SOME ORGANOTRANSITION METAL CHEMISTRY OF THE CARBON-CARBON TRIPLE BOND

by

GEORGE ANTHONY KOUTSANTONIS
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The Department of Physical and Inorganic Chemistry
The University of Adelaide

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SUMMARY

This thesis presents some new aspects of alkyne chemistry on mono- or poly- nuclear transition metal complexes.#

Complexes containing unsaturated carbenes, such as vinylidene, have received considerable attention over the past decade. Chapter One describes addition of halogen (Cl_2, Br_2 or I_2) to ruthenium or osmium σ-acetylides to give cationic halovinylidene complexes, such as $[Ru\{C{=}C(I)Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)][I_3]^*$ and $[Ru\{C{=}CBr\text{-}(C_6H_4Br\text{-}4)\}(PPh_3)_2(\eta\text{-}C_5H_5)][Br_3]^*$. Reactions of the bromo- complex with nucleophiles resulted in formal displacement of Br^+ and the formation of $Ru(C_2C_6H_4Br\text{-}4)\text{-}(PPh_3)_2(\eta\text{-}C_5H_5)$.

Isomerisation of terminal alkynes to vinylidenes on transition metal centres occurs readily. The use of HC_2SiMe_3, in the presence of NH_4PF_6, has resulted in the preparation of the sought-after parent vinylidene complexes $[Ru\{C{=}CH_2\}(L)_2(\eta\text{-}C_5H_5)][PF_6]$ [$L{=}PPh_3$, $L_2{=}dppe$, $L{=}PMe_3$]. The complexes $[RuCl_2(PMe_3)_2(\eta\text{-}C_5H_5)][PO_2F_2]$ and $[Ru\{H_2C_4(SiMe_3)_2\}(PMe_3)(\eta\text{-}C_5H_5)][PF_6]$ have also been isolated. The vinylidene complexes are readily deprotonated by either basic alumina or $KOBu^t$ to give the rather unstable ethynyl complexes $Ru(C_2H)(L)_2(\eta\text{-}C_5H_5)$. Reaction of the CCH_2 complex ($L{=}PPh_3$) with water or MeOH gave $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ and $[Ru\{C(OMe)\text{-}Me\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]^*$, respectively; the latter complex was also obtained from reaction of $[Ru(NCMe)\text{-}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ with HC_2SiMe_3 in methanol. The

analogous dppe complex was obtained from the reaction of ethyne with $\mathrm{RuCl(dppe)(\eta\text{-}C_5H_5)}$ in methanol in the presence of $\mathrm{NH_4PF_6}$, but in the presence of $\mathrm{AgPF_6}$ a complex tentatively formulated as $\mathrm{[Ru(\eta^2\text{-}HC_2H)(dppe)(\eta\text{-}C_5H_5)][PF_6]}$ was obtained. The Ru-C(sp) bond in the ethynyl complex $\mathrm{Ru(C_2H)(PPh_3)_2\text{-}(\eta\text{-}C_5H_5)}$ does not exhibit the remarkable stability towards halogens found in arylacetylides and is readily cleaved by bromine giving $\mathrm{RuBr(PPh_3)_2(\eta\text{-}C_5H_5)}$. Attempts to prepare aryldiazovinylidenes are described.

Chapter Two deals with some chemistry of the electron deficient alkyne, $\mathrm{C_2(CO_2Me)_2}$. Reactions with $\mathrm{RuCl(PPh_3)_2\text{-}(\eta\text{-}C_5H_5)}$ in the presence of $\mathrm{NH_4PF_6}$ afforded $\mathrm{RuCl\{\eta^4\text{-}CH(CO_2Me)=C(CO_2Me)C(CO_2Me)=CH(CO_2Me)\}(\eta\text{-}C_5H_5)}$, also obtained in much higher yield from the reaction between $\mathrm{RuCl(\eta^4\text{-}C_8H_{12})(\eta\text{-}C_5H_5)}$ and tetramethyl (*z,z*)-1,3-butadiene-1,2,3,4-tetracarboxylate. The analogous iodo* complex has also been obtained, from $\mathrm{RuI(PPh_3)_2(\eta\text{-}C_5H_5)}$. Two interesting cyclo-oligomerization products, $\mathrm{Ru(\eta\text{-}C_5H_5)\text{-}\{\eta^5\text{-}C_6H(CO_2Me)_6\}^*}$ and $\mathrm{Ru(\eta\text{-}C_5H_5)\{\eta^5\text{-}C_8H(CO_2Me)_8\}^*}$, resulting from novel tri- and tetramerization of the alkyne, were also isolated.

A re-investigation of the reaction between $\mathrm{C_2(CO_2Me)_2}$ and $\mathrm{RuH(PPh_3)_2(\eta\text{-}C_5H_5)}$ is described. Other products isolated from this reaction are the bis-insertion product, $\overline{\mathrm{Ru\{C(CO_2Me)=C(CO_2Me)C(CO_2Me)}}\mathrm{=CH(CO_2Me)\}(PPh_3)(\eta\text{-}C_5H_5)}$ and the 1/2 $\mathrm{PPh_3/C_2(CO_2Me)_2}$ adduct. Isomerisation of $\mathrm{Ru\{C(CO_2Me)C=CH(CO_2Me)\}(PPh_3)_2(\eta\text{-}C_5H_5)}$ from the original *cis* configuration is followed by chelation of the ester CO-group with concomitant displacement of one $\mathrm{PPh_3}$ ligand. The resulting chelate reacts with CO to give the (*z*)-$\mathrm{Ru\{C(CO_2Me)C=CH(CO_2Me)\}(CO)(PPh_3)(\eta\text{-}C_5H_5)^*}$. The complexes,

$RuX(dppf)(\eta\text{-}C_5H_5)$, {dppf=1,1′-bis-diphenylphosphinoferrocene; X=H*, Cl and $C(CO_2Me)=CH(CO_2Me)$} are also described.

Chapter Three describes the reaction of AgC_2Ph with $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$, which afforded the novel phenylacetylide oligomers $\{Ru(PPh_3)(\eta\text{-}C_5H_5)\}_2\{\mu\text{-}C_8Ph_4\}^*$ and $\{Ru(PPh_3)(\eta\text{-}C_5H_5)\}_2\{\mu\text{-}C_{10}Ph_4(C_6H_4)\}^*$; both contain unusual diruthena polycyclic systems.

The synthesis and reactivity of some bimetallic clusters is discussed in Chapter Four. Reactions between $Ir(C_2Ph)(CO)_2(PPh_3)_2$ and iron carbonyls $[Fe(CO)_5$ or $Fe_2(CO)_9]$ gave the new iron-iridium clusters $Fe_2Ir(\mu_3\text{-}\eta^2\text{-}C_2Ph)(CO)_8\text{-}(PPh_3)^*$ (A), $Fe_2Ir(\mu_3\text{-}\eta^2\text{-}C_2Ph)(CO)_7(PPh_3)_2$ and $FeIr_2(\mu_3\text{-}\eta^2\text{-}PhC_2C_2Ph)(CO)_7(PPh_3)_2{}^*$. Formation of the $FeIr_2$ complex involves a novel oxidative coupling of two phenylacetylide units. The Fe_2Rh cluster analogous to (A), has also been prepared. Complex (A) reacted with hydride or sodium amalgam to form an anion which could be protonated to give the hydrido- alkyne cluster, $Fe_2Ir(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(CO)_8\text{-}(PPh_3)$ and the isomeric hydrido-vinylidene cluster $Fe_2Ir(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}CCHPh)(CO)_8(PPh_3)$.* The same vinylidene complex was obtained by addition of H_2 to (A) and by thermal isomerisation of the alkyne cluster. Auration of the anion gave $AuFe_2Ir(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(CO)_8(PPh_3)$, $Au_2Fe_2Ir(\mu_4\text{-}\eta^2\text{-}C_2Ph)\text{-}(CO)_7(PPh_3)_3{}^*$ and $Au_3Fe_2Ir(CCHPh)(CO)_7(PPh_3)_4$. The reaction of (A) with $[O\{Au(PPh_3)\}_3][BF_4]/[ppn][Co(CO)_4]$ resulted in a much higher yield of the di-gold cluster; the analogous rhodium complex was obtained similarly.

Reactions of complex (A) with tertiary phosphines or phosphites resulted in either nucleophilic addition to the α-carbon of the acetylide ligand to give the zwitterionic complex $Fe_2Ir\{\mu_3-\eta^2-PhCC(PEt_3)\}(CO)_8(PEt_3)^*$ (B) or simple substitution at Ir to give the mono- or di-substituted complexes [for PEt_3, PMe_2Ph and $P(OMe)_3$]. Complex (B) rearranges, to form $Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_8(PEt_3)$ and $Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_7(PEt_3)_2$.

The molecular structures of the complexes marked with an asterisk have been determined by single crystal X-ray studies.

STATEMENT

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference is made in the text of this thesis.

I consent to this thesis being made available for photocopying and loan.

GEORGE A. KOUTSANTONIS

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ABBREVIATIONS

Å	angstroms
acac	acetylacetonate
AR	analytical reagent
Ar	Aryl
atm	atmospheres
av.	average
Bu^n	normal butyl
Bu^s	secondary butyl
Bu^t	tertiary butyl
ca	circa
Calc	Calculated
cp	cyclopentadienyl
d	days
dec	decomposed
DMAD	dimethyl acetylenedicarboxylate
dppe	1,1'-bis(diphenylphosphino)ethane
dppf	1,1'-bis(diphenylphosphino)ferrocene
dppm	1,1'-bis(diphenylphosphino)methane
e	electron
Ed.	Editors
ESR	electron spin resonance
Et	ethyl
eV	electron volts
fac	facial
g	grams
h	hours
Hz	hertz
kJ	kilojoules

kV	kilovolts
L	ligand or litre
Lit.	literature value
M	metal or molarity
Me	methyl
mer	meridional
mol	molarity
mg	milligrams
MHz	megahertz
min	minutes
ml	millilitres
mmol	millimoles
m.p.	melting point
OAc	acetate
p	page
Ph	phenyl
ppn	bis(triphenylphosphine)iminium
Pr	propyl
Pr^i	isopropyl
py	pyridine
Ref.	references
R_f	retardation factor
sec.	seconds
thf	tetrahydrofuran
tlc	thin-layer chromatography
vol.	volume
x	halide or anion

For Infrared Spectroscopy (i.r.)

br	broad
cm^{-1}	wavenumbers
m	medium
s	strong
sh	shoulder
vs	very strong
vw	very weak
w	weak

For X-ray crystallography

Dcalc	Density calculated
esd	estimated standard deviation
F	structure factor(s)
F_o	observed structure factor(s)
F_c	calculated structure factor(s)

For Mass spectrometry (MS)

EIMS	Electron Impact Mass Spectra
FAB MS	Fast Atom Bombardment Mass Spectra
$[M]$	molecular ion
m/z	mass per unit charge

For Nuclear Magnetic Resonance Spectroscopy (NMR)

δ	chemical shift (parts per million)
d	doublet
J	coupling constant
m	multiplet
s	singlet
t	triplet

NUMBERING OF COMPLEXES

The numbering of complexes applies only to the chapter being discussed in the text as each chapter is self-contained.

CHAPTER ONE

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SYNTHESIS AND REACTIVITY OF NEW VINYLIDENE AND ACETYLIDE COMPLEXES

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INTRODUCTION

It is well known that transition metals stabilise reactive organic species by complexation. Of these vinylidene (:C=CH$_2$), is the simplest unsaturated carbene and is the tautomer of ethyne, HC$_2$H. Recent kinetic and trapping experiments[1a] with ethyne/benzene and ethyne/toluene mixtures pyrolysed at > 820K have given evidence for the fast ethyne/carbene equilibrium,

$$HC{\equiv}CH \longleftrightarrow H_2C{=}C:$$

which precedes carbene addition to the aromatic ring. The activation energy of this pyrolysis is 155(8) kJ mol^{-1} while the lifetime of the free vinylidene species[1b] has been calculated at 10^{-11} sec. The formation of transition metal complexes containing unsaturated cationic carbenes (vinylidenes) was described many years ago.[2] Rational routes to these complexes were not found until some time later[3-5] leading to a rapid development of the area, which has been reviewed.[6]

Four general methods have been employed for the preparation of mononuclear vinylidene complexes,[6]

(i) from 1-alkynes via a formal 1,2-hydrogen shift;

e.g. fac-W(CO)$_3$(dppe)(thf) + HC$_2$Ph $\longrightarrow$

mer-W(CCHPh)(CO)$_3$(dppe)[7]

(ii) by addition of electrophiles to metal acetylide complexes;

e.g. Rh(C$_2$Ph)[N(CH$_2$CH$_2$PPh$_2$)$_3$] + H$^+$ $\longrightarrow$

[Rh(CCHPh){N(CH$_2$CH$_2$PPh$_2$)$_3$}]$^+$ [8]

(iii) by deprotonation of carbyne complexes;

e.g. $Mo(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta-C_5H_5) + LiBu^n \longrightarrow$

$Li[Mo(CCHBu^t)\{P(OMe)_3\}_2(\eta-C_5H_5)]$ [9]

(iv) by formal dehydration of acyl complexes;

e.g. $Fe(COCH_3)(CO)(PPh_3)(\eta-C_5H_5) + (CF_3SO_2)_2O \longrightarrow$

$[Fe(CCH_2)(CO)(PPh_3)(\eta-C_5H_5][CF_3SO_2]$ [10]

Of relevance to the present work are routes (i) and (ii).

The 1,2-hydrogen shift undergone by many 1-alkynes on reaction with certain transition metal complexes has proved a useful entry into vinylidene complexes and the mechanism for alkyne-vinylidene transformation has excited much discussion.

Two possible pathways for this isomerisation on metal centres have been considered.

(i) oxidative addition of the alkyne to the metal centre to give a hydrido-alkynyl complex which then isomerises by a 1,3-hydrogen shift from the metal to C_β

(ii) intra-molecular reaction of an initially formed η^2-complex leading to a formal 1,2-hydrogen shift which involves the prior slippage of the alkyne to an η^1-mode of co-ordination.

Silvestre and Hoffmann performed Extended Hückel Molecular Orbital calculations to define the 1,2-hydrogen shift and they concluded that the latter mechanism was most likely as the alternative oxidative addition mechanism was considered to require a prohibitively large amount of energy to promote the migration of the H atom from the metal to the β-carbon of the acetylide.[11]

The formation of the intermediate η^2-complex, and its rearrangement to the corresponding η^1-vinylidene, has been observed in the ruthenium series.[12] Ethyne or propyne reacted with $RuCl(PMe_3)_2(\eta-C_5H_5)$ in methanol to give $[Ru(\eta^2-HC_2R)(PMe_3)_2(\eta-C_5H_5)]^+$ (R=H,Me). In the one case (R=Me) the propyne intermediate underwent first-order rearrangement in MeOH or MeCN to the vinylidene $[Ru(CCHMe)(PMe_3)_2(\eta-C_5H_5)]^+$ with a half life of 5.5 min at 40°C in MeCN; at higher temperatures in MeCN the free alkyne is regenerated in high yield with the formation of $[Ru(MeCN)(PMe_3)_2(\eta-C_5H_5)]^+$. The η^2-ethyne complex is more stable, with a half-life > 5 h at 60°C.[12]

Werner and co-workers have isolated hydrido-alkynyl complexes which are intermediates in the conversion of Rh and Ir η^2-alkynes to vinylidene complexes.[13] The transformations observed, however, required considerable lengths of time at elevated reaction temperatures.

Kostić and Fenske[14] have explained many of the physical, structural and chemical properties of mononuclear acetylide complexes. Co-ordination of acetylide anion to a metal centre has the effect of localizing the electron density in the Highest Occupied Molecular Orbital on the β-carbon. The addition of electrophiles to the electron-rich β-carbon of metal acetylides has been described on many occasions[6] and is perhaps the best entry into mononuclear vinylidene complexes.

Iron and ruthenium acetylide complexes are remarkably strong carbon-centred bases. For example $Ru(C_2Me)(PMe_3)_2(\eta-C_5H_5)$ is protonated by $MH(CO)_3(\eta-C_5H_5)$ (M=Cr,Mo,W) to give the salts $[Ru(CCHMe)(PMe_3)_2(\eta-C_5H_5)][M(CO)_3(\eta-C_5H_5)]$.[15]

Alkylation of iron or ruthenium acetylides with alkyl halides has provided a powerful method for the introduction of a wide variety of functional groups.[16] Extension of this reaction to a variety of halogenated organics has given many disubstituted vinylidene complexes containing alkyl, alkenyl and alkynyl substituents.[17]

Addition of the tropylium cation to a series of acetylide complexes afforded orange cycloheptatrienylvinylidene derivatives[18, 19] $[M\{CCR(C_7H_7)\}(L)_2(\eta\text{-}C_5H_5)]^+$ (M=Fe,Ru,Os). Their reactions were characterised by ready displacement of the $C_7H_7^+$ group and formation of the metal acetylide. Thus, NaOMe gave C_7H_7OMe, and $K[HB(CHMeEt)_3]$ gave C_7H_8 as the organic products, while in MeOH, the methoxy(benzyl)carbene complex was found. Similar reaction of $Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$ with $C_7H_7^+$ gave $[Fe(CO)_3(\eta\text{-}C_5H_5)]^+$ via the vinylidene complex (detected by FAB MS) and thf cations.

Complexes containing azovinylidene ligands were prepared by addition of aryldiazonium salts to iron, ruthenium and osmium acetylides. In these complexes, the azo group could be protonated and alkylated, and could enter into cyclometallation reactions, e.g. with $Mn(CH_2Ph)(CO)_5$.[18,20] The aryldiazovinylidene complexes reactivity towards nucleophiles was analogous to that of the cycloheptatrienyl vinylidenes and was characterised by cleavage of the aryldiazo group.

The electrophilic addition of H^+ to the β-carbon of $Fe(C_2H)(dppe)(\eta\text{-}C_5H_5)$ allowed the preparation of the first unsubstituted vinylidene complex $[Fe(C{=}CH_2)(dppe)(\eta\text{-}C_5H_5)]^+$, over a decade ago.[21] This complex was also obtained from the reaction of $FeCl(dppe)(\eta-C_5H_5)$ with C_2H_2 or HC_2SiMe_3 in MeOH but under similar conditions the ruthenium complex, $RuCl(PPh_3)_2(\eta-C_5H_5)$ gave 75% $[Ru\{C(OMe)Me\}(PPh_3)_2(\eta-C_5H_5)]^+$ by rapid addition of MeOH to the intermediate vinylidene.[16]

An extremely useful method for generating transition metal acetylide complexes is the deprotonation of intermediate monosubstituted vinylidene complexes.[6,16] Recently pentamethylcyclopentadienyl iron and ruthenium acetylides have been prepared by this route.[22] Electrochemical studies on these complexes showed the ruthenium complexes were more difficult to oxidize than the iron analogues. Permethylation of the cyclopentadienyl ring depressed E° values and the nature of the alkynyl substituent had little effect on E° values, although the bulkier substituents, e.g. Bu^t, had a pronounced effect on the chemical reversibility of the system. The E° values were strongly dependent upon the degree of phosphine substitution although comparison of data for $Ru(C_2Ph)(dppe)(\eta-C_5H_5)$ and $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ suggest little effect on exchanging dppe for two PPh_3 ligands. An adjunct to this work was the isolation of stable radical cations, $[Mo(C_2R)(dppe)(\eta-C_7H_7)]$-$[BF_4]$,[23] it is pertinent to note that the fragments $Mo(\eta-C_7H_7)$ and $Ru(\eta-C_5H_5)$ are isoelectronic. Subsequently, these radical cations were shown to undergo coupling at C_β of the alkynyl ligand to afford divinylidene-bridged dimers, $[Mo_2(dppe)_2(\eta-C_7H_7)_2(\mu-C_4R_2)]$.[24]

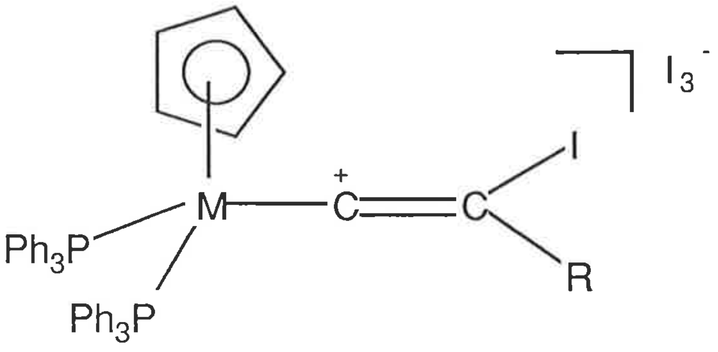
This chapter describes reactions of some ruthenium and osmium σ-acetylides with halogens and the reactions of the resulting novel halo-vinylidenes.

Although iron complexes containing vinylidene, :$C=CH_2$, have been known for some time, the analogous complexes of ruthenium were unknown. The reaction of some ruthenium chloride complexes with terminal acetylenes and the reactions of the resulting unsubstituted vinylidene complexes are also described herein.

RESULTS AND DISCUSSION

A. Preparation of halovinylidenes

(a) Reaction of iodine - Addition of iodine to a tetrahydrofuran solution of $M(C_2R)(PPh_3)_2(\eta-C_5H_5)$ resulted in an immediate change in colour from bright yellow to dark green. Suitable work-up procedures gave green crystalline salts of the novel iodovinylidene complexes $[M\{C{=}C(I)(R)\}(PPh_3)_2(\eta-C_5H_5)][I_3]$.

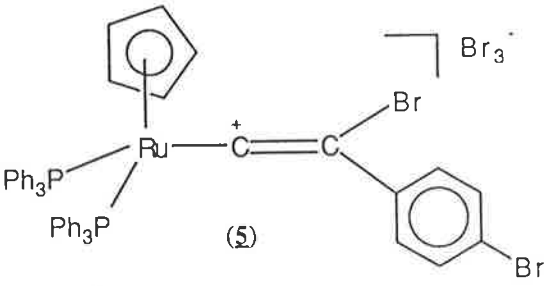


	R	M
(1)	Ph	Ru
(2)	Me	Ru
(3)	C_6F_5	Ru
(4)	Ph	Os

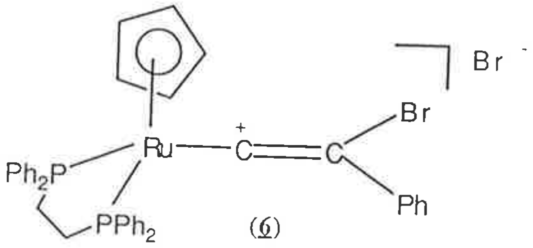
Elemental microanalysis indicated the presence of iodine, although it was not possible to obtain reliable halogen analyses for these complexes. Their infrared spectra contain medium to strong bands between 1690-1638 cm^{-1} assigned to the $\nu(C{=}C)$ mode, these values being consistent with those values found in other vinylidene complexes.[25] The ^1H NMR spectra contain little useful structural information; the C_5H_5 resonances are singlets between δ 5.3-5.5 and the expected phenyl resonances are at *ca* δ 7.3. Complexes (1), (3) and (4) proved to be too insoluble in the common NMR solvents to obtain informative $^{13}C\{^1H\}$ spectra. Complex (2), however, exhibited a characteristic low-field triplet at δ 325.9, coupled to two ^{31}P nuclei (J 15Hz), and was assigned to $C\alpha$ of the vinylidene unit.

The spectrum also contained resonances at δ 18.6 and 128.7-133.9 assigned to the methyl and phenyl groups, respectively; the resonances associated with the β-carbon probably lie under the phenyl resonances. The identity of complex (1) was unambiguously determined by X-ray structure analysis and will be discussed below in comparison with a related bromovinylidene.

(b) Reactions of bromine - The addition of neat bromine, in excess, to a tetrahydrofuran solution of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ produced a dark green solution, work-up affording dark green crystals of $[Ru\{C{=}C(Br)\text{-}(C_6H_4Br\text{-}4)\}(PPh_3)_2(\eta\text{-}C_5H_5)][Br_3]$ (5) in essentially quantitative yield. In contrast, addition of bromine (in CCl_4) to $Ru(C_2Ph)(dppe)(\eta\text{-}C_5H_5)$ resulted in the immediate precipitation of the related bromo(phenyl)vinylidene complex $[Ru\{C{=}C(Br)Ph\}(dppe)(\eta\text{-}C_5H_5)][Br]$ (6) .



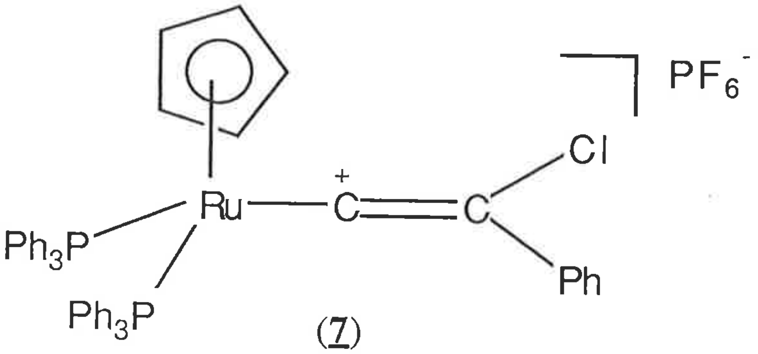
(5)



(6)

Complexes (5) and (6) were identified by the usual spectroscopic techniques and microanalyses. Their infrared spectra contained strong $\nu(C{=}C)$ bands (at 1638 and 1640 cm^{-1}, respectively) consistent with those observed in the iodo analogues (1) - (4). Both complexes contained molecules of Et_2O of crystallisation; signals for these were observed in the proton NMR spectra, obscuring the methylene protons in (6), along with singlet resonances at δ 5.35 and 5.63, for (5) and (6) respectively, assigned to the cyclopentadienyl groups. The phenyl protons were found in the region between δ 6.5-8.0. The relatively low solubility of (5) in the common NMR solvents allowed the assignment of only the C_5H_5 (δ97.2) and phenyl (δ 128.0-135.0) resonances in the proton decoupled ^{13}C NMR spectrum of (5). Subsequent structural analysis of (5) by a single crystal X-ray study revealed the phenyl group originally present on the phenylacetylide ligand had also been brominated *para* to the C=C double bond (see below). A deficiency of bromine in its reaction with $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ also resulted in the formation of the 4-bromophenyl complex, so that the ring substitution either precedes, or is concurrent with, the addition of bromine to the β-carbon of the acetylide ligand. In contrast, bromination of $Ru(C_2Ph)(dppe)(\eta\text{-}C_5H_5)$ afforded only the bromo(phenyl)-vinylidene possibly due to its relative insolubility under the prevailing reaction conditions.

(c) Reaction of chlorine with $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ - Chlorine in diethyl ether reacts with $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ in tetrahydrofuran to give a green solution. After metathesis of the counter ion, the chloro(phenyl)vinylidene complex (7) was isolated, in moderate yield. The complex was tentatively identified by microanalysis and infrared spectroscopy [ν(C=C) 1650 and ν(PF) 840 cm^{-1}]. The proton NMR contained signals, assigned to the cyclopentadienyl and phenyl groups, at δ 5.63 and 7.10-7.73,



(7)

respectively. Subsequently a FAB mass spectrum confirmed the identity of (7) and will be discussed below (see p.37)

Crystal structures of $[Ru\{C=C(I)Ph\}(PPh_3)_2(\eta-C_5H_5)][I_3]$ (1) and $[Ru\{C=C(Br)(C_6H_4Br-4)\}(PPh_3)_2(\eta-C_5H_5)][Br_3]$ (5)

It is convenient to compare the structures of the two cations in (1) and (5). These are shown in Figures 1 and 2, together with the numbering schemes used; Table 1 summarises pertinent bond parameters determined for each complex. Table 2 collects some structural parameters obtained for the vinylidene linkage in some related ruthenium-vinylidene complexes.

The cations in (1) and (5) contain the now familiar ruthenium (II) atoms coordinated by the C_5H_5 group and two PPh_3 ligands; nearly octahedral geometry is achieved by co-ordination of the halovinylidene ligand in the sixth position. The $Ru-C(C_5H_5)$ distances lie within the ranges 2.250(5)-2.284(5) and 2.226(1)-2.306(11)Å (parameters given for (1) and (5), respectively), with the longest Ru-C separation being approximately *trans* to the vinylidene ligand. The two Ru-P distances [2.337(2) and 2.356(2); 2.366(5) and 2.366(5)Å, respectively] are normal for this type of complex.

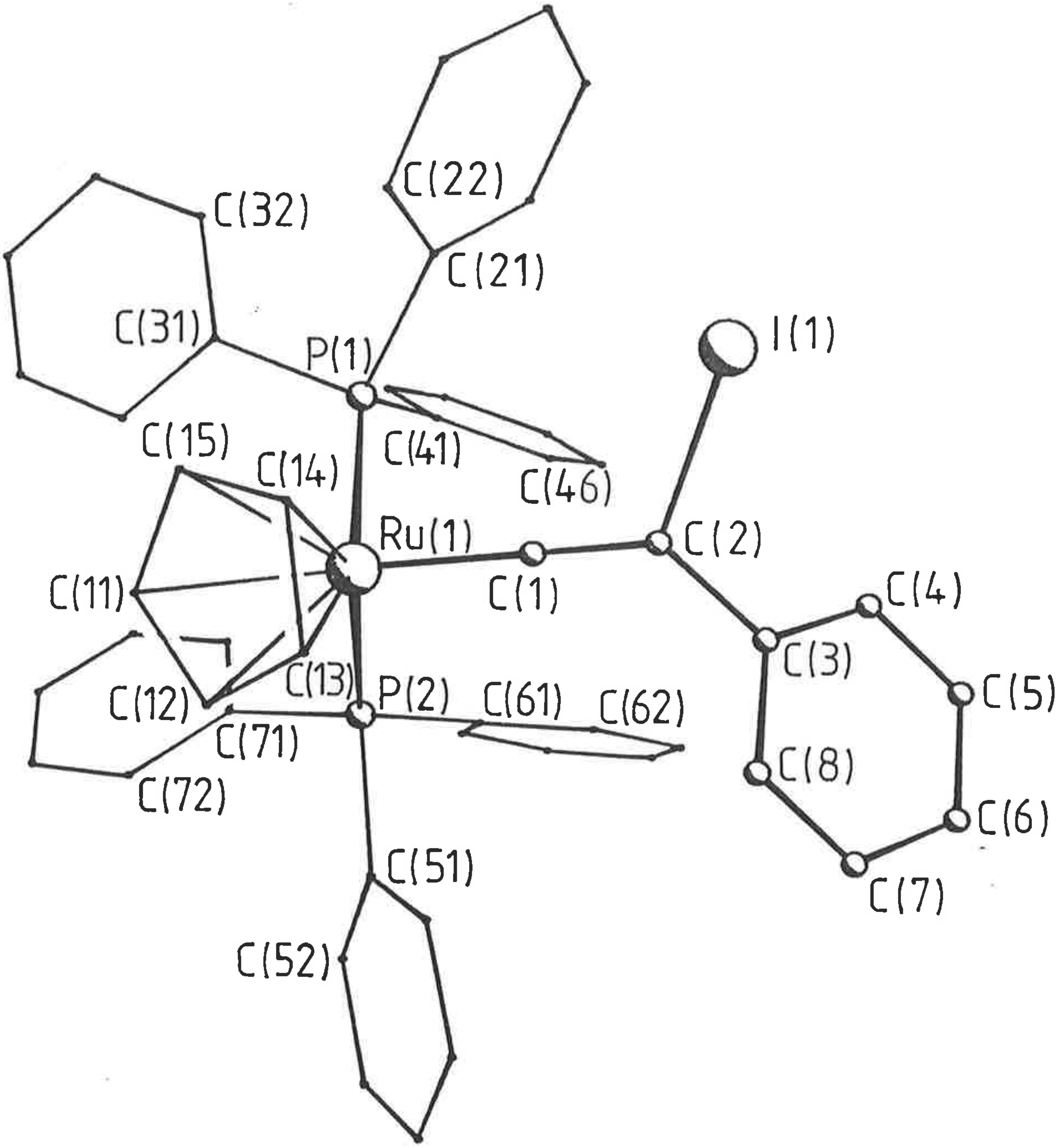


Figure 1: PLUTO plot of the structure of the cation in $[Ru\{C{=}C(I)Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)][I_3]$ (1) (by B.K. Nicholson)

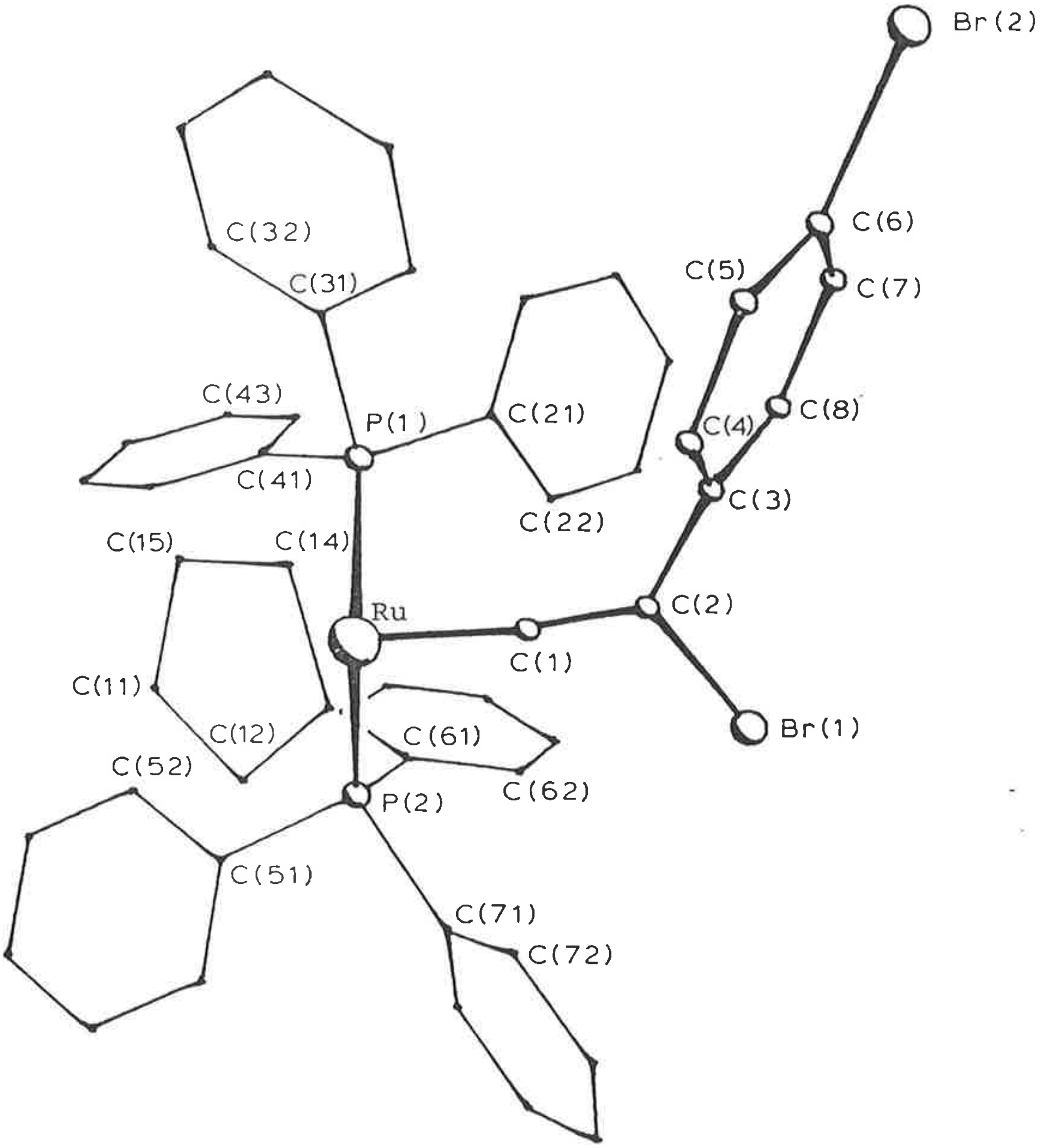
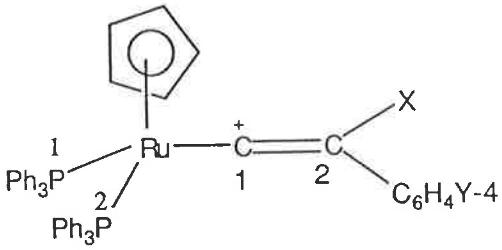


Figure 2: PLUTO plot of the structure of the cation in $[Ru\{C{=}C(Br)(C_6H_4Br\text{-}4)\}(PPh_3)_2(\eta\text{-}C_5H_5)]$-$[Br_3]$ (5) (by B.K. Nicholson).

Table 1

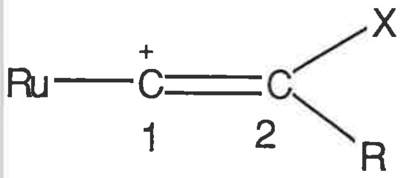
Selected bond distances (Å) and angles (°) for complexes (1) and (5)



	(1)	(5)
	X=I	X=Br
	Y=H	X=Br
Ru-C(1)	1.839(7)	1.85(1)
C(1)-C(2)	1.31(1)	1.31(2)
C(2)-X	2.124(7)	1.93(2)
C(2)-C(Ar)	1.49(1)	1.49(2)
Ru-P(1)	2.337(2)	2.366(5)
Ru-P(2)	2.356(2)	2.366(5)
Ru-C(C_5H_5) (Av)	2.26	2.26
P(1)-Ru-P(2)	97.0(1)	103.3(2)
P(1)-Ru-C(1)	89.6(2)	88.2(5)
P(2)-Ru-C(1)	97.4(2)	93.6(5)
Ru-C(1)-C(2)	171.0(7)	169.4(14)
C(1)-C(2)-X	115.7(6)	116.8(13)
C(1)-C(2)-C_6H_4Y	129.4(7)	126.8(15)

Table 2

Bond distances (Å) and angles (°) of the vinylidene linkage in some ruthenium complexes



	R=Ph X=C_7H_7	R=Me X=H	R=Me X=Ph	R=Ph X=$N_2C_6H_3Me_2$	R=Me X=Me
Ru-C(1)	1.848(9)	1.845(7)	1.863(10)	1.823(9)	1.88
C(1)-C(2)	1.32(1)	1.313(10)	1.293(15)	1.34(1)	1.29
Ru-C(1)-C(2)	174.9(6)	180(2)	172.8(1)	169.9	168.1
C(1)-C(2)-R	121.1(6)	125.1(6)	117.0(11)	121.4(8)	-
C(1)-C(2)-X	118.1(7)	-	125.1(12)	114.4(8)	-
Ref.	18	51	27	18	6

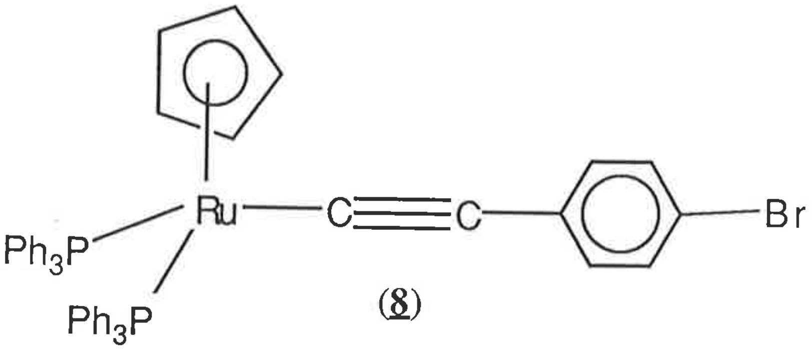
The Ru-C(vinylidene) separations are 1.839(7) [(1)] and 1.85(1)Å [(5)], providing evidence for considerable multiple bond-order and, hence, back-bonding into the unsaturated ligand [*cf* Ru-CO 1.869(2)Å in Ru(CO)(PPh$_3$)$_2$(η-C$_5$H$_5$)$^+$[26] and Ru-Cα 1.86(1)Å in Ru{C=CMePh}(PPh$_3$)$_2$(η-C$_5$H$_5$)].[27] This experimental observation supports theoretical arguments that extensive transfer of charge onto the vinylidene ligand occurs *via* its *p* and π^* orbitals.[14] This was also supported by studies of manganese complexes[3] whose infrared spectra suggested that vinylidene ligands are stronger π acceptors than CO.

The C(1) - C(2) bonds for (1) and (5) have lengths of 1.31(1) and 1.31(2)Å, respectively, both of which are short for C=C bonds. The Ru-C=C moiety is slightly bent at the α-carbon [angles Ru-C(1)-C(2) 171.0(7) and 169.4(14)°], while angles at the β-carbon in (1) [C(1)-C(2)-I(1) 115.7(6), C(1)-C(2)-C(3) 129.4(7), I(1)-C(2)-C(3) 114.9(5)°] show bending of the C-I bond caused by the mutual interaction of the I and metal atoms. The C(2)-I(1) bond length [2.124(7)Å] is similar to that in CH$_2$=CHI [2.092(5)Å[28a]].

The geometry of the tri-iodide anion differs somewhat from those that have been found previously, with I-I separations of 2.896(1) (d^1), 2.923(1)Å (d^2), and angle I(3)-I(2)-I(4) 174.7(1)°. A recent survey[28b] quotes ranges of 2.794-2.850(d^1) and 3.005-3.123Å(d^2), with angles of 176.3-179.9°; in the case of (1) the smaller difference between d^1 and d^2 is no doubt a result of little interaction between the anion and the complex cation.

Reactions of $[Ru\{C{=}C(Br)(C_6H_4Br\text{-}4)\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (5)

Attempted elaboration of the vinylidene moiety by the addition of H^- or OMe^-, using $K[BH(CHMeEt)_3]$ or NaOMe, respectively, was unsuccessful. Treatment of a tetrahydrofuran solution or CH_2Cl_2 solution of (5) with the above reagents, respectively, resulted in the formal displacement of Br^+ and the formation of $Ru(C_2C_6H_4Br\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)$ (8). This compound was readily characterised by elemental microanalysis, and from its infrared and EI mass spectra. The infrared spectrum was particularly informative, the strong absorption at 2076 cm^{-1} being assigned to $\nu(C{=}C)$ of the phenylacetylide ligand.



(8)

The resonances at δ 4.32 and 7.14 in the proton NMR spectrum are assigned to the cyclopentadienyl and phenyl protons, respectively, the former being at characteristically higher field than the analogous signals in the cationic complexes (1) - (7). The EI mass spectrum contained a molecular ion at m/z 872.

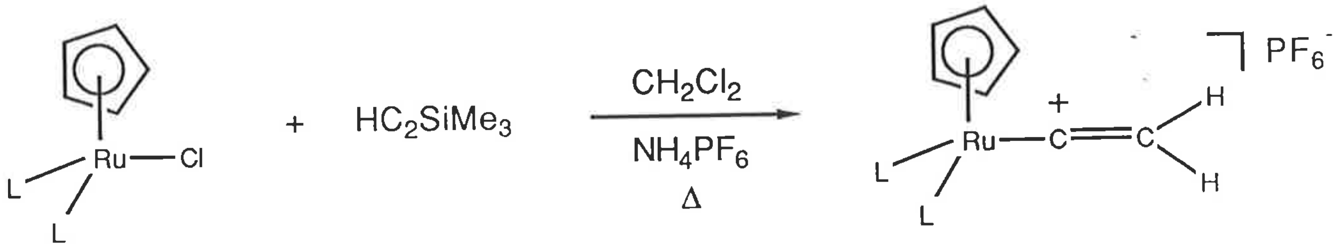
The reactivity shown by complex (5) is perhaps not surprising, since the formation of the halovinylidene complexes occurs by formal addition of the electrophile X^+ to the β-carbon of the acetylide. In this behaviour these complexes resemble the cycloheptatrienyl[18,19] and aryldiazovinylidene[20] complexes.

Synthesis of unsubstituted vinylidene complexes

Reaction between $RuCl(L)_2(\eta-C_5H_5)$ and HC_2SiMe_3

(a) $L=PPh_3$ or L_2=dppe - Several years ago, Davies and co-workers[16] found that treatment of FeCl(dppe)-($\eta-C_5H_5$) in methanol in the presence of NH_4PF_6 with acetylene or trimethylsilylacetylene generated the unsubstituted vinylidene complex.

Heating mixtures of $RuCl(L)_2(\eta-C_5H_5)$ ($L=PPh_3$, L_2=dppe), HC_2SiMe_3 and NH_4PF_6 in dichloromethane gave essentially quantitative yields of the corresponding ruthenium vinylidenes (9) and (10).



L = PPh_3 (**9**), L_2= dppe (**10**)

The synthesis of complex (10) requires more severe reaction conditions (90°C, 48 h) than does (9) (oil bath at *ca* 60°C, 7 h) necessitating the use of a closed vessel in the formation of (10) to prevent the loss of HC_2SiMe_3.

The relative stability of the two complexes is different, complex (10) being more readily oxidized than (9) even in the solid state. The presence of $[Ru(CO)(dppe)(\eta-C_5H_5)]^+$

was found in solid samples of (10) by infrared spectroscopy [ν(CO) 1990 cm^{-1}] after exposure to air.

Spectral and microanalytical techniques were used to characterise the complexes (9) and (10). Characteristic ν(C=C) bands were observed [(9) 1628; (10) 1641 cm^{-1}] in the infrared spectra and the strong absorption at *ca* 840 cm^{-1} confirmed the presence of PF_6^- counter ion in both complexes. Apart from the usual signals observed for the phenyl and cyclopentadienyl moieties the ^1H NMR spectra of (9) and (10) contained triplets at δ 4.34 and 3.19, respectively, assigned to the vinylidene protons, coupled to two equivalent ^{31}P nuclei with *J* 1.5 and 2.0 Hz, respectively. The $^{13}C\{^1H\}$ NMR spectra contain C_5H_5 resonances at δ 95.0 and 93.4 for (9) and (10), respectively, which are characteristic of cationic complexes. Most informative were the resonances of the α and β carbons; the former appeared as triplets by coupling with the two ^{31}P nuclei and their low field position is typical of vinylidene complexes [(9): 347.2, *J*(PC) 15Hz; (10): 343, *J*(PC) 18Hz]. The β-carbons of (9) and (10) resonate as singlets at δ 99.9 and 96.7, respectively, considerably upfield from the analogous resonances in other substituted vinylidene complexes. The C_β resonance in CCR_2 complexes is assumed to lie under the phenyl region at *ca* δ 130. In the monosubstituted complex $[Ru(C{=}CHMe)(PPh_3)_2(\eta\text{-}C_5H_5)]$-$[CF_3CO_2]$[25] the β-carbon was found at δ 109.0 while the analogous resonance in $[Ru(C{=}CMePh)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ was observed at δ 125.2[25]. These data suggest a higher electon density at the β-carbon in complexes (9) and (10) than in mono- or disubstituted vinylidenes. The β-carbon of [Ru(C=CH_2)-(PMe_3)$_2$(η-C_5H_5)][PF_6] was found at δ 92.7,[12] i.e. at higher field, than (9) and (10), consistent with the presence of the more electron donating PMe_3 ligands. The solvent signals of deuteroacetone (*ca* δ 30) are presumably obscuring the expected dppe methylene resonances of (10).

L_2 = PMe_3

Recently, Bullock[12] reported isolation of [Ru{C=CH_2}-(PMe_3)$_2$(η-C_5H_5)][PF_6] (11) from the reaction between HC_2SiMe_3 and RuCl(PMe_3)$_2$(η-C_5H_5) (12) in the presence of NH_4PF_6 in MeOH. Independently, a study of this reaction in dichloromethane was undertaken in conjunction with the preceding reactions.

Heating (12) in dichloromethane containing HC_2SiMe_3 in the presence of NH_4PF_6 provided an excellent synthesis of complex (11). The complex was readily identified by microanalysis and spectral data.

The infrared spectrum contained the now familiar ν(C=C) band at 1625 cm^{-1} and a ν(PF) band at *ca* 840 cm^{-1}; and the ^1H NMR spectrum contained a multiplet at δ1.62 and a singlet at δ 5.42 which were assigned to the PMe_3 and C_5H_5 protons, respectively. The vinylidene protons appeared as a triplet [*J*(HP) 2Hz] and δ 3.76. The identity of this complex was confirmed from its FAB mass spectrum, as discussed below

On one occasion a similar reaction of (12) with HC_2SiMe_3 in dichloromethane was continued for 48 h whereupon a dark suspension was obtained. Filtration gave an unidentified paramagnetic solid (13).

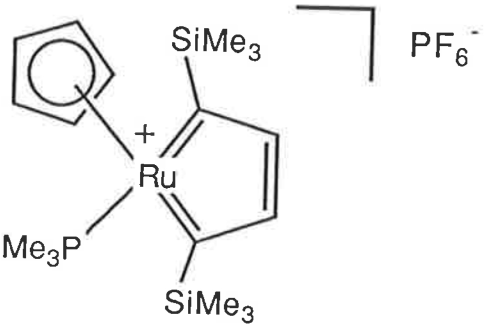
Microanalysis indicated a low carbon percentage and the presence of nitrogen. Presumably this derives from ammonium ion present in the reaction mixture. Qualitative magnetic susceptibility measurements indicated that the complex was paramagnetic but it did not prove possible to obtain either ESR or NMR spectra.

Concentration of the filtrate obtained from the experiment above resulted in the crystallisation of another complex formulated as $[RuCl_2(PMe_3)_2(\eta\text{-}C_5H_5)][PO_2F_2]$ (14) on the basis of microanalytical and spectroscopic data. The presence of the partially hydrolysed anion was confirmed by infrared spectroscopy; there were strong bands at 1055 [ν(PO)] and 840 [ν(PF)] cm^{-1}.[29] The proton NMR spectrum indicated the presence of C_5H_5 and PMe_3 ligands with resonances at δ 2.06 and 6.12, respectively. These data correspond closely with those found for the known complex $[RuCl_2(PMe_3)_2(\eta\text{-}C_5H_5)]$-$[PF_6]$[30] obtained from the reaction of chlorine with (12), which gave a precipitate of the hexafluorophosphate salt. The identity of the cation in (14) was further confirmed by its FAB mass spectrum which contained a base peak at *m/z* 389, corresponding to the molecular cation which fragmented by loss of Cl.

Preparative tlc of the supernatant liquid gave a major mauve band which was crystallised to give $[Ru(HC_2SiMe_3)_2$-$(PMe_3)(\eta\text{-}C_5H_5)][PF_6]$ (15) in low yield. The formulation of this complex followed from the analytical results, and the proton NMR spectrum, which contained two signals at δ 0.27 and 0.36 assigned to two inequivalent trimethylsilyl groups. The signals for the PMe_3 and C_5H_5 ligands were found at δ 1.38 [d, *J*(PH), 13Hz) and 5.40, respectively.

The cyclopentadienyl resonance lies over a signal which could not be resolved. The infrared spectrum confirmed the presence of trimethylsilyl groups giving rise to a strong absorption of 1250 cm^{-1} assigned to the $\nu(SiCH_3)$ deformation. The expected strong $\nu(SiCH_3)$ stretch at 841 cm^{-1} [31] was not observed and probably lies under the broad $\nu(PF)$ band. In the FAB mass spectrum the molecular cation is also the base peak fragmenting principally by the loss of $SiMe_3$; at *m/z* 272 a peak corresponding to, $[Me_3P(HC_2SiMe_3)]^+$ was found.

The structure shown below is postulated for (15).



(15)

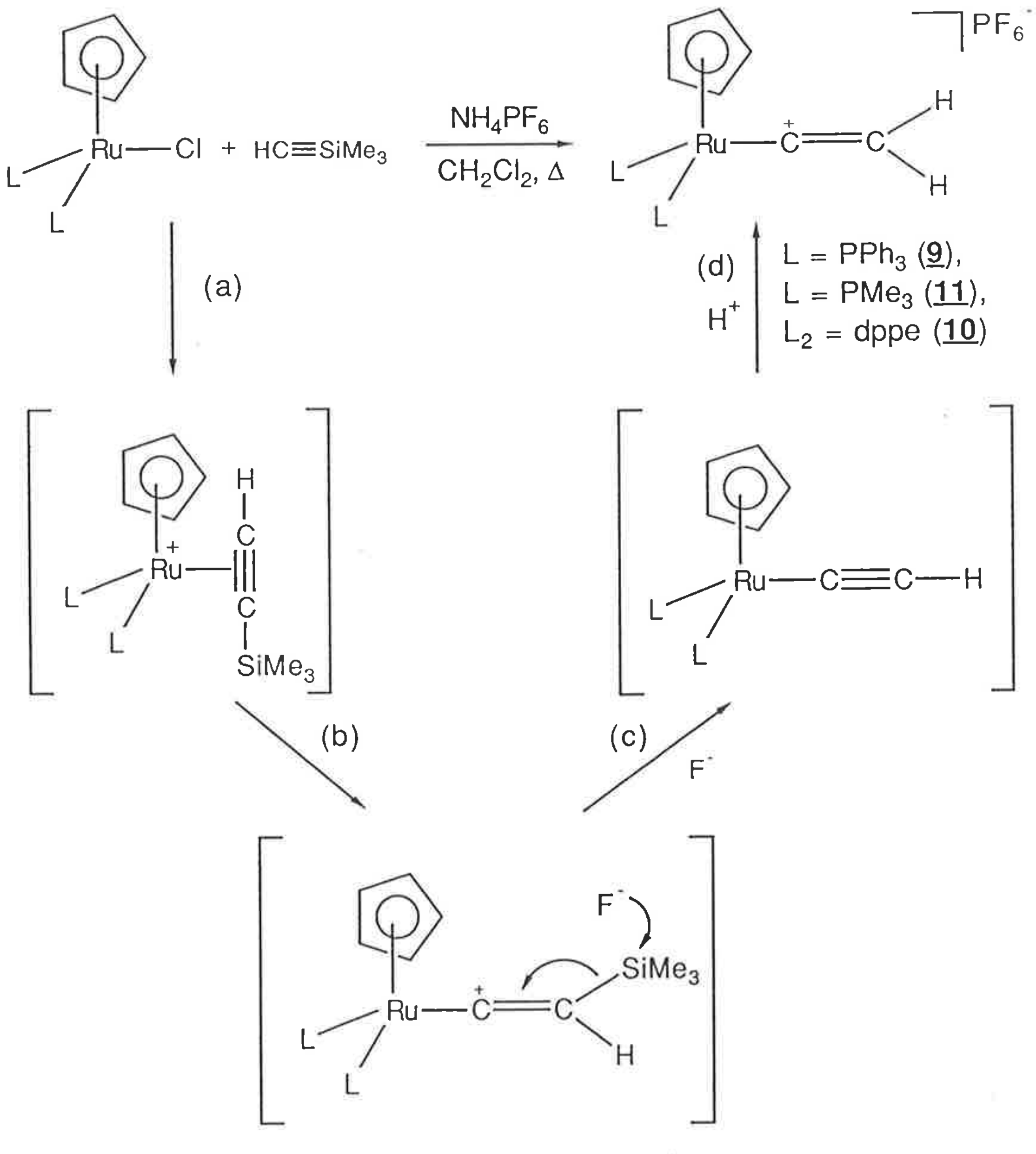
This metallacyclopentatriene structure has precedent in the structurally characterised complex $RuBr(C_4Ph_2H_2)$-$(\eta$-$C_5H_5)$ (16) [32] formed by cyclodimerisation of two molecules of phenylacetylene at the Ru(II) centre in a reaction with $RuBr(\eta^4$-$C_8H_{12})(\eta$-$C_5H_5)$. An alternative ruthenium (IV) metallacyclopentadiene structure cannot be entirely ruled out for (15) as the two $SiMe_3$ groups in (15) are found to be magnetically inequivalent while complex (16) has crystallographic mirror symmetry and the $RuC_4Ph_2H_2$ ruthenacycle is essentially planar, this symmetry being reflected in the NMR spectra (^1H and ^{13}C).

The reaction of $RuCl(PMe_3)_2(\eta-C_5H_5)$ with HC_2SiMe_3 in dichloromethane in the presence of NH_4PF_6 gave, in the strict absence of oxygen or moisture, the expected vinylidene complex $[Ru(C=CH_2)(PMe_3)_2(\eta-C_5H_5)][PF_6]$ (11). Presumably the presence of water or oxygen or both gave rise to complexes (13), (14) and (15). It was not possible to determine the mechanism operating in these latter reactions but it is likely that either the vinylidene or trimethylsilylvinylidene is formed initially. Partial hydrolysis of the PF_6^- ion would explain the presence of the $PO_2F_2^-$ counter ion present in complex (14). This has been found in several other cases, one example being the reaction of the phenyldiazovinylidene $[Ru(C=CPhN=NPh)(PPh_3)_2(\eta-C_5H_5)][PF_6]$ with $HPF_6\cdot OEt_2$ giving $[Ru(C=CPhN=NPh)(PPh_3)_2(\eta-C_5H_5)][PO_2F_2]$.[20]

Possible mechanism for the formation of the unsubstituted vinylidene complexes

As mentioned previously, the formal 1,2-hydrogen shift undergone by many 1-alkynes on transition metal centres has proved to be a useful entry into vinylidene complexes.

The mechanism suggested for the reaction of HC_2SiMe_3 at the ruthenium centres studied is shown in Scheme 1. Initially it is envisaged that the alkyne co-ordinates in an η^2 fashion and then rearranges, by either of the routes mentioned previously, to a coordinated trimethylsilylvinylidene group. This has been shown in the reaction of $RuCl(PMe_3)_2(\eta-C_5H_5)$ with alkynes giving initially $Ru(\eta^2\text{-alkyne})(PMe_3)_2(\eta-C_5H_5)$ [alkyne = HC_2Me or HC_2H] which were found to



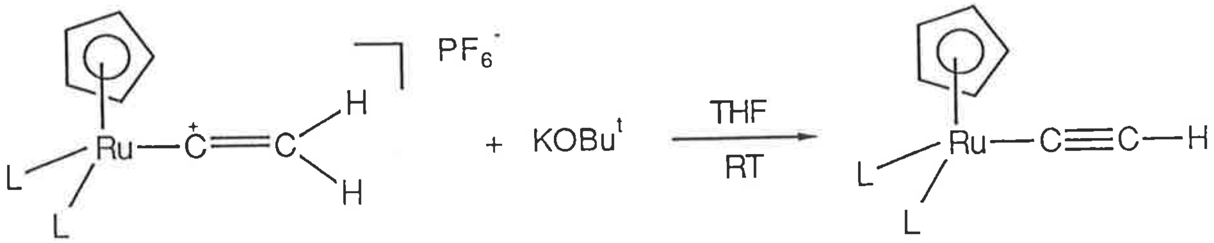
Scheme 1. Possible mechanism of formation of the unsubstituted vinylidene complexes.

rearrange thermally to the corresponding vinylidene complexes. The next step [Scheme 1(c)] postulates cleavage of the C-Si bond with fluoride ion. The affinity of the trimethylsilyl group for fluoride ion is well known, and advantage of this fact is taken in organic chemistry to remove the $SiMe_3$ moiety where it is used to protect a functional group.[33] Fluoride ion required for this step is presumably present in the hygroscopic NH_4PF_6 salt used in this reaction, or by partial hydrolysis of this salt despite precautions taken to dry this material *in vacuo* before use. Nucleophilic attack on halo-, cycloheptatrienyl-[19] and aryldiazo-[20] vinylidenes has been shown to cleanly generate σ-acetylide complexes. Step (d) involves the protonation of the parent acetylide complex at the β-carbon; i.e. electrophilic addition to that electron-rich carbon. Protonation of the related iron complex $Fe(C{\equiv}CH)(dppe)$-$(\eta$-$C_5H_5)$ giving the spectroscopically characterised parent vinylidene complex was reported over a decade ago.[21]

Preparation of ethynyl complexes

Several methods have been described for the synthesis of transition metal acetylides; one method is deprotonation of mono-substituted vinylidene complexes[16,25]. It was this route that led to the parent acetylide complexes described below. Two methods of deprotonating the unsubstituted vinylidenes (9), (10) and (11) were used.

Elution of a dichloromethane solution of $[Ru(C{=}CH_2)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (9), though a column of basic alumina gave a yellow solution from which yellow $Ru(C{\equiv}CH)(PPh_3)_2(\eta\text{-}C_5H_5)$ (17) was obtained. A more convenient preparation of the ethynyl complexes involved treating tetrahydrofuran solutions of the vinylidenes (9), (10) and (11) with $KOBu^t$.



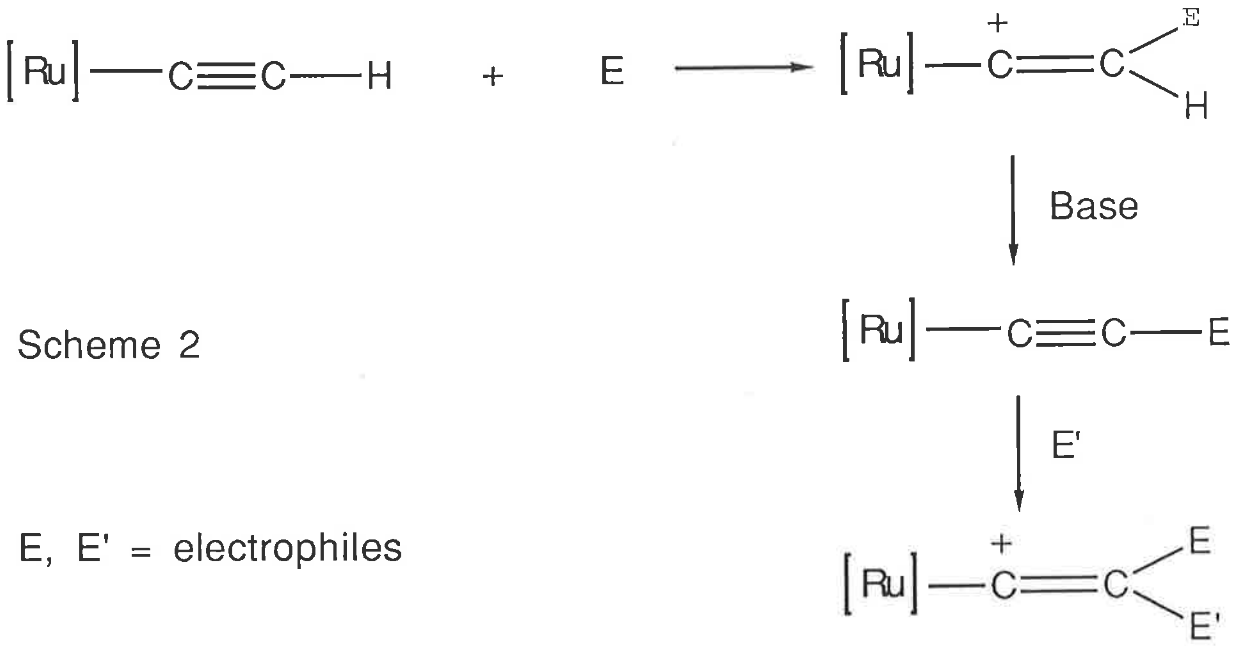
L = PPh_3 (17),
L_2 = dppe (18),
L = PMe_3 (19)

These reactions could be followed by infrared spectroscopy, by disappearance of the medium intensity $\nu(C{=}C)$ band [at *ca* 1620 cm^{-1}] with concomitant appearance of a $\nu(C{\equiv}C)$ band at *ca* 1940 cm^{-1} in tetrahydrofuran.

Characterisation of the extremely air sensitive ethynyl complexes relied principally on their spectroscopic properties. Only complex (18) gave a reliable microanalysis. The infrared spectra of all the complexes contained bands characteristic of the $-C{\equiv}CH$ moiety at *ca* 1940 cm^{-1}; those of (17) and (18) also have weak $\nu(CH)$ bands at 3295 and 3288 cm^{-1}, respectively. The low value for $\nu(C{\equiv}C)$ is found in other unsubstituted transition metal acetylides which generally have $\nu(C{\equiv}C)$ below 2000 cm^{-1}[34]. The alkynyl protons in the ^{1}H NMR of complexes (17) - (19) were found as triplets at δ 1.95, 1.13 and 1.29, respectively, all showing a *ca* 2Hz coupling to the two equivalent ^{31}P nuclei. The cyclopentadienyl resonances shifted to low field with respect to the corresponding resonances in the vinylidene complexes and were found at δ 4.46, 4.74 and 4.55, respectively. The proton NMR of complexes (17) and (18) contained phenyl resonances in the usual region; (18) also contained resonances associated with the dppe methylene protons at δ 2.33 and 2.75. The PMe_3 ligands of complex (19) gave a multiplet at δ 1.41. The $^{13}C\{^{1}H\}$ NMR spectra contained signals for Cα and Cβ at δ 107.1 and 108.0 (Cα), and 96.6 and 95.2 (Cβ) [for (17) and (18), respectively]. The α-carbon resonances were assigned by virtue of the coupling they showed to the two equivalent ^{31}P nuclei [*ca* 20Hz], giving rise to a triplet signal. The expected cyclopentadienyl, methylene and phenyl resonances were found in the usual regions. The FAB mass spectra of complexes (17) - (19) all showed pseudo molecular ions corresponding to $[M + H]^{+}$ at *m/z* 717, 591 and 345, respectively. The principal fragmentation route was loss of the acetylide ligand giving the base peaks: $[Ru(PPh_3)(C_5H_5)]^{+}$, $[Ru(dppe)(C_5H_5)]^{+}$ and $[Ru(PMe_3)(C_5H_5)]^{+}$.

Reactions of ethynyl complexes

These ethynyl complexes provided an opportunity to further functionalise the acetylide linkage by taking advantage of the nucleophilic C_β atom (Scheme 2). Attack of one electrophile (E) would give a monosubstituted vinylidene, which after depronation and reaction with a second electrophile (E or E´) would give the disubstituted vinylidene.



Scheme 2

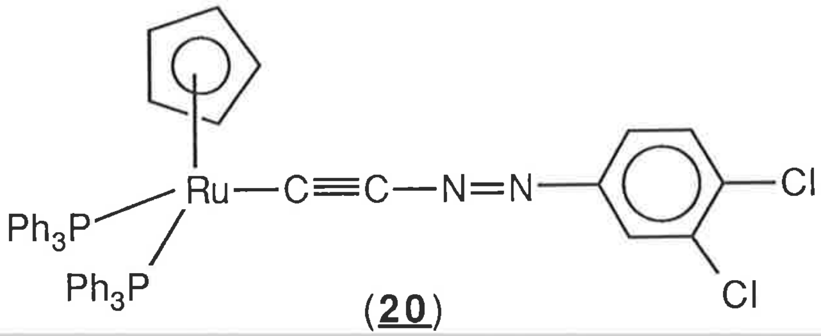
E, E' = electrophiles

Attempted synthesis of aryldiazovinylidenes

Dichloromethane solutions of the ethynyl complex (17) react readily with an equivalent amount of $[ArN_2][X]$ [X= BF_4, PF_6; Ar= Ph, $(C_6H_3Me\text{-}3,4)$, $(C_6H_3Cl_2\text{-}2,3)$] to give highly coloured and air sensitive solutions. On exposure to air these solutions rapidly become yellow and infrared spectroscopy indicated the presence of $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ [ν(CO) 1974 cm^{-1}][35], this complex is also formed from the reaction of (9) with water in tetrahydrofuran.

As this complex is the oxidation product of a large number of vinylidene complexes[6] it is suggested that an aryldiazovinylidene is initially formed which is extremely unstable with respect to aerial oxidation. Some confirmation of this was achieved from the reaction of (17) with $[PhN_2][PF_6]$ in dichloromethane. This gave a maroon solution which was quickly filtered into excess stirred diethyl ether giving a red-brown solid. FAB mass spectrometry of this solid indicated the presence of $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5]^+$ (*m/z* 719) and the spectrum also contained a molecular ion at *m/z* 821 corresponding to $[Ru\{C{=}C(H){-}N{=}N{-}Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ which fragmented by the loss of N_2.

It was, however, possible to deprotonate the intermediate vinylidene formed from the reaction of (17) with $[3,4\text{-}C_6H_3Cl_2N_2][BF_4]$ at low temperatures. The initially-formed red dichloromethane solution was passed through a short column of basic alumina giving neutral orange product tentatively identified as the aryldiazoacetylide complex (20).



(20)

Characterisation is based on its spectroscopic properties. The infrared spectrum has a characteristic strong $\nu(C\equiv C)$ band at 2002 cm^{-1} and the FAB mass spectrum contained a pseudo molecular ion at m/z 889 corresponding to $[M + H]^+$ which lost PPh_3 to give $[Ru(C_2N_2C_6H_3Cl_2)(PPh_3)(C_5H_5)]^+$. Another fragment ion is formed by loss of the aryldiazo moiety and the peak corresponding to $[Ru(PPh_3)(\eta\text{-}C_5H_5)]^+$ is the base peak. The formation of this aryldiazoacetylide represents a facile synthesis of the $C\equiv C\text{-}N=N$ system and the formation of a C-N bond.

Reaction of (17) with bromine

As was seen previously, arylacetylides react readily with halogens to give halo-vinylidene complexes. However, treatment of a tetrahydrofuran solution of (17) with a solution of bromine in CCl_4 immediately gave a red-brown solution from which was isolated the known compound $RuBr(PPh_3)_2(\eta\text{-}C_5H_5)$ (21).[36] This implies a facile cleavage of the Ru-C(sp) bond giving the ruthenium bromide complex (21) and presumably bromoethyne. In this reactivity the ethynyl complexes do not resemble the substituted acetylides discussed previously. The reason for this is probably steric, the smaller hydrogen atom allowing attack on the Ru-C(sp) bond.

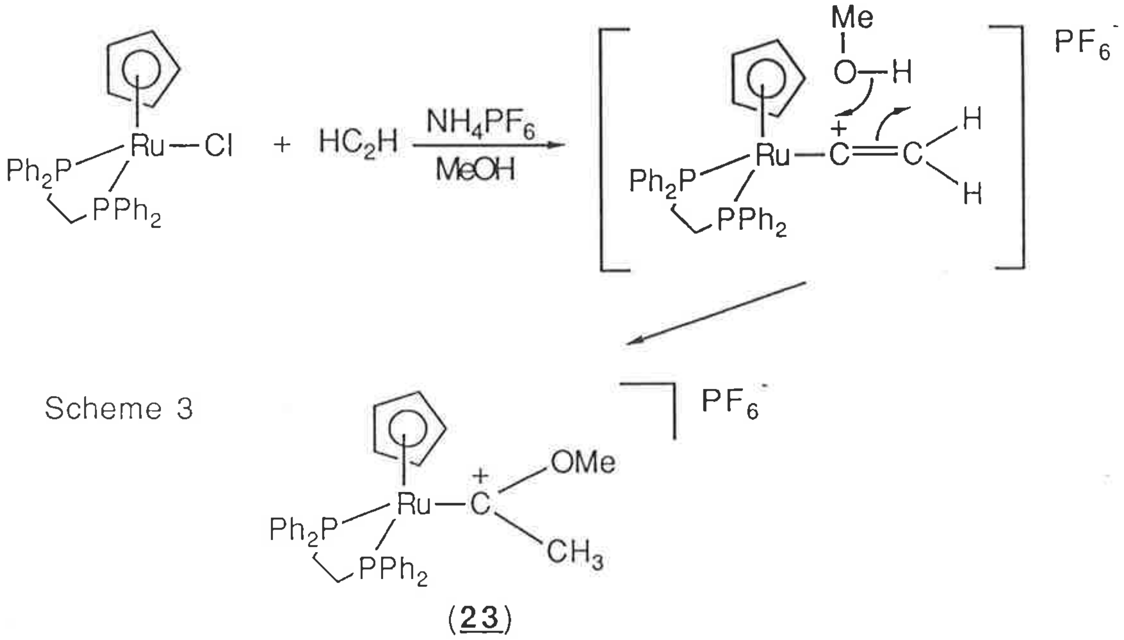
The reactivity of $Ru(C\equiv CH)(PPh_3)_2(\eta\text{-}C_5H_5)$ (17) also differs from that of the substituted acetylides insofar as solutions of (17) rapidly attain a green colouration if exposed to atmospheric oxygen. Green solutions are also obtained from the reaction of (17) with the oxidants $C_7H_7^+$ and MeI which NMR and FAB mass spectrometry indicate both contain mixtures of products. The FAB mass spectrum, however, contains a peak tentatively assigned to the binuclear ion $[\{Ru(PPh_3)_2(\eta-C_5H_5)\}_2C_4H_2]^{2+}$, possibly with a structure similar to that of the structurally-characterised diirondivinylidene, $[Fe_2(\mu-C_4Me_2)(dppe)_2(\eta-C_5H_5)_2][BF_4]_2$, reported recently[37]. This latter complex was formed by oxidative coupling of the corresponding mononuclear vinylidene. A mixture of products was obtained from similar reactions of the analogous CCH_2 complex.[37]

Complexes obtained from reactions in which vinylidene complexes are implicated

The first reactions undertaken by the author in attempts to prepare the parent vinylidene complex (9) involved passing a stream of ethyne through refluxing suspensions or solutions of $RuCl(PPh_3)_2(\eta-C_5H_5)$ in MeOH, thf or CH_2Cl_2 in the presence of NH_4PF_6. This approach gave mixtures of solid products (as shown by FAB MS and NMR) which were inseparable by chromatography. The FAB mass spectra of these solids contained peaks at *m/z* 717 assignable to $[Ru(CCH_2)(PPh_3)_2(C_5H_5)]^+$; higher mass peaks related to the *m/z* 717 peak by sequential addition of C_2H_2 were also found indicating the presence of up to four molecules of ethyne in the product. The FAB MS spectrum also contained peaks related to these ions by loss of PPh_3. It was assumed that ethyne was being oligomerised at the ruthenium centre. Similar products were obtained from reactions between the acetonitrile complex $[Ru(NCMe)(PPh_3)_2(\eta-C_5H_5)][BPh_4]$ and ethyne.

The dppe complex $RuCl(dppe)(\eta-C_5H_5)$ reacted in acetonitrile in the presence of NH_4PF_6 or $AgBF_4$ to give the known complexes $[Ru(NCMe)(dppe)(\eta-C_5H_5)][X]$ (X=PF_6 or BF_4).[38] In dichloromethane, however, the chloro complex reacts with $AgPF_6$ to give a red solution which lightens considerably when ethyne is passed through it. After suitable work-up a pale yellow precipitate of the complex $[Ru(\eta^2-HC_2H)(dppe)(\eta-C_5H_5)][PF_6]$ (22) was obtained. Tentative characterisation of this complex rests on its spectroscopic properties. The infrared spectrum contained a weak ν(C≡C) band at 1750 cm^{-1} characteristic of a co-ordinated acetylene together with a strong band ν(PF) band at 841 cm^{-1}. The FAB mass spectrum contained a molecular cation at *m/z* 591 and another (base) peak formed by loss of HC_2H. This fragmentation differs from that of the unambiguously characterised vinylidene, $[Ru(C=CH_2)$-$(dppe)(\eta-C_5H_5)][PF_6]$ (10), whose FAB mass spectrum has the molecular cation as the base peak.

The chloro complex $RuCl(dppe)(\eta-C_5H_5)$ reacts with ethyne in methanol in the presence of NH_4PF_6 to give a moderate yield of the methoxy(methyl)carbene complex, $[Ru\{C(OMe)Me\}(dppe)(\eta-C_5H_5)][PF_6]$ (23), identified by microanalysis and spectral properties. The infrared spectrum contained strong ν(C-O) and ν(PF) bands at 1247 and 840 cm^{-1}. A molecular cation was observed at *m/z* 623 in the FAB mass spectrum which was also the base peak. Other fragmentations involved loss of -OMe and C(OMe)Me fragments. There have been many reports describing the formation of alkoxycarbene complexes from 1-alkynes[39] in which vinylidene complexes were implicated as intermediates. Subsequently, vinylidene complexes were shown to react with alcohols to give alkoxycarbene complexes.[40] A similar mechanism is thought to be operating in the reaction of the chloro complex with HC_2H in methanol;



Scheme 3

(23)

The analogous PPh_3 complexes, $[Ru\{C(OMe)Me\}(PPh_3)_2(\eta-C_5H_5)]$-$[X][X= PF_6$ (24), Cl (25))] were obtained from the reaction of either $[Ru(NCMe)(PPh_3)_2(\eta-C_5H_5)][PF_6]$ or $RuCl(PPh_3)_2$-$(\eta-C_5H_5)$ with HC_2SiMe_3 in methanol or from the reaction of the vinylidene (9) with MeOH to give (24). Complex (24) has been obtained previously[16], from the reaction of $RuCl(PPh_3)_2(\eta-C_5H_5)$ with HC_2SiMe_3 in MeOH although no characterisation data was presented. The methoxy(methyl)-carbene complexes (24) and (25) were characterised by spectroscopic methods and microanalysis. The spectroscopic data for the cations are essentially identical and only that found for (24) will be discussed. A strong ν(C-O) band was found at 1270 cm^{-1} for the C-OMe group together with the usual ν(PF) band. In the ^{1}H NMR spectrum the methoxy and methyl protons of the carbene ligands appear as sharp singlets at δ 3.28 and 3.03, respectively. Similarly, the ^{13}C NMR spectrum contains singlets at δ 46.4 and 60.7, assigned to Me and OMe, respectively. In the ^{13}C NMR spectrum of (<u>24</u>) the triplet signal at δ 309.2 is assigned to the electron deficient carbene carbon which shows a 12Hz coupling to the two ^{31}P nuclei. Other resonances in the ^{1}H and ^{13}C NMR spectra were consistent with the ligands present. Interestingly, the FAB mass spectrum did not have the molecular cation as base peak that is generally found in other cationic complexes. The molecular cation, *m/z* 749, fragments by loss of Me, C(OMe)Me and PPh_3. The crystal structure of (24) was determined, and is discussed below.

<u>X-ray structure of $[Ru\{C(OMe)Me\}(PPh_3)_2(\eta-C_5H_5)][PF_6]$ (24)</u>

The cation is shown in Figure 3. The structure determination confirms the presence of the methoxy(methyl)carbene ligand (Table 3 collects relevant interatomic parameters). The coordination about the ruthenium atom is distorted octahedral, with the C_5H_5 group occupying three facial sites [Ru-C 2.232(8)-2.292(8), or 2.26Å] and the other three positions being taken up by the two P atoms of the tertiary phosphines [Ru-P(1) 2.332(2); Ru-P(2) 2.336(2)Å] and the carbene ligand [Ru-C(6) 1.931(9)Å].

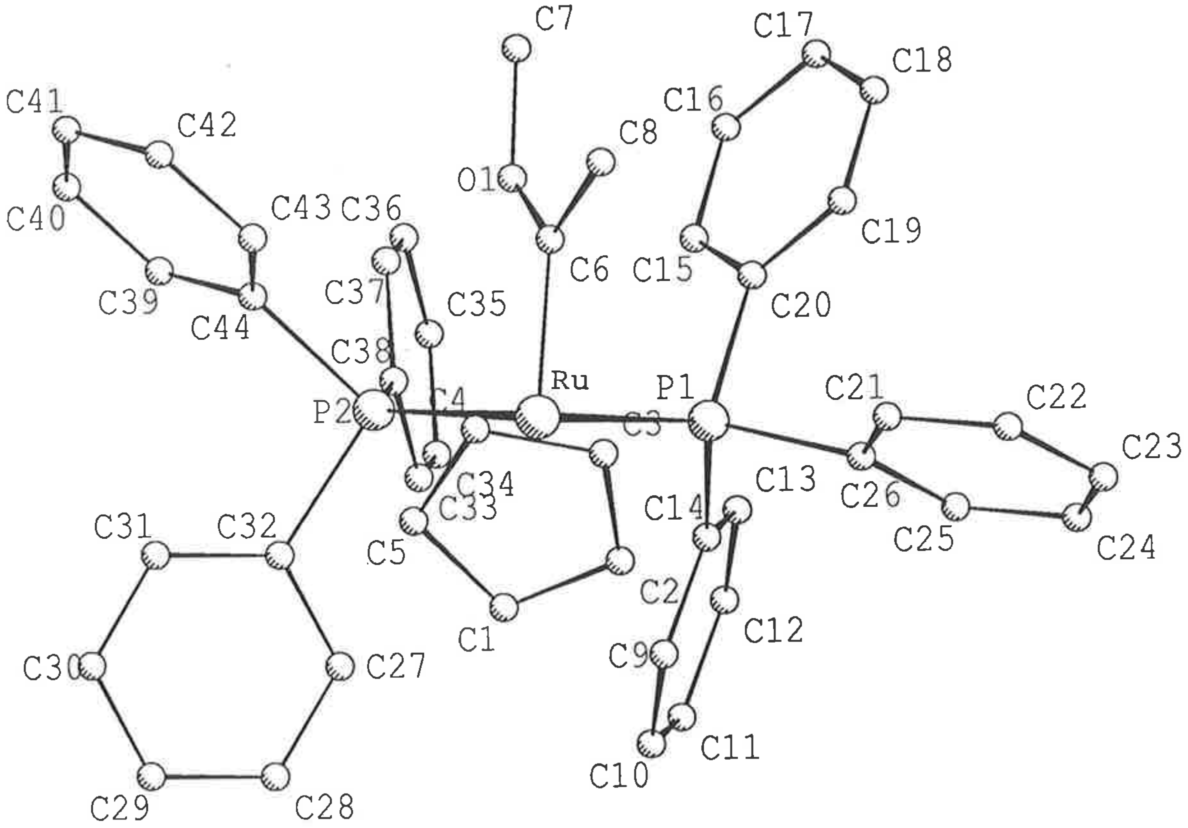
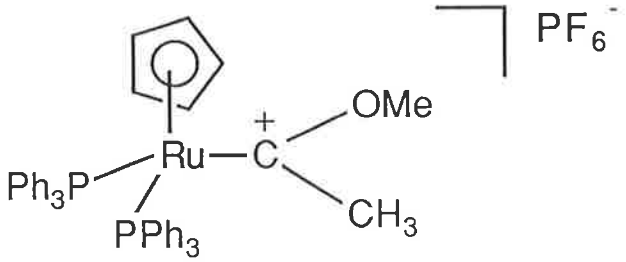


Figure 3: PLUTO plot of the structure of the cation in $[Ru\{C(OMe)Me\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (24) showing the atom-numbering scheme.

Table 3

Selected interatomic parameters for (24)



Bond distances (Å)			Bond angles (°)	
Ru-C(C$_5$H$_5$)	1	2.292(8)	P(1)-Ru-P(2)	101.3(1)
	2	2.244(8)	P(1)-Ru-C(6)	86.6(2)
	3	2.257(8)	P(2)-Ru-C(6)	89.8(2)
	4	2.232(8)	Ru-C(6)-O(1)	120.9(6)
	5	2.250(8)	Ru-C(6)-C(8)	124.8(7)
Ru-P(1)		2.333(2)	O(1)-C(6)-C(8)	114.3
Ru-P(2)		2.336(2)	C(6)-O(1)-C(7)	122.9(7)
Ru-C(6)		1.931(9)		
C(6)-C(8)		1.50(1)		
C(5)-O(1)		1.44(1)		

These values fall within the range found for several other related cyclopentadienyl ruthenium complexes. Complex (24) is isomorphous with [Ru{C(OMe)Et}-$(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (26)[27] and both complexes have similar Ru-Cα bond lengths [1.931(9)(24) and 1.959(6)Å (26)]. These values are intermediate between the distances for the singly bonded Ru-C(sp) in $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$[26] [Ru-C(sp) 2.016(3)Å] and Ru-C(sp^2) in [Ru{C=CPh(I)}-$(PPh_3)_2(\eta\text{-}C_5H_5)][I_3]$ (1) [1.839(7)Å], in which appreciable Ru-C multiple bond character is implied. In the carbene ligand, the α-carbon is sp^2 hybridized, with angles at C(6) of 120.9(6) and 124.8(7)° for Ru-C(6)-O(1) and Ru-C(6)-C(8), respectively; bond lengths from the α-carbon to the methyl and methoxy groups are normal at 1.50(1) and 1.44(1)Å, respectively.

FAB mass spectra of vinylidene complexes

The technique of fast atom bombardment (FAB) mass spectrometry is well suited to the study of ionic and high molecular weight compounds which cannot be volatilised in a conventional electron-impact source. Since the initial report of the utility of FAB mass spectrometry in organo-transition metal chemistry[41] there has been a wide variety of studies described and reviewed.[42,43] FAB MS has proved very useful for the study of cationic vinylidene compounds including the complexes in this chapter. Also included is a discussion of the related cycloheptatrienyl[18,19] - and aryldiazovinylidene[20] complexes.

The major fragmentation route for the halo-, cycloheptatrienyl-, and aryldiazo-vinylidene complexes is loss of the electrophile, added initially in their formation to the corresponding σ-acetylide complex (Tables 4, 6 and 7). The unsubstituted vinylidene complexes (9), (10) and (11) have remarkably stable molecular cations which are also the base peaks (Table 5). Strong peaks corresponding to the loss of ethyne are also found.

The ions $[Ru(C_2R)(PPh_3)_2(C_5H_5)]^+$ in the spectra of (2), (6) and (7), decompose by loss of C_2R, PPh_3 and in the case of (2) loss of C_6H_5 was also observed. Ions corresponding to the carbonyl cation $[Ru(CO)(L)_2(C_5H_5)]^+$, which is the oxidation product of most vinylidene complexes, were found in the spectra of (6) and (7). The base peaks are either $[Ru(PPh_3)(C_5H_5)]^+$ or $[Os(dppe)(C_5H_5)]^+$.

The unsubstituted vinylidene complex (9) has a particularly simple FAB spectrum which contains a molecular cation, and an ion related to it by loss of PPh_3. The only other metal containing ion corresponds to $[Ru(PPh_3)(C_5H_5)]^+$. The spectrum of (9) differs from those of (10) and (11) in not having a peak corresponding to loss of CCH_2. This suggests that the Ru-Cα interaction present in (9) is stronger than in (10) or (11) as a result of back-bonding and this mirrors the relative stability of the three complexes. The spectrum of (10) contains a peak at higher *m/z* corresponding to a water adduct, $[M + H_2O]^+$ and ions reflecting the breakdown of the dppe ligand at *m/z* 378 ($[M - PPh_2C_2H_4]^+$) and *m/z* 352 ($[M - C_2H_2 - PPh_2C_2H_4)$ were also found. Unlike the disubstituted vinylidene complexes, the spectra of (9), (10) and (11)

Table 4. FAB mass spectra of halovinylidene complexes (2), (6) and (7)

Complex	$[M]^+$	$[M+O]^+$	$[M-X]^+$	$[M-X-L]^+$	$[Ru(L)_2(C_5H_5)]^+$	$[Ru(L)(C_5H_5)]^+$	$[Ru(CO)(L)_2(C_5H_5)]^+$	Other ions[d]
(2)[a]	857[e]	7	730	468	691	429		391, $[Ru(C_2Me)(PPh_2)(C_5H_5)]^+$, 36
	(57)	–	(37)	(27)	(23)	(100)	–	350, $[Ru(PPh_2)(C_5H_5)-2H]^+$, 29
(6)[b]	745	761	666	–	565	–	591	380, $[Ru(C_2H_4PPh_2)(C_5H_5)]^+$, 18
	(56)	(5)	(49)		(100)		(32)	
(7)[c]	827	843	792	530	691	429	719	612, $[Ru(PPh_2)(PPh_3)(C_5H_5)]^+$, 4
	(53)	(1)	(6)	(33)	(13)	(100)	(4)	565, $[M-PPh_3]$, 3
								465, $[Ru(C_2Ph)(PPh_3)]^+$, 70
								453, $[Ru(C_2Ph)(PPh_2)(C_5H_5)]^+$, 30
								352, $[Ru(PPh_2)(C_5H_5)]^+$, 27
								287, $[Ru(PPh_2)]^+$, 21
								244, $[RuPh(C_5H_5)]^+$, 18

(a) X=I, R=Me, L=PPh_3 (b) X=Br, R=Ph, L_2 =dppe (c) X=Cl, R=Ph, L=PPh_3 (d) *m/z*, assignment, relative intensity
(e) *m/z* (relative intensity).

Table 5

FAB mass spectra of the unsubstituted vinylidene complexes (9), (10) and (11)

Complex	$[M]^+$	$[M-C_2H_2]^+$	$[Ru(L)-(C_5H_5)]^+$	Other ions[c]
(9)[a]	717[d] (100)	-	429 (60)	455 $[M-PPh_3]$,51
(10)[b]	591 (100)	565 (71)	-	609,$[M+H_2O]$,6 514,$[M-Ph]$,5 488,$[M-C_2H_2-Ph]^+$,5 378,$[M-PPh_2C_2H_4]^+$,11 352,$[M-C_2H_2-PPh_2C_2H_4]^+$,20
(11)	345 (100)	319 (39)	243 (11)	167,$[Ru(C_5H_5)]^+$,0.5

(a) $L=PPh_3$ (b) $L=PMe_3$ (c) *m/z*, assignment, relative intensity

(d) *m/z*, relative intensity.

Table 6. FAB mass spectra of some cycloheptatrienylvinylidene complexes.[19]

Column entries in the form m/z (relative intensity)

Complex	$[M]^+$	$[M\text{-Ph}]^+$	$[M\text{-C}_7\text{H}_7]^+$	$[\text{M(L)}_2(\text{C}_5\text{H}_5)]^+$	$[\text{M(PPh}_2)(\text{C}_5\text{H}_5)]^+$	Other assigned ions
(27)[a]	711[e] (5)	634 (3)	620 (100)	519 (80)	306 (47)	555, $[M\text{-C}_7\text{H}_7\text{-C}_5\text{H}_5]^+$, 5 454, $[\text{Fe(dppe)(C}_5\text{H}_5)\text{-C}_5\text{H}_5]^+$, 12 519, $[\text{Fe(dppe)(C}_5\text{H}_5)\text{-C}_5\text{H}_5]^+$, 8 426, $[\text{Fe(PPh}_2)_2]^+$, 50 398, $[\text{dppe}]^+$, 7 332, $[\text{Fe(C}_2\text{H}_2\text{PPh}_2)(\text{C}_5\text{H}_5)]^+$, 9 320, $[\text{Fe(CH}_2\text{PPh}_2)(\text{C}_5\text{H}_5)]^+$, 15
(28)[b]	757 (7)	680 (5)	666 (50)	565 (100)	350 (61)	911, $[M\text{+matrix}]^+$, 1 379, $[\text{Ru(C}_2\text{H}_4\text{PPh}_2)(\text{C}_5\text{H}_5)]^+$, 33
(29)[c]	973 (42)	-	882 (62)	691 (9)	352 (24)	989, $[M\text{+O}]^+$ 2 954, $[M\text{-F}]^+$, 4 863, $[M\text{-F-C}_7\text{H}_7]^+$, 6 619, $[\text{Ru(C}_2\text{C}_6\text{F}_5)(\text{PPh}_3)(\text{C}_5\text{H}_5)]^+$, 17 448, $[\text{RuF(PPh}_3)(\text{C}_5\text{H}_5)]^+$, 17 429, $[\text{Ru(PPh}_3)(\text{C}_5\text{H}_5)]^+$, 100 287, $[\text{Ru(PPh}_2)]^+$, 14 244, $[\text{RuPh(C}_5\text{H}_5)]^+$, 28 167, $[\text{Ru(C}_5\text{H}_5)]^+$, 14

(a) L_2=dppe, M=Fe (b) L_2=dppe, M=Ru (c) L =PPh_3, M=Ru

(d) m/z, assignment, relative intensity

(e) m/z (relative intensity).

Table 7. FAB mass spectra of some aryldiazovinylidene complexes[20]

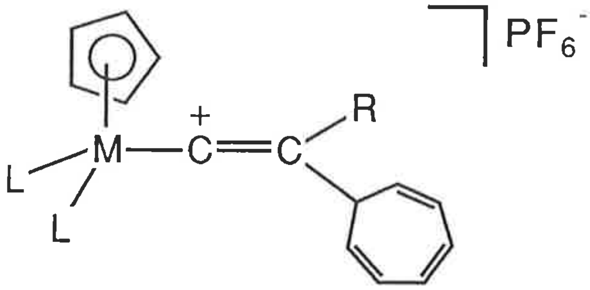
Column entries are in the form *m/z* (relative intensity)

Complex	$[M]^+$	$[M\text{-}N_2]^+$	$[M\text{-}N_2Ar]^+$	$[M\text{-}PPh_3]^+$	$[M(PPh_3)_2\text{-}(C_5H_5)]^+$	$[M(C_2R)\text{-}(C_5H_5)]^+$	$[M(PPh_3)\text{-}(C_5H_5)]^+$	$[M(PPh)\text{-}(C_5H_5)]^+$	Other assigned ions[g]
(30)[a]	880 (15)	-	730 (7)	618 (8)	691 (4)	-	428[d] (100)	-	
(31)[b]	1015 (3)	-	882 (33)	753 (6)	691 (5)	358 (23)	429-427[e] (100)	352 (-)[f]	896, $[M\text{-}NAr]^+$, 2 863, $[M\text{-}N_2Ar\text{-}F]^+$, 4 634, $[M\text{-}PPh_3\text{-}NAr]^+$, 5 620, $[M\text{-}PPh_3\text{-}N_2Ar]^+$, 23 601, $[M\text{-}PPh_3\text{-}N_2Ar\text{-}F]^+$, 7 543, $[Ru(C_2C_6F_5)(PPh_2)(C_5H_5)]^+$, 80 524, $[Ru(C_2C_6F_5)(PPh_2)(C_5H_5)]^+$, 10 287, $[Ru(PPh_2)]^+$, 33 244, $[RuPh(C_5H_5)]^+$, 10 210, $[Ru(PPh)]^+$, 21 167, $[Ru(C_5H_5)]^+$, 20
(32)[c]	987 (7)	959 (12)	-	725 (32)	781 (33)	-	519 (80)	442 (100)	1141, $[M\text{+matrix}]^+$, 17 879, $[(M\text{+matrix})\text{-}PPh_3]^+$, 42 809, $[Os(CO)(PPh_3)_2(C_5H_5)]^+$, 9 697, $[M\text{-}N_2\text{-}PPh_3]^+$, 24 620, $[Os(C_2Ph)(PPh_3)(C_5H_5)]^+$, 64

(a) Ar=$C_6H_4NO_2$-4, M=Ru, R=Me (b) Br=$C_6H_3Me_2$-3,4, M=Ru, R=C_6F_5

(c) Ar=Ph, M=Os, R=Ph (d) assignment $[Ru(PPh_3)(C_5H_5)\text{-}H]^+$

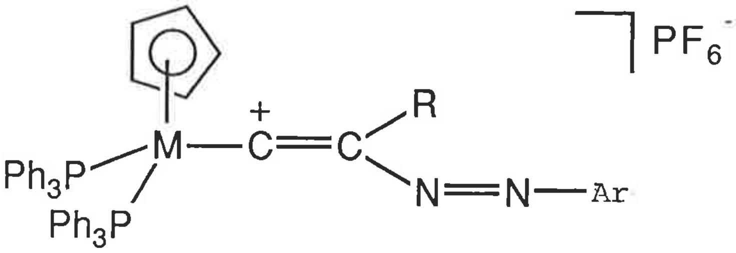
(e) assignment $[Ru(PPh_3\text{-}nH)(C_5H_5)]^+$ (g) *m/z*, assignment, relative intensity



(**27**) M = Fe, L_2 = dppe, R = Ph

(**28**) M = Ru, L_2 = dppe, R = Ph

(**29**) M = Ru, L = PPh_3, R = C_6F_5



(**30**) M = Ru, R = Me, Ar = $C_6H_4NO_2$-4

(**31**) M = Ru, R = C_6F_5, Ar = $C_6H_3Me_2$-3,4

(**32**) M = Os, R = Ph, Ar = Ph

have the molecular cations as the base peaks.

The molecular cations of the cycloheptatrienyl vinylidene complexes (Table 6) fragment by competitive loss of the two vinylidene substituents; loss of C_7H_7 is favoured. The base peak in the spectrum of (27) corresponds to $[Fe(C_2Ph)(dppe)(C_5H_5)]^+$ (*m/z* 620), strong analogous ions were found in the spectra of (28) and (29). The peak at *m/z* 620 in the spectrum of (27) fragments by loss of C_2Ph to give $[Fe(dppe)(C_5H_5)]^+$ and an unusual loss of C_5H_6 from this ion gave $[Fe\{C_2H_3(PPh_2)_2\}]^+$, which can be formulated as containing a 5e donor $[C_2H_3(PPh_3)]^-$ ligand. Other breakdown routes include elimination of C_6H_6 or C_2H_4 molecules; at lower *m/z* ions containing PPh_2, CH_2PPh_2 and $C_2H_2PPh_2$ fragments attached to the $Fe(C_5H_5)$ moiety were found. Fragmentation of the ruthenium analogue (28) proceeds more cleanly, the base peak being $[Ru(dppe)(C_5H_5)]^+$ which loses PPh_2 and C_2H_4. The most interesting feature of the spectrum of (29) is the peak at *m/z* 448 assigned to $[RuF(PPh_3)(C_5H_5)]^+$ probably formed by transfer of fluorine to the metal with elimination of $C_2C_6F_4$. The molecular cation fragments by competitive loss of Ph, C_7H_7 and F. The latter fragmentation gives a peak at *m/z* 954 which further decomposes by loss of C_7H_7 giving an ion at *m/z* 863 assigned to $[Ru(C_2C_6F_4)(PPh_3)_2(C_5H_5)]^+$.

The aryldiazo-complexes (Table 7) all contain ions corresponding to the molecular cation; the osmium complex (32) also forms a matrix adduct ion at higher *m/z*. Two major fragmentation routes are loss of PPh_3 and of the aryldiazo group. In the case of (31) loss of arylnitrene occurs while with (<u>32</u>) loss of N_2 gives an ion at *m/z* 959. The base peaks are centred on *m/z* 427 for (<u>30</u>) and (<u>31</u>) while the analogous ion at *m/z* 519 ($[Os(PPh_3)(C_5H_5)]^+$) is found, the relative intensity of the phosphido ion $[Os(PPh_2)(C_5H_5)]^+$ is greater.

CONCLUSIONS

Ruthenium and osmium σ-acetylide complexes react with halogens to give cationic halovinylidene derivatives; in one case halogenation of the phenyl group of a phenylacetylide ligand has also occurred. These can be isolated as polyhalide (Br_3^-, I_3^-) salts and nucleophiles such as H^- or $\bar{O}Me^-$ displace X^+ to give the corresponding acetylide complex.

The reaction of ruthenium-halide complexes with HC_2SiMe_3 in CH_2Cl_2 in the presence of NH_4PF_6 represents an excellent synthesis of unsubstituted vinylidene complexes $[Ru(C{=}CH_2)(L)_2(\eta\text{-}C_5H_5)]^+$, ($L{=}PPh_3, PMe_3$; L_2=dppe). These cations were readily deprotonated by basic alumina or $KOBu^t$ giving the unsubstituted σ-acetylide complexes $Ru(C_2H)(L)_2(\eta\text{-}C_5H_5)$ and this parallels the reactivity of mono-substituted vinylidene complexes. These new vinylidene complexes also react with water and alcohols in a similar manner to other vinylidene complexes.

The addition of Br_2 to a solution of $Ru(C_2H)(PPh_3)_2(\eta\text{-}C_5H_5)$ results in the cleavage of the Ru-C(sp) bond which is in direct contrast to the reactivity of the substituted ruthenium σ-acetylides.

Complexation of the transient vinylidene moiety to transition metals has afforded the opportunity to study reactions of this species.

EXPERIMENTAL

General conditions

All reactions were performed under nitrogen using dried degassed solvents; no special precautions were taken to exclude air during workup since most complexes proved to be stable in air as solids and for short times in solution except for the syntheses and reactions of the unsubstituted vinylidene and acetylide complexes, when Schlenk techniques were used to exclude oxygen. Solvents used for Chromatrography and spectroscopy were LR and spectroscopic grade, respectively. All other solvents were AR grade and were dried and distilled under a nitrogen atmosphere. The light petroleum spirit used was a fraction of b.p. 62-66°C. Melting points were measured in sealed capillaries using a Gallenkamp melting point apparatus and are uncorrected.

Column chromatography was performed under N_2, using water-jacketed columns (15 x 350 or 35 x 350 mm) with silica (200-325 Mesh, AJAX), Florisil (60-100 Mesh, BDH), neutral alumina (100-125 Mesh, activity:grade 1, Fluka) and basic alumina (100-125 Mesh, activity:grade 1, Woelm) as adsorbents; preparative tlc was on 20 x 20 cm plates coated with Kieselgel 60 GF_{254} (Merck, Darmstadt).

A small autoclave (Roth, 100 ml) equipped with Teflon gaskets and a glass liner was used for pressurised reactions at less than 80 atm. Low pressure syntheses were performed in thick-walled Carius tubes fitted with Rotaflo high vacuum taps.

Microanalyses were performed by the Canadian Microanalytical Service, New Westminster, British Columbia, Canada.

Instrumentation

Infrared: Perkin-Elmer 683 double-beam and Perkin-Elmer 1720 X FT spectrometers, NaCl optics, calibrated using polystyrene absorption at 1601.4 cm^{-1}.

NMR: Bruker CXP300 (^{1}H NMR at 300.13 MHz, ^{31}P NMR at 121.49 MHz, ^{13}C NMR at 75.47 MHz) and Bruker WP80 (^{1}H NMR at 80 MHz, ^{13}C NMR at 20.1 MHz). Chemical shifts (300K) to low field are denoted positive; internal references were $SiMe_4$ (^{13}C and ^{1}H NMR); the external reference for ^{31}P NMR was 0.1M HCl/0.01M H_3PO_4 in D_2O (δ + 0.8 ppm). The shifts quoted for the ^{31}P NMR spectra are relative to 85% H_3PO_4. With spectra recorded in non-deuterated solvents, D_2O in a concentric tube was used for the field lock.

Mass spectra: FAB mass spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon or xenon were used as FAB gases, with source pressures typically 10^{-6} bar; the FAB gun voltage was 7.5kV current 1mA. The ion-accelerating potential was 7 kV. The samples were made up as *ca* 0.5 M solution in CH_2Cl_2; a drop was added to a drop of matrix (3-nitrobenzyl alcohol), and the mixture was applied to the FAB probe tip Spectra reported below in the form: *m/z*, assignment, relative intensity; multi-isotopic species are normalized on the most abundant metal isotope. All metal-containing ions with relative intensities greater than 10% of the base peak are listed as well as assigned minor ions. Peaks marked with an asterisk are the strongest of multiplets related to the assigned formulation by addition or loss of one or two H atoms. Most of the spectra were recorded within two minutes of sample introduction to avoid any decomposition and/or side reactions. EI mass spectra were obtained on a GEC-Kratos MS3074 mass spectrometer (70eV ionizing energy, 4kV accelerating potential).

Starting materials

Literature methods were used to prepare RuCl(L)$_2$-(η-C_5H_5) (L=PPh_3,[44] PMe_3;[45] L_2=dppe),[38] Ru(C_2R)(PPh_3)$_2$-(η-C_5H_5) (R=Ph,[44] C_6F_5,[25] Me),[25] Ru(C_2Ph)(dppe)(η-C_5H_5),[25] Os(C_2Ph)(PPh_3)$_2$(η-C_5H_5)[25] and [Ru(NCMe)(PPh_3)$_2$(η-C_5H_5)]-[PF_6].[46] The diazonium salt, [3,4-$C_6H_3Cl_2N_2$][BF_4] was made by diazotisation of the appropriate aniline with $NaNO_2$/HBF_4; HC_2SiMe_3 (Fluka) and KOBu^t (Fluka) were obtained commercially. Ethyne (Commonwealth Industrial Gases) was pre-purified by passage through H_2SO_4 (conc.).

Syntheses

A. Preparation of halovinylidenes

(a) Reaction of iodine

(i) with Ru(C_2Ph)(PPh_3)$_2$(η-C_5H_5) - Addition of iodine (160 mg, 0.603 mmol) to a stirred solution of Ru(C_2Ph)(PPh_3)$_2$-(η-C_5H_5) (200 mg, 0.253 mmol) in thf (20 ml) resulted in an immediate colour change to dark green. After 20 min and evaporation to dryness, the residue was extracted with CH_2Cl_2 (*ca* 2 ml) and the extract filtered into excess stirred diethyl ether to give green microcrystals of [Ru{C=C(I)Ph}-(PPh_3)$_2$(η-C_5H_5)][I_3] (1) (281 mg, 85%). An analytical sample was recrystallised from CH_2Cl_2/EtOH, m.p. 134-135°C (dec.). [Found: C, 44.85; H, 3.11; I, 36.56; $C_{49}H_{40}I_4P_2Ru$ requires C, 45.29; H, 3.10; I, 39.06%]. Infrared (Nujol): ν(C=C) 1638s; other bands at 1590w, 1518w, 1480sh, 1438m, 1435m, 1412w, 1310w, 1187w, 1160w, 1092s, 1075w, 1040w, 1018w, 998w, 845s, 823m, 770w, 745s, 722w, 705w, 695vs, 613w cm^{-1}. ^1H NMR: $[(CD_3)_2CO]$ 5.46 (s, 5H, C_5H_5); 7.57 (m, 35H, Ph).

(ii) with $Ru(C_2Me)(PPh_3)_2(\eta-C_5H_5)$ - As in (i) above, iodine (200 mg, 0.788 mmol) and $Ru(C_2Me)(PPh_3)_2(\eta-C_5H_5)$ (200 mg, 0.274 mmol) afforded $[Ru\{C=C(I)Me\}(PPh_3)_2(\eta-C_5H_5)]$-$[I_3]$ (2) as dark olive-green crystals (293 mg, 86%), m.p. 140-142°C (dec.). [Found: C, 42.55; H, 3.10; I, 40.03, *M* (mass spectrometry) 857; $C_{44}H_{39}I_4P_2Ru$ requires C, 42.68; H, 3.15; I, 41.00%; *M* 857]. Infrared (Nujol): $\nu(C=C)$ 1690m; other bands at 1482m, 1438s, 1370w, 1185w, 1080m, 1035w, 1000m, 836w, 823w, 750m,742m, 699s, 665m cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 2.22 (s, 3H, Me); 5.26 (s, 5H, C_5H_5); 7.03-7.39 (m, 30H, Ph). $^{13}C\{^1H\}$ NMR: $\delta(CDCl_3)$ 15.6 (s, Me); 95.1 (s, C_5H_5); 127.7-133.9 (m, Ph); 325.9 [t, *J*(PC) 15Hz, Ru=C].

(iii) with $Ru(C_2C_6F_5)(PPh_3)_2(\eta-C_5H_5)$ - As in (i) above, iodine (150 mg, 0.59 mmol) and $Ru(C_2C_6F_5)(PPh_3)_2(\eta-C_5H_5)$ (200 mg, 0.227 mmol) gave $[Ru\{C=C(I)C_6F_5\}(PPh_3)_2(\eta-C_5H_5)]$-$[I_3]$ (3) as dark green microcrystals (118 mg, 38%), m.p. 124-125°C. [Found: C, 41.40; H, 2.55; I, 34.52; $C_{49}H_{35}F_5I_4P_2Ru$ requires C, 42.36: H, 2.54; I, 36.53%]. Infrared (Nujol): $\nu(C=C)$ 1652m; other bands at 1588w, 1519s, 1497vs, 1482m, 1439s, 1310w, 1188w, 1159w, 1131w, 1100m, 1091m, 1012w, 1000w, 934s, 857w, 835w, 828w, 752s, 745s, 739w, 705sh, 697vs, 660m cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 5.40 (s, 5H, C_5H_5); 7.27-7.36 (m, 30H, Ph).

(iv) with $Os(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ - As in (i) above, iodine (73 mg, 0.288 mmol) and $Os(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ (80 mg, 0.091 mmol) afforded $[Os\{C{=}C(I)Ph\}(PPh_3)_2(\eta-C_5H_5)]$-$[I_3]$ (4) as dark green crystals (63 mg, 50%), m.p. 198-199°C. [Found: C, 41.97; H, 2.93; I, 35.46; $C_{49}H_{40}I_4OsP_2$ requires C, 42.36; H, 2.54; I, 36.53%]. Infrared (Nujol): ν(C=C) 1640m; other bands at 1360w, 1260m, 1100m, 1090s, 1000w, 842m, 825m, 742s, 722m, 696s, 660m cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 5.44 (s, 5H, C_5H_5); 6.9-7.4 (m, 35H, Ph).

(b) Reactions of bromine

(i) with $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ - Neat bromine (1 ml, excess) was added dropwise to a stirred solution of $Ru(C_2Ph)$-$(PPh_3)_2(\eta-C_5H_5)$ (1000 mg, 1.26 mmol) in thf (10 ml) to give immediately a dark green solution. After 15 min, evaporation to dryness, extraction of the residue with CH_2Cl_2 (*ca* 5 ml) and filtration into excess Et_2O afforded green microcrystals of $[Ru\{C{=}C(Br)(C_6H_4Br\text{-}4)\}(PPh_3)_2(\eta-C_5H_5)][Br_3]\cdot Et_2O$ (5) (1401 mg, 88%). [Found: C, 47.01; H, 3.38; Br, 30.25; $C_{49}H_{39}Br_5P_2Ru\cdot C_4H_{10}O$ requires C, 46.54; H,3.11; Br, 31.60%]. Infrared (KBr): ν(C=C) 1638s; other bands at 3060w, 2930w, 2860w, 1482s, 1435s, 1412w, 1392w, 1315w, 1272w, 1178w, 1160w, 1092s, 1072m, 1029w, 1009w, 1000m, 848m, 825m, 752sh, 740s, 730m, 695vs, 685sh, 660w, 538s, 523vs, 574w, 498m, 490m, 465w, 441w, 426w cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 1.21 [t, *J*(HH) 7Hz, 6H, $(C\mathit{H}_3CH_2)_2O$; 3.48 [q, 4H $(CH_3C\mathit{H}_2)_2O$]; 5.35 (s, 5H, C_5H_5), 6.6-7.5 (m, 34H, Ph). $^{13}C\{^1H\}$ NMR: $\delta(CDCl_3)$ 17.2 (s, C_5H_5); 128.0-135.0 (m, Ph).

Metathesis of the tribromide counter ion was achieved by stirring a solution of the vinylidene with a twofold excess of NH_4PF_6 in CH_2Cl_2. [Found: C, 52.12; H, 3.77; Br, 15.06;

$C_{49}H_{39}Br_2F_6P_3Ru$ requires C, 53.72; H, 3.59; Br, 14.59%].

(ii) with $Ru(C_2Ph)(dppe)(\eta-C_5H_5)$ - To a stirred solution of $Ru(C_2Ph)(dppe)(\eta-C_5H_5)$ (200 mg, 0.30 mmol in thf (15 ml) was added a bromine solution (20 ml of *ca* 0.038 mmol ml^{-1} solution in CCl_4; 0.75 mmol) resulting in formation of a green precipitate of $[Ru\{C{=}C(Br)Ph\}(dppe)(\eta-C_5H_5)][Br]\cdot 0.5\ Et_2O$ (6) (251 mg, 100%). Dark green crystals, m.p. 79-80°C (dec.) were obtained from addition of Et_2O to a concentrated CH_2Cl_2/EtOH solution of (6). [Found: C, 55.97; H, 4.60; Br, 18.73; *M* (mass spectrometry) 745; $C_{39}H_{34}Br_2P_2Ru\cdot 0.5\ Et_2O$ requires C, 57.09; H, 4.56; Br, 18.53%; *M* 745]. Infrared (Nujol): ν(C=C) 1640s; other bands at 1488sh, 1445s, 1439vs, 1419m, 1358w, 1312w, 1100s, 1071w, 1045m, 1000w, 880w, 850m, 831m, 798w, 758m, 750m, 742m, 718s, 706s, 690s, 618m cm^{-1}. ^{1}H NMR: $\delta(CDCl_3)$ 1.20 [t, *J*(HH) 7Hz, 3H, $(CH_3CH_2)_2O$]; 2.5-3.8 [m, 6H, PCH_2 + $(CH_3CH_2)_2O$]; 5.63 (s, 5H, C_5H_5); 7.34 (m, 25H, Ph).

(c) Reaction of chlorine with $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$

A stirred solution of $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ (200 mg, 0.25 mmol) in thf (20 ml) was treated with a solution of chlorine [6 ml of a 0.13 mmol ml^{-1} solution in Et_2O; 0.77 mmol] immediately giving a green solution. After 20 min, the solution was filtered and evaporated to dryness. The residue was extracted with CH_2Cl_2 (20 ml) and NH_4PF_6 (300 mg, 1.84 mmol) was added to the solution. After 10 min, addition of EtOH to the filtered solution and reduction in volume resulted in the formation of emerald green needles of $[Ru\{C=C(Cl)Ph\}(PPh_3)_2(\eta-C_5H_5)][PF_6]$ (7) (70 mg, 28%), m.p. 139-141°C (dec.). [Found: C, 56.95; H, 4.07; Cl, 8.93; *M* (mass spectrometry) 827; $C_{49}H_{40}ClF_6P_3Ru$ requires C, 60.53; H, 4.14; Cl, 7.04%; *M* 827]. Infrared (Nujol): ν(C=C) 1650s, ν(PF) 840vs(br); other bands at 1483s, 1430s, 1416m, 1312m, 1270m, 1220w, 1160m, 1092s, 1075sh, 1030w, 1020w, 1000m, 880m, 860vs, 790m, 745sh, 739s, 697vs, 640sh, 635w, 620w cm^{-1}. ^{1}H NMR: δ($CDCl_3$) 5.63 (s, 5H, C_5H_5), 7.10-7.73 (m, 35H, Ph).

B. Reaction of $[Ru\{C=C(Br)(C_6H_4Br-4)\}(PPh_3)_2(\eta-C_5H_5)][PF_6]$ (5)

(a) with $K[BH(CHMeEt)_3]$ - Treatment of a green solution of (5) (200 mg, 0.182 mmol) in thf (10 ml) with $K[BH(CHMeEt)_3]$ (0.4 ml of a 0.5 mol L^{-1} solution in thf; 0.20 mmol) gave a yellow solution. Addition of MeOH (10 ml) and reduction in volume (to *ca* 5 ml) gave a yellow precipitate of $Ru(C_2C_6H_4Br-4)(PPh_3)_2(\eta-C_5H_5)$ (8) (101 mg, 64%), m.p. 192-197°C (dec.). [Found: C, 67.40; H, 4.82; Br, 9.01; *M* (EI mass spectrometry) 872; $C_{49}H_{39}BrP_2Ru$ requires C, 67.59; H, 4.51; Br, 9.18%; *M* 872). Infrared (Nujol): ν(C≡C) 2076vs; other bands at 1587w, 1482s, 1436s, 1210w, 1185w, 1160w, 1095m, 1090m, 1068m, 1005m, 828m, 822w, 810w, 800w, 759m, 747m, 739w, 699vs cm^{-1}. ^{1}H NMR: δ($CDCl_3$) 4.32 (s, 5H, C_5H_5); 7.14 (m, H, Ph + C_6H_4).

(b) with Sodium methoxide - A solution of (5) (200 mg, 0.182 mmol) in CH_2Cl_2 (20 ml) was treated with NaOMe (0.5 ml of *ca* 1 mol L^{-1} solution in MeOH; 0.5 mmol) giving a yellow solution. After filtering, addition of MeOH (10 ml) and concentration of the solution (to *ca* 5 ml) a yellow powder of (<u>8</u>) was obtained (84 mg, 53%). Identified by comparison of its ^{1}H NMR and i.r. spectra with those of an authentic sample.

C. <u>Synthesis and reactivity of vinylidene complexes</u>

(a) <u>Reaction between RuCl(L)$_2$(η-C$_5$H$_5$) and HC$_2$SiMe$_3$</u>

(i) <u>L=PPh$_3$</u> - A mixture of RuCl(PPh$_3$)$_2$(η-C$_5$H$_5$) (400 mg, 0.551 mmol), HC$_2$SiMe$_3$ (0.32 ml, 2.26 mmol) and NH$_4$PF$_6$ (180 mg, 1.10 mmol) in dry, distilled CH$_2$Cl$_2$ (40 ml) was heated in an oil bath (58-65°C) for 7 h. The suspension was filtered into excess stirred diethyl ether giving a light yellow precipitate of [Ru(C=CH$_2$)(PPh$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$] (<u>9</u>) (410 mg, 86%), m.p. >150°C (dec.). [Found: C, 60.11; H, 4.30; *M* (mass spectrometry) 717; C$_{43}$H$_{37}$F$_6$P$_3$Ru requires C, 59.94; H, 4.33%; *M* 717]. Infrared (Nujol): ν(C=C) 1628m, ν(PF) 844vs(br); other bands 3057w, 1434s, 1092m, 1071m, 1025w, 1010w, 1000w, 935vw, 930vw, 920vw, 880m, 750m, 748m, 741m, 700s, 695s cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 4.34 [t, *J*(PH) 2Hz, 2H, C=CH$_2$]; 5.09 (s, 5H, C$_5$H$_5$); 7.0-7.42 (m, 36H, Ph). ^{13}C{^{1}H} NMR: δ[CH$_2$Cl$_2$,Cr(acac)$_3$] 95.0 (s, C$_5$H$_5$); 99.9 (s, C$_\beta$); 128.0-134.0 (m, Ph); 347.2 [t, *J*(PC) 15Hz, C$_\alpha$].

(ii) <u>L$_2$=dppe</u> - A mixture of RuCl(dppe)(η-C$_5$H$_5$) (116 mg, 0.193 mmol), HC$_2$SiMe$_3$ (0.20 ml, 1.42 mmol) and NH$_4$PF$_6$ (121 mg, 0.742 mmol) in CH$_2$Cl$_2$ (10 ml) was sealed in a Carius tube under vacuum and heated at 90°C for 48 h. The turbid solution was transferred to a Schlenk tube, reduced in volume (*ca* 5 ml) and filtered into excess stirred diethyl ether (*ca* 100 ml) to give a pale yellow precipitate of $[Ru\{C{=}CH_2\}(dppe)(\eta\text{-}C_5H_5)][PF_6]$ (<u>10</u>) (100 mg, 70%) m.p. >150°C (dec.). [Found: C, 54.00; H, 4.18; *M* (mass spectrometry) 591 $C_{33}H_{31}F_6P_3Ru$ requires C, 53.88; H, 4.25%; *M* 591]. Infrared (thf): ν(C=C) 1631 cm^{-1}; (Nujol): ν(C=C) 1641m, ν(P-F) 841vs(br); other bands 1426s, 1421m, 1307w, 1161w, 1105m, 1068m, 1009w, 1001w, 929w, 876m, 860vs, 851vs, 755m, 748m, 725m, 715m, 706m, 700s, 691m, 680m, 653m cm^{-1}. ^1H NMR: $\delta(CD_2Cl_2)$ 2.95 (m, 4H, PCH_2); 3.19 [t, *J*(PH) 1.5Hz, 2H, $C{=}CH_2$]; 5.37 (s, 5H, C_5H_5); 7.16-7.57 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR: $\delta[(CD_3)_2CO, Cr(acac)_3]$ 93.4 (s, C_5H_5); 96.7 (s, C_β); 130.0-136.0 (m, Ph); 343.0 (t, *J*(PH) 18Hz, C_α].

(iii) <u>$L{=}PMe_3$</u> - As in (i) above, $RuCl(PMe_3)_2(\eta\text{-}C_5H_5)$ (201 mg, 0.568 mmol), HC_2SiMe_3 (0.32 ml, 2.12 mmol) and NH_4PF_6 (187 mg, 1.15 mmol) after 24 h afforded a light yellow precipitate of $[Ru\{C{=}CH_2\}(PMe_3)_2(\eta\text{-}C_5H_5)]$-$[PF_6]$ (<u>11</u>) (242 mg, 87%), m.p. >150°C (dec.). [Found: C, 31.70; H, 5.30%; *M* (mass spectrometry) 345: $C_{13}H_{25}F_6P_3Ru$ requires C, 31.91; H, 5.15%, *M* 345]. Infrared (Nujol): ν(C=C) 1625; ν(P-F) 840; other bands 1325w, 1312w, 1300m, 1240w, 1020w, 970w, 950m, 880w, 865w, 820m, 741w, 715w, 680w cm^{-1}. ^1H NMR: $\delta(CD_2Cl_2)$ 1.62 (m, 18H, PMe); 3.76 [t, *J*(PH) 2.4Hz, $C{=}CH_2$]; 5.42 (s, 5H, C_5H_5).

Alternatively, a mixture of $RuCl(PMe_3)_2(\eta-C_5H_5)$ (91 mg, 0.26 mmol), HC_2SiMe_3 (0.05 ml, 35 mg, 0.36 mmol) and NH_4PF_6 (110 mg, 0.68 mmol) in CH_2Cl_2 (10 ml) was heated at reflux for 3 d. Filtration yielded a dark green paramagnetic powder which was not identified (71 mg). [Found: C, 5.74; H, 2.89; N; 8.19%]. The green solution was concentrated (*ca* 5 ml) to give crystals of a second green complex characterised as $[RuCl_2(PMe_3)_2(\eta-C_5H_5)]$-$[PO_2F_2] \cdot 2CH_2Cl_2$ (<u>14</u>) (18 mg, 14%), m.p. >150°C (dec.). [Found: C, 23.60; H, 4.10; *M* (mass spectrometry) 389; $C_{11}H_{23}Cl_2F_2O_2P_3 \cdot 2CH_2Cl_2$ requires C, 23.63; H, 4.12%; *M* 389]. Infrared (Nujol): ν(PO) 1055s(br); ν(PF) 840vs(br); other bands 3125m, 1420s, 1309w, 1295sh, 1290s, 1285m, 748m, 740m, 675m cm^{-1}. ^1H NMR: $\delta[(CD_3)_2CO]$ 2.06 (m, 18H, PMe_3); 6.12 (s, 5H, C_5H_5). FAB MS: 389, $[M]^+$, 100; 354, $[M - Cl]$, 19. The supernatant solution was then separated by preparative tlc (acetone-light petroleum; 1:1) giving a major mauve band (R_f 0.75) which was crystallised from C_6H_6/EtOH to give mauve crystals of $[Ru(HC_2SiMe_3)_2(PMe_3)(\eta-C_5H_5)][PF_6]$(<u>15</u>) (12 mg, 8%), m.p. 150°C (dec.). [Found: C, 36.86; 5.89; *M* (mass spectrometry) 439; $C_{18}H_{34}F_6P_2RuSi_2$ requires C, 37.04; H, 5.87%; *M* 439]. Infrared (Nujol): ν(SiMe) 1250s, ν(PF) 840vs(br); other bands 1312w, 1304w, 1297m, 1250s, 1190m, 1109w, 1092m, 979m, 965m, 959m, 940w, 910w, 878s, 762m, 740w, 722w, 700w cm^{-1}. ^1H NMR: $\delta[(CD_3)_2CO]$ 0.27 (s, 9H, $SiMe_3$); 0.36 (s, 9H, $SiMe_3$); 1.38 [d, *J*(PH) 13Hz, 9H, PMe_3]; 5.40 (s, 5H, C_5H_5). FAB MS: 439, $[M]^+$, 100; 366, $[M - SiMe_3]$, 33; 272, $[PMe_3 + (HC_2SiMe_3)_2]^+$, 46; several high peaks were found at *m/z* 495, 523, 548, 563, 577, 603.

D. Preparation of ethynyl complexes

(a) $Ru(C_2H)(PPh_3)_2(\eta\text{-}C_5H_5)$ (17)

(i) Method A: A solution of $[Ru\{C{=}CH_2\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (50 mg, 0.058 mmol) in dry, degassed CH_2Cl_2 (5 ml) was passed through a column of basic alumina (1 x 10 cm). Elution with CH_2Cl_2 afforded a yellow fraction which was evaporated to dryness to give an oily residue. Trituration with dry, degassed light petroleum afforded an air sensitive yellow powder of $Ru(C_2H)(PPh_3)_2(\eta\text{-}C_5H_5)$ (17) (25 mg, 60%), m.p. >150°C (dec.). A reliable analysis was not obtained. Infrared (Nujol): ν(CH) 3295, $\nu(C{\equiv}C)$ 1940m; other bands 1590w, 1578w, 1550w, 1485w, 1438w, 1265w, 1190w, 1160w, 1090m, 1000w, 832w, 810w, 795w, 750w, 740m, 722w, 700s cm^{-1}. ^1H NMR: $\delta(CD_2Cl_2)$ 1.95 [t, J(PH) 2.3Hz, ≡CH]; 4.46 (s, 5H, C_5H_5) 7.1-7.7 (m, 30H, Ph). $^{13}C\{^1H\}$ NMR: $\delta[CH_2Cl_2, Cr(acac)_3]$ 85.5 (s, C_5H_5); 96.6 (s, C_β); 107.1, [t, J(PH) 22Hz, C_α); 127.0-140.0 (m, Ph). FAB MS: 717, $[M + H]^+$, 39; 691, $[M - C_2H]^+$, 14; 455, $[M - PPh_3]^+$, 24; 429, $[Ru(PPh_3)(C_5H_5)]^+$, 100; 351, $[Ru(PPh_3)(C_5H_5) - C_6H_6]^+$, 20. Further elution with CH_2Cl_2 afforded trace amounts of a green fraction which was not identified.

(ii) Method B: A solution of $[Ru\{C{=}CH_2\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$(50 mg, 0.058 mmol) in thf (10 ml) was treated with $KOBu^t$ (10 mg, 0.089 mmol) and stirred for 20 min, after which time the reaction was adjudged complete [the disappearance of the i.r. $\nu(C{=}C)$ band of (9) was monitored]. The yellow solution was evaporated to dryness and the residue extracted with Et_2O until the extracts were colourless.

Addition of light petroleum to the filtered extracts and concentration resulted in the formation of a yellow precipitate of $Ru(C_2H)(PPh_3)_2(\eta\text{-}C_5H_5)$ (17) (32 mg, 77%), identified by comparison of its i.r. and FAB spectra with those of an authentic sample.

(b) $Ru(C_2H)(dppe)(\eta\text{-}C_5H_5)$ - Using Method B, $[Ru\{C{=}CH_2\}(dppe)(\eta\text{-}C_5H_5)][PF_6]$ (45 mg, 0.061 mmol), $KOBu^t$ (10 mg, 0.089 mmol) in thf (10 ml) gave a yellow powder of $Ru(C_2H)(dppe)(\eta\text{-}C_5H_5)$ (18) (27 mg, 75%), m.p. >150° (dec.). [Found: C, 65.63; H, 5.26%; *M* (mass spectrometry) 591; $C_{33}H_{31}P_2Ru$ requires C, 67.22; H, 5.12%; *M* 590]. Infrared (thf): $\nu(C{\equiv}C)$ 1941 cm^{-1}. (Nujol): $\nu(CH)$ 3288w; $\nu(C{\equiv}C)$ 1938s; other bands 1585w, 1434s, 1100w, 1026w, 999w, 869w, 841w, 796w, 744m, 722m, 697s, 674m cm^{-1}. ^1H NMR: $\delta(CD_2Cl_2)$ 1.13 [t, *J*(PH) 2Hz, 1H, $\equiv CH$]; 2.33, 2.75 (m, 4H, PCH_2CH_2P); 4.74 (s, 5H, C_5H_5); 7.10-7.90 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR: $\delta[CH_2Cl_2, Cr(acac)_3]$ 27.7 (m, PCH_2CH_2P); 82.7 (s, C_5H_5); 95.2 (s, C_β); 108.0 [t, *J*(PH) 20Hz, C_α]; 127.5-134.1 (m, Ph). FAB MS: 591, $[M + H]^+$, 43; 565, $[M - C_2H]$, 100; 513, $[M - Ph]^+$, 16.

(c) $Ru(C_2H)(PMe_3)_2(\eta\text{-}C_5H_5)$ - Using Method B, $[Ru\{C{=}CH_2\}(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (30 mg, 0.061 mmol), $KOBu^t$ (10 mg, 0.089 mmol) in thf (10 ml) gave a yellow precipitate of $Ru(C_2H)(PMe_3)_2(\eta\text{-}C_5H_5)$ (19) (18 mg, 86%), m.p. >150°C (dec.). Infrared (thf): 1941 cm^{-1}. ^1H NMR: $\delta(CD_2Cl_2)$ 1.29 [t, *J*(PH) 2Hz, 1H, $\equiv CH$], 1.41 (m, 18H, PMe_3); 4.55 (s, 5H, C_5H_5). FAB MS: 345, $[M + H]^+$, 27; 320, $[M - C_2H]^+$, 100; 243, $[Ru(PMe_3)(C_5H_5)]^+$, 10.

E. Reactions of $[Ru(C{=}CH_2)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$

(a) with Methanol - A solution of $[Ru(C{=}CH_2)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (50 mg, 0.058 mmol) in CH_2Cl_2 (10 ml) was treated with MeOH (5 ml, excess) and stirred for 2 h. Reduction in volume afforded yellow crystals of $[Ru\{C(OMe)Me\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (24) (39 mg, 75%), identified by comparison of its ^1H NMR and FAB MS spectra with those of an authentic sample (see below p.60).

(b) with water - A solution of $[Ru\{C{=}CH_2\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (100 mg, 0.116 mmol) in thf (20 ml) was treated with water (3 drops) and the mixture stirred for 16 h. Reduction in volume (to *ca* 10 ml) and addition of Et_2O (40 ml) resulted in the formation of a light yellow precipitate of $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (60 mg, 60%). Identified by comparison of its i.r. and ^1H NMR spectra with those of an authentic sample.[35]

F. Reactions of alkynyl complexes

Reactions of $Ru(C_2H)(PPh_3)_2(\eta\text{-}C_5H_5)$

(a) with bromine - A solution of (17) (75 mg, 0.105 mmol) in thf (10 ml) was treated dropwise with bromine (0.6 ml of 31 mg ml^{-1} solution in CCl_4) to give an immediate colour change from yellow to red. Evaporation and separation of the residue by preparative tlc (acetone-light petroleum; 1:1) gave one major band (R_f 0.79, orange) which was crystallised from CH_2Cl_2/MeOH to give orange crystals of $RuBr(PPh_3)_2(\eta\text{-}C_5H_5)$ (21) (47 mg, 58%). Identified by comparison of its ^1H NMR and i.r. spectra with those of an authentic sample.[36]

(b) with $[3,4\text{-}C_6H_3Cl_2N_2][BF_4]$ - To a solution of $Ru(C_2H)(PPh_3)_2(\eta\text{-}C_5H_5)$ (55 mg, 0.077 mmol) in thf (10 ml) at -64°C was added solid $[3,4\text{-}C_6H_3Cl_2N_2][BF_4]$ resulting immediately in formation of a red solution. Concentration and filtration through basic alumina (1 x 10 cm) gave a dark orange solution. Addition of light petroleum and further concentration afforded dark orange crystals of $Ru(C_2N{=}NC_6H_3Cl_2\text{-}3,4)(PPh_3)_2(\eta\text{-}C_5H_5)$ (20) (8 mg, 12%). Infrared: (Nujol) $\nu(C{\equiv}C)$ 2002vs(br); other bands 1485m, 1440m, 1310s, 1240v, 1215w, 1095m, 1050w, 1005w, 868w, 832w, 820w, 795w, 782w, 750m, 745w, 721w, 697w, 668w cm^{-1}. FAB MS: 889^*, $[M + H]^+$, 12; 717, $[M - N_2C_6H_3Cl_2]^+$, 15; 691, $[Ru(PPh_3)_2(\eta\text{-}C_5H_5)]^+$, 15; 627, $[M - PPh_3]^+$, 3; 467, $[M - PPh_3 - HNC_6H_3Cl_2]^+$, 15; 453, $[M - PPh_3\text{-}HN_2C_6H_3Cl_2]^+$, 20; 429, $[Ru(PPh_3)(C_5H_5)]^+$, 100.

G. Reaction of $[Ru(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ with HC_2SiMe_3 in methanol

To a suspension of $[Ru(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (245 mg, 0.279 mmol) in MeOH (15 ml) was added HC_2SiMe_3 (0.05 ml, 0.361 mmol) and the mixture was refluxed for 2 h. Filtration of the solution yielded a light yellow solid $[Ru\{C(OMe)Me\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (24) . Concentration of the supernatant yielded a second crop of (24) as yellow crystals (total yield: 166 mg, 67%), m.p. 150°C (dec.). [Found: C, 58.87; H, 4.63; *M* (mass spectrometry) 749; $C_{44}H_{41}F_6OP_3Ru$ requires C, 58.86; H, 4.60%; *M* 749]. Infrared (Nujol): $\nu(C\text{-}O)$ 1270s, $\nu(P\text{-}F)$ 840vs(br); other bands 3150w, 3070w, 1480m, 1470s, 1440m, 1360m, 1350m, 1185m, 1160w, 1095m, 1030w, 1020w, 1005m, 1000s, 975w, 930w, 880s, 760s, 742s, 742s, 700vs cm^{-1}. ^{1}H NMR: δ($CDCl_3$) 3.03 (s, 3H, Me); 3.28 (s, 3H, OMe); 4.75 (s, 5H, C_5H_5); 7.0-7.4 (m, 30H, Ph). $^{13}C\{^{1}H\}$ NMR: δ($CDCl_3$) 46.4 (s, Me); 60.7 (s, OMe); 91.4 (s, C_5H_5); 128.2-136.1 (m, Ph); 309.15 [t, *J*(PH) 12Hz, Ru-C_α]. FAB MS: 749, [*M*]$^+$, 24; 719, [*M* - 2Me], 0.75; 691, [*M* - C(OMe)Me]$^+$, 9*; 626*, [Ru(PPh_3)$_2$, 1.3; 486, [*M* - PPh_3]$^+$, 18; 471*, [*M* - PPh_3 - Me]$^+$, 2.4; 457, [*M* - PPh_3 - 2Me], 3.7; 441, [*M* - PPh_3 - OMe - Me]$^+$, 37; 429, [Ru(PPh_3)(C_5H_5)]$^+$, 100.

H. Reaction of RuCl(PPh_3)$_2$(η-C_5H_5) with HC_2SiMe_3 in Methanol

A suspension of RuCl(PPh_3)$_2$(η-C_5H_5) (211 mg, 0.291 mmol) and HC_2SiMe_3 (0.05 ml, 0.361 mmol) was heated at reflux point for 30 min. The light yellow solution was evaporated to dryness, the residue extracted with CH_2Cl_2 (*ca* 2 ml) and filtered into excess stirred Et_2O giving a light yellow precipitate of [Ru{C(OMe)Me}(PPh_3)$_2$(η-C_5H_5)][Cl] (<u>25</u>) (187 mg, 82%), m.p. >150°C (dec.). Infrared (Nujol): ν(C-O) 1270s; other bands 1470m, 1438m, 1352m, 1347m, 1186m, 1160w, 1095w, 1030w, 1005m, 1000s, 974w, 930w, 760s, 742s, 700vs cm^{-1}. ^{1}H NMR: δ($CDCl_3$) 3.02 (s, 3H, Me); 3.26 (s, 3H, OMe); 4.75 (s, 5H, C_5H_5); 7.0-7.4 (m, 30H, Ph). FAB MS: 749, [*M*]$^+$, 16; 735*, [*M* - CH_3], 3; 719, [*M* - 2Me]$^+$, 12; 691, [*M* - C(OMe)Me]$^+$, 7; 625*, [Ru(PPh_3)$_2$] 1.3; 547, [*M* - PPh_3 - 2Me]$^+$, 1.3; 486*, [*M* - PPh_3]$^+$, 3; 471*, [*M* - PPh_3 - Me]$^+$, 4; 457, [*M* - PPh_3 - 2Me]$^+$, 10; 429 [Ru(PPh_3)(C_5H_5)]$^+$, 100; 352, [Ru(PPh_2)(C_5H_5)]$^+$, 11.

I. Reaction of $RuCl(dppe)(\eta-C_5H_5)$ with ethyne

(a) in methanol - A suspension of $RuCl(dppe)(\eta-C_5H_5)$ (118 mg, 0.197 mmol) and NH_4PF_6 (32 mg, 0.196 mmol) was stirred in HC_2H saturated MeOH (10 ml) for 40 h. Filtration of the solution yielded light yellow crystals of $[Ru\{C(OMe)Me\}(dppe)(\eta-C_5H_5)][PF_6]$ (26) Concentration of the supernatant yielded a second crop. (Total yield 80 mg, 53%), m.p. >200°C (dec.). [Found: C, 53.51; H, 4.53; *M* (mass spectrometry), 623; $C_{34}H_{35}F_6OP_3Ru$ requires C, 53.20; H, 4.60%; *M* 623]. Infrared (Nujol): ν(C-O) 1247s, ν(P-F) 840vs(br); other bands 1438s, 1310w. 1268w, 1180w, 1160w, 1105m, 1095w, 1030w, 1200m, 894s, 828s, 750m, 720w, 700s, 678m, 650w cm^{-1}. FAB MS: 623, $[M]^+$, 100; 593, $[(M - OMe) + H]^+$, 17; 565, $[Ru(dppe)(C_5H_5)]^+$, 29; 488, $[Ru(dppe)(C_5H_5) - Ph]^+$, 3;

(b) in the presence of $AgPF_6$ - A solution of $RuCl(dppe)(\eta-C_5H_5)$ (224 mg, 0.373 mmol) in CH_2Cl_2 (20 ml) was treated with $AgPF_6$ (130 mg, 0.514 mmol) giving an immediate precipitate (AgCl) and a dark red solution. Through this was bubbled HC_2H for 45 min, resulting in a lightening of the solution colour to pale orange. The solution was concentrated and filtered through celite into excess stirred Et_2O giving a pale yellow precipitate of $[Ru(\eta^2-HC_2H)(dppe)(\eta-C_5H_5)][PF_6]$(22)(111mg,40%), m.p. >100°C (dec.). [Found: C, 48.55; H, 4.14; *M* (mass spectrometry) 591 $C_{33}H_{31}F_6P_3Ru$ requires C, 53.88; H, 4.25%; *M* 591]. Infrared (Nujol): ν(CH) 3210w, 3158w, ν(C≡C) 1750w, ν(PF) 841vs(br); other bands 1440s, 1300m, 1190w, 1140m, 1100m, 1075m, 1000 cm^{-1}. FAB MS: 591, $[M]^+$, 19; 565, $[M - HC_2H]^+$, 100;

X-ray structure determination of (24)

General techniques and details given below apply to the structure of (24), determined by the author.

A suitable crystal (0.50 x 0.18 x 0.50 mm) of was grown from $CDCl_3$/MeOH by solvent diffusion at ambient temperature and was mounted on a glass fibre using cyanoacrylate 'super glue'. Lattice parameters were determined from a least squares fit to the setting angles of 25 high angle reflections[47] on an Enraf-Nonius CAD-4F four circle diffractometer using graphite monochromated MoK_α ($\lambda = 0.7107$ Å). The crystal was found to be orthorhombic with systematic absences $h00{:}h=2n$; $0k0{:}k=2n$ and $00l{:}l=2n$ uniquely defining the space group $P2_12_12_1$ (D_2^4, No.19).

Crystal data $C_{44}H_{41}F_6OP_3Ru$ of (24), M 893.8, orthorhombic, space group $P2_12_12_1$ (D_2^4, No.19), $a = 11.934(4)$, $b = 14.858(4)$, $c = 22.287(4)$ Å, $V = 3952(2)$ Å^3, Dcalc = 1.502 g cm^{-3}, $Z = 4$, $F(000) = 1824$, $T = 293(2)$K, θ range 1.5-25°; of 4300 measured reflections 3219 were found to be unique, with $I \geqq 2.5\sigma(I)$, μ0.531 mm^{-1}, absorption correction applied; maximum and minimum transmission factors 0.860 and 0.794. Intensity data were measured using a $\omega{:}2\theta$ scan technique in the range $-14 \leqq h \leqq 0, -17 \leqq k \leqq 0, -23 \leqq l \leqq 3$ with the inclusion of some high-angle Friedel pairs. Three reference reflections ($\bar{2}\bar{2}2$, $\bar{1}\bar{2}\bar{1}$, $0\bar{2}1$) were monitored every 3600 sec of X-ray exposure time to check for crystal and machine stability; no appreciable variation in the net intensity values was observed. Data reduction and the application of Lorentz and polarization corrections were undertaken using the programs PREABS and PROCES[48]. No correction for extinction was made.

An analytical absorption correction was applied using the SHELX 76[49] system of programs. Reflections with intensities $I<2.5\sigma(I)$ were rejected; while equivalent reflections were averaged.

The ruthenium atom position was determined from a Patterson map and the remaining non-hydrogen atoms were located by means of subsequent Fourier difference maps. The structure was refined by full matrix least squares procedures on 247 parameters based on F.[49] Phenyl groups were refined as hexagonal rigid rings (C-C 1.39Å) with isotropic thermal parameters. Anisotropic thermal parameters were employed for the remaining non-hydrogen atoms; hydrogen atoms were included in their calculated positions (0.97Å). In the final refinement cycles the weighting scheme, $w = [\sigma^2(F) + |g| - F^2]^{-1}$ was employed and at convergence g = 0.0006 and R = 0.046 for the preferred chirality. Bond lengths, valence angles, non-bonding distances and their standard deviations were all calculated using SHELX 76 and diagrams were drawn using PLUTO. All programs were implemented on the VAX11/785 computing system at the University of Adelaide. Neutral atom scattering factors for C, H, F, O and P were those listed in SHELX 76 and those for Ru were corrected for f' and f''.[50]
The listings of observed (F_o), and calculated (F_c) structure factors along with positional and thermal parameters for the structure are in the appendices.

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CHAPTER TWO

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SOME REACTIONS OF DIMETHYLACETYLENE DICARBOXYLATE AT CYCLOPENTADIENYL RUTHENIUM CENTRES

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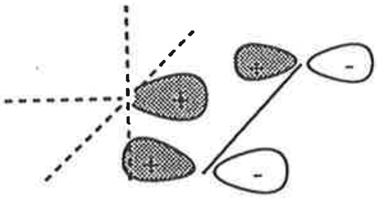
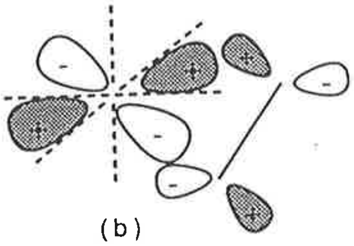
INTRODUCTION

Acetylenes occupy a prominent place in organotransition metal chemistry in view of their ability, in the presence of transition metals, to undergo an interesting and complex range of reactions. These can be as simple as ligand substitution, to give π-acetylene complexes, and as complex as cyclooligomerisation reactions giving dimers, trimers and tetramers. In many reactions it is often assumed that simple π-acetylene complexes act as intermediates in the formation of more complex products.[1]

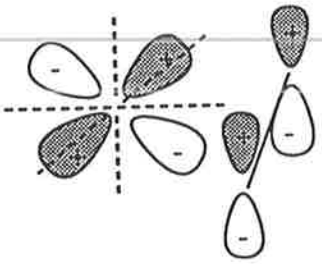
Coordination of an acetylene to a transition metal *via* a π-interaction results in two basic structural alterations to the carbon skeleton, (i) a deviation from linearity giving a *cis*-bent structure and (ii) the acetylenic C≡C distance increases by an amount which approximately parallels the strength of the metal acetylene bonding interaction.[2] The extent to which the acetylene is modified on coordination can be rationalised in terms of the orbital interactions shown below.



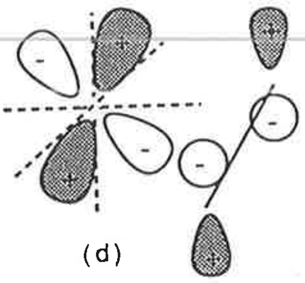
(a)



(b)



(c)



(d)

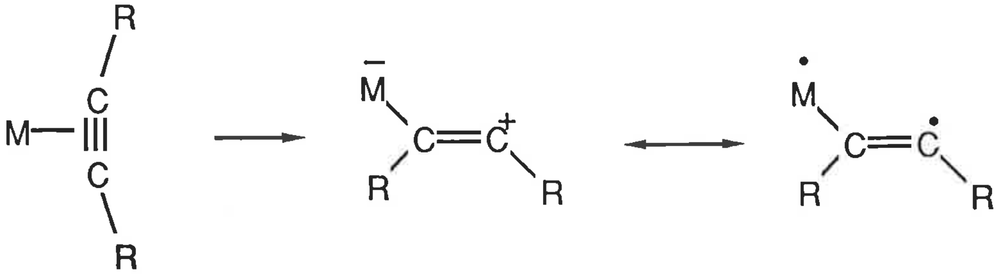
On the basis of overlap considerations above the major contributions to the metal acetylene bond will come from interactions (a) and (b).[1,3,4] The bonding involves the synergic action of (a), which arises from donations from the filled π-orbital in the plane of the metal acetylene linkage (π_y) to an empty σ-type orbital on the metal, and (b), where back donation of electron density from filled metal d-type orbitals to the antibonding counterpart of πy occurs. Important in determining the extent to which each interaction contributes, is the metal present, its oxidation state, other ligands attached to the metal and the electron withdrawing or donating ability of the acetylenic substituents.[1]

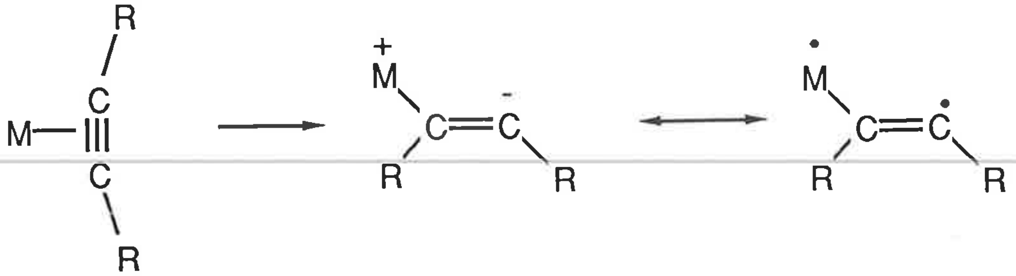
Interaction (a) predominates in the π-acetylene complexes of the early transition elements particularly those in high oxidation states and with electron donating substituents on the acetylene while interaction (b) is favoured by the later transition metals and acetylenes bearing electron withdrawing substituents.[1]

For some cases it is possible that orbital interactions (c) and (d) make some contribution to metal-alkyne bonding, involving the π_z and π_z^* orbitals of the C≡C bond.[1,3,4] However, overlap considerations suggest that back donation *via* interaction (d) can probably be neglected and Otsuka and Nakamura[3] suggest that (c) can result in a net increase in bonding if there are suitable empty d-type orbitals on the metal. This is the case with early transition metals in high oxidation states whereas with the later transition metals, with low oxidation states and full d-orbitals, interaction (c) would have a destabilising, antibonding effect.[3]

Otsuka and Nakamura[3] also point out that the extra stability gained from a bonding interaction of this type [(c)] enables the isolation of π-bonded acetylene complexes. However, with the later transition metals, where the interaction becomes non-bonding, complexes containing more than one π-bonded acetylene are rarely isolated[1] as the acetylenes exhibit a greater propensity to undergo cyclisation reactions.

The destabilising interaction (c) results in the activation of acetylenes by complexation to transition metals and has been discussed in terms of the $\eta^2 \rightarrow \eta^1$ transformation depicted in equations 1 and 2.


(1)


(2)

The cationic form (equation 1) is expected to contribute significantly in complexes where electron donating substituents are present on the acetylene whereas electron withdrawing groups will stabilise the anionic form (equation 2). Intermediates of this latter type are frequently invoked in reactions of $C_2(CF_3)_2$ and dimethylacetylene dicarboxylate (DMAD) with metal complexes.

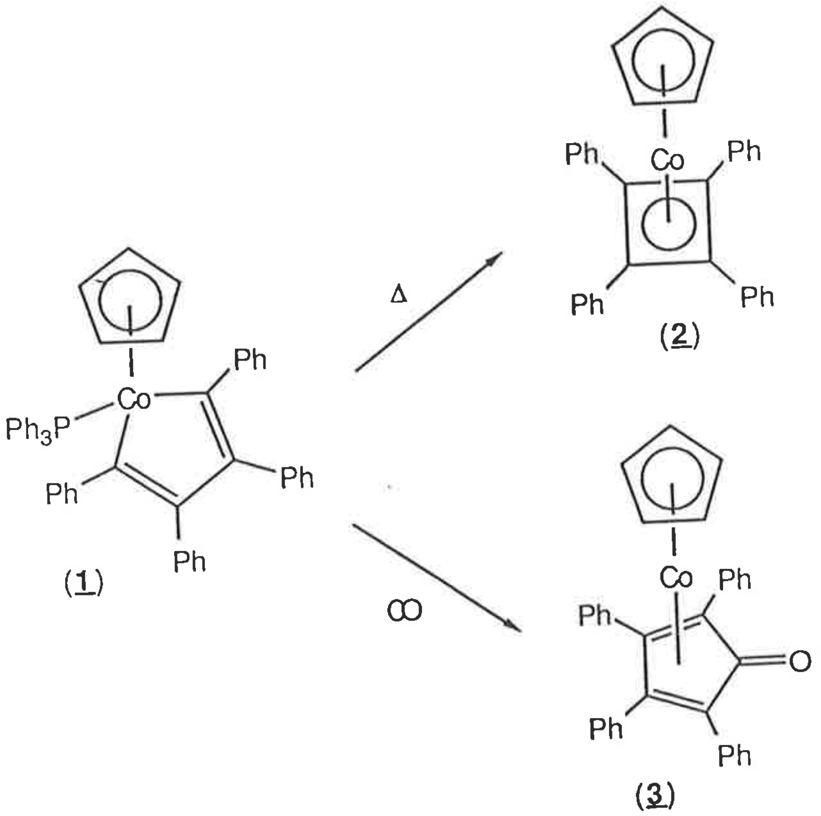
A large number of inorganic and organometallic compounds of transition metals have the ability to cyclooligomerise and polymerise acetylenes.[5] Cyclooligomerisation of acetylenes in the absence of metal complexes is subject to the conservation of orbital symmetry if the reactions proceed in a concerted manner. Consequently, formally forbidden thermal cyclisation reactions of acetylenes are expected to proceed stepwise rather than by a concerted mechanism.[1]

An old but interesting example of the ability of metals to catalyse forbidden pericyclic reactions is the nickel-promoted cyclisation of acetylenes to give cyclooctatetrenes.[6] A comprehensive summary of the work in this area has been recently published as an introduction to an elegant labelling study of ethyne tetramerisation[7] in the presence of Ni catalysts. This study made it possible to eliminate several mechanistic possibilities, including those involving cyclobutadiene or benzene intermediates and mechanisms that randomise alkyne carbons by complete cleavage of triple bonds. It was concluded that cyclooctatetrene formation probably proceeds with either a stepwise or concerted mechanism of formation. The latter process involves the nickel atom acting as a template with all four acetylene molecules simultaneously bound to the metal prior to coupling while the former involves metallacyclic intermediates in which each acetylene unit is added in a distinct step.[7]

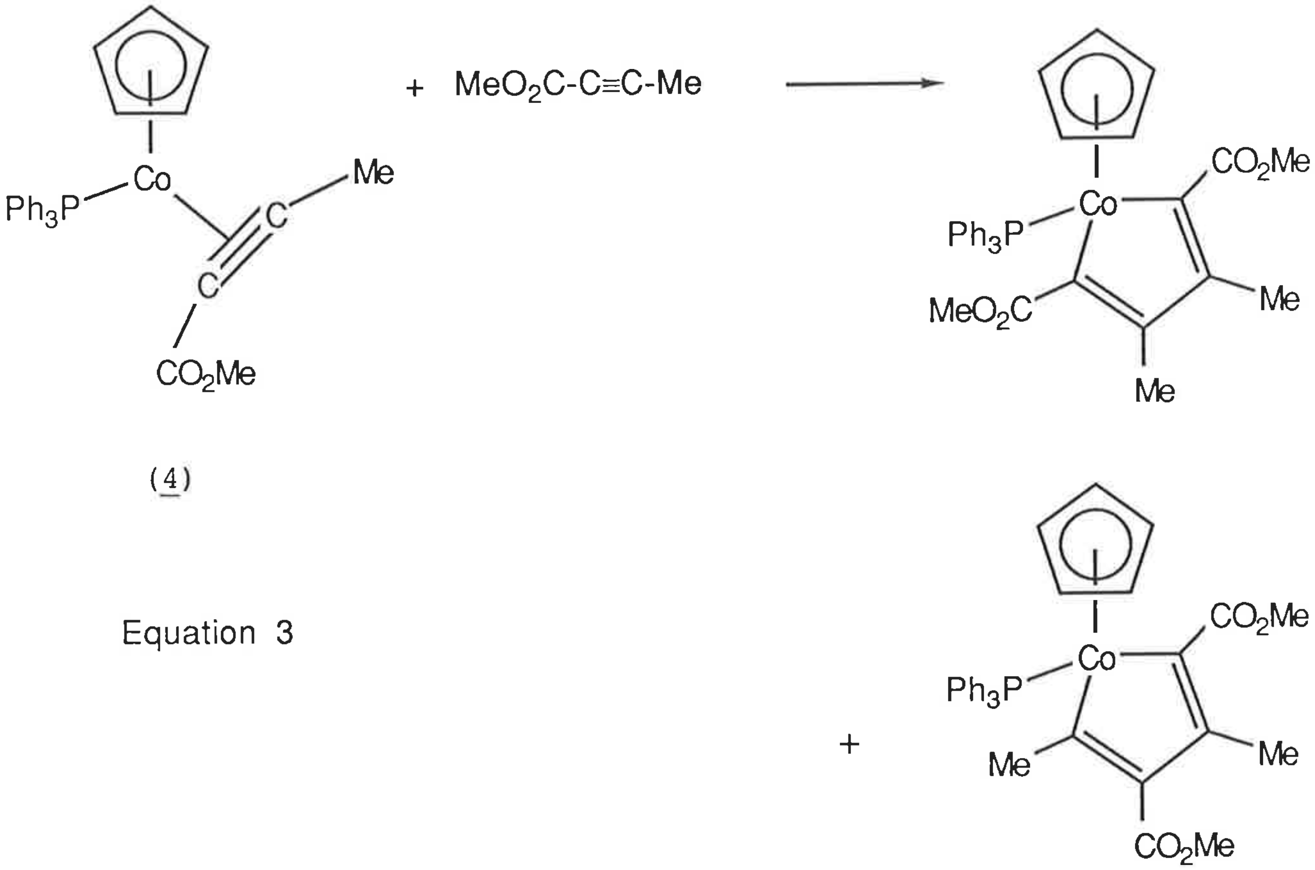
Acetylene Oligomerisation

Dimerisation of acetylenes on metal centres frequently leads to metallacyclopentadiene or cyclobutadiene complexes, which in some cases have proved to be capable of interconversion.[8,9]

Yamazaki and co-workers reported that the metallacycle (1), which was obtained from the reaction of a monoacetylene precursor with PhC_2Ph, underwent either reductive cyclisation to the cyclobutadiene (2) or reacted with CO to give a metallacyclopentadienone (3).[10] They subsequently showed that the monoacetylene complex (4) reacted with different acetylenes to



produce isomeric metallacycles but of the three possible isomers only two were formed[11] (equation 3).

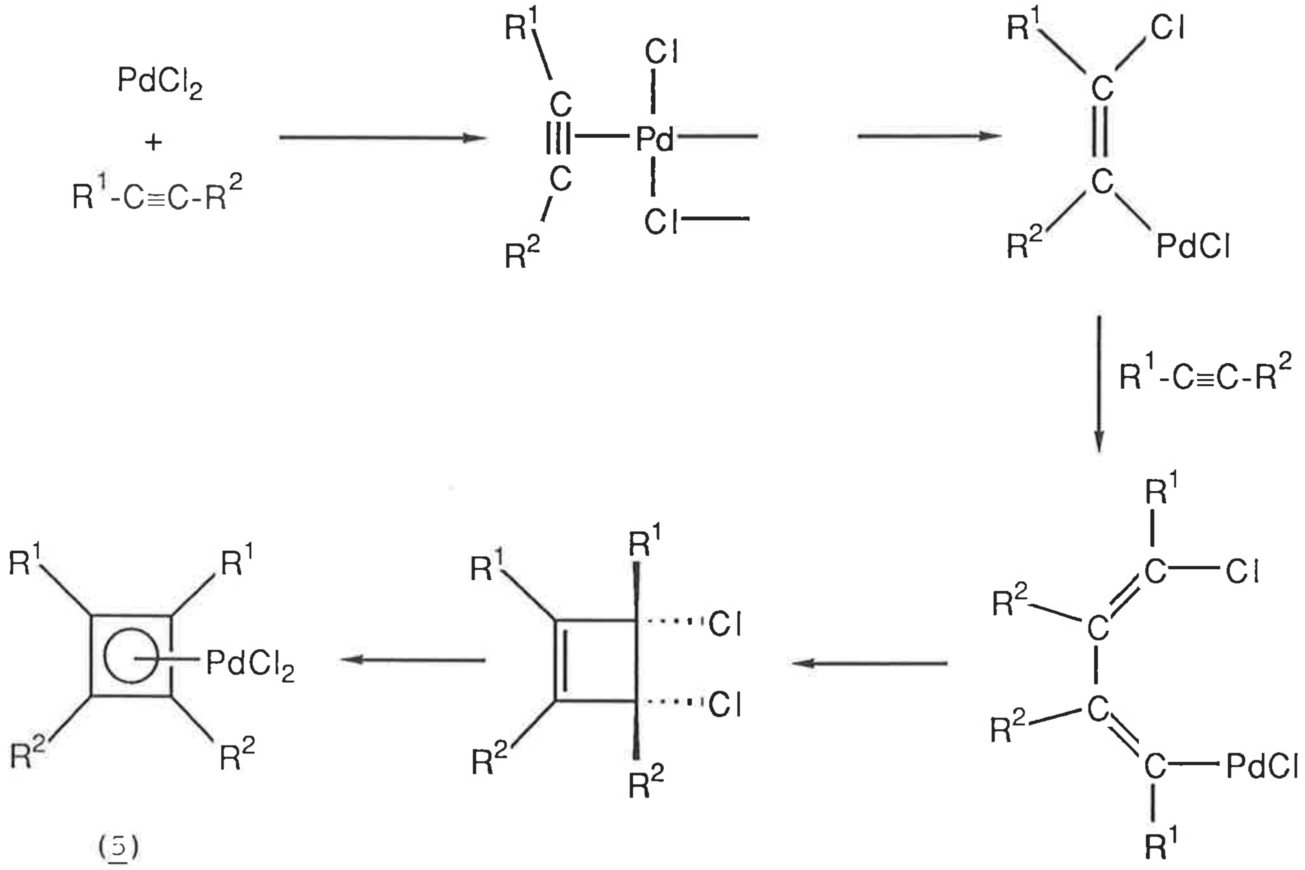


(4)

Equation 3

Two mechanisms were proposed to account for these features, one of which involved a bis-acetylene complex intermediate and the other involved a dipolar species (*cf* equation 2). It was concluded that the former mechanism was most probable as polar solvents had no effect on reaction rate.[11] The regio selectivity observed in such reactions is thought to be governed by preferential arrangements, allowing for steric effects, of the two acetylenes in the intermediate complex.[1]

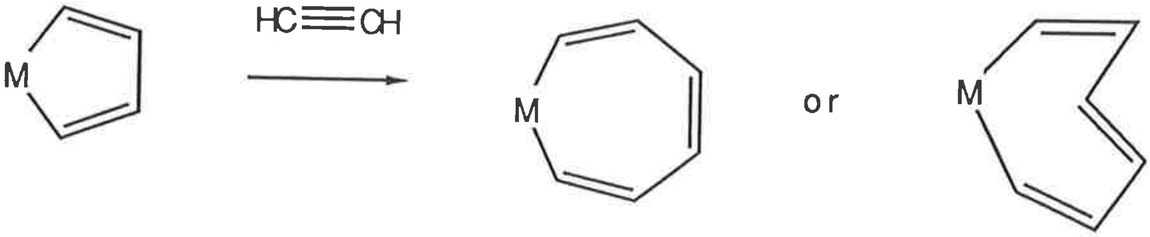
Dimerisation of acetylenes need not proceed via a metallacyclic intermediate. For the formation of substituted cyclobutadiene complexes from disubstituted alkynes with $PdCl_2$, Maitlis[12] proposed a sequence of coordination, insertion and ring closure reactions resulting in the formation of a cyclobutene intermediate which isomerises to the cyclobutadiene product (5).



Scheme 1

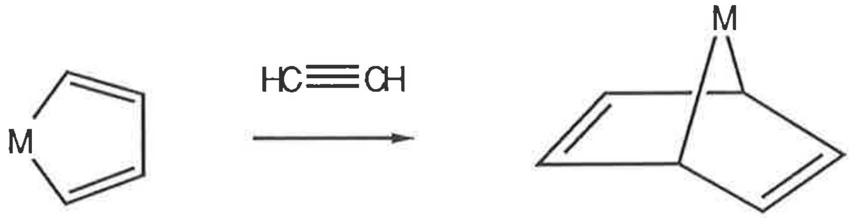
Cyclotrimerisation to form benzene derivatives has probably been the most studied of all metal-promoted reactions of acetylenes and a number of reviews concerned partly or wholly with the subject have appeared.[5,8,13] Cyclobutadiene intermediates were initially suggested as possible intermediates in the cyclotrimerisation reaction but this idea was soon abandoned because isolated cyclobutadiene complexes do not react with alkyne However, in one case Russian workers[15] obtained the complex Nb(CO)(η^2-PhC$_2$Ph)(η^4-C$_4$Ph$_4$)(η-C$_5$H$_5$) (6), from the reaction of the bis-acetylene complex $Nb(CO)$-$(\eta^2$-$PhC_2Ph)_2(\eta$-$C_5H_5)$ with excess PhC_2Ph in benzene, which was found to decompose by releasing Ph_6C_6 on heating. Although the concerted reaction is formally allowed it has been suggested that a step-wise oxidative mechanism might be operating in the formation of (6).[16]

Otsuka and Nakamura[3] have suggested that cyclotrimerisation proceeds via insertion of the acetylene into a metal carbon π-bond of an initially formed metallacyclopentadiene leading to a metallacycloheptatriene (Equation 4). Complexes of this type have been isolated.[21]



Equation 4

An alternative view suggested is Diels-Alder addition of an acetylene to the diene moiety of the metallacyclopentadiene generating a bicyclic intermediate[18] (equation 5). In either case the final step is reductive elimination of the arene.

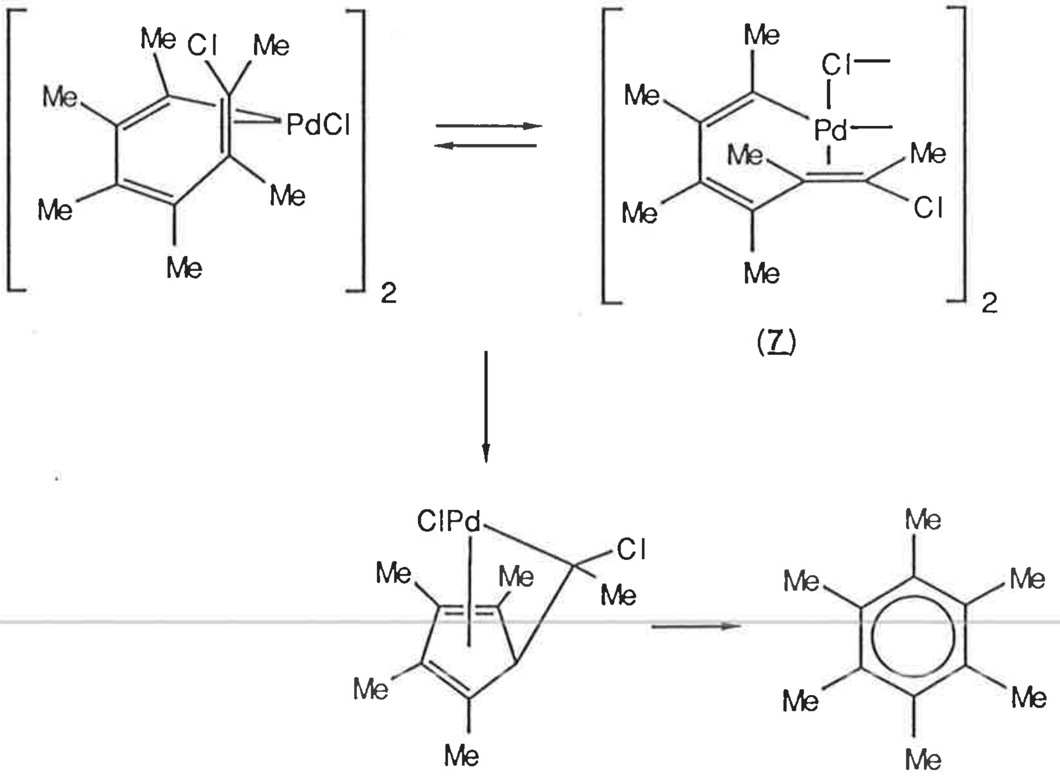


Equation 5

It has been assumed that π-coordination of the acetylene precedes either of the two suggested mechanisms and this assumption is supported by Collman and co-workers[19] who observed that blocking the vacant coordination site of $IrCl\{C_4(CO_2Me)_4\}(PPh_3)_2$ with CO, completely inhibited the cyclotrimerisation of DMAD. More recently,[20] the complexes $IrMe(CO)(PPh_3)_2$ and $IrMe(CO)(PPh_3)_2\{C_2(CO_2Me)_2\}$ were found to be active cyclotrimerisation catalysts for DMAD. The mechanism suggested requires the production of a vacant coordination site by methyl migration leading to $Ir(COMe)(PPh_3)_2\{C_2(CO_2Me)_2\}_2$ (a neopentyl analogue was structurally characterised) which then rearranges to a metallacyclopentadiene complex. It is notable that the halide complexes $IrX(CO)(PPh_3)_2$ are inactive for cyclotrimerisation.[19]

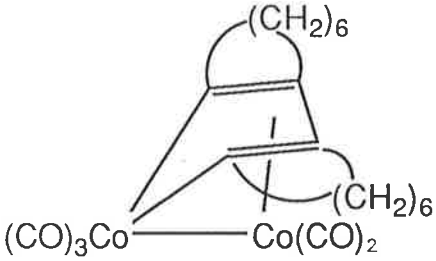
It was found that the metallacycle $Co(C_4Me_4)(PPh_3)(\eta-C_5H_5)$ catalyses the cyclotrimerisation of 2-butyne according to a rate law consistent with prior dissociation of the phosphine ligand.[18] In contrast, the PMe_3 analogue is unreactive towards 2-butyne even at elevated temperatures whereas DMAD reacted with $Co(C_4Me_4)(PMe_3)(\eta\text{-}C_5H_5)$ to give dimethyl 3,4,5,6-tetramethylphthalate at room temperature. In this latter reaction it was suggested that a Diels-Alder cycloaddition has occurred which further illustrates the importance of the nature of the alkyne in determining the mechanism which operates in cyclotrimerisation reactions.

Cyclotrimerisation in the palladium systems investigated by Maitlis[12] does not proceed via metallacyclic intermediates. Instead he again proposes a sequence of acetylene coordination and insertion reactions leading to intermediate (7) which undergoes ring closure via a cyclopentadiene complex to yield free benzenes (Scheme 2).



Scheme 2

Dinuclear complexes also undergo a diverse range of reactions with acetylenes. These include cyclooligomerisations in which metallacyclopentadienes are again thought to be intermediates. The novel metallacyclopentadiene (8) was isolated from the reaction of cyclooctyne with $Co_2(CO)_8$[22] and was found to catalytically cyclotrimerise cyclooctyne.

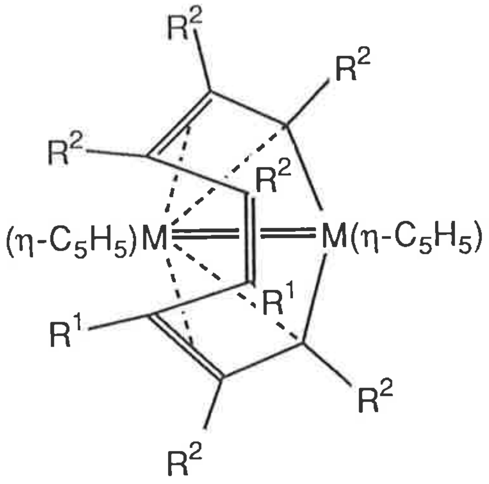


(**8**)

Tetramerisation

The Reppe, metal catalysed assembly of acetylenes into cyclooctatetrane has already been mentioned. Monosubstituted alkynes are also readily cyclotetramerised, with both simple and functionalised tetramers available,[23] using Ni catalysts.

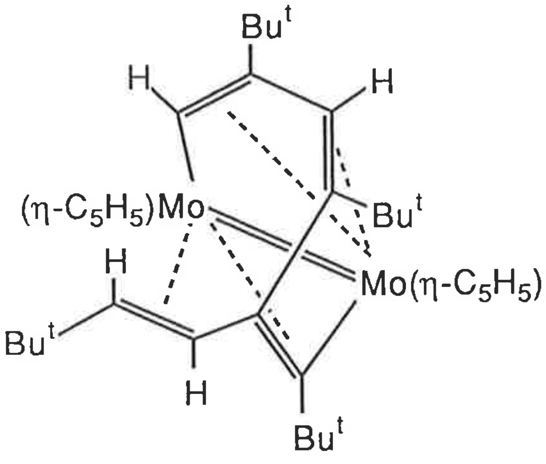
Metal complexes containing acetylene tetramers are rarer. Some binuclear complexes have been obtained by Stone and Knox who found that step-wise addition of acetylenes to $\{M(CO)_2(\eta\text{-}C_5H_5)\}_2$ (M= Cr, Mo, W) led to binuclear complexes (9) containing carbon chains constructed of four acetylene units.[24]



(**9**; R^1, R^2 = H, Ph, CO_2Me)
(not all combinations)

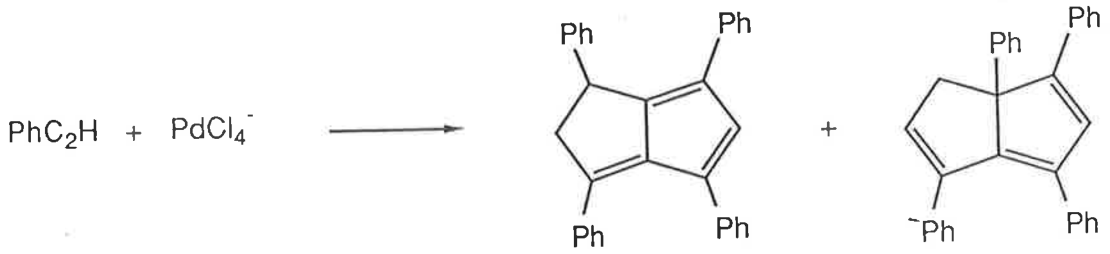
A complex similar to (9) was obtained from the reduction of $[Mo(MeCN)(MeC_2Me)_2(\eta-C_5H_5)]BF_4$ with $Na[Fe(CO)_2(\eta-C_5H_5)]$.[25] Extention of this reaction to $[Mo(NCMe)(\eta^2-Bu^tC_2H)_2(\eta-C_5H_5)][BF_4]$[26] afforded two dinuclear acetylene tetramers; $[Mo_2\{\mu-(\sigma,\eta^3:\eta^2:\eta^3,\sigma-C_8H_4Bu^t{}_4)\}(\eta-C_5H_5)_2]$ (10) and $Mo_2\{\mu-(\sigma,\eta^3:\eta^3,\sigma-H=CHBu^tC_6H_2Bu^t{}_3)\}(\eta-C_5H_5)_2]$ (11). Both complexes were characterised crystallographically and (10) was found to be structurally similar to (9) while (11) was described as having a vinyl substituted C_6 'flyover' ligand.

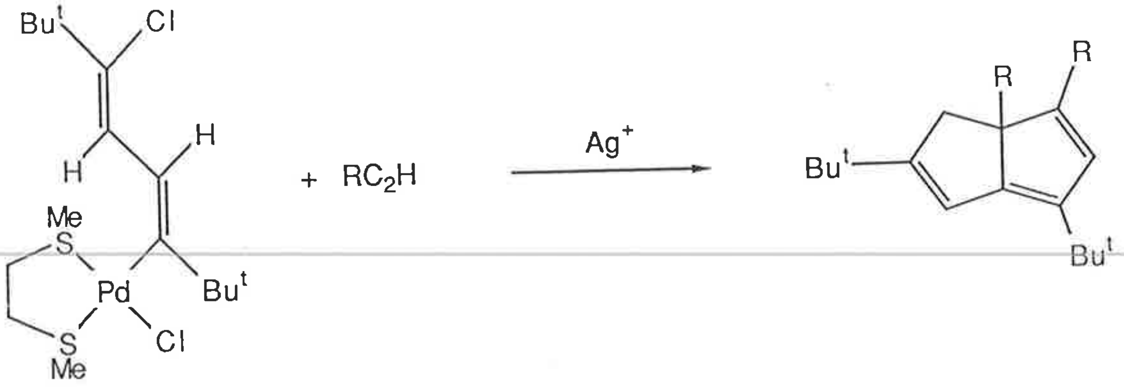
Maitlis and co-workers[12,27] found that the reaction of phenylacetylene with $PdCl_4{}^{2-}$ gave dihydropentalene organic tetramers (Equation 6).



(**11**)

Similar organic compounds were also obtained from the reaction of other terminal acetylenes with the butadienyl complex (12). The formation of these organic compounds can be rationalised in terms of an extention of Schemes 1 and 2.[12]



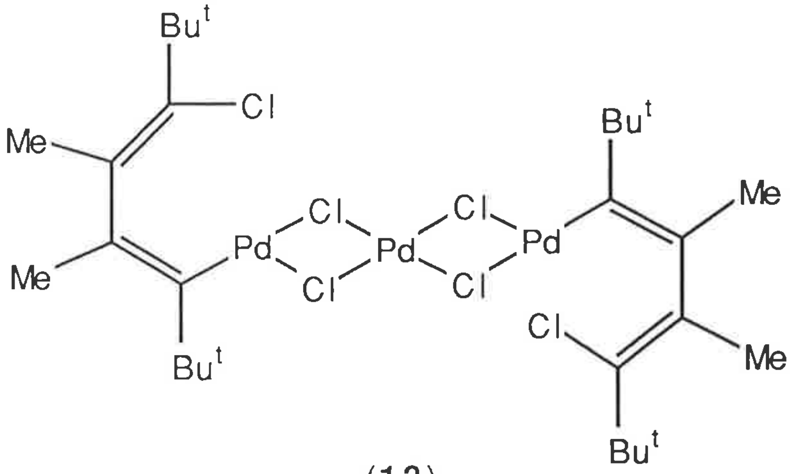


(**12**)

Equation 6

Linear oligomerisation

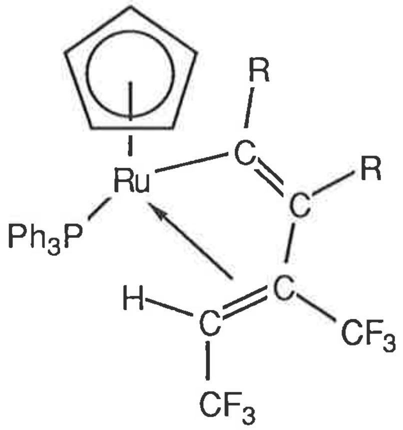
The best characterised system for the di-, tri-, and tetramerisation of acetylenes by transition metals is the previously mentioned Pd (II) system of Maitlis.[12] He suggests that the key intermediates are σ-butadienyl complexes, an example of which was obtained from the reaction of $PdCl_2(PhCN)_2$ with Bu^tC_2Me,[28] (13). These butadienyl complexes are formed by *cis* insertion of a previously coordinated acetylene molecule into a PdCl bond.



(**13**)

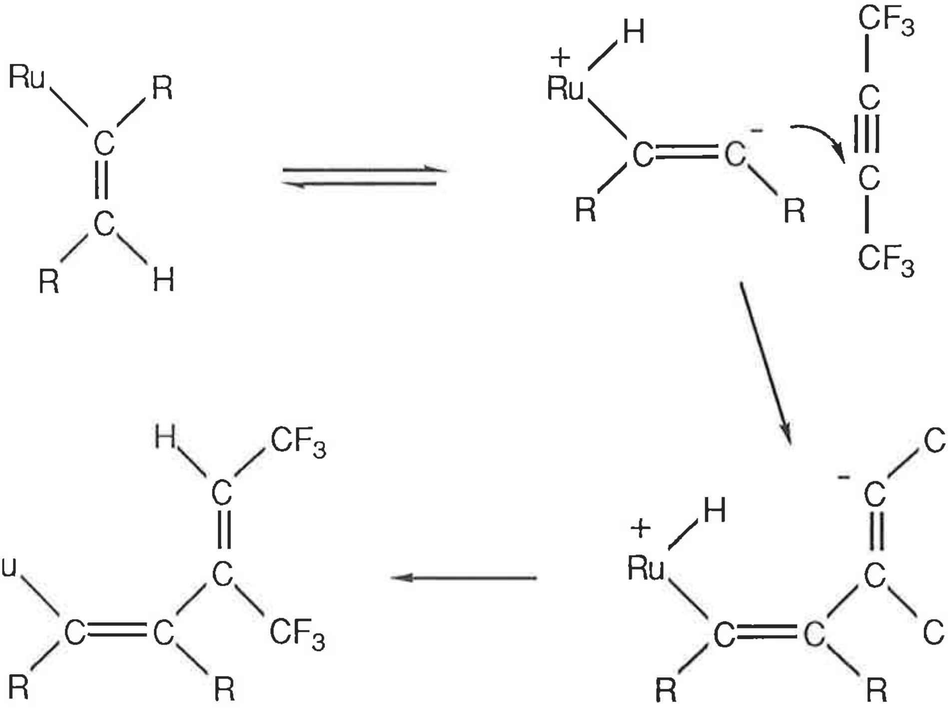
The insertion of acetylenes into metal-hydrogen bonds represents one of the fundamental processes of organometallic chemistry.[3,29] Such insertion reactions may proceed with either *cis* or *trans* addition of the alkyne and it has been pointed out that determination of the product stereochemistry is not trivial.[3,30,31] A recent reinvestigation of the insertion of DMAD into the ReH bond of $ReH(\eta\text{-}C_5H_5)_2$ found that the original stereochemical assignments of Dubeck and Schell[32] were incorrect and that the first formed vinyl complex has *trans* or (Z) stereochemistry. A slow isomerisation to *cis* stereochemistry was observed at 75°C even in the absence of the platinum catalyst mentioned in the original literature.[32]

The ruthenium hydride complex $RuH(PPh_3)_2(\eta-C_5H_5)$ (14) was also found to insert DMAD and hexafluorobut-2-yne[33,34] affording simple mono-insertion products $Ru\{(E)-C(R)=CH(R)\}-(PPh_3)_2(\eta-C_5H_5)$ [(15) $R=CF_3$; (16) $R= CO_2Me$, respectively]. In the hexafluorobut-2-yne reaction the acetylene was also found to oligomerise giving the bis-insertion butadienyl complex, $\overline{Ru\{C(CF_3)=C(CF_3)C(CF_3)=}CH(CF_3)\}(PPh_3)-(\eta-C_5H_5)$ (17). Hexafluorobut-2-yne also reacted with



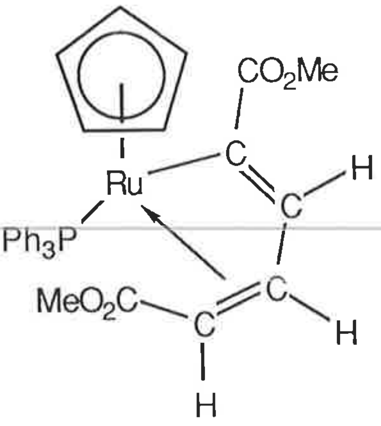
(**17**) $R = CF_3$
(**18**) $R = CO_2Me$

complex (16) to give a butadienyl complex (18) analogous to (17). In this reaction the second acetylene apparently does not simply insert into the Ru-C bond but instead apparently inserts into the CH bond of the vinyl ligand of (16). This type of insertion has also been observed by other workers.[35] To explain this unexpected result an ionic mechanism has been proposed in which the hydrogen is transferred back to the metal during the reaction (Scheme 3).

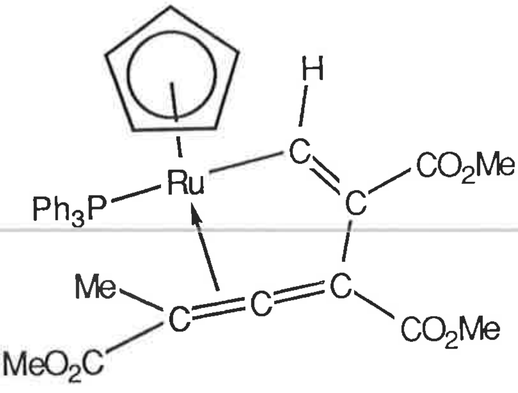


Scheme 3

Reaction between RuX(PPh$_3$)$_2$(η-C$_5$H$_5$) (X= H, Me, or CH$_2$Ph) and HC$_2$R[36] (R= CO$_2$Me, COMe, CF$_3$ or C$_6$F$_5$) was also the source of other novel oligomerisation products containing one, two or three alkyne molecules. Among the products isolated from the reaction of (<u>14</u>) with HC$_2$CO$_2$Me was the butadienyl complex Ru{C(CO$_2$Me)=C(H)C(H)=C(H)-(CO$_2$Me)}(PPh$_3$)(η-C$_5$H$_5$) (<u>19</u>) and the pentatrienyl complex Ru{C(H)=C(CO$_2$Me)C(CO$_2$Me)=C=C(Me)(CO$_2$Me)}(PPh$_3$)(η-C$_5$H$_5$) (<u>20</u>)

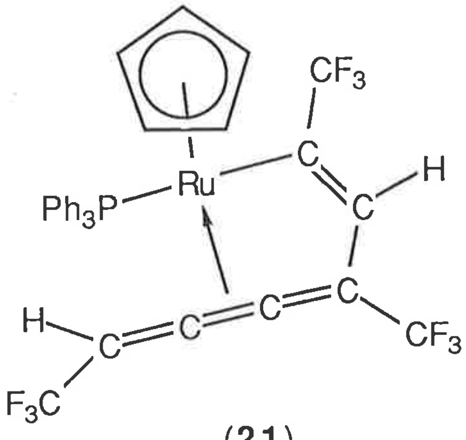


(**19**)



(**20**)

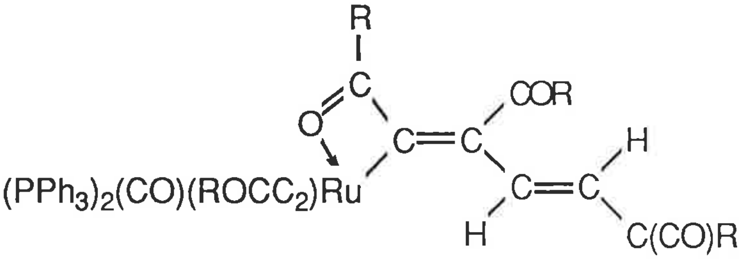
in which the acetylene was dimerised and trimerised, respectively. The methyl- and benzyl complexes gave only dimers analogous to (19) in their reaction with HC_2CO_2Me. The reaction of HC_2CF_3 with the methyl complex $RuMe(PPh_3)_2(\eta-C_5H_5)$ afforded a novel structurally characterised cumulene derivative, $\overline{Ru\{C(CF_3)=C(H)C(CF_3)=C}=C=C(H)(CF_3)\}(PPh_3)(\eta-C_5H_5)$ (21) in which the acetylene was trimerised.



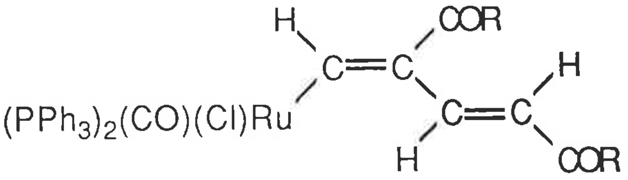
(21)

Reaction between alkynes and the chloride bridged cyclopalladated dimers $\{\overline{Pd(C_6H_4NHMe=O})\}_2(\mu-Cl)_2$ and $\{\overline{Pd(C_6H_4NHCMe=N}Ph)\}_2(\mu-Cl)_2$ has also resulted in the isolation of products in which one, two or three alkynes inserted into Pd-C bonds.[37] Earlier workers had reported the insertion of hexafluorobut-2-yne into the Ru-C bond of $Ru(C_6H_4PPh_2)(PPh_3)_2(\eta-C_5H_5)$ in which a bis-insertion product was isolated.[38]

Spanish workers[39] have found that $RuHCl(CO)(PPh_3)_3$ (22) readily inserts HC_2Ph, $HC_2(C_3H_7)$ and PhC_2Ph in CH_2Cl_2 to give red vinyl complexes $RuCl(RC{=}CHR')(CO)(PPh_3)_2$ (23) (R= H, R' = C_3H_7, Ph; R= R' = Ph) in which one phosphine ligand was eliminated. They later found[40] that complex (22) reacts readily with activated acetylenes RC_2R' (R= CO_2Me, CO_2Et, COMe and R = H; R=R' = CO_2Me) giving mixtures of products, from which complexes containing one, two or three alkyne molecules could be isolated. Two types of bis-insertion products were isolated $RuCl\{HC{=}C(CO_2R)C(H){=}C(H)(CO_2R)\}(CO)(PPh_3)_2$ (24) and $Ru\{R(O)C\}{-}C{=}C(H)C(H){=}C(H)(COR)][C{\equiv}C(COR)](CO)(PPh_3)_2$ (25). The mono-insertion products were analogous to complexes (23).



(25)

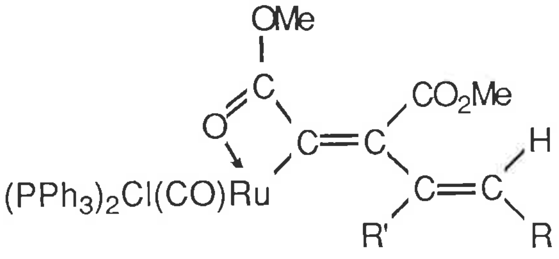


(24)

R= OMe, OEt

Complexes (24) and (25) were believed[41] to derive from insertion of alkynes into Ru-C bonds of initially formed vinyl complexes. Support for this was gained from the isolation of 'mixed' bis-insertion products $RuCl\{MeO(O)CC{=}C(CO_2Me)C(R'){=}CH(R)\}(CO)(PPh_3)_2$ (26).

(R´= R=H, Me, Ph; R´= H, R= C_3H_7, Bu^t, $SiMe_3$, Ph) from the reaction of vinyl complexes analogous to (<u>23</u>) with DMAD.[41]



(**<u>26</u>**)

Structural studies of complexes (<u>23</u>), (<u>24</u>), (<u>25</u>) and (<u>26</u>) allowed their stereochemistry to be unambiguously determined and from these it was determined that *cis* addition of acetylenes had occurred.

It is interesting to note that in the insertion oligomerisation reaction so far discussed only acyclic oligomers have been found except in cases where ketonic oxygens of ester groups also coordinate to metal atoms.

This acyclic oligomerisation of acetylenes is also observed in the insertion reactions of terminal acetylenes (HC≡CR´) into the Re-C bond of Re[(*E*)-{CH=CHR}](η-C_5H_5)$_2$ which affords butadienyl complexes Re[(*E,E*)-{CH=C(R´)C(H)-=C(R)(H)}](η-C_5H_5)$_2$[42] (R,R´=COMe, CO_2Me).

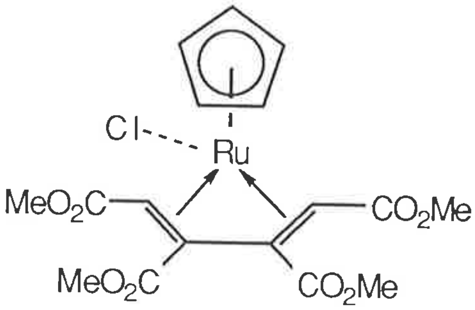
The first part of this chapter describes the reaction of dimethylacetylene dicarboxylate (DMAD) with RuX$(PPh_3)_2$-(η-C_5H_5)(X= Cl,I) and the second section describes the reinvestigation of the reaction between DMAD and RuH$(PPh_3)_2$-(η-C_5H_5).

RESULTS AND DISCUSSION

A. Reaction of Dimethyl acetylenedicarboxylate with some Cyclopentadienyl ruthenium complexes

(a) $RuCl(PPh_3)_2(\eta-C_5H_5)$ - Heating a suspension of $RuCl(PPh_3)_2(\eta-C_5H_5)$ and dimethyl acetylenedicarboxylate (DMAD), in the presence of NH_4PF_6, in refluxing methanol for *ca* 1 hour gave a complex mixture of products. Chromatography allowed the isolation of one major product, identified by the usual spectroscopic and microanalytical techniques as $RuCl\{\eta^4-CH(CO_2Me)=C(CO_2Me)C(CO_2Me)=CH(CO_2Me)\}-(\eta-C_5H_5)$ (27). The infrared spectrum of complex (27) contained strong to medium intensity bands at 1760, 1738, 1710 and 1697 cm^{-1}, which were assigned to the ν(C=O) stretching vibrations of the ester groups with the corresponding ν(C-O) bands being found at 1283, 1228, 1199 and 1163 cm^{-1}. The proton NMR spectrum contains five signals: that at δ 5.58 (s, 5H) was readily assigned to the C_5H_5 protons, and the singlets at δ 3.87 (6H) and 3.73 (6H) were assigned to two sets of equivalent CO_2Me protons. The two proton singlet at δ 2.00 was assigned to the butadiene protons. A molecular ion was observed in the FAB mass spectrum of complex (27) at *m/z* 488. Ions related to this by the loss of Cl, CO_2Me and (CO_2Me + 2OMe) were observed at *m/z* 453, 429 and 391, respectively. A metal-free (base) peak was observed at *m/z* 284 and was assigned to $[C_4(CO_2Me)_4]^+$.

The preceding data are consistent with the structure shown below.



(27)

The only tractable product obtained from a similar reaction carried out in refluxing toluene was hexamethyl mellitate, $C_6(CO_2Me)_6$, identified by comparison of its spectral properties (^1H NMR, EI MS) and melting point with those reported in the literature.[19]

The symmetrical nature of the NMR spectra suggests *E,E* stereochemistry for the butadiene moiety. Unfortunately crystals suitable for an X-ray structure determination could not be obtained to confirm this assignment.

Complex (27) was obtained in higher yield (60%) from the reaction of $RuCl(\eta^4-C_8H_{12})(\eta-C_5H_5)$ and tetramethyl (*Z,Z*)-1,3-butadiene-1,2,3,4-tetracarboxylate in MeOH at 60°C. The product obtained was shown to be identical (i.r., NMR) with the complex isolated from the reaction above.

(b) $RuI(PPh_3)_2(\eta-C_5H_5)$ - A suspension of the iodo-complex, NH_4PF_6 and DMAD in MeOH was refluxed for *ca* 10 h and the complex mixture obtained was separated by preparative tlc. Three major products were isolated and identified as $RuI\{\eta^4-CH(CO_2Me)=C(CO_2Me)C(CO_2Me)=CH(CO_2Me)\}(\eta-C_5H_5)$ (28), $Ru(\eta-C_5H_5)\{\eta^5-C_6H(CO_2Me)_6\}$ (29) and tetramethyl (*Z*,*Z*)-1,3-butadiene-1,2,3,4-tetracarboxylate (30) (Scheme 4.) by microanalytical and spectroscopic techniques.

In a similar reaction, $RuI(PPh_3)_2(\eta-C_5H_5)$, NH_4PF_6 and DMAD in MeOH were refluxed for 72 h. An appreciable amount of solid starting material was recovered by filtration. From the filtrate, after suitable work-up, a complex mixture of compounds was obtained. The major products isolated were (28) (16%), (29) (9%) and a product not previously observed which was formulated as $Ru(\eta-C_5H_5)\{\eta^5-C_8H(CO_2Me)_8\}$ (31).

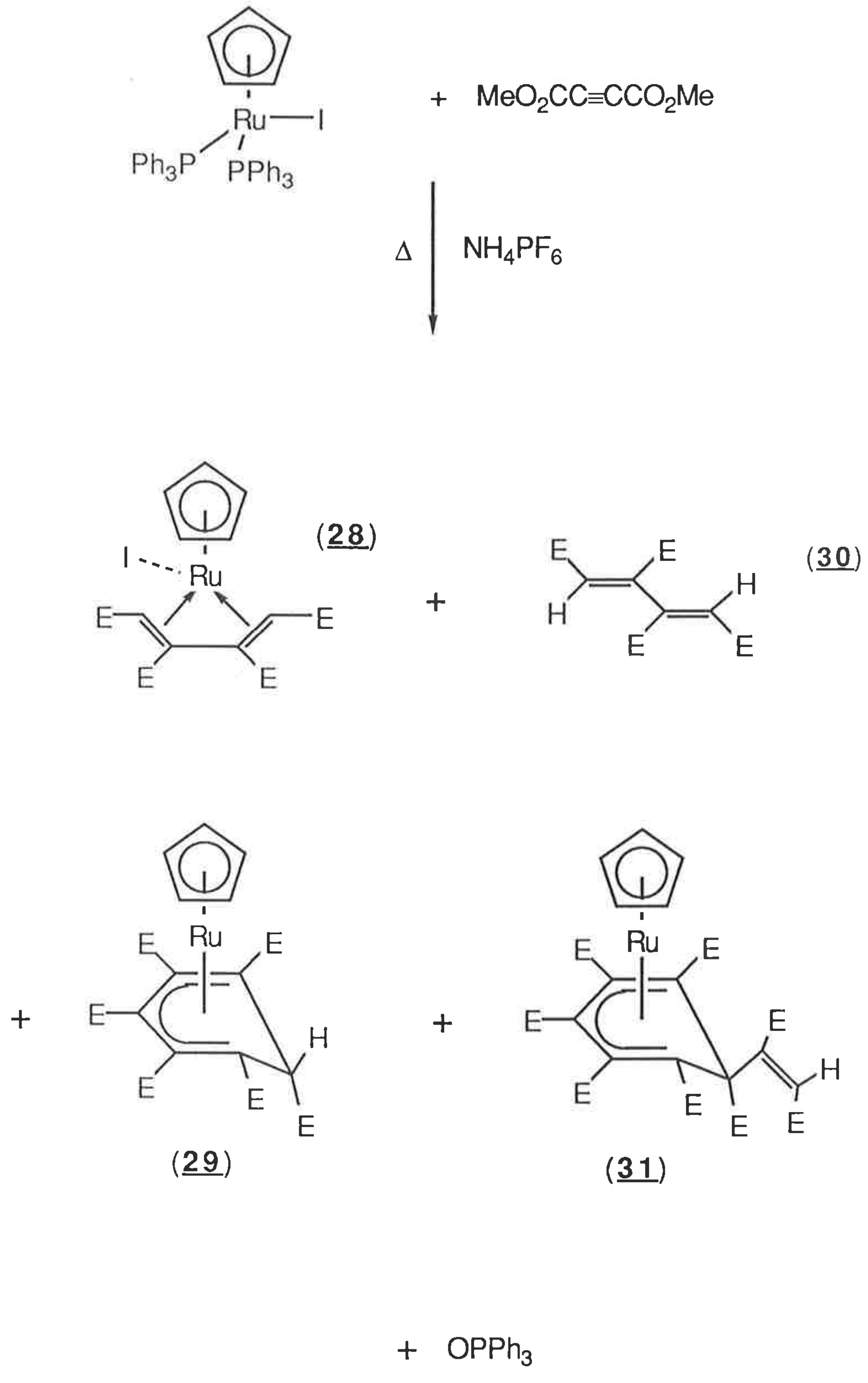
The molecular structures of complexes (28), (29) and (31) were determined unambiguously by X-ray crystallography.

Molecular structure of $RuI\{\eta^4-CH(CO_2Me)=C(CO_2Me)C(CO_2Me)=CH(CO_2Me)\}(\eta-C_5H_5)$ (28)

A plot of the structure of (28) is shown in Figure 1; Table 1 collects relevant bond distances and angles. The coordination about the ruthenium atom can be considered distorted octahedral with the C_5H_5 group occupying three positions and the other sites being taken up by the I atom and the butadiene ligand.

The Ru-C(C_5H_5) distances lie in the range 2.27(3)-2.14(3)Å (2.20Å av.) These values are within the ranges found for several other related complexes.[43,44]

The Ru-I distance [2.727(2)Å] is close to the Ru-I length in (*R*)-[$RuI(CO)(PPh_3)\{\eta-(S,R,S)-(-)-C_5H_4$ neomenthyl}] [2.708(1)Å].[45]



Scheme 4 E = CO_2Me

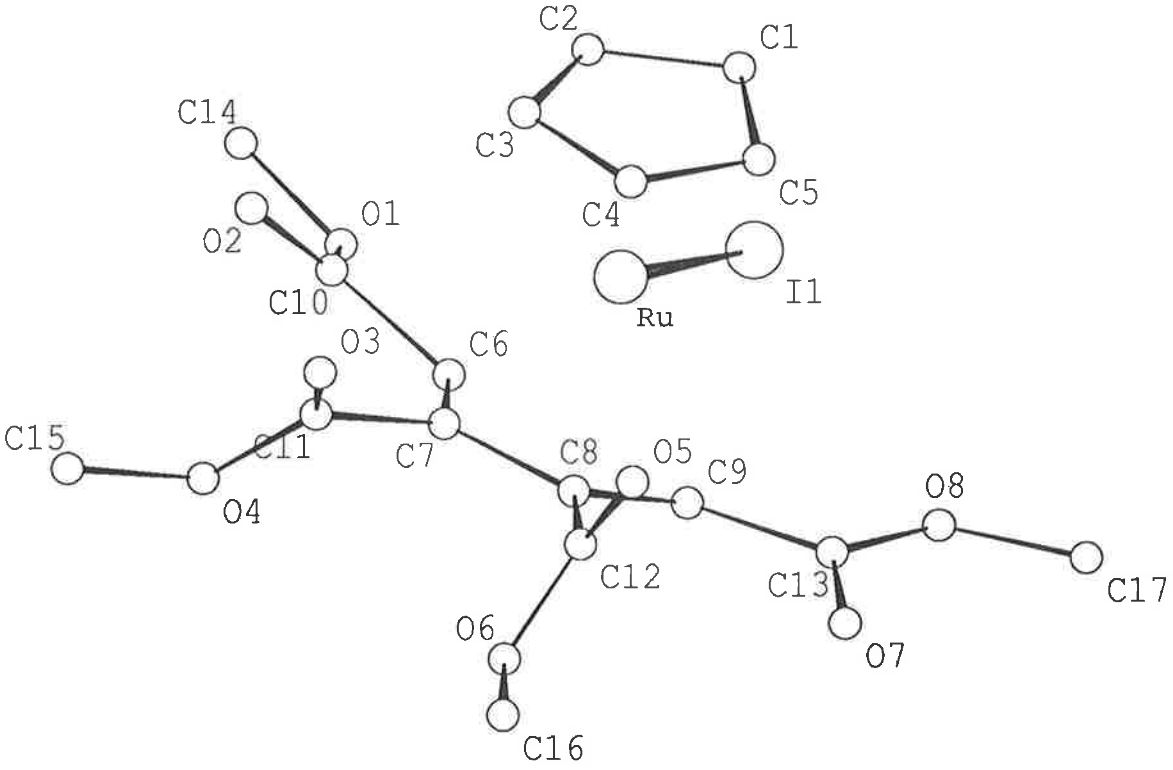


Figure 1. PLUTO plot of the molecular structure of RuI{η^4-CH(CO_2Me)=C(CO_2Me)C(CO_2Me)-=CH(CO_2Me)}(η-C_5H_5) (28) (by E.R.T. Tiekink)

Table 1. Selected interatomic parameters for (28)

Bond distances (Å)

Ru	---	I	2.727(2)	C(1)	---	Ru	2.265(33)
C(2)	---	Ru	2.199(24)	C(3)	---	Ru	2.232(34)
C(4)	---	Ru	2.173(24)	C(5)	---	Ru	2.143(30)
C(6)	---	Ru	2.202(21)	C(7)	---	Ru	2.147(22)
C(8)	---	Ru	2.145(18)	C(9)	---	Ru	2.217(25)
C(10)	---	C(6)	1.519(32)	C(7)	---	C(6)	1.389(32)
C(11)	---	C(7)	1.511(33)	C(8)	---	C(7)	1.484(29)
C(12)	---	C(8)	1.472(34)	C(9)	---	C(8)	1.374(33)
Ru	---	C(C_5H_5)	2.20(av.)	C(13)	---	C(9)	1.528(32)

Bond angles (°)

C(7)	-	Ru	-	I	116.8(6)
C(7)	-	C(6)	-	C(10)	112(3)
C(8)	-	C(9)	-	C(13)	118(2)
C(6)	-	C(7)	-	C(8)	118(2)
C(6)	-	C(7)	-	C(11)	128(2)
C(8)	-	C(7)	-	C(11)	115(2)
C(7)	-	C(8)	-	C(9)	116(2)
C(7)	-	C(8)	-	C(12)	123(2)
C(9)	-	C(8)	-	C(12)	121(2)

The C_4-carbons [C(6) - C(9)] of the butadiene moiety lie in a plane and are essentially equidistant from the ruthenium atom; the dihedral angle between the C_4 plane and the C_5H_5 ring plane is 20.4°. The Ru-butadiene carbon distances are in the range 2.15(2) - 2.22(3)Å (2.18Å av.) and are similar to the corresponding interaction in Ru{C(CO$_2$Me)=C(CO$_2$Me)C(CF$_3$)=CH(CF$_3$)}(PPh$_3$)(η-C$_5$H$_5$) (18) [2.185(5), 2.171(6)Å].[55] The other distances in the butadiene ligand of (28) are C(9) - C(8) [1.37(3)Å] and C(7) - C(6) [1.39(3)Å] which are similar to the length of the coordinated double bond in (18) [1.428(7)Å]. The 'middle' bond of the butadiene ligand can be considered to be a single bond [1.48(3)Å] and the angles C(9)C(8)C(7) and C(6)C(7)C(8) [116(2), 118(2)°] are consistent with sp^2 hybridised carbons. Only the ester group attached to C(9) appears to be coplanar with the butadienyl moiety. The interatomic parameters for the four ester groups are similar and will not be discussed further.

Spectroscopic data obtained for complex (28) was in accord with the determined structure. The nujol infrared spectrum contained four strong bands corresponding to ν(C=O) stretching vibrations at 1762, 1740, 1712s and 1700s cm^{-1}. The ^1H NMR spectrum of (28) was very similar to that of (27) and contained a singlet at δ 5.57 which was assigned to the C_5H_5 protons. The other singlets at δ 3.85 and 3.66 were assigned to two sets of equivalent methoxy proton resonances, integrating as six protons each. The ester groups attached to C(9), C(6) and C(7), C(8), respectively, in complex (28) appear to have essentially the same chemical environment and this is reflected in the ^1H NMR spectrum. The protons attached to C(9) and C(6) are found to resonate at δ 2.02 which is similar to the analogous butadienyl proton resonance in (18) (δ 2.18). These values suggest significant withdrawal of electron density from the butadiene double bonds probably coupled with a metal shielding effect.

The low field singlets at δ 171.0 and 165.4 in the $^{13}C\{^1H\}$-NMR spectrum of complex (28) were assigned to two sets of equivalent ester carbonyl carbons. The signal at δ 91.1 was assigned to the C_5H_5 carbons while the nearby resonance at δ 92.8 was assigned to the quaternary C(8) and C(7) carbons on the basis of its much smaller relative intensity, which is consistent with the longer relaxation time expected for these carbons. This value is considerably up-field from the Ru-C(vinyl) resonances found for some $Ru\{C(CO_2Me)=CH(CO_2Me)\}(L)_2(\eta-C_5H_5)$ complexes[46] (*ca* δ 175). The =CH resonances in these latter complexes were at much lower field (*ca* δ 160) than the analogous resonance in complex (28) (δ 47.9) this is consistent with withdrawal of electron density from the carbons. The methoxy carbons gave two equal intensity singlets at δ 51.7 and 53.4. A molecular ion was observed at *m/z* 580 in the FAB mass spectrum of (28). Other ions related to this by loss of OMe, CO_2Me, and I were found at *m/z* 549, 521 and 453, respectively. The metal free ion at *m/z* 286 was assigned to $[C_4(CO_2Me)_4H_2]^+$ and ions related to this by loss of OMe and CO_2Me were found at *m/z* 255 and 227, respectively.

The preceding data confirm the structure of (28) and the similarity of the spectroscopic data to those found for (27) strongly suggests that (27) has a closely related structure.

Structures of $Ru(\eta-C_5H_5)\{\eta^5-C_6H(CO_2Me)_6\}$ (29) and $Ru(\eta-C_5H_5)\{\eta^5-C_8H(CO_2Me)_8\}$ (31)

The molecular structures of complexes (29) and (31) are shown in Figures 2 and 3, respectively. Relevant interatomic parameters for both complexes are collected in Table 2. Complexes (29) and (31) are obviously related and result from the tri- and tetra-merisation of DMAD, and differ by the replacement of the endocyclic H atom attached to C(11) in (29) by the $-C(CO_2Me)=CH(CO_2Me)$ unit in (31). Coordination about the ruthenium atoms in both complexes can be considered distorted octahedral with the η^5-C_6 and C_5H_5 ligands in each complex occupying three coordination positions, respectively.

Least squares planes through the C_5H_5 rings in complexes (29) and (31) are 1.83 and 1.84Å distant from their respective ruthenium atoms. The planes bonded by C(6) - C(10) in the coordinated portion of the η^5-C_6 ligands, in (29) and (31), are found somewhat closer to the ruthenium [1.66 and 1.65Å , respectively] than the cyclopentadienyl rings in each complex. The acute dihedral angles between the planes defined by C(6)-C(10) and C(6)C(11)C10), within the cyclohexadienyl ligands of (29) and (31), are 47.6 and 55.2°, respectively. In addition the dihedral angles between the η^5-C_6 plane and the C_5H_5 plane in (29) and (31) are 2.1 and 7.2°. The larger angles in (31) are probably a result of steric interaction of

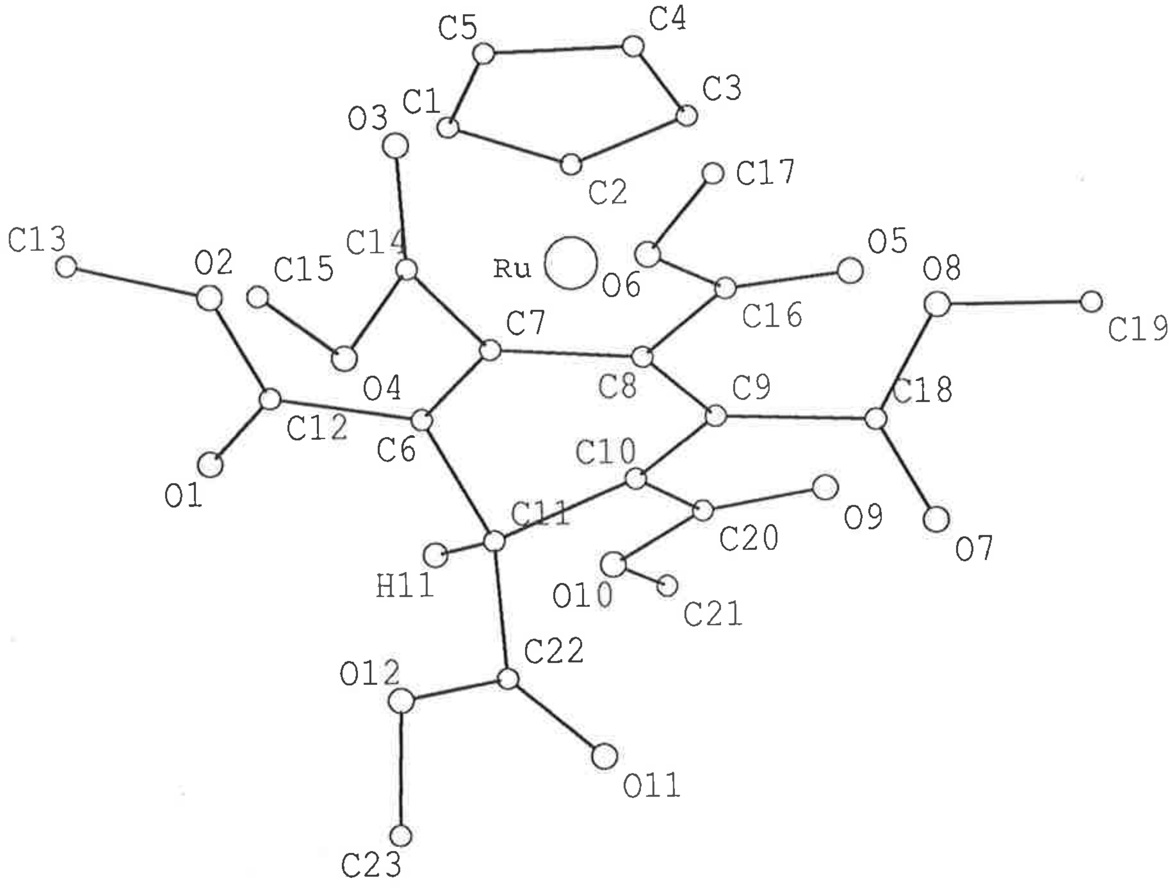


Figure 2. PLUTO plot of the molecular structure of Ru(η-C_5H_5){η^5-$C_6H(CO_2Me)_6$} (29) (by E.R.T. Tiekink)

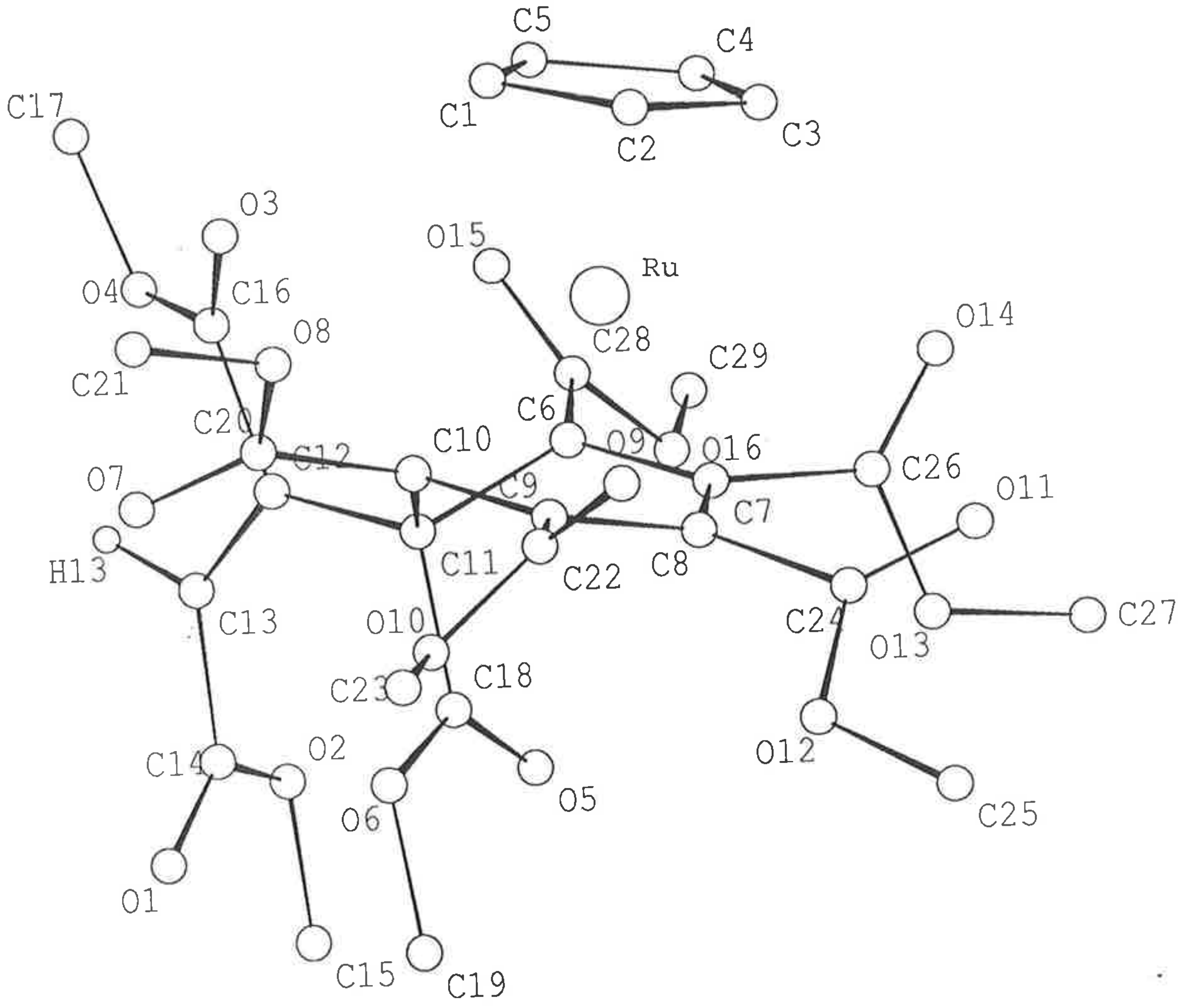


Figure 3. PLUTO plot of the molecular structure of $Ru(\eta\text{-}C_5H_5)\{\eta^5\text{-}C_8H(CO_2Me)_8\}$ (31) (by B.K. Nicholson)

Table 2. Selected bond distances (Å) and angles (°) for complexes (29) and (31)

	(29)	(31)
Ru - $C(C_5H_5)$ 1	2.201(3)	2.207(2)
Ru - $C(C_5H_5)$ 2	2.202(3)	2.231(3)
Ru - $C(C_5H_5)$ 3	2.186(3)	2.216(3)
Ru - $C(C_5H_5)$ 4	2.174(3)	2.183(2)
Ru - $C(C_5H_5)$ 5	2.181(3)	2.178(2)
Ru - C(6)	2.193(2)	2.154(3)
Ru - C(7)	2.138(2)	2.125(3)
Ru - C(8)	2.181(2)	2.178(3)
Ru - C(9)	2.148(2)	2.146(3)
Ru - C(10)	2.183(3)	2.189(3)
Ru - C(11)	2.773(2)	-
C(6) - C(7)	1.429(3)	1.422(4)
C(7) - C(8)	1.444(3)	1.437(4)
C(8) - C(9)	1.451(4)	1.429(4)
C(9) - C(10)	1.425(4)	1.440(4)
C(10) - C(11)	1.514(3)	1.529(4)
C(6) - C(11)	1.511(3)	1.552(4)
C(12) - C(13)	-	1.333(5)
C(6) - C(7) - C(8)	117.4(2)	117.3(2)
C(7) - C(8) - C(9)	118.2(2)	118.4(3)
C(8) - C(9) - C(10)	118.4(2)	118.3(3)
C(9) - C(10) - C(11)	117.5(2)	114.6(2)
C(10) - C(11) - C(6)	101.8(2)	97.9(2)
C(11) - C(6) - C(7)	119.2(2)	115.7(2)
C(11) - C(12) - C(13)	-	125.4(3)
C(12) - C(13) - C(14)	-	132.5(3)
C(13) - C(12) - C(16)	-	116.1(3)
dihedral angle between C(1) - C(5) plane and C(6) - C(10) plane	2.1	7.2

the pendant bis(methoxycarbonyl)vinyl group attached to C(11) with the rest of the molecule. These latter dihedral angles may be compared with those of ruthenocene[47] (0.0°) and Ru(η-C_5H_5)[η-$C_5(CO_2Me)_5$][48] (1.5°). In this latter complex the $C_5(CO_2Me_5)$ ring is closer to the ruthenium than is the C_5H_5 ring, the distances from the ruthenium atom being 1.796 and 1.817Å, respectively. This phenomenon was also observed in the previously discussed structure of (28), in which the plane containing the butadiene carbons is 0.15Å closer to the ruthenium than the C_5 plane of the cyclopentadienyl ring. A possible reason for the closer approach of the C_6 ligand in (28) and (31) is that, in the ligands containing electron withdrawing CO_2Me groups, compensation for loss of electron density is made by stronger Ru-ligand back donation thereby shortening the bonds between the metal and the η^5-C_6 ligands. The individual Ru-C(C_5H_5) and Ru-C_6 distances are similar for (29) and (31).

The range of C-C distances found in the C_5H_5 ring of (4) [1.383(5) - 1.429(5)Å] correspond with those in ruthenocene[47] [1.428 - 1.438Å]. The C-C distances for the coplanar atoms [C(6)-C(10)] vary from 1.425(4) to 1.451(4)Å in (28) and from 1.422(4) to 1.440(4)Å in (31). The single bond distances to the uncoordinated ring carbons are 1.511(3)Å [C(6)-C(11)] and 1.514(3)Å [C(10)-C(11)] in (29) and 1.552(4)Å [C(6)-C(11)] and 1.529(4)Å [C(10)-C(11)] in (31).

The ester group attached to C(11) in (29) is *exo*-cyclic with a hydrogen in the *endo* position which is replaced by a bis(methoxycarbonyl)vinyl group in complex (31). The vinyl proton, attached to C(13) in (31), was located in the structure determination and is included in a fixed position. The vinyl moiety carries the two CO_2Me groups in a mutually *trans* configuration with the C=C distance [C(12)-C(13) 1.333(5)Å] comparable to that found in $Pt(H)\{(Z)\text{-}C(CO_2Me)=CH(CO_2Me)\}(PBu^nBu^t{}_2)_2$ [49] (32) [1.37(2)Å]. The angle C(12)- C(13)-C(14) in (31) is 132.5(3)° with the analogous angle in the platinum compound being slightly smaller [124.8(8)°].

The ruthenium atoms in (29) and (31) achieve an eighteen electron configuration by five electron donations from the C_5H_5 and η^5-cyclohexadienyl ligands.

Spectroscopic data obtained for (29) and (31) are in good agreement with the determined structures and comparison of the data allows complete assignment.

Their infrared spectra contain very strong broad absorptions between 1730 - 1700 cm^{-1} which are assigned to the stretching vibrations of the ester groups ν(C=O) with the corresponding strong ν(C-O) absorptions found between 1210 - 1270 cm^{-1}. A weak ν(C=C) band was also found at 1640 cm^{-1} in the infrared spectrum of (31). The methoxy groups attached to the η^5-C_6 ring gave signals with relative intensities 3/9/6 in the ^1H NMR spectra of complexes (29) (δ 3.55, 3.84 and 3.76) and (31) (3.52, 3.59 and 3.76), respectively.

The two methoxy resonances of the $-C(CO_2Me)=CH(CO_2Me)$ group attached to C(11) are found at δ 3.80 and 3.81 in the proton spectrum of (31) with the *endo*-proton of complex (29) giving a resonance at δ 4.54. Signals at δ 5.04 and 5.15 were assigned to the cyclopentadienyl protons of (29) and (31), respectively.

The $^{13}C\{^1H\}$ NMR spectrum of (29) contained resonances for the methoxy carbons at δ 51.6, 52.1 and 53.0 and the *exo*-carbon C(11) resonance was found at δ 42.4. The signal at δ 84.5 was assigned to the C_5H_5 carbons. Of the remaining ring carbons only C(6), C(10) and C(7),C(8), C(9) are likely to be in similar chemical environments and therefore the signals at δ 87.8 and 94.9 were assigned to these carbons, respectively. The three low field resonances at 166.5, 167.1 and 171.7 were assigned to the carbonyl resonances of the ester groups.

The FAB mass spectra of (29) and (31) contained molecular ions at *m/z* 594 and 737($[M + H]^+$) respectively, and ions related to these by loss of OMe and CO_2Me at *m/z* 535 and 677 ($[M - CO_2Me]^+$). The ion at *m/z* 477 in the FAB spectrum of (29) was assigned the formula $[Ru(C_5H_5)\text{-}\{C_6H_2(CO_2Me)_4\}]$ from which was observed the sequential loss of four "$C_2H_2O_2$" groups giving an ion at *m/z* 244 assigned to $[Ru(C_5H_5)(C_6H_6)]^+$. Both these cations can be assigned stable 18e configurations. A similar effect has been observed in the FAB mass spectrum of $Ru(\eta\text{-}C_5H_5)\{\eta\text{-}C_5(CO_2Me)_5\}$.[50] Loss of C_6H_6 was observed from the ion at *m/z* 244 giving a peak corresponding to $[Ru(C_5H_5)]^+$. The ion at *m/z* 594 in the FAB spectrum of (31) can be related to the parent ion by loss of $C_2(CO_2Me)_2$.

The butadiene (30) isolated from the reaction of $RuI(PPh_3)_2(\eta\text{-}C_5H_5)$ and DMAD was identified by comparison of its spectral data (EI MS and ^1H NMR) with literature values.[51]

A small amount of $OPPh_3$ was also isolated from the reaction.

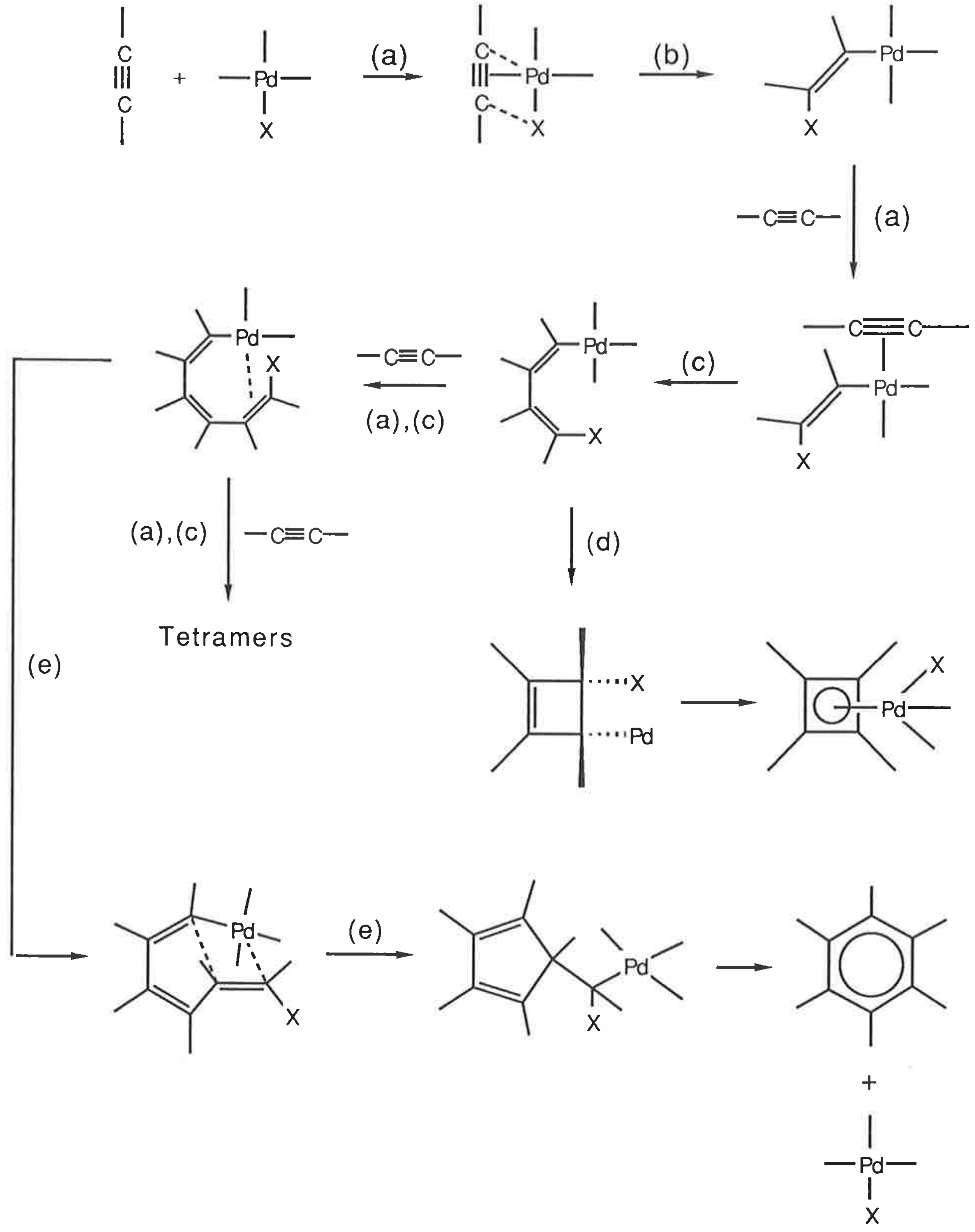
The formation of (31) containing a vinyl cyclohexadienyl ligand to the author's knowledge represents an unprecedented tetramerisation of DMAD on a mononuclear ruthenium centre.

The reaction of $RuI(PPh_3)_2(\eta-C_5H_5)$,$C_2(CO_2Me)_2$ and $HPF_6 \cdot OEt_2$ in MeOH at reflux gave a complex mixture of products. After suitable work-up, one of these products was readily identified as complex (28) and the only other compound isolated was the organic species $C_6(CO_2Me)_6$.

The mechanism for the formation of (27), (28), (29) and (31) is still unclear and is obviously complex judging from the numerous trace bands obtained after thin layer chromatographic separation of the product mixtures obtained in these reactions.

It appears that complex (28) is formed independently of complexes (29) and (31), because (29) and (31) are not formed from the reaction of (28) with excess DMAD.

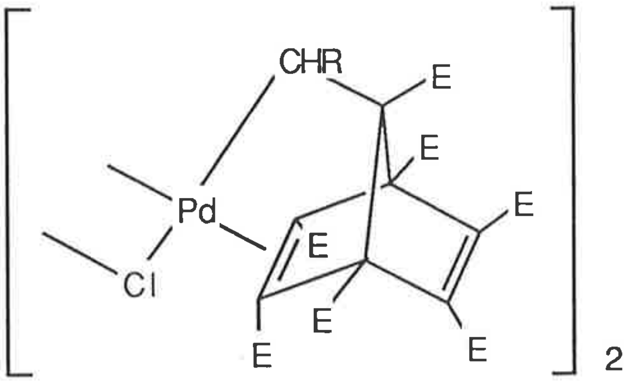
Maitlis and co-workers[12] have previously described the tri- and tetramerisation of DMAD on palladium systems such as $PdCl_2(PhCN)_2$. The proposed mechanism (Scheme 5) features step-wise addition of acetylene molecules and provides a route for the formation of possible tetramers and acetylene cyclotrimerisation products. The first stage [step (a)] is the formation of a π acetylene complex, followed by *cis*-ligand insertion step (b). The further reaction of these vinyl intermediates is by fast step-wise *cis*-addition into Pd-C bonds; oligomerisation proceeds in this way [step (c)]. Maitlis determined that the extent


C
C
Pd
X
(a)
C
C
Pd
X
(b)
Pd
X
—C≡C—
(a)
—C≡C—
Pd
X
(c)
Pd
X
—C≡C—
(a),(c)
Pd
X
(a),(c)
—C≡C—
Tetramers
(d)
(e)
X
Pd
X
Pd
Pd
X
(e)
Pd
X
+
Pd
X

Scheme 5

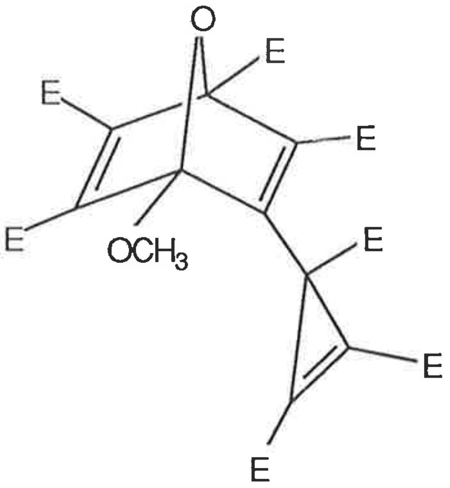
of this reaction was governed by the size of the acetylenic substituents. Bulky substituents, e.g. phenyl, cause the reaction to cease after two acetylenes have added and lead to processes like step (d). For smaller substituents (e.g. methyl) three or four acetylenes can be incorporated before rearrangement or decomposition reactions [e.g. step (e)] become fast with respect to further oligomerisation.

Products obtained from the reaction of $PdCl_2(PhCN)_2$ and DMAD in methanol include the complex

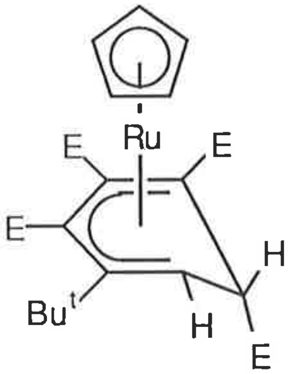


together with $HC_5(Co_2Me)_5$ and $C_6(CO_2Me)_6$.[52]

It is also interesting to note that DMAD tetramerizes spontaneously to give the cyclopropenyloxanorbornadiene compound below,[53]

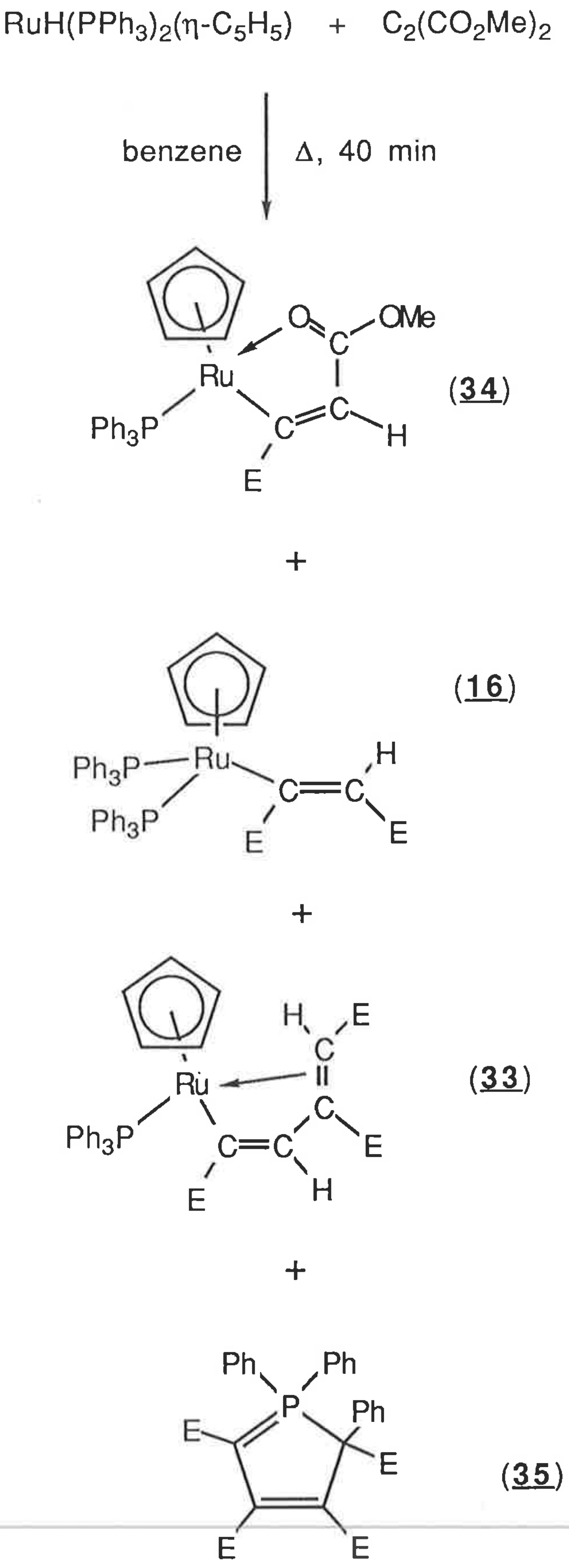


The reaction of Ru{C(CO$_2$Me)=C(CO$_2$Me)C(CO$_2$Me)=CH(CO$_2$Me) -(PPh$_3$)(η-C$_5$H$_5$) (33) with HC$_2$Bu^t gave a structurally characterised product analogous to (29).[54]



(c) $RuH(PPh_3)_2(\eta\text{-}C_5H_5)$ (14) - Reactions between the hydride complex and alkynes have given a number of interesting products, including vinyl, butadienyl, and cumulenyl complexes.[34] Two complexes were reported to have been obtained from the reaction of DMAD and $RuH(PPh_3)_2(\eta\text{-}C_5H_5)$:[34] the 1:1 adduct $Ru\{(E)C(CO_2Me){=}CH(CO_2Me)\}(PPh_3)_2(\eta\text{-}C_5H_5)$ (16) and the chelate complex $Ru\{C(CO_2Me){=}CHC(O)OMe\}(PPh_3)(\eta\text{-}C_5H_5)$ (34). For (16) the assignment of geometry was not clear cut, but on the basis of a small value of J(PH) (*ca* 7Hz) found for the vinyl proton, and the ready conversion to (34), the *trans* configuration was originally preferred[34] (for the following discussion, *cis* and *trans* refer to the mutual configuration of the two CO_2Me groups). However, it was recognised that the stereochemistry of the isolated complex was not necessarily the initial stereochemistry, since a facile isomerisation might have occurred. In this regard it is relevant to recall that the first formed *trans* adduct of DMAD with $ReH(\eta\text{-}C_5H_5)_2$ isomerises on heating in benzene.[32]

A reinvestigation of the reaction between DMAD and $RuH(PPh_3)_2(\eta\text{-}C_5H_5)$ (14) was undertaken. The original preparation of $Ru\{C(CO_2Me){=}CH(CO_2Me)\}(PPh_3)_2(\eta\text{-}C_5H_5)$ (16) was carried out in diethyl ether for 5 h and gave over 90% isolated yields. In contrast, reaction in refluxing benzene for 40 min afforded four products (Scheme 6): complex (16), the cyclic vinyl complex (34), yellow $Ru\{C(CO_2Me){=}C(CO_2Me)C(CO_2Me){=}CH(CO_2Me)\}(PPh_3)(\eta\text{-}C_5H_5)$ (33) and the PPh_3/DMAD adduct (35). The new complex (33) was identified by elemental microanalysis and spectroscopic data. Full stereochemical characterisation was achieved by a single crystal X-ray study.



Scheme 6 $E = CO_2Me$

Structure of Ru{C(CO$_2$Me)=C(CO$_2$Me)C(CO$_2$Me)=CH(CO$_2$Me)-(PPh$_3$)(η-C$_5$H$_5$)   (33)

The structural study confirmed the 1,3,4-η^3-butadienyl structure, a diagram of which is given in Figure 4 (see also Table 3).

The ruthenium atom is coordinated by the C$_5$H$_5$ group [Ru-C(C$_5$H$_5$) 2.207(6) - 2.247(7)Å, av. 2.228Å], the PPh$_3$ ligand [Ru-P 2.346(2)Å], and the butadienyl group, which is attached by the σ-bonded carbon [Ru-C(6) 2.060(6)Å] and the 'outer' C=C double bond of the butadiene [Ru-C(8) 2.189(6), Ru-C(9) 2.194(6)Å]. These distances may be compared with those found in (17), Ru{C(CO$_2$Me)=C(CO$_2$Me)C(CF$_3$)=CH(CF$_3$)}-(PPh$_3$)(η-C$_5$H$_5$) (18) and Ru{C(Ph)=C(Ph)C(Ph)=CH(Ph)}-{P(OMe)$_3$}(η-C$_5$H$_5$) (36) (Table 4). No significant differences were found.

Spectroscopic data obtained for complex (33) were in accord with the determined structure. Strong ν(C=O) bands were found at 1716 and 1699 cm^{-1} in the infrared spectrum, with a weak band assigned to a ν(C=C) vibration at 1585 cm^{-1}. The ^{1}H and ^{13}C{^{1}H} spectra were readily assigned, the former containing three sharp singlet resonances between δ 3.13 - 3.80 with relative intensities 3/6/3, assigned to the OMe groups, together with a vinyl proton resonance at δ 2.22, which is coupled to a single ^{31}P nucleus. The ^{13}C{^{1}H} NMR spectrum shows four resonances between δ 50.7 - 52.1 which were assigned to the methoxycarbons with the resonances at δ 45.4 and 62.8 assigned to C(8) and C(9), respectively. A singlet was found for the cyclopentadienyl carbons at δ 89.5 with the Ru-C(6) signal being found, characteristically, at δ 162.5 [d, *J*(PC) 16Hz]. The methoxycarbonyl resonances were found at δ 172.6,

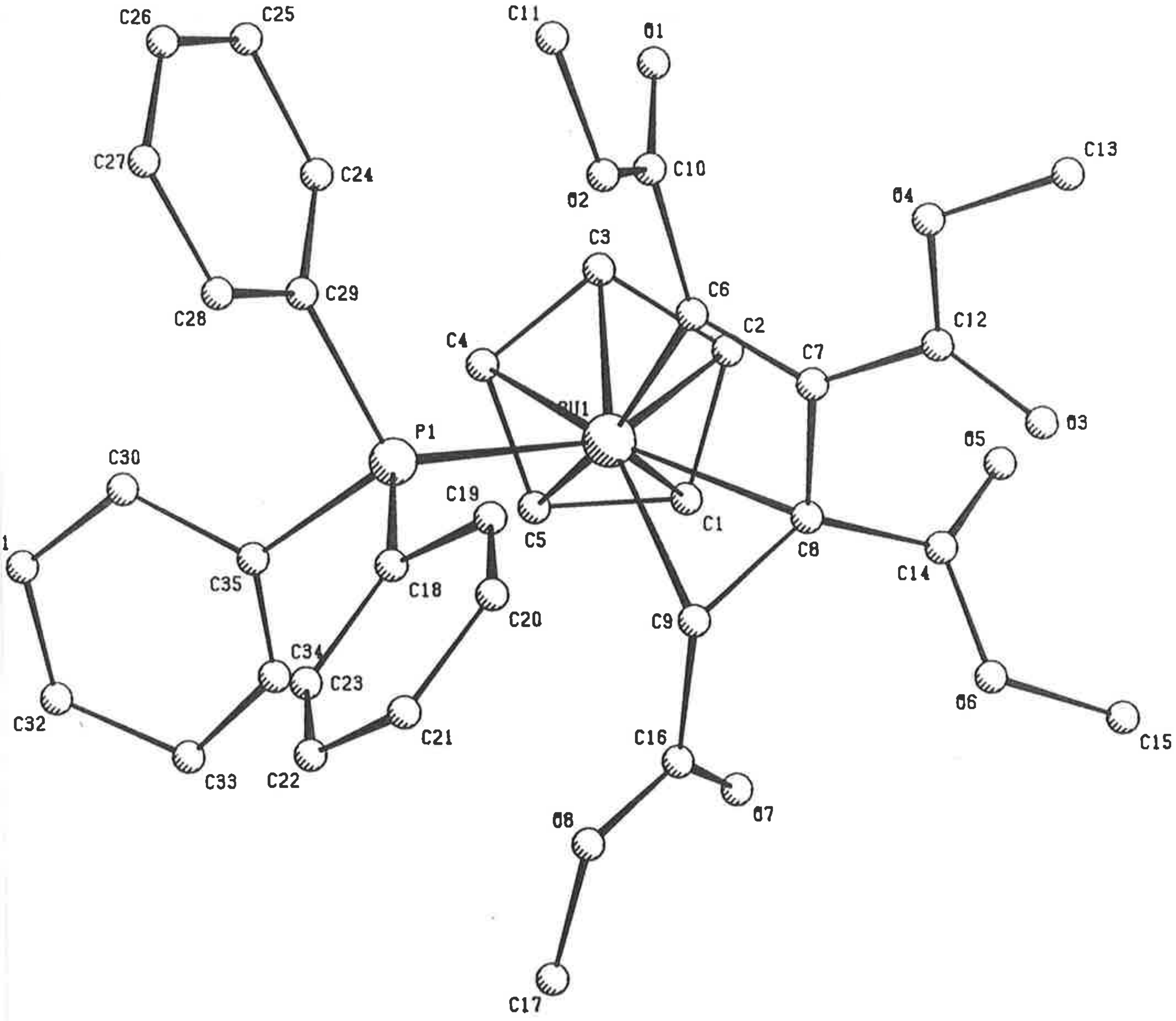


Figure 4. Molecular structure of $Ru\{C(CO_2Me)=C(CO_2Me)C(CO_2Me)=CH(CO_2Me)\}(PPh_3)(\eta\text{-}C_5H_5)$ (33)

(by M.R. Snow and E.R.T. Tiekink)

Table 3. Selected bond lengths and valence angles for $Ru\{C(CO_2Me)=C(CO_2Me)C(CO_2Me)=CH(CO_2Me)\}$-$(PPh_3)(\eta\text{-}C_5H_5)$ (33)

Bond distances (Å)

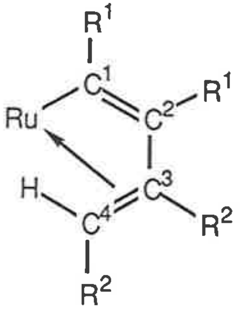
Ru(1) - C(1)	2.207(6)	P(1) - C(18)	1.833(4)
Ru(1) - C(2)	2.219(6)	P(1) - C(29)	1.839(4)
Ru(1) - C(3)	2.247(7)	P(1) - C(35)	1.835(4)
Ru(1) - C(4)	2.225(7)	C(6) - C(7)	1.36(1)
Ru(1) - C(5)	2.243(7)	C(6) - C(10)	1.48(1)
Ru(1) - C(cp)(av)	2.228	C(7) - C(8)	1.52(1)
Ru(1) - P(1)	2.346(2)	C(7) - C(12)	1.43(1)
Ru(1) - C(6)	2.060(6)	C(8) - C(9)	1.42(1)
Ru(1) - C(7)	2.663(6)	C(8) - C(14)	1.50(1)
Ru(1) - C(8)	2.189(6)	C(9) - C(16)	1.50(1)
Ru(1) - C(9)	2.194(6)		

Bond angles (°)

P(1) - Ru(1) - C(6)	88.9(2)	Ru(1) - C(6) - C(7)	100.4(4)
P(1) - Ru(1) - C(8)	117.7(2)	Ru(1) - C(6) - C(10)	132.2(5)
P(1) - Ru(1) - C(9)	88.1(2)	C(6) - C(7) - C(8)	104.7(5)
C(6) - Ru(1) - C(8)	64.6(2)	C(6) - C(7) - C(12)	131.6(6)
C(6) - Ru(1) - C(9)	84.7(2)	C(7) - C(8) - C(9)	117.7(6)
Ru(1) - P(1) - C(18)	119.0(1)	C(7) - C(8) - C(14)	114.4(6)
Ru(1) - P(1) - C(29)	117.0(1)	C(8) - C(9) - C(16)	122.3(6)
Ru(1) - P(1) - C(35)	111.5(2)		

Table 4

Some structural parameters for η^3-butadienylruthenium complexes



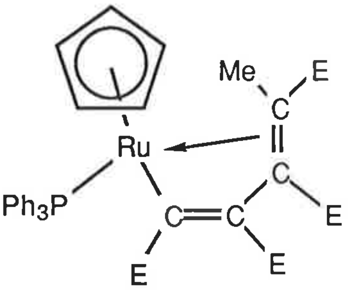
Complex	(33)	(17)	(18)	(36)
R^1	CO_2Me	CF_3	CO_2Me	Ph
R^2	CO_2Me	CF_3	CF_3	Ph
Bond distances (Å)				
Ru-C(1)	2.060(6)	2.05	2.082(1)	2.070(7)
Ru-C(3)	2.189(6)	2.16	2.185(5)	2.248(7)
Ru-C(4)	2.194(6)	2.19	2.171(6)	2.253(7)
C(1)-C(2)	1.355(9)	1.33	1.348(7)	1.330(9)
C(2)-C(3)	1.515(8)	1.51	1.509(8)	1.509(9)
C(3)-C(4)	1.421(9)	1.42	1.428(7)	1.418(10)
Bond angles (deg)				
Ru-C(1)-C(2)	100.4(4)	[a]	99.4	[a]
C(1)-C(2)-C(3)	104.7(5)	[a]	105.5(4)	[a]
C(2)-C(3)-C(4)	117.7(6)	[a]	117.2(4)	[a]
Reference	This work	[33]	[55]	[57]

[a] Not available.

173.0 and 174.4. The FAB mass spectra of (<u>33</u>) gave a molecular ion at *m/z* 714 and ions related to this by loss of MeOH and CO_2Me were also found at *m/z* 682 and 655, respectively.

Compound (<u>35</u>) was identified as the yellow 1:2 adduct of PPh_3 with DMAD by comparison with an authentic sample prepared as described by Johnson and Tebby.[56]

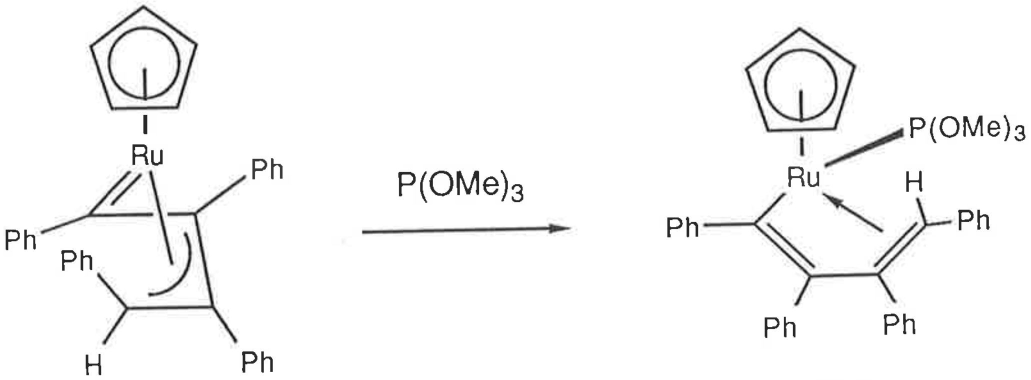
The formal insertion of two alkyne molecules into Ru-H or Ru-C bonds was first observed in the previously mentioned reaction between $RuH(PPh_3)_2(\eta-C_5H_5)$ and $C_2(CF_3)_2$[34] and subsequently in the addition of DMAD to $RuMe(PPh_3)_2$-$(\eta-C_5H_5)$ generating the butadienyl complexes (<u>17</u>) and (<u>37</u>), respectively.



(**<u>37</u>**; E = CO_2Me)

Complex (<u>33</u>) was not observed in the initial studies of the reaction between the hydride and DMAD, although, as we have now shown, it can be isolated as a stable yellow crystalline solid if the reaction conditions are modified. It has been shown previously[34] that the vinyl complex (<u>16</u>) reacts with $C_2(CF_3)_2$ to give the mixed insertion product (<u>18</u>), where the entering alkyne has apparently inserted into the vinylic C-H bond of (<u>16</u>)

in contrast to the Ru-H or Ru-C insertions discussed earlier. The related tetraphenylbutadienyl complex (36) was obtained from the reaction of the σ,η^3(5e)-butadienyl [Ru=C(Ph)-η^3-{C(Ph)C(Ph)CH(Ph)}(η-C_5H_5)] (38) with the two electron donor $P(OMe)_3$.[57]



(**38**)

(**36**)

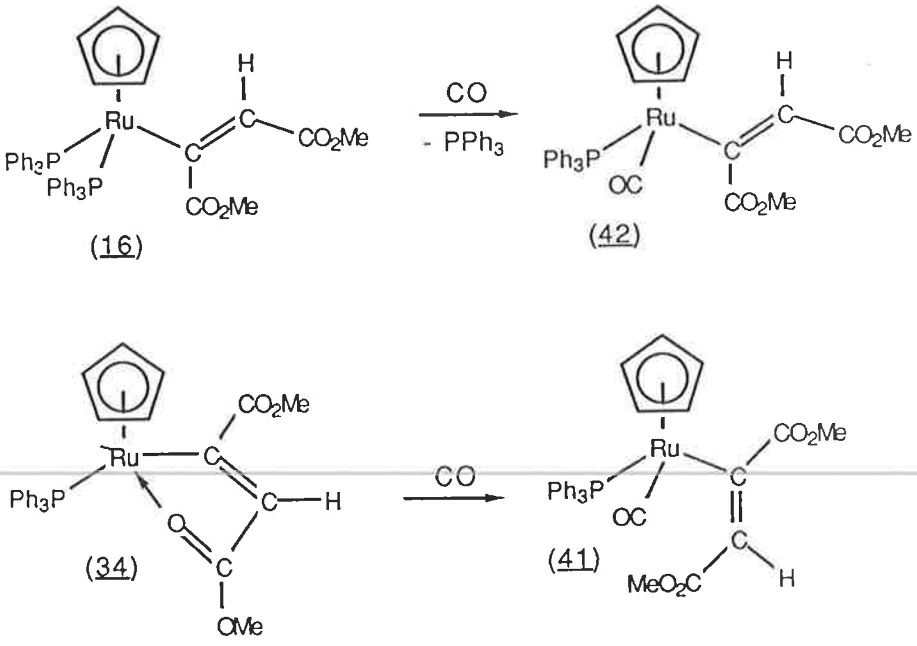
Stereochemistry and isomerisation of the MC(CO_2Me)=CH(CO_2Me) group

The chief interest in these reactions was the configuration of the attached 1,2-bis(methoxycarbonyl)ethenyl group of (16) and methods for the determination of stereochemistry of these groups were sought, without recourse to X-ray structural studies.

Complexes related to (16) had been prepared previously by the reaction of RuH(L-L)(η-C_5H_5) [L-L=dppm,dppe] with DMAD[46] which afforded the yellow complexes Ru{(C(CO_2Me)=CH(CO_2Me)}(L-L)(η-C_5H_5) [L-L = dppm (39), dppe (40)]. Similarly, the osmium analogue of (16) was prepared.[46] The molecular structure of (40) was determined and it was clear that the two CO_2Me groups were in a mutual *cis* configuration.

Conversion of complex (16) into complex (34) was originally achieved by thermolysis, with concomitant loss of PPh_3.[34] It was found that addition of MeI to a solution of (16) in refluxing toluene rapidly gave a white precipitate of $[PMePh_3]I$; the resulting red solution gave (34) in > 80% yield, after chromatography. This represented a considerable improvement in the yield.

The carbonylation of (34) under mild conditions (12.5 atm, 100°C, 2 h) gave a yellow solution from which was obtained, after suitable work-up, a complex readily formulated as $Ru\{C(CO_2Me)=CH(CO_2Me)\}(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (41), from its spectroscopic properties. An isomeric yellow compound (42) was obtained from the carbonylation (40 atm, 110°C, 21 h) of (16) in a $MeOH/CH_2Cl_2$ mixture. (42) was found to have different spectroscopic properties (*cf* $\nu(C\equiv O)$ 1954 cm^{-1} (41); $\nu(C\equiv O)$ 1940 cm^{-1} (42)].



Scheme 7

The monocarbonyl complexes (41) and (42) provided the opportunity to see whether spectroscopic differention could be made between *cis* and *trans* isomers (Scheme 7) as the stereochemistry of complex (41) was unambiguously determined by X-ray crystallography.

Molecular structure of Ru{(*Z*)-C(CO_2Me)=CH(CO_2Me)}(CO)(PPh_3)-(η-C_5H_5) (41)

A molecule of (41) is shown in Figure 5 (see also Table 5). The vinyl group has mutually *trans* - CO_2Me groups and this was expected as (41) was obtained from the opening of the chelate ring in complex (34). Coordination of the ruthenium atom to the vinyl group [Ru-C 2.080(8)Å], a CO ligand [Ru-C 1.847(7)Å], the PPh_3 ligand [Ru-P 2.310(2)Å] and the η-C_5H_5 group [Ru-C(C_5H_5) 2.250 - 2.264(7) or 2.258Å] is unexceptional and as found in previously discussed structures, the ruthenium coordination is distorted octahedral.

Comparing the structure of (41) with the structures of some related molecules such as (40)[46], Pd{(*E*)-C(CO_2Me)=CH-(CO_2Me)}(C_2Ph)(PEt_3)$_2$ (43)[58], Pt($C_6H_4PPh_2$){(*E*)-C(CO_2Me)=CH-(CO_2Me)}(PPh_3) (44)[59], RuCl{(*Z*)-C(CO_2Me)=CCl(CO_2Me)}(CO)$_2$-(PPh_3)$_2$(45)[60], *trans* PtH{(*Z*)-C(CO_2Me)=CH(CO_2Me)}($PBu^nBu^t{}_2$)$_2$ (32)[49], or [N(PPh_3)$_2$][Pt{(*E*)-C(CO_2Et)=CCl(CO_2Pr^i)}Cl_2(CO)] (46)[61] (Table 6) it is evident that there are no significant differences in the C(CO_2Me)=CH(CO_2Me) groups.

The structure determination unequivocally established the configurations of the vinyl ligand in complex (41). Furthermore, since the carbonylation of (16), and the reaction between RuH(CO)(PPh_3)(η-C_5H_5) and DMAD[62] both afforded (42), it is likely that *cis* addition of the metal

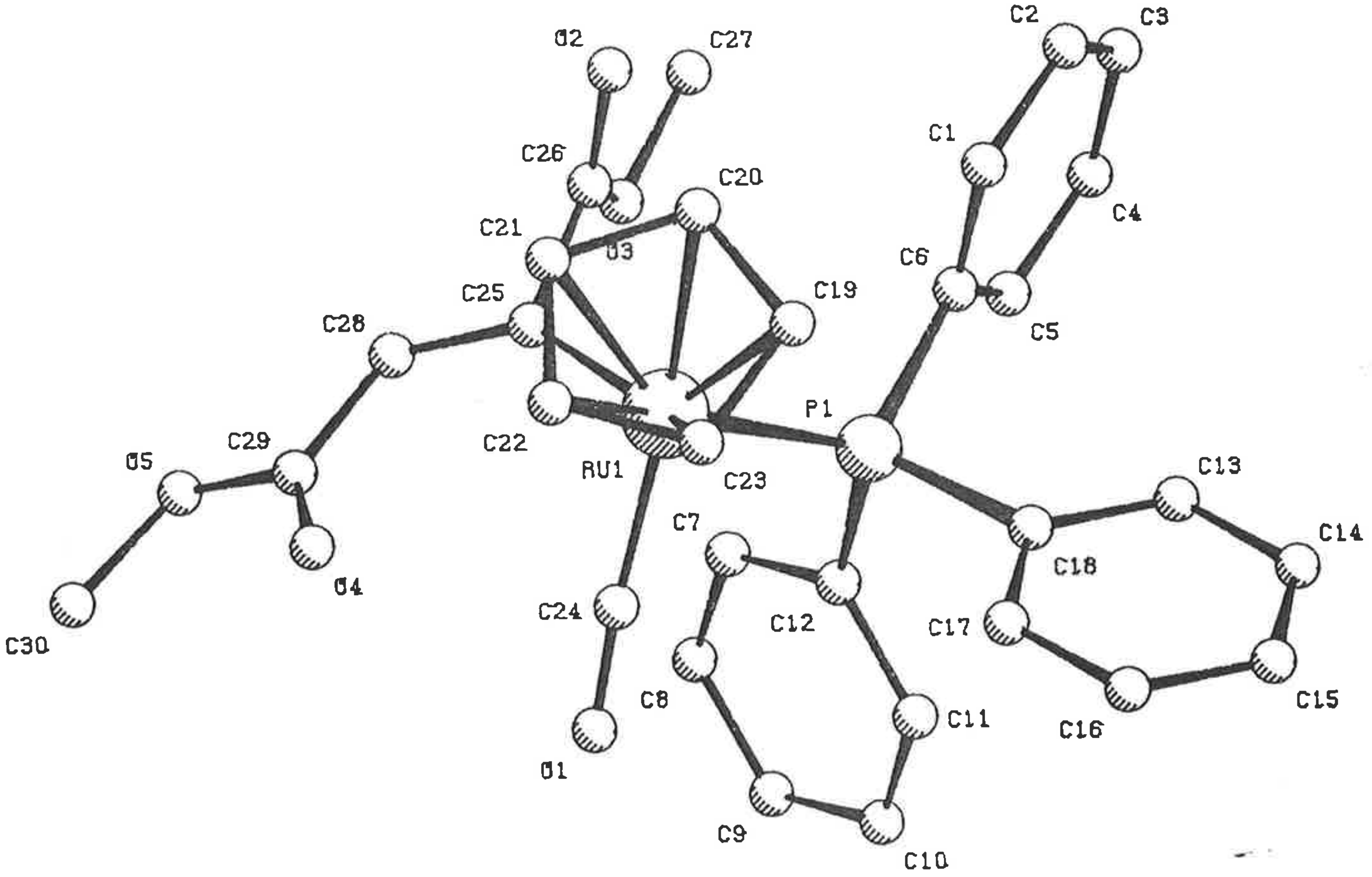


Figure 5. PLUTO plot of the molecular structure of $Ru\{(Z)\text{-}C(CO_2Me){=}CH(CO_2Me)\}(CO)(PPh_3)\text{-}(\eta\text{-}C_5H_5)$ (41) (by M.G. Humphrey)

Table 5. Selected bond lengths and bond angles for

$Ru\{(Z)\text{-}C(CO_2Me)=CH(CO_2Me)\}(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (41)

Bond lengths (Å)

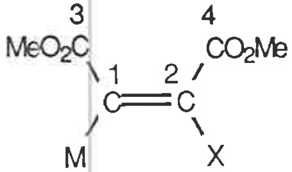
Ru(1) - C(19)	2.256(5)	Ru(1) - C(25)	2.080(8)
Ru(1) - C(20)	2.250(7)	P(1) - C(6)	1.822(4)
Ru(1) - C(21)	2.255(6)	P(1) - C(12)	1.837(4)
Ru(1) - C(22)	2.263(7)	P(1) - C(18)	1.829(5)
Ru(1) - C(23)	2.264(8)	O(1) - C(24)	1.151(8)
Ru(1) - C(cp)(av.)	2.258	C(25) - C(26)	1.49(1)
Ru(1) - C(24)	1.847(7)	C(25) - C(28)	1.37(1)
Ru(1) - P(1)	2.310(2)	C(28) - C(29)	1.46(1)

Bond angles (°)

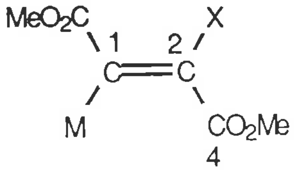
P(1) - Ru(1) - C(24)	85.0(2)	Ru(1) - C(24) - O(1)	174.6(7)
P(1) - Ru(1) - C(25)	94.7(2)	Ru(1) - C(25) - C(26)	114.7(6)
C(24) - Ru(1) - C(25)	93.1(3)	Ru(1) - C(25) - C(28)	133.2(5)
Ru(1) - P(1) - C(6)	119.8(2)	C(26) - C(25) - C(28)	111.5(7)
Ru(1) - P(1) - C(12)	113.9(2)	C(25) - C(28) - C(29)	124.6(7)
Ru(1) - P(1) - C(18)	113.5(1)		

Table 6

Stereochemistry of some $M\{C(CO_2Me)=CX(CO_2Me)\}$groups



(**A**) *cis*



(**B**) *trans*

Complex	(40)	(43)[a]	(44)	(45)	(41)	(32)	(46)
M	Ru	Pd	Pt	Ru	Ru	Pt	Pt
X	H	H	H	Cl	H	H	Cl
Configuration	A	A	A	A	B	B	B
Bond lengths (Å)							
M-C(1)	2.07(1)	2.05(2)	2.026(8)	2.16(2)	2.080(8)	2.086(12)	1.97(2)
C(1)-C(2)	1.43(2)	1.38(2)	1.337(12)	1.41(3)	1.373(10)	1.37(2)	1.31(2)
C(1)-C(3)	1.47(2)	1.48(2)	1.508(13)	1.49(3)	1.494(9)	1.50(2)	1.56(3)
C(2)-C(4)	1.53(2)	1.48(3)	1.480(13)	1.49(3)	1.462(10)	1.49(2)	1.51(3)
Bond angles (deg)							
M-C(1)-C(2)	126.1(10)	94.5(5)	126.7(7)	129.9(14)	133.2(5)	129.9(5)	129.9(11)
M-C(1)-C(3)	113.7(10)	91.7(4)	122.8(6)	114.7(15)	114.7(6)	117.9(5)	112.6(9)
C(3)-C(1)-C(2)	120.1(11)	123(2)	120.5(8)	114.5(18)	111.5(7)	111.8(8)	117.4(9)
C(1)-C(2)-C(4)	124.3(13)	121(2)	126.4(9)	122.1(14)	124.6(7)	124.8(8)	124.4(8)
C(1)-C(2)-X	-	-	-	122.4(16)	-	-	125.8(10)
C(4)-C(2)-X	-	-	-	115.4(17)	-	-	109.8(8)
Reference	(46)	(58)	(59)	(60)	this work	(49)	(61)

[a] Average of two values

hydride occurred and that (42) is indeed the *cis*-isomer of (41). Although the synthesis of (42) had been reported[62] previously only the ^{1}H NMR data was published. Therefore a full characterisation was undertaken including obtaining ^{1}H NMR and $^{13}C\{^1H\}$ NMR data for comparison with those obtained for the new complex (41). Tables 7 and 8 contain ^{1}H and $^{13}C\{^1H\}$-NMR data for complexes (41) and (42) relevant to the following discussion in comparison to data obtained for similar complexes. Other resonances and assignments for (41) and (42) are in the experimental sections of this chapter.

The ^{1}H NMR spectra for complexes (41) and (42) show similarities. In the *cis*-isomer, the vinyl CH resonance is at higher field than in the *trans*-isomer because of the shielding effect of metal electron density; the observed values are δ 5.33 and 6.60, respectively. The magnitude of the J(PH) coupling is also different, having values of 2 and 1 Hz, in (41) and (42), respectively; the *trans* coupling in other compounds containing the PC=CH moiety is usually twice the *cis*-coupling.[63] The chemical shifts of the two OMe resonances are found to differ by only *ca* 0.02 ppm in the *cis*-isomer, compared with *ca* 0.8 ppm in the *trans*-isomer; this is consistent with the CO_2Me groups being in more similar environments in the former complex. There is also observed a separation of the two OMe resonances of *ca* 0.3 ppm in the chelate complex (34).

The $^{13}C\{^1H\}$ NMR spectra of the isomeric complexes also show differences in the CO_2Me resonances.

Table 7

^{1}H NMR spectra (CDCl$_3$) of some MLL´{C(CO$_2$Me)=CH(CO$_2$Me)}(η-C$_5$H$_5$) complexes

MLL´	Configuration	Chemical shifts (ppm)[a]		
		CO$_2$Me	CH=	C$_5$H$_5$
[b]Ru(PPh$_3$)$_2$ (16)	*cis*	3.27s,3.96s	4.55s	4.15s
[b]Os(PPh$_3$)$_2$	*cis*	3.25s,3.95s	4.75t (1.0)	4.30s
[b]Ru(dppm) (39)	*cis*	3.15s,3.25s	5.00s (-)	4.80s
[b]Ru(dppe) (40)	*cis*	3.19s,3.52s	4.29s (-)	4.44s
[c]Ru(CO)(PPh$_3$) (41)	*trans*	2.88s,3.66s	6.60d (2.0)	4.98s
[c]Ru(CO)(PPh$_3$) (42)	*cis*	3.55s,3.57s	5.33d (1.0)	4.98s
[b]Ru(CNBu^t)(PPh$_3$)	*cis*	3.55s,3.58s	5.60d (2.0)	4.80s
[b]Ru(PPh$_3$) (34)	*trans* (chelate)	3.21s,3.49s	6.20d (2.5)	4.41s
[b]Os(PPh$_3$)	*trans* (chelate)	3.30s,3.45s	5.90d (1.0)	4.65s

[a] *J*(HP) (Hz) in parentheses. [b] Ref. 49 [c] This work

Table 8

^{13}C NMR spectra ($CDCl_3$) of some $RuLL'\{C(CO_2Me)=CH(CO_2Me)\}(\eta\text{-}C_5H_5)$ complexes

LL	Configuration	Chemical shifts (ppm)				
		CO_2Me	C_5H_5	$CH=$	RuC^a	CO_2Me
[b]$(PPh_3)_2$ (16)	*cis*	49.51s, 50.31s	86.25s	163.0s	182.2t (16)	182.5s
[b]dppm	*cis*	50.05s	85.6s	162.45s	191.9t (0.5)	181.45s
[c](CO)(PPh_3) (41)	*trans*	49.9s 50.25s	87.45s	168.65s	172.7d (11)	178.25s 178.4s
[c](CO)(PPh_3) (42)	*cis*	50.5s	87.95s	162.3s	176.6d (13)	179.65s
[b]$(CNBu^t)(PPh_3)$	*cis*	50.0s 50.3s	84.95s	162.45s	137.05d (44)	180.4s, 186.7s
[b]PPh_3 (34)	*trans* (chelate)	50.55s, 50.6s	77.25s	116.25s	179.1d (17)	176.4s

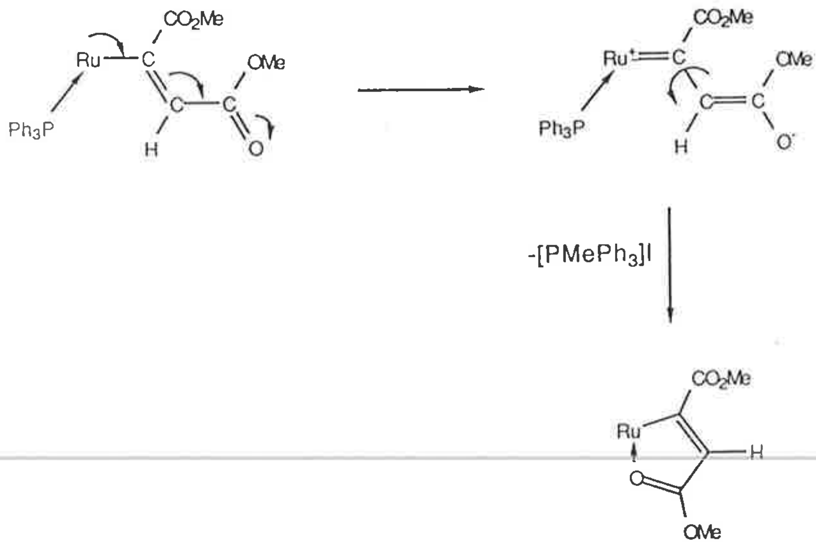
[a] *J*(CP) (Hz) in parentheses. [b] Ref. 46 [c] This work

In the *cis* isomer (42), both groups are accidentally equivalent, with OMe and CO resonances at 50.5 and 179.6, respectively, whereas in the *trans* isomer (41) two sets of resonances are found, at δ 49.9 and 50.2, and δ 178.3 and 178.4, respectively. Other resonances are readily assigned to C_5H_5 (δ 88.0 and 87.5 ppm, respectively), CH (δ 162.3 and 168.7), RuC(δ 176.6 and 172.7) and Ru-CO carbons (204.7 and 205.0). The metal-bonded carbons show 11-13(Ru-C) or 21 Hz (Ru-CO) coupling to phosphorus.

It is evident that the effects of differing geometry of the vinyl ligand on the NMR spectra are subtle, and of limited use in assigning the stereochemistry unless both isomers are available for study.

The isomerisation reaction. Conversion of (16) to (34)

It was previously suggested that the initial *cis* adduct might transform into the *trans* isomer by virtue of a partial withdrawal of electron density from the C=C double bond on to the β-ester carbonyl group (Scheme 8).



Scheme 8. One PPh_3 and C_5H_5 ligands omitted for clarity.

The reduction in C=C bond order would allow rotation of the $CH(CO_2Me)$ group about this bond, a possible driving force being the extra stability derived from chelation of the ester carbonyl group.

The isomerisation proceeds quite slowly on heating, but the reaction is accelerated by addition of MeI to the solution of complex (16). In this way, the displaced PPh_3 ligand is removed as $[PMePh_3]I$, which separates from the solution, and the possibility of a competing reaction involving recoordination of the phosphine ligand is lessened.

Preparation of some complexes containing 1,1´-bis(diphenylphosphino)ferrocene(dppf)

The ready exchange of the two PPh_3 ligands in $RuCl(PPh_3)_2(\eta-C_5H_5)$ for dppf occurred in refluxing benzene, (16 h); orange crystals of $RuCl(dppf)(\eta-C_5H_5)$ (47) were formed, which were characterised by elemental microanalyses and conventional spectroscopic methods. In particular, the ^1H NMR spectrum contained five resonances between δ 4.03 and 5.18 of relative intensities 2/5/2/2/2 assigned to ring protons of the three cyclopentadienyl groups. The EI mass spectrum contained a parent ion at m/z 756, which fragmented by loss of HCl and C_6H_5, while the relatively strong doubly charged $[M]^{2+}$ and $[M - Cl]^{2+}$ ions were also present.

Conversion of the chloro complex (47) into the hydrido complex $RuH(dppf)(\eta-C_5H_5)$ (48) was achieved by treating it with NaOMe in methanol which is a well known route into hydride complexes.[64] This complex was fully characterised by an X-ray diffraction study.

Structure of RuH(dppf)(η-C_5H_5) (48)

The unit cell of (48) consists of two discrete molecules; no intermolecular contacts are shorter than normal van der Waals separations. Figure 6 (see also Table 9) shows a plot of one of the two independent molecules, which differ from one another only in the orientation of the phenyl rings. The ruthenium is in a distorted octahedral environment, being coordinated by the cyclopentadienyl group [Ru-C(C_5H_5) 1.198(20) - 2.242(19), av. 2.217Å (molecule 1); 2.226(14) - 2.275(16), av. 2.242Å (molecule 2)], the dppf ligand [Ru-P 2.263(4), 2.246(3)Å (molecule 1); 2.258(3), 2.265(3)Å (molecule 2)] and the hydride ligand. The hydride ligand was not located unambiguously, although two residual electron density peaks were located in positions approximately *cis* to the chelating phosphorus atoms.

The geometry of the dppf ligand is of interest, and may be compared with those found in Mo(CO)$_4$(dppf) (49)[65], NiBr$_2$(dppf) (50)[65], PdCl$_2$(dppf)[65] (51), NiCl$_2$(dppf)[66] (52) and the uncoordinated ligand, dppf (53).[66] These previous studies have noted that the steric requirements of the various metal atoms lead to differences in the ring tilt, phosphorus atom separation and conformation. In (48), the angle between the ring plane normals is 4.9° (6.3° in molecule 2) [(49) 2.2, (50) 6.2, (51) 4.5, (52) 6.2°, (53) 0.0°], while the P....P distances in the two molecules of (48) are 3.43 and 3.55Å [(49) 3.78, (50) 3.57, (51) 3.45Å], with the P-RuP angles 99.1(1) and 95.5(1)° (49) 95.3, (50) 102.5, (52) 105.0, (51) 98.0°). In (48), as expected, the distortions more nearly approach those found in the octahedral molybdenum complex, rather than those found for tetrahedral nickel complexes or square-planar palladium; in all cases, the

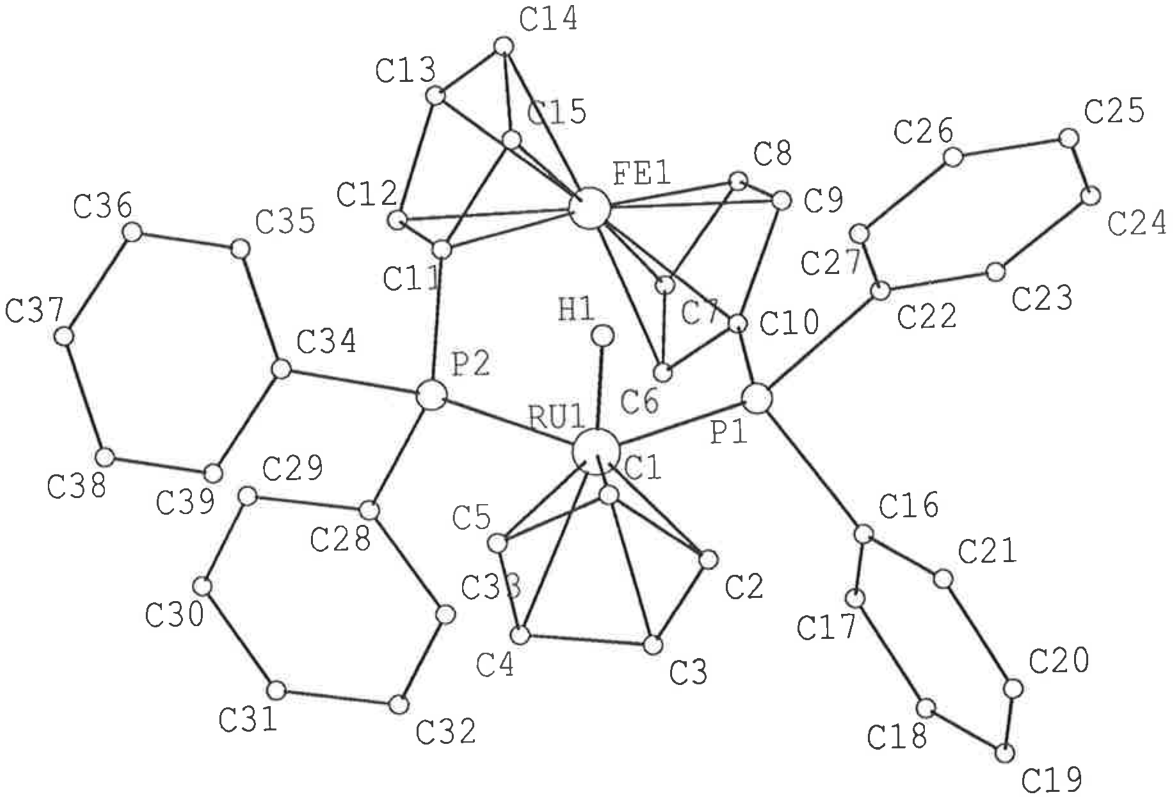


Figure 6. PLUTO plot of molecule 1 of RuH(dppf)(η-C_5H_5) (48). The metal bonded hydrogen is shown at the location of residual electron density in the difference map (by M.R. Snow and E.R.T. Tiekink)

Table 9

Selected interatomic parameters for one molecule of RuH(dppf)-(η-C_5H_5) (48)

Bond lengths (Å)

Ru(1) - P(1)	2.263(4)
Ru(2) - P(2)	2.246(3)
Ru(1) - C(1)	2.24(2)
Ru(1) - C(2)	2.21(1)
Ru(1) - C(3)	2.22(1)
Ru(1) - C(4)	2.22(2)
Ru(1) - C(5)	2.20(2)
Fe(1) - C(6)	2.01(1)
Fe(1) - C(7)	2.02(2)
Fe(1) - C(8)	2.04(2)
Fe(1) - C(9)	2.04(1)
Fe(1) - C(10)	2.06(9)
Fe(1) - C(11)	2.03(2)
Fe(1) - C(12)	2.01(1)
Fe(1) - C(13)	2.05(1)
Fe(1) - C(14)	2.06(1)
Fe(1) - C(15)	2.02(2)
P(1) - C(10)	1.80(1)
P(1) - C(16)	1.873(8)
P(1) - C(22)	1.875(9)
P(2) - C(11)	1.81(1)
P(2) - C(28)	1.865(8)
P(2) - C(34)	1.87(1)

Bond angles (°)

P(1) - Ru(1) - P(2)	99.1(1)
Ru(1) - P(1) - C(10)	124.4(4)
Ru(1) - P(1) - C(16)	113.4(3)
Ru(1) - P(1) - C(22)	115.9(3)
Ru(1) - P(2) - C(11)	118.9(4)
Ru(1) - P(2) - C(28)	118.7(2)
Ru(1) - P(2) - C(34)	111.5(3)
C(16) - P(1) - C(22)	98.3(3)
C(16) - P(1) - C(10)	101.7(5)
C(22) - P(1) - C(10)	99.0(5)
C(28) - P(2) - C(34)	99.6(4)
C(28) - P(2) - C(11)	103.8(5)
C(34) - P(2) - C(11)	101.4(5)
P(1) - C(10) - Fe(1)	124.7(8)
P(2) - C(11) - Fe(1)	122.9(5)
C(10) - Fe(1) - C(11)	107.5(5)

the geometries are more or less distorted from ideal to accommodate the steric requirements of the various ligands.

The spectroscopic data obtained for (48) were consistent with the determined structure. The infrared spectrum of (48) contained a broad weak band at 1975 cm^{-1} which was assigned to ν(Ru-H). The ^1H NMR spectrum confirmed the formation of the metal bonded hydride,

a high-field triplet at δ -11.5 being observed. The cyclopentadienyl protons resonated between δ 3.89 and 4.49 giving three peaks of relative intensity 4:5:4. A pseudo molecular ion was found at *m/z* 722 which consisted of overlapping multiplets assigned to $[M]^+$ and $[M - H]^+$ in the EI mass spectrum. Ions related to the molecular ion by the loss of C_6H_6 and further loss of C_5H_6 were found at *m/z* 644 and 578, respectively, while a relatively strong doubly charged ion was found at 361 ($[M]^{2+}$).

The insertion reaction of (48) with DMAD was also examined. The vinyl complex Ru{C(CO_2Me)=CH(CO_2Me)}-(dppf)(η-C_5H_5) (54) was obtained from the hydride and DMAD in refluxing benzene. There was no evidence for the presence of a bis-insertion product analogous to (33). Complex (54) was characterised on the basis of micro-analytical and spectroscopic data. The infrared spectrum contained familiar ν(C=O) vibrations at 1709 and 1698 cm^{-1} while a ν(C=C) band was found at 1540 cm^{-1}. The proton NMR contained singlet resonances at δ 3.31 and 3.45 assigned to the OMe signals while the signal at δ 6.36 [s, 1H] was assigned to the vinyl proton. Comparison of these values with those in Table 7 suggest the assignment of the configuration of the vinyl group as *cis* on the basis of lack of coupling of the =CH proton to the ^{31}P nuclei and favourable comparison of the OMe resonances of (<u>54</u>) with those found for complex (<u>40</u>).

The multiplet between δ 3.06 - 4.81 was assigned to the dppf cyclopentadienyl protons while the Ru-C_5H_5 protons gave a singlet at δ 4.33 and the multiplet between δ 7.1 - 7.6 was assigned to the phenyl protons.

A molecular ion at *m/z* 864 was observed in the EI mass spectrum of complex (<u>54</u>) and ions related to it by the loss Me, OMe, CO_2Me and $Fe(C_5H_5)_2$ were found at *m/z* 849, 833, 805 and 678, respectively. The ion at *m/z* 721 was assigned to $[Ru(dppf)(C_5H_5)]^+$ and doubly charged ions at *m/z* 432, 402.5, 360.5, 327.5 and 332 were assigned to $[M]^{2+}$, $[M - CO\,Me]^{2+}$, $[Ru(dppf)(C_5H_5)]^{2+}$, $[Ru(dppf)-H]^+$ and $Ru(dppf)(C_5H_5) - Ph]^{2+}$.

EXPERIMENTAL

General conditions and instrumentation used were as described in Chapter 1.

Starting materials

Literature methods were used to prepare $RuCl(PPh_3)_2(\eta-C_5H_5)$[67], $RuI(PPh_3)_2(\eta-C_5H_5)$[68], $RuH(PPh_3)_2(\eta-C_5H_5)$[64] and $RuCl(\eta^4-C_8H_{12})(\eta-C_5H_5)$[69]. Commercial $C_2(CO_2Me)_2$ (Fluka) was routinely distilled before use and commercial NH_4PF_6 (Aldrich) was used as received.

Syntheses

A. Reaction between $C_2(CO_2Me)_2$ and $RuX(PPh_3)_2(\eta-C_5H_5)$

(a) X=Cl - A mixture of $RuCl(PPh_3)_2(\eta-C_5H_5)$ (200 mg, 0.284 mmol), NH_4PF_6 (46 mg, 0.284 mmol) and $C_2(CO_2Me)_2$ (0.05 ml, 0.408 mmol) in MeOH (25 ml) was heated at reflux point until a clear dark brown solution was obtained, *ca* 1h. Evaporation and separation of the residue by preparative tlc (acetone-light petroleum; 1:1) gave eleven bands.
Band 1, (R_f 0.51, yellow) was crystallised from Et_2O/pentane to give orange microcrystals of $RuCl[\eta^4-CH(CO_2Me)=C(CO_2Me)C(CO_2Me)=CH(CO_2Me)](\eta-C_5H_5)$ (27) (13 mg, 9%), m.p. 154-155°C. [Found: C, 41.86; H, 3.93; *M* (mass spectrometry) 488; $C_{17}H_{19}ClO_8Ru$ requires C, 41.80; H, 3.93%; *M* 488]. Infrared (Nujol): $\nu(C=O)$ 1760s, 1738m, 1710vs, 1697s; $\nu(CO)$ 1283s, 1228vs, 1199s, 1163s cm^{-1}; other bands at 3107m, 1343m, 1180m, 1016w, 989m, 968m, 841m, 763w cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 2.00 (s, 2H, 2x =CH); 3.73 (s, 6H, 2x CO_2Me); 3.87 (s, 6H, 2x CO_2Me); 5.58 (s, 5H, C_5H_5). FAB MS: 488, $[M]^+$, 26; 453, $[M - Cl]^+$, 75; 429, $[M - CO_2Me]^+$, 6; 391, $[M - CO_2Me - 2\ OMe]^+$, 17; 284, $[C_4(CO_2Me)_4]^+$, 100.

The only product isolated from a similar reaction carried out in refluxing toluene was $C_6(CO_2Me)_6$ (32 mg, 5%. The remaining bands were present in trace amounts or intractable (baseline), and were not identified.

(b) X=I

(i) A mixture of $RuI(PPh_3)_2(\eta\text{-}C_5H_5)$ (694 mg, 0.85 mmol), NH_4PF_6 (144 mg, 0.88 mmol) and $C_2(CO_2Me)_2$ (1.05 ml, 8.54 mmol) in MeOH (200 ml) was heated at reflux point for 10.5 h. Evaporation and separation of the residue by preparative tlc (acetone-cyclohexane-CH_2Cl_2; 1:4:5) gave ten bands. Band 1, (*R*$_f$ 0.69, red) was further separated by preparative tlc (as above, double development) to give two bands. Band 1, (*R*$_f$ 0.73, red) was crystallised from CH_2Cl_2/MeOH to give red crystals of $RuI[\eta^4\text{-}CH(CO_2Me)\text{-}{=}C(CO_2Me)C(CO_2Me){=}CH(CO_2Me)](\eta\text{-}C_5H_5)$ (28) (72 mg, 15%), m.p. 161-163°C. [Found: C, 35.04; H, 3.26; *M* (mass spectrometry) 580; $C_{17}H_{19}IO_8Ru$ requires C, 35.24; H; 3.31%; *M* 580]; Infrared (Nujol): ν(C=O) 1762s, 1740m, 1712s, 1700s, ν(CO) 1350m, 1285m, 1230s; other bands at 1200m, 1160m, 1020w, 990m, 970w, 930w, 843w, 835w, 801w, 775w, 761w, 720w cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 2.07 (s, 2H, 2x =CH); 3.66 (s, 6H, 2x OMe); 3.85 (s, 6H, 2x CO_2Me); 5.57 (s, 5H, C_5H_5). $^{13}C\{^1H\}$ NMR: $\delta(CDCl_3)$ 47.9 (s, =CH); 51.7 (s, OMe); 53.4 (s, OMe); 91.1 (s, C_5H_5); 92.8 (s, -C=); 165.4 (s, C=O); 171.0 (s, C=O). FAB MS: 580, $[M]^+$, 16; 549, $[M - OMe]^+$, 19; 521, $[M - CO_2Me]^+$, 2; 453, $[M - I]^+$, 39; 394, $[M - I - CO_2Me]^+$, 32; 286, $[C_4(CO_2Me)_4H_2]^+$, 3; 255, $[C_4(CO_2Me)_4H_2 - OMe]^+$, 27; 227, $[C_4(CO_2Me)_4H_2 - CO_2Me]^+$, 32; 154, ?, 100. Band 2, (*R*$_f$ 0.77, colourless) was crystallised from MeOH to give white crystals of tetramethyl (*z*,*z*)-1,3-butadiene-1,2,3,4-

tetracarboxylate (<u>30</u>) (59 mg, 2%) m.p. 90°C. [Found: *M* (EI mass spectrometry) 286; $C_{12}H_{14}O_4$ requires *M* 286]. ^1H NMR: δ($CDCl_3$) 3.73 (s, 6H, 2x OMe); 3.87 (s, 6H, 2x OMe), 6.00 (s, 2H, 2x =CH) [Lit.[51] m.p. 90°C. ^1H NMR: δ($CDCl_3$) 3.75, 3.88 and 6.09 respectively]. Band 2, (R_f 0.54, yellow) was further separated by preparative tlc (acetone-cyclohexane-CH_2Cl_2; 1:4:5) to give two bands. The major band (R_f 0.57, yellow) was crystallised from CH_2Cl_2/cyclohexane to give yellow prisms of $Ru(\eta\text{-}C_5H_5)[\eta^5\text{-}C_6H(CO_2Me)_6]$ (<u>29</u>) (100 mg, 20%), m.p. 165-166°C. [Found: C, 46.47; H, 4.07; *M* (mass spectrometry) 594; $C_{23}H_{24}O_{12}Ru$ requires C, 46.62; H, 3.91%; *M* 594]. Infrared (KBr): ν(C=O) 1750vs, 1730vs(br), 1700s; ν(C-O) 1225vs(br); other bands at 2960m, 1438vs, 1420m, 1395m, 1350m, 1330m, 1325m, 1115s, 1100w, 1002s, 992s, 822s, 800m, 791m cm^{-1}. ^1H NMR: δ($CDCl_3$) 3.55 (s, 3H, OMe); 3.76 (s, 6H, 2x OMe); 3.84 (s, 9H, 3x OMe); 4.54 (s, 1H, CH); 5.04 (s, 5H, C_5H_5). $^{13}C\{^1H\}$ NMR: δ($CDCl_3$) 42.4 (s, CH); 51.6 (s, OMe); 52.1 (s, 2x OMe); 53.0 (s, 3x OMe); 84.5 (s, C_5H_5); 87.8 [s, C(6), C(10)]; 94.9 [s, C(7), C(8), C(9)]; 166.5 (s, 2x CO_2Me); 167.1 (s, CO_2Me); 171.7 (s, 3x CO_2Me). FAB MS: 594, $[M]^+$, 3; 563, $[M - OMe]^+$, 29; 535, $[M - CO_2Me]^+$, 100; 477, $[Ru(C_5H_5)\{C_6H_2(CO_2Me)_4\}]^+$, 65; 419, $[Ru(C_5H_5)\{C_6H_3(CO_2Me)_3\}]^+$, 41; 361, $[Ru(C_5H_5)\text{-}\{C_6H_4(CO_2Me)_2\}]^+$, 47; 303, $[Ru(C_5H_5)\{C_6H_5(CO_2Me)\}]^+$, 5; 244, $[Ru(C_5H_5)(C_6H_6)]^+$, 7; 167, $[Ru(C_5H_5)]^+$, 8. Band 3, (R_f 0.17, orange) was crystallised from MeOH/EtOAc to give white crystals of Ph_3PO (66 mg, 14%). Identified by comparison of its m.p. and infrared spectrum with those of an authentic sample. The remaining bands were present in trace amounts, or intractable (baseline), and were not identified.

(ii) A similar reaction between $RuI(PPh_3)_2(\eta-C_5H_5)$ (1030 mg, 1.26 mmol), NH_4PF_6 (205 mg, 1.26 mmol) and $C_2(CO_2Me)_2$ (0.6 ml, 4.88 mmol) in MeOH (75ml) was continued for 72 h. Filtration of the resulting orange suspension gave an orange powder of unreacted $RuI(PPh_3)_2(\eta-C_5H_5)$ (460 mg, 37%). The orange filtrate was evaporated to dryness and the residue separated by preparative tlc (acetone-cyclohexane-CH_2Cl_2; 1:4:5) to give eleven bands. Band 1, (R_f 0.69, red) was crystallised to give red crystals of (<u>28</u>) (16 mg, 4%), identified by comparison of its infrared and FAB spectra with those of the sample prepared as above. Band 2, (R_f 0.60, yellow) was further separated by preparative tlc (acetone-cyclohexane-CH_2Cl_2); 1:10:9) into two bands. Band 1, (R_f 0.90 yellow) was crystallised from CH_2Cl_2/cyclohexane to give yellow prisms of (<u>29</u>) (37 mg, 9%). Band 2, (R_f 0.88, yellow) was crystallised from CH_2Cl_2/cyclohexane to give yellow prisms of $Ru(\eta-C_5H_5)\{\eta^5-C_8H(CO_2Me)_8\}$ (<u>31</u>) (32 mg, 6%), m.p. 240-241°C. [Found: C, 47.28; H, 4.13; [*M* + H] (mass spectrometry) 737; $C_{29}H_{30}O_{16}Ru$ requires C, 47.35; H, 4.11%; *M* 736]. Infrared (KBr): ν(C=O) 1740vs(br); ν(C=C) 1640w; ν(C-O) 1270vs, 1255vs, 1230vs, 1210vs; other bands at 1365s, 1355m, 1340vs, 1320m, 1175s, 1142s, 1130s, 1110m, 1025m, 1010m, 1000s, 995s, 918w, 820s cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 3.52 (s, 3H, OMe); 3.59 (s, 9H, 3x OMe); 3.76 (s, 6H, 2x OMe); 3.80 (s, 3H, OMe); 3.81 (s, 3H, OMe); 5.15 (s, 5H, C_5H_5); 6.63 (s, 1H, =CH). FAB MS: 737, $[M + H]^+$, 3; 706, $[(M + H) - OMe]^+$, 50; 677, $[M - CO_2Me]^+$, 100; 619, $[(M - 2CO_2Me) + H]^+$, 3; 604, $[M - CO_2Me - Me]^+$, 594, $[M - C_2(CO_2Me)_2]^+$, 1; 559, $[M - 3CO_2Me]^+$; 2; 167, $[Ru(C_5H_5)]^+$, 6.

(iii) A mixture of $RuI(PPh_3)_2(\eta-C_5H_5)$ (200 mg, 0.339 mmol) and $C_2(CO_2Me)_2$ (0.33 ml, 2.68 mmol) in MeOH was treated with $HPF_6.OEt_2$(*ca* 1 drop) and refluxed for 16 h. The clear orange solution was evaporated to dryness and the residue separated by preparative tlc (acetone-light petroleum; 1:4) to give eleven bands. Band 1 (R_f 0.80, orange) gave solid $RuI(PPh_3)_2(\eta-C_5H_5)$ (20 mg, 10%). Band 2 (R_f 0.40, red) was crystallised from CH_2Cl_2/MeOH to give red crystals of (<u>28</u>) (11 mg, 11%). Identified by comparison of its i.r. and FAB mass spectrum with those of an authentic sample. Band 3 (R_f 0.14, orange) was crystallised from MeOH to give white prisms of $C_6(CO_2Me)_6$ (90 mg, 24%), identified by comparison of its i.r. and ^1H NMR spectra with those of an authentic sample.[19]

(c) <u>X=H</u> - A mixture of $RuH(PPh_3)_2(\eta-C_5H_5)$ (502 mg, 0.73 mmol) and $C_2(CO_2Me)_2$ (0.25 ml, 2.03 mmol) in benzene (50 ml) was heated (82-86°C) for 45 min. The resulting red solution was evaporated and the residue was chromatographed (Florisil, 3 x 20 cm). Elution with light petroleum removed traces of unreacted $C_2(CO_2Me)_2$. Further elution with acetone-light petroleum (1:10) gave an orange fraction which was crystallised from Et_2O/light petroleum to give red crystals of $\overline{\mathrm{Ru[C(CO_2Me)=CHC(O}}\mathrm{)OMe](PPh_3)(\eta-C_5H_5)}$ (<u>34</u>) (26 mg, 6%), identified by comparison of its m.p. and i.r. spectrum with those of an authentic sample.[34] Further elution with acetone-light petroleum (1:4) gave a yellow product which was crystallised from Et_2O/light petroleum to give yellow microcrystals of $Ru[(E)-C(CO_2Me)=CH(CO_2Me)](PPh_3)_2(\eta-C_5H_5)$ (<u>16</u>) (308 mg, 51%), identified by comparison of its m.p. and i.r.

spectrum with those of an authentic sample. A second yellow band was eluted with acetone-light petroleum (1:3) and crystallised from Et_2O/pentane to give yellow crystals of $Ru[C(CO_2Me)=C(CO_2Me)C(CO_2Me)=CH(CO_2Me)](PPh_3)(\eta-C_5H_5)$ (33) (106 mg, 20%), m.p. 180-181°C. [Found: C, 58.81; H, 4.64; M (mass spectrometry) 714; $C_{35}H_{33}O_8PRu$ requires C, 58.90; H, 4.66%; M 714). Infrared (Nujol): ν(C=O) 1716vs, 1699s; ν(C=C) 1585w; Other bands at 1310m, 1250(sh), 1212s, 1192m, 1150m, 1140m, 1093m, 1012w, 895w, 785w, 758w, 745w, 697m cm^{-1}. ^1H NMR: δ($CDCl_3$) 2.22 [d, J(PH) 16Hz, 1H, =CH]; 3.13 (s, 3H, OMe); 3.60 (s, 6H, 2x OMe); 3.80 (s, 3H, OMe); 4.89 (s, 5H, C_5H_5); 7.2-7.4 (m, 15H, Ph). $^{13}C\{^1H\}$ NMR: δ($CDCl_3$) 45.4 [s, C(8)]; 50.7 (s, OMe); 51.0 (s, OMe); 51.1 (s, OMe); 52.1 (s, OMe); 159.0 [s, C(7)]; 162.8 [s, C(9)], 89.5 (s, C_5H_5), 128.3-134.6 (m, Ph); 62.5 [d, J(PC) 16Hz, Ru-C(6)]; 172.6 (s, CO_2Me); 173.0 (s, 2x CO_2Me); 174.4 (s, CO_2Me). FAB MS: 714, $[M]^+$, 29; 682, $[M - MeOH]^+$, 12; 655, $[M - CO_2Me]^+$, 15; 429, $[Ru(PPh_3)(C_5H_5)]^+$, 100; 262, $[PPh_3]^+$, 31; 167, $[Ru(C_5H_5)]^+$, 18. Further elution with the same solvent gave a second yellow fraction. This was further separated by preparative tlc (acetone-light petroleum; 1:1) to give one major band, (R_f 0.36, yellow) which was crystallised from CH_2Cl_2/light petroleum to give $Ph_2P=C(CO_2Me)C(CO_2Me)=C(CO_2Me)C(Ph)(CO_2Me)$ (35) (60 mg, 12%), m.p. 248-249°C. [Found: M (mass spectrometry) 546; $C_{30}H_{27}O_8P$ requires M 546] (Lit.[56] 248-250°C).

B. Reaction between $C_4H_2(CO_2Me)_4$ and $RuCl(\eta^4-C_8H_{12})-(\eta-C_5H_5)$

$RuCl(\eta^4-C_8H_{12})(\eta-C_5H_5)$ (54 mg, 0.175 mmol) was added to a solution of tetramethyl (*z*,*z*)-1,3-butadiene-1,2,3,4-tetracarboxylate in MeOH (17 ml) and the mixture heated at 60°C for 3.5 h. The resulting yellow-orange solution was filtered through alumina, evaporated to dryness and the residue crystallised from Et_2O/light petroleum to give orange crystals of (27) (51 mg, 60%), shown to be identical (i.r., NMR) with the complex isolated from reaction A(a) above.

C. Reaction of $Ru[(E)-C(CO_2Me)=CH(CO_2Me)](PPh_3)_2(\eta-C_5H_5)$

(i) with MeI - A mixture of (16) (400 mg, 0.48 mmol) and MeI (2280 mg, 16.1 mmol) in toluene (25 ml) was refluxed for 45 min resulting in the precipitation of a white powder of $[PMePh_3]I$ (198 mg, 88%). Identified by comparison of its m.p. and ^1H NMR with those of an authentic sample. The filtrate was evaporated and the resulting red oil chromatographed (silica, 3 x 20). Elution with Et_2O afforded a red-orange band which was collected, evaporated to dryness and the residue crystallised from Et_2O/light petroleum to give red crystals of (34) (219 mg, 80%), identified by comparison of its m.p. and i.r. spectrum with those of an authentic sample.[34]

(ii) with carbon monoxide - A solution of (16) (300 mg, 0.36 mmol) in $MeOH-CH_2Cl_2$ (1:5, 60 ml) was carbonylated in an autoclave (40 atm, 110°C, 21 h) giving a pale yellow solution which was evaporated to dryness. Separation of the residue by preparative tlc (acetone-light petroleum; 1:1) gave seven bands of which only the major band (R_f 0.6, yellow) was isolated. Crystallisation from Et_2O/light petroleum gave yellow microcrystals of $Ru[(E)-C(CO_2Me)-=CH(CO_2Me)](CO)(PPh_3)(\eta-C_5H_5)$(42) (140 mg, 65%), m.p. 165-168°C. [Found: C, 60.10; H, 4.58; $C_{30}H_{27}O_5PRu$ requires C, 60.00; H, 4.50%]. Infrared (Nujol): ν(RuCO) 1940vs(br); ν(C=O) 1708s, 1690s; ν(C=C) 1557s; other bands at 1482sh, 1441sh, 1438s, 1325s, 1212s, 1191m, 1167sh, 1154vs, 1100sh, 1095m, 1074w, 1023m, 1009m, 1000sh, 960w, 870w, 855sh, 849m, 841m, 832w, 810w, 750m, 725w, 710sh, 700w, 661m cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 3.55 (s, 3H, OMe); 3.57 (s, 3H, OMe); 4.98 (s, 5H, C_5H_5); 5.33 [d, J(PH) 1Hz, 1H, =CH], 7.37 (m, 15H, Ph). $^{13}C\{^1H\}$ NMR: $\delta(CDCl_3)$ 50.5 (s, 2x OMe); 88.0 (s, C_5H_5); 128.0-136.0 (m, Ph); 162.3 (s, =CH); 176.6 [d, J(PC) 13Hz, RuC]; 179.7 (s, 2x CO_2Me); 204.7 [d, J(PC) 21Hz, RuCO].

D. Reaction of $\overline{Ru[C(CO_2Me)=CHC(O}{)}OMe](PPh_3)(\eta-C_5H_5)$ with CO

A red solution of (34) (254 mg, 0.44 mmol) in thf (20 ml) was carbonylated in a small autoclave (12.5 atm, 100°C, 2 h). The resulting yellow solution was evaporated to dryness and the residue separated by preparative tlc (Et_2O-light petroleum; 1:1) to give six bands. The only band isolated (R_f 0.52, yellow) was crystallised from Et_2O/light petroleum to give light yellow crystals of $Ru[(Z)-C(CO_2Me)=CH(CO_2Me)](CO)(PPh_3)(\eta-C_5H_5)$ (41) (173 mg, 66%), m.p. 128-130°C. [Found: C, 60.17; H, 4.65; $C_{30}H_{27}O_5PRu$ requires C, 60.00; H, 4.50%]. Infrared (Nujol): ν(Ru-CO) 1954vs(br); ν(C=O) 1718s, 1700s; ν(C=C) 1556s; other bands at 1540w, 1482w, 1440w, 1396sh, 1355w, 1322m, 1208s, 1188s, 1162vs, 1096s, 1020m, 1014s, 1000sh, 995sh, 862w, 845m, 835w, 825w, 814m, 798w, 762m, 752m, 724w, 703m, 694w, 668w cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 2.88 (s, 3H, OMe); 3.66 (s, 3H, OMe); 4.98 (s, 5H, C_5H_5); 6.60 [d, J(PH) 2Hz, 1H, =CH]; 7.25 (m, 15H, Ph). $^{13}C\{^1H\}$ NMR:

δ($CDCl_3$) 49.9 (s, OMe); 50.3 (s, OMe); 87.5 (s, C_5H_5); 127.7-136.6 (m, Ph); 168.7 (s, =CH); 172.7 [d, *J*(PC) 11Hz, RuC] 178.3 (s, *C*O_2Me); 178.4 (s, *C*O_2Me); 205.0 [d, *J*(PC) 21Hz, RuCO].

E. Preparation of RuX(dppf)(η-C_5H_5) [dppf = 1,1 -bis (diphenylphosphino)ferrocene]

(i) X=Cl - A solution of RuCl(PPh_3)$_2$(η-C_5H_5) (178 mg, 0.245 mmol) and dppf (135 mg, 0.244 mmol) in benzene (25 ml) was heated at reflux for 16 h. The orange solution was evaporated to dryness and the residue crystallised from CH_2Cl_2/EtOH to give orange crystals of RuCl(dppf)(η-C_5H_5)(47) (128 mg, 69%), m.p. 203-204°C (dec.). [Found: C, 61.10; H, 4.50; *M* (mass spectrometry) 756; $C_{39}H_{33}ClFeP_2Ru$ requires C, 62.00; H, 4.40%; *M* 756]. Infrared (Nujol): 1437s, 1315w, 1115w, 1110m, 1091s, 1070w, 1060w, 1044m, 1038m, 820m, 808s, 761w, 742m, 738m, 695s, 631m, 625m cm^{-1}. ^{1}H NMR: δ($CDCl_3$) 4.03, 4.24, 4.31, 5.18 [m, 8H, $(C_5H_4)_2Fe$]; 4.11 (s, 5H, C_5H_5); 7.2-8.0 (m, 20H, Ph). EI MS: 756, $[M]^+$, 80; 720, $[M - HCl]^+$, 64; 654, $[M - HCl - C_5H_6]^+$, 3; 642, $[M - Cl - C_6H_6]^+$, 16; 576, $[M - HCl - C_5H_6 - C_6H_6]^+$, 6; 554, $[dppf]^+$, 48; 507, $[M - C_5H_4PPh_2]^+$, 28; 476, $[dppf\text{-}C_6H_6]^+$, 24; 472, $[FeRu(C_5H_4PPh_2)(C_5H_5)]^+$, 4; 416, $[Ru(C_5H_4PPh_2)(C_5H_5)]^+$, 58; 378, $[M]^{2+}$, 10; 360, $[M - HCl]^{2+}$, 6; 339, $[Ru(C_5H_4PPh)(C_5H_5)]^+$, 100; 305, $[Fe(C_5H_4PPh_2)]^+$, 9; 262, $[PPh_3]^+$, 13.

(ii) X=H - A suspension of RuCl(dppf)(η-C_5H_5) (108 mg, 0.143 mmol) in methanol (25 ml) containing NaOMe (1 ml of a *ca* 1 mol.L^{-1} solution in MeOH) was heated at reflux for 15 min. The yellow powder which precipitated was collected, washed with MeOH (2 x 5 ml) and light petroleum (2 x 10 ml), and dried under vacuum to give RuH(dppf)(η-C_5H_5)(48) (78 mg, 75%), m.p. 198-200° (dec.). [Found: C, 64.70; H, 5.10; *M* (mass spectrometry) 722; $C_{39}H_{34}FeP_2Ru$ requires C, 64.90; H, 4.80%; *M* 722]. Infrared (Nujol): ν(RuH) 1975w(br); Other bands at 1590w, 1435s, 1310w, 1180w, 1160m, 1105w, 1090s, 1070w, 1041m, 1029w, 850w, 835w, 825w, 800m, 755w, 745m, 720w, 708m, 697s cm^{-1}. ^{1}H NMR: δ(C_6D_6) -11.5[t, *J*(PH) 35 Hz, 1H, RuH]; 3.89 (s, 4H, C_5H_4); 4.38 (s, 5H, C_5H_5); 4.49 (s, 4H, C_5H_4); 7.16 (m, 13H, Ph); 7.95 (m, 7H, Ph). EI MS: 722, $[M]^+$ + $[M - H]^+$, 100; 644, $[M - C_6H_6]^+$, 36; 578, $[M - C_5H_6 - C_6H_6]^+$, 18; 566, $[M - 2(C_6H_6)]^+$, 17; 536, $[FeRu(C_5H_4)_2(PPh_2)(C_5H_5)]^+$, 24; 471, $[FeRu(C_5H_4PPh_2)(C_5H_5)]^+$, 52; 395, $[FeRu(C_5H_4PPh)(C_5H_5)]^+$, 11; 361, $[M]^{2+}$, 36; 339, $[Ru(C_5H_4PPh)(C_5H_5)]^+$, 67.

(iii) <u>X=[C(CO$_2$Me)=CH(CO$_2$Me)]</u> - A mixture of RuH(dppf)(η-C_5H_5) (78 mg, 0.108 mmol) and $C_2(CO_2Me)_2$ (63 mg, 0.44 mmol) in benzene was heated at reflux for 4 h. The resulting yellow solution was evaporated to dryness and the residue was crystallised from CH_2Cl_2/EtOH to give a light yellow cotton-like mass of Ru[C(CO$_2$Me)=CH(CO$_2$Me)](dppf)(η-C_5H_5) (<u>54</u>) (72 mg, 77%), m.p. 269-270°C (dec.). [Found: C, 62.40; 4.90; *M* (mass spectrometry) 864; $C_{45}H_{40}FeO_4P_2Ru$ requires C, 62.60; H, 4.70%; *M* 864]. Infrared (Nujol): ν(C=O) 1708s, 1698s; ν(C=C) 1540s; Other bands at 1435s, 1328w, 1190s, 1178m, 1160m, 1142s, 1090s, 1040w, 1035w, 1005m, 832w, 828w, 752m, 723w, 701s cm^{-1}. ^{1}H NMR: δ($CDCl_3$) 3.31 (s, 3H, OMe); 3.45 (s, 3H, OMe); 3.06, 4.25, 4.38, 4.81 [m, 8H, $(C_5H_4)_2Fe$]; 4.33 (s, 5H, C_5H_5); 6.36 (s, 1H, =CH); 7.1-7.6 (m, 20H, Ph). EI MS: 864, $[M]^+$, 56; 849, $[M - Me]^+$, 0.5; 833, $[M - OMe]^+$, 0.3; 818, $[M - Me - OMe]^+$, 0.7; 805, $[M - CO_2Me]^+$, 6; 721, $[Ru(dppf)(C_5H_5)]^+$, 33; 678, $[M - Fe(C_5H_5)_2]^+$, 8; 655, $[Ru(dppf) - H]^+$, 12; 644, $[Ru(dppf)(C_5H_5)-Ph]^+$, 10; 554,

$[dppf]^+$, 100; 535, $[721 - Fe(C_5H_5)_2]^+$, 2; 497, $[Ru\{C_2H(CO_2Me)_2\}(PPh_2)(C_5H_5)]^+$, 8; 476, $[dppf - C_6H_6]^+$, 43; 471, $[FeRu(C_5H_3PPh_2)(C_5H_5)]^+$, 25; 432. $[M]^{2+}$, 9; 416, $[Ru(C_5H_4PPh_2)(C_5H_5)]^+$, 5; 402.5, $[M - CO_2Me]^{2+}$, 3; 381, $[dppf-C_5H_5PPh]^+$, 8; 360.5, $[721]^{2+}$, 7; 339, $[Ru(C_5H_4PPh)(C_5H_5)]^+$, 5 ; 327.5, $[655]^{2+}$, 3; 322, $[644]^{2+}$, 32; 310, $[Ru\{CO_2Me)_2\}(C_5H_5)]^+$, 2.

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CHAPTER THREE

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OLIGOMERISATION REACTIONS OF AgC_2Ph

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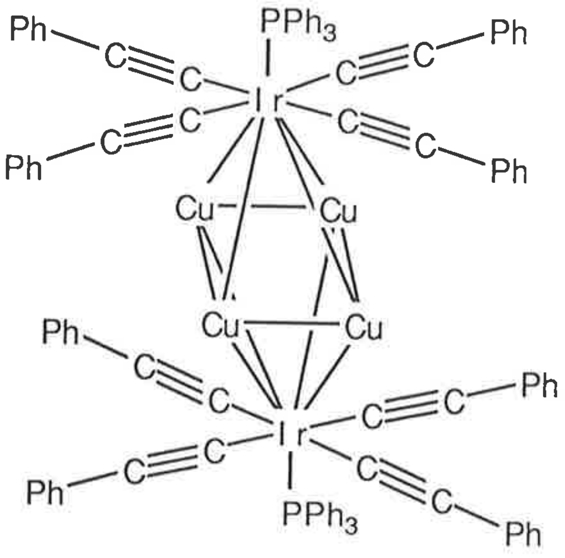
INTRODUCTION

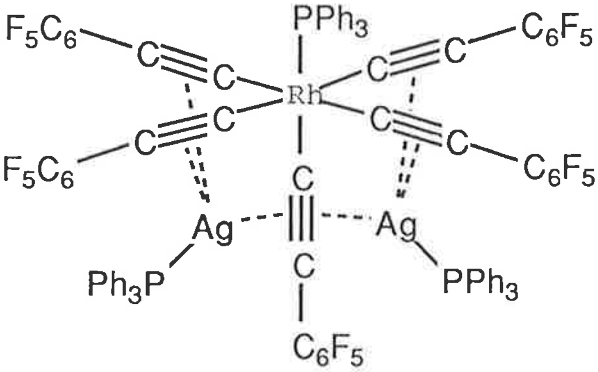
Reactions between group 11 metal acetylides and transition metal halides have proved to be a fruitful source of unusual types of mixed-metal complexes.

Some time ago, the novel hexanuclear iridium-copper cluster $Cu_4Ir_2(C_2Ph)_8(PPh_3)_2$ (1) was obtained from the reaction of $IrCl(CO)(PPh_3)_2$ and copper phenylacetylide[1] in refluxing benzene. Each acetylenic fragment is σ-bonded to iridium and participates in a π- interaction with a copper atom. Extension of this reaction to other Ir and Rh chlorides and selected copper arylacetylides gave a series of analogous mixed metal clusters $M_2Cu_4(C_2Ar)_8(PPh_2R)_2$ [M= Ir, Rh; Ar= Ph, C_6H_4Me-4 , C_6H_4F-4 , C_6F_5; R= Ph, Me; not all combinations].



(1)

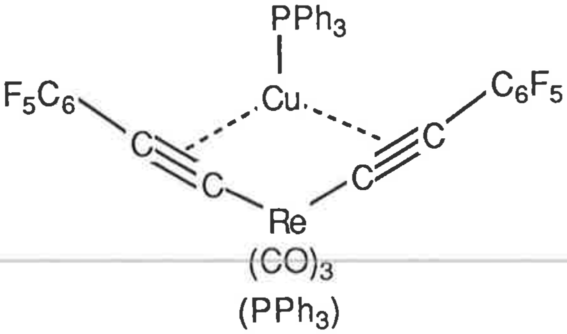
Similarly the reactions between the silver arylacetylides AgC_2Ar (Ar= Ph or C_6F_5) and $RhCl(PPh_3)_3$ or $IrCl(CO)(PPh_3)_2$ in refluxing toluene have given the analogous hexanuclear compounds $M_2Ag_4(C_2Ar)_8(PPh_3)_2$ (M= Rh, Ir) as well as the zwitterionic complexes $[Ag(PPh_3)]^+[M(C_2C_6F_5)_4(PPh_3)_2]^-$ and $[Ag(PPh_3)]^+_2[Rh(C_2C_6F_5)_5(PPh_3)]^{2-}$ (2). This latter complex was structurally characterised.[2a,3]



(**2**)

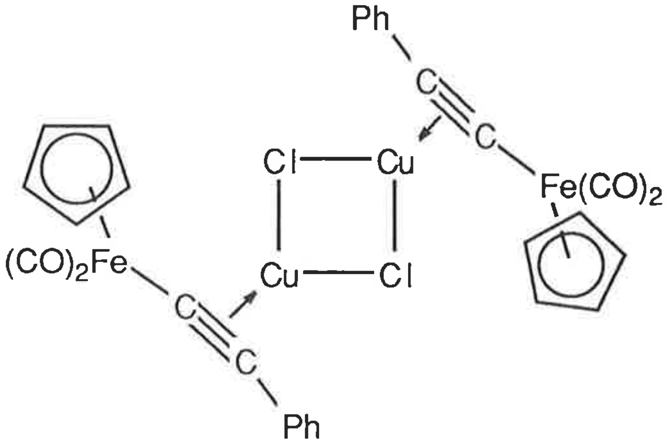
Also isolated from these reactions were small amounts of PhC≡C-C≡CPh, $OPPh_3$ and $[AgCl(PPh_3)]_4$.

These studies were even further extended to the Group VII elements, in which it was found that the reaction between *cis*-$[ReCl(CO)_3(PPh_3)_2]$ and $Cu(C_2C_6F_5)$ yielded $[CuCl(PPh_3)]_4$, the σ-acetylide complex $Re(C_2C_6F_5)(CO)_3(PPh_3)_2$ and the crystallographically characterised complex $[CuRe(C_2C_6F_5)_2(CO)_3(PPh_3)_2]$[4] (3).



(**3**)

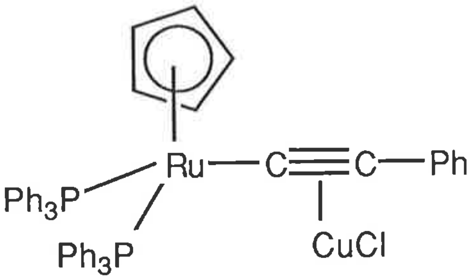
The reaction between CuC_2Ar (Ar= Ph, C_6H_4-4, C_6H_4F-4 or C_6F_5) and $Pt(C_2H_4)(PPh_3)_2$ afforded the bis(acetylide) complexes $Pt(C_2Ar)_2(PPh_3)_2$,[5] which were also obtained from the reaction of *cis*-$PtCl_2(PPh_3)_2$ and CuC_2Ar.



(**5**)

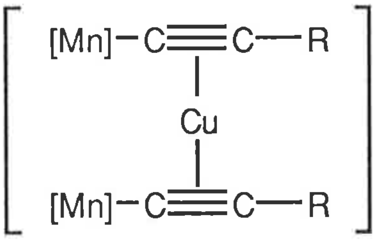
The iron and ruthenium halide complexes $FeX(CO)_2$-(η-C_5H_5)(X= Cl, Br) and $RuCl(PPh_3)_2(\eta$-$C_5H_5)$ (4) also react readily with CuC_2Ar. The iron complex[6] (X= Cl; Ar= Ph) afforded the dimeric compound (5) while the ruthenium complex[7] gave the monomeric compound (6). Complexes (5) and (6) are better prepared from the reaction of $Fe(C_2Ph)(CO)_2(\eta$-$C_5H_5)$ or $Ru(C_2Ph)(PPh_3)_2(\eta$-$C_5H_5)$ (7)

with CuCl, respectively.[6,7] The π-complexed copper (I) chloride was removed from (6) using the tridentate phosphine $MeC(CH_2PPh_2)_3$.



(6)

Spanish workers[8] found that manganese complexes, $[Mn(C_2R)(CO)_3(dppe)]$ (μ-CuCl) (8) [(a) R= CH_2OMe, (b) R= Bu^t, (c) R= Ph], similar to (6) were obtained from the reaction of the corresponding acetylides with CuCl. They were also able to obtain the cationic complexes $\{[Mn(C_2Bu^t)(CO)_3(dppe)][\mu\text{-}MP(C_6H_4Me\text{-}2)_3]\}^+$ (9) [(a) M= Cu; (b) M= Ag; (c) M= Au] from the reaction of one equivalent of the acetylide with a 1:1 ratio of $AgBF_4$ and $P(C_6H_4Me\text{-}2)_3$. Complexes (8a) and (8b) react readily with $TlPF_6$ in the presence of the corresponding acetylide to give the dimeric complexes (10).



[Mn] = $Mn(CO)_3(dppe)$

R = CH_2OMe, Bu^t

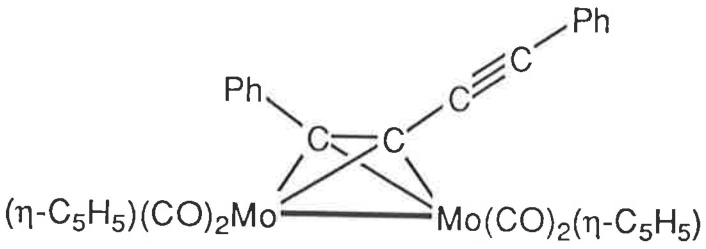
(**10**)

The analogous silver (11) and gold (12) complexes (for R= Bu^t) were prepared directly from the acetylide complex $Mn(C_2Bu^t)(CO)_3(dppe)$ in a reaction with $AgBF_4$ and AuCl(tht)-(tht = tetrahydrothiophene), respectively. Complexes (10) - (12) reacted with excess chloride ion in CH_2Cl_2 giving different results depending on the π-complexed metal. Thus, the copper complex (R= Bu^t) gave $Mn(C_2Bu^t)(CO)_3(dppe)$ and (8b) while the gold complex (12) reacted slowly giving a 1:1 mixture of acetylide and $MnCl(CO)_3$dppe. However, complex (11) reacted instantly giving $Mn(C_2Bu^t)(CO)_3(dppe)$ and AgCl.

Copper-acetylide complexes are implicated in the mechanism for copper-amine catalysed oxidative coupling of terminal alkynes. It is more than a hundred years since Glaser[9] observed that phenylacetylene underwent smooth aerial oxidative coupling to 1,4-diphenyl-1,3-butadiyne when cuprous chloride in ammonia was used as a catalyst. The Glaser copper-amine system has been used in various modifications for many years and the O_2/Cu^I/amine oxidation system has been extended to C-C coupling of a variety of compounds.[10]

Oxidative coupling of acetylide groups has also been observed more recently. The reaction of NaC_2Ph with $TiCl_2(\eta^5-C_5H_4Me)_2$ resulted in the oxidative coupling of two phenylacetylide anions which gave a complex containing a 1,4-diphenyl-1,3-butadiyne ligand complexed to two $Ti(\eta^5-C_5H_4Me)_2$ moieties.[11]

A complex (13) containing this ligand was also obtained from the thermal decomposition, in the solid state or in octane at 110-115°C, of $Mo(C_2Ph)(CO)_3(\eta-C_5H_5)$.[12] Complex (13) and the analogous C_6H_4F-4 complex were unstable with

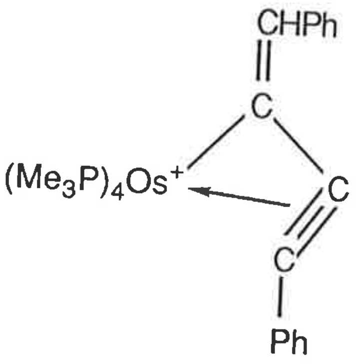


(13)

respect to thermolysis.

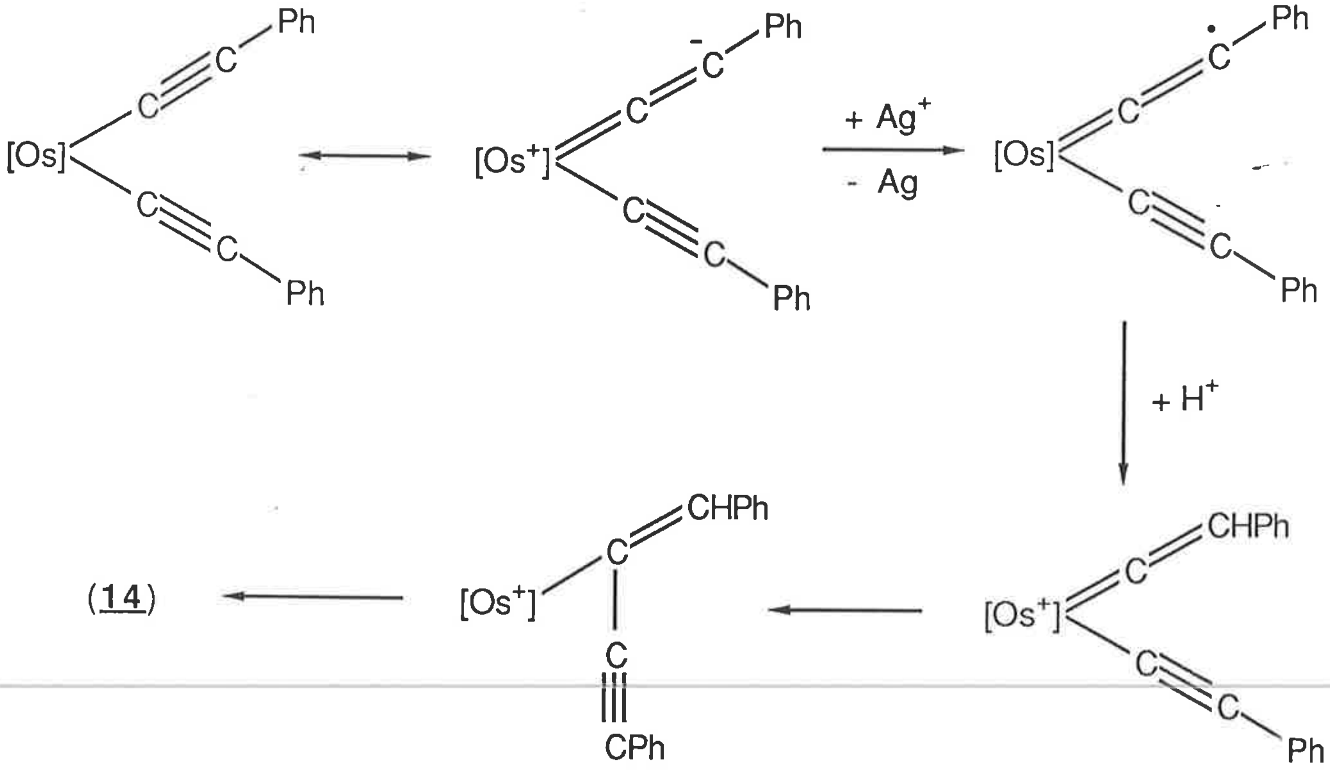
It is of interest that no free phenylacetylene or 1,4-diphenyl-1,3-butadiyne was found in the reaction mixture.

The product of the reaction between *cis*-$[Os(C_2Ph)_2(PMe_3)_4]$ and $AgPF_6$, $[Os(\eta^3-PhC_3{=}CHPh)(PMe_3)_4][PF_6]$[13] (14), contains a novel C_4 ligand produced by oxidative coupling of the two acetylide ligands. X-ray structural characterisation showed that the unsaturated hydrocarbon unit forms a strictly planar ligand system which occupies two *cis*-positions in the octahedral complex cation.



(**14**)

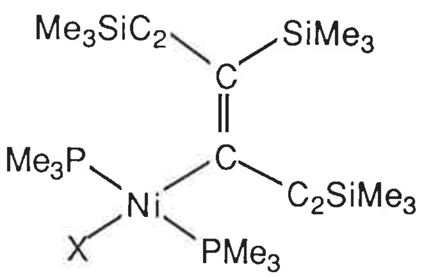
A radical mechanism[13] is proposed for the oxidative coupling reaction leading to (14) (Scheme 1). Silver ion acts to oxidize one of the acetylide ligands causing the



Scheme 1 [Os] = Os(PMe$_3$)$_4$

deposition of solid silver. Hydrogen atom abstraction from the solvent followed by addition of the remaining phenylacetylide ligand to the α-carbon of the intermediate vinylidene ligand, then coordination to the osmium atom of the $-C\equiv CPh$ unit gave complex (14). It is believed that this reaction sheds some light on the mechanism of dimerisation of alkynes by transition metal compounds.[13]

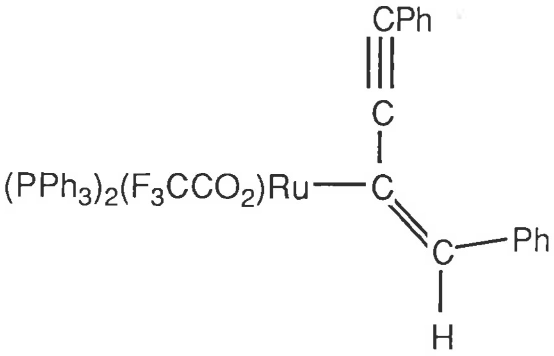
The mono acetylide nickel compounds $NiX(C_2SiMe_3)(PMe_3)_2$ (X= Cl, Br) were obtained by an oxidative addition of ClC_2SiMe_3 to the nickel (O) complexes $Ni(PMe_3)_4$ or $Ni(CO)(PMe_3)_3$; the bromo complex was obtained following halide exchange.[14] In exchanging for iodide an oxidative trimerisation of acetylide groups occurred in solution. The chloro- and bromo- complexes above undergo a similar thermally induced rearrangement in the crystalline state giving $NiX\{C(C_2SiMe_3)=C(SiMe_3)(C_2SiMe_3)\}(PMe_3)_2$ [(15)-(17); X= Cl, Br, I] as well as Ni, $Ni(PMe_3)_4$ and $NiX_2(PMe_3)_2$(3)



(15) - (17)

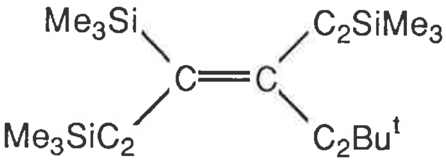
A series of reactions discounted the possibility of 1,3-butadiyne intermediates in the preceding reactions and therefore a mechanism involving vinylidene intermediates was proposed.[14]

Ruthenium and osmium complexes containing similar vinylacetylide ligands were prepared from the reaction of either $MH(O_2CF_3)(CO)(PPh_3)_2$ or $M(O_2CCF_3)_2(CO)(PPh_3)_2$ (M= Ru, Os) with phenylacetylene.[26] The initial products are assumed to be the acetylide complexes $M(C_2R)(O_2CCF_3)$-$(CO)(PPh_3)_2$ which react further with PhC_2H to give bright yellow complexes, $Ru\{C(C_2Ph)=CHPh\}(O_2CCF_3)(CO)(PPh_3)_2$ (For M= Ru, R= Ph), presumably via a vinylidene intermediate.



When M= Os a brown hydrocarbon polymer is obtained, production of which appears to be catalytic. The ruthenium complex and its osmium analogue $Os\{C(C_2Ph)=CHPh\}(O_2CCF_3)$-$(CO)(PPh_3)_2$ are better obtained by the addition of 1,4-diphenyl-1,3-butadiyne to the hydrides $MH(O_2CCF_3)(CO)(PPh_3)_2$.

Substitution of the halide in complex (<u>17</u>) by LiC_2Bu^t gave *trans*-$Ni(C_2Bu^t)\{C(C_2SiMe_3)=C(SiMe_3)(C_2SiMe_3)\}(PMe_3)_2$ which under an atmosphere of CO reductively eliminates (<u>18</u>),



(<u>**18**</u>)

i.e. coupling of the sp^2 carbon of the vinyl ligand in (<u>17</u>) to the sp carbon of the C_2Bu^t ligand.[14]

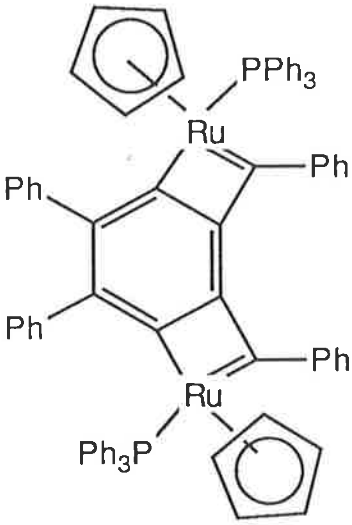
It has been briefly shown that the reaction of metal acetylide complexes with metal halide complexes or themselves gives a variety of interesting products.

As mentioned previously, $[Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)]$-($\mu$-CuCl) (<u>6</u>) was obtained from the reaction of $RuCl(PPh_3)_2$-(η-C_5H_5) (<u>4</u>) and $Cu(C_2Ph)$. It was reasoned that the use of $Ag(C_2Ph)$ would be expected to afford a less stable π-adduct and therefore provide a better synthesis of $Ru(C_2Ph)(PPh_3)(\eta-C_5H_5)$. Interestingly, the reaction proceeded in a totally unexpected manner.

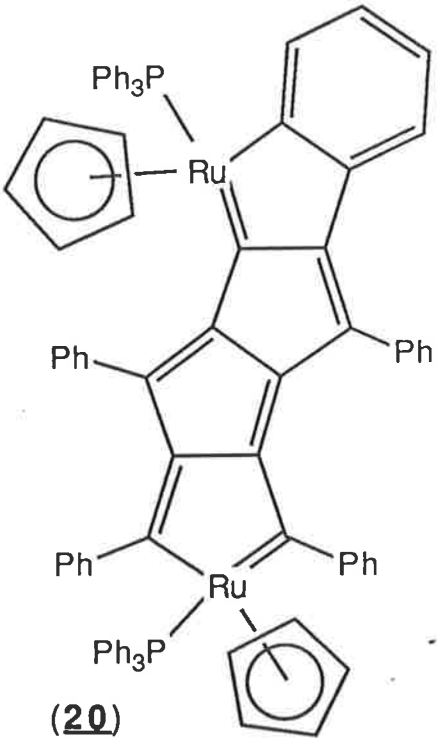
RESULTS AND DISCUSSION

Reaction of $RuCl(PPh_3)_2(\eta-C_5H_5)$ (4) with AgC_2Ph

A mixture of the two compounds in refluxing toluene rapidly darkens and deposits metallic silver. From the cooled reaction mixture two intensely coloured binuclear products were isolated, $\{Ru(PPh_3)(\eta-C_5H_5)\}_2(\mu-C_8Ph_4)$ (19) and $\{Ru(PPh_3)(\eta-C_5H_5)\}_2\{\mu-C_{10}Ph_4(C_6H_4)\}$ (20) by column chromatography.



(**19**)



(**20**)

The best yields of complex (19) (15 - 24%) were obtained by quenching the reaction when spot tlc of the reaction mixture showed that all of (4) had been consumed. Continued reaction results in decomposition of (19) as was shown in a separate reaction where pyrolysis of (19) in toluene leads to complete decomposition after 30 min. Complex (20) was obtained as a minor product.

The binuclear compounds do not have any distinguishing spectroscopic features except for their FAB mass spectra; (19) contains cyclopentadienyl resonances at δ 4.69 and 87.0 in its ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra, respectively. The instability of (<u>19</u>) in solution precluded the observation of the expected lowfield carbene resonances. The FAB mass spectra, however, showed parent ions at *m/z* 1262 and at 1363 for (<u>19</u>) and (<u>20</u>) respectively, suggesting that (<u>20</u>) was related to (<u>19</u>) by the addition of a phenylacetylide unit. These ions fragment principally by the loss of Ph, PPh_3 and $Ru(PPh_3)(\eta-C_5H_5)$ groups.

Single crystal X-ray studies established the molecular structures of both complexes unambiguously.

<u>X-ray crystal structures of (19) and (20)</u>

The structure of (<u>19</u>) (Figure 1) shows that the complex consists of a C_8Ph_4 ligand bridging two $Ru(PPh_3)(\eta-C_5H_5)$ moieties and can be considered to be a diruthena 4|6|4 tricyclic system. (Relevant bond distances and angles are collected in Table 1). Each metal atom has approximate octahedral co-ordination, with Ru(1)-C_5H_5(av) 2.26Å, Ru(2)-C_5H_5(av) 2.25Å, Ru(1)-P(1) 2.308(2), and Ru(2)-P(2) 2.310Å, and achieves an 18 electron configuration by virtue of Ru-C(σ) and Ru-C(Carbene) interactions with C(11)[2.062(7)Å] and C(14)[2.051(7)Å], and with C(17)[1.982(7)Å] and C(24) [1.997(7)Å], respectively. The central Ru_2C_8 fragment, defined by Ru(1)-C(11)-C(17)-C(24)-Ru(2), is planar within experimental error. The small bite of the ligand results in severe distortions within the four membered RuC_3 rings as shown by the angles at carbon [C(11)C(12)C(17) 99.1(6); C(14)C(13)C(24) 99.5(6)°] and at Ru[C(11)Ru(1)C(17) 64.8(3);

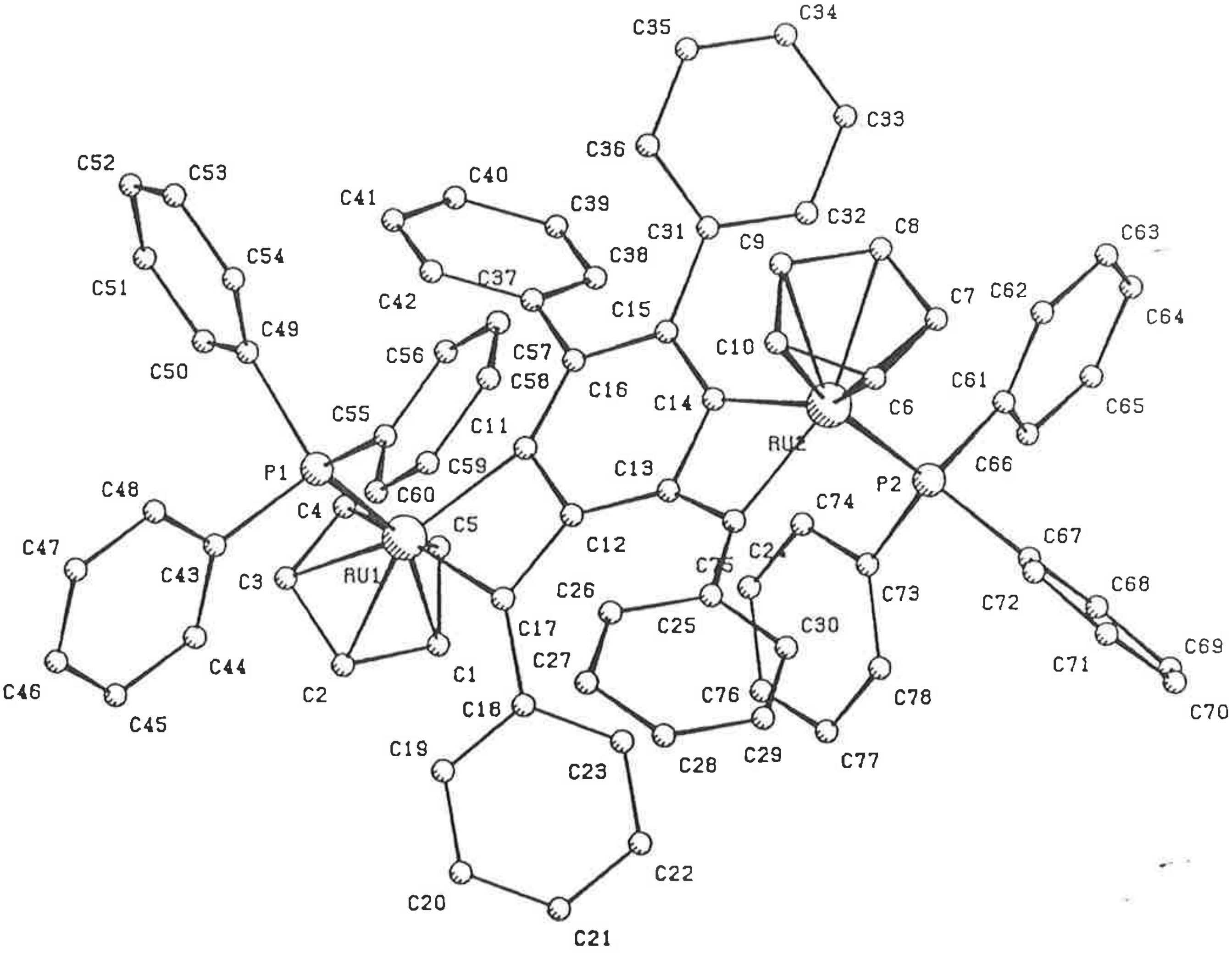


Figure 1: PLUTO plot of the molecular structure of $\{Ru(PPh_3)(\eta-C_5H_5)\}_2(\mu-C_8Ph_4)$ (19) (by M.R. Snow and E.R.T. Tiekink)

Table 1. Selected interatomic parameters for (19)

Bond distances (Å)

P(1)-Ru(1)	2.308(2)	P(2)-Ru(2)	2.310(2)
C(11)-Ru(1)	2.062(7)	C(13)-Ru(2)	2.627(7)
C(17)-Ru(1)	1.982(7)	C(24)-Ru(2)	1.997(7)
C(14)-Ru(2)	2.051(7)	C(12)-C(11)	1.411(9)
C(16)-C(11)	1.398(10)	C(13)-C(12)	1.437(10)
C(17)-C(12)	1.436(10)	C(14)-C(13)	1.411(10)
C(24)-C(13)	1.432(9)	C(15)-C(14)	1.419(9)
C(16)-C(15)	1.434(10)	C(31)-C(15)	1.491(8)
C(37)-C(16)	1.500(9)	C(18)-C(17)	1.472(8)
C(25)-C(24)	1.475(8)	Ru(1)-C(C_5H_5)	2.26 av.
C(12)-Ru(1)	2.630(7)	Ru(2)-C(C_5H_5)	2.25 av.

Bond angles (°)

C(17)-Ru(1)-P(1)	92.2(2)	C(14)-Ru(2)-C(13)	32.2(2)
C(17)-Ru(1)-C(11)	64.8(3)	C(24)-Ru(2)-C(6)	105.4(3)
C(24)-Ru(2)-P(2)	93.1(2)	C(24)-Ru(2)-C(8)	152.8(3)
C(24)-Ru(2)-C(7)	141.0(3)	C(24)-Ru(2)-C(10)	93.7(3)
C(24)-Ru(2)-C(9)	116.8(3)	C(24)-Ru(2)-C(14)	64.8(3)
C(24)-Ru(2)-C(13)	32.6(2)	Ru(1)-C(11)-C(12)	96.6(5)
C(11)-Ru(1)-P(1)	90.1(2)	Ru(2)-C(14)-C(13)	97.0(5)
C(12)-Ru(1)-P(1)	90.1(2)	C(11)-C(12)-C(17)	99.1(6)
C(12)-Ru(1)-C(11)	32.2(2)	C(14)-C(13)-C(24)	99.5(6)
C(17)-Ru(1)-C(12)	32.6(2)	C(12)-C(17)-Ru(1)	99.4(5)
C(13)-Ru(2)-P(2)	91.9(2)	C(13)-C(24)-Ru(2)	98.7(4)

C(14)Ru(2)C(24) 64.8(3)°]. The cross-ring Ru....C separations [Ru(1)-C(12) 2.630(7) and Ru(2)-C(13) 2.627(Å)] are too long for there to be any significant bonding interaction.

Complex (<u>19</u>) may be formally represented as a diruthenadicyclobutadieno [*a,c*] benzene, although the e.s.d.'s in C-C bond lengths do not allow a determination of the degree of bond localisation in the six membered ring.

The structure of the purple complex (<u>20</u>) (Figure 2, bond lengths and angles in Table 2) contains two Ru(PPh_3)-(η-C_5H_5) moities joined by a polycyclic system formed from five C_2Ph units, one of which has been cyclometallated. Each metal atom exists in a distorted octahedral environment with Ru(1)-C_5H_5(av) 2.29Å, Ru(2)-C_5H_5(av) 2.28Å, Ru(1)-P(1) 2.310(5)Å and Ru(2)-P(2) 2.321(5)Å. As was found in (<u>19</u>) the ruthenium atoms in (<u>20</u>) are bonded to the polycyclic ligand via Ru-C(σ) [Ru(1)-C(14) 2.036(14), Ru(2)-C(22) 2.059(16)Å] and Ru-C(Carbene) interactions [Ru(1)-C(11) 1.963(15); Ru(2)-C(20) 1.910(15)Å]. The planar, pentacyclic 14-atom Ru_2C_{12} system contains several unusual features. The nine central carbon atoms C(12) - C(20) form a methylenepentalene nucleus fused to a metallocyclopentadiene [involving Ru(2)]. The maximum deviation from the mean plane through atoms Ru(1)Ru(2), C(11)-C(26) is 0.18(2)Å for C(23) and the maximum deviation from the plane defined by C(11)-C(26) is 0.16(2)Å for C(20) with Ru(1) and Ru(2) 0.016(2) and 0.112(1)Å out of the plane, respectively. The dihedral angle between the plane bounded by C(16)-C(20) (P1) and the plane through C(12)C(13)C(15)C(16)C(17)(P2) is 1.4°. Plane P1 has a dihedral

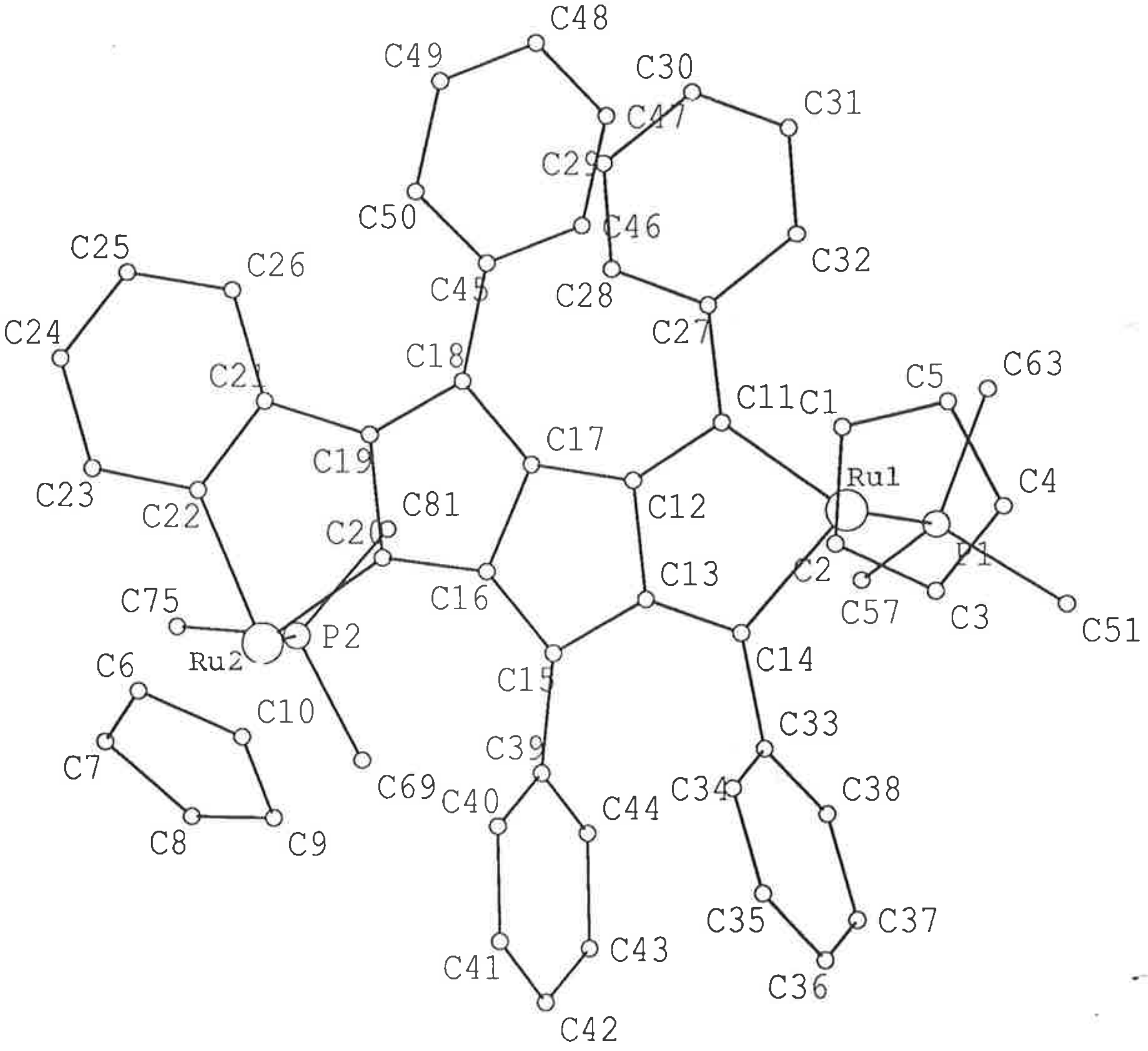


Figure 2: PLUTO plot of the molecular structure of $\{Ru(PPh_3)(\eta\text{-}C_5H_5)\}_2\{\mu\text{-}C_{10}Ph_4(C_6H_4)\}$ (<u>20</u>) (by M.R. Snow and E.R.T. Tiekink) - only ipso carbons of phosphine bound phenyl groups are shown for clarity.

Table 2. Selected interatomic parameters for (20)

Bond distances (Å)

P(1)-Ru(1)	2.310(5)	C(14)-Ru(1)	2.036(14)
C(11)-Ru(1)	1.963(15)	C(22)-Ru(2)	2.059(16)
P(2)-Ru(2)	2.321(5)	C(27)-C(11)	1.487(17)
C(20)-Ru(2)	1.910(15)	C(17)-C(12)	1.413(19)
C(12)-C(11)	1.440(20)	C(15)-C(13)	1.438(19)
C(13)-C(12)	1.470(19)	C(16)-C(15)	1.381(20)
C(14)-C(13)	1.374(18)	C(17)-C(16)	1.454(19)
C(33)-C(14)	1.496(19)	C(18)-C(17)	1.437(20)
C(39)-C(15)	1.488(19)	C(45)-C(18)	1.482(19)
C(20)-C(16)	1.492(20)	C(21)-C(19)	1.457(19)
C(19)-C(18)	1.415(20)	C(26)-C(21)	1.423(21)
C(20)-C(19)	1.517(20)	C(24)-C(23)	1.422(22)
C(22)-C(21)	1.411(20)	C(26)-C(25)	1.414(20)
C(23)-C(22)	1.415(20)	Ru(1)-C(C_5H_5)	2.27 (av.)
C(25)-C(24)	1.367(22)	Ru(2)-C(C_5H_5)	2.28 (av.)

Bond angles (°)

C(11)-Ru(1)-P(1)	95.8(5)	C(24)-C(23)-C(22)	119.6(16)
C(14)-Ru(1)-P(1)	90.3(4)	C(26)-C(25)-C(24)	121.7(16)
C(20)-Ru(2)-P(2)	100.4(5)	C(13)-C(12)-C(11)	110.6(13)
C(22)-Ru(2)-C(20)	80.8(6)	C(17)-C(12)-C(13)	106.2(13)
C(12)-C(11)-Ru(1)	117.5(11)	C(15)-C(13)-C(12)	108.7(13)
C(17)-C(12)-C(11)	143.1(15)	C(13)-C(14)-Ru(1)	114.7(10)
C(14)-C(13)-C(12)	116.2(13)	C(17)-C(16)-C(15)	110.2(13)
C(15)-C(13)-C(14)	135.2(15)	C(20)-C(16)-C(17)	108.9(13)
C(16)-C(15)-C(13)	107.1(14)	C(18)-C(17)-C(12)	142.5(15)
C(20)-C(16)-C(15)	141.0(15)	C(19)-C(18)-C(17)	107.4(14)
C(16)-C(17)-C(12)	107.8(13)	C(21)-C(19)-C(18)	136.1(15)
C(18)-C(17)-C(16)	109.5(13)	C(16)-C(20)-Ru(2)	139.4(12)
C(20)-C(19)-C(18)	111.0(13)	C(19)-C(20)-C(16)	102.7(12)
C(21)-C(19)-C(20)	112.9(14)	C(26)-C(21)-C(19)	125.0(15)
C(19)-C(20)-Ru(2)	117.3(10)	C(21)-C(22)-Ru(2)	117.1(11)
C(22)-C(21)-C(19)	111.8(15)	C(23)-C(22)-C(21)	117.7(15)
C(26)-C(21)-C(22)	123.2(13)	C(25)-C(24)-C(23)	121.2(16)
C(23)-C(22)-Ru(2)	125.1(13)	C(25)-C(26)-C(21)	116.6(14)

angle of 3.0° to the plane through Ru(2)C(20)C(19)C(21)C(22) while the similar angle between plane P2 and Ru(1)C(11)C(14) is 6.2°. This ring system is the first example of a pentalene-metal complex which does not involve the metal stabilising this system by π-complexation. The short Ru(1)-C(11) and Ru(2)-C(20) distances and longer Ru(1)-C(14) and Ru(2)-C(12) single bonds, effectively localise the conjugated double bonds in the molecule (e.s.d.'s in individual C-C distances preclude further confirmation of this feature).

Although the portion C(19)-C(22) attached to Ru(2) can be formally related to Ru(C_2Ph) precursors, both C(11) and C(14) bear phenyl groups and cannot be so related.

The Ru=C interactions found in (19) and (20) are further examples of the growing number of complexes containing this bonding feature in the chemistry of ruthenium carbon-bonded ligands; other examples include the "allylic" complex Ru{η^3-C$(CN)_2$C(Ph)C=C$(CN)_2$}(PPh_3)(η-C_5H_5) (21),[15] the (5e)-butadienyl derivative Ru{η^4-C(Ph)C(Ph)C(Ph)CH(Ph)}(η-C_5H_5)(22)[16] and the metallocyclopentatriene, RuBr(CPhCHCHCPh)(η-C_5H_5)[17] (23). Table 3 collects some relevant bond angles and distances and allows comparison with (19) and (20). It is obvious that all the complexes contain Ru-C bonds of some multiple character. The relatively long distances found in (19) may be a result of steric strain in the four membered rings.

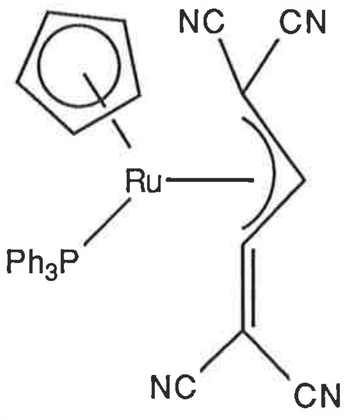
Some related reactions

The formation of such extended polycyclic systems is unprecedented, although Maitlis[18] found that tetramerisation of phenylacetylene by palladium salts gave dihydropentalene compounds (Equation 1) not incorporating the metal atoms.

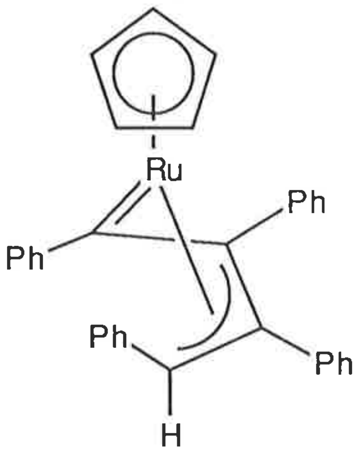
Table 3

Some bond distances (Å) and angles (°) for complexes (21), (22) and (23)

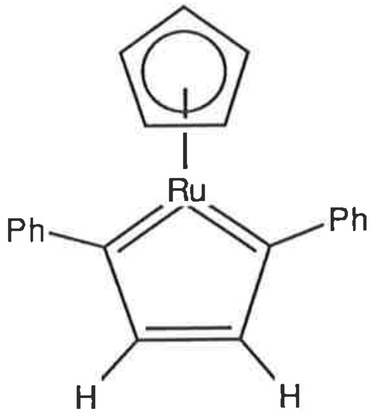
	(21)	(22)	(23)
Ru-C(1)	1.919(5)	1.896(5)	1.942(6)
Ru-C(2)	2.135(4)	2.204(5)	-
Ru-C(3)	2.231(4)	2.152(4)	-
angle at Ru	-	32.0(3) RuC(1)C(2)	78.7(4) C(1)RuC(C1´)
Ref.	15	16	17



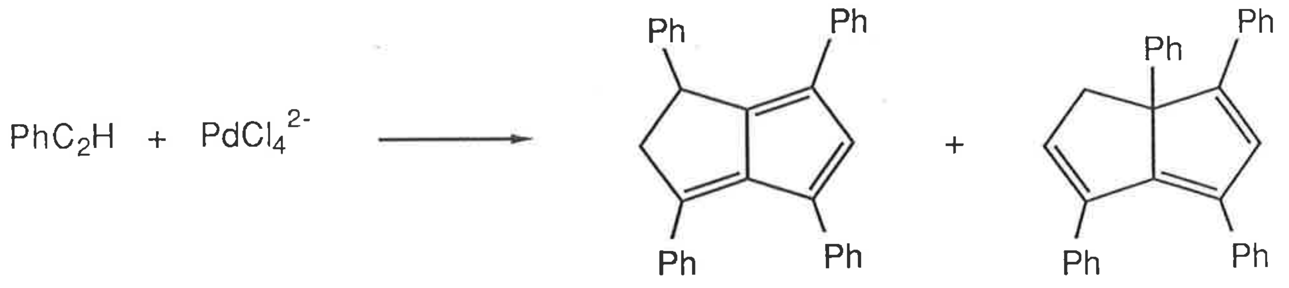
(21)



(22)

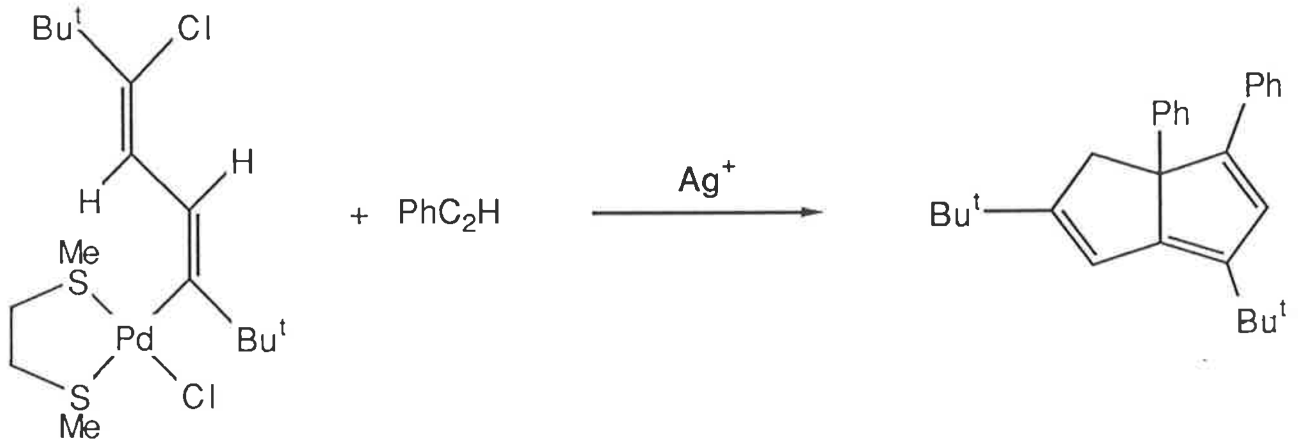


(23)



Equation 1

The silver ion mediated reaction of phenylacetylene with a palladium butadienyl complex also gave a dihydropentalene compound (Equation 2).



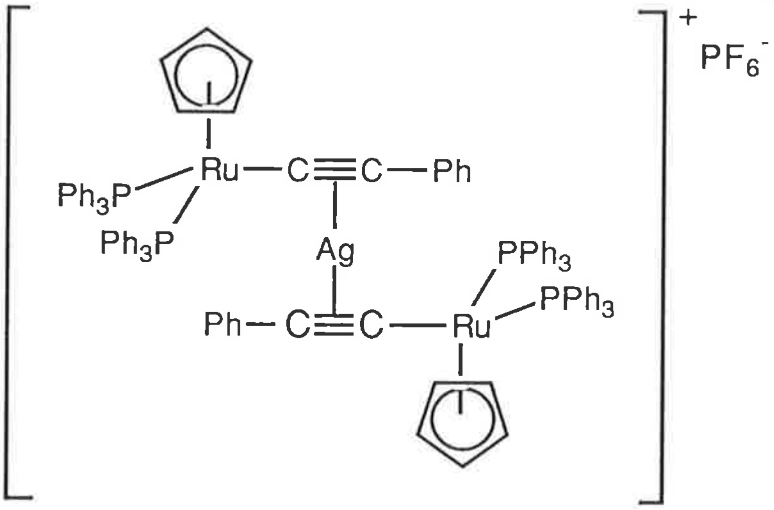
Equation 2

Several reactions were undertaken in an attempt to determine the mechanism operating in the reaction of (4) with AgC_2Ph.

Although (20) is formally related to (19) by the addition of one more phenylacetylide unit, there is apparently an alternative pathway operating in the formation of (20), insofar as (20) cannot be obtained from the reaction of (19) with excess AgC_2Ph in toluene. Complex (19) is also not obtained from any combination of $[Ru(S)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ (S = Solvent), AgC_2Ph and/or PhC_2C_2Ph. However, the reaction of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (7) and AgC_2Ph gives (19) (in 9% yield) only after the addition of one equivalent of AgCl. This suggests that silver ion mediates the oligomerisation of the phenylacetylide units.

(i) Reaction of (7) with $AgPF_6$ (2:1) - Addition of a toluene suspension of $AgPF_6$ to a solution of (7), also in toluene, at 0°C causes the precipitation of the yellow complex $[\{Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)\}_2Ag][PF_6]$ (24) in essentially quantitative yield. Complex (24) is an air-stable solid that decomposes on silica tlc plates to give (7) and Ag. Characterisation of (24) rests on its spectroscopic properties, supported by elemental microanalysis. The infrared spectrum is distinguished by the shift of the $\nu(C{\equiv}C)$ stretching mode to lower wavenumber than that found for (7) [1984m, 1943s; c.f. 2068m cm^{-1} in (24) and (7)[19] respectively] and by the presence of a strong, broad band at 839 cm^{-1} assigned to $\nu(P\text{-}F)$ of a PF_6^- counter ion. The proton NMR spectrum contains a multiplet at δ 7.25 and a singlet at δ 4.41 assigned to the phenyl and cyclopentadienyl groups, respectively. The $^{13}C\{^1H\}$ NMR spectrum similarly shows a multiplet at δ 128.3-138.1 and a singlet at δ 86.15, also assigned to the phenyl and cyclopentadienyl carbons, respectively. A signal at δ 91.1 is assigned to C_β of the acetylide ligands; the $C\alpha$ resonance ~~was not observed and this was probably due to decomposition~~ of the sample.

Assignment was confirmed by FAB MS, the spectrum showing a parent ion at m/z 1692 $[M + H]^+$ which fragments with competitive loss of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$, Ag and PPh_3 groups. The ion at m/z 529 assigned to $[Ru(C_2C_6H_4)(PPh_3)(C_5H_5)]^+$ loses C_6H_4 to give an ion containing a C_2 fragment; which is lost to give the base peak $[Ru(PPh_3)(\eta\text{-}C_5H_5)]^+$. The preceding data suggest the structure shown below:



(**<u>24</u>**)

This structure is consistent with the lowering of bond order of the C≡C moieties by π complexation to Ag^+. An unsymmetrical co-ordination is most likely, because of steric factors. Similar i.r. spectra to that of (<u>24</u>) were given by the closely related $[\{Ru(C_2Ph)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)\}_2Cu][PF_6]$ (<u>25</u>)[20] obtained from the reaction of $Ru(C_2Ph)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (<u>26</u>) and $[Cu(NCMe)_4][PF_6]$ [(<u>25</u>) ν(C≡C) 1992m, 1948s; (<u>26</u>) ν(C≡C) 2085 cm^{-1}], and the structurally characterised complex $Ru\{C_2Ph(CuCl)\}(PPh_3)_2(\eta\text{-}C_5H_5)$ (<u>6</u>) [(<u>6</u>) ν(C≡C) 1979m, 1934m; (<u>7</u>) ν(C≡C) 2076 cm^{-1}] obtained both from the reaction of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (<u>4</u>) with CuC_2Ph[7] and from the reaction of (<u>7</u>) with CuCl.[7]

This tendency of phenylacetylide units to act as η^2-ligands for the coinage metals is also shown by $Mn(C_2Ph)-(CO)_3(dppe)$ ($R=CH_2OMe$,Bu^t or Ph),[8] which coordinate Cu, Ag and Au in a similar manner to (6) and in the case of Cu a structurally characterised 2:1 adduct was obtained, *viz.* $[\{Mn(C_2Bu^t)(CO)_3(dppe)\}_2Cu][PF_6]$ (10b),[8] (Figure 3).

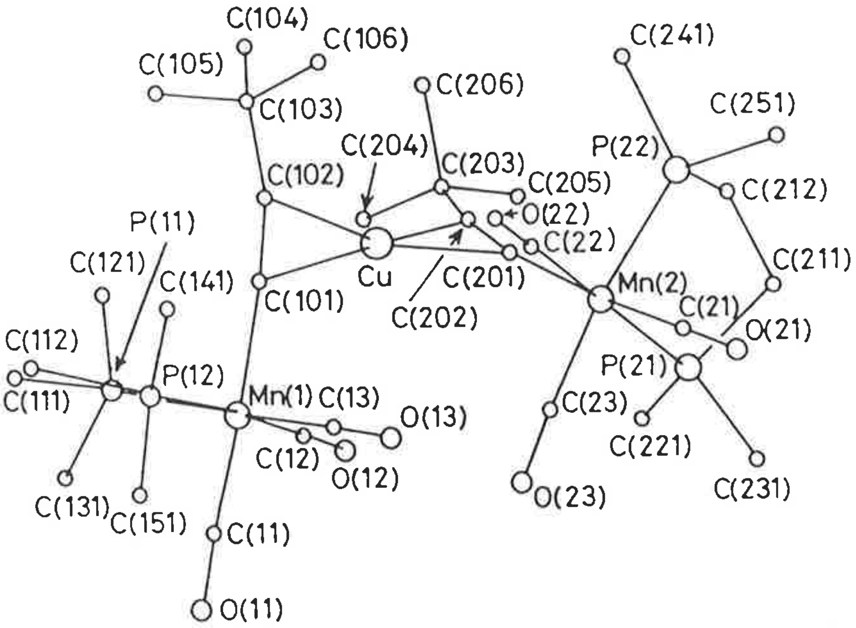
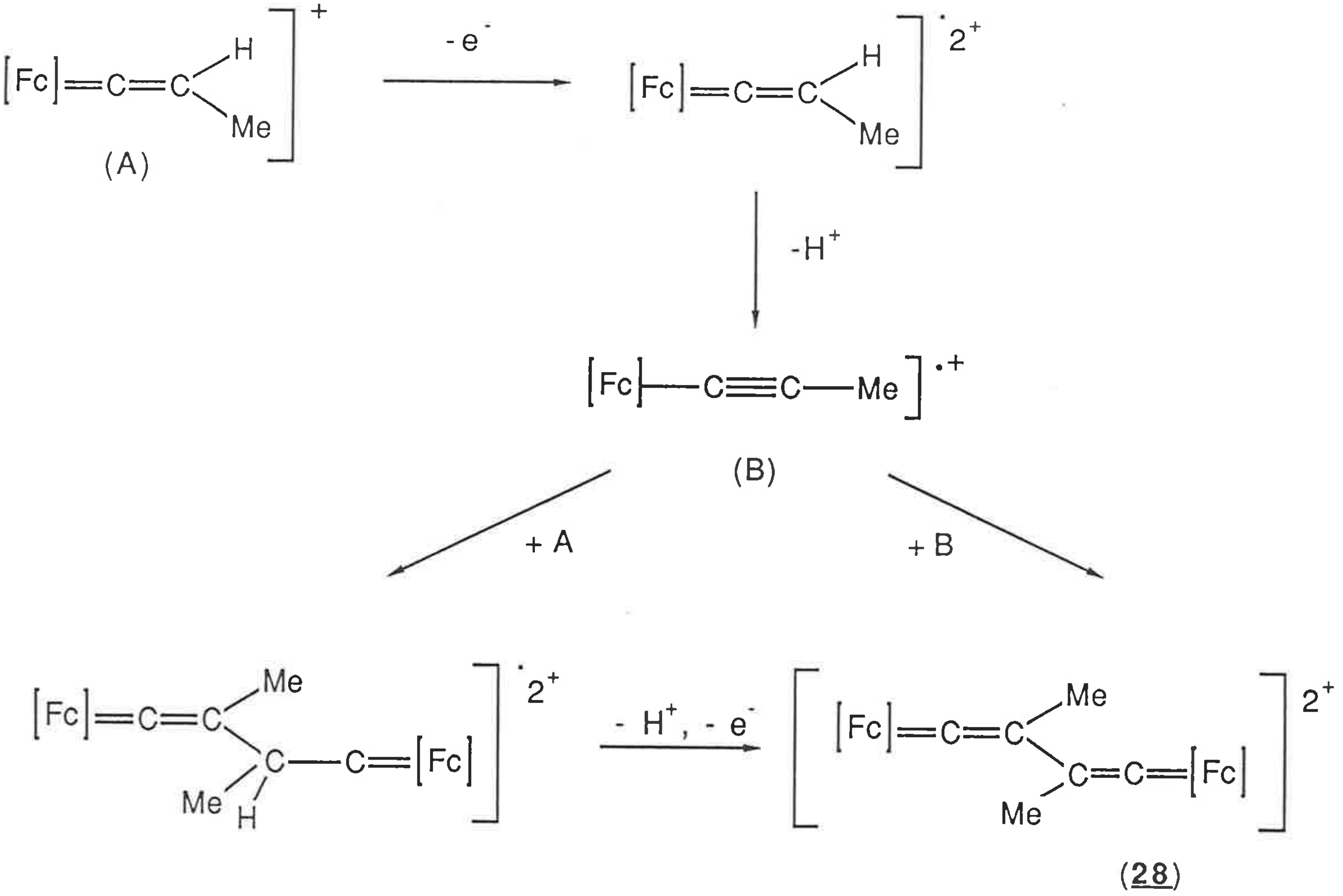


Figure 3

There is pseudotetrahedral coordination around the copper with Cu-C(acetylide) bonds averaging 2.081(1)Å.[8] Mean planes bonded by the respective acetylide carbons, manganese and copper atom have a dihedral angle of 71(1)°. This accommodates the steric bulk of both the Bu^t and $Mn(CO)_3(dppe)$ groups, although steric interaction between the bulkier manganese moieties probably cause the angle C(101)CuC(201) [158.4(5)°] to be larger than C(202)CuC(102) [145.6(5)°]. The characteristic "bending back" of the acetylide substituents suggests that some π-back bonding is occurring even allowing for steric effects [Mn(1)C(101)C(102) 170.5(10)° and C(103)C(102)C(101) 164.0(14)°].

(ii) the Reaction of (7) with $AgPF_6$ (1:1) - Reaction of equimolar amounts of $AgPF_6$ and (7) resulted in the immediate precipitation of yellow (24). Upon dissolution of this precipitate in dichloromethane the solution rapidly darkens to a red/pink solution from which was isolated the divinylidene $[\{Ru(PPh_3)_2(\eta\text{-}C_5H_5)\}_2(\eta\text{-}C_4Ph_2)][PF_6]_2$ (27) as a pale apricot powder, characterised by elemental microanalysis and its spectral properties. Broad medium intensity bands at 1626 and 1587 cm^{-1}, in the infrared spectrum, are assigned to $\nu(C{=}C)$ of the vinylidene ligand and the strong broad absorption at 841 cm^{-1} to $\nu(P\text{-}F)$ of the counter ions. Two equal intensity resonances were found in the ^1H NMR spectrum at δ 5.42, 5.59 and were assigned to two inequivalent C_5H_5 groups; the phenyl resonances were found in the usual region. The $^{13}C\{^1H\}$ NMR spectrum contained two peaks at δ 91.1 and 95.5 and were assigned to the C_5H_5 moieties. An unresolved peak found at low field at δ 347.6 is only tentatively assigned to the α-carbon as no coupling to phosphorus was observed. A signal for the β-carbons was not observed and probably lies under the phenyl signals. It should be noted that in the $^{13}C\{^1H\}$ spectrum of the phenylvinylidene complex $[Ru\{C{=}CHPh\}(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$, the α-carbon shows a 24 Hz coupling to the two equivalent ^{31}P nuclei.[19] The ^1H NMR spectrum of the analogous iron complex, $[\{Fe(dppe)(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_4Ph_2)][PF_6]$[21] contains two peaks at δ 5.1 and 5.7, the former assigned to C_5H_5 rings and the latter to the phenyl groups of the divinylidene ligand. The reliability of the ^{13}C NMR data obtained for complex (27) must be questioned because of decomposition of the complex during accumulation. The NMR data for (27) seems to be inconsistent with a divinylidene structure therefore characterisation is tentative and requires an X-ray structure determination to unambiguously characterise (27), when suitable single crystals become available.

The FAB mass spectrum of (27) was much more informative with the highest peak being found at m/z 1729 $[M + PF_6]^+$; an ion at m/z 1583 corresponds to $[M - H]^+$. Experimentally, ions generated by the FAB process are generally found to be univalent as multicharged ions are relatively rare in the gas phase, having high enthalpies of formation. In the case of complexes $[X^{2+}][Y^-]_2$ the lower aggregate $[X + Y]^+$ is usually found as the highest monopositive ion.[22] In this context the ion corresponding to $[M - H]^+$ is unusual. Competitive loss of PPh_3 and $Ru(PPh_3)(C_5H_5)$ from this ion is observed. Interestingly, a peak corresponding to $[Ru(C_4Ph_2)(PPh_3)(C_5H_5)]^+$ is also observed at m/z 631. Loss of the C_4 ligand gives the usual base peak $[Ru(PPh_3)(C_5H_5)]^+$. Complex (27) has precedent in the crystallographically characterised complex, $[\{Fe(dppe)(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_4Me_2)][BF_4]_2$ (28), obtained by oxidation of the mononuclear vinylidene complex $[Fe(C{=}CHMe)(dppe)(\eta\text{-}C_5H_5)][BF_4]$ with iodosobenzene.[23] A radical mechanism has been posited for the formation of (28) (Scheme 2), but the possibility of other pathways has not been dismissed. It was not possible to obtain (28) directly from $Fe(C_2Me)(dppe)(\eta\text{-}C_5H_5)$ using Cu^{2+}, Ag^+ or anodic oxidation and it was concluded that an acidic proton was



Scheme 2: [Fc] = Fe(dppe)(η-C_5H_5)

probably necessary for the formation of (28).

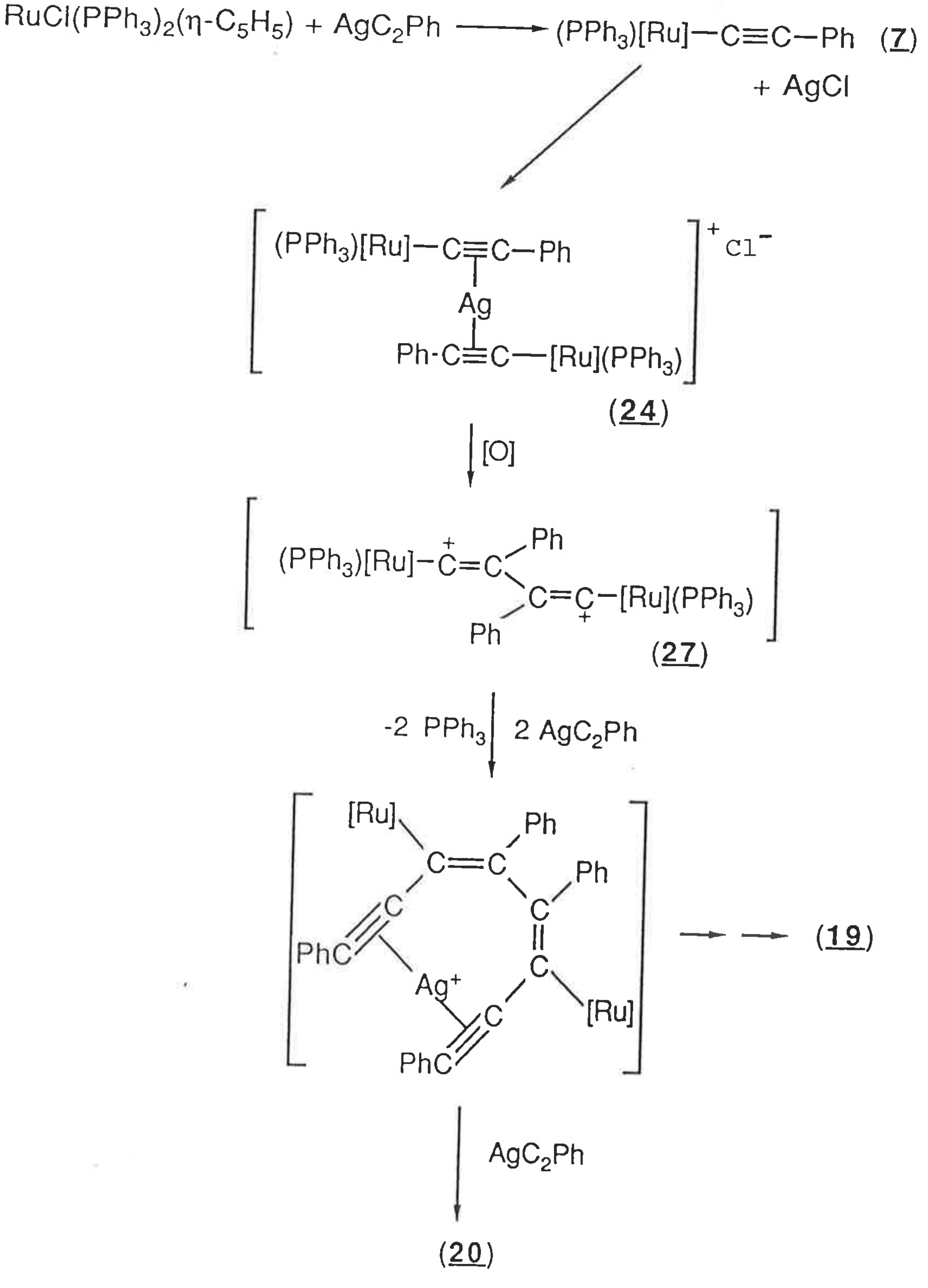
More recently,[24] the radical cations $[Mo(C{\equiv}CR)(dppe)(\eta\text{-}C_7H_7)]^+$ (R=Ph, Bu^n), prepared from the neutral acetylide complexes by oxidation with $[Fe(\eta\text{-}C_5H_5)_2]^+$, were found to undergo coupling at the β-carbon of the acetylide ligand to afford the divinylidene-bridged, products $[\{Mo(dppe)(\eta\text{-}C_7H_7)\}_2(\mu\text{-}C_4R_2)]^{2+}$. The phenyl derivative was crystallographically characterised.

The reaction of complex (26) with $[Cu(NCMe)_4][PF_6]$ also yielded, as a byproduct, the $P(OMe)_3$ complex analogous to (27).[20]

Postulated reaction mechanism for the formation of (19) and (20)

The cyclic ligand in (19) contains a C_4 backbone [C(11)C(16)C(15)C(14)] which can be formally related to the divinylidene linkage in (27). Therefore, a complex similar to (27) is thought to be a possible intermediate in the formation of (19) (Scheme 3).

The initial step probably involves the formation of the σ-acetylide complex $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (7) and AgCl. The silver ion then oxidatively couples the acetylide ligands, probably through the intermediacy of (24), giving (27). Nucleophilic attack at both α-carbons by phenylacetylide anions follows, possibly with loss of PPh_3 to accommodate the steric requirements of the bulky acetylide groups at Cα and allowing interaction of these groups with the metal atoms, which are then coupled with the assistance of Ag^+. The coupling of unsubstituted alkyne carbons by copper ion is well known.[9]



Scheme 3: [Ru] = Ru(PPh$_3$)(η-C$_5$H$_5$)

The formation of complex (20) can also be rationalised by the intermediacy of (27). Here a further phenylacetylide moiety is coupled and subsequent rearrangement gives (20). This latter process requires little of the bond rupture and reformation required if (20) resulted from the addition of AgC_2Ph to (19). However, the true mechanism operating in the reaction of $RuCl(PPh_3)_2(\eta-C_5H_5)$ with AgC_2Ph must be more complicated than that shown in Scheme 3, as the reaction of either (24) or (27) with AgC_2Ph does not give any (19) or (20). This suggests that the chloride ion might play an important but as yet undetermined role.

EXPERIMENTAL

General conditions and instrumentation used were as described in Chapter 1.

Starting materials

Literature methods were used to prepare RuCl$(PPh_3)_2$-$(\eta$-$C_5H_5)$[25] and Ru$(C_2Ph)(PPh_3)_2(\eta$-$C_5H_5)$.[19] Silver phenylacetylide was obtained from the addition of PhC_2H in ethanol to aqueous ammoniacal solutions of $AgNO_3$; $AgPF_6$ is commercially available and was used as received (Pennwalt Chemicals, Tulsa, Oklahoma).

Syntheses

A. (i) Reaction of RuCl$(PPh_3)_2(\eta$-$C_5H_5)$ with AgC_2Ph

A suspension of RuCl$(PPh_3)_2(\eta$-$C_5H_5)$ (127 mg, 0.175 mmol) and AgC_2Ph (130 mg, 0.622 mmol) was heated in refluxing toluene (30 ml) for 1 hr. The resulting mixture was filtered and the filtrate was evaporated to dryness and the residue was chromatographed (Florisil; 3 x 20 cm). Elution with acetone-light petroleum (1:9) gave a blue-green band which was crystallised from CH_2Cl_2/EtOH to give dark blue crystals of $\{Ru(PPh_3)(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_8Ph_4)$ (19) (27 mg, 24%), m.p. >239°C (dec.). [Found: C, 70.50; 4.64; *M* (mass spectrometry) 1262; $C_{78}H_{60}P_2Ru_2.CH_2Cl_2$ requires C, 70.48; H, 4.63%; *M* 1262]. Infrared (Nujol): 1438m, 1089w, 790w, 740w, 720w, 645m cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 4.69 (s, 10H, C_5H_5); 6.40-7.30 (m, 50H, Ph). $^{13}C\{^1H\}$ NMR: $\delta(CDCl_3)$ 87.0 (s, C_5H_5); 124.9-134.6 (m, Ph); 138.3 [d, *J*(PC) 37 Hz, Ru-C]; Ru=C, not detected. FAB MS: 1262, $[M]^+$, 65; 1185, $[M - Ph]^+$, 0.7; 1000, $[M - PPh_3]^+$, 13; 833, $[M - Ru(PPh_3)(C_5H_5)]^+$, 4; 738, $[M - 2PPh_3]^+$, 100; 429, $[Ru(PPh_3)(C_5H_5)]^+$, 70. Further elution of the column afforded a purple fraction which was crystallised from $CH_2Cl_2/EtOH$ to give purple crystals of $\{Ru(PPh_3)(\eta\text{-}C_5H_5)\}_2\{\mu\text{-}C_{10}Ph_4\text{-}(C_6H_4)\}$ (20) (3 mg, 0.5%), m.p. >250°C (dec.). [Found: M (mass spectrometry) 1363; $C_{86}H_{64}P_2Ru_2$ requires M 1363]. FAB MS: 1363, $[M]^+$, 1; 1101, $[M - PPh_3]^+$, 0.5; 839, $[M - 2PPh_3]^+$, 3; 429, $[Ru(PPh_3)(\eta\text{-}C_5H_5)]^+$, 5; 391, $[C_7Ph_3(C_6H_4)]^+$, 100.

(ii) Reaction of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (7) with $AgC_2Ph/AgCl$ by M.L. Williams

A suspension of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (7) (500 mg, 0.632 mmol) and AgC_2Ph (140 mg, 0.498 mmol) in toluene (50 ml) was treated with AgCl (90 mg, 0.627 mmol) 5 min after reaching reflux. After 15 min the dark blue suspension was cooled. Work up as (1) above gave (19) (35 mg, 9%), identified by comparison of its spot tlc behaviour and FAB mass spectrum with those of an authentic sample prepared as above.

(iii) Reaction of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$(7) with $AgPF_6$

(a) in ratio 2:1 - A solution of (7) (500 mg, 0.632 mmol) in toluene (50 ml) was treated with a suspension of $AgPF_6$ (80 mg, 0.32 mmol) in toluene (10 ml) giving immediately a yellow precipitate of $[\{Ru(PPh_3)_2(\eta\text{-}C_5H_5)\text{-}(C_2Ph)\}_2Ag][PF_6]$ (24) (436 mg, 75%), m.p. >190°C (dec.). [Found: C, 63.32; H, 4.64; M (mass spectrometry) 1692; $C_{98}H_{80}AgF_6P_5Ru_2$ requires C, 64.11; H, 4.39%; M + H 1692]. Infrared (Nujol): $\nu(C{\equiv}C)$ 1984m, 1943s, $\nu(PF)$ 839s(br); other bands 1593m, 1570m, 1495w, 1481s, 1433s, 1312w, 1187w, 1161w, 1089s, 1028w, 1000w, 913w, 874w, 813w, 785w, 752s, 737s, 696vs, 557vs. ^1H NMR: $\delta[(CD_3)_2CO]$ 4.41 (s, 10H, C_5H_5); 7.25 (m, 70H, Ph). $^{13}C\{^1H\}$ NMR:

$\delta[(CD_3)_2CO]$ 86.2 (s, C_5H_5); 91.1 (s, C_β); 128.3-138.1 (m, Ph). FAB MS: 1692, $[M + H]^+$, 2; 901*, $[M - Ru(C_2Ph)\text{-}(PPh_3)_2(C_5H_5)]^+$, 23; 792, $[M - Ru(C_2Ph)(PPh_3)_2(C_5H_5) - Ag]^+$, 16; $[Ru(PPh_3)_2(C_5H_5)]^+$, 11; 639*, $[M - Ru(C_2Ph)(PPh_3)_2\text{-}(C_5H_5) - PPh_3]^+$, 24; 529, $[Ru(C_2C_6H_4)(PPh_3)(C_5H_5)]^+$, 31; 453, $[Ru(C_2)(PPh_3)(C_5H_5)]^+$, 61; 429, $[Ru(PPh_3)(C_5H_5)]^+$, 100.

(b) in ratio 1:1 - A solution of (7) (100 mg, 0.126 mmol) in toluene (12 ml) was treated with a suspension of $AgPF_6$ (33 mg, 0.130 mmol) in toluene (10 ml) giving immediately a yellow suspension. After stirring for 10 min, CH_2Cl_2 (10 ml) was added. The colour of the solution gradually changed to red pink with deposition of solid Ag. After 30 min, the solution was filtered through celite and the filtrate evaporated to dryness. Extraction of the residue with CH_2Cl_2 (*ca* 5 ml) and filtration into excess stirred Et_2O gave a pale apricot precipitate of $[\{Ru(PPh_3)_2\text{-}(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_4Ph_2)][PF_6]_2$ (27) (93 mg, 82%), m.p. 150°C (dec.). [Found: C, 62.55; H, 4.34; *M* (mass spectrometry) 1538; $C_{98}H_{80}F_{12}P_6Ru_2$ requires C, 62.82; H, 4.30%; *M* (M − H) 1583]. Infrared (Nujol): ν(C=C) 1626m, 1587m; ν(PF) 841vs(br); other bands 1437s, 1311m, 1187m, 1160m, 1091s, 1028w, 1000w, 744s, 723s, 696s, 667w cm^{-1}. ^1H NMR: $\delta[(CD_3)_2CO]$ 5.42 (s, 5H, C_5H_5); 5.59 (s, 5H, C_5H_5); 7.21 (m, 70H, Ph). $^{13}C\{^1H\}$ NMR: $\delta[CH_2Cl_2, Cr(acac)_3]$ 91.1, 95.5 (2 x s, C_5H_5) 129.0-134.0 (m, Ph); 347.6 (s, $C\alpha$?). FAB MS: 1729, $[M + PF_6]^+$, 1; 1583, $[M - H]^+$, 23; 1321, $[(M - H) - PPh_3]^+$, 1; 1059, $[(M - H) - 2PPh_3]^+$, 2; 892, $[(M - H) - Ru(PPh_3)(C_5H_5)]^+$, 7; 796, $[(M - H) - 3PPh_3]^+$, 6; 691, $[Ru(PPh_3)_2(\eta\text{-}C_5H_5)]^+$, 20; 631, $[Ru(C_4Ph_2)(PPh_3)(C_5H_5)]^+$, 12; 429, $[Ru(PPh_3)(C_5H_5)]^+$, 100.

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CHAPTER FOUR

Page

SYNTHESIS AND REACTIVITY OF SOME MIXED METAL CLUSTERS

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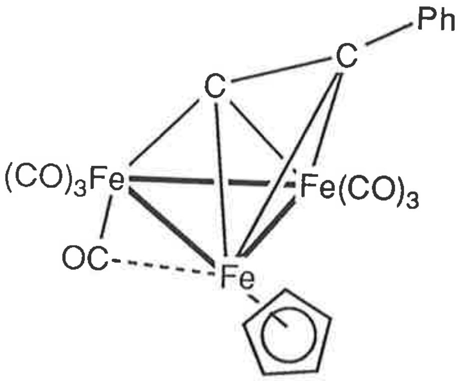
INTRODUCTION

The reactivity exhibited by mixed-metal clusters as a result of the presence of dissimilar metals within the molecules has seen interest in their chemistry blossom over recent years; especially in the field of alkyne substituted metal clusters.[1-6] A fruitful source of novel and interesting structures in the early years of organometallic chemistry was the addition of metal substrates to acetylenes.[7,8] Similar reactions with metal acetylides and iron or cobalt carbonyls often result in heterometallic compounds, e.g.[9,10]

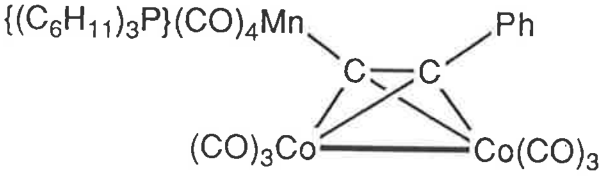
$Fe(C_2Ph)(CO)_2(\eta-C_5H_5) + Co_2(CO)_8 \rightarrow Co_2\{\mu-\eta^2-PhC_2Fe(CO)_2-(\mu-C_5H_5)\}(CO)_6$ (1).



(2)

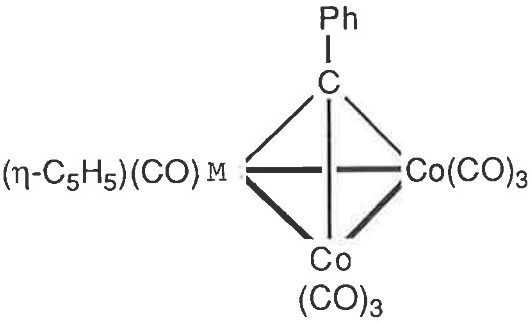
The analogous reaction with $Fe_2(CO)_9$ gave the cluster complex, $Fe_3(\mu_3-\eta^2-C_2Ph)(CO)_7(\eta-C_5H_5)$ (2) which can also be obtained from the reaction of the CuCl adduct of $Fe(C_2Ph)(CO)_2(\eta-C_5H_5)$ and $Fe_2(CO)_9$.[11] Russian workers have reported the isolation of trinuclear clusters, $Fe_2M(\mu_3-\eta^2-C_2Ph)(CO)_8(\eta-C_5H_5)$, from the reaction of $M(C_2Ph)(CO)_3(\eta-C_5H_5)$ (M= Cr, Mo, W) with $Fe_2(CO)_9$.[12]

A more recent example is the cobalt-manganese complex, $Co_2[\mu-\eta^2-PhC_2Mn(CO)_4\{P(C_6H_{11})_3\}](CO)_6$ (3) which was obtained from the reaction of $Co_2(CO)_8$ and the appropriate σ-acetylide complex.[13]



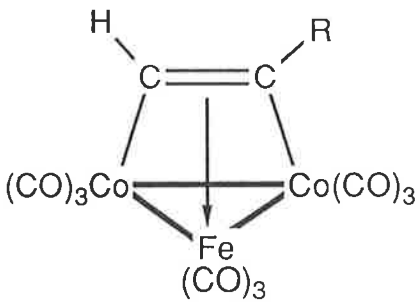
(**3**)

Complex (1) and the analogous ruthenium complex undergo a non-destructive reaction with oxygen which results in the net loss of one acetylide carbon and the formation of the alkylidyne-bridged clusters[14] $Co_2M(\mu_3-CPh)(CO)_7(\eta-C_5H_5)$ (4) [(4a) M= Fe; (4b) M= Ru]

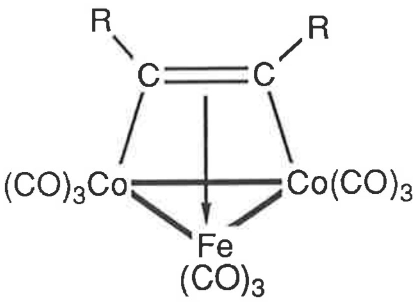


(**4**)

Vahrenkamp and co-workers[15] have provided other examples of hetero- or mixed metal clusters from the reaction of alkyne-bridged dicobalt complexes with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$, affording the bimetallic μ_3-η^2-alkyne clusters (5)



(**5**)

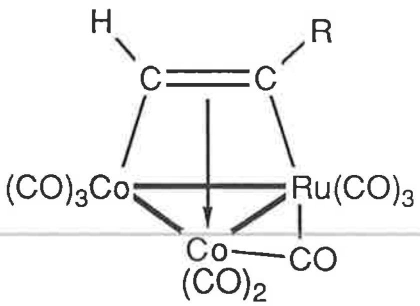


(**6**)

(R = H, Me, Et, Ph, Bu^t)

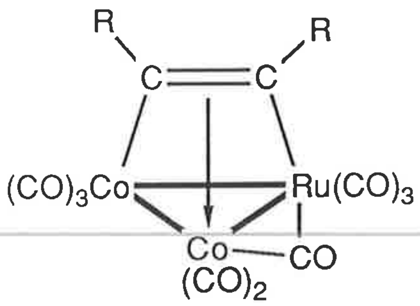
and (6) in which the formal π bond is directed towards the less electron rich metal.

The homologous Co_2Ru (7) and (8) clusters were obtained from the reaction of alkynes HC_2R or RC_2R with $RuCo_2(CO)_{11}$ in boiling hexane.[16]



(**7**)

(R = H, Me, Ph, Bu^t)

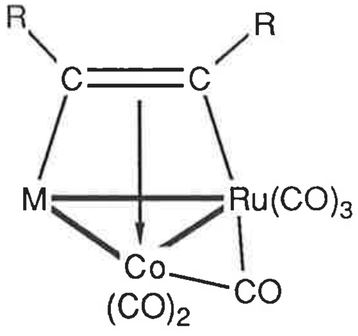


(**8**)

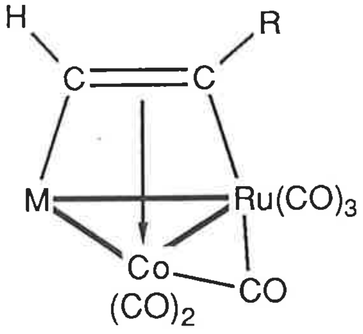
(R = Me, Et, Ph)

Complexes (7) and (8) do not conform to the generally observed trend[3] in μ_3-$\eta^2(2\sigma,\pi)$ alkyne, mixed metal clusters in that the π-bond is not directed towards the least electron rich metal present in the complex.

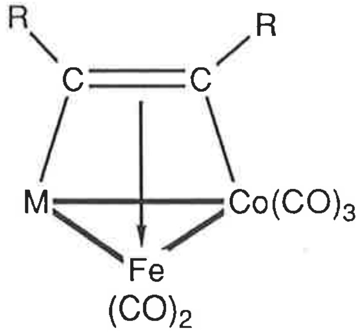
Subjection of complexes (6), (7) and (8) to metal exchange reactions[17] with sources of the fragments '$Ni(\eta-C_5H_5)$', '$Mo(CO)_2(\eta-C_5H_5)$' and '$W(CO)_2(\eta-C_5H_5)$' lead to the formation of chiral trimetallic clusters,[15] in which one of the $Co(CO)_3$ groups originally present in (6), (7) and (8) have been preferentially exchanged.



(**9**)



(**10**)



(**11**)

M = $Ni(\eta-C_5H_5)$, $Mo(CO)_2(\eta-C_5H_5)$, $W(CO)_2(\eta-C_5H_5)$

R = H, Me, Et, Ph, Bu^t

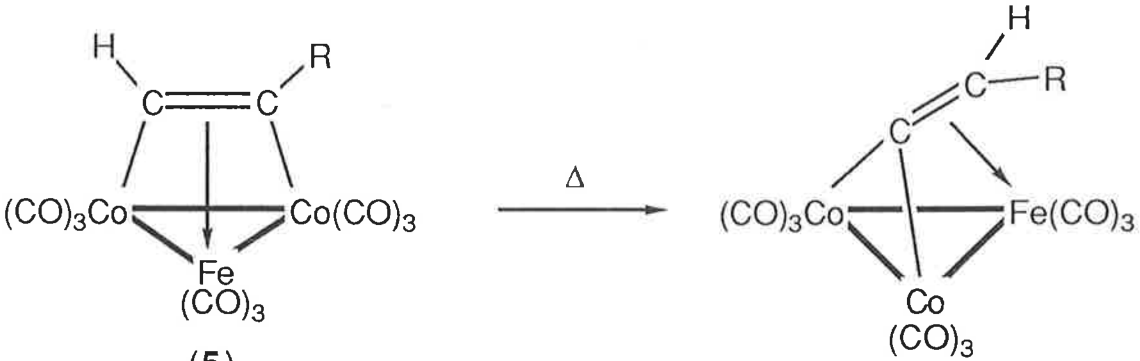
(not all combinations)

In boiling hexane, the terminal alkyne clusters (5), (7) and (10) were found to rearrange by H migration into vinylidene bridged clusters (12), (13) and (14). The nature of the mechanism for this 1-alkyne→vinylidene transformation has been the subject of considerable discussion in which Silvestre and Hoffmann have made an important contribution.[18] They believe that the isomerisation proceeds via a hydrido acetylide intermediate, formed by oxidative addition to the cluster.

The diastereoselectivity of the alkyne-vinylidene transformation varied between 0 and 100%, depending on R and M; the geometry is not determined by steric considerations. Only one isomer was found for all the CoMoW and CoRuW complexes, and for the CoFeM (M= Mo, W) complexes with R= Bu^t. The 'Ni(η-C_5H_5)' containing clusters showed no stereoselectivity, with equal proportion of isomers being found, as observed by NMR[15].

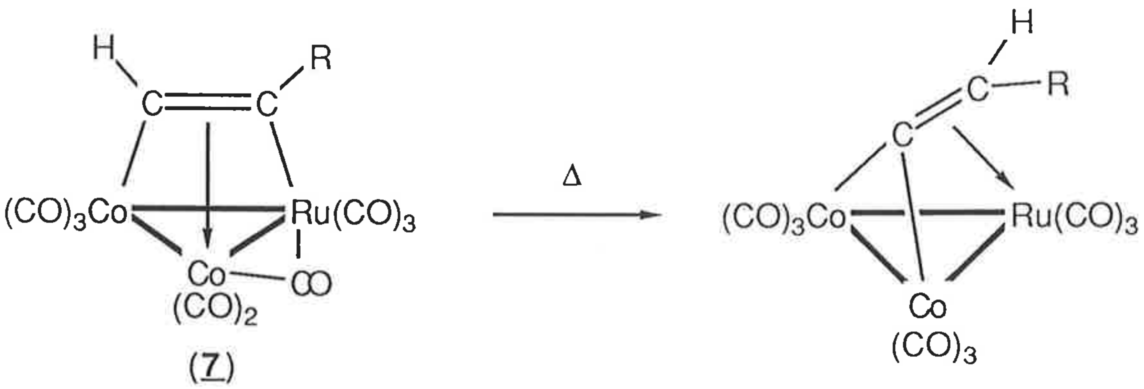
The best route to chiral μ_3-vinylidene FeCoM clusters (15) was through metal exchange reactions on the corresponding $FeCo_2$ vinylidene clusters.

It is interesting to note that in the alkyne→vinylidene rearrangement [(5)→(12) and (7)→(13)] the vinylidene ligand is bound in an η^2-fashion to the least electron-rich metal even though in clusters (7) the η^2-alkyne interaction is directed towards the Co atom. This apparent anomaly in complex (7) is thought not to be the result of any particular electronic requirement but simply emphasises the facile fluxional motion in the complex frozen out at low temperature.[18] Dynamic ^1H NMR spectroscopy showed the activation barriers for fluctuation of the alkyne ligand to be 63-66 kJ mol^{-1}.


H
R
C
C
(CO)$_3$Co
Co(CO)$_3$
Fe
(CO)$_3$
Δ
H
C
R
C
(CO)$_3$Co
Fe(CO)$_3$
Co
(CO)$_3$

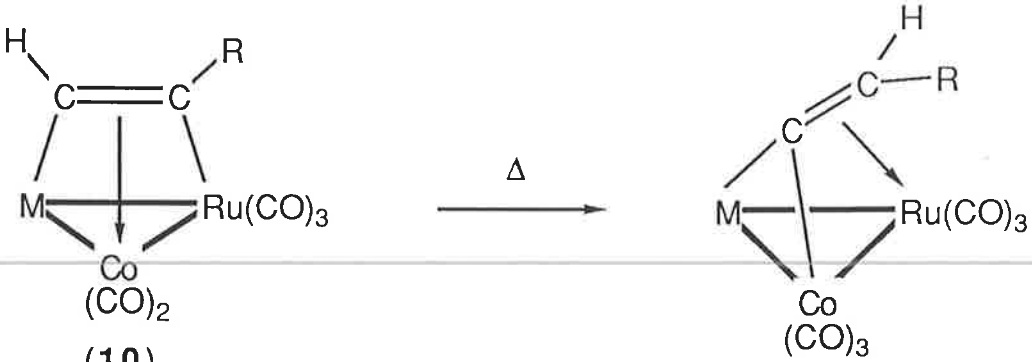
(**5**)

(**12**)


H
R
C
C
(CO)$_3$Co
Ru(CO)$_3$
Co
CO
(CO)$_2$
Δ
H
C
R
C
(CO)$_3$Co
Ru(CO)$_3$
Co
(CO)$_3$

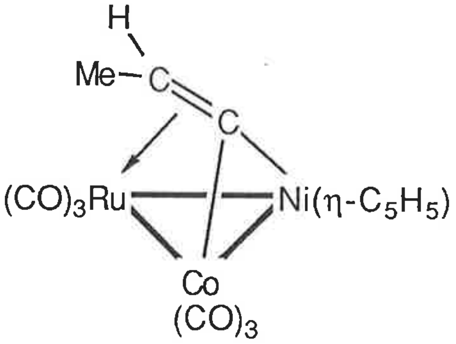
(**7**)

(**13**)

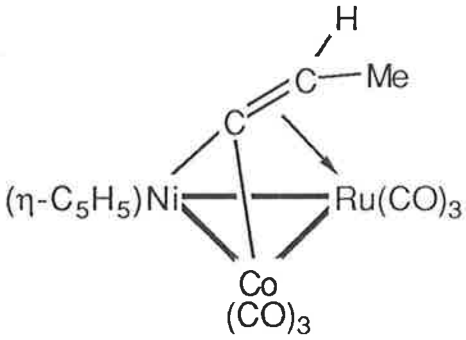

H
R
C
C
M
Ru(CO)$_3$
Co
(CO)$_2$
Δ
H
C
R
C
M
Ru(CO)$_3$
Co
(CO)$_3$

(**10**)

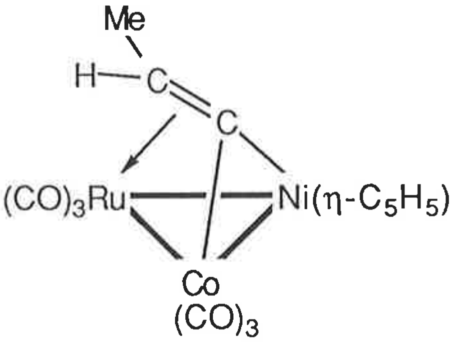
(**14**)


H
Me
C
C
(CO)3Ru
Ni(η-C5H5)
Co
(CO)3

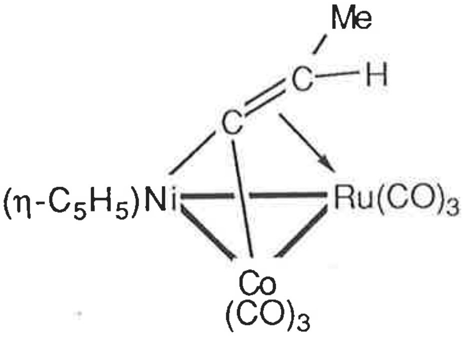
(S,S)


H
C
Me
C
(η-C5H5)Ni
Ru(CO)3
Co
(CO)3

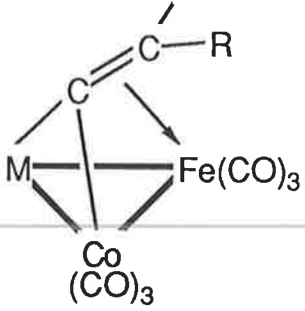
(R,R)


Me
H
C
C
(CO)3Ru
Ni(η-C5H5)
Co
(CO)3

(S,R)


Me
C
H
C
(η-C5H5)Ni
Ru(CO)3
Co
(CO)3

(R,S)


H
C
R
C
M
Fe(CO)3
Co
(CO)3

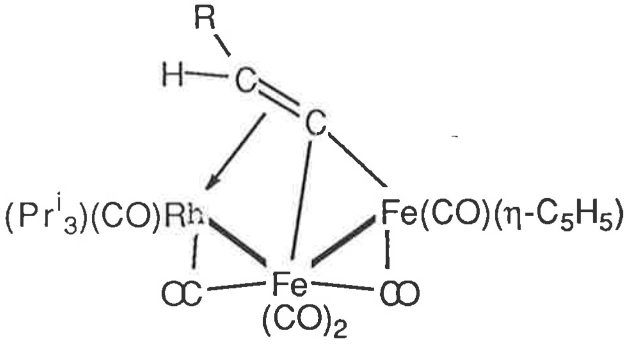
(**<u>15</u>**)

The alkyne complex (7) (R= Bu^t) and the vinylidene complex (13) (R= Bu^t) were both crystallographically characterised,[16] from which it could be seen that the conversion is associated with a gradual inclination of the C=C bond with respect to the metal triangle.[16] When these structures are compared to μ_3-η^2-acetylide clusters, such as $HRu_3(CO)_9(C_2Bu^t)$[19], it is obvious that the angles associated with this inclination define a significant erection of the C=C unit above the Co_2Ru triangle with angles increasing from *ca* 2° → *ca* 20° → *ca* 50°, for HCCR→H/CCR→CCHR, respectively. There is a slight extension of the C-C bond from 1.34 → 1.37Å. These observations support the theoretical conclusions of Silvestre and Hoffmann[18] that the alkyne→vinylidene isomerisation probably proceeds via H migration to and from the metal core.

The CO substitution chemistry for $Co_2Fe(\mu_3$-η^2-$MeC_2Me)$-$(CO)_9$ and for alkyne and vinylidene clusters containing Co_2Fe triangles[20] was investigated. In the case of Co_2Fe clusters, substitution at cobalt was observed exclusively. For the Co_2Ru clusters Co- as well as Ru-substituted products were isolated, of which in all cases Co-substitution is kinetically favoured and Ru-substitution is thermodynamically favoured. The thermally induced Co-Ru migration of the phosphine ligands was realised in several cases; the migratory aptitude decreases in the sequence PMe_3, PMe_2Ph, $PMePh_2$, PPh_3. Competitive experiments with Co_2Fe-$(\mu_3$-η^2-$MeC_2Me)(CO)_9$, $Co_2Ru(\mu_3$-η^2-$MeC_2Me)(CO)_9$ and PPh_3

demonstrated the higher substitutional lability of the Co_2Fe cluster with phosphine transfer from the Co_2Fe to the Co_2Ru cluster being observed. Disubstituted clusters were also obtained. The disubstituted vinylidene clusters had one phosphine attached to Ru and one to cobalt with the C=C unit η^2-bonded to ruthenium. The similar alkyne clusters each had phosphines distributed to Ru and Co with the C=C unit formally σ-bonded to these metals and the η^2-interaction directed towards the other $Co(CO)_3$ unit.[20]

Small amounts of vinylidene substituted clusters (16)



(16) R = H, Me, Ph

were obtained from the reaction of the mononuclear vinylidene complex $Rh(=C=CH_2)(PPr^i_3)(\eta-C_5H_5)$ with $Fe_2(CO)_9$ in thf.[21] Interestingly there was a transfer of the cyclopentadienyl ligand from rhodium to iron to give the isolated product.

The alkyne-bridged clusters $Co_2Ru(\mu_3-\eta^2-RC\equiv CH)(CO)_9$ (7) can be deprotonated, at low temperature, with a variety of bases generating an anionic species which when protonated regenerated the starting cluster.†

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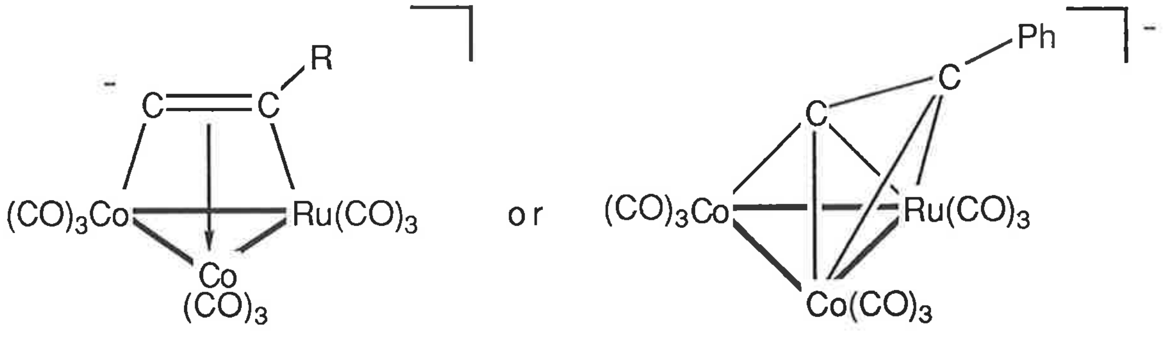
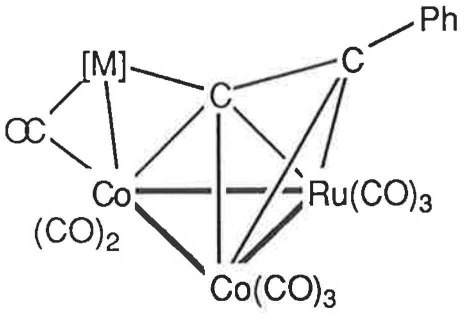
†W. Bernhardt and H. Vahrenkamp, *J. Organomet. Chem.*, 1988, 355, 427.



If the deprotonation is performed in triethylamine in the presence of catalytic amounts of CuI, the complexes $FeCl(CO)_2(\eta-C_5H_5)$, $RuCl(CO)_2(\eta-C_5H_5)$, $NiCl(PPh_3)(\eta-C_5H_5)$ and $MoCl(CO)_3(\eta-C_5H_5)$ can be incorporated into the clusters generating novel $RuCo_2M$ (<u>17</u>) metal frameworks with μ_4-η^2-acetylide ligands.†



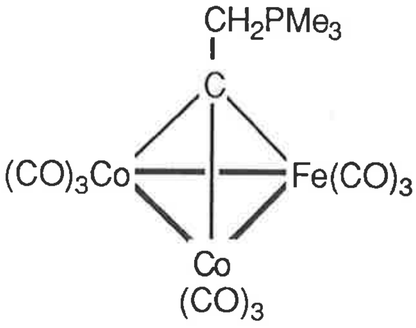
(<u>17</u>)

$[M] = Fe(CO)(\eta-C_5H_5)$, $Ru(CO)_2(\eta-C_5H_5)$,
$Ni(\eta-C_5H_5)$, $Mo(CO)_2(\eta-C_5H_5)$

---

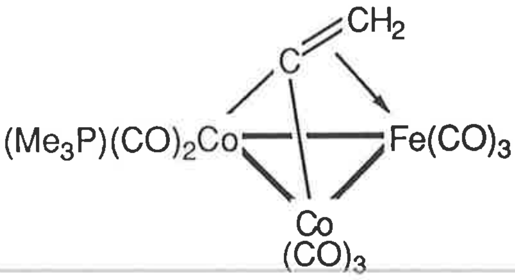
† W. Bernhardt and H. Vahrenkamp, *J. Organomet. Chem.*, 1988, <u>355</u>, 427.

The reaction of $CoFe_2(\mu_3\text{-}\eta^2\text{-}CCH_2)(CO)_9$ with PMe_3 below 0°C gave the black zwitterionic complex (18), which is isosteric with $Co_3(\mu_3\text{-}\eta^1\text{-}CCH_2SiMe_3)(CO)_9$. The outer carbon is completely removed from bonding with the metals,



(**18**)

the C-C bond being inclined at 82° to the Co_2Fe plane.[22] Addition of PMe_3 to the hydrocarbyl ligand competes with CO-substitution at the Co atoms which predominates at higher temperatures so that on heating, (18) rearranges to (19). Increasing the bulk of the tertiary phosphine



(**19**)

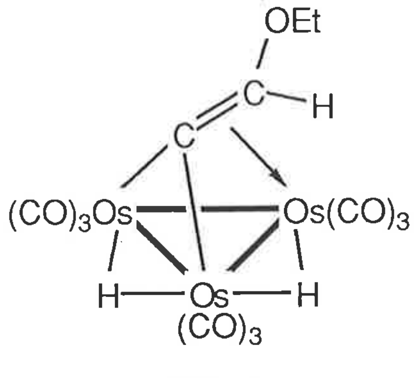
has the same effect, the adduct being increasingly labile with PMe_2Ph and $PMePh_2$, and not being formed at all with PPh_3.

This pattern of reactivity is not restricted to vinylidene complexes. The trinuclear osmium and ruthenium compounds $Os_3(\mu_3\text{-}\eta^2\text{-}C_2Ph)(CO)_9(PPh_2)$ (20) and $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C_2Ph)(CO)_9(PPh_2)$ (21) readily undergo attack by phosphites and amines with additions to the acetylide carbon atoms.[23] Similarly, the $\mu_2\text{-}\eta^2$-acetylide complexes $M_2(C_2Ph)(CO)_6(PPh_2)$ (M= Fe, Ru) react smoothly with isonitriles at 0° giving excellent yields of adducts $M_2\{C(CNR)CPh\}(CO)_6(PPh_2)$ together with small amounts of the substitution products.

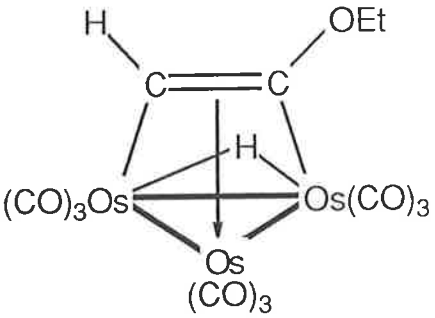
The group R on the acetylide appears to play a significant role in the reactivity of the triple bond towards nucleophiles. For $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C_2Bu^t)(CO)_9$ reaction with phosphites, phosphines and isonitriles yields only substitution products of the type $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C_2Bu^t)(CO)_8(L)$. Carbonyl substitution on the hydride cluster occurs regiospecifically for phosphorus ligands with the ligand occupying an equatorial site.[23]

The μ_3-acetylide complexes $Os_3(\mu\text{-}H)_3(\mu_3\text{-}\eta^2\text{-}C_2R)(CO)_9$ (22) (R= H, Me, Ph or CMe_2OH) and $Os_3(\mu\text{-}H)(\mu_2\text{-}\eta^2C_2Ph)(CO)_{10}$ form 1:1 adducts with PMe_2Ph giving zwitterionic complexes containing phosphonium centres with negative charges formally on the metal atoms.[24] This phosphine also adds to bridging vinyl ligands in triosmium clusters.[25]

Nucleophilic addition at μ_3-alkyne triosmium clusters has been described recently.[26] The μ_3-acetylide complex $Os_3(\mu\text{-}H)(\mu_3\text{-}\eta^2C_2H)(CO)_9$ (22a) reacts smoothly with ethanol to give two isomeric adducts (23a) and (23b) in



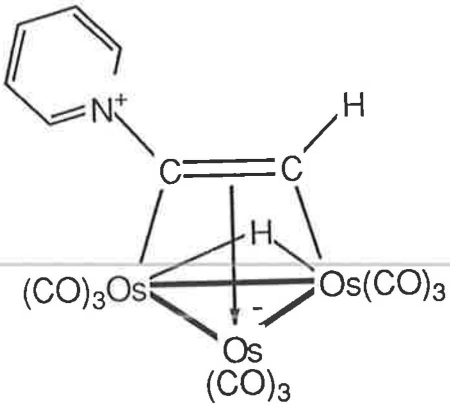
(**23a**)



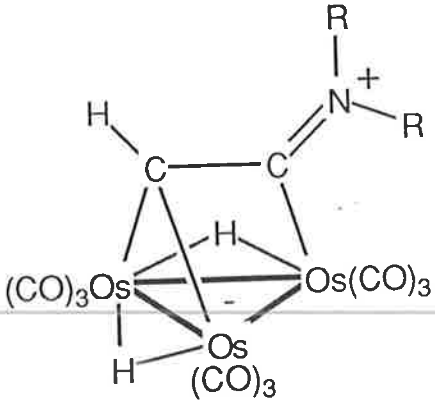
(**23b**)

21 and 78% yield, respectively,[27a,b] Complexes (23a) and (23b) are derived by ethoxy group addition at the β- and α- carbons respectively. Similarly the reaction of H_2O with $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}C_2H)(CO)_9]^+$ leads to $Os_3(\mu\text{-}H)_3(\mu_3\text{-}CH)(CO)_9$, after CO loss, and $Os_3(\mu\text{-}H)_3(\mu_3\text{-}CCHO)(CO)_9$ also by nucleophilic attack at the α- and β- carbon atoms, respectively.[27a]

Complex (22a) also forms adducts with pyridine (24), ammonia (25) and diethylamine (26).



(**24**)



(**25**) R = H
(**26**) R = Et

The zwitterionic pyridine adduct readily loses pyridine in the absence of free pyridine to regenerate (22a) but complexes (25) and (26) do not lose R_2NH even under acidic conditions.[27c] Complexes (25) and (26) do not adopt the normal μ_3-η^2 parallel structure found for Os_3 clusters and the C-C axis of the organic ligand is perpendicular to an Os-Os bond.[27c] Proton NMR experiments determined that the attachment of the Et_2NC_2H ligand in (26) as a whole to the Os_3 triangle is rigid. These observations were rationalised in terms of the π-donor ability of the NR_2 substituent being strong enough to rotate the $R_2NC{\equiv}CH$ ligand from a parallel to perpendicular orientation.

It is of note that the adducts (24), (25) and (26) are the products of exclusive nucleophilic addition to the α-carbon which is in contrast to the reactivity of H_2O and EtOH towards (22a), in which appreciable amounts of β-carbon attack products are formed.

Clusters containing μ_3-acetylide ligands show considerable nucleophilic reactivity at the acetylide α-carbon; this feature being confirmed by ultraviolet-photoelectron spectroscopy.[28] Carbon-13 NMR data for a range of iron group polynuclear acetylide complexes with μ_2-η^2, μ_3-η^2 and μ_4-η^2 alkynyl groups has been presented.[29] For doubly bridging μ_2-η^2-acetylides of Fe, Ru and Os, the α-carbon resonance lies in the range δ 65 - 110 downfield of TMS, while β-carbon shifts are found over the range δ 90 - 110. In μ_3-η^2-complexes the α-carbon lies in the region δ 115 - 220 and is always downfield of the β-carbon resonance (δ 43 - 153). For μ_4-η^2-acetylides, the α-carbon is also downfield of β-carbon resonances with values lying in the ranges δ 185 - 230 and δ 91 - 165, respectively. The α-carbon resonance generally moves to lower field in the sequence μ_2-η^2<μ_3-η^2<μ_4-η^2 as the number of metals interacting with the acetylide unit increases. This obvious deshielding of the α-carbon is attributed to the development of a positive change density on this atom due to coordination to electrophilic $M(CO)_2$ fragments.[29] A "metal effect" on the Cα shifts is also observed with a shift to low field in the sequence Fe-Ru-Os.[29]

The C_2 hydrocarbyl moiety shows varying degrees of saturation on trinuclear clusters. In acetone, alkynes reacted with $[Fe_3(\mu\text{-}H)(CO)_{11}]^-$ to give $[Fe_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}CCHR)\text{-}(CO)_9]^-$ (R= Ph, Pr; CO_2Me, COMe) as dark brown or dark red solids. Initial formation of $[Fe_3(\mu_3\text{-}CCH_2R)(CO)_{10}]^-$ probably occurs; heating the vinylidene under CO (20 atm) gave the alkylidyne complex, which on refluxing in acetone, reformed the vinylidene.[30] At higher temperatures (refluxing 2-methoxyethanol), the acetylide anions $[Fe_3\text{-}(\mu_3\text{-}\eta^2\text{-}C_2R)(CO)_9]^-$ (R= Pr, Ph) were formed, thus completing the transformation RC≡CH → CCH_2C → RCH=C= → RC≡C- on the Fe_3 cluster.

This chapter describes the preparation of some bimetallic clusters of iron and iridium, examples of which are rare. The reactivity of a μ_3-η^2-acetylide cluster is also examined.

RESULTS AND DISCUSSION

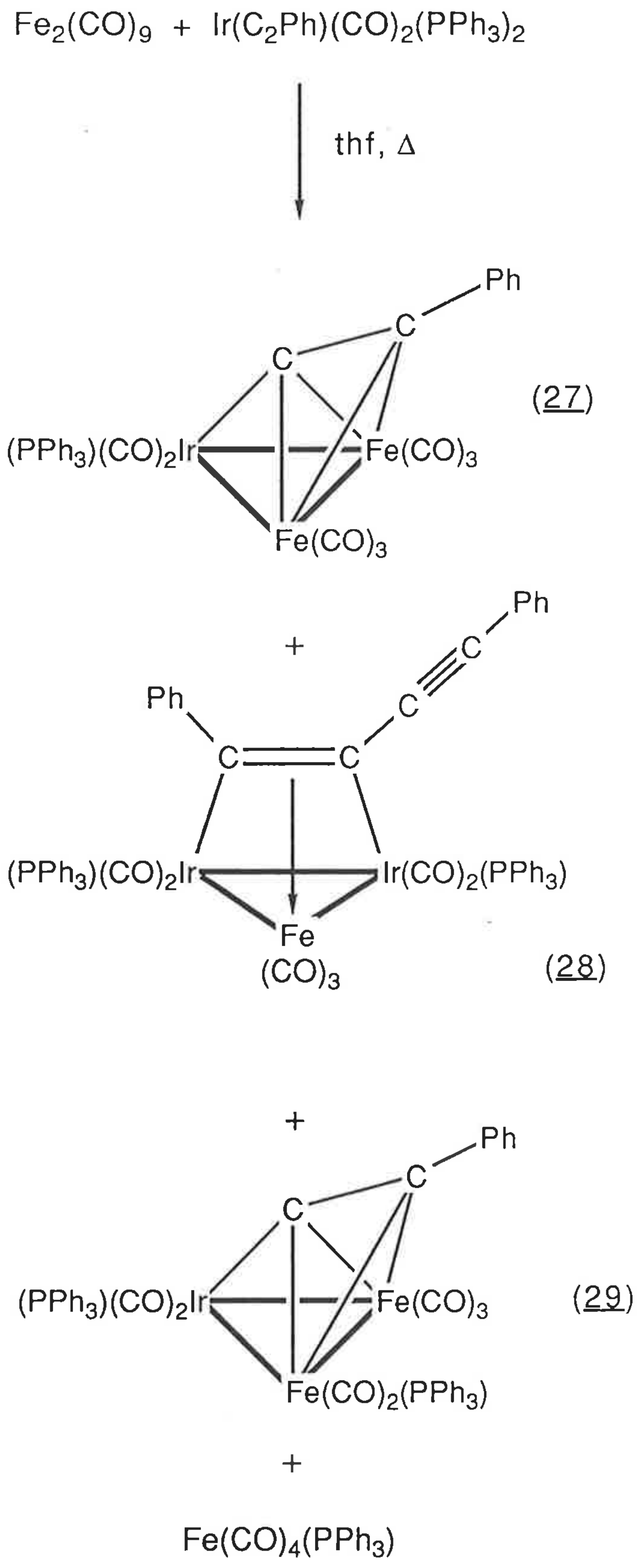
Reaction of $Ir(C_2Ph)(CO)_2(PPh_3)_2$ with $Fe_2(CO)_9$

A suspension of $Ir(C_2Ph)(CO)_2(PPh_3)_2$ and $Fe_2(CO)_9$ was found to react readily in refluxing tetrahydrofuran to give a mixture of four products (Equation 1). Initial chromatographic separation afforded pure fractions containing $Fe(CO)_4(PPh_3)$ and the expected trinuclear cluster $Fe_2Ir(\mu_3\text{-}\eta^2\text{-}C_2Ph)(CO)_8(PPh_3)$ (27) in 33% yield. Fractional crystallisation of the band eluted last gave poor yields of the di-iridium cluster, $FeIr_2(\mu_3\text{-}\eta^2\text{-}PhC_2C_2Ph)(CO)_7(PPh_3)_2$ (28) and secondly, $Fe_2Ir(\mu_3\text{-}\eta^2\text{-}C_2Ph)(CO)_7(PPh_3)_2$ (29).

Complexes (27), (28), and (29) were formulated by the usual microanalytical and spectroscopic techniques. The molecular structures of complexes (27) and (28) were determined by X-ray crystallography.

Structure of $Fe_2Ir(\mu_3\text{-}\eta^2\text{-}C_2Ph)(CO)_8(PPh_3)$ (27)

The molecular structure of (27) is shown in Figure 1, while Table 1 collects the bond distances and angles. The iridium and iron atoms adopt a triangular arrangement with the two iridium-iron distances being essentially equal [Ir-Fe(1) 2.701(1) and Ir-Fe(2) 2.693(1)Å]. These values are similar to the value found for the non-CO bridged vector in the only other structurally characterised Ir-Fe cluster, $(\eta^5\text{-}C_5Me_5)IrFe_2(CO)_9$[31] (30) [Ir-Fe(2) 2.698(7)Å] and significantly shorter than the Ir-Fe bond [2.960(1)Å] in $FeIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$[32] (31) the only other structurally characterised iron-iridium metal complex.


Fe2(CO)9 + Ir(C2Ph)(CO)2(PPh3)2
thf, Δ
(27)
(28)
(29)
Fe(CO)4(PPh3)
Ph
C
(PPh3)(CO)2Ir
Fe(CO)3
Fe(CO)2(PPh3)
Ir(CO)2(PPh3)
Fe
(CO)3
+

Equation 1

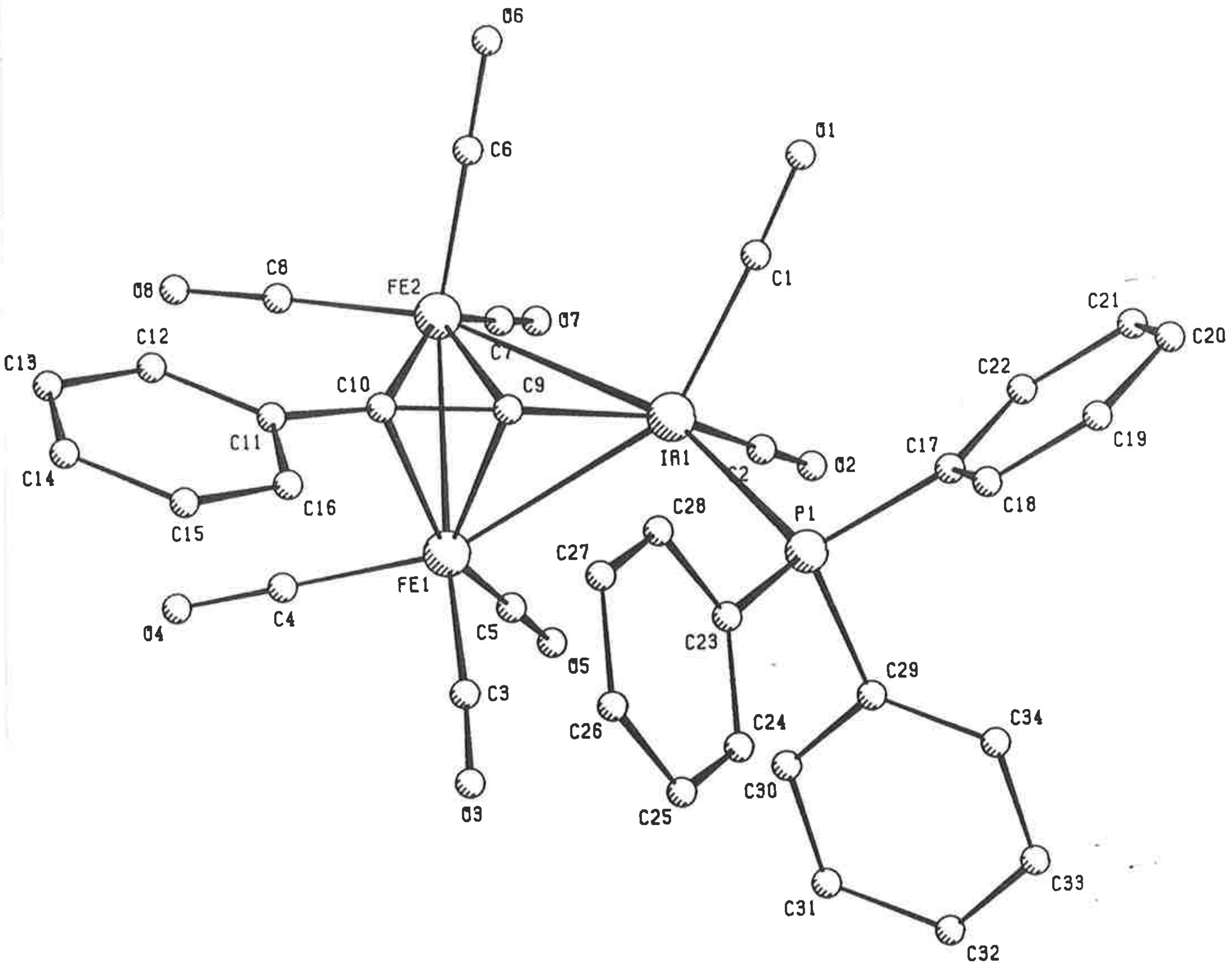


Figure 1. PLUTO plot of the molecular structure of $Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_8(PPh_3)$ (27)
(By E.R.T. Tiekink)

Table 1. Selected interatomic parameters for

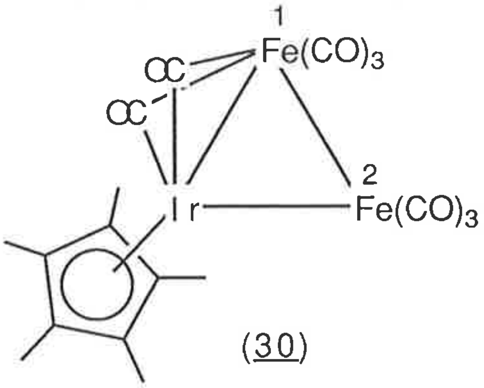
$Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_8(PPh_3)$ (27)

Bond Lengths

Fe(1) ---	Ir	2.701(1)	C(10) ---	C(9)	1.294(10)
P(1) ---	Ir	2.351(2)	Fe(2) ---	Ir	2.693(1)
Fe(2) ---	Fe(1)	2.483(2)	C(9) ---	Ir	1.934(7)
C(9) ---	Fe(1)	2.050(8)	C(10) ---	Fe(1)	2.133(8)
C(8) ---	Fe(2)	1.761(10)	C(9) ---	Fe(2)	2.087(7)
C(10) ---	Fe(2)	2.098(7)			

Bond Angles

Fe(2)	- C(9)	- Ir	84.0(3)	C(9)	- Fe(2)	- Ir	45.6(2)
C(10)	- C(9)	- Ir	152.9(6)	C(10)	- Fe(2)	- Fe(1)	54.7(2)
C(10)	- C(9)	- Fe(2)	72.5(5)	C(10)	- Fe(2)	- C(9)	36.0(3)
C(9)	- C(10)	- Fe(1)	68.5(5)	Fe(2)	- C(9)	- Fe(1)	73.7(3)
C(11)	- C(10)	- C(9)	143.7(7)	C(10)	- C(9)	- Fe(1)	75.5(5)
Fe(2)	- Ir	- Fe(1)	54.8(1)	Fe(2)	- C(10)	- Fe(1)	71.8(2)
P(1)	- Ir	- Fe(2)	153.6(1)	C(9)	- C(10)	- Fe(2)	71.5(4)
C(1)	- Ir	- Fe(2)	96.1(3)	P(1)	- Ir	- Fe(1)	104.7(1)
C(9)	- Ir	- Fe(1)	49.2(2)	C(9)	- Ir	- Fe(2)	50.4(2)
C(9)	- Ir	- P(1)	104.3(2)	Fe(2)	- Fe(1)	- Ir	62.4(1)
C(9)	- Fe(1)	- Fe(2)	53.8(2)	C(9)	- Fe(1)	- Ir	45.5(2)
C(10)	- Fe(1)	- Ir	80.1(2)	C(10)	- Fe(1)	- C(9)	36.0(3)
Fe(1)	- Fe(2)	- Ir	62.7(1)	C(10)	- Fe(2)	- Ir	80.9(2)
				Fe(1)	- C(9)	- Ir	85.3(3)



(<u>30</u>)

The Fe-Fe separation in complex (<u>27</u>) [2.483(2)Å] is shorter than the analogous distances in (<u>30</u>) as expected from the presence of a bridging acetylide group in the former complex. The Ir-P1 distance [2.351(2)Å] implies that a conventional 2e-donor interaction of a tertiary phosphine with a metal atom is present and this value is close to that observed in (<u>31</u>) [2.349(2)Å] for the terminal Ir-PPh$_3$ bond. The bridging acetylide ligand adopts the familiar μ_3-η^2-(σ+2π) or η^2-|| bonding mode with the C≡C and Ir-C$_\alpha$ distances [1.294(10) and 1.934(7)Å, respectively] consistent with those found in other homo- and heterometallic μ_3-η^2-acetylide clusters.[3] The symmetric disposition of the bridging acetylide ligand is evidenced by its distance from the two iron atoms [Fe(1)-C(9),C(10) 2.050(8), 2.233(8)Å; Fe(2)-C(9),C(10)2.087(7), 2.098(7)]. Coordination at the metal atom is completed by carbonyl ligands [Ir-CO 1.894Å av.; Ir-C-O 176.8° av.; Fe-CO 1.771Å av.; Fe-C-O 177.5° av.]. An electron count shows that the C$_2$Ph ligand functions as a 5e-donor to the cluster which is electron precise (48e) and gives rise to a *closo*, trigonal bipyramidal, 6 skeletal electron pair (SEP), 5 vertex structure.

Spectroscopic data obtained for complex (27) are in accord with the crystallographically determined structure. Its solution infrared spectrum showed only terminal ν(CO) bands, which gave a seven-band pattern. Resonances found at δ 174.5 and 212.1 in the $^{13}C\{^{1}H\}$ NMR spectrum were assigned to carbonyl ligands on the iridium and iron atoms, respectively, by comparison with similar resonances in the related complexes, $FeRh(\mu-PPh_2)(CO)_4(PEt_3)_2$[32] and $Ir_4(CO)_7$-$(\mu-CO)_3$ (1,5-Cyclooctadiene).[33] The observation of only two signals suggests that the carbonyls on both metals are fluxional at ambient temperature or are accidentally equivalent. The C_α(δ 165.5, s) and C_β(δ 99.6, s) signals were in environments similar to those of other μ_3-η^2-acetylide clusters.[29] A resonance at δ 14.9 in the $^{31}P\{^{1}H\}$ NMR spectrum was assigned to PPh_3 [*cf* δ 14.0 for Ir-PPh_3 in the related complex, $FeIr(\mu-PPh_2)(CO)_5(PPh_3)_2$].[32] The FAB mass spectrum showed a molecular ion at *m/z* 892 which fragmented by stepwise loss of eight carbonyl ligands.

Structure of $FeIr_2(\mu_3-\eta^2-PhC_2C_2Ph)(CO)_7(PPh_3)_2$ (28)

The molecular structure of (28) is shown in Figure 2. Relevant bond distances and angles are listed in Table 2. Although the accuracy of the determination only allows the molecular connectivities to be seen, some discussion of the structure will be given.

The three metal atoms form a triangular arrangement in which the Ir-Fe distances [2.613(8) and 2.617(8)Å] are similar to those found in (27) and (30). The homometallic bond distance [Ir(2)-Ir(1) 2.743(4)Å] is comparable to

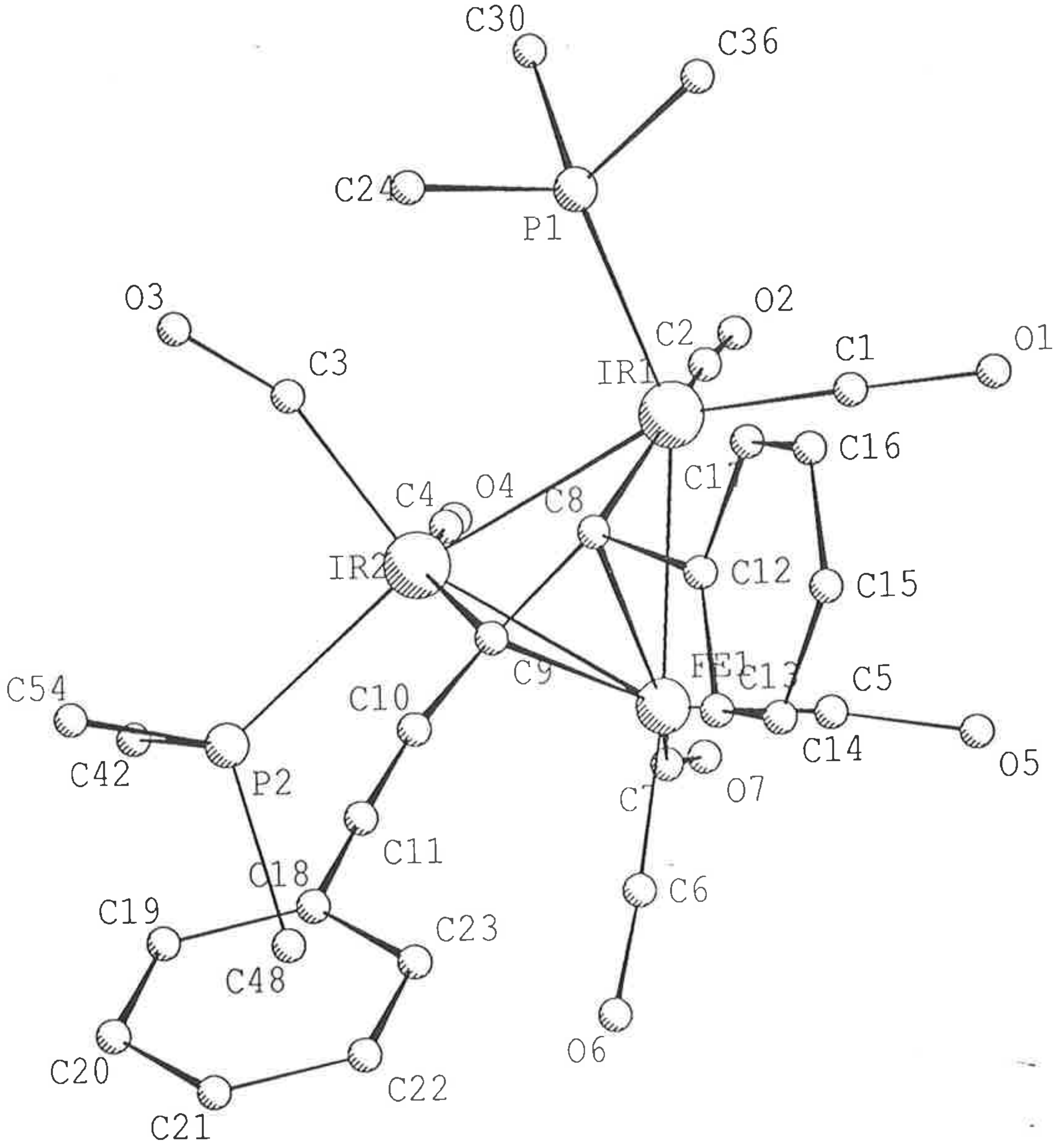


Figure 2. PLUTO plot of the molecular structure of $FeIr_2(\mu_3-\eta^2-PhC_2C_2Ph)(CO)_7(PPh_3)_2$ (28) (by E.R.T. Tiekink) - only ipsocarbons of phosphine bound phenyl groups are shown for clarity.

the average Ir-Ir bond length [2.73Å av.] in the Ir_4 cluster; [$Ir_4(CO)_{10}$(1,5-cyclooctadiene)].[33] The two phosphorus atoms are disposed essentially *trans* to each other with respect to the Ir-Ir vector and with bond lengths [Ir(1)-P(1) 2.33(2) and Ir(2)-P(2) 2.36(2)Å] similar to those found in the previously mentioned complexes. The most interesting feature of complex (<u>28</u>) is the presence of the diphenyl diacetylene ligand. The crystallographic data suggests the ligand adopts the familiar μ_3-η^2-(||) bonding mode[4] designating a parallel arrangement of the coordinated alkyne carbons with respect to the Ir-Ir vector. The two formal σ-bonds are Ir(1)-C(8) 1.92(5) and Ir(2)-C(9) 2.18(5)Å while the π-bond lengths are C(9)-Fe 2.17(5) and C(8)-Fe 2.18(5)Å. The coordinated C_2 moiety shows the expected lengthening[34] [C(8)-C(9) 1.40(2) compared with the uncoordinated triple bond. [C(10)-C(11) 1.22(7)Å]. The pendant phenyl acetylene moiety is essentially linear [C(9)C(10)C(11) 174(5)°; C(10)C(11)C(18) 172(6)°]. The alkyne ligand adopts a distorted parallel coordination but does not approach perpendicular coordination; the Ir(2)-C(8) [2.78Å] distance is non bonding. This distortion suggests a bonding mode in between η^2-|| and η^2-$\perp$. This is possibly due to a solid state freezing out of oscillatory motion that has been noted for other η^2-|| complexes in solution.[35,36] The carbonyl ligands are unexceptional. A formal electron count shows that none of the metals are electron deficient and that the μ_3-η^2-alkyne ligand acts as a 4e-donor to the electron precise (48e) cluster. Spectroscopic data were in accord with the structure of complex (<u>28</u>).

Table 2. Selected interatomic parameters for the structure of (28)

Ir(2) --- Ir(1)	2.743(4)	Fe --- Ir(1)	2.613(8)
P(1) --- Ir(1)	2.333(17)	P(2) --- Ir(2)	2.356(17)
Fe --- Ir(2)	2.627(8)	C(4) --- Ir(2)	1.899(50)
C(9) --- Ir(2)	2.176(51)	C(9) --- Fe	2.168(52)
C(8) --- Fe	2.178(48)	C(9) --- C(8)	1.400(17)
C(10) --- C(9)	1.436(70)	C(11) --- C(10)	1.216(68)
C(18) --- C(11)	1.350(70)	C(8) --- Ir(1)	1.917(51)

Fe - Ir(1) - Ir(2)	58.7(2)	P(1) - Ir(1) - Ir(2)	100.6(4)
P(1) - Ir(1) - Fe	149.0(5)	C(8) - Ir(1) - Fe	54.9(14)
C(8) - Ir(1) - Ir(2)	70.8(12)	Fe - Ir(2) - Ir(1)	58.2(2)
C(8) - Ir(1) - P(1)	98.3(14)	P(2) - Ir(2) - Fe	107.6(4)
P(2) - Ir(2) - Ir(1)	164.7(4)	C(9) - Ir(2) - Ir(1)	70.3(11)
C(9) - Ir(2) - Fe	52.6(13)	C(9) - Ir(2) - P(2)	97.0(12)
Ir(2) - Fe - Ir(1)	63.1(2)	C(8) - Fe - Ir(2)	70.1(12)
C(8) - Fe - Ir(1)	46.1(13)	C(9) - Fe - Ir(1)	73.0(12)
C(9) - Fe - Ir(2)	52.9(13)	C(9) - C(8) - Ir(1)	118.8(38)
Fe - C(8) - Ir(1)	79.0(19)	Fe - C(9) - Ir(2)	74.4(17)
C(9) - C(8) - Fe	70.8(27)	C(8) - C(9) - Fe	71.6(30)
C(8) - C(9) - Ir(2)	99.9(35)	C(10) - C(9) - Fe	125.6(33)
C(10) - C(9) - Ir(2)	126.6(31)	C(11) - C(10) - C(9)	173.9(52)
C(10) - C(9) - C(8)	132.4(47)		

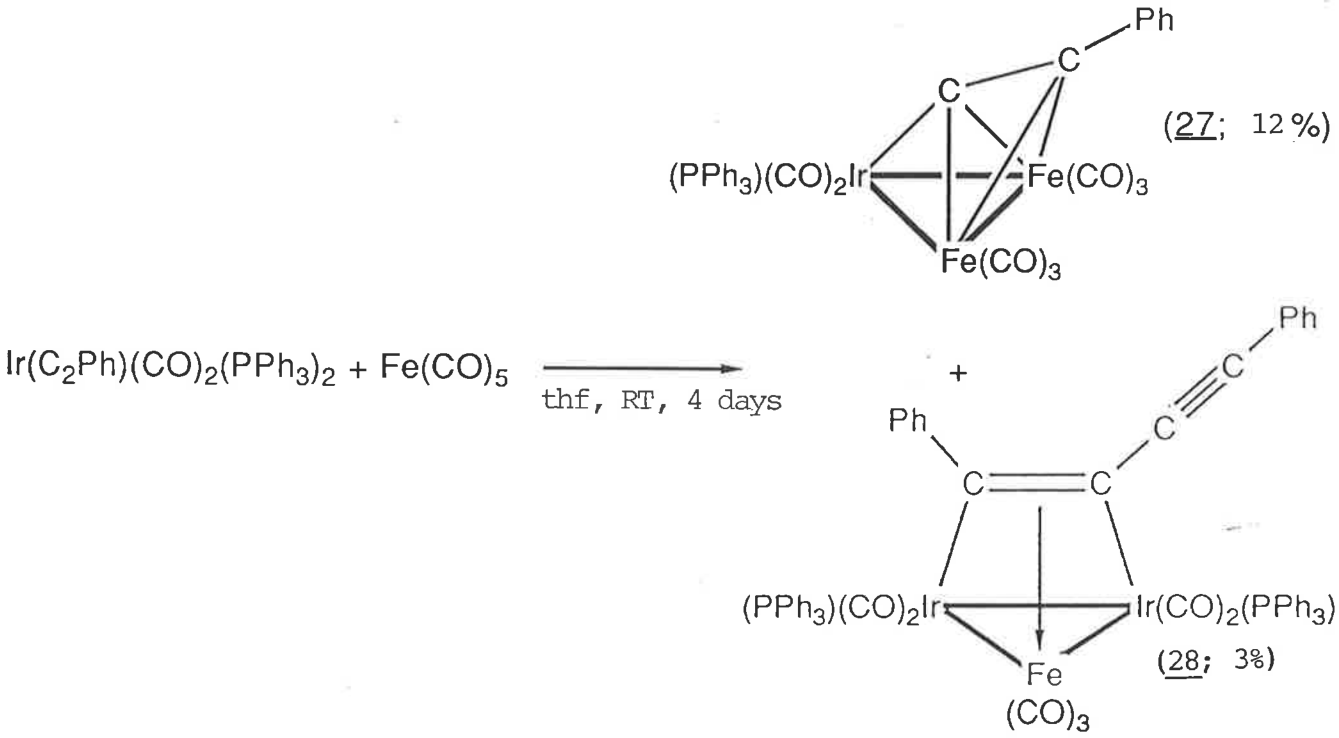
The FAB mass spectrum of (28) contained a molecular ion at *m/z* 1362 which decomposed by stepwise loss of six CO groups and C_2Ph.

The phosphorus atoms in (28) P(1) and P(2), attached to Ir(1) and Ir(2), respectively, (*cf.* Figure 2), are in different relative chemical environments and this is reflected in the $^{31}P\{^{1}H\}$ NMR spectrum of (28) which contained two singlets at δ 8.5 and -15.2 and were assigned to the two PPh_3 ligands.

The other trinuclear diiron-iridium cluster isolated from the reaction of Ir(C$_2$Ph)(CO)$_2$(PPh$_3$)$_2$ and Fe$_2$(CO)$_9$ was Fe$_2$Ir(μ_3-η^2-C$_2$Ph)(CO)$_7$(PPh$_3$)$_2$ (29). Its solution i.r. spectrum comprised a six-band pattern showing only terminal ν(CO) bands. The ^{1}H NMR spectrum contained a multiplet resonating between δ 7.1-7.7 for the phenyl protons. Singlet resonances at δ 180.1 and 243.8 in the ^{13}C{^{1}H} NMR spectrum are assigned to iridium-carbonyl and iron-carbonyl signals, respectively. The signal at δ 80.0 was assigned to Cβ and the signal for Cα was not observed. The phenyl resonances were found in the usual region. The ^{31}P{^{1}H} NMR was particularly informative and contained two resonances at δ -8.1 and 76.4. The former was assigned to IrPPh$_3$ and the latter was assigned to FePPh$_3$ [*cf* δ 74.2 in FeIr(μ-PPh$_2$)(CO)$_5$(PPh$_3$)$_2$ (31)][32]. The FAB mass spectrum of (28) showed a molecular ion at *m/z* 1126 which fragmented by consecutive loss of seven CO groups.

Reaction between Ir(C$_2$Ph)(CO)$_2$ and Fe(CO)$_5$

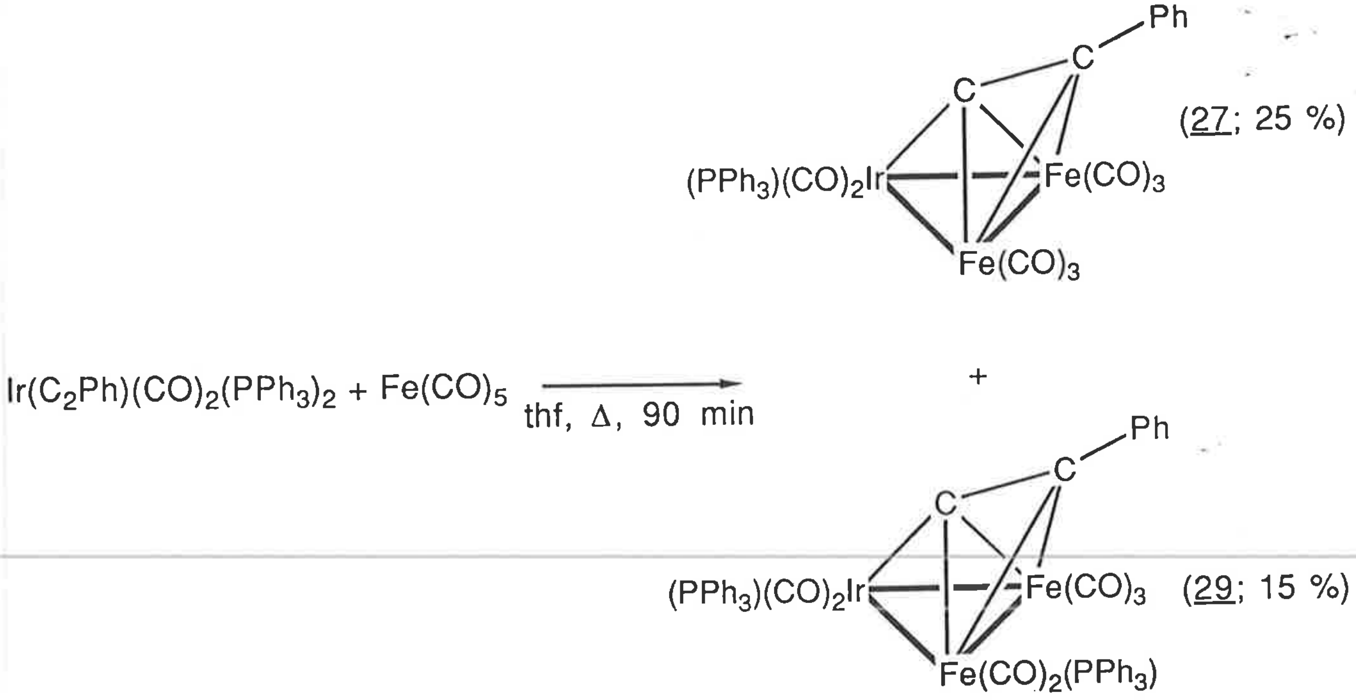
It was of interest to study the chemistry of compound (27) and a higher yielding synthesis was sought. However, stirring a tetrahydrofuran solution of Ir(C$_2$Ph)(CO)$_2$(PPh$_3$)$_2$ and Fe(CO)$_5$ at ambient temperature for 4 days resulted in a much lower yield of (27) (12%), after thin layer chromatographic separation. The only other major tractable product was (28) (3%).



(27; 12 %)

(28; 3%)

In a similar reaction, a refluxing thf solution of $Ir(C_2Ph)(CO)_2(PPh_3)_2$ and $Fe(CO)_5$ afforded a higher yield of (27) (25%) than the previously mentioned room temperature reaction. Complex (29) was also obtained in 15% yield.



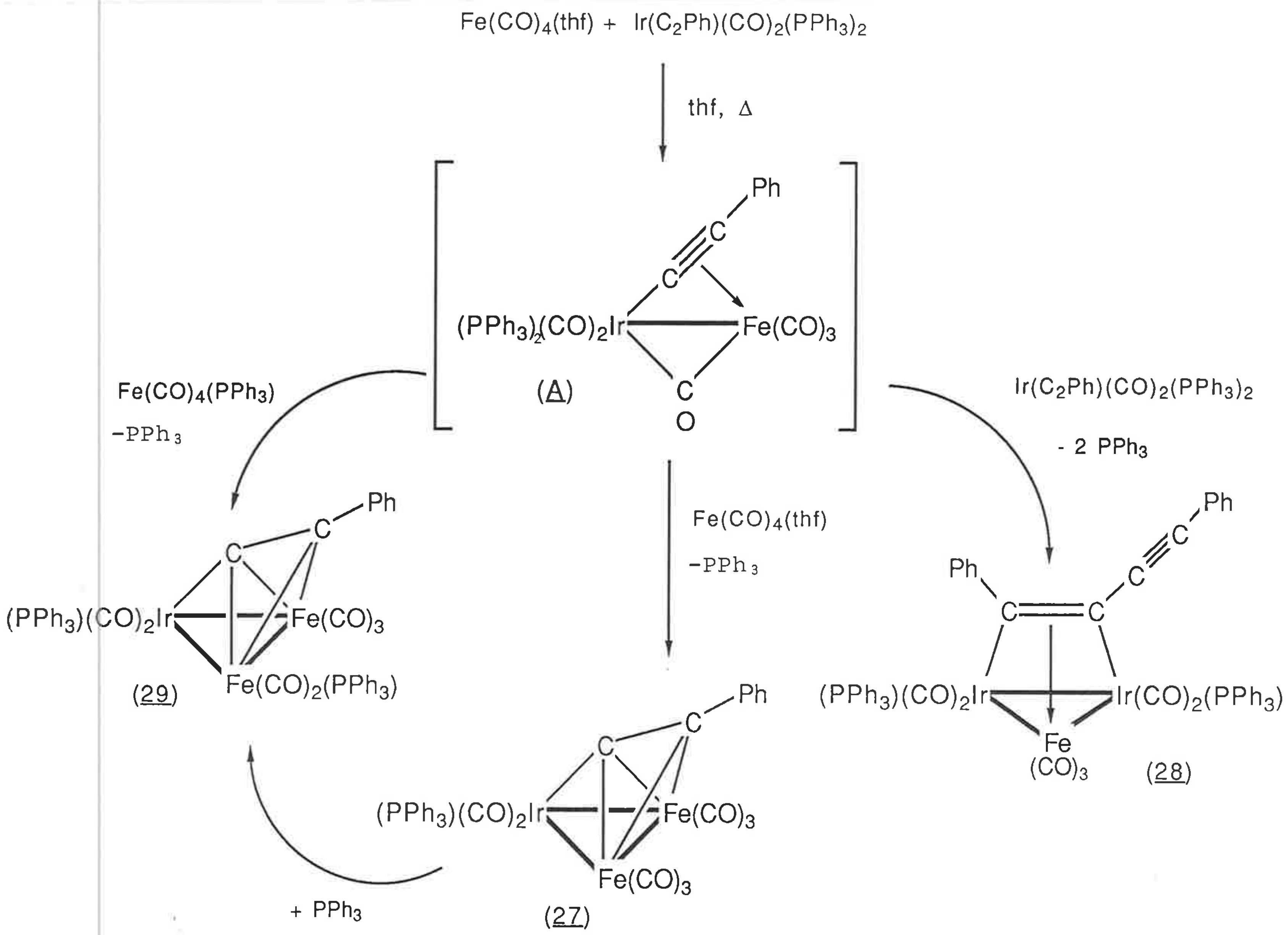
(27; 25 %)

(29; 15 %)

B. Preparation of $Fe_2Rh(\mu_3-\eta^2-C_2Ph)(CO)_8(PPh_3)$ (4)

A suspension of $Rh(C_2Ph)(CO)(PPh_3)_2$ and $Fe_2(CO)_9$ in tetrahydrofuran rapidly darkens to red when heated at 60°C for a short time. Preparative tlc enabled the isolation of two major products. One was the well-known $Fe_3(CO)_{12}$. The other product was identified as $Fe_2Rh(\mu_3-\eta^2-C_2Ph)(CO)_8(PPh_3)$ (32) on the basis of microanalytical and spectroscopic data. The infrared spectrum of (32) was similar to that of complex (27) and contained only terminal $\nu(CO)$ bands. The ^1H NMR spectrum contained a multiplet at δ 7.32 which was assigned to the phenyl proton resonances. The phenyl carbon resonances of (32) were found between δ 128-134 in the $^{13}C\{^1H\}$ NMR spectrum. The only other signal in this spectrum was found at δ 212.1 and as no ^{103}Rh coupling was observed it was assigned to carbonyl groups on the Fe. The $^{31}P\{^1H\}$ NMR spectrum contained a doublet signal at δ 15.6 with *J* (RhP) 122Hz; this value is comparable to that observed in $RhRu_3(\mu_3-PPh)(\mu_2-CO)(CO)_8(PPh_3)$ [$\delta(RhPPh_3)$ 30.9 and *J* (RhP) 128Hz].[37] A weak molecular ion was found at *m/z* 802 in the FAB MS of complex (32) which decomposed by consecutive loss of eight CO groups.

A possible mechanism for the formation of complexes (27), (28) and (29) is pictured in Scheme 1. When $Ir(C_2Ph)(CO)_2(PPh_3)_2$ is dissolved in solvents such as $CHCl_3$ or CH_2Cl_2 carbon monoxide is rapidly liberated giving the four coordinate square planar complex, $Ir(C_2Ph)(CO)(PPh_3)_2$.[38] This monocarbonyl complex undergoes addition reactions readily at the metal centre and in some cases at the triple bond of the acetylide moiety.[38] It is possible that this monocarbonyl acetylide complex may react with a coordinatively

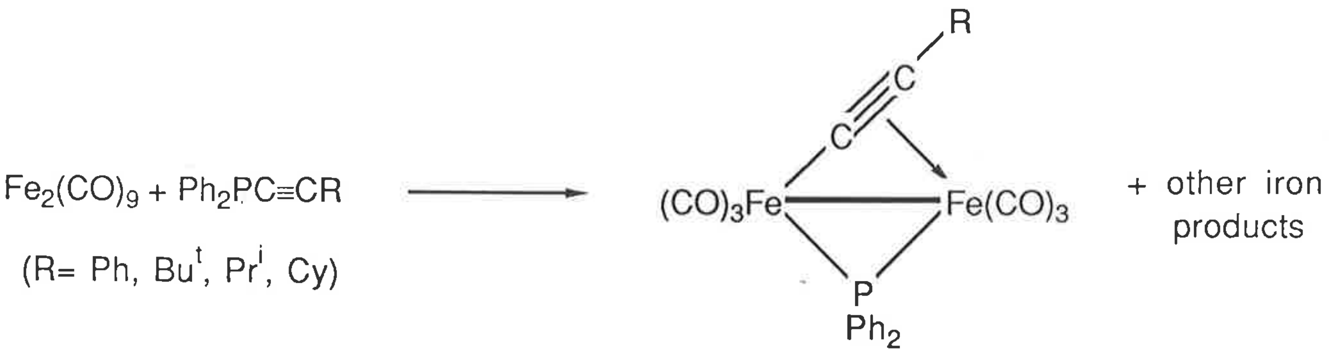

Fe(CO)4(thf) + Ir(C2Ph)(CO)2(PPh3)2
thf, Δ
(PPh3)2(CO)2Ir
Fe(CO)3
Ph
C
C
O
(A)
Fe(CO)4(PPh3)
-PPh3
Fe(CO)4(thf)
-PPh3
Ir(C2Ph)(CO)2(PPh3)2
- 2 PPh3
(PPh3)(CO)2Ir
Fe(CO)2(PPh3)
(29)
+ PPh3
(PPh3)(CO)2Ir
Fe(CO)3
Fe(CO)3
(27)
(PPh3)(CO)2Ir
Ir(CO)2(PPh3)
Fe
(CO)3
(28)

Scheme 1

unsaturated iron fragment to form the binuclear intermediate (A). It has been known for some time that the reaction of $Fe_2(CO)_9$ with tetrahydrofuran produces a tetracarbonyl iron fragment stabilized by a solvent molecule[39] (Equation 2).

$$Fe_2(CO)_9(thf) \longrightarrow Fe(CO)_4(thf) + Fe(CO)_5. \qquad \text{(Equation 2)}$$

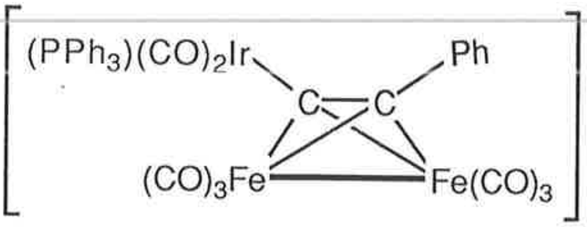
Carty and co-workers have reported the isolation of binuclear complexes similar to the postulated intermediate (A) from the reaction of phosphinoacetylenes with $Fe_2(CO)_9$ in benzene[40] (Equation 3).



(Equation 3)

These complexes readily undergo phosphine substitution at the iron centre which has the acetylide ligand σ-bonded to it.

Reaction of an intermediate of type (A) with a further '$Fe(CO)_4$' unit followed by loss of PPh_3 would give complex (27). This probably proceeds by initial coordination of the '$Fe(CO)_4$' unit to the acetylide triple bond giving adduct (B) which then condenses by virtue of the presence of the late transition



(B)

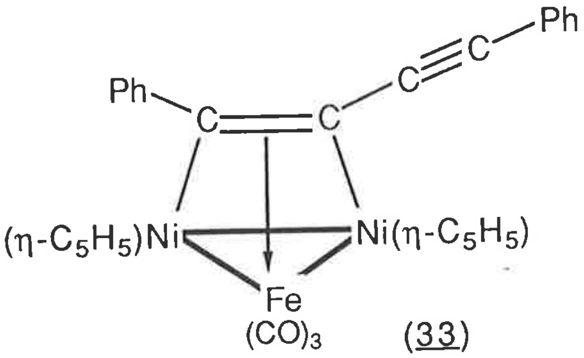
metal being of sufficient size to form metal-metal bonds with iron. Similar $M_2\{\mu-\eta^2\text{-acetylide}\}(CO)_6$ complexes are known [M = Co,Fe] and were described in the introduction to this chapter.

The formation of complex (29) could be easily explained by employing a similar reaction pathway to that postulated for the formation of complex (27) i.e. intermediate (A) and a $Fe(CO)_4(PPh_3)$ fragment. This, however, ignores the well-known substitution inertness of $Fe(CO)_4(PPh_3)$,[41] (obtained as a product in the reaction of $Ir(C_2Ph)(CO)_2(PPh_3)_2$ with $Fe_2(CO)_9$). Another possible route to complex (28) is CO-substitution of intermediate (A) with PPh_3 liberated in the formation of complex (27), this new intermediate would then react with an '$Fe(CO)_4$'-fragment in a similar manner to that postulated for the formation of complex (27). A pathway which also cannot be discounted is simple CO-substitution of complex (27), although the Fe atoms are not the preferred site of phosphine attack (see later).

Similarly, the reaction of intermediate (A) with one equivalent of $Ir(C_2Ph)(CO)_2(PPh_3)_2$, probably proceeds with initial coordination of the carbon-carbon triple bond of the incoming acetylide to the $Fe(CO)_3$ moiety of intermediate (A). Subsequent rearrangement involves an acetylide-acetylide coupling reaction of which there are few examples in the literature.[42,43]

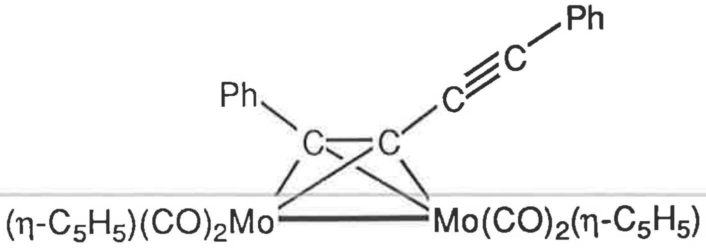
Several complexes containing the ligand 1,4-diphenyl-1,3-butadiyne have been reported. Some involve addition of the diyne as a ligand[42,44,47] or oxidative coupling

of phenyl acetylide groups on metal centres.[42,43]
A mixed metal analogue of complex (28) has been described, although not structurally characterised; $FeNi_2(\mu_3\text{-}\eta^2\text{-}PhC_2C_2Ph)\text{-}(CO)_3(\eta\text{-}C_5H_5)_2$ (33) was obtained from the reaction of $[Ni(\eta\text{-}C_5H_5)]_2\{\mu\text{-}PhC_2C_2Ph\}$[8] and iron carbonyl. Complex (33) was also obtained from the reaction of $Ni(C_2Ph)(PPh_3)\text{-}(\eta\text{-}C_5H_5)$ with $Fe_2(CO)_9$ along with the binuclear complex $FeNi(C_2Ph)(CO)_3(PPh_3)(\eta\text{-}C_5H_5)$ (34),[48] this latter complex could be important in regard to the validity of (A) as a reaction intermediate (Scheme 1).



(33)

Thermal decomposition of $Mo(C_2Ph)(CO)_3(\eta\text{-}C_5H_5)$ at *ca*. 110°C in octane results in the coupling of phenylacetylide units to give the structurally characterised, $[Mo(CO)_2(\eta\text{-}C_5H_5)]_2\text{-}(\mu\text{-}\eta^2\text{-}PhC_2C_2Ph)$ (35).[43]



(35)

Reactivity of $Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_8(PPh_3)$ (27)

Treatment of (27) with sodium amalgam in tetrahydrofuran at low temperature followed by protonation (H_3PO_4), and subsequent work-up afforded the hydrido vinylidene complex $Fe_2Ir(\mu-H)(\mu_3-\eta^2-CCHPh)(CO)_8(PPh_3)$ (36), in low yield (2%) and the hydrido alkyne cluster $Fe_2Ir(\mu-H)(\mu_3-\eta^2-HC_2Ph)(CO)_8$-$(PPh_3)$ (37) in 47% yield. The complexes were identified by the standard spectroscopic and microanalytical techniques; the structure of (36) was determined unambiguously by X-ray diffraction methods.

Structure of $Fe_2Ir(\mu-H)(\mu_3-\eta^2-CCHPh)(CO)_8(PPh_3)$ (36)

The structure of (36) is shown in Figure 3 (see also Table 3). There is a familiar triangular arrangement of the metal atoms with the two Ir-Fe distances in (36) [Fe(1)-Ir 2.705(1); Fe(2)-Ir 2.656(1)Å] being comparable to the two Ir-Fe distances in the starting acetylide cluster (27) [Fe(1)-Ir 2.701(1); Fe(2)-Ir 2.693(1)Å] and to the other Ir-Fe distances mentioned previously. The Fe-Fe separation shows a significant lengthening compared to the analogous distance in (27)(*ca.* 0.11Å) and suggests that the hydride present in the complex bridges this bond and this is supported by the 'splayed-out' nature of C(5)O(5) and C(6)O(6). The Ir-P(1) distance [2.362(1)Å] is unexceptional and similar to the analogous interaction in (27) [2.351(2)Å] and (28) [2.33(2) and 2.36(2)Å]. The hydrocarbon moiety interacts in a distorted η^2-fashion with Fe(2) [C(9)-Fe(2), C(10)-Fe(2) 2.806(4), 2.282(5), respectively] while C(9) is within bonding distance of Fe(1) [1.900(5)Å], and Ir [2.034(5)Å]. The C(9)-C(10) distance [1.406(7)Å] has appreciably lengthened

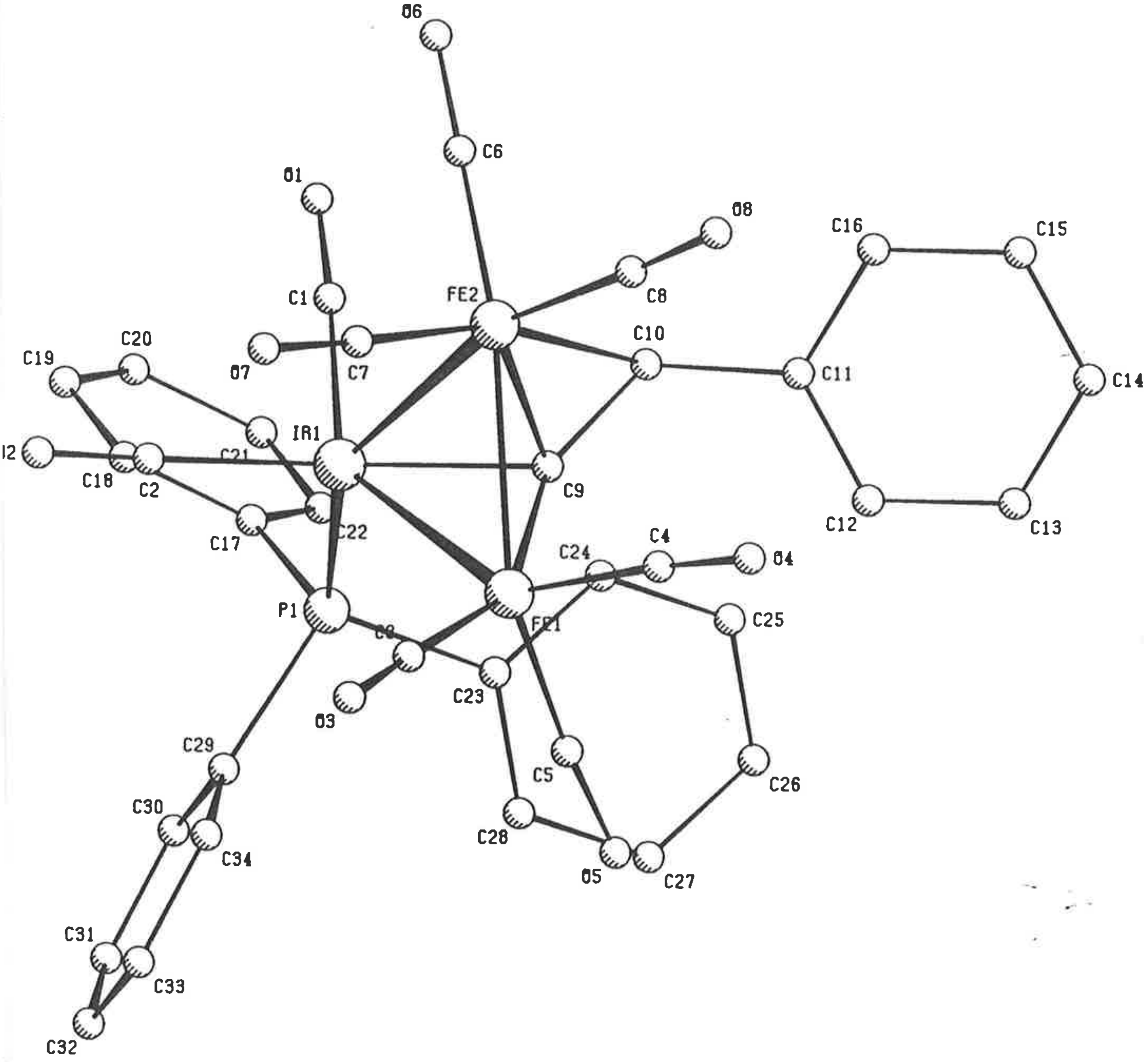


Figure 3. PLUTO plot of the molecular structure of $Fe_2Ir(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}CCHPh)(CO)_8(PPh_3)$ (36) (by M.R. Snow and E.R.T. Tiekink)

Table 3. Selected interatomic parameters for $Fe_2Ir(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}CCHPh)(CO)_8(PPh_3)$ (36)

Bond distances (Å)

Fe(1) --- Ir	2.705(1)	O(8) --- C(8)	1.145(7)
P(1) --- Ir	2.362(1)	Fe(2) --- Ir	2.656(1)
Fe(2) --- Fe(1)	2.591(1)	C(9) --- Ir	2.034(5)
C(9) --- Fe(1)	1.900(5)	C(10) --- Fe(2)	2.282(5)
C(9) --- Fe(2)	2.006(4)	C(17) --- P(1)	1.830(3)
C(29) --- P(1)	1.832(4)	C(10) --- C(9)	1.406(7)
C(23) --- P(1)	1.826(4)		

Bond angles (°)

Fe(2) - Ir - Fe(1)	57.8(1)	P(1) - Ir - Fe(1)	106.4(1)
P(1) - Ir - Fe(2)	148.9(1)	C(9) - Ir - Fe(2)	48.4(1)
C(9) - Ir - Fe(1)	44.5(1)	Fe(2) - Fe(1) - Ir	60.2(1)
C(9) - Fe(1) - Fe(2)	50.2(1)	C(9) - Fe(1) - Ir	48.7(2)
Fe(1) - Fe(2) - Ir	62.0(1)	C(9) - Fe(2) - Fe(1)	46.7(1)
C(9) - Fe(2) - Ir	49.3(1)	C(10) - Fe(2) - Ir	77.7(1)
C(10) - Fe(2) - Fe(1)	78.6(1)	Fe(1) - C(9) - Ir	86.8(2)
C(10) - Fe(2) - C(9)	37.6(2)	Fe(2) - C(9) - Fe(1)	83.0 (2)
Fe(2) - C(9) - Ir	82.2(2)	C(10) - C(9) - Fe(1)	138.5(4)
C(10) - C(9) - Ir	128.7(4)	C(9) - C(10) - Fe(2)	60.5(3)
C(10) - C(9) - Fe(2)	81.9(3)	C(1) - Ir - Fe(1)	139.8(2)

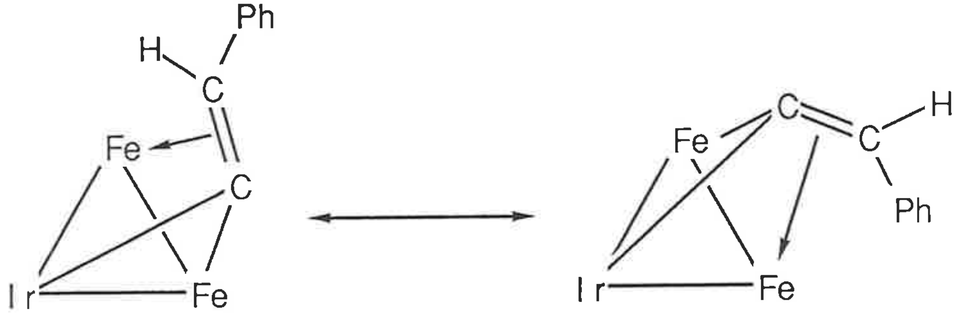
from the corresponding value in (27) [1.294(10)Å]. These data are consistent with the presence of a μ_3-η^2 vinylidene ligand and the distorted side-on coordination of the ligand to Fe(2) is also shown by the mixed-metal vinylidene clusters, $Co_2Ru(\mu_3$-η^2-CCHR)(CO)$_9$ (R=Ph,Bu^t),[16,49] in which the vinylidene ligands are η^2 bound to the ruthenium atom with *ca.* 0.34Å difference in Ru-C distances.

The precise position of the bridging hydride ligand was not found from the structure determination. A formal electron count shows that Fe(1) is electron deficient, suggesting that the hydride ligand bridges Fe(1)-Fe(2).

The spectroscopic data agree with this formulation. The infrared spectrum contains only terminal ν(CO) absorptions giving an eight band pattern. The ^{1}H NMR spectrum contains signals at δ 7.35, which were assigned to the phenyl groups and δ 6.93, which was assigned to the CH proton of the vinylidene unit although it shows no coupling to phosphorus [*cf.* similar values in $Co_2Ru(\mu_3$-η^2-CCHPh)(CO)$_9$ at δ 6.89[16] and Ru_3Au_2-(μ_3-η^2-CCHBu^t)(CO)$_8$(PPh$_3$)$_2$ at δ 6.30[50]]. There are two doublets of equal intensity which integrate as 0.5H each showing a 13Hz coupling to ^{31}P. This suggests that (36) exists as a mixture of isomers in solution possibly resulting from the vinylidene fragment switching from an η^2-bonding mode from Fe(2) to Fe(1) (Scheme 2).

The signal for the vinylidene proton is relatively broad and could, in fact, be the product of two overlapping doublets which are not resolved as a result of the vinylidene proton exhibiting a smaller coupling to ^{31}P than the metal bound hydride.

The ^{13}C{^{1}H} NMR has signals at δ 126-130 assigned to the phenyl carbons. Two peaks at δ 101.7 and 145.5 are

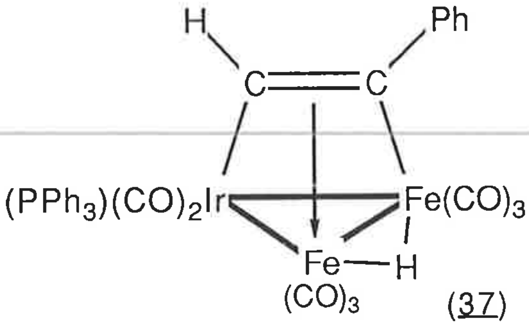


Scheme 2

assigned to C_α and C_β of the vinylidene moiety, respectively. The former resonance was assigned with the aid of an off-resonance decoupling experiment. A sharp singlet at δ 5.1 in the $^{31}P\{^1H\}$ NMR spectrum was assigned to PPh_3 bound to the Ir above. The FAB MS showed a molecular ion at *m/z* 894 together with a fragmentation pattern due to successive loss of eight CO ligands.

Spectroscopic data confirmed that complex (37) was also related to (27) by the addition of two hydrogens. The ^1H NMR spectrum contained a high field doublet at δ -23.48 [*J*(PH) 12Hz] and was assigned to a bridging hydride ligand. A characteristic low-field doublet signal at δ 7.81 [d, *J*(PH) 5Hz, 1H] was found for the CH proton of the alkynyl unit. The singlet at δ 112.5 in the $^{13}C\{^1H\}$ NMR spectrum was assigned to the alkynyl carbons with the aid of an off-resonance decoupling experiment. The resonances at δ 152.8 and 171.2 were assigned to carbonyl ligands on Ir while the peaks at *ca.* δ 210 were assigned to the analogous Fe signals. The FAB mass spectrum contained a molecular ion at *m/z* 894 and fragmentation ions formed by stepwise loss of eight CO ligands.

The preceding data suggest that complex (37) has the structure shown in Figure 4.



(37)

Figure 4

Figure 4

The μ_3-η^2-|| alkyne bonding mode is one of the most common found in either homo- or hetero-metallic alkyne clusters.[3] The structure postulated for (37) is consistent with the observation of the trend shown by (μ_3-η^2-||)-bonded alkyne clusters, in which the formal ρ-bond is directed towards the least electron rich metal.

Complexes (36) and (37) appear to be the result of hydride addition to the acetylide ligand and protonation at the cluster core of complex (27). This was confirmed by the reaction of (27), in tetrahydrofuran, with *K*-Selectride [K{BH(CHMeEt)$_3$}; a source of H$^-$] followed by protonation (H_3PO_4). This reaction gave a similar distribution of products as the reaction of (27) with sodium amalgam/H_3PO_4 and suggests this latter reaction proceeds by simple hydride abstraction from the solvent followed by protonation at the cluster core. These results are consistent with the electrophilic nature of Cα of μ_3-η^2-acetylide clusters leading to the formation of alkynes, parallel to one edge of the cluster,[51] and hence to structures comparable to (37).

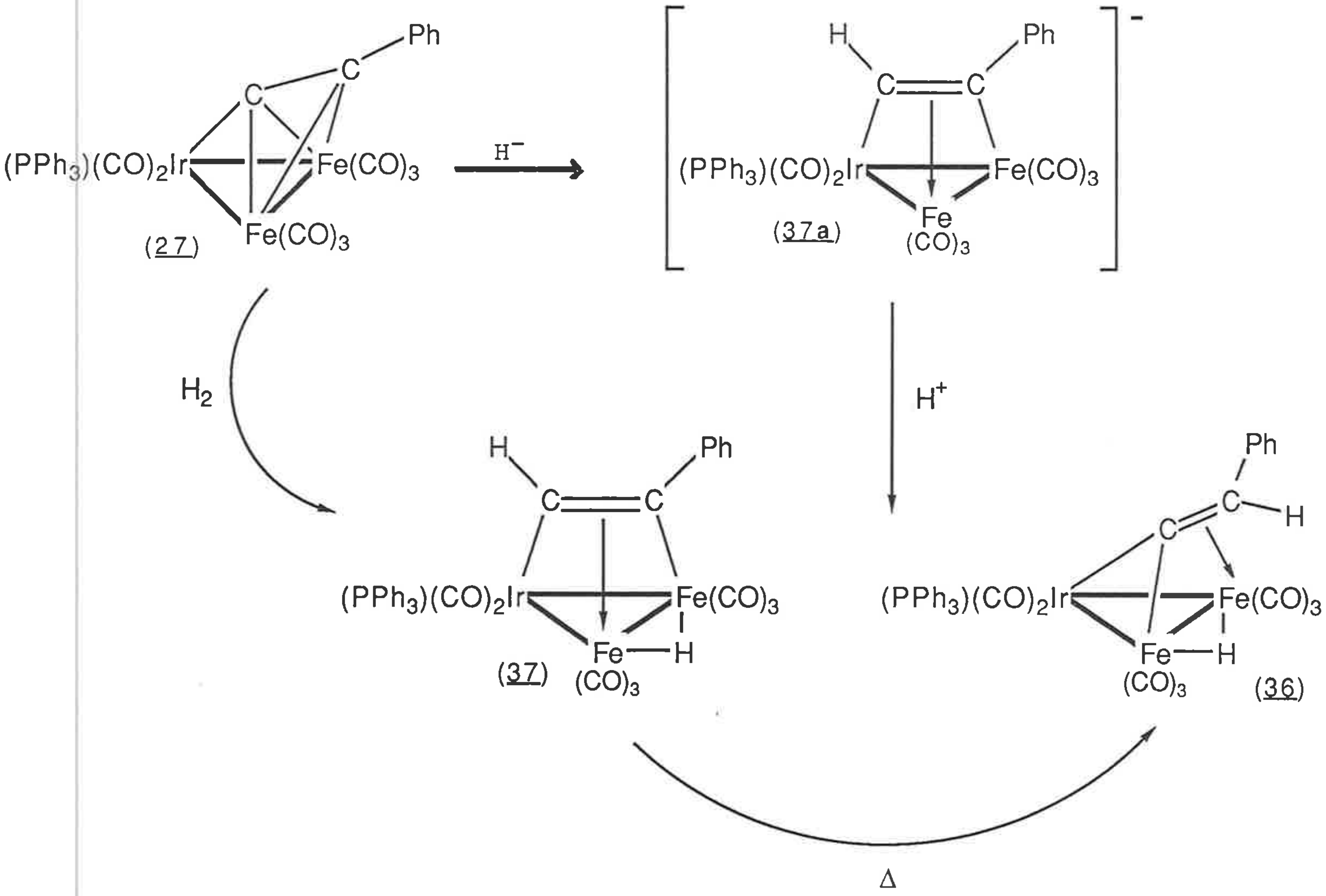
These H$^-$/H$^+$ reactions correspond, at least formally, to the addition of hydrogen to the acetylide cluster (27). Indeed, the hydrogenation of (27) in cyclohexane, resulted in the isolation, after suitable work-up, of the hydrido-vinylidene cluster (36) which was identified by comparison with an authentic sample. The major product from this reaction, however, was an unidentified brown complex, (38). Its infrared spectrum contained two bridging (1855m, 1820m cm^{-1}) as well as six terminal ν(CO) bands.

The only distinguishing features of its ^{1}H NMR spectrum were a broad singlet at δ -23 assigned to a metal bridging hydride ligand and the ubiquitous phenyl resonances at δ 7.47. It was not possible to obtain a FAB mass spectrum of (38) using any of the established solvent matrices. It was also not possible to obtain crystals suitable for X-ray structural analysis. There is no evidence for the identity of (38) at this time due to the obvious complexity of the reaction; there were at least eleven compounds observed after thin-layer chromatographic separation. However, in several cases the hydrogenation of hydrocarbyl containing clusters results in reduction of the hydrocarbyl ligand [52, 53] e.g. hydrogenation of $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C_2Bu^t)(CO)_9$ gives alkylidyne complex $Ru_3(\mu\text{-}H)_3(\mu_3\text{-}CCH_2Bu^t)(CO)_9$.[52] It is interesting to note that hydrogenation of (36), under the same conditions as (27) results only in decomposition while similar hydrogenation of (37) gave a multitude of products, one of which was identified as (38).

Pyrolysis of $Fe_2Ir(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(CO)_8$ (37)

Heating a toluene solution of (37) at reflux for 90 min results in almost quantitative conversion to the vinylidene cluster (36). This represents a formal 1,2-hydrogen shift, a subject which has aroused much recent interest, in mononuclear[54,55] as well as cluster chemistry.[15a,16,49,56]

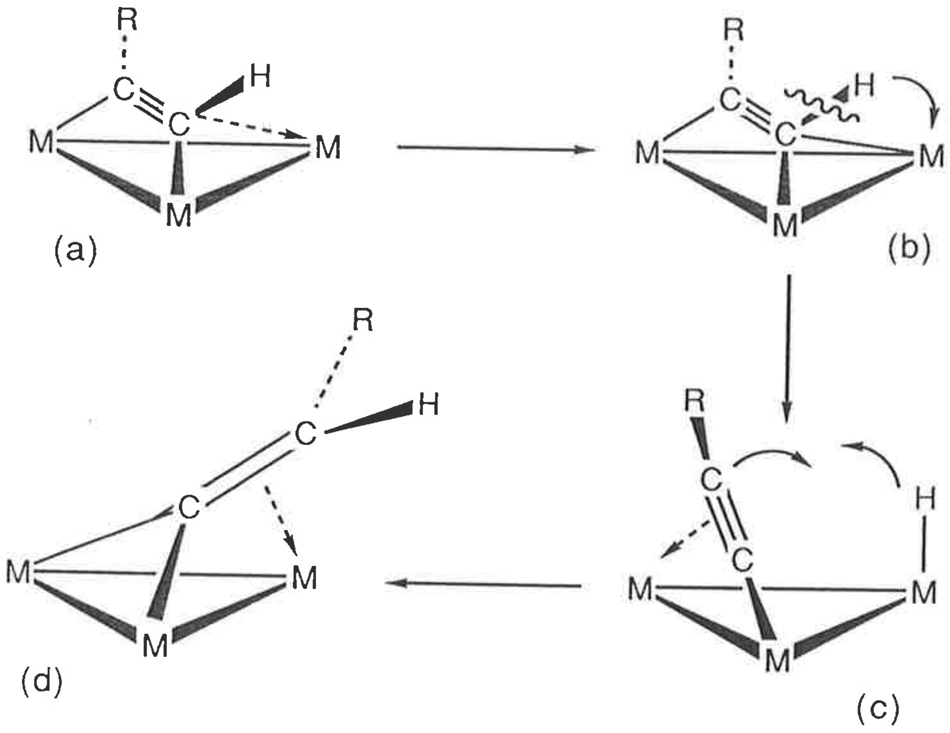
The transformation of complex (27) by successive addition of H^-/H^+ into a hydrido alkyne cluster followed by thermal rearrangement to a vinylidene cluster (36) is depicted in Scheme 3. Although (36) is obtained from the reaction of H^-/H^+ with the acetylide cluster it is, in fact, a minor



Scheme 3 Transformation of acetylide cluster (27) into vinylidene cluster (36) and alkyne cluster (37)

product (<5%) while the alkyne cluster (37) is by far the major product. A theoretical study[57] on the acetylide cluster, $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C_2Me)(CO)_9$ indicated that the most likely site of nucleophilic attack was at C_α. Experimentally, Deeming[27] has shown that nucleophilic attack on $Os(\mu\text{-}H)\text{-}(\mu_3\text{-}\eta^2\text{-}C_2H)(CO)_9$ is predominately at $C\alpha$ while attack at $C\beta$ is also possible. We believe initial H^- attack at C_α of (27) gives the anionic alkyne intermediate (37a) (Scheme 3) and protonation at the metal core gives the alkyne cluster (37). It is not possible to say conclusively at this time whether H^- attack at C_β affords an analogous anionic vinylidene intermediate, which after protonation gives (36) because of the facile nature of the thermal rearrangement of (37) to (36). This rearrangement was found to occur in solution even at room temperature, albeit slowly. An alternative explanation for the formation of (36) is initial H^- attack at the metal core giving an anionic hydrido-acetylide cluster which then rearranges to an anionic vinylidene intermediate giving (36) after protonation.

The addition of H^-/H^+ corresponds to the formal addition of H_2 to the cluster and it is probable that the initially formed product in the hydrogenation of (27) is complex (37) which then under the prevailing reaction conditions rearranges to (36). As mentioned previously alkyne-vinylidene interconversion on metal clusters has been the subject of a theoretical study[18] in which Silvestre and Hoffmann concluded that in bi- and tri-nuclear systems the isomerisation proceeded via a hydrido acetylide intermediate, formed by oxidative addition of the CH bond of the alkyne to the cluster. (Scheme 4).



Scheme 4

In mononuclear complexes the analogous process was calculated to be of higher energy than a situation involving η^1-alkyne slippage and consequent 1,2-hydrogen shift.[18] Reactions between $Co_2Ru(CO)_{11}$ and HC_2R gave μ_3-alkyne complexes which rearranged in boiling hexane to μ_3-vinylidene complexes.[16,49] Both complexes for R=Bu^t were characterised crystallographically from which it could be seen that the conversion is associated with a gradual inclination of C=C bond with respect to the M_3 plane. The extremely facile interconversion of the hydrido acetylide cluster $Ru_3Pt(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CBu^t)(CO)_9$-(dppe) to the tautomeric vinylidene cluster $Ru_3Pt(\mu_4\text{-}\eta^2\text{-}C{=}CHBu^t)(CO)_9(dppe)$ occurs at ambient temperatures[56] and lends support to the mechanism proposed by Silvestre and Hoffmann[18] (Scheme 4).

Synthesis of trimetallic clusters by incorporation of gold fragments

Addition of $[O\{Au(PPh_3)\}_3][BF_4]/[ppn][Co(CO)_4]$ to (27) resulted in the formation of the pentanuclear cluster $Au_2Fe_2Ir(\mu_4-\eta^2-C_2Ph)(CO)_7(PPh_3)_3$ (39). This complex was characterised unambiguously by X-ray structural analysis as well as spectroscopic and microanalytical techniques.

Structure of $Au_2Fe_2Ir(\mu_4-\eta^2-C_2Ph)(CO)_7(PPh_3)_3$

The molecular structure of (39) is shown in Figure 5. Table 4 collects significant bond distances and valence angles for (39). The structure of (39) is closely related to the structure of (27), the major difference being the co-ordination of a $Au_2(PPh_3)_2$ unit to the Ir atom with an additional interaction between Au(2) and C(8) of the acetylide ligand. The cluster metal core comprises a 'bow-tie' arrangement of the five metal atoms with the two halves of the tie defined by the Ir(1)Fe(1)Fe(2) and Ir(1)Au(1)Au(2) triangles. The dihedral angle between the planes is 86.0°. The Ir-Fe [2.709(3)Å, 2.744(4)Å], Fe-Fe [2.501(5)Å] and Ir-P(1) [2.287(6)Å] distances are all comparable to those found in complex (27). The Au-Ir distances [Ir-Au(1) 2.6331; Ir-Au(2) 2.726(1)Å] are close to that expected from the sum of the metallic radii (2.794Å)[58] and the Ir-Au(1) interaction falls within the range found for the analogous distance in other mixed-metal clusters (2.593-2.675Å)[58]. The coordination mode of the acetylide ligand in (39) can be described as distorted $\mu_4-\eta^2-(\perp)$[56] with the angle between the C≡C axis and the bridged Fe(1)-Fe(2) vector being *ca* 103°. The Ir-C_α distance [1.957(23)Å] and C≡C distance [1.340(31)Å]

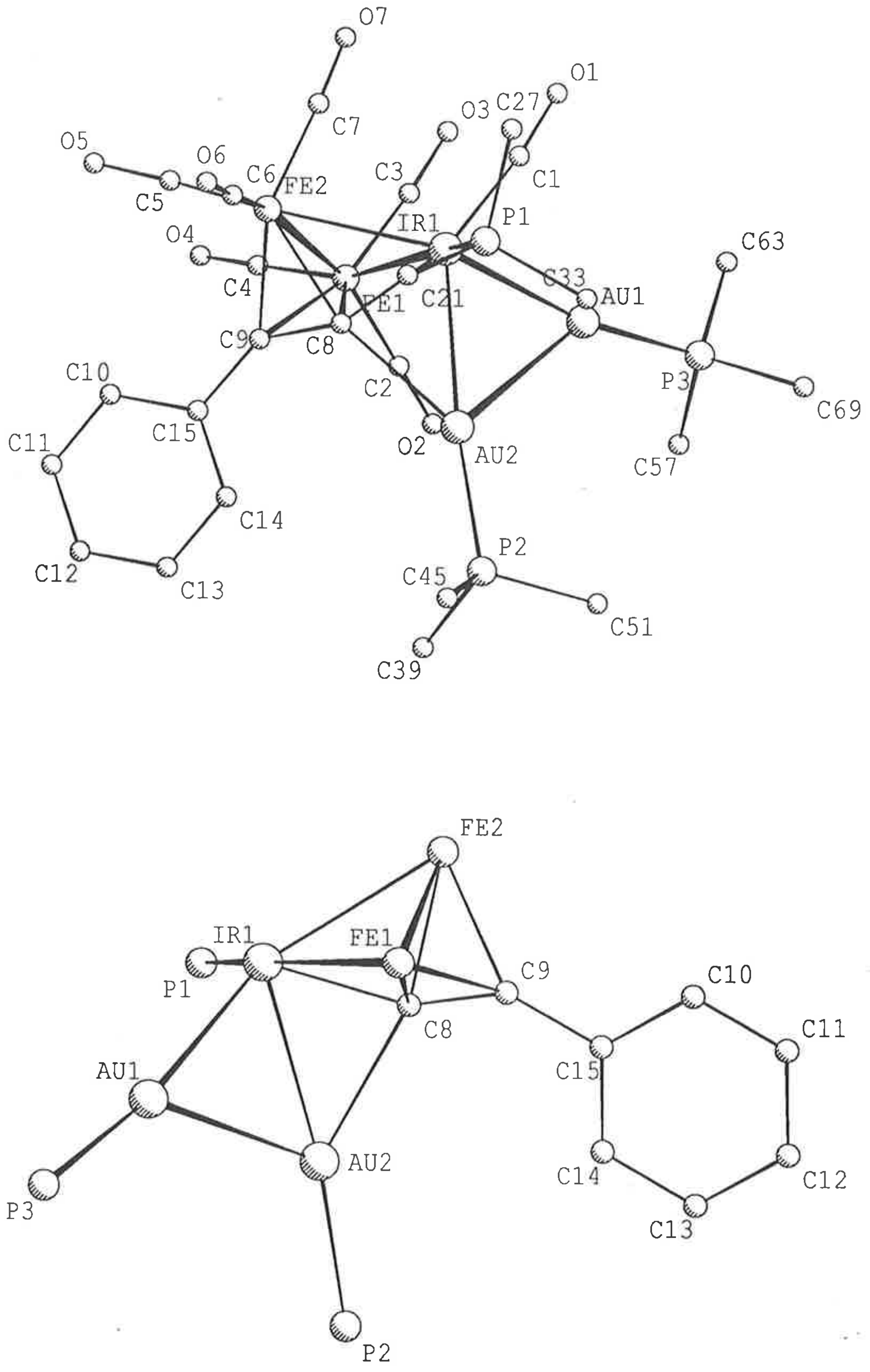


Figure 5. PLUTO plot of the molecular structure of $Au_2IrFe_2(\mu_4-\eta^2-C_2Ph)(CO)_7(PPh_3)_3$ (39)

Table 4. Selected interatomic parameters for (39)

Bond distances (Å)

Au(2) --- Au(1)	2.847(1)	C(8) --- Au(2)	2.387(22)
P(3) --- Au(1)	2.269(6)	Au(2) --- Ir(1)	2.726(1)
Au(1) --- Au(2)	2.847(1)	Fe(2) --- Ir(1)	2.744(4)
Au(1) --- Ir(1)	2.633(1)	Fe(2) --- Fe(1)	2.501(5)
Fe(1) --- Ir(1)	2.709(3)	Au(2) --- P(2)	2.269(6)
Ir(1) --- C(8)	1.957(23)	Au(1) --- P(3)	2.269(6)
Fe(2) --- C(8)	2.079(23)	Fe(1) --- C(8)	2.074(23)
Fe(1) --- C(9)	2.141(22)	C(9) --- C(8)	1.340(31)
Ir(1) --- Au(2)	2.726(1)	Fe(2) --- C(9)	2.063(23)
Ir(1) --- P(1)	2.287(6)		

Bond angles (°)

Ir(1) - Au(1) - Au(2)	59.5	Fe(2) - C(9) - Fe(1)	73.0(8)
P(3) - Au(1) - Ir(1)	166.0(2)	C(8) - C(9) - Fe(2)	71.8(14)
Ir(1) - Au(2) - Au(1)	56.3	P(3) - Au(1) - Au(2)	132.7(2)
P(2) - Au(2) - Ir(1)	170.0(2)	P(2) - Au(2) - Au(1)	122.4(2)
C(8) - Au(2) - Ir(1)	44.4(6)	C(8) - Au(2) - Au(1)	91.2(6)
Au(2) - Ir(1) - Au(1)	64.1	C(8) - Au(2) - P(2)	142.6(6)
Fe(1) - Ir(1) - Au(2)	86.5(1)	Fe(2) - Ir(1) - Au(1)	144.8(1)
Fe(2) - Ir(1) - Au(2)	107.1(1)	Fe(2) - Ir(1) - Fe(1)	54.6(1)
Fe(2) - Fe(1) - Ir(1)	63.4(1)	C(8) - Fe(2) - Fe(1)	52.9(6)
Fe(1) - Fe(2) - Ir(1)	62.0(1)	Fe(1) - C(8) - Au(2)	113.0(10)
C(8) - Fe(2) - Ir(1)	45.3(6)	Fe(2) - C(8) - Au(2)	160.2(10)
Ir(1) - C(8) - Au(2)	77.0(7)	Fe(2) - C(8) - Fe(1)	74.1(8)
Fe(1) - C(8) - Ir(1)	84.4(10)	C(9) - C(8) - Ir(1)	151.4(19)
Fe(2) - C(8) - Ir(1)	85.6(9)	C(9) - C(8) - Fe(2)	70.5(13)
C(9) - C(8) - Au(2)	128.7(17)	C(8) - C(9) - Fe(1)	68.7(14)
C(9) - C(8) - Fe(1)	74.2(13)	Fe(1) - Ir(1) - Au(1)	90.3(1)

fall within the values found for μ_4-η^2($\perp$) acetylide ligands[39] and are comparable to those in (27). An interesting feature of the structure of (39) is the Au(2)-C(8) interaction [2.387(22)Å]. Gold-carbon interactions have been noted previously in the complexes [(η-C_5H_5)Fe-(η-C_5H_4)Au_2(PPh_3)$_2$][BF_4],[59] [AuW_2(μ-CC_6H_4Me-4)$_2$(CO)$_4$(η-C_5H_5)$_2$]-[PF_6],[60] and [(η^5-C_5H_5)MoMn(μ-PPh_2){μ-σ:η^4-CH(Me)-CHCHAu(PMe_2Ph)}(CO)$_4$][61] where Au-C contacts of 2.16(3), 2.12(2) and 2.19(1)Å, respectively, were found. The longer distance in (39) might be a result of steric interaction between the PPh_3 ligand on Ir, which is bonded *cis* to Cα of the acetylide ligand, and the AuPPh_3 group interacting with Cα.

In (39) the seven CO groups are distributed three to each iron and one to the iridium. Although the least hindered site of attack on the iridium atom in (27) is the position occupied by C(2)O(2) (see Figure 1), which is *trans* to Cα of the acetylide ligand, comparison of the two structures suggests that C(1)O(1) has been substituted by Au_2(PPh_3)$_2$ which allows interaction of the digold unit with Cα.

Spectroscopic data obtained for (39) were in accord with the determined structure and will be discussed in conjunction with the characterisation data obtained for the analogous rhodium compound Au_2Fe_2Rh(μ_4-η^2-C_2Ph)(CO)$_7$-(PPh_3)$_3$ (40). Complexes (39) and (40) were obtained from the addition of [ppn][Co(CO)$_4$] and [O{Au(PPh_3)}$_3$][BF_4] to thf solutions of (27) and (32) respectively, at room temperature. For both cases thin layer chromatographic separation gave good yields of (27) and (32) as well as the binuclear complex

$AuCo(CO)_4(PPh_3)$. The infrared spectra of (39) and (40) were similar and contained only terminal ν(CO) bands. Multiplets, assigned to phenyl group resonances, were the only signals observed in the ^1H NMR spectra of (39) and (40); the compounds proved too insoluble to obtain ^{13}C spectra. The $^{31}P\{^1H\}$ NMR spectrum of (40) contained two broad singlets at δ 40.8 and 47.8 which were assigned to $AuPPh_3$ also a sharp doublet at δ 52.6 was assigned to $RhPPh_3$ on the basis of the observed 141 Hz coupling to ^{103}Rh. By analogy the broad singlets at δ 42.8 and 47.6 and the sharp singlet at δ 30.6 were assigned to $AuPPh_3$ and $IrPPh_3$, respectively, in the $^{31}P\{^1H\}$ NMR spectrum of (39). The FAB mass spectra of (39) and (40) contained weak pseudomolecular ions at *m/z* 1784 and *m/z* 1694, respectively, corresponding to [*M* + H] and [*M* + 2H], respectively. These ions decomposed by successive loss of seven CO groups and $AuPPh_3$. Both the spectra of (39) and (40) contained strong ions at *m/z* 721 and *m/z* 459 assigned to $[Au(PPh_3)_2]^+$ and $[Au(PPh_3)]^+$, respectively. An ion corresponding to $[\{Au_2(PPh_3)_2\}H]^+$ was also found at *m/z* 919 in the FAB spectrum of (39).

Various routes to (39) were investigated. For preparative purposes it was found that treatment of the acetylide cluster (27) with $[ppn][Co(CO)_4]/[O\{Au(PPh_3)\}_3][BF_4]$ was the best synthesis (83%), however, the reacticn of (27) with $[O\{Au(PPh_3)\}_3][BF_4]$ alone also gave (39) but the yield was considerably lower (24%). The orange solution obtained from the reaction of the gold oxonium salt with $[ppn][Co(CO)_4]$ in thf did not react with (27) to form (39). This suggests that the cluster may have been reacting with an unstable intermediate

'$\{Au(PPh_3)\}_2O$' formed by removal of $Au(PPh_3)$ from the oxonium salt as $AuCo(CO)_4(PPh_3)$. Recently it has been found that [ppn][Cl] or [ppn][OAc]/$[O\{Au(PPh_3)\}_3][BF_4]$ achieves the same results giving in the former case $AuCl(PPh_3)$ as a side product which can be recycled.[62]

This gold oxonium/anion reagent appears to be useful in introducing digold '$Au_2(PPh_3)_2$' units into clusters which have the facility to lose CO readily, obviating the requirement that the cluster be a dianion or multihydride complex. Various methods of introducing one, two or three $AuPh_3$ units have been developed,[50,58,65-67] but no rational route to digold substitution of neutral clusters has appeared.

Evans and Mingos[68] have examined the bonding tendencies of $Au(PPh_3)$ fragments and have shown that these groups have a single sp-hybridised orbital which makes them isolobal with H,CH_3,$Co(CO)_4$. Lauher and Wald[69] have argued that the isolobal relationship between H and $AuPPh_3$ may be used to provide evidence for hydrido-ligand positions in transition metal complexes.

It is thought that the isolobal relationship between $Au(PPh_3)$ and H is of limited use in predicting structures when more than one gold atom is present.[65b,68,70] This is because of the propensity of gold to form Au-Au bonds. However, the digold unit '$Au_2(PPh_3)_2$' is isolobal with H_2 and complex (39) might model the way hydrogen reacts with complex (27). The formal addition of H_2 ($\equiv H^-/H^+$) to (27) was demonstrated previously giving initially the hydrido-alkyne cluster (37) which was shown to rearrange thermally to the hydrido-vinylidene cluster (36). Similarly, hydrogenation of (27) gave (36) which we believe derives from initially formed (37) (see Scheme 3).

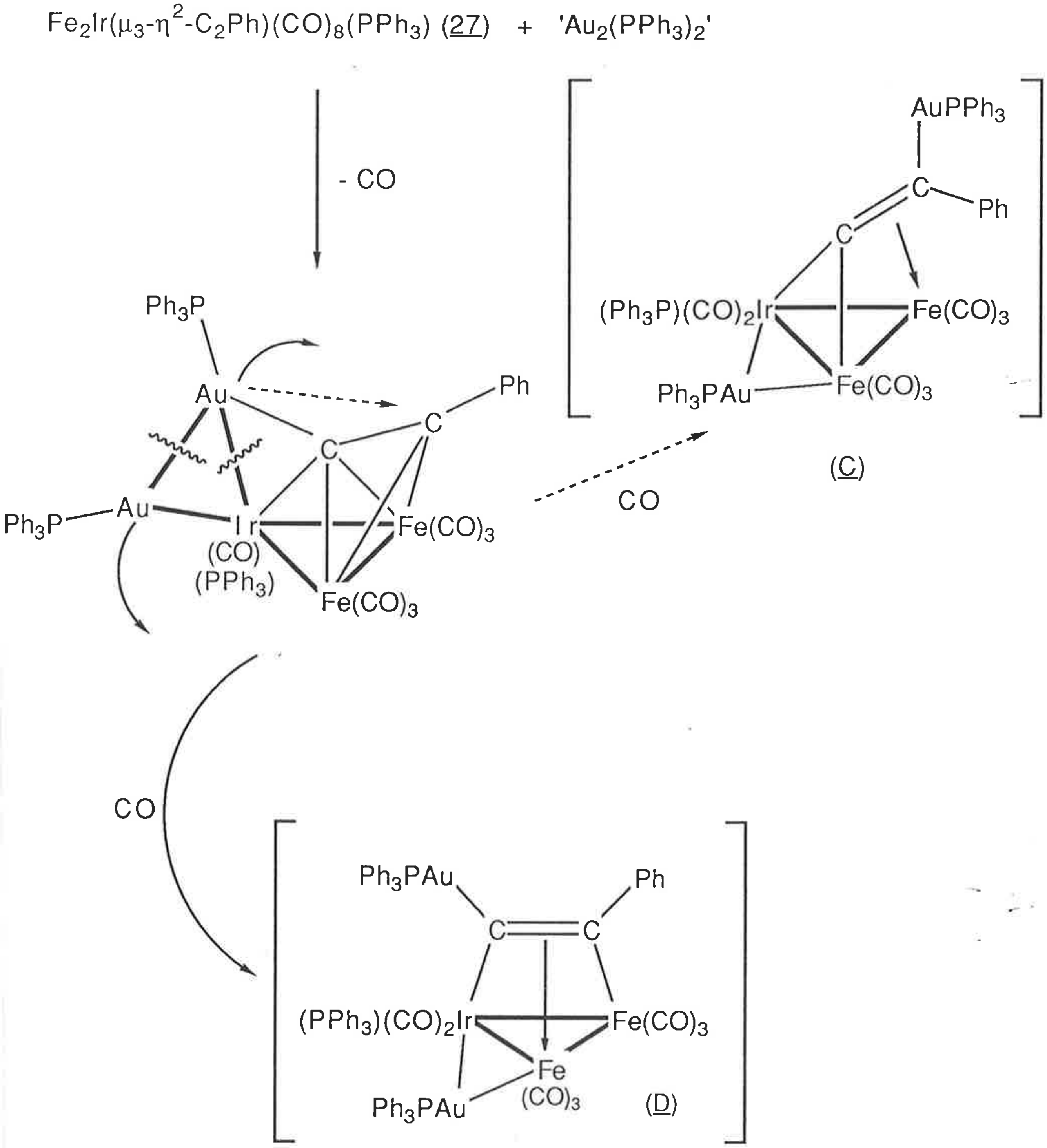
Formal substitution of a CO group by $Au_2(PPh_3)_2$ results in the formation of (39) (Scheme 5). A situation can be envisaged in which cleavage of the Au-Au bond and one of the Ir-Au bonds could give rise to structures (C) and (D) which are isolobal with (36) and (37), respectively. However, no evidence was found for the formation of complexes of this type in the pyrolysis or hydrogenation of complex (39). A simple electron count requires the acetylide ligand to contribute 5e, the digold unit contributes 2e to give an electron precise count of 48 electrons. The conversion of the acetylide ligand into the 4e donor depicted in (C) or (D) requires the addition of two electrons; and this might be achieved by the addition of CO.

Although on the surface it seems that '$Au_2(PPh_3)_2$' might be used to model the reaction of H_2 on clusters this analogy must be treated with caution. The reaction of '$Au_2(PPh_3)_2$' with the pentanuclear cluster $Ru_5(\mu_5\text{-}\eta^2\text{-}P\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$[71] was found not to parallel the reaction of H_2 with this cluster.[53]

Reactions of an iron-iridium cluster anion with aurating reagents

The trigold-oxonium reagent $[O\{Au(PPh_3)\}_3][BF_4]$ was first reported by Nesmeyanov et al[72] and has since been shown to introduce up to three $Au(PPh_3)$ moieties onto cluster anions.[50,65-67]

As was discussed earlier the reaction of (27) with Na/Hg or $K[BH(CHMeEt)_3]$ is believed to generate a hydrido-anion. Tetrahydrofuran solutions of the anion, generated using


Fe₂Ir(μ₃-η²-C₂Ph)(CO)₈(PPh₃) (27) + 'Au₂(PPh₃)₂'
- CO
Ph₃P
Au
Ph₃P
Au
Ir
(CO)
(PPh₃)
C
C
Ph
Fe(CO)₃
Fe(CO)₃
CO
AuPPh₃
C
Ph
C
(Ph₃P)(CO)₂Ir
Fe(CO)₃
Ph₃PAu
Fe(CO)₃
(C)
CO
Ph₃PAu
Ph
C
C
(PPh₃)(CO)₂Ir
Fe(CO)₃
Fe
(CO)₃
Ph₃PAu
(D)

Scheme 5

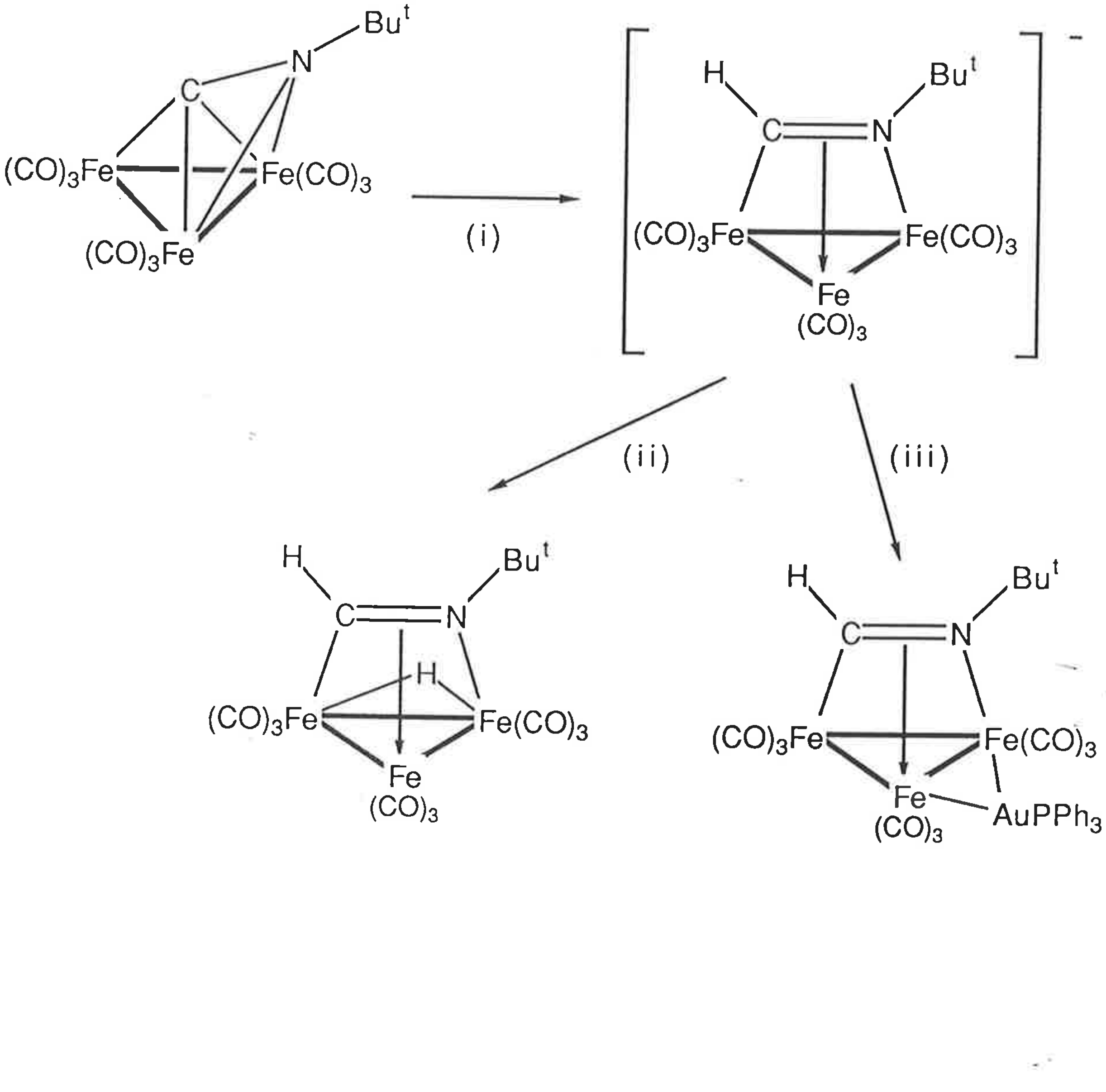
sodium amalgam, reacted readily with the gold-oxonium reagent. The dark red solutions which were obtained afforded numerous bands after thin-layer chromatographic separation. The major band was crystallised and identified as $AuFe_2Ir(\mu_3-\eta^2-HC_2Ph)(CO)_8(PPh_3)_2$ (<u>41</u>) by microanalytical and spectroscopic data. A small amount of (<u>39</u>) (15%) was also isolated and identified by comparison of its spectral data to an authentic sample prepared as described previously.

The solution infrared spectrum of complex (<u>41</u>) contained only six terminal ν(CO) bands. The ^1H NMR spectrum contained resonances at δ 7.14-7.62 which were assigned to the phenyl groups. A characteristic low field signal was found at δ 9.18 [d, *J*(PH) 13Hz, 1H] and was assigned to the CH proton of an alkyne unit [*cf* similar values in $Co_2Ru(\mu_3-\eta^2-HC_2Ph)(CO)_9$ at δ 9.53[16]]. The multiplet between δ 126.0-135.0 in the $^{13}C\{^1H\}$ NMR spectrum, assigned to the phenyl groups, and the signal at δ 102.5, assigned to the alkyne carbons, were the only resonances observed. The FAB mass spectrum contained a weak pseudomolecular ion at *m/z* 1353 ($[M + H]^+$) which decomposed by the step-wise loss of eight CO groups and an $Au(PPh_3)$ fragment. The gold containing ions at *m/z* 721 and *m/z* 459 were assigned to $[Au(PPh_3)_2]^+$ and $[Au(PPh_3)_2]^+$, respectively.

Although the isolobal analogy between $AuPPh_3$ and H has been demonstrated in cases where the hydride ligand has been located in the molecular structure of a complex, as in, for example, $NiOs_3(\mu\text{-}H)_3(CO)_9(\eta\text{-}C_5H_5)$, and the corresponding $AuNiOs_3$ cluster has been shown to have the $Au(PPh_3)$ unit occupying the position of the H atom which it replaces.[73] Unfortunately, crystals suitable for an X-ray structure determination of either (<u>37</u>) or (<u>41</u>) could not be obtained therefore the precise position of the $Au(PPh_3)$ group cannot be stated. In most examples of mixed metal clusters, however, $AuPR_3$ units are usually found in a μ_2-edge bridging or μ_3-face capping situation but μ_4- and μ_5- modes are also encountered.[58]

Complex (<u>41</u>) is also obtained from the reaction of the anion of (<u>27</u>) generated using either Na/Hg or $K[BH(CHMeEt)_3]$ in thf, and $AuCl(PPh_3)$; small amounts of (<u>39</u>) were also obtained. This observation supports the premise that initial nucleophilic attack of H^- occurs at Cα of the acetylide ligand in (<u>27</u>). Bruce and Nicholson[74] observed a similar reaction with $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)$. The cluster band isocyanide was found to add H^- to give $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}HCNBu^t)]^-$, which could be protonated or aurated to give $Fe_3(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}HCNBu^t)(CO)_9$ and $AuFe_3(\mu_3\text{-}\eta^2\text{-}HCNBu^t)(CO)_9PPh_3$, respectively (Scheme 6).

The reaction of (<u>27</u>) with $K[HB(CHMeEt)_3]$ followed by the oxonium reagent gave a number of compounds, after suitable work-up, one of which was identified as $Au_3Fe_2Ir(C_2HPh)(CO)_7(PPh_3)_4$ (<u>42</u>). A small amount of (<u>39</u>) was also identified by comparison of its spectral data with a sample prepared

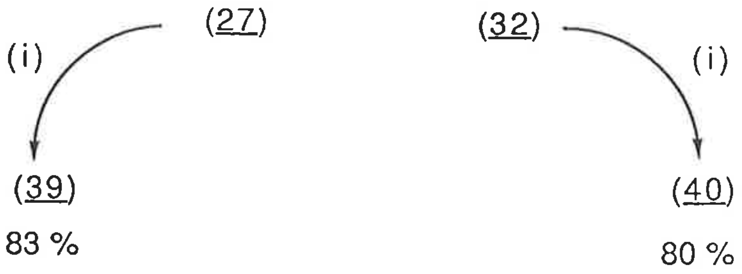


Scheme 6: (i) K[HB(CHMeEt)$_3$]; (ii) H$^+$ (iii) AuCl(PPh$_3$).

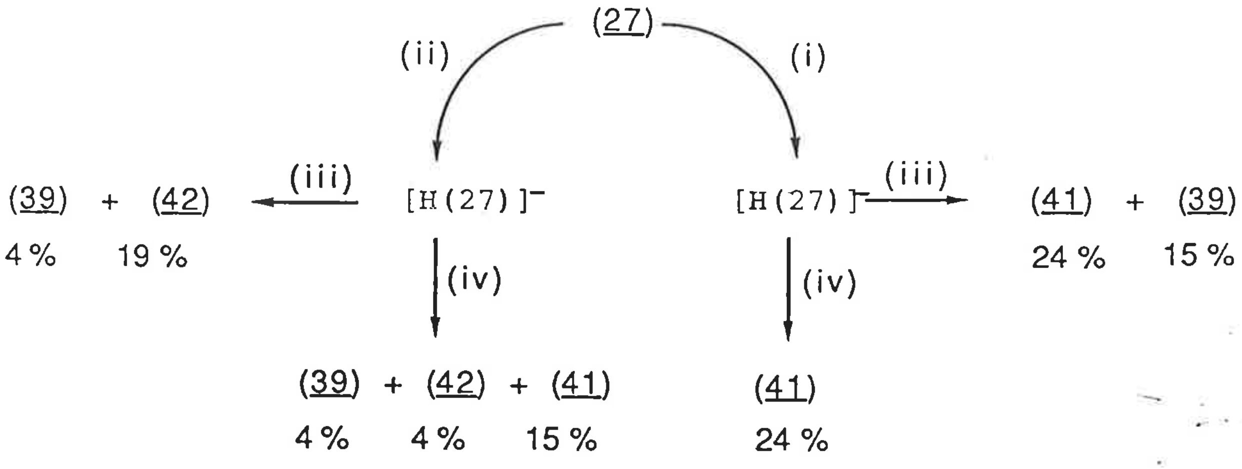
previously. Complex (42) gave microanalytical data which were consistent with the presence of two CH_2Cl_2 molecules of crystallisation. This was confirmed by the observation of a peak at δ 5.3 in the ^{1}H NMR spectrum of (42). The broad unresolved peak at δ 7.05 is barely separate from the phenyl resonances but might be assigned to the -CCHR of a vinylidene ligand although it seems to be of too low field for such an assignment when compared with the resonances of the analogous protons in the extensive series of μ_3-vinylidenc compounds reported by Vahrenkamp *et al.*[15,16] Simple electronic book-keeping requires a 4e donor ligand to be present in (42) rather than the 5e acetylide ligand. The FAB mass spectrum of complex (42) contained a molecular ion at *m/z* 2242 and ions related to this by successive loss of six CO groups and loss of PPh_3. Gold containing ions were found at *m/z* 1377, 1115 and 721 and were assigned to $[Au_3(PPh_3)_3]^+$, $[Au_2(PPh_3)_2]^+$ and $[Au(PPh_3)_2]^+$, respectively. It is not surprising that a tris-gold adduct has been found given the nature of the aurating reagent used. What is unclear at this time is the disposition of the three $Au(PPh_3)$ units in the structure of (42).

No reaction was found between complex (39) and gold oxonium therefore stepwise addition of three $Au(PPh_3)$ groups giving (42) can probably be ruled out. It has been stated that the principle which seems to govern construction of multi-$Au(PR_3)$ containing clusters is that the first unit occupies the position of H in the corresponding hydride cluster, if steric effects allow. The successive gold atoms add to the least hindered triangular faces next to existing gold atoms. This leads to a compact arrangement of face-sharing tetrahedra with as many adjacent gold atoms as possible.[58,65b] Thus, it is likely that complex (<u>42</u>) contains a $Au_3(PPh_3)_3$ ligand attached to the iron-iridium triangle on the opposite face to that occupied by the hydrocarbyl ligand.

Scheme 7 summarises the auration of iron-iridium clusters discussed in this work.

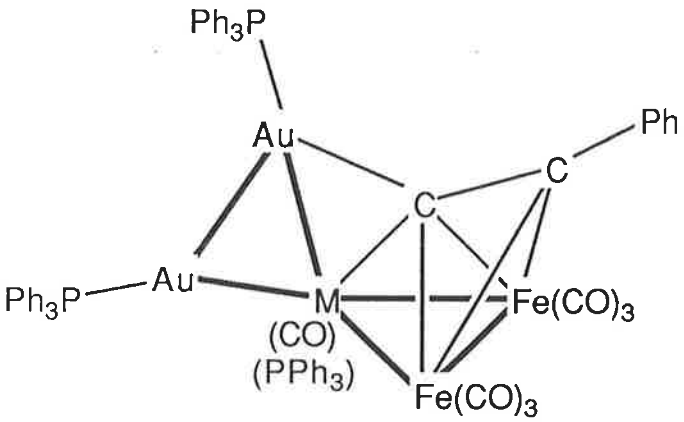


Scheme 7(a) (i) $[O\{Au(PPh_3)_3][BF_4]$ / $[ppn][Co(CO)_4]$

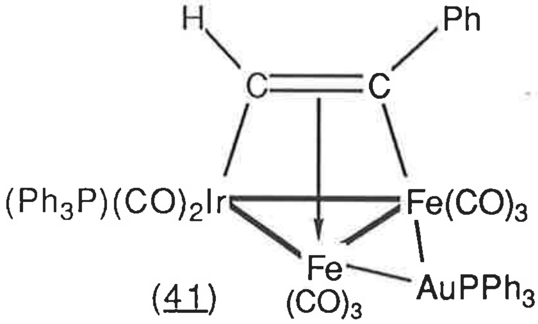


Scheme 7(b) (i) Na/Hg, thf; (ii) $K[HB(CHMeEt)_3]$;
(iii) $[O\{Au(PPh_3)_3][BF_4]$; (iv) $AuCl(PPh_3)$

Scheme 7



M = Ir (39), Rh (40)



(41)

$Au_3Fe_2Ir(C_2HPh)(CO)_7(PPh_3)_4$

(42)

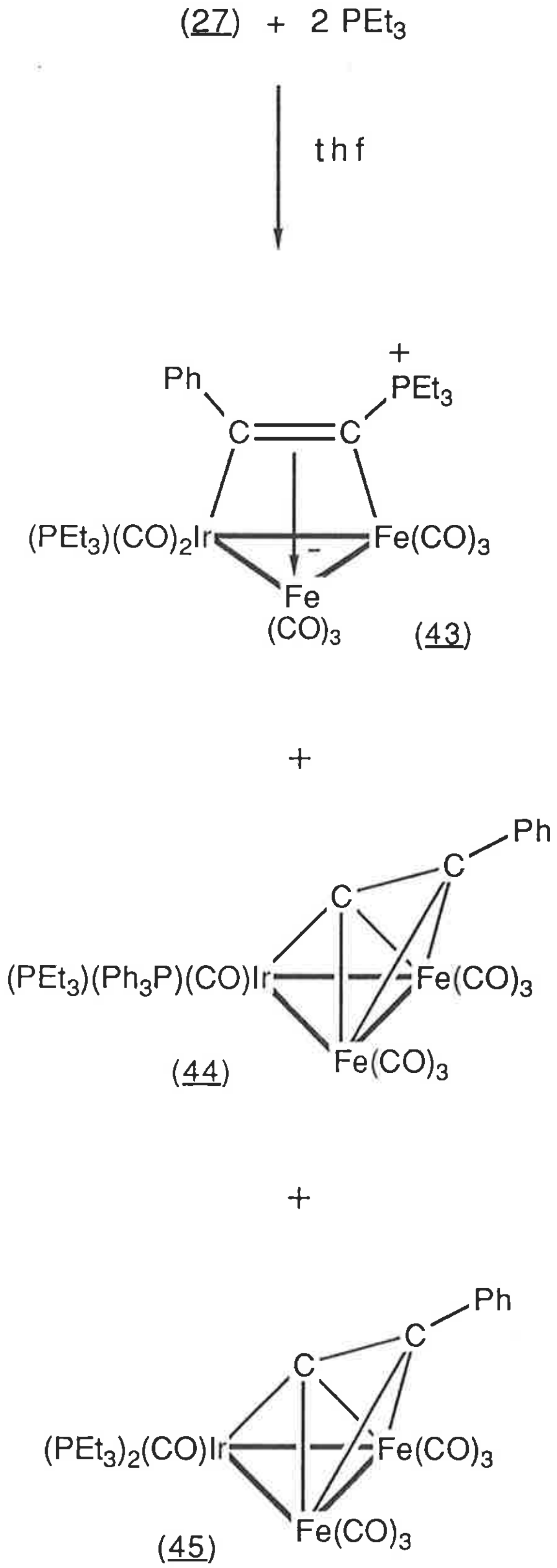
Reactions of $Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_8(PPh_3)$ (27) with some tertiary phosphines and phosphites

(a) Reaction of (1) with PEt_3

Treatment of a solution of (27) in thf at room temperature with a twofold excess of PEt_3 gave three compounds: the zwitterionic, $Fe_2Ir(\mu_3-\eta^2-PhC_2PEt_3)(CO)_8(PEt_3)$ (43) and substitution products, $Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_7(PEt_3)(PPh_3)$ (44) and $Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_7(PEt_3)_2$ (45) (Scheme 8). Complexes (43), (44) and (45) were identified by the usual spectroscopic and microanalytical techniques and in the case of (43), by X-ray structure analysis.

Structure of $Fe_2Ir(\mu_3-\eta^2-PhC_2PEt_3)(CO)_8(PEt_3)$ (43)

The molecular structure of (43) is shown in Figure 6 and Table 5 collects relevant bond distances and angles. The Ir-Fe and Fe-Fe distances in (43) are comparable to the analogous distances in the other structurally characterised Ir-Fe clusters prepared in this work, which are collected in Table 6.


(27) + 2 PEt3
thf
Ph
+
PEt3
C
C
(PEt3)(CO)2Ir
Fe(CO)3
-
Fe
(CO)3
(43)
+
Ph
C
C
(PEt3)(Ph3P)(CO)Ir
Fe(CO)3
Fe(CO)3
(44)
+
Ph
C
C
(PEt3)2(CO)Ir
Fe(CO)3
Fe(CO)3
(45)

Scheme 8

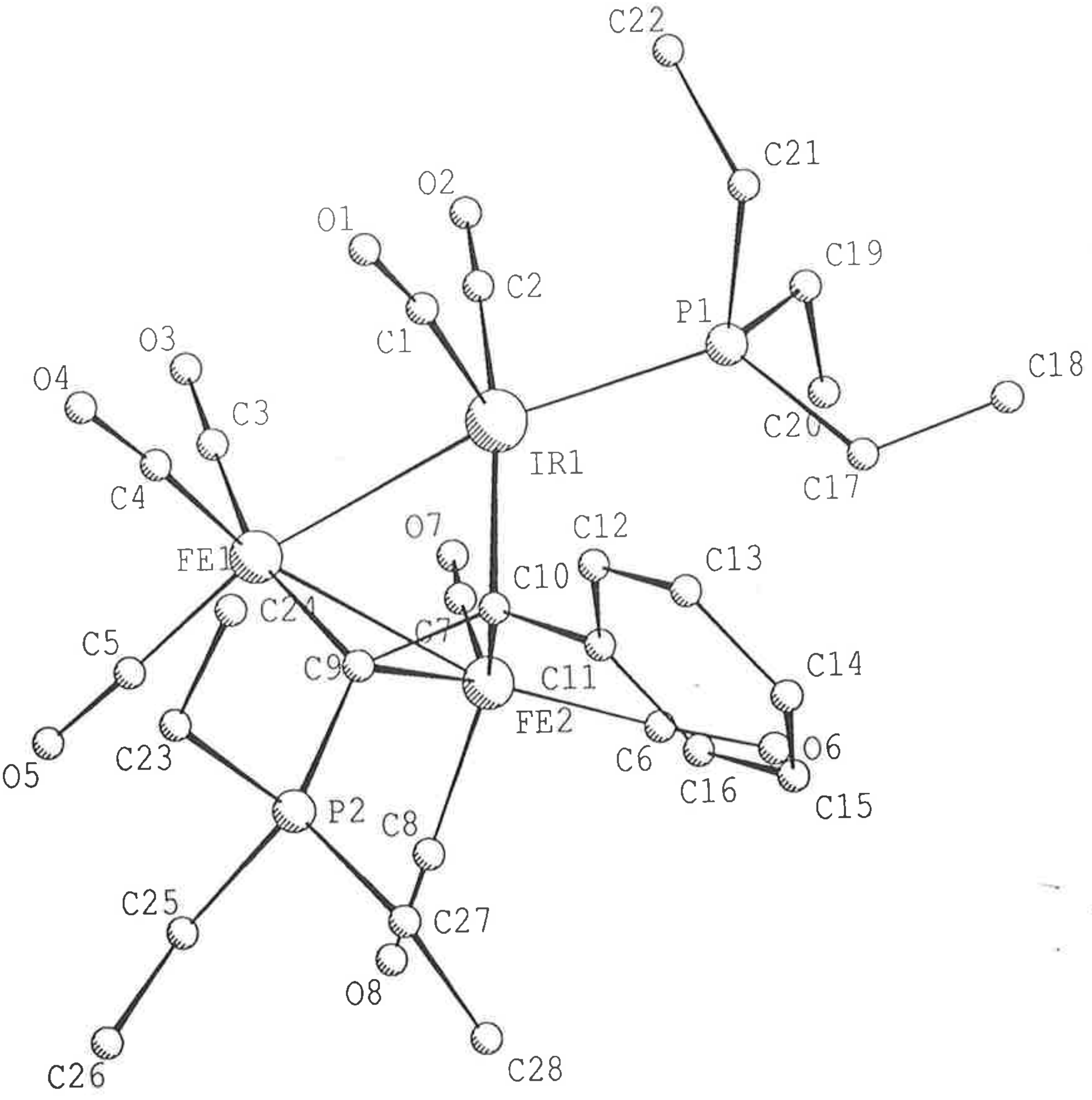


Figure 6. PLUTO plot of the molecular structure of $Fe_2Ir(\mu_3-\eta^2-PhC_2PEt_3)(CO)_7(PEt_3)$ (43) (by E.R.T. Tiekink)

Table 5. Selected bond lengths and angles for the molecular structure of (43).

Bond lengths (Å)

Fe(1)--- Ir	2.662(2)	Fe(2)--- Ir	2.642(2)
P(1) --- Ir	2.371(4)	C(10)--- Ir	2.056(15)
Fe(2)--- Fe(1)	2.538(3)	C(10)--- Fe(2)	2.086(14)
C(9) --- Fe(1)	1.858(20)	C(9) --- P(2)	1.861(18)
C(9) --- Fe(2)	2.075(20)	C(10)--- C(9)	1.478(14)

Angles (°)

Fe(2) - Ir - Fe(1)	57.2(1)	C(1) - Ir - Fe(1)	93.5(6)
P(1) - Ir - Fe(2)	110.4(1)	C(10) - Ir - Fe(2)	50.9(4)
C(10) - Ir - Fe(1)	71.2(4)	Fe(2) - Fe(1) - Ir	61.0(1)
Fe(1) - Fe(2) - Ir	61.8(1)	C(9) - Fe(2) - Fe(1)	46.2(1)
C(9) - Fe(2) - Ir	71.0(1)	C(10) - Fe(2) - Ir	49.9(4)
C(10) - Fe(2) - Fe(1)	73.5(4)	Fe(2) - C(9) - Fe(1)	80.2(1)
C(10) - C(9) - Fe(1)	113.0(6)	C(10) - C(9) - Fe(2)	69.6(6)
C(10) - C(9) - P(2)	117.1(6)	Fe(2) - C(10) - Ir	79.2(5)
C(9) - C(10) - Ir	102.3(7)	C(9) - C(10) - Fe(2)	68.8(5)
P(1) - Ir - Fe(1)	167.5(1)	C(9) - Fe(1) - Fe(2)	53.7(1)

Table 6

Selected metal-metal and metal ligand distances (Å) in new structurally characterised iron-iridium complexes obtained from this work.

Complex	Ir(1)-Fe(1)	Ir(1)-Fe(2)	Fe(1)-Fe(2)	Ir(1)-Ir(2)	Ir(2)-Fe(1)	Ir(1)-Au	Au-Au	Ir-P	Au-P	Ir-CO av.	Fe-CO av.
(27)	2.701(1)	2.693(1)	2.483(2)	-	-	-	-	2.351(2)	-	1.894	1.771
(28)	2.613(8)	-	-	2.743(4)	2.627(8)	-	-	2.33(2) 2.36(2)	-	1.90	1.77
(36)	2.705(1)	2.656(1)	2.591(1)	-	-	-	-	2.362(1)	-	1.904	1.788
(39)	2.709(3)	2.744(4)	2.501(5)	-	-	2.633(1) 2.726(1)	2.847(1)	2.287(6)	2.269(6) 2.269(6)	1.85	1.75
(43)	2.662(2)	2.642(2)	2.538(3)	-	-	-	-	2.371(4)	-	1.89	1.77

(a) Numbering schemes used in this table are as per the corresponding figures in the text.

The alkyne ligand is bonded to Fe(1) and Ir(1) via σ-interactions and to Fe(2) in a π-fashion. The acetylene-metal bonding can be considered μ^3-η^2-|| with the Fe-C (π-alkyne) bond distances [Fe(2)-C(10) 2.09(1); Fe(2)-C(9) 2.08(2)Å] lying within the range of values normally associated with trinuclear alkyne complexes.[4]
The formal σ-bond Ir(1)-C(10) [2.06(2)Å] is comparable to the analogous interactions in complex (<u>28</u>) [2.18(5), 1.92(5)Å] while the other σ-interaction in (<u>43</u>) [Fe(1)-C(9) 1.89(2)Å] does not differ from the similar distance in [$Fe_2Ni(\mu_3$-η^2-$C_2Ph_2)$-$(CO)_6(\eta$-$C_5H_5)]^-$ [1.907(5)Å][4].

Attachment of the PEt_3 moiety to Cα results in the formation of a phosphonium centre on P(2). The zwitterionic complex, $Os_3(\mu$-H)$(\mu_3$-η^2-$HC_2PMe_2Ph)(CO)_9$ contains a similar phosphonium centre 1.76(2)Å distant from the alkyne carbon to which it is attached.[24] The analogous interaction in complex (<u>43</u>) [P(2)-C(9) 1.86(2)Å] is slightly longer but comparable to the P-C(sp^2) distances [1.798-1.800(7)Å] in related phosphonium salts.[75] The C-C lengths [C(9)-C(10) 1.48(1)Å] is similar to the analogous interaction in (<u>28</u>) [1.40(2)Å] and is within the range found for μ_3-η^2-alkyne ligands. The bonding is best described as a zwitterionic contribution from the alkyne ligand with the positive charge on the phosphorus and the negative charge on Fe(1). A formal electron count indicated that Fe(1) is electron deficient, thus formulation of the negative charge on this atom fulfills its electronic requirements. It is obvious from the position of the phenyl ring on the alkyne ligand that initial attack of the phosphine was at C_α of the acetylide ligand and subsequent to that a rotation of the ligand has occurred reflecting the previously mentioned flexibility of parallel-coordinated alkyne ligands.

Recent literature[51,76] has discussed the transformation of μ_3-η^2-$\perp$ acetylide or alkyne clusters which have *closo*, trigonal bipyramidal, 6 skeletal electron pair (SEP), 5 vertex structures to μ_3-η^2-$||$ alkyne clusters with *nido*, 7 SEP, 5 vertex structures, by the addition of two electrons, either electrochemically or by the addition of a 2e donor. Opinion differs as to whether the alkyne ligand is viewed simply as a 4e-donor, which is generally accepted for *nido* μ_3-η^2-$||$ clusters, or alternatively as six- or five-electron donors and are considered to be a part of the cluster skeleton, as espoused by Wade.[77] The latter theory allows the *closo*-μ_3-η^2-$\perp$ cluster to attain a 48e count and the former theory suggests that these clusters are electronically unsaturated 46e clusters. Support for this former hypothesis was gained in the electrochemical reduction of *closo*-$Fe_3(\mu_3$-η^2-$\perp$-$RC_2R)(CO)_9$ which gives the spectroscopically characterised $[Fe_3(\mu_3$-η^2-$||$-$RC_2R)(CO)_9]^{2-}$.[76] However, Sappa[51] found that addition of a 2e donor ligand, PPh_3, to $Fe_2Ni(\mu_3$-η^2-$\perp$-$C_2Bu^t)(CO)_6(\eta$-$C_5H_5)$ gave the CO-substitution product rather than addition product resulting in alkyne re-orientation.

This transformation is probably best viewed as the simple addition of one skeletal electron pair to the *closo* 5 vertex trigonal bipyramidal cluster giving a *nido* 5 vertex octahedral cluster. This behaviour was predicted by theoretical considerations.[78 79]

Obviously, the major product (43) obtained from the reaction of PEt_3 with (27) supports the 46e hypothesis although phosphine substitution products were also observed.

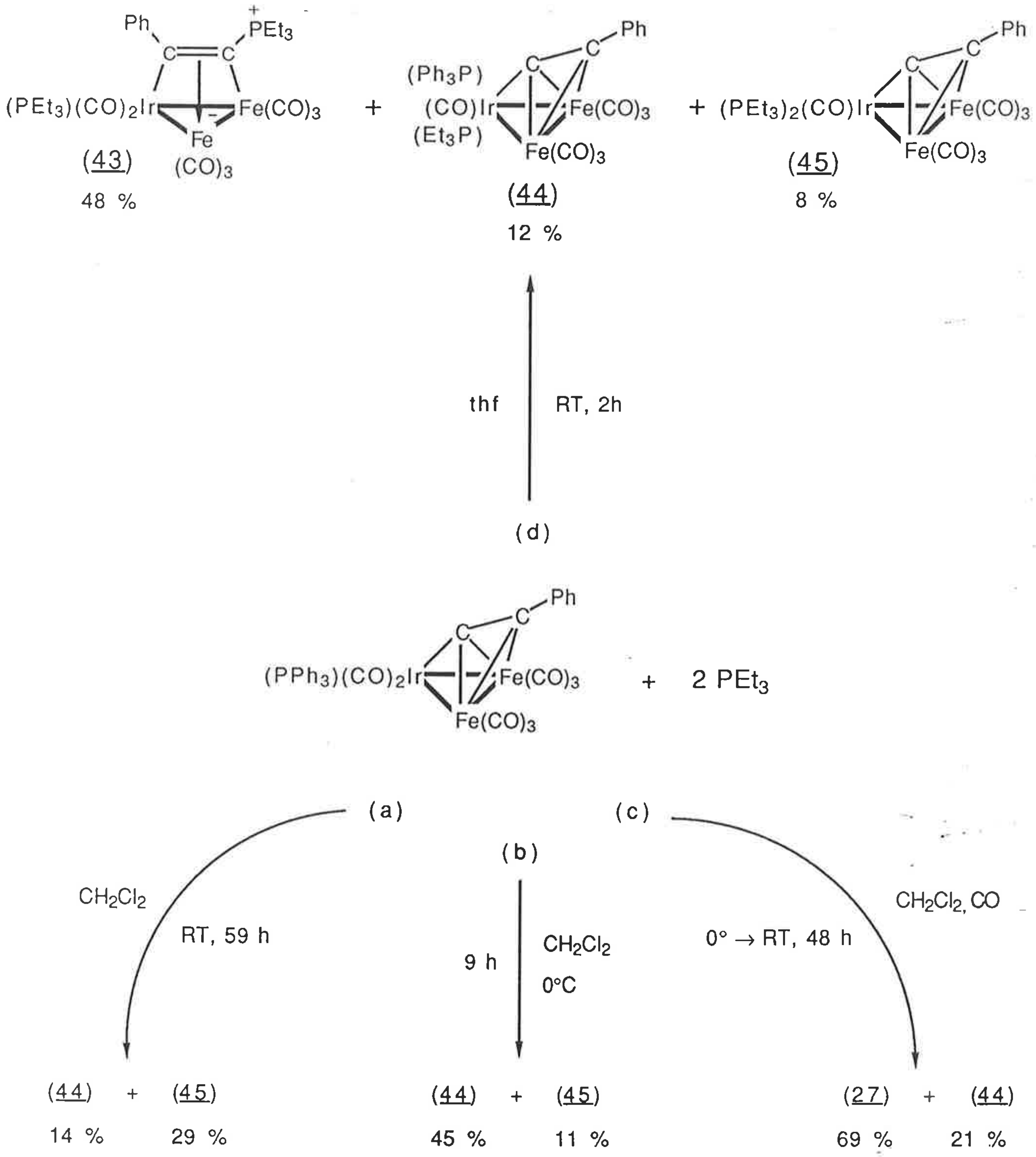
The spectroscopic data obtained for complex (43) were in accord with the determined structure.

Only terminal $\nu(CO)$ bands were found in the solution infrared spectrum of (43) giving a four-band pattern in CH_2Cl_2. From the ^1H NMR spectrum it was obvious that substitution of the PPh_3 ligand by PEt_3 had occurred. The multiplets centered on δ 0.91 and 1.13 were assigned to the CH_3 resonances of the PEt_3 moieties while the methylene groups gave multiplets centered on δ 1.43 and 1.70. The remaining multiplet at δ 7.15 was assigned to the phenyl protons of the alkyne ligand. Two resonances were observed in the $^{31}P\{^1H\}$ NMR spectrum at δ -10.2 and δ 38.3. The latter signal was assigned to the phosphonium centre on the basis of its low field position {*cf* free PEt_3 (δ -20)[80] on forming the phosphonium salt $[Et_3PCl]Cl$(δ 114)[67]} while the former signal (δ -10.2) is assigned to the Ir-PEt_3 resonance [*c.f* $\delta(IrPEt_3)$ -8.5 in $(dppe)Rh(\mu\text{-}H)_3Ir(PEt_3)_3$].[81] The FAB mass spectrum of (43) contained a molecular ion at *m/z* 866 which fragmented with the step-wise loss of eight CO groups. The strong metal free ion at *m/z* 219 was assigned to $[PEt_3C_2Ph]^+$.

The minor products from the reaction of (27) with PEt_3 were isolated by crystallisation after thin-layer chromatographic separation. Complexes (44) and (45) had very similar but distinguishable solution infrared ν(CO) spectra containing four terminal bands. The ^1H NMR spectrum of (44) contained multiplets at δ 0.91 and 1.58 which were assigned to the methyl and methylene protons, respectively, of the coordinated phosphine ligands and a multiplet at δ 7.42 which was assigned to phenyl protons of the acetylide group. The $^{31}P\{^1H\}$ NMR spectrum of (44) contained two resonances at δ 5.8 and 22.3; the lower field resonance was assigned to $Ir-PPh_3$ and the higher field resonance was assigned to $Ir-PEt_3$. A similar trend in $^{31}P\{^1H\}$ chemical shifts was observed in complexes $FeRh(\mu-PPh_2)-(CO)_4(PR_3)$ (R= Ph, Et) where assignment was aided by the observation of ^{103}Rh coupling. The ^1H NMR spectrum of complex (45) contained multiplets at δ 1.16 and 2.10 which were assigned to the PEt_3 groups and the phenyl protons resonated in the usual region. A singlet at δ 7.6 was observed in the $^{31}P\{^1H\}$ NMR spectrum of (45) and was assigned to two equivalent $IrPEt_3$ resonances. Complexes (44) and (45) gave molecular ions in their FAB mass spectra at *m/z* 982 and 838, respectively, both fragmenting through successive loss of seven CO groups.

The reaction of (27) with two equivalents of PEt_3 was performed under several different reaction conditions in an attempt to determine the mechanism operating in this system (see Scheme 9).

The best yield of complex (45) was obtained from extended reaction times but was accompanied by a poor yield of (44); no evidence of complex (43) being present was found.


Ph
PEt3
(PEt3)(CO)2Ir
Fe(CO)3
Fe
(CO)3
(43)
48 %
+
(Ph3P)
(CO)Ir
(Et3P)
Fe(CO)3
Fe(CO)3
Ph
(44)
12 %
+ (PEt3)2(CO)Ir
Fe(CO)3
Fe(CO)3
Ph
(45)
8 %
thf
RT, 2h
(d)
(PPh3)(CO)2Ir
Fe(CO)3
Fe(CO)3
Ph
+ 2 PEt3
(a)
CH2Cl2
RT, 59 h
(44) + (45)
14 % 29 %
(b)
9 h
CH2Cl2
0°C
(44) + (45)
45 % 11 %
(c)
CH2Cl2, CO
0° → RT, 48 h
(27) + (44)
69 % 21 %

Scheme 9

Similarly, complex (43) was not present after work-up of the analogous reaction at low temperature although a reasonable yield of (44) and a small amount of (45) were isolated.

It was observed in the $^{31}P\{^1H\}$ NMR spectrum of (43) that, with time, the signals attributable to (43) decreased with concomitant increase in size of a new resonance at δ 7.6 which was readily assigned to complex (45). This suggested that (43) underwent thermal conversion to (45) and this was confirmed by the pyrolysis reaction of (43) in dichloromethane which gave (45) in 80% yield, after suitable work-up. A minor product of the pyrolysis reaction was identified as the PEt_3 analogue of (27), $Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_8(PEt_3)$ (46). This complex is better prepared (*ca* 50% yield) from direct carbonylation of (45) (25 atm, 80°C, 3h). Complex (46) was identified spectroscopically, having a very similar infrared ν(CO) spectrum to that of complex (27) and containing six terminal ν(CO) bands. A high field resonance at δ -12.5 in the $^{31}P\{^1H\}$ NMR spectrum of (46) was assigned to $IrPEt_3$. Characterisation was supported by observation of a molecular ion at *m/z* 748 in the FAB mass spectrum of (46) and ions related to $[M]^+$ by step-wise loss of eight CO groups was also observed.

The conversion of the zwitterion (43) to (45) has precedent in the previously mentioned conversion of (18) - (19), where a structure determination revealed that substitution had occurred at the metal to which the vinylidene ligand was σ-bonded in the starting cluster.[22] This phenomenon was not observed with the zwitterionic alkyne cluster, $Os_3(\mu-H)(\mu_3-\eta^2-HC_2PMe_2Ph)(CO)_9$.[24]

The regiospecific substitution of a phosphine on the metal σ-bound to an acetylide ligand has been observed for $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C_2Bu^t)(CO)_9$[82] and was confirmed by subsequent structural studies. These data support the formulation of (45) as a bis-Ir substituted acetylide cluster.

The reaction of complex (27) with only one equivalent of PEt_3 in CH_2Cl_2 resulted in complexes (43), (44) and (45) being isolated in 20, 17 and 4% yields, respectively, also 58% of (27) was recovered. This result suggests that competitive reaction between phosphine addition at C of (27) and CO-substitution at the Ir atom occurs. Complex (45) is probably formed by thermal conversion of (43), although bis-substitution at the iridium cannot be ruled out. The addition reaction, however, is further complicated by PPh_3-substitution and rotation of the alkyne ligand.

Variable-Temperature $^{31}P\{^1H\}$ NMR experiment

The reaction of two equivalents of PEt_3 with complex (27) was monitored by $^{31}P\{^1H\}$ NMR over a 205 - 293K temperature range in a further effort to elucidate the mechanism operating in this reaction. The spectra obtained are given in Figure 7. The two most intense signals in the low temperature spectrum (205K) were readily assigned to the coordinated PPh_3 ligand in (27) (*ca* δ 15.0) and free PEt_3 (*ca* δ -20). However, the appearance of two low intensity signals at *ca* δ -5 and 40 demonstrated that the reaction of (27) with PEt_3 begins below 205K. These latter signals gradually increase in size with increase in temperature with concomitant decrease in size of the signals due to the starting materials. The position of the new signals suggest the formation of a complex similar to (43) [*cf*

Figure 7. Variable temperature $^{31}P\{^{1}H\}$ NMR experiment.

Reaction of $Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_8(PPh_3)$ (27) with PEt_3

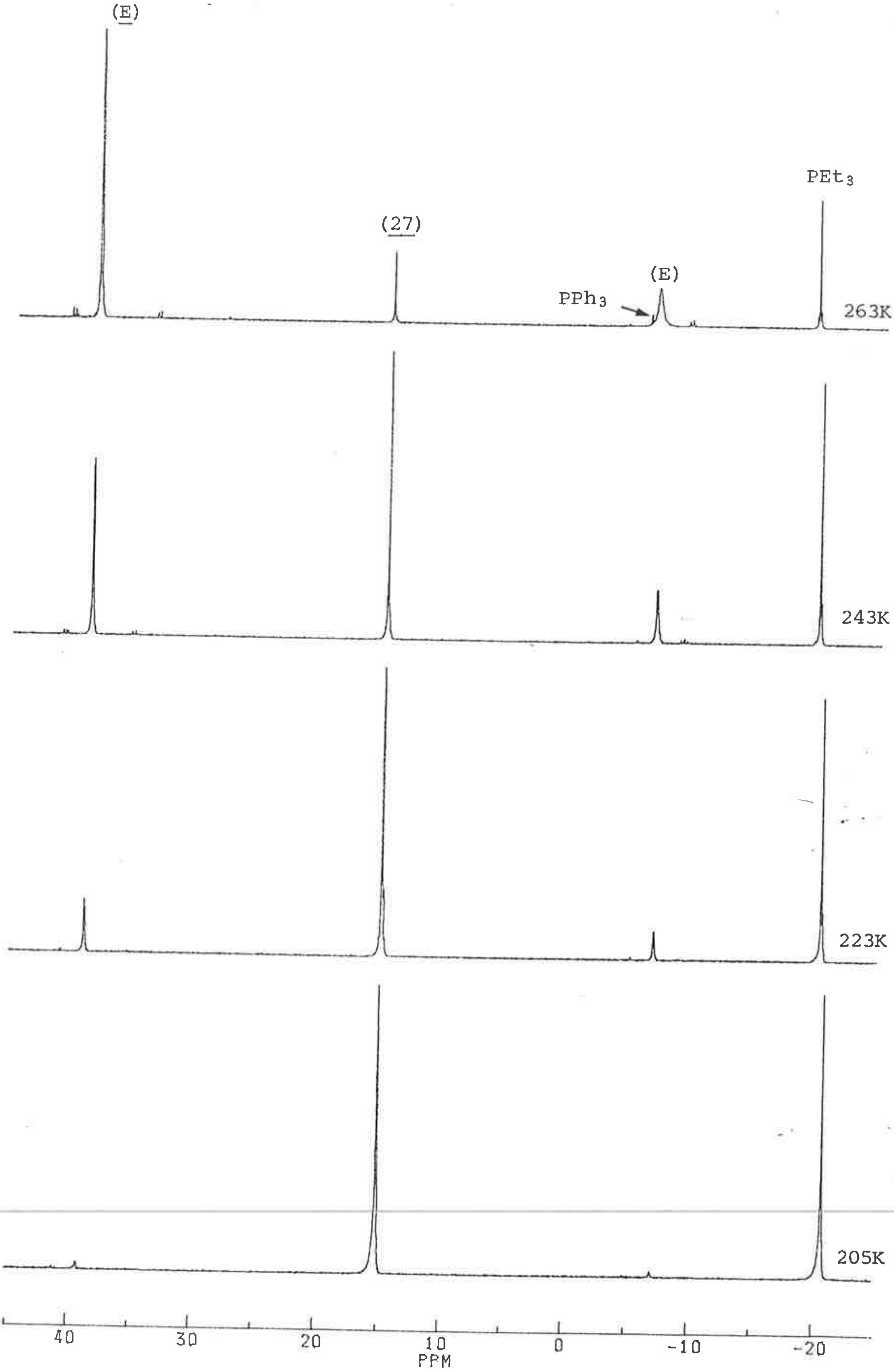
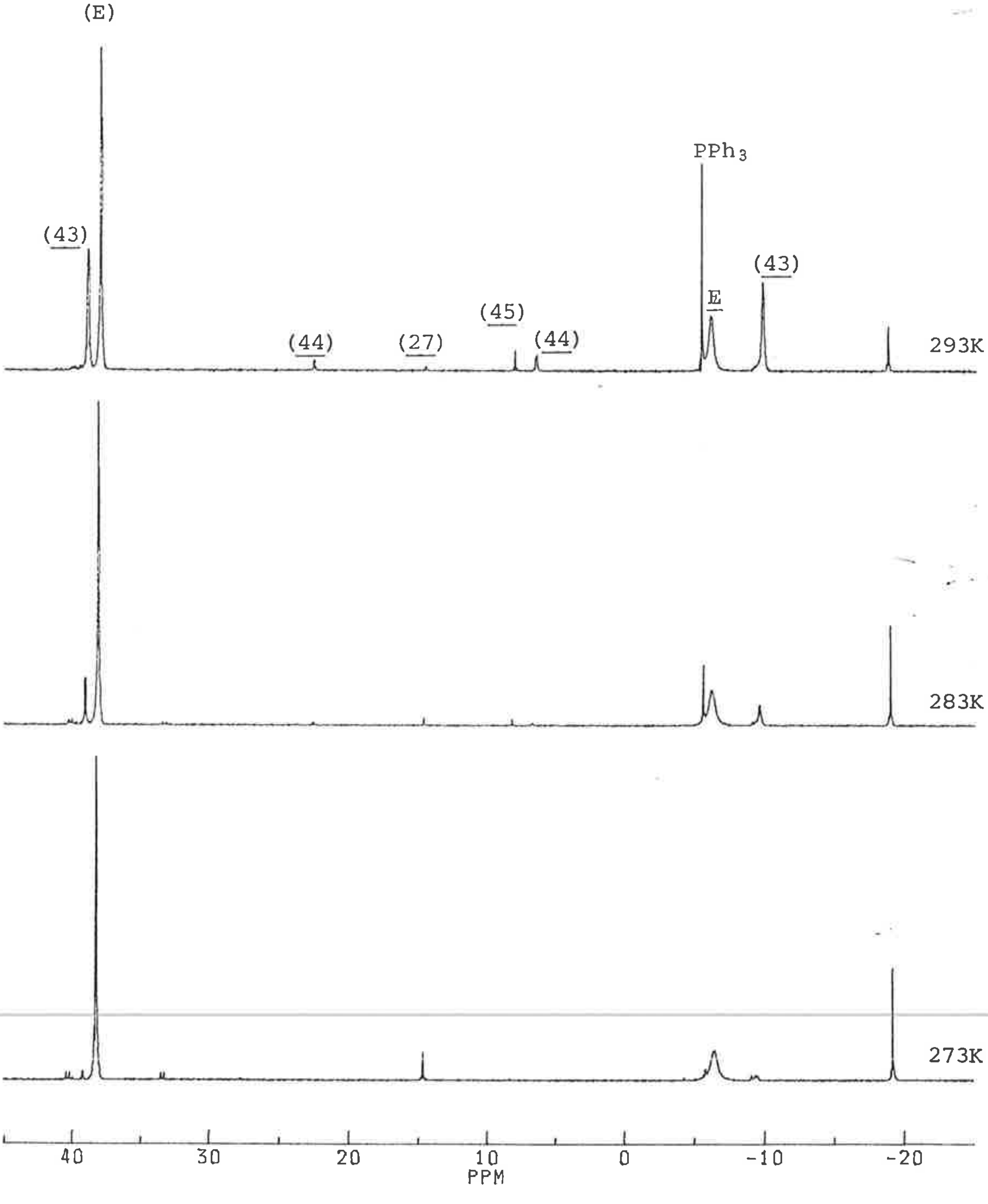
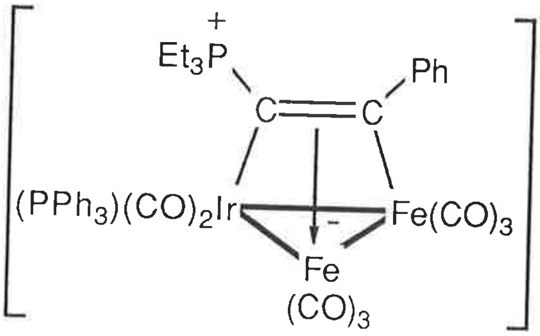


Figure 7 (continued)



δ(C_2PEt_3) 38.3; δ($IrPEt_3$) -10.2] but the abundant presence of free PEt_3 and the lack of a signal attributable to free PPh_3 suggest that the new signals arise from a similar zwitterionic intermediate, denoted (E). The structure shown below is postulated for (*E*).



(<u>E</u>)

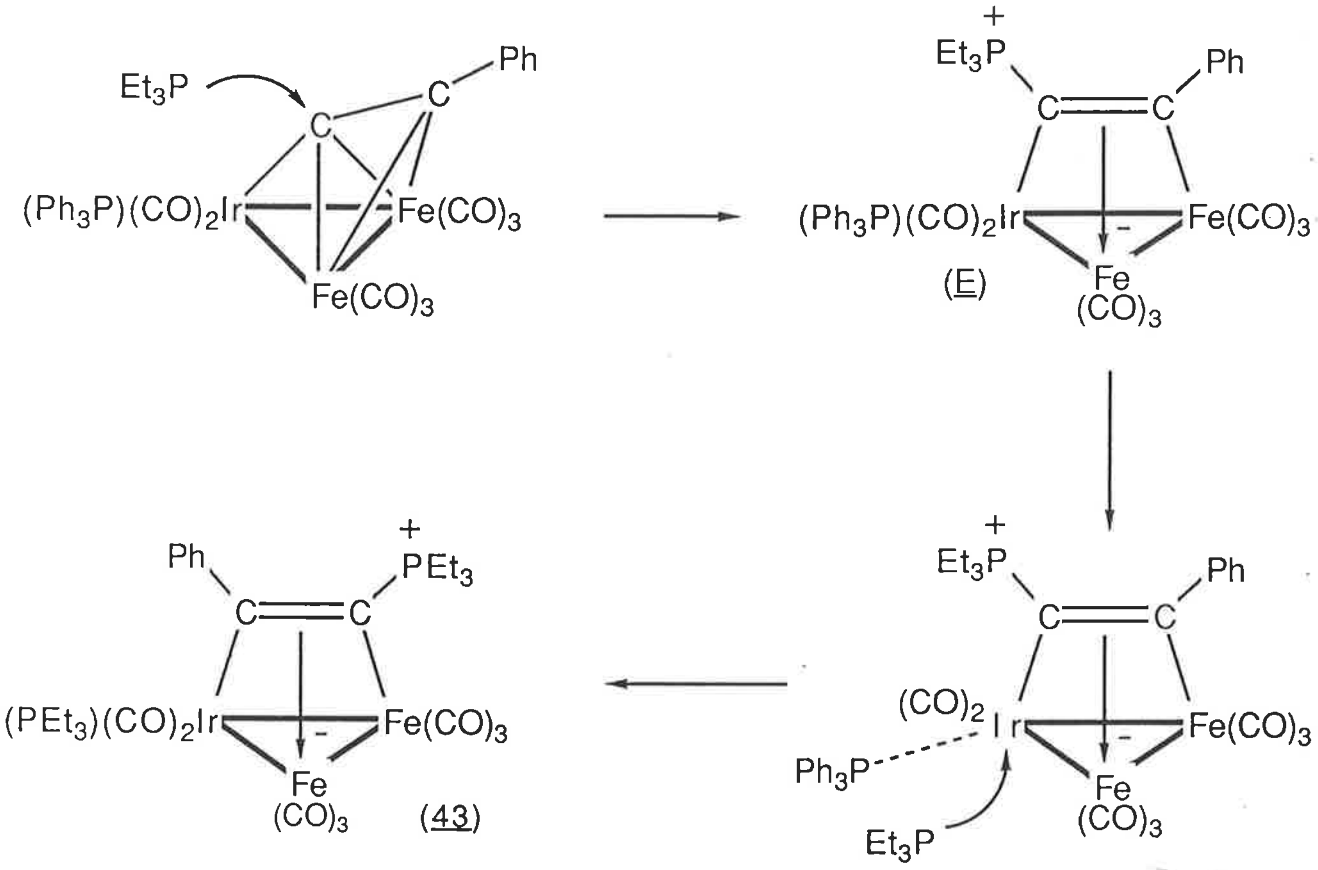
It was established previously that nucleophilic attack on complex (<u>27</u>) occurs at C_α of the acetylide ligand. The signal at *ca.* δ 40 is assigned to a phosphonium centre in (*E*) and the signal at *ca.* δ -5 is assigned to Ir-PPh_3. This latter signal broadens considerably with increasing temperature. This is probably due to a fluxional process involving the coordinated PPh_3 ligand undergoing localised site exchange as a result of steric interaction with the relatively bulky PEt_3 moiety believed to be attached to C_α in (*E*).

A signal attributable to free PPh_3 (*ca.* δ -7) is first observed at 263K, and is seen to increase in size with concomitant decrease in signal due to free PEt_3; accompanied with the appearance of signals attributable to complex (43), (only visible in expanded spectra) which are more pronounced at 273K. Further increase in temperature results in the signals due to (43) and free PPh$_3$ increasing while the resonances of (E) diminish in size. This suggests that dissociation of PPh$_3$ from iridium is concomitant with the formation of (43).

A separate ^{31}P{^{1}H} NMR study of a preparative scale reaction mixture of (27) with two equivalents of PEt$_3$ at room temperature showed negligible amounts of (E) remained after two hours. Small intensity signals attributable to complexes (44) and (45) are observed at 283K. The mechanism believed to be operating in this reaction is shown in Scheme 10.

Initial nucleophillic attack of PEt$_3$ on Cα gives intermediate (E) and as a result of steric interaction the PPh$_3$ ligand attached to Ir becomes labile allowing substitution by a second PEt$_3$ group. It is unclear at this time whether substitution precedes or is concomitant with alkyne rotation.

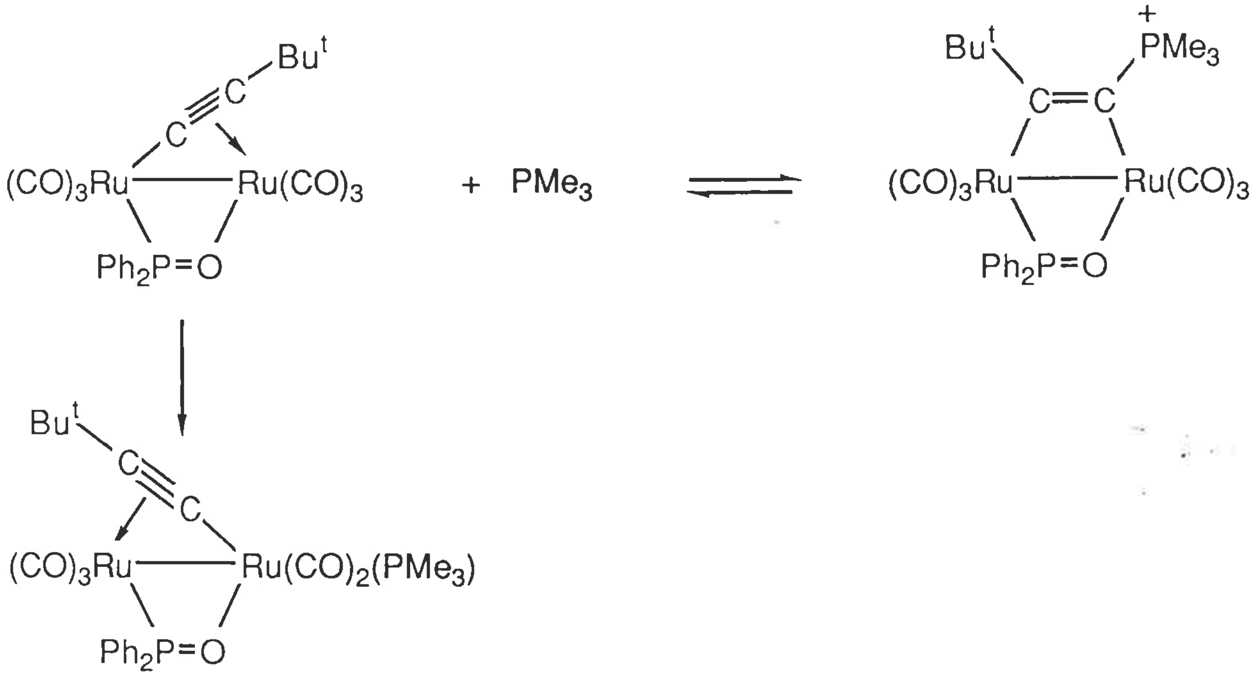
It is possible to postulate several mechanisms for the formation of (44); either intramolecular CO-substitution by PEt$_3$ attached to Cα of intermediate (E), or possibly intermolecular CO-substitution at Ir of (27) by PEt$_3$. Although, the formation of (45) can be rationalized by thermal conversion of (43), an alternative mechanism is initial CO-substitution of (E) by PEt$_3$ at Ir, followed by intramolecular substitution of PPh$_3$ by the PEt$_3$ group bound to Cα in (E). The reaction is obviously complex judging by the numerous unidentified low-intensity signals


Et$_3$P
Ph
C
C
(Ph$_3$P)(CO)$_2$Ir
Fe(CO)$_3$
Fe(CO)$_3$
+
Et$_3$P
Ph
C
C
(Ph$_3$P)(CO)$_2$Ir
Fe(CO)$_3$
-
Fe
(CO)$_3$
(E)
+
Et$_3$P
Ph
C
C
(CO)$_2$
Ir
Fe(CO)$_3$
-
Ph$_3$P
Fe
(CO)$_3$
Et$_3$P
Ph
+
PEt$_3$
C
C
(PEt$_3$)(CO)$_2$Ir
Fe(CO)$_3$
-
Fe
(CO)$_3$
(43)

Scheme 10

present in the spectra.

Recently, Carty and Fogg[83] have reported the reaction of PMe_3 with $Ru_2(\mu\text{-}\eta^2\text{-}C_2Bu^t)(\mu\text{-}Ph_2P{=}O)(CO)_6$ which gives a *ca* 1:1 ratio of the bis- and unsubstituted compounds. They suggest that the mono-substituted product is more rapidly substituted than the unsubstituted complex. $^{31}P\{^1H\}$ NMR evidence is consistent with initial nucleophilic attack at C_α of the acetylide which produces a zwitterionic two carbon bridge in which flipping of the acetylide has occurred.



The reaction of (27) with other phosphines and phosphites

It proved impossible to grow suitable crystals of either (44) or (45) in order to confirm their formulation by X-ray crystallographic methods. Therefore some other group 15 bases were tried.

(a) PMe$_2$Ph - Treatment of a solution of (27) in thf with *ca* two equivalents of PMe$_2$Ph resulted in an immediate darkening in colour. Suitable work-up gave $Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_7(PMe_2Ph)_2$ (47) in 65% yield readily identified by the usual spectroscopic and microanalytical techniques. The solution infrared spectrum of (47) was similar to those of complexes (44) and (45) and contained only four terminal ν(CO) bands. The multiplets at δ 1.97 and 7.68 in the ^{1}H NMR spectrum of (47) were assigned to the methyl resonances of the PMe$_2$Ph ligands and the phenyl groups of PMe$_2$Ph and C$_2$Ph, respectively. The $^{31}P\{^1H\}$ NMR spectrum of (47) contained a singlet at δ 16.0 which was assigned to two equivalent Ir-PMe$_2$Ph resonances. The FAB mass spectrum contained a molecular ion at *m/z* 878 which fragmented by the usual loss of CO-groups.

(b) with P(OMe)$_3$ - The reaction of (27) with two equivalents of P(OMe)$_3$ in thf at 45°C gave, after thin-layer chromatographic separation, two major products. These were identified by the usual spectroscopic and microanalytical techniques as $Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_7\{P(OMe)_3\}(PPh_3)$ (48) and $Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_7\{P(OMe)_3\}_2$ (49). The solution infrared spectra of (48) and (49) were similar to the spectra of (45) and (47) and contained only terminal ν(CO) bands. The doublet signals at δ 3.47 [*J*(PH) 8Hz] and 3.65 [*J*(PH) 13Hz] in the ^{1}H NMR spectra of (48) and (49), respectively, were assigned to the methyl groups of the P(OMe)$_3$ ligands. Both complexes gave [M]$^+$ ions in their FAB mass spectra at *m/z* 988 [(48)]

and 850 [(49)], each fragmenting with consecutive loss of seven CO groups.

The $^{31}P\{^{1}H\}$ NMR spectrum of (49) contained a singlet at δ 112.2 which was assigned to two equivalent Ir-P(OMe)$_3$ resonances.

Crystals of complex (47) were obtained but they decomposed in the X-ray beam and, therefore, were not suitable for a structural study. Well-formed single crystals of (48) or (49) could not be obtained.

There was no evidence for the formation of complexes analogous to (43) which is readily identified by its characteristic infrared ν(CO) spectrum.

The reaction of (27) with PMe$_2$Ph and P(OMe)$_3$ resulted in the bis-substitution products and for P(OMe$_3$) the mono-substitution product. For P(OMe)$_3$ this is readily explained in the decreased basicity with respect to PEt$_3$, even though P(OMe)$_3$ has a smaller cone angle than PEt$_3$. Dimethylphenylphosphine on the other hand has both smaller cone angle and is relatively more basic than PEt$_3$, but gave the bis-substitution product. Perhaps in this case nucleophilic attack at Cα and subsequent conversion to the bis-substitution product [analogous to the (43) → (45) conversion] is too rapid to isolate a zwitterionic intermediate.

^{31}P NMR studies on some iron-iridium clusters

The ^{31}P NMR data gathered in the course of this work (Table 7) proved invaluable in formulating the cluster complexes obtained. The presence of dissimilar metals allowed conclusive assignments to be made as to which metal

Table 7 $^{31}P\{^1H\}$ NMR data for mixed metal clusters obtained in this work.

Complex [a,b]	δ(Ir-PPh_3)	δ(Rh-PPh_3)	δ(Fe-PPh_3)	δ(Au-PPh_3)	δ(Ir-PEt_3)	δ(Ir-PMe_2Ph)	δ(Ir-$P(OMe)_3$)
$Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_8(PPh_3)$ (27)	14.9	-	-	-	-	-	-
$FeIr_2(\mu_3-\eta^2-PhC_2C_2Ph)(CO)_7(PPh_3)_2$ (28)	8.5 -15.2	-	-	-	-	-	-
$Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_7(PPh_3)_2$ (29)	-8.1	-	76.4	-	-	-	-
$Fe_2Ir(\mu-H)(\mu_3-\eta^2-C{=}CHPh)(CO)_8(PPh_3)$ (36)	5.1	-	-	-	-	-	-
$Au_2Fe_2Ir(\mu_4-\eta^2-C_2Ph)(CO)_7(PPh_3)_3$ (39)	30.6	-	-	42.9[e] 47.6	-	-	-
$Fe_2Ir(\mu_3-\eta^2-PhC_2PEt_3)(CO)_8(PEt_3)$ (43)	-	-	-	-	-10.2[f]	-	-
$Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_7(PEt_3)(PPh_3)$ (44)	22.3	-	-	-	5.8	-	-
$Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_7(PEt_3)_2$ (45)	-	-	-	-	7.6	-	-
$Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_7(PMe_2Ph)_2$ (47)	-	-	-	-	-	16.0	-
$Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_7\{P(OMe)_3\}_2$ (49)	-	-	-	-	-	-	112.2
$Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_8(PEt_3)$ (46)	-	-	-	-	-12.5	-	-
$Fe_2Rh(\mu_3-\eta^2-C_2Ph)(CO)_8(PPh_3)$ (32)	-	15.6[c]	-	-	-	-	-
$Au_2Fe_2Rh(\mu_4-\eta^2-C_2Ph)(CO)_7(PPh_3)_3$ (40)	-	52.6[d]	-	40.8[e] 47.8	-	-	-

(a) External reference 0.1 M HCl/0.01 M H_3PO_4 in D_2O (δ0.8)

(b) solvent CH_2Cl_2

(c) doublet, *J*(RhP) 122Hz

(d) doublet, *J*(RhP) 141Hz

(e) broad signals

(f) (C^+PEt_3) 38.3

the PR_3 ligand was attached. A metal effect was observed in M-PPh_3 resonances in which the general trend was the shift to lower field in the sequence Ir>Rh>Fe. The Rh resonances were easily assigned on the basis of observed ^{103}Rh coupling. Iridium-PEt_3 shifts ranged in value from δ -12.5 - 7.46 while Ir-PPh_3 shifts were found in the range δ -8.0 - 30.6. These ranges show considerable overlap but the Fe-PPh_3 resonance of (29) was at significantly lower field (δ 76.4). Complexes (47) and (49) had signals at δ 16.0 and 112.2, respectively, which were assigned to Ir-PMe_2Ph and Ir-P(OMe) , respectively, and reflected the differing basicity of the coordinated phosphines.

Replacement of CO in complexes (27) and (32) by $Au_2(PPh_3)_2$ resulted in downfield shifts of their respective M-PPh_3 resonances.

The phosphonium centre in (43) resonated at δ 38.3, considerably downfield from free PEt_3.

The chemical shift data obtained for the mixed-metal clusters described in this work allowed the assignment of M-PR_3 resonances. However, the utility of ^{31}P NMR studies in characterising clusters relies on having a large body of data for comparison.

CONCLUSIONS

The reaction of $Ir(C_2Ph)(CO)_2(PPh_3)_2$ and iron carbonyls has afforded new iron-iridium trinuclear clusters. In one of these clusters $FeIr_2(\mu_3\text{-}\eta^2\text{-}PhC_2C_2Ph)(CO)_7(PPh_3)_2$, an oxidative coupling of two phenylacetylide moieties has occurred.

It has been established that $Fe_2Ir(\mu_3\text{-}C_2Ph)(CO)_8(PPh_3)$ (<u>27</u>) undergoes nucleophilic attack at $C\alpha$ by H^- and PEt_3 and is substitutionally labile at the Ir towards relatively basic phosphines.

Reduction of the bridging acetylide ligand was achieved by the step-wise addition of H^-/H^+ and the products isolated were the hydrido-alkyne and hydrido-vinylidene clusters $Fe_2Ir(\mu\text{-}H)(\mu_3\text{-}HC_2Ph)(CO)_8(PPh_3)$ and $Fe_2Ir(\mu\text{-}H)(\mu_3\text{-}C{=}CHPh)(CO)_8(PPh_3)$, respectively. The reduction is also achieved by direct hydrogenation of the acetylide cluster which gives the hydrido-vinylidene cluster in comparable yield. This latter complex is also the thermal isomerisation product of the alkyne cluster which is another example of the facile alkyne vinylidene transformation on a cluster framework. The vinylidene cluster was found to be structurally similar to the congeneric Co_2Fe and Co_2Ru μ_3-vinylidene cluster prepared by Vahrenkamp and co-workers with the hydrocarbon moiety interacting in a distorted η^2-fashion with one of the less electron rich metals present in the complex.

The acetylide cluster $Fe_2Ir(\mu_3\text{-}\eta^2\text{-}C_2Ph)(CO)_8(PPh_3)$ reacted with hydride or sodium amalgam to form an anion which was aurated using $AuCl(PPh_3)$ or $[O\{Au(PPh_3)\}_3]$-$[BF_4]$ to give mono-, di- or tri-gold adducts. The Au-C interaction present in the structure of the digold cluster $Au_2Fe_2Ir(\mu_4\text{-}\eta^2\text{-}C_2Ph)(CO)_7(PPh_3)_2$ leads us to believe that the '$Au_2(PPh_3)_2$' unit may model an intermediate stage of addition of dihydrogen to the acetylide cluster.

The digold cluster was best prepared from the reaction of the neutral acetylide cluster with $[O\{Au(PPh_3)\}_3]$-$[BF_4]/[ppn][Co(CO)_4]$. This reagent is believed to be a source of '$Au_2(PPh_3)_2$' units, which are capable of replacing labile CO groups, and provides a rational route to the preparation of digold clusters.

Reactions of (27) with PEt_3 resulted in nucleophilic addition to the α-carbon of the acetylide ligand affording the zwitterionic complex $Fe_2Ir(\mu_3\text{-}\eta^2\text{-}PhC_2PEt_3)(CO)_8(PEt_3)$ in which an apparent reorientation of alkyne ligand has occurred, presumably for steric reasons. A variable temperature $^{31}P\{^1H\}$ NMR experiment suggested that this complex is formed via similar zwitterionic complex which has not yet been isolated. The addition reaction competes with CO- and PPh_3- substitution, which occur exclusively at the Ir atom to give the mono- or di- substituted clusters, $Fe_2Ir(\mu_3\text{-}\eta^2\text{-}C_2Ph)(CO)_7(PEt_3)(PPh_3)$ and $Fe_2Ir(\mu_3\text{-}\eta^2\text{-}C_2Ph)$-$(CO)_7(PEt_3)_2$. This latter complex was found to be the thermal rearrangement product of (43) suggesting that intramolecular migration of ligands from C to Ir may occur. Reaction of (27) with PMe_2Ph and $P(OMe)_3$ also gave analogous di-substituted clusters. In its reactions with tertiary

Phosphines $Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_8(PPh_3)$ resembles the previously mentioned $FeCo_2$ complex where substitution was observed exclusively at the Group 9 metal; (27) was stable towards thermally induced phosphine migration unlike the phosphine substituted Co_2Ru clusters.

The reactions of (27) clearly demonstrate the readiness of this *closo* formally 46e acetylide cluster to enter into reactions with nucleophiles to give electronically more saturated clusters.

EXPERIMENTAL

General conditions and instrumentation used were as described in Chapter 1.

Starting materials

Literature methods were used to prepare $Ir(C_2Ph)(CO)_2(PPh_3)_2$,[38] $Rh(C_2Ph)(CO)(PPh_3)_2$,[84] $AuCl(PPh_3)$,[85] $[O\{Au(PPh_3)\}_3][BF_4]$,[72] and $[ppn][Co(CO)_4]$.[86] Iron carbonyls [$Fe(CO)_5$ and $Fe_2(CO)_9$] and phosphines (PEt_3 and PMe_2Ph) were purchased from Strem Chemicals and used as received; $P(OMe)_3$ (Strem) was distilled from 4Å molecular sieves before use. Hydrogen (Commonwealth Industrial Gases) and carbon monoxide (Matheson Gas Products) were commercial products. Orthophosphoric acid (H_3PO_4,Sp.Gr.1.75) was obtained from B.D.H. Chemicals.

Syntheses

A. Reaction of $Ir(C_2Ph)(CO)_2(PPh_3)_2$

(a) with $Fe_2(CO)_9$ - A mixture of $Ir(C_2Ph)(CO)_2(PPh_3)_2$ (2140 mg, 2.45 mmol) and $Fe_2(CO)_9$ (1068 mg, 2.94 mmol) in thf (60 ml) was refluxed for 50 min. After filtration, the resulting red solution was evaporated to dryness and the residue chromatographed (Alumina, 3 x 20 cm). Elution with CH_2Cl_2-light petroleum (1:10) gave a light yellow fraction which was evaporated to dryness *in vacuo* and the residue crystallised from acetone/light petroleum to give light-yellow crystals of $Fe(CO)_4(PPh_3)$ (390 mg, 31%), m.p. 198-199°C. Infrared (cyclohexane): $\nu(CO)$ 2055m, 1985m, 1950vs cm^{-1} [Lit.[87] m.p. 201-203°C. Infrared (CCl_4): $\nu(CO)$ 2059m, 1984m, 1946vs cm^{-1}]. Further elution with CH_2Cl_2-light petroleum (1:4), followed by removal of solvent *in vacuo* and crystallisation from CH_2Cl_2/MeOH gave dark red crystals of $Fe_2Ir(\mu_3\text{-}\eta^2\text{-}C_2Ph)(CO)_8(PPh_3)$(27) (721 mg, 33%), m.p. >150°C (dec.). [Found: C, 45.82; H, 2.26; M (mass spectrometry) 892; $C_{34}H_{20}Fe_2IrO_8P$ requires C, 45.81; H, 2.26%; M 892]. Infrared (cyclohexane): ν(CO) 2072m, 2035s, 2022s, 2008s, 1981m, 1969m, 1952w; (thf): ν(CO) 2066m, 2029vs, 2015s, 1999vs, 1967m, 1957m cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 7.44 (m, Ph). $^{13}C\{^1H\}$ NMR: $\delta[CDCl_3, Cr(acac)_3]$ 99.6 (s, C_β); 128.2-134.2 (m, Ph); 165.5 (s, C_α); 174.5 (s, 2x CO, IrCO); 212.1 (s, 6x CO, FeCO). $^{31}P\{^1H\}$ NMR: $\delta(CH_2Cl_2)$ 14.9 (s, PPh_3). FAB MS: 892, $[M]^+$, 24; 864, $[M - CO]^+$, 100; 780, $[M - 4CO]^+$, 17, 752, $[M - 5CO]$, 7; 724, $[M - 6CO]^+$, 68; 696, $[M - 7CO]^+$, 54; 667, $[M - 8CO]$, 8. Elution with CH_2Cl_2-light petroleum (10:1) gave an orange fraction which was evaporated to dryness and the residue crystallised from CH_2Cl_2/MeOH to give an orange powder of $FeIr_2(\mu_3\text{-}\eta^2\text{-}PhC_2C_2Ph)(CO)_7(PPh_3)_2$ (28) (341 mg, 20%) m.p. 190° (dec.). [Found: C, 50.93; H, 2.93; M (mass spectrometry) 1363; $C_{59}H_{40}FeIr_2O_7P_2\cdot 0.5CH_2Cl_2$ requires C, 50.84; H, 2.94%; M 1363]. Infrared (CH_2Cl_2): ν(CO) 2055s, 2024s, 2006s, 1996m, 1978w, 1956w cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 5.31 (s, 1H, CH_2Cl_2); 7.41 (m, Ph). $^{31}P\{^1H\}$ NMR: $\delta(CH_2Cl_2, 205K)$ 8.46 (s, Ir-PPh_3); -15.24 (s, Ir-PPh_3). FAB MS: 1362*, $[M]$*, 22; 1334, $[M - CO]^+$, 7; 1306, $[M - 2CO]^+$, 3; 1261*, $[M - C_2Ph]^+$, 4; 1278, $[M - 3CO]^+$, 100; 1250, $[M - 4CO]^+$, 22; 1222, $[M - 5CO]^+$, 60; 1194, $[M - 6CO]^+$, 14. Reduction in volume of the supernatant and cooling (*ca* 10°C) resulted in red crystals of $Fe_2Ir(\mu_3\text{-}\eta^2\text{-}C_2Ph)(CO)_7(PPh_3)_2$ (29) (64 mg, 2%), m.p. >173° (dec.). [Found: C, 55.01; H, 3.73; *M* (mass spectrometry) 1126; $C_{51}H_{35}Fe_2IrO_7P_2$ requires C, 54.41; H, 3.13%; *M* 1126]. Infrared (CH_2Cl_2): ν(CO) 2042s, 2014sh, 1997vs, 1965m, 1941m, 1920sh cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 7.1-7.7 (m, Ph). $^{13}C\{^1H\}$ NMR: $\delta[CDCl_3, Cr(acac)_3]$ 80.0 (s, C_β); 127.3-137.4 (m, Ph); 180.1 (s, Ir-CO); 213.8 (s, 6x CO, Fe-CO); $C\alpha$ - not observed. $^{31}P\{^1H\}$ NMR: $\delta(CH_2Cl_2)$ -8.1 (s, Ir-PPh_3); 76.4 (s, Fe-PPh_3). FAB MS: 1126, $[M]^+$, 2; 1098, $[M - CO]^+$, 3; 1042, $[M - 3CO]^+$, 68; 1014, $[M - 4CO]^+$, 5; 986, $[M - 5CO]^+$, 89; 958, $[M - 6CO]^+$, 100; 930, $[M - 7CO]^+$, 34. Evaporation of the supernatant and separation of the residue by preparative tlc (acetone-light petroleum; 1:4) afforded a major dark red band (R_f 0.68), after triple development, crystallisation from CH_2Cl_2/MeOH gave red crystals of (29) (17 mg, <1%).

(b) with $Fe(CO)_5$ at ambient temperature - A solution of $Ir(C_2Ph)(CO)_2(PPh_3)_2$ (101 mg, 0.116 mmol) and $Fe(CO)_5$ (0.05 ml, 0.380 mmol) in thf (10 ml) was stirred at ambient temperature for 4 d, after which time the reaction was adjudged complete (tlc). The resulting dark orange solution was evaporated to dryness and the residue separated by preparative tlc (acetone-light petroleum, 1:4, doubly developed) to give four bands. Band 1, (R_f 0.66, yellow, trace) not identified. Band 2 (R_f 0.62, red-brown) was crystallised from CH_2Cl_2/MeOH to give dark red crystals of (27) (12 mg, 12%). Band 3 (R_f 0.46, orange) was crystallised from CH_2Cl_2/light petroleum to give orange crystals of (28) (9 mg, 12%). Band 4 (Baseline, brown) intractable. Bands 2 and 3 were identified by comparison of their i.r. ν(CO)

FAB mass and $^{31}P\{^1H\}$NMR spectra with those of authentic samples prepared above.

(c) with $Fe(CO)_5$ at elevated temperature - A solution of $Ir(C_2Ph)(CO)_2(PPh_3)_2$ (100 mg, 0.114 mmol) and $Fe(CO)_5$ (0.05 ml, 0.380 mmol) in thf (10 ml) was heated at 100°C for 30 min. Analysis of the reaction mixture (tlc) indicated that all the $Fe(CO)_5$ had been consumed leaving unreacted $Ir(C_2Ph)(CO)_2(PPh_3)_2$. A further portion of $Fe(CO)_5$ (0.05 ml, 0.380 mmol) was added and the reaction continued for a further 1 h. Evaporation and preparative tlc (acetone-light petroleum; 1:3) revealed seven bands. Band 1 (R_f 0.86, colourless) not identified. Band 2, (R_f 0.74, brown) $Fe(CO)_5$ (identified by comparison of its i.r. ν(CO) spectrum with that of an authentic sample). Band 3, (R_f 0.62, red-brown) was crystallised from CH_2Cl_2/MeOH to give dark red crystals of (27) (25 mg, 25%). Band 4, (R_f 0.52, dark red) was crystallised from CH_2Cl_2/MeOH to give dark red crystals of (29) (19 mg, 15%). Bands 5 and 6 (R_f's 0.49 and 0.46, respectively) were present in trace amounts and not identified. Bands 3 and 4 were identified by comparison of their i.r. ν(CO), FAB mass and $^{31}P\{^1H\}$ NMR spectra with those of authentic samples prepared above.

B. Reaction of $Rh(C_2Ph)(CO)(PPh_3)_2$ with $Fe_2(CO)_9$

A suspension of $Rh(C_2Ph)(CO)(PPh_3)_2$ (380 mg, 0.502 mmol) and $Fe_2(CO)_9$ (734 mg, 2.02 mmol) in thf (15 ml) was heated at 60°C for 15 min, after which time the reaction was adjudged complete (tlc). The dark red reaction mixture was cooled and filtered to remove unreacted $Fe_2(CO)_9$ (90 mg, 12%). The filtrate was evaporated to dryness and the residue separated by preparative tlc (acetone-light petroleum;

1:4) giving ten bands. Band 1, (R_f 0.85, green) $Fe_3(CO)_{12}$ (2 mg, 0.2%). Identified by comparison of its i.r. ν(CO) spectrum with that of an authentic sample.[88] Band 2, (R_f 0.62, colourless) trace, not identified. Band 3, (R_f 0.53, dark red-brown) was crystallised from CH_2Cl_2/MeOH to give dark red crystals of $Fe_2Rh(\mu_3-\eta^2-C_2Ph)(CO)_8(PPh_3)$ (32) (105 mg, 26%), m.p. 155-156°C. [Found: C, 50.59; H, 2.59; *M* (mass spectrometry) 802; $C_{34}H_{20}Fe_2O_8PRh$ requires C, 50.91; H, 2.51%; *M* 802]. Infrared (cyclohexane): ν(CO) 2068m, 2037s, 2019vs, 2011sh, 1983m, 1963sh, 1968m cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 7.32 (m, Ph). $^{13}C\{^1H\}$ NMR: $\delta[(CDCl_3, Cr(acac)_3]$ 128.1-133.7 (m, Ph); 212.1 (s, Fe-CO); the remaining carbons were not observed. $^{31}P\{^1H\}$ NMR: $\delta(CH_2Cl_2)$ 15.6 [d, *J*(RhP) 122 Hz]. FAB MS: 802, $[M]^+$, 2; 774, $[M - CO]^+$, 3; 690, $[M - 4CO]^+$, 100; 662, $[M - 5CO]^+$, 2; 634, $[M - 6CO]^+$, 32: 606 $[M - 7CO]^+$, 26; 579, $[M - 8CO]^+$, 8. The remaining bands were present in trace amounts and were not identified.

C. Reaction of $Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_8(PPh_3)$ with

(a) Sodium amalgam - A solution of (27) (163 mg, 0.183 mmol) in thf (15 ml) was added to a freshly prepared sample of sodium amalgam (*ca* 100 mg Na in 1.0 ml Hg) at -64°C and stirred for 15 min. The dark red reaction mixture was warmed to 0°C and stirred for a further 1 h. After standing for a period to allow the amalgam to settle, the solution was transferred *via* syringe to a schlenk flask and filtered through celite. The solution was then treated with H_3PO_4 (5 drops, excess) and stirred at 0°C for 10 min. The dark red solution was evaporated to dryness, the residue extracted with CH_2Cl_2/water (25:10) and filtered through phase separating paper. The organic layer was evaporated to dryness and the residue was separated by preparative tlc (acetone-CH_2Cl_2-light petroleum; 7:1:12) giving ten bands. Band 1 (R_f 0.67, red-pink) was crystallised from Et_2O/light petroleum to give red crystals of $Fe_2Ir(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}CCHPh)\text{-}(CO)_8(PPh_3)$ (36) (3 mg, 2%). Identified by comparison of its spot tlc behaviour and i.r. ν(CO) spectrum with those of a sample prepared below (p.274) Band 2 (R_f 0.61, orange-brown) crystallised from Et_2O/light petroleum to give dark red crystals of $Fe_2Ir(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(CO)_8(PPh_3)$ (37) (77 mg, 47%), m.p. >150°C (dec.). [Found: C, 45.41; H, 2.56; *M* (mass spectrometry) 894; $C_{34}H_{21}Fe_2IrO_8P$ requires C, 45.71; H, 2.48%; *M* 894]. Infrared (cyclohexane): ν(CO) 2076w, 2047s, 2023m, 2009vs, 1986m, 1970m, 1955w cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 7.81 [d, *J*(PH) 5Hz, 1H, CH]; 7.1-7.5 (m, 20H, Ph); -23.48 [d, *J*(PH) 12Hz, 1H, Fe-H]. $^{13}C\{^1H\}$ NMR: $\delta[CDCl_3, Cr(acac)_3]$ 112.5 (s, H*C*CPh); 126.5-133.4 (m, Ph); 152.8 (s, Ir-CO); 171.2 (m, Ir-CO); 210.4, 212.1, 213.0 Fe-CO). FAB MS: 894, $[M]^+$, 19; 838, $[M - 2CO]^+$, 3; 810, $[M - 3CO]^+$, 100; 782, $[M - 4CO]^+$, 33; 754, $[M - 5CO]^+$, 19; 726, $[M - 6CO]^+$, 83; 698, $[M - 7CO]^+$, 13; 670 $[M - 8CO]^+$, 4. The remaining eight bands were present in trace amounts and were not identified.

(b) with K-Selectride, $K[BH(CHMeEt)_3]$ - A solution of (27) (103 mg, 0.116 mmol) in thf (20 ml) at 0°C was treated with $K[BH(CHMeEt)_3]$ (0.16 ml of a 1.0 mol L^{-1} solution in thf, 0.16 mmol), and stirred for 60 min. The now darkened solution was warmed to ambient temperature and H_3PO_4 (3 drops, excess) was added. After stirring for a further 10 min, the solution was evaporated to dryness and the residue extracted with equal volumes of CH_2Cl_2/H_2O (10 ml).

The organic layer was separated by filtration through phase separating paper and then evaporated to dryness. The residue was separated by preparative tlc (acetone-light petroleum; 1:4) giving twelve bands. Band 1 (R_f 0.92, red-pink) gave solid $Fe_2Ir(\mu-H)(\mu_3-\eta^2-CCHPh)(CO)_8(PPh_3)$ (36) (3 mg, 3%) and was identified by comparison of its spot tlc behaviour and i.r. ν(CO) spectrum with that of an authentic sample (see p.274). Band 2 (R_f 0.86, red-brown) was crystallised from Et_2O/light petroleum giving dark red crystals of (37) (20 mg, 19%), identified by comparison of its i.r. ν(CO), ^1H NMR and FAB mass spectra with those of an authentic sample. Band 3 (R_f 0.42, orange) was crystallised from CH_2Cl_2/light petroleum (2 mg) but was not identified. Infrared (cyclohexane): ν(CO) 2084m, 2052s, 2020m, 2010s, 1994m, 1981m, 1964w cm^{-1}.

(c) with dihydrogen - A solution of (27) (48 mg, 0.054 mmol) in cyclohexane (20 ml) was hydrogenated in an autoclave (30 atm., 80°C, 7 h). The resulting brown suspension was filtered, the filtrate evaporated to dryness and the residue separated by preparative tlc (acetone-light petroleum; 1:4) to give eleven bands. Band 1 (R_f 0.87, red) gave solid $Fe_2Ir(\mu-H)(\mu_3-\eta^2-CCHPh)(CO)_8(PPh_3)$ (36) (1 mg, 2%), identified by comparison of its spot tlc behaviour and i.r. ν(CO) spectrum with those of an authentic sample (see p.274) Bands 3 and 4 (R_f's 0.75 and 0.68, respectively) contained trace amounts and were not identified. Band 5, (R_f 0.61, brown) was crystallised from CH_2Cl_2/pentane to give brown needles of (38) (12 mg), m.p. >150°C (dec.). [Found: C, 42.08; H, 2.46]. Infrared (cyclohexane): ν(CO) 2064m, 2043m, 2029s, 2009s, 1997m, 1970m, 1855m, 1820m cm^{-1}.

^{1}H NMR: δ(CD_2Cl_2) -23.0 [s(br), 1H, MH]; 7.47 (m, 20H, Ph). Not identified. Band 7, (*R*$_f$ 0.50, yellow) (1 mg). Infrared (cyclohexane): ν(CO) 2053m, 2004sh, 1999s, 1981w, 1802m, 1791m cm^{-1}. Not identified.

The remaining bands were present in trace amounts and were not identified.

D. Hydrogenation of $Fe_2Ir(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}CCHPh)(CO)_8(PPh_3)$ (36) and $Fe_2Ir(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(CO)_8(PPh_3)$ (37)

Hydrogenation of (36), under the same conditions as above resulted only in decomposition, while the hydrogenation of (37) (20 mg, 0.022 mmol) as above resulted in many bands (after preparative tlc). One of these was identified as (38) (5 mg), by spot tlc analysis and i.r. ν(CO) spectroscopy.

E. Pyrolysis of $Fe_2Ir(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(CO)_8(PPh_3)$ (37)

A solution of (37) (42 mg, 0.047 mmol) in toluene (15 ml) was heated at reflux for 1.5 h, after which time the reaction was adjudged complete (tlc). The burgundy coloured solution was evaporated to dryness and the residue separated by preparative tlc (acetone-light petroleum; 1:4) to give one major band (*R*$_f$ 0.78, red). Crystallisation from hexane gave dark red crystals of $Fe_2Ir(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}CCHPh)(CO)_8(PPh_3)$ (36) (35 mg, 83%), m.p. >200°C (dec.). [Found: C, 44.99; H, 2.53; *M* (mass spectrometry) 894; $C_{34}H_{21}Fe_2IrO_8P$ requires C, 45.71; H, 2.48%; *M* 894]. Infrared (cyclohexane): ν(CO) 2072m, 2045vs, 2022s, 2009vs, 1986s, 1971m, 1961w, 1954w cm^{-1}. ^{1}H NMR: ($CDCl_3$) -17.959 [d, *J*(PH) 13Hz, 0.5H, FeH]; -17.962 [d, *J*(PH) 13Hz, 0.5H, FeH]; 6.93 (s, 1H, CC*H*Ph); 7.35 (m, 20H, Ph). ^{13}C{^{1}H} NMR: δ[$CDCl_3$, $Cr(acac)_3$] 101.7 (s, C*C*HPh); 126.0-134.0 (m, Ph); 145.5 (s, *C*CHPh); 170.2, 176.1 (s, 2xIr-CO);

209.8, 212.7, 214.0, 247.8 (m, Fe-CO). $^{31}P\{^1H\}$ NMR: $\delta(CH_2Cl_2)$ 5.1 (s, Ir-PPh_3). FAB MS: 894, $[M]^+$, 5; 866, $[M - CO]^+$, 5; 810, $[M - 3CO]^+$, 89; 782, $[M - 4CO]^+$, 33; 754, $[M - 5CO]^+$, 22; 726, $[M - 6CO]^+$, 100; 698, $[M - 7CO]^+$, 70; 670, $[M - 8CO]^+$, 9.

F. Incorporation of gold into some mixed metal clusters

(a) the reaction of $[O\{Au(PPh_3)\}_3][BF_4]$/$[ppn][Co(CO)_4]$ with

(i) $Fe_2Ir(\mu_3\text{-}\eta^2\text{-}C_2Ph)(CO)_8(PPh_3)$ (27) - A solution of (27) (54 mg, 0.061 mmol) in thf (20 ml) at ambient temperature wastreated successively with $[O\{Au(PPh_3)\}_3][BF_4]$ (90 mg, 0.061 mmol) and $[ppn][Co(CO)_4]$ (45 mg, 0.063 mmol). After *ca* 1 min the red-brown mixture cleared to an orange solution. Evaporation and preparative tlc (acetone-light petroleum; 3.5:10) afforded two bands. Band 1 (R_f 0.53, colourless) gave solid $AuCo(CO)_4(PPh_3)$ (35 mg), identified by comparison of its i.r. ν(CO) spectrum with that of an authentic sample.[96] Band 2 (R_f 0.17, orange) was crystallised from CH_2Cl_2/MeOH to give orange crystals of $Au_2Fe_2Ir(\mu_4\text{-}\eta^2\text{-}C_2Ph)(CO)_7(PPh_3)_3$ (39) (90 mg, 83%), m.p. >150°C (dec.). [Found: C, 45.97; H, 2.74; M (mass spectrometry) 1784; $C_{69}H_{50}Au_2Fe_2IrO_7P_3$ requires C, 46.51; H, 2.83%; M 1783]. Infrared (CH_2Cl_2): ν(CO) 2018m, 1978m, 1962m, 1885w, 1876sh cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 7.33 (m, Ph). $^{13}C\{^1H\}$ NMR: $\delta[CDCl_3, Cr(acac)_3]$ 126.0-134.0 (m, Ph); 215.2 (m, Fe-CO). $^{31}P\{^1H\}$ NMR: $\delta(CH_2Cl_2)$ 30.6 (s, Ir-PPh_3); 42.8 [s(br), $AuPPh_3$]; 47.6 [s(br), $AuPPh_3$]. FAB MS: 1784, $[M + H]^+$, 6; 1699, $[M - 3CO]^+$, 50; 1671, $[M - 4CO]^+$, 2; 1643, $[M - 5CO]^+$, 47; 1615, $[M - 6CO]^+$, 74; 1587 $[M - 7CO]^+$, 3; 1324, $[M\text{-}AuPPh_3]^+$, 5; 919, $[\{Au_2(PPh_3)_2\} + H]^+$, 12; 721, $[Au(PPh_3)_2]^+$, 100; 459, $[Au(PPh_3)]^+$, 53.

(ii) $Fe_2Rh(\mu_3-\eta^2-C_2Ph)(CO)_8(PPh_3)$ (32) - A solution of (32) (40 mg, 0.050 mmol) in thf (10 ml) at 20°C was treated successively with $[O\{Au(PPh_3)\}_3][BF_4]$ (75 mg, 0.051 mmol) and $[ppn][Co(CO)_4]$ (36 mg, 0.051 mmol). The initial dark red suspension cleared to a dark brown-black solution. Evaporation and preparative tlc (acetone-light petroleum; 1:2.5) afforded one major band (R_f 0.30, black) which was crystallised from CH_2Cl_2/MeOH to give black crystals of $Au_2Fe_2Rh(\mu_4-\eta^2-C_2Ph)(CO)_7(PPh_3)_3$ (40) (68 mg, 80%), m.p. >200°C (dec.). [Found:- C, 48.84; H, 2.94; M (mass spectrometry) 1694; $C_{69}H_{50}Au_2Fe_2O_7P_3Rh$ requires C, 48.16; H, 2.98%; M 1692]. Infrared (CH_2Cl_2): ν(CO) 2008s, 1981m, 1970s, 1954s, 1904w cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 7.32 (m, Ph). $^{31}P\{^1H\}$ NMR: $\delta(CH_2Cl_2)$ 40.8 [s(br), $AuPPh_3$]; 47.8 [s(br), $AuPPh_3$]; 52.6 [d, J(RhP) 141Hz, $RhPPh_3$]. FAB MS: 1694, $[M + 2H]^+$, 4; 1609, $[M - 3CO]^+$, 17; 1524, $[M - 6CO]^+$, 28; 1496, $[M - 7CO]^+$, 13; 1234, $[M - Au(PPh_3)]^+$, 12; 721 $[Au(PPh_3)_2]^+$, 100; 459, $[Au(PPh_3)]^+$, 91.

(b) Reactions of $Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_8(PPh_3)$ (27)

(i) with $[O\{Au(PPh_3)\}_3][BF_4]$ - A solution of (27) (31 mg, 0.035 mmol) in thf (10 ml) was treated with $[O\{Au(PPh_3)\}_3][BF_4]$ (51 mg, 0.035 mmol) and the resulting suspension stirred for 24 h. The dark orange solution was evaporated to dryness and the residue separated by preparative tlc (acetone-light petroleum; 3·5:10) to give five bands. Bands 1 and 2 (R_f 0.88 and 0.85, respectively) contained trace amounts and were not identified. Band 3, (R_f 0.45, orange) was crystallised from CH_2Cl_2/MeOH to give orange crystals of (39) (15 mg, 24%). Identified by comparison of its i.r. ν(CO) and FAB mass spectra with those of an authentic sample. The remaining bands were present in trace amounts and were not identified.

(ii) with $K[BH(CHMeEt)_3]$ and $[O\{Au(PPh_3)\}_3][BF_4]$ - A solution of (27) (50 mg, 0.056 mmol) in thf (10 ml) at -64°C was treated with $K[BH(CHMeEt)_3]$ (0.1 ml of a 1.0 mol L^{-1} solution in thf; 0.10 mmol). After 5 min the red-brown solution was warmed to ambient temperature and stirred for 35 min, after which the darkened solution was cooled to -64°C. After 15 min, $[O\{Au(PPh_3)\}_3][BF_4]$ (95 mg, 0.064 mmol) was added and the mixture warmed to ambient temperature. After stirring for 30 min the solution was evaporated to dryness and the residue separated by preparative tlc (CH_2Cl_2-acetone-cyclohexane; 6:1:4) to give eight bands. Bands 1, 2 and 3 (R_f's 0.96, 0.93 and 0.90 respectively) contained only trace amounts and were not identified. Band 4 (R_f 0.86, black-brown) was further separated by preparative tlc (CH_2Cl_2-acetone-cyclohexane 6:1:4) to give two bands. Band 1 (R_f 0.72, orange) was crystallised from CH_2Cl_2/MeOH to give orange crystals of (39) (4 mg, 4%) which was identified by comparison of its i.r. ν(CO) and FAB mass spectra with those of an authentic sample. Band 2 (R_f 0.67, black) was crystallised from CH_2Cl_2/MeOH to give black needles of a compound formulated as $Au_3Fe_2Ir(C_2HPh)(CO)_7(PPh_3)_4$ (42) (24 mg, 19%), m.p. >200°C (dec.). [Found: C, 45.43; H, 2.82; M(mass spectrometry) 2242; $C_{87}H_{66}Au_3Fe_2IrO_7P_4\cdot CH_2Cl_2$ requires C, 45.40; H, 2.90%; M 2242]. Infrared (CH_2Cl_2): ν(CO) 2024w, 1988s, 1962m, 1933m, 1918w, 1893w cm^{-1}. ^1H NMR: δ($CDCl_3$) 5.31 (s, CH_2Cl_2); 7.00-7.54 (m, Ph). FAB MS: 2242, $[M]^+$, 0.4; 2214, $[M - CO]^+$, 0.5; 2186 $[M - 2CO]^+$, 0.9; 2158, $[M - 3CO]^+$, 0.9; 2130, $[M - 4CO]^+$, 16; 2102 $[M - 5CO]^+$, 10; 2074, $[M - 6CO]^+$, 2; 2048, $[M - 7CO]^+$, 0.6; 1896, $[M - 3CO - PPh_3]^+$, 6; 1868, $[M - 4CO - PPh_3]^+$, 5; 1840, $[M - 5CO - PPh_3]^+$, 21; 1812, $[M - 6CO - PPh_3]^+$, 18; 1377, $[Au_3(PPh_3)_3]^+$, 62; 1115, $[Au_3(PPh_3)_2]^+$, 14; 721, $[Au(PPh_3)_2]^+$, 100.

(iii) with sodium amalgam and $[O\{Au(PPh_3)\}_3][BF_4]$ - A solution of (27) (55 mg, 0.062 mmol) in thf (10 ml) was added to a freshly prepared sample of sodium amalgam (*ca* 100 mg Na in 1.0 ml Hg) and the mixture was stirred at ambient temperature for 1 h. The dark red solution was filtered through celite, cooled to 0°C and $[O\{Au(PPh_3)\}_3][BF_4]$ (92 mg, 0.062 mmol) was added. The mixture was warmed to ambient temperature and stirred for 1 h. Evaporation and preparative tlc (CH_2Cl_2-acetone-cyclohexane; 4:1:5) gave ten bands. Band 1 (R_f 0.76, red) was crystallised from CH_2Cl_2/light petroleum to give dark red rosettes of $AuFe_2Ir(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(CO)_8(PPh_3)_2$ (41) (20 mg, 24%), m.p. >176°C (dec.). [Found: C, 45.82; H, 2.89; *M* (mass spectrometry) 1353; $C_{52}H_{36}AuFe_2IrO_8P$ requires C, 46.24; H, 2.61%; *M* 1352]. Infrared (CH_2Cl_2): ν(CO) 2040m, 2008sh, 1999vs, 1985s, 1959m, 1923m cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 7.14-7.62 (m, 35H, Ph); 9.18 [d, *J*(PH) 13Hz, 1H, $\underline{H}C_2Ph$]. $^{13}C\{^1H\}$ NMR: $\delta(CDCl_3)$ 102.5 (s, H*C*CPh); 126.0-135.0 (m, Ph); other carbon resonances were not observed. FAB MS: 1353, $[M + H]^+$, 2; 1296, $[M - 2CO]^+$, 9; 1268, $[M - 3CO]^+$, 41; 1240, $[M - 4CO]^+$, 39; 1212, $[M - 5CO]^+$, 33; 1184, $[M - 6CO]^+$, 81; 1156, $[M - 7CO]^+$, 100; 1128, $[M - 8CO]^+$, 7; 1079, $[M - Au(C_6H_3)]^+$, 14; 894, $[(M + H) - Au(PPh_3)]^+$, 15; 721, $[Au(PPh_3)_2$, 60; 459, $[Au(PPh_3)]^+$, 46. Band 5, (R_f 0.62, orange) was crystallised from CH_2Cl_2/light petroleum to give orange crystals of (39) (14 mg, 15%). Identified by comparison of its i.r. ν(CO) and FAB mass spectra with those of an authentic sample. The remaining bands were present in trace amounts and were not identified.

(iv) with sodium amalgam and AuCl(PPh$_3$) - To a freshly prepared sample of sodium amalgam (*ca* 180 mg Na in 1.0 ml of Hg) was added a solution of (27) (82 mg, 0.092 mmol) in thf (10 ml) and the mixture stirred for 20 min. The dark red solution was transferred *via* syringe to a schlenk flask and filtered through celite into a solution of AuCl(PPh$_3$) (50 mg, 0.101mmol) in thf (10 ml) and stirred for 1 h. Evaporation and preparative tlc (acetone-light petroleum; 1:4) afforded eight bands. The major band (R_f 0.69, red-pink) was further separated by preparative tlc (CH$_2$Cl$_2$-acetone-cyclohexane; 6:1:4) to give a major band (R_f 0.72, red-pink) which was crystallised from CH$_2$Cl$_2$/heptane to afford red crystals of (41) (30 mg, 24%). Identified by comparison of i.r. ν(CO) and ^{1}H NMR spectra with those of an authentic sample. The remaining bands were present in trace amounts and were not identified.

(v) with K[BH(CHMeEt)$_3$] and AuCl(PPh$_3$) - A solution of (27) (50 mg, 0.056 mmol) in thf (10 ml) was treated with K[BH(CHMeEt)$_3$] (0.08 ml of 1mol L^{-1} solution in thf, 0.08 mmol) and stirred for 1 h at ambient temperature. The solution was cooled to 0°C and AuCl(PPh$_3$) (40 mg, 0.081 mmol) was added followed by a gradual warming to ambient temperature. After stirring for 1 h, the mixture was evaporated to dryness and the residue separated by preparative tlc (acetone-light petroleum, 1:3) to give eleven bands. Band 1, (R_f 0.064, red-brown) gave solid (27) (10 mg, 20%). Band 3, (R_f 0.53, red-pink) gave solid (41) (9 mg, 15%). Band 7, (R_f 0.38, orange) gave solid (39) (15 mg, 19%) and Band 8, (R_f 0.32, dark red-black) gave solid (42) (4 mg, 4%). These bands were identified by comparison of their i.r. ν(CO) spectra and spot tlc behaviour with those of authentic samples. The remaining bands were present in trace amounts and were not identified.

G. Reaction of $Fe_2Ir(\mu_3\text{-}\eta^2\text{-}C_2Ph)(CO)_8(PPh_3)$(27) with some tertiary phosphines and phosphites

(a) Reaction of (27) with PEt_3

(i) in thf at ambient temperature - A solution of (27) (102 mg, 0.114 mmol) in thf (20 ml) was treated with PEt_3 (0.05 ml, 0.34 mmol) and stirred at ambient temperature for 2 h, after which time the reaction was adjudged complete [the disappearance of the i.r. ν(CO) bands of (27) at 2066, 2029 and 1999cm^{-1} were monitored]. Evaporation of the dark red solution to dryness and fractional crystallisation of the residue from CH_2Cl_2/MeOH gave dark red crystals of $Fe_2Ir(\mu_3\text{-}\eta^2\text{-}PhC_2PEt_3)(CO)_8(PEt_3)$(43) (40 mg, 41%), m.p. 195-197°C. [Found: C, 38.68, H, 4.06; *M* (mass spectrometry) 866; $C_{28}H_{35}Fe_2IrO_8P_2$ requires C, 38.86; H, 4.08%; *M* 866]. Infrared (CH_2Cl_2): ν(CO) 2038s, 1985vs, 1952s, 1915s cm^{-1}. ^{1}H NMR: δ($CDCl_3$) 0.91 (m, 9H, $IrPCH_2C\mathit{H}_3$); 1.13 (m, 9H, $C\text{-}PCH_2C\mathit{H}_3$); 1.43 (m, 6H, $IrPC\mathit{H}_2CH_3$); 1.70 (m, 6H, $CPC\mathit{H}_2CH_3$); 7.15 (m, 5H, Ph). $^{31}P\{^1H\}$ NMR: δ(CH_2Cl_2) -10.2 (s, Ir-PEt_3); 38.3 (s, C_2PEt_3). FAB MS: 866, $[M]^+$, 6; 839, $[(M - CO) + H]^+$, 5; 810, $[M - 2CO]^+$, 12; 782, $[M - 3CO^+$, 100; 754, $[M - 4CO]^+$, 66; 726, $[M - 5CO]^+$, 12; 698, $[M - 6CO]^+$, 25; 770, $[M - 7CO]^+$, 27; 742, $[M - 8CO]^+$, 26; 219, $[PEt_3C_2Ph]^+$, 81. The supernatant was evaporated to dryness and the residue separated by preparative tlc (acetone-light petroleum; 1:3) to give nine bands. Band 1, (R_f 0.94, colourless) gave solid PPh_3. Identified by tlc and mixed melting point. Band 2, (R_f 0.58, red-pink) was crystallised from CH_2Cl_2/MeOH to give dark red crystals of (43) (7 mg, 7%). Identified by comparison of its i.r. ν(CO) and FAB mass spectra with those of an authentic sample. Band 3, (R_f 0.55, red-brown) was crystallised from

CH_2Cl_2/MeOH to give dark red crystals of $Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_7(PEt_3)(PPh_3)$ (44) (12 mg, 11%), m.p. 194-195°C. [Found: C, 47.41; H, 3.64; *M* (mass spectrometry) 982; $C_{39}H_{35}Fe_2IrO_7P_2$ requires C, 47.72; H, 3.59%; *M* 982]. Infrared (CH_2Cl_2): ν(CO) 2030s, 1983vs(br), 1945sh, 1932m cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 0.91 (m, 9H, PCH_2CH_3); 1.58 (m, 6H PCH_2CH_3); 7.42 (m, 20H, Ph). $^{31}P\{^1H\}$ NMR: $\delta(CH_2Cl_2)$ 5.8 (s, Ir-PEt_3); 22.3 (s, Ir-PPh_3). FAB MS: 982, $[M]^+$, 6; 954, $[M - CO]^+$, 3; 898, $[M - 3CO]^+$, 100; 870, $[M - 4CO]^+$, 4; 842, $[M - 5CO]^+$, 6; 814, $[M - 6CO]^+$, 90; 786, $[M - 7CO]^+$, 11; 758, $[M - 8CO]^+$, 7. Band 4, (R_f 0.49, brown-red) was crystallised from CH_2Cl_2/MeOH to give dark-red crystals of $Fe_2Ir(\mu_3-\eta^2-C_2Ph)(CO)_7(PEt_3)_2$ (45) (8 mg, 8%), m.p. >150°C (dec.). [Found: C, 38.67; H, 4.17; *M* (mass spectrometry) 838; $C_{27}H_{35}Fe_2IrO_7P_2$ requires C, 38.72; H, 4.21%; *M* 838]. Infrared (CH_2Cl_2): ν(CO) 2027s, 1978vs(br), 1939sh, 1922m cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 1.16 (m, 18H, PCH_2CH_3); 2.10 (m, 12H, PCH_2CH_3); 7.50 (m, 5H, Ph). $^{31}P\{^1H\}$ NMR: $\delta(CH_2Cl_2)$ 7.6 (s, Ir-PEt_3). FAB MS: 838, $[M]^+$, 22; 810, $[M - CO]^+$, 45; 782, $[M - 2CO]^+$. 40; 754, $[M - 3CO]^+$, 30; 726, $[M - 4CO]^+$, 100; 698, $[M - 5CO]^+$, 31; 670, $[M - 6CO]^+$, 35; 642, $[M - 7CO]^+$, 81. The remaining bands were present in trace amounts and were not identified.

(ii) in CH_2Cl_2 at ambient temperature - A solution of (27) (40 mg, 0.045 mmol) in CH_2Cl_2 (5 ml) was treated with PEt_3 (0.9 ml of a *ca* 0.1 mmol ml^{-1} solution in CH_2Cl_2, 0.09 mmol) and the resulting dark red solution was stirred for 59 h. Evaporation and preparative tlc (acetone-light petroleum; 1:4) afforded eight bands. Band 1, (R_f 0.42, red-brown) was crystallised from CH_2Cl_2/MeOH to give dark red crystals of (44) (6 mg, 14%). Band 2, (R_f 0.36, brown-red) was crystallised from CH_2Cl_2/MeOH to give dark red crystals of (45) (11 mg, 29%). Bands 1 and 2 were identified by comparison of their i.r. ν(CO) and ^{1}H NMR spectra with those of authentic samples. The remaining bands were present in trace amounts and were not identified.

(iii) in CH_2Cl_2 at 0°C - A solution of (30 mg, 0.034 mmol) in CH_2Cl_2 (5 ml) at 0°C was treated with PEt_3 (0.75 ml of *ca* 0.1 mmol ml^{-1} solution in CH_2Cl_2, 0.075 mmol) and stirred for 9 h. The dark red solution was evaporated to dryness (at 0°C) and the mixture separated by preparative tlc (acetone-light petroleum; 1:4) to give six bands after double development. Band 1 (R_f 0.60, red-brown) was crystallised from CH_2Cl_2/MeOH to give dark red crystals of (44) (15 mg, 45%). Band 2, (R_f 0.54, brown-red) was crystallised from CH_2Cl_2/MeOH to give dark red crystals of (45) (3 mg, 11%). Bands 1 and 2 were identified by comparison of their i.r. ν(CO) spectra and spot tlc behaviour with those of authentic samples. The remaining bands were present in trace amounts and were not identified.

(iv) in CH_2Cl_2 at 0°C under a carbon monoxide atmosphere - A solution of (27) (26 mg, 0.029 mmol) in CH_2Cl_2 (20 ml) saturated with CO was treated with PEt_3 (0.65 ml of *ca* 0.1 mmol ml^{-1} solution in CH_2Cl_2, 0.065 mmol) and stirred under a CO atmosphere for 1 h. The solution was warmed to ambient temperature and stirred for 48 h. Evaporation and preparative tlc (acetone-light petroleum; 1:3) gave two bands. Band 1 (R_f 0.55, brown-red) gave solid (27) (18 mg, 69%). Band 2, (R_f 0.41, brown-red) was crystallised from CH_2Cl_2/MeOH to give dark-red crystals of (44) (6 mg, 21%). Bands 1 and 2 were identified by comparison of their i.r. ν(CO) and FAB mass spectra with those of authentic samples.

(v) in CH_2Cl_2 with one equivalent of PEt_3 - A solution of (27) (60 mg, 0.067 mmol) in CH_2Cl_2 (10 ml) was treated with PEt_3 (0.01 ml, 0.068 mmol) and stirred for 2 h. Evaporation and preparative tlc (acetone-light petroleum; 1:4) gave three bands. Band 1 (R_f 0.67, red) was crystallised from CH_2Cl_2/MeOH to give dark-red crystals of (27) (35 mg, 58%). Band 2 (R_f 0.53, red) was further separated by preparative tlc (CH_2Cl_2-acetone-cyclohexane; 40:15:65) giving three bands. Band 1 (R_f 0.79, brown-red) gave solid (44) (11 mg, 17%). Band 2 (R_f 0.72, red) gave solid (43) (12 mg, 20%). Band 3 (R_f 0.66, red) gave solid (45) (2 mg, 4%). Bands 1, 2 and 3 were identified by comparison of their $^{31}P\{^1H\}$ NMR and i.r. ν(CO) spectra with those of authentic samples.

(b) Reaction of (27) with PMe_2Ph - A solution of (50 mg, 0.056 mmol) in thf (20 ml) was treated with PMe_2Ph (0.12 ml of *ca* 1 mmol ml^{-1} solution in thf, 0.12 mmol). An immediate darkening in colour to deep red was observed. After 40 m the solution was evaporated to dryness and the residue chromatographed (Florisil, 1 x 10 cm). Elution with light petroleum removed traces of unreacted PMe_2Ph. Further elution with acetone-light petroleum (1:4) gave a red eluate. Removal of the solvent *in vacuo* and crystallisation of the residue from CH_2Cl_2/heptane afforded dark red crystals of $Fe_2Ir(\mu_3\text{-}\eta^2\text{-}C_2Ph)(CO)_7(PMe_2Ph)_2$ (47) (32 mg, 65%) m.p. 185-186°C. [Found C, 42.16; H, 3.12; *M* (mass spectrometry) 878, $C_{31}H_{27}Fe_2IrO_7P_2$ requires C, 42.43; H, 3.10%; *M* 878]. Infrared (CH_2Cl_2): ν(CO) 2032m, 1985s(br), 1948sh, 1930w cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 1.97 (m, 12H, PCH_3Ph); 7.68 (m, 15H, Ph). $^{31}P\{^1H\}$ NMR: $\delta(CH_2Cl_2)$ 16.0 (Ir-PMe_2Ph). FAB MS: 878, $[M]^+$, 8; 850, $[M - CO]^+$, 8; 794, $[M - 3CO]^+$, 100; 738, $[M - 5CO]^+$, 74; 710, $[M - 6CO]^+$, 53; 682, $[M - 7CO]^+$, 21.

(c) Reaction of (27) with $P(OMe)_3$ - A solution of (50 mg, 0.056 mmol) in thf (20 ml) was treated with $P(OMe)_3$ (0.80 ml of 0.113 mmol ml^{-1} solution in thf, 0.090 ml) and stirred at ambient temperature for 2 h. The solution was heated to 45°C and stirred for a further 17 h, during which time the solution colour changed from red-brown to orange. Evaporation and preparative tlc (acetone-light petroleum, 1:4) gave five bands of which the two major bands were isolated. Band 1, (R_f 0.5, red) was crystallised from Et_2O/light petroleum to give red crystals of Fe_2Ir-

(μ_3-η^2-C_2Ph)(CO)$_7$[P(OMe)$_3$](PPh$_3$) (48) (6 mg, 11%), m.p. 197-199°C. [Found: C, 43.12; H, 3.05; *M* (mass spectrometry) 988; $C_{36}H_{29}Fe_2IrO_{10}P_2$ requires C, 43.79; H, 2.96; *M* 988]. Infrared (cyclohexane): ν(CO) 2044s, 1999vs, 1965w, 1950m cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 3.47 [d, *J*(PH) 8Hz, 9H, POCH$_3$]; 7.41 (m, 20H, Ph). FAB MS: 988, [*M*]$^+$, 3; 960, [*M* - CO]$^+$, 4; 904, [*M* - 3CO]$^+$, 94; 845, [*M* - 5CO]$^+$, 26; 820, [*M* - 6CO]$^+$, 100; 792, [*M* - 7CO]$^+$, 10. Band 2, (R_f 0.45, orange) was crystallised from Et$_2$O/light petroleum to give orange crystals of Fe_2Ir(μ_3-η^2-C_2Ph)(CO)$_7$[P(OMe)$_3$]$_2$ (49) (34 mg, 72%), m.p. 203-205°C. [Found: C, 29.58; H, 2.76; *M* (mass spectrometry) 850; $C_{21}H_{23}Fe_2IrO_{13}P_2$ requires C, 29.70; H, 2.73%, *M* 850]. Infrared (cyclohexane): ν(CO) 2048m, 2006sh, 1998s, 1964w, 1949m cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 3.65 [d, *J*(PH) 13Hz, 18H, POCH$_3$]; 7.55 (m, 5H, Ph). ^{31}P{^{1}H} NMR: δ(CH$_2$Cl$_2$) 112.2 [s, Ir-P(OMe)$_3$]. FAB MS: 850, [*M*]$^+$, 6; 822, [*M* - CO]$^+$, 18; 794, [*M* -2CO]$^+$, 19; 766, [*M* - 3CO]$^+$, 6; 748, [*M* - 4CO]$^+$, 54; 720, [*M* - 5CO]$^+$, 100; 692, [*M* - 6CO]$^+$, 63; 651, [*M* - 7CO]$^+$, 18.

H. Pyrolysis of Fe_2Ir(μ_3-η^2-PhC_2PEt_3)(CO)$_8$(PEt$_3$)

A solution of (43) (20 mg, 0.013 mmol) in CH$_2$Cl$_2$ (20 ml) was heated at reflux, while being purged with nitrogen, for 8 h. Evaporation and preparative tlc afforded four bands. Band 1 (R_f 0.88, orange) gave solid Fe_2Ir(μ_3-η^2-C_2Ph)-(CO)$_8$(PEt$_3$) (46) (2 mg, 12%). Identified by comparison of its i.r. ν(CO) and FAB mass spectra with those of an authentic sample (see below). Band 2 (R_f, 0.78, red) was not identified. Infrared (CH$_2$Cl$_2$): ν(CO) 2029s, 1983vs(br), 1942sh, 1931w cm^{-1}. Band 3, (R_f 0.71, red) was crystallised from CH_2Cl_2/MeOH to give dark red crystals of (45) (15 mg, 80%). Identified by comparison of its i.r. ν(CO) and FAB mass spectra with those of an authentic sample.

I. Carbonylation of $Fe_2Ir(\mu-\eta^2-C_2Ph)(CO)_7(PEt_3)_2$

A solution of (45) (20 mg, 0.023 mmol) in cyclohexane (20 ml) was carbonylated in an autoclave (25 atm, 80°C, 3 h) and the resulting brown-orange solution was filtered, evaporated to dryness and the residue separated by preparative tlc (acetone-light petroleum; 1:4) to give six bands. Only the major band (R_f 0.58, orange) was isolated and gave solid $Fe_2Ir(\mu_3,\eta^2-C_2Ph)(CO)_8(PEt_3)$ (46) (8 mg, 47%), m.p. >150°C (dec.). Infrared (CH_2Cl_2): (CO) 2064s, 2024vs, 1994s, 1963m, 1950m, 1934sh cm^{-1}. $^{31}P\{^1H\}$ NMR: δ(CH_2Cl_2) -12.5 (s, Ir-PEt_3). FAB MS: 748, $[M]^+$, 28; 720, $[M - CO]^+$, 62; 692, $[M - 2CO]^+$, 16; 664, $[M - 3CO]^+$, 100; 636, $[M - 4CO]^+$, 78; 608, $[M - 5CO]^+$, 13; 580, $[M - 6CO]^+$, 24; 552, $[M - 7CO]^+$, 31; 524, $[M - 8CO]$, 9.

J. ^{31}P NMR experiment. Variable temperature study (205K-293K) of the reaction of (27) with two equivalents of PEt_3

A solution of (27) (88 mg, 0.099 mmol) in CH_2Cl_2 (2 ml), cooled in a liquid nitrogen bath, was treated with PEt_3 (0.030 ml, 24 mg, 0.203 mmol). The 10 mm NMR tube which was used for this reaction was then transferred to the probe of NMR spectrometer (see General Experimental Conditions) which had been previously cooled to 205K.

At each temperature, between 1500 - 2001 transients were collected over 8192 points, with a sweep width of 9804 Hz. The spectra were referenced to internal PEt_3 (δ - 19.0).

At the end of the NMR experiment, the dark red solution was evaporated to dryness and the residue fractionally crystallised from CH_2Cl_2/MeOH, to give dark red crystals of (43)(58 mg, 68%), which was identified by comparison of its i.r. ν(CO) and FAB spectra with those of an authentic sample prepared as above. The supernatant was evaporated to dryness and the residue separated by preparative tlc (acetone-light petroleum; 1:3) to give 12 bands which were present in trace amounts and were not identified.

X-ray structure determination of (39)

General techniques and details given below apply to the structure of (39) , determined by the author.

A suitable crystal (0.11 x 0.18 x 0.11 mm) of (39) was grown from CH_2Cl_2/EtOH by solvent diffusion at 10°C and was mounted on a glass fibre using cyanoacrylate 'super glue'.

Lattice parameters were determined from a least squares fit to the setting angles of 25 high angle reflections on an Enraf-Nonius CAD-4F four-circle diffractomater[89] using graphite monochromated Mo$K\alpha$ (λ = 0.7107Å). The crystal was found to be monoclinic with systematic absences hkl:$h+k$=2n and $h0l$:l=2n defining the space group Cc (C_s^4 No.9) or $C2/c$ (C_{2h}^6,No.15); subsequent analysis confirmed Cc as the true space group.

Crystal data $Au_2Fe_2Ir(\mu_4\text{-}\eta^2\text{-}C_2Ph)(CO)_7(PPh_3)_3\cdot EtOH$

M 1828.0, monoclinic, space group Cc (C_s^4 , No.9), a = 12.956(1), b = 26.604(4), c =19.190(2)Å, β = 97.14 (3)°, V = 6563.1Å^3, Dcalc = 1.850 gcm^{-3}, Z = 4, F (000) = 3511 T = 293(2) K.

Intensity data were measured using a $\omega:2\theta$ scan technique measured in the range $-13 \leq h \leq 13$, $0 \leq k \leq 20$, $-20 \leq l \leq 1$. Three standard reflections $(20\bar{2}, 53\bar{2}, 5\bar{3}\bar{2})$ were monitored every hour of X-ray exposure time, to check for crystal and machine stability. Data reduction and application of Lorentz and polarization corrections were undertaken with the programs PREABS[90] and PROCES.[90] An analytical absorption correction was applied using the SHELX-76[91] system of programs, θ range 1.5-22.5°; of 4616 measured reflections 4508 were found to be unique, with $\underset{\sim}{I} \geq 2.5\sigma(\underset{\sim}{I})$, μ 69.87 cm^{-1}, maximum and minimum transmission factors 0.2964 and 0.1983, R and R_w values 0.0476 and 0.0467. Reflections with intensities $\underset{\sim}{I} \geq 2.5\sigma(\underset{\sim}{I})$ were rejected; while equivalent reflections were averaged.

The metal atom positions were found, using direct methods (SHELXS-86)[92] and remaining non-hydrogen atoms were located by means of Fourier difference maps. The structure was refined by full-matrix least squares procedures in which the function $\Sigma\, w\, \Delta^2$ was minimized, where w was the weight applied to each reflection and $\Delta = \left\| F_o \right| - \left| F_c \right\|$. Phenyl rings were included as hexagonal rigid groups (C-C 1.39Å) with isotropic thermal parameters and anisotropic thermal parameters were used for the core atoms [Au,Fe,Ir,-C(8),C(9) and P]. The heavy atom positions were found to be disordered such that about each atom two residual electron density peaks were located approximately 1Å from the parent atom. These were modelled successfully with 2% occupancy factors. Hydrogen atoms were placed in calculated positions (0.97Å) with common group thermal parameters.

The solvent molecule of crystallisation, EtOH, was refined with constrained bond lengths (C-O 1.45, C-C 1.53Å) owing to high thermal motion associated with the molecule.

In the final refinement cycles the following weighting was employed: $w = [\sigma^2(I) + |g| F^2]^{-1}$, at convergence $g = 0.005857$, $R = 0.0476$ and R_w 0.0467. The SHELX[91] procedure UNDO was used to determine the absolute configuration (R_g 0.0713 cf. R_g 0.0606 for the preferred configuration. Bond lengths, valence angles, non bonding distances and their standard deviations were all calculated using SHELX 76.[91] least squares planes and dihedral angles were calculated using the program LSPLAN[93] and diagrams from PLUTO.[94] All programs were implemented on the VAX11/785 computing system at the University of Adelaide. Neutral atom scattering factors for C, H, O and P were those listed in SHELX-76[91] and those for Au, Ir and Fe were obtained from the International Tables, the values being corrected for anomalous dispersion.

The listings of observed (F_o), calculated (F_c) structure factors, positional and thermal parameters for the structure are in Appendix 2.

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APPENDIX 1. Supplementary data for [Ru{C(OMe)Me}-$(PPh_3)_2(\eta-C_5H_5)][PF_6]$ (24) (Chapter 1).

Table 1.1	Fractional atomic coordinates and thermal parameters for non-hydrogen atoms
Table 1.2	Positional and thermal parameters for hydrogen atoms
Table 1.3	Interatomic distances
Table 1.4	Interatomic angles
Table 1.5	Observed and calculated structure factors

Table 1.1. Fractional atomic coordinates (X 10^5 for Ru; X 10^4 for remaining non-hydrogen atoms) and thermal parameters (X 10^4 for Ru and 10^3 for remaining non-hydrogen atoms)

Atom	x	y	z	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Ru	-19498(4)	253(4)	-18001(2)	342(3)	315(2)	277(3)	48(3)	38(3)	36(3)
P(1)	-3116(2)	-746(1)	-1136(1)	30(1)	35(1)	27(1)	3(1)	0(1)	0(1)
P(2)	-654(2)	-1093(1)	-2047(1)	32(1)	40(1)	29(1)	-3(1)	1(1)	2(1)
P(3)	-6043(3)	-1339(2)	-3908(1)	116(2)	58(1)	56(1)	9(1)	27(2)	-18(1)
F(1)	-5517(9)	-2140(6)	-3545(4)	201(3)	107(2)	102(2)	40(2)	-6(3)	-5(3)
F(2)	-5472(10)	-682(6)	-3487(7)	243(3)	110(3)	281(3)	-48(3)	-97(3)	-28(3)
F(3)	-6585(7)	-567(5)	-4292(4)	163(3)	104(2)	119(2)	44(2)	42(2)	33(2)
F(4)	-4979(9)	-1331(8)	-4288(6)	174(3)	249(3)	197(3)	140(3)	103(3)	69(3)
F(5)	-6492(11)	-1975(6)	-4365(6)	311(3)	137(3)	225(3)	-68(3)	-151(3)	46(3)
F(6)	-7071(9)	-1387(9)	-3529(6)	167(3)	301(3)	249(3)	135(3)	129(3)	52(3)
O(1)	-394(4)	-255(3)	-852(2)	47(2)	57(2)	29(2)	-10(2)	-2(2)	-5(2)
C(1)	-2807(6)	202(6)	-2712(4)	48(2)	75(3)	32(2)	16(2)	0(2)	8(2)
C(2)	-3399(7)	684(6)	-2272(4)	50(2)	79(2)	52(2)	33(2)	1(2)	30(2)
C(3)	-2725(8)	1370(6)	-2023(4)	86(3)	48(2)	45(2)	14(2)	4(2)	29(2)
C(4)	-1683(8)	1305(6)	-2309(4)	78(3)	44(2)	59(2)	25(2)	4(2)	8(2)
C(5)	-1698(8)	607(6)	-2722(4)	73(2)	68(2)	24(2)	23(2)	13(2)	20(2)
C(6)	-1057(6)	344(5)	-1109(4)	38(2)	40(2)	42(2)	-1(2)	12(2)	-7(2)
C(7)	310(7)	-52(7)	-337(4)	58(2)	90(3)	53(2)	-19(3)	-16(2)	7(3)
C(8)	-1045(9)	1253(5)	-825(5)	91(3)	38(2)	94(3)	-17(2)	8(3)	-15(2)
C(9)	-4024(3)	-1896(3)	-1983(2)	51(2)					
C(10)	-4381(3)	-2718(3)	-2217(2)	65(2)					
C(11)	-4380(3)	-3485(3)	-1856(2)	55(2)					
C(12)	-4023(3)	-3430(3)	-1261(2)	56(2)					
C(13)	-3667(3)	-2607(3)	-1027(2)	42(2)					
C(14)	-3667(3)	-1840(3)	-1388(2)	35(1)					
C(15)	-1903(4)	-1678(3)	-247(2)	45(2)					
C(16)	-1484(4)	-1804(3)	331(2)	59(2)					
C(17)	-1747(4)	-1192(3)	784(2)	62(2)					
C(18)	-2429(4)	-452(3)	659(2)	57(2)					
C(19)	-2848(4)	-326(3)	81(2)	42(2)					
C(20)	-2585(4)	-938(3)	-372(2)	31(1)					
C(21)	-4480(3)	749(3)	-881(2)	50(2)					
C(22)	-5426(3)	1168(3)	-642(2)	60(2)					
C(23)	-6337(3)	652(3)	-453(2)	68(2)					
C(24)	-6302(3)	-284(3)	-505(2)	60(2)					
C(25)	-5357(3)	-703(3)	-744(2)	53(2)					

Table 1.1 (continued)

Atom	x	y	z	U(11)
C(26)	-4446(3)	-186(3)	-933(2)	35(1)
C(27)	-1809(3)	-1789(3)	-3046(2)	50(2)
C(28)	-1966(3)	-2000(3)	-3650(2)	67(2)
C(29)	-1099(3)	-1865(3)	-4060(2)	73(2)
C(30)	-74(3)	-1520(3)	-3865(2)	62(2)
C(31)	83(3)	-1309(3)	-3261(2)	50(2)
C(32)	-785(3)	-1444(3)	-2851(2)	38(1)
C(33)	-1210(3)	-2916(3)	-1807(2)	50(2)
C(34)	-1137(3)	-3724(3)	-1491(2)	59(2)
C(35)	-396(3)	-3802(3)	-1009(2)	60(2)
C(36)	272(3)	-3073(3)	-844(2)	63(2)
C(37)	199(3)	-2264(3)	-1160(2)	51(2)
C(38)	-542(3)	-2186(3)	-1642(2)	33(1)
C(39)	1665(4)	-1350(3)	-2088(2)	56(2)
C(40)	2781(4)	-1069(3)	-2091(2)	72(2)
C(41)	3037(4)	-156(3)	-2041(2)	70(2)
C(42)	2179(4)	476(3)	-1987(2)	62(2)
C(43)	1063(4)	195(3)	-1984(2)	48(2)
C(44)	807(4)	-718(3)	-2035(2)	38(1)

Where the anisotropic thermal parameter is given by the following expression:

$$T_{aniso}=\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*}U_{22} + l^2c^{*2}U_{33} + 2hka^{*}b^{*}U_{12} + 2hla^{*}c^{*}U_{13} + 2klb^{*}c^{*}U_{23})].$$

Table 1.2. Positional (X 10^4) and thermal parameters for hydrogen atoms.

Atom	x	y	z	U(11)
H(1)	-3112(6)	-347(6)	-2985(4)	105(3)
H(2)	-4251(7)	544(6)	-2138(4)	105(3)
H(3)	-2970(8)	1851(6)	-1684(4)	105(3)
H(4)	-970(8)	1732(6)	-2217(4)	105(3)
H(5)	-1009(8)	401(6)	-3005(4)	105(3)
H(71)	771(7)	-646(7)	-207(4)	117(3)
H(72)	-206(7)	168(7)	33(4)	117(3)
H(73)	891(7)	477(7)	-456(4)	117(3)
H(81)	-1609(9)	1692(5)	-1066(5)	117(3)
H(82)	-208(9)	1527(5)	-840(5)	117(3)
H(83)	-1315(9)	1198(5)	-364(5)	117(3)
H(9)	-4025(3)	-1302(3)	-2262(2)	89(2)
H(10)	-4658(3)	-2761(3)	-2677(2)	89(2)
H(11)	-4657(3)	-4122(3)	-2037(2)	89(2)
H(12)	-4023(3)	-4024(3)	-982(2)	89(2)
H(13)	-3390(3)	-2565(3)	-567(2)	89(2)
H(15)	-1700(4)	-2152(3)	-598(2)	89(2)
H(16)	-956(4)	-2376(3)	428(2)	89(2)
H(17)	-1422(4)	-1290(3)	1232(2)	89(2)
H(18)	-2632(4)	22(3)	1010(2)	89(2)
H(19)	-3376(4)	247(3)	-16(2)	89(2)
H(21)	-3775(3)	1149(3)	-1027(2)	89(2)
H(22)	-5453(3)	1892(3)	-602(2)	89(2)
H(23)	-7069(3)	976(3)	-268(2)	89(2)
H(24)	-7007(3)	-683(3)	-359(2)	89(2)
H(25)	-5330(3)	-1427(3)	-784(2)	89(2)
H(27)	-2481(3)	-1894(3)	-2729(2)	89(2)
H(28)	-2759(3)	-2267(3)	-3801(2)	89(2)
H(29)	-1220(3)	-2028(3)	-4527(2)	89(2)
H(30)	598(3)	-1415(3)	-4182(2)	89(2)
H(31)	876(3)	-1042(3)	-3110(2)	89(2)
H(33)	-1783(3)	-2855(3)	-2180(2)	89(2)
H(34)	-1654(3)	-4289(3)	-1619(2)	89(2)
H(35)	-340(3)	-4428(3)	-765(2)	89(2)
H(36)	845(3)	-3133(3)	-471(2)	89(2)
H(37)	715(3)	-1699(3)	-1032(2)	89(2)
H(39)	1467(4)	-2056(3)	-2128(2)	89(2)
H(40)	3446(4)	-1558(3)	-2133(2)	89(2)
H(41)	3901(4)	61(3)	-2043(2)	89(2)
H(42)	2377(4)	1183(3)	-1948(2)	89(2)
H(43)	398(4)	684(3)	-1943(2)	89(2)

Table 1.3. Interatomic distances (Å)

P(1)	---	Ru	2.333(2)	P(2)	---	Ru	2.336(2)
C(1)	---	Ru	2.290(8)	C(2)	---	Ru	2.248(8)
C(3)	---	Ru	2.257(8)	C(4)	---	Ru	2.238(8)
C(5)	---	Ru	2.250(8)	C(6)	---	Ru	1.932(8)
C(14)	---	P(1)	1.842(5)	C(20)	---	P(1)	1.838(5)
C(26)	---	P(1)	1.848(5)	C(32)	---	P(2)	1.873(5)
C(38)	---	P(2)	1.863(5)	C(44)	---	P(2)	1.830(5)
F(1)	---	P(3)	1.570(8)	F(2)	---	P(3)	1.515(10)
F(3)	---	P(3)	1.572(8)	F(4)	---	P(3)	1.527(9)
F(5)	---	P(3)	1.490(10)	F(6)	---	P(3)	1.490(9)
C(6)	---	O(1)	1.321(9)	C(7)	---	O(1)	1.455(10)
C(2)	---	C(1)	1.405(12)	C(5)	---	C(1)	1.454(12)
C(3)	---	C(2)	1.411(13)	C(4)	---	C(3)	1.402(12)
C(5)	---	C(4)	1.387(12)	C(8)	---	C(6)	1.491(11)

Table 1.4. Interatomic angles (°)

P(2)	- Ru	- P(1)	101.2(1)	C(1)	- Ru	- P(1)	110.7(2)
C(1)	- Ru	- P(2)	99.7(2)	C(2)	- Ru	- P(1)	93.0(2)
C(2)	- Ru	- P(2)	135.1(3)	C(2)	- Ru	- C(1)	36.0(3)
C(3)	- Ru	- P(1)	109.3(2)	C(3)	- Ru	- P(2)	148.1(2)
C(3)	- Ru	- C(1)	61.3(3)	C(3)	- Ru	- C(2)	36.5(3)
C(4)	- Ru	- P(1)	145.5(2)	C(4)	- Ru	- P(2)	113.0(2)
C(4)	- Ru	- C(1)	61.1(3)	C(4)	- Ru	- C(2)	60.2(3)
C(4)	- Ru	- C(3)	36.3(3)	C(5)	- Ru	- P(1)	148.0(2)
C(5)	- Ru	- P(2)	88.3(2)	C(5)	- Ru	- C(1)	37.3(3)
C(5)	- Ru	- C(2)	60.5(3)	C(5)	- Ru	- C(3)	60.9(3)
C(5)	- Ru	- C(4)	36.0(3)	C(6)	- Ru	- P(1)	86.7(2)
C(6)	- Ru	- P(2)	89.8(2)	C(6)	- Ru	- C(1)	157.8(3)
C(6)	- Ru	- C(2)	133.7(3)	C(6)	- Ru	- C(3)	100.6(3)
C(6)	- Ru	- C(4)	96.8(3)	C(6)	- Ru	- C(5)	124.1(3)
C(14)	- P(1)	- Ru	116.9(2)	C(20)	- P(1)	- Ru	117.3(2)
C(20)	- P(1)	- C(14)	105.6(2)	C(26)	- P(1)	- Ru	116.5(1)
C(26)	- P(1)	- C(14)	99.5(2)	C(26)	- P(1)	- C(20)	98.0(2)
C(32)	- P(2)	- Ru	111.6(2)	C(38)	- P(2)	- Ru	123.6(2)
C(38)	- P(2)	- C(32)	103.1(2)	C(44)	- P(2)	- Ru	114.2(2)
C(44)	- P(2)	- C(32)	100.3(2)	C(44)	- P(2)	- C(38)	101.0(2)
F(2)	- P(3)	- F(1)	89.4(6)	F(3)	- P(3)	- F(1)	177.5(5)
F(3)	- P(3)	- F(2)	93.0(6)	F(4)	- P(3)	- F(1)	87.6(5)
F(4)	- P(3)	- F(2)	87.9(7)	F(4)	- P(3)	- F(3)	91.9(5)
F(5)	- P(3)	- F(1)	90.9(5)	F(5)	- P(3)	- F(2)	173.6(8)
F(5)	- P(3)	- F(3)	86.6(5)	F(5)	- P(3)	- F(4)	85.6(8)
F(6)	- P(3)	- F(1)	90.1(6)	F(6)	- P(3)	- F(2)	93.0(8)
F(6)	- P(3)	- F(3)	90.3(5)	F(6)	- P(3)	- F(4)	177.5(7)
F(6)	- P(3)	- F(5)	93.5(8)	C(7)	- O(1)	- C(6)	123.2(7)
C(2)	- C(1)	- Ru	70.3(5)	C(5)	- C(1)	- Ru	69.8(4)
C(5)	- C(1)	- C(2)	104.9(8)	C(1)	- C(2)	- Ru	73.6(4)
C(3)	- C(2)	- Ru	72.1(5)	C(3)	- C(2)	- C(1)	110.8(8)
C(2)	- C(3)	- Ru	71.4(4)	C(4)	- C(3)	- Ru	71.1(5)
C(4)	- C(3)	- C(2)	106.1(8)	C(3)	- C(4)	- Ru	72.6(5)
C(5)	- C(4)	- Ru	72.5(5)	C(5)	- C(4)	- C(3)	109.9(9)
C(1)	- C(5)	- Ru	72.8(5)	C(4)	- C(5)	- Ru	71.5(5)
C(4)	- C(5)	- C(1)	108.1(8)	O(1)	- C(6)	- Ru	120.7(5)
C(8)	- C(6)	- Ru	124.4(7)	C(8)	- C(6)	- O(1)	114.9(7)
C(13)	- C(14)	- P(1)	123.0(1)	C(9)	- C(14)	- P(1)	116.8(1)
C(19)	- C(20)	- P(1)	119.4(1)	C(15)	- C(20)	- P(1)	120.6(1)
C(25)	- C(26)	- P(1)	119.7(1)	C(21)	- C(26)	- P(1)	119.6(1)
C(31)	- C(32)	- P(2)	121.6(1)	C(27)	- C(32)	- P(2)	118.2(1)
C(37)	- C(38)	- P(2)	119.4(1)	C(33)	- C(38)	- P(2)	120.6(1)
C(43)	- C(44)	- P(2)	120.4(1)	C(39)	- C(44)	- P(2)	119.6(1)

Table 1.5. Observed and calculated structure factors

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CPRU(PPH3)2[C(OME)CH3] 4/112 PAGE 1

H	K	L	10FO	10FC
2	0	0	185	187
4	0	0	280	260
6	0	0	394	414
8	0	0	1257	1264
10	0	0	512	568
12	0	0	367	342
1	1	0	2095	2250
2	1	0	1137	1082
3	1	0	1635	1667
4	1	0	224	194
6	1	0	327	308
7	1	0	1058	1057
8	1	0	158	152
9	1	0	959	966
12	1	0	132	129
0	2	0	2346	2561
1	2	0	125	115
2	2	0	1915	1904
3	2	0	850	854
4	2	0	741	753
5	2	0	220	193
6	2	0	380	372
7	2	0	253	257
8	2	0	913	968
9	2	0	525	476
10	2	0	572	538
12	2	0	331	283
13	2	0	229	275
1	3	0	1110	1137
2	3	0	372	366
3	3	0	643	613
4	3	0	802	795
5	3	0	395	375
6	3	0	147	149
7	3	0	547	592
9	3	0	564	560
10	3	0	214	191
11	3	0	435	449
12	3	0	296	278
13	3	0	108	74
0	4	0	261	236
1	4	0	516	528
2	4	0	1250	1244
3	4	0	938	917
4	4	0	302	316
5	4	0	964	905
6	4	0	566	537
7	4	0	206	223
8	4	0	416	436
10	4	0	451	465
11	4	0	227	248
12	4	0	462	460
13	4	0	197	183
1	5	0	1289	1329
2	5	0	353	387
3	5	0	563	584
4	5	0	455	457
7	5	0	493	486
8	5	0	292	274
9	5	0	406	413
10	5	0	202	198
11	5	0	490	539
0	6	0	1376	1362
1	6	0	572	575
2	6	0	817	801
3	6	0	261	249
5	6	0	167	167
6	6	0	284	313
7	6	0	235	222
8	6	0	268	291
9	6	0	146	134
10	6	0	614	640
11	6	0	148	137
12	6	0	219	236
1	7	0	777	775
3	7	0	333	375
4	7	0	477	478
6	7	0	83	87
7	7	0	464	414
8	7	0	196	165
9	7	0	398	391
10	7	0	191	176
11	7	0	238	249
13	7	0	191	152
0	8	0	931	978
1	8	0	262	272
2	8	0	139	181
4	8	0	294	311
5	8	0	298	328
8	8	0	422	468
10	8	0	357	342
12	8	0	144	171
1	9	0	559	576
3	9	0	246	231
5	9	0	259	225
7	9	0	389	372
8	9	0	211	216
9	9	0	571	592
0	10	0	693	759
2	10	0	492	483
3	10	0	363	400
4	10	0	201	231
5	10	0	412	378
6	10	0	153	197
8	10	0	620	594
9	10	0	189	182
10	10	0	241	266
1	11	0	1027	1047
2	11	0	341	405
5	11	0	197	175
7	11	0	449	429
9	11	0	385	382
11	11	0	272	271
0	12	0	300	284
2	12	0	635	623
4	12	0	225	211
6	12	0	392	389
8	12	0	477	510
9	12	0	157	128
10	12	0	352	323
1	13	0	461	439
2	13	0	156	131
3	13	0	586	618
5	13	0	243	227
7	13	0	416	415
9	13	0	372	347
0	14	0	641	643
1	14	0	222	167
2	14	0	374	326
4	14	0	121	98
5	14	0	201	204
6	14	0	322	304
8	14	0	392	395
1	15	0	405	385
2	15	0	148	134
3	15	0	360	358
7	15	0	342	314
0	16	0	533	532
1	16	0	247	248
2	16	0	330	320
3	16	0	197	194
6	16	0	293	278
1	17	0	300	310
2	17	0	162	167
1	0	1	672	690
2	0	1	599	635
3	0	1	397	393
4	0	1	339	323
5	0	1	621	692
6	0	1	158	179
7	0	1	439	461
8	0	1	130	132
9	0	1	148	108
11	0	1	397	380
13	0	1	215	223
-14	1	1	324	303
-11	1	1	186	193
-10	1	1	248	297
-9	1	1	170	188
-8	1	1	253	251
-7	1	1	207	203
-6	1	1	911	908
-5	1	1	294	282
-4	1	1	552	542
-3	1	1	1031	983
-2	1	1	1512	1505
-1	1	1	641	645
0	1	1	129	125
1	1	1	652	647
2	1	1	1477	1499
3	1	1	1022	966
4	1	1	566	550
5	1	1	322	297
6	1	1	897	910
7	1	1	209	211
8	1	1	256	257
9	1	1	190	187
10	1	1	255	302
11	1	1	221	193
12	1	1	220	219

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CPRU(PPH3)2[C(OME)CH3] 4/112 PAGE 2

H	K	L	10FO	10FC
14	1	1	323	304
-14	2	1	137	126
-13	2	1	234	246
-12	2	1	191	201
-11	2	1	251	252
-10	2	1	136	162
-8	2	1	341	343
-7	2	1	605	613
-6	2	1	113	135
-5	2	1	297	311
-4	2	1	269	238
-3	2	1	863	861
-2	2	1	1126	1072
-1	2	1	1353	1352
0	2	1	1557	1559
1	2	1	1355	1336
2	2	1	1112	1066
3	2	1	844	835
4	2	1	293	258
5	2	1	315	322
6	2	1	135	145
7	2	1	624	623
8	2	1	343	337
10	2	1	168	165
11	2	1	256	256
13	2	1	241	245
-14	3	1	253	244
-12	3	1	426	413
-8	3	1	335	330
-7	3	1	167	186
-6	3	1	317	331
-5	3	1	714	699
-4	3	1	1638	1617
-3	3	1	364	345
-2	3	1	893	877
-1	3	1	1109	1098
0	3	1	157	147
1	3	1	1142	1093
2	3	1	894	847
3	3	1	386	344
4	3	1	1632	1601
5	3	1	709	713
6	3	1	295	315
7	3	1	142	178
8	3	1	347	344
12	3	1	435	416
13	3	1	139	188
14	3	1	272	250
-13	4	1	432	452
-12	4	1	190	186
-11	4	1	260	258
-10	4	1	101	117
-9	4	1	319	294
-8	4	1	396	383
-7	4	1	423	426
-5	4	1	982	1041
-4	4	1	664	622
-3	4	1	1246	1231
-2	4	1	461	445
-1	4	1	604	573
0	4	1	616	610
1	4	1	593	556
2	4	1	445	425
3	4	1	1225	1210
4	4	1	667	628
5	4	1	1008	1039
6	4	1	158	185
7	4	1	422	423
8	4	1	393	381
9	4	1	322	294
10	4	1	101	116
11	4	1	240	257
12	4	1	204	187
13	4	1	428	454
-13	5	1	226	217
-12	5	1	498	484
-10	5	1	252	216
-7	5	1	293	243
-6	5	1	979	946
-5	5	1	807	795
-4	5	1	1467	1451
-3	5	1	598	550
-2	5	1	760	749
-1	5	1	540	497
0	5	1	799	797
1	5	1	554	497
2	5	1	778	756
3	5	1	628	573
4	5	1	1448	1429
5	5	1	813	790
6	5	1	968	945
7	5	1	298	239
9	5	1	110	115
10	5	1	247	215
12	5	1	509	483
13	5	1	217	218
-13	6	1	397	398
-12	6	1	224	219
-11	6	1	336	351
-10	6	1	137	164
-7	6	1	252	275
-6	6	1	458	441
-5	6	1	1216	1225
-4	6	1	989	957
-3	6	1	1001	1001
-2	6	1	328	324
-1	6	1	655	623
0	6	1	182	206
1	6	1	644	613
2	6	1	334	320
3	6	1	1008	1004
4	6	1	989	954
5	6	1	1199	1218
6	6	1	442	435
7	6	1	253	285
11	6	1	332	351
12	6	1	251	224
13	6	1	395	395
-13	7	1	287	269
-12	7	1	373	366
-11	7	1	236	252
-10	7	1	280	283
-8	7	1	397	383
-7	7	1	329	313
-6	7	1	570	557
-5	7	1	433	464
-4	7	1	894	909
-3	7	1	772	753
-2	7	1	958	937
-1	7	1	429	425
0	7	1	78	87
1	7	1	446	433
2	7	1	939	943
3	7	1	774	756
4	7	1	886	901
5	7	1	442	455
6	7	1	516	558
7	7	1	342	313
8	7	1	402	385
10	7	1	274	284
11	7	1	231	257
12	7	1	382	361
13	7	1	278	266
-12	8	1	197	197
-11	8	1	278	271
-10	8	1	179	182
-9	8	1	205	187
-8	8	1	210	221
-7	8	1	345	327
-6	8	1	590	569
-5	8	1	665	644
-4	8	1	440	447
-3	8	1	593	574
-2	8	1	671	655
-1	8	1	697	686
0	8	1	554	546
1	8	1	740	683
2	8	1	683	654
3	8	1	599	572
4	8	1	419	440
5	8	1	642	637
6	8	1	602	558
7	8	1	345	331
8	8	1	210	222
9	8	1	191	185
10	8	1	186	182
11	8	1	284	267
12	8	1	183	196
-10	9	1	300	295
-8	9	1	247	241
-7	9	1	125	139
-6	9	1	725	727
-5	9	1	481	452
-4	9	1	499	521
-3	9	1	428	438
-2	9	1	618	688
-1	9	1	623	665
0	9	1	186	182
1	9	1	656	662
2	9	1	624	688

Table 1.5 (continued)

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR   CPRU(PPH3)2[C(OME)CH3] 4/112                                PAGE  3

  H  K  L 10FO 10FC       H  K  L 10FO 10FC       H  K  L 10FO 10FC       H  K  L 10FO 10FC       H  K  L 10FO 10FC

  3  9  1  407  423       4 11  1  680  725      -5 15  1  110   75      -5  1  2  442  400       4  2  2  688  682
  4  9  1  493  519       5 11  1  421  428      -4 15  1  375  373      -4  1  2  229  241       5  2  2  163  133
  5  9  1  495  464       6 11  1  537  546      -3 15  1  148  147      -3  1  2  924  932       6  2  2  538  519
  6  9  1  717  728       7 11  1  134  133       3 15  1  139  146      -2  1  2  989 1010       7  2  2 1060 1042
  8  9  1  234  246       8 11  1  167  143       4 15  1  386  372      -1  1  2 1000 1019       8  2  2  493  478
 10  9  1  303  298      10 11  1  204  194       6 15  1  198  199       0  1  2 1660 1725       9  2  2  653  664
-11 10  1  143  143      -9 12  1  188  176      -6 16  1  171  153       1  1  2 1034 1043      10  2  2  503  480
 -8 10  1  151  122      -8 12  1  121  103      -5 16  1  329  317       2  1  2 1012 1023      11  2  2  303  333
 -7 10  1  412  430      -7 12  1  196  220      -3 16  1  281  260       3  1  2  931  916      12  2  2  249  280
 -6 10  1  242  251      -6 12  1  182  195       3 16  1  276  263       4  1  2  252  248      13  2  2  168  151
 -5 10  1  555  545      -5 12  1  459  450       5 16  1  321  318       5  1  2  428  393     -13  3  2  149  137
 -4 10  1  234  250      -4 12  1  349  330       6 16  1  174  150       6  1  2  372  381     -12  3  2  296  271
 -3 10  1  541  530      -3 12  1  387  385      -3 17  1  195  188       7  1  2  604  616     -11  3  2  356  376
 -2 10  1  589  538       3 12  1  391  394      -2 17  1  242  213       8  1  2 1021 1027     -10  3  2  587  618
 -1 10  1  512  503       4 12  1  332  326       2 17  1  213  214       9  1  2  373  396      -9  3  2  236  228
  0 10  1  262  259       5 12  1  451  437       3 17  1  168  191      10  1  2  366  356      -8  3  2  593  600
  1 10  1  526  509       7 12  1  209  223       0  0  2 1726 1729      11  1  2  190  201      -7  3  2  548  524
  2 10  1  573  532      -8 13  1  160  146       1  0  2 2628 2855      12  1  2  349  312      -6  3  2  435  437
  3 10  1  546  538      -6 13  1  232  224       2  0  2 1141 1138      13  1  2  106  125      -5  3  2  900  869
  4 10  1  242  260      -4 13  1  408  388       3  0  2 1455 1415     -13  2  2  150  146      -4  3  2  146  161
  5 10  1  509  521      -3 13  1  211  237       4  0  2  180  167     -12  2  2  272  289      -3  3  2  522  544
  6 10  1  256  249      -2 13  1  239  217       5  0  2  109   72     -11  2  2  289  335      -2  3  2  357  342
  7 10  1  422  433      -1 13  1  128  116       6  0  2  212  192     -10  2  2  523  480      -1  3  2  865  850
  8 10  1  116  119       0 13  1  273  316       7  0  2  475  526      -9  2  2  655  670       0  3  2 3365 3668
 10 10  1  257  245       2 13  1  226  216       8  0  2  951  965      -8  2  2  477  475       1  3  2  897  861
 -8 11  1  126  146       3 13  1  206  228       9  0  2  731  748      -7  2  2 1079 1037       2  3  2  325  305
 -7 11  1  123  133       4 13  1  404  391      10  0  2  425  419      -6  2  2  551  527       3  3  2  528  549
 -6 11  1  558  547       5 13  1  141  135      11  0  2  268  274      -5  2  2  168  141       4  3  2  152  167
 -5 11  1  423  422       6 13  1  232  220      13  0  2  158  182      -4  2  2  679  690       5  3  2  898  867
 -4 11  1  685  731      -5 14  1  338  336     -12  1  2  334  310      -3  2  2  900  862       6  3  2  431  444
 -3 11  1  402  443      -4 14  1  208  230     -11  1  2  217  212      -2  2  2 2288 2280       7  3  2  563  527
 -2 11  1  283  256      -3 14  1  351  364     -10  1  2  357  350      -1  2  2 1055 1100       8  3  2  595  616
 -1 11  1  228  242       3 14  1  354  359      -9  1  2  363  386       0  2  2  523  551       9  3  2  249  240
  1 11  1  218  233       4 14  1  243  235      -8  1  2 1002 1020       1  2  2 1022 1065      10  3  2  614  620
  2 11  1  310  273       5 14  1  344  330      -7  1  2  597  620       2  2  2 2239 2261      11  3  2  344  369
  3 11  1  386  432      -6 15  1  207  201      -6  1  2  334  366       3  2  2  907  879      12  3  2  291  276
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR   CPRU(PPH3)2[C(OME)CH3] 4/112                                PAGE  4

  H  K  L 10FO 10FC       H  K  L 10FO 10FC       H  K  L 10FO 10FC       H  K  L 10FO 10FC       H  K  L 10FO 10FC

-12  4  2  262  247      -1  5  2  743  727      10  6  2  407  396       0  8  2  964 1009      -6 10  2  149  135
-11  4  2  205  194       0  5  2  551  595      11  6  2  267  269       1  8  2  743  741      -5 10  2  187  182
-10  4  2  521  507       1  5  2  794  750     -12  7  2  166  197       2  8  2  595  617      -4 10  2  214  228
 -9  4  2  329  319       2  5  2  240  204     -11  7  2  216  190       4  8  2  291  259      -3 10  2  347  332
 -8  4  2  246  250       3  5  2 1075 1084     -10  7  2  185  192       5  8  2  164  167      -2 10  2  309  333
 -7  4  2  784  736       4  5  2  405  412      -9  7  2  397  372       6  8  2  175  180      -1 10  2  467  501
 -6  4  2  395  404       5  5  2  199  190      -8  7  2  318  310       7  8  2  180  175       0 10  2  588  595
 -5  4  2  324  327       6  5  2  390  380      -7  7  2  258  235       8  8  2  460  433       1 10  2  470  492
 -4  4  2  335  343       7  5  2  306  310      -6  7  2  276  257       9  8  2  364  342       2 10  2  317  335
 -3  4  2  647  650       8  5  2  180  214      -5  7  2  409  384      10  8  2  255  248       3 10  2  352  332
 -2  4  2  822  838       9  5  2  348  335      -4  7  2  259  233      11  8  2  205  203       4 10  2  219  234
 -1  4  2  222  243      10  5  2  368  376      -3  7  2  323  315      12  8  2  175  165       5 10  2  178  177
  0  4  2  285  296      11  5  2  336  320      -2  7  2  860  865     -10  9  2  218  199       7 10  2  375  345
  1  4  2  217  232      12  5  2  204  199      -1  7  2  838  829      -9  9  2  408  388       8 10  2  329  334
  2  4  2  874  856      13  5  2  156  159       0  7  2  381  371      -8  9  2  471  506       9 10  2  319  305
  3  4  2  647  635     -11  6  2  255  266       1  7  2  862  809      -7  9  2  392  388      10 10  2  280  287
  4  4  2  337  343     -10  6  2  396  398       2  7  2  901  873      -5  9  2  258  257     -11 11  2  176  187
  5  4  2  325  323      -9  6  2  296  284       3  7  2  323  312      -4  9  2  328  315     -10 11  2  274  275
  6  4  2  410  409      -8  6  2  238  255       4  7  2  242  224      -3  9  2  285  279      -9 11  2  313  294
  7  4  2  790  734      -7  6  2  139  152       5  7  2  421  382      -2  9  2  264  264      -8 11  2  355  342
  8  4  2  247  255      -6  6  2  224  234       6  7  2  274  261      -1  9  2  478  495      -7 11  2  272  269
  9  4  2  324  324      -5  6  2  210  225       7  7  2  265  248       0  9  2  781  749      -6 11  2  223  238
 10  4  2  512  500      -4  6  2  271  231       8  7  2  320  312       1  9  2  484  483      -4 11  2  311  278
 11  4  2  206  194      -3  6  2  298  302       9  7  2  398  376       2  9  2  268  259      -3 11  2  216  253
 12  4  2  264  246      -2  6  2 1010 1025      10  7  2  168  199       3  9  2  296  289      -2 11  2  410  415
-12  5  2  204  201      -1  6  2  642  635      11  7  2  208  192       4  9  2  338  315      -1 11  2  418  427
-11  5  2  337  318       0  6  2  580  606      12  7  2  178  193       5  9  2  245  260       0 11  2  954  966
-10  5  2  360  370       1  6  2  668  656     -12  8  2  135  158       7  9  2  395  386       1 11  2  444  441
 -9  5  2  333  328       2  6  2 1025 1023     -10  8  2  219  252       8  9  2  481  518       2 11  2  399  403
 -8  5  2  174  215       3  6  2  295  291      -9  8  2  360  331       9  9  2  415  388       3 11  2  222  246
 -7  5  2  287  295       4  6  2  253  228      -8  8  2  435  433      10  9  2  218  205       4 11  2  333  282
 -6  5  2  371  382       5  6  2  213  231      -6  8  2  178  186      11  9  2  158  137       6 11  2  223  250
 -5  5  2  197  189       6  6  2  225  233      -5  8  2  157  171     -10 10  2  280  283       7 11  2  219  268
 -4  5  2  408  418       7  6  2  145  142      -4  8  2  291  254      -9 10  2  315  303       8 11  2  345  350
 -3  5  2 1069 1090       8  6  2  255  265      -2  8  2  576  614      -8 10  2  325  335       9 11  2  315  298
 -2  5  2  250  233       9  6  2  301  281      -1  8  2  723  740      -7 10  2  363  339      10 11  2  280  274
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Table 1.5 (continued)

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CPRU(PPH3)2[C(OME)CH3] 4/112

PAGE 5

H	K	L	10FO	10FC	H	K	L	10FO-	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-10	12	2	196	217	-4	14	2	176	139	3	0	3	1740	1777	-12	3	3	206	231	-5	6	3	230	236
-9	12	2	353	340	-3	14	2	273	290	4	0	3	858	900	-11	3	3	302	317	-4	6	3	1061	1087
-7	12	2	431	428	-2	14	2	355	373	6	0	3	821	827	-9	3	3	391	388	-3	6	3	140	144
-6	12	2	159	133	-1	14	2	547	536	7	0	3	159	174	-8	3	3	479	450	-2	6	3	523	524
-4	12	2	105	85	0	14	2	385	413	8	0	3	301	250	-7	3	3	518	553	-1	6	3	520	506
-3	12	2	584	593	1	14	2	548	535	9	0	3	316	349	-5	3	3	1055	1130	0	6	3	1210	1171
-2	12	2	299	277	2	14	2	369	387	11	0	3	98	139	-4	3	3	329	334	-11	7	3	347	345
-1	12	2	513	521	3	14	2	271	287	12	0	3	172	150	-3	3	3	1821	1833	-9	7	3	135	153
0	12	2	228	243	4	14	2	146	137	14	0	3	290	301	-2	3	3	369	368	-8	7	3	293	314
1	12	2	510	527	5	14	2	123	110	-14	1	3	164	201	-1	3	3	742	747	-7	7	3	453	446
2	12	2	296	278	7	14	2	279	289	-13	1	3	223	216	0	3	3	331	298	-6	7	3	88	76
3	12	2	583	590	-7	15	2	174	174	-11	1	3	151	165	-12	4	3	455	422	-5	7	3	729	726
4	12	2	123	84	-6	15	2	248	227	-10	1	3	422	432	-10	4	3	180	178	-4	7	3	90	119
6	12	2	152	127	-5	15	2	162	136	-8	1	3	115	72	-9	4	3	247	243	-3	7	3	1533	1580
7	12	2	439	428	-3	15	2	262	258	-7	1	3	897	939	-8	4	3	344	368	-2	7	3	233	208
8	12	2	171	193	-2	15	2	421	402	-6	1	3	856	836	-7	4	3	326	304	-1	7	3	212	213
9	12	2	342	340	-1	15	2	351	377	-5	1	3	671	706	-6	4	3	1011	1039	0	7	3	731	707
10	12	2	227	221	0	15	2	260	250	-4	1	3	907	851	-4	4	3	1452	1500	-12	8	3	294	298
-8	13	2	375	364	1	15	2	368	377	-3	1	3	1287	1323	-3	4	3	376	376	-11	8	3	128	84
-6	13	2	373	375	2	15	2	407	399	-2	1	3	971	963	-2	4	3	1133	1159	-10	8	3	257	246
-5	13	2	166	171	3	15	2	264	263	-1	1	3	971	957	-1	4	3	1008	1032	-9	8	3	251	259
-4	13	2	210	200	6	15	2	227	226	-14	2	3	266	253	0	4	3	254	249	-8	8	3	164	172
-3	13	2	409	425	7	15	2	195	179	-13	2	3	139	159	-13	5	3	346	363	-7	8	3	312	303
-2	13	2	535	517	-2	16	2	368	368	-12	2	3	324	334	-11	5	3	290	306	-6	8	3	846	848
-1	13	2	423	428	-1	16	2	329	315	-10	2	3	208	232	-9	5	3	275	278	-5	8	3	269	237
0	13	2	523	547	0	16	2	291	283	-9	2	3	144	147	-7	5	3	449	461	-4	8	3	870	870
1	13	2	383	417	1	16	2	315	315	-8	2	3	314	347	-6	5	3	299	287	-3	8	3	187	161
2	13	2	522	514	2	16	2	361	366	-7	2	3	278	307	-5	5	3	1078	1107	-2	8	3	1081	1100
3	13	2	398	422	3	16	2	171	146	-6	2	3	1204	1216	-4	5	3	167	166	-1	8	3	284	296
4	13	2	199	195	-1	17	2	276	278	-5	2	3	491	470	-3	5	3	681	746	0	8	3	302	277
5	13	2	134	165	0	17	2	265	258	-4	2	3	1331	1355	-2	5	3	536	502	-11	9	3	236	220
6	13	2	357	381	1	17	2	260	275	-3	2	3	311	339	-1	5	3	285	279	-10	9	3	157	198
7	13	2	128	136	2	17	2	119	163	-2	2	3	1312	1334	-12	6	3	431	420	-9	9	3	296	287
8	13	2	361	364	3	17	2	134	143	-1	2	3	1103	1068	-10	6	3	150	148	-7	9	3	535	531
-7	14	2	285	286	1	0	3	1588	1708	0	2	3	700	695	-8	6	3	362	390	-6	9	3	304	304
-6	14	2	256	252	2	0	3	817	740	-13	3	3	353	373	-6	6	3	790	810	-5	9	3	752	746

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CPRU(PPH3)2[C(OME)CH3] 4/112

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H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-4	9	3	167	159	-3	12	3	349	377	1	15	3	136	159	-4	1	4	334	330	10	3	4	748	752
-3	9	3	705	724	-1	12	3	140	146	3	15	3	332	323	-3	1	4	476	445	-11	4	4	448	473
-2	9	3	287	324	0	12	3	297	299	4	15	3	224	241	-2	1	4	2000	2023	-9	4	4	521	514
-1	9	3	605	617	2	12	3	177	162	5	15	3	321	314	-1	1	4	347	299	-8	4	4	287	287
0	9	3	488	502	3	12	3	346	385	6	15	3	112	95	0	1	4	1572	1617	-7	4	4	332	324
-11	10	3	138	141	4	12	3	535	544	7	15	3	171	163	8	1	4	691	680	-5	4	4	370	341
-8	10	3	262	269	5	12	3	188	196	-4	16	3	281	266	9	1	4	201	209	-4	4	4	653	611
-7	10	3	201	169	6	12	3	387	378	-3	16	3	156	153	10	1	4	599	571	-3	4	4	804	798
-6	10	3	679	679	8	12	3	215	213	-2	16	3	149	128	-11	2	4	332	319	-2	4	4	537	547
-5	10	3	237	211	-6	13	3	212	208	0	16	3	289	303	-9	2	4	525	555	-1	4	4	996	1033
-4	10	3	467	451	-5	13	3	353	355	1	16	3	117	141	-8	2	4	409	416	0	4	4	145	147
-3	10	3	303	289	-4	13	3	227	200	2	16	3	136	123	-7	2	4	630	635	8	4	4	304	290
-2	10	3	761	786	-3	13	3	414	382	4	16	3	275	267	-6	2	4	247	214	9	4	4	504	514
-1	10	3	143	127	-2	13	3	272	254	-3	17	3	227	201	-5	2	4	615	577	10	4	4	166	162
0	10	3	84	66	-1	13	3	231	233	1	17	3	196	170	-4	2	4	123	111	-12	5	4	292	279
-11	11	3	159	173	0	13	3	113	112	3	17	3	218	198	-3	2	4	1312	1341	-10	5	4	590	583
-10	11	3	146	172	2	13	3	277	253	0	0	4	2147	2070	-2	2	4	685	681	-8	5	4	306	297
-9	11	3	176	154	3	13	3	408	387	1	0	4	1044	1028	-1	2	4	1341	1342	-6	5	4	456	480
-7	11	3	301	306	4	13	3	211	194	2	0	4	1344	1341	0	2	4	789	763	-5	5	4	266	276
-6	11	3	172	185	5	13	3	348	342	3	0	4	463	379	8	2	4	414	416	-4	5	4	484	481
-5	11	3	558	597	7	13	3	151	172	5	0	4	388	401	9	2	4	505	546	-3	5	4	632	610
-4	11	3	206	231	-4	14	3	534	531	6	0	4	228	225	-12	3	4	189	174	-2	5	4	999	1035
-3	11	3	354	306	-3	14	3	223	202	7	0	4	665	678	-11	3	4	124	151	-1	5	4	565	578
-2	11	3	465	479	-2	14	3	181	197	9	0	4	367	384	-10	3	4	768	761	0	5	4	1167	1190
-1	11	3	225	241	-1	14	3	199	208	10	0	4	312	356	-9	3	4	307	311	8	5	4	315	301
3	11	3	327	295	2	14	3	186	207	11	0	4	247	255	-8	3	4	679	700	-12	6	4	110	46
4	11	3	208	229	3	14	3	206	201	12	0	4	193	208	-7	3	4	243	283	-11	6	4	364	371
5	11	3	547	577	4	14	3	533	522	13	0	4	208	200	-6	3	4	497	497	-9	6	4	477	452
6	11	3	148	180	5	14	3	139	142	14	0	4	203	190	-5	3	4	277	268	-7	6	4	415	394
7	11	3	293	315	7	14	3	108	132	-11	1	4	216	222	-4	3	4	348	368	-6	6	4	353	398
9	11	3	173	154	-7	15	3	171	160	-10	1	4	604	570	-3	3	4	696	702	-5	6	4	329	326
-8	12	3	247	219	-5	15	3	326	317	-9	1	4	220	211	-2	3	4	1501	1560	-4	6	4	484	510
-7	12	3	241	225	-4	15	3	239	243	-8	1	4	685	683	-1	3	4	838	839	-3	6	4	774	800
-6	12	3	405	387	-3	15	3	328	329	-7	1	4	407	407	0	3	4	599	596	-2	6	4	302	310
-5	12	3	174	198	-1	15	3	165	168	-6	1	4	344	336	8	3	4	693	711	-1	6	4	1005	1049
-4	12	3	516	536	0	15	3	143	109	-5	1	4	370	370	9	3	4	293	307	7	6	4	373	378

Table 1.5 (continued)

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR   CPRU(PPH3)2[C(OME)CH3] 4/112
                                                                                          PAGE  7
  H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC

  8  6  4  101   98     -4  9  4  233  260     -4 12  4  342  316      5  0  5  729  786      8  2  5  307  318
  9  6  4  480  448     -3  9  4  225  200     -3 12  4  321  320      6  0  5  611  651      9  2  5  192  197
-12  7  4  223  202     -2  9  4  611  592     -2 12  4  270  244      8  0  5  251  243     10  2  5  439  466
-10  7  4  455  468     -1  9  4  317  313     -1 12  4  403  403      9  0  5  136  128    -13  3  5  257  274
 -9  7  4  254  274      0  9  4  915 1018     -9 13  4  172  175     10  0  5  227  212    -12  3  5  213  220
 -8  7  4  493  511      4  9  4  238  268     -8 13  4  182  190     12  0  5  248  270    -11  3  5  320  337
 -7  7  4  306  321      6  9  4  298  302     -7 13  4  221  220     13  0  5  155  147     -9  3  5  355  331
 -6  7  4  482  524    -11 10  4  229  243     -6 13  4  280  268    -13  1  5  301  330     -8  3  5  229  214
 -5  7  4  116  103     -9 10  4  500  507     -3 13  4  189  218    -12  1  5  114  130     -7  3  5  549  537
 -4  7  4  188  201     -7 10  4  504  481     -2 13  4  572  571    -11  1  5  238  235     -6  3  5  571  571
 -3  7  4  348  390     -6 10  4  213  260     -1 13  4  174  195    -10  1  5  148  125     -5  3  5  563  590
 -2  7  4  968 1029     -5 10  4  458  465      0 13  4  251  228     -9  1  5  423  386     -4  3  5  456  468
 -1  7  4  591  599     -4 10  4  461  514     -8 14  4  202  202     -8  1  5  308  318     -3  3  5 1033 1065
  0  7  4 1011 1115     -3 10  4  201  224     -7 14  4  247  271     -7  1  5  794  844     -2  3  5  850  839
  6  7  4  486  518     -2 10  4  279  280     -5 14  4  199  181     -6  1  5  859  852     -1  3  5  512  552
  7  7  4  317  319     -1 10  4  772  795     -4 14  4  206  189     -5  1  5 1085 1157      0  3  5  170  168
  8  7  4  484  509      1 10  4  776  793     -3 14  4  353  378     -4  1  5  677  646      8  3  5  236  219
  9  7  4  265  279      2 10  4  283  273     -2 14  4  149  158     -3  1  5  327  338      9  3  5  364  332
-11  8  4  203  201      3 10  4  220  242     -1 14  4  407  406     -2  1  5  402  385    -13  4  5  204  205
 -9  8  4  671  681      4 10  4  468  516      0 14  4  343  345     -1  1  5 1105 1082    -12  4  5  275  244
 -8  8  4  156  167      5 10  4  461  463     -7 15  4  177  168      0  1  5 1045  984    -11  4  5  234  229
 -7  8  4  754  761      6 10  4  226  268     -6 15  4  193  177      8  1  5  311  315    -10  4  5  147  114
 -6  8  4  293  290      7 10  4  503  487     -3 15  4  159  181      9  1  5  423  386     -9  4  5  212  187
 -5  8  4  126  142    -10 11  4  377  380     -2 15  4  398  404    -13  2  5  166  183     -7  4  5  536  556
 -4  8  4  238  234     -8 11  4  363  371     -1 15  4  172  179    -12  2  5  242  227     -6  4  5  687  676
 -3  8  4  642  658     -6 11  4  188  189      0 15  4  362  395    -10  2  5  445  465     -5  4  5  449  459
 -1  8  4  868  929     -5 11  4  310  334     -3 16  4  236  233     -9  2  5  191  199     -4  4  5 1118 1168
  6  8  4  280  288     -4 11  4  263  282     -2 16  4  208  199     -8  2  5  311  312     -3  4  5 1205 1241
  7  8  4  726  760     -3 11  4  168  124     -1 16  4  338  358     -7  2  5  280  293     -2  4  5  648  607
  8  8  4  179  168     -2 11  4  264  242      0 16  4  157  145     -6  2  5  945  949     -1  4  5  346  316
-12  9  4  180  187     -1 11  4  400  376     -2 17  4  216  213     -5  2  5  720  691      0  4  5  118   98
-11  9  4  114   75      0 11  4  620  631      0 17  4  413  426     -4  2  5 1226 1255      7  4  5  543  557
-10  9  4  333  347     -9 12  4  310  301      1  0  5  674  649     -3  2  5 1266 1232      9  4  5  219  188
 -8  9  4  768  795     -8 12  4  208  199      2  0  5 1228 1255     -2  2  5   92  104    -13  5  5  193  194
 -6  9  4  306  306     -7 12  4  292  301      3  0  5  809  808     -1  2  5  847  811    -12  5  5  215  217
 -5  9  4  155  129     -6 12  4  157  143      4  0  5 1312 1305      0  2  5  869  789    -11  5  5  105  130
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR   CPRU(PPH3)2[C(OME)CH3] 4/112
                                                                                          PAGE  8
  H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC

-10  5  5  166  175      0  7  5  242  285     -8 10  5  186  207     -2 13  5  275  258     -9  1  6  486  503
 -9  5  5  317  313      6  7  5  457  463     -7 10  5  355  334     -1 13  5  211  255     -8  1  6  204  207
 -8  5  5  122  127      8  7  5  238  250     -6 10  5  684  658      0 13  5  148  128     -7  1  6  381  383
 -6  5  5  685  698      9  7  5  189  191     -5 10  5  360  369     -7 14  5  171  170     -6  1  6  356  355
 -5  5  5  697  679    -11  8  5  240  275     -4 10  5  487  489     -6 14  5  330  306     -5  1  6  453  462
 -4  5  5  530  539    -10  8  5  145  135     -3 10  5  494  482     -5 14  5  229  228     -4  1  6  102   54
 -3  5  5  836  871     -8  8  5  441  408     -2 10  5  561  573     -4 14  5  550  553     -3  1  6 1032  970
 -2  5  5  551  570     -7  8  5  283  305      1 10  5  121  131     -2 14  5  306  290     -2  1  6  360  366
 -1  5  5  265  257     -6  8  5  358  402      2 10  5  559  572      0 14  5  238  259     -1  1  6  429  453
  0  5  5  614  667     -5  8  5  677  679      3 10  5  489  485     -6 15  5  210  210      0  1  6 2394 2350
  8  5  5  144  126     -4  8  5  357  360      4 10  5  462  473     -5 15  5  465  455      8  1  6  204  212
  9  5  5  312  315     -3  8  5  450  444      5 10  5  352  367     -4 15  5  177  179      9  1  6  491  499
-13  6  5  215  192     -2  8  5  647  626      6 10  5  675  655     -3 15  5  362  339     10  1  6  153  130
-12  6  5  201  201      0  8  5  480  493     -7 11  5  314  322     -2 15  5  108  102    -13  2  6  105   99
-11  6  5  282  281      5  8  5  660  664     -6 11  5  272  286     -1 15  5  139  134    -10  2  6  595  593
 -8  6  5  214  208      6  8  5  361  397     -5 11  5  346  339      0 15  5  236  206     -9  2  6  157  158
 -7  6  5  451  440      7  8  5  298  313     -4 11  5  435  399     -5 16  5  192  202     -8  2  6  394  399
 -6  6  5  456  430      8  8  5  421  403     -3 11  5  529  516     -4 16  5  316  300     -7  2  6  189  178
 -5  6  5  630  645    -11  9  5  139  115     -2 11  5  268  280     -3 16  5  162  178     -6  2  6  671  648
 -4  6  5  730  753    -10  9  5  137  159     -1 11  5  626  599     -2 16  5  242  221     -5  2  6  378  329
 -3  6  5  612  578     -9  9  5  188  225      0 11  5  297  299     -1 16  5  318  301     -4  2  6  165  188
 -2  6  5  287  336     -8  9  5  103   85     -9 12  5  157  183      0 17  5  266  235     -3  2  6  488  430
 -1  6  5  227  232     -7  9  5  571  545     -8 12  5  193  173      0  0  6  559  512     -2  2  6 1161 1134
  0  6  5  267  254     -6  9  5  423  442     -7 12  5  250  249      1  0  6 1166 1090     -1  2  6  761  666
  6  6  5  435  417     -5  9  5  307  308     -6 12  5  480  470      2  0  6 1535 1442      0  2  6  356  370
  7  6  5  459  452     -4  9  5  583  603     -5 12  5  267  256      3  0  6  673  713    -11  3  6  392  409
  8  6  5  212  212     -3  9  5  393  371     -4 12  5  658  675      4  0  6  254  266    -10  3  6  199  185
-12  7  5  251  248     -2  9  5  378  397     -3 12  5  331  329      5  0  6  344  300     -9  3  6  705  682
-10  7  5  192  201     -1  9  5  322  319     -2 12  5  346  379      7  0  6  385  363     -8  3  6  235  266
 -8  7  5  235  245      3  9  5  383  361     -1 12  5  216  210      8  0  6  543  575     -7  3  6  454  456
 -6  7  5  468  479      4  9  5  592  604      0 12  5  229  253      9  0  6  248  224     -6  3  6  519  535
 -5  7  5  659  665      5  9  5  310  303     -7 13  5  279  275     10  0  6  597  600     -5  3  6  450  450
 -4  7  5  814  774      6  9  5  446  432     -6 13  5  199  189     11  0  6  159  114     -4  3  6  367  319
 -3  7  5  592  577      7  9  5  578  537     -5 13  5  533  521     12  0  6  167  159     -3  3  6  552  582
 -2  7  5  633  647    -10 10  5  144  141     -4 13  5  224  254    -11  1  6  319  321     -2  3  6  355  375
 -1  7  5  288  307     -9 10  5  114  114     -3 13  5  553  526    -10  1  6  180  129     -1  3  6 1048 1006
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Table 1.5 (continued)

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR   CPRU(PPH3)2[C(OME)CH3] 4/112                                          PAGE  9
   H   K   L  10FO  10FC       H   K   L  10FO  10FC       H   K   L  10FO  10FC       H   K   L  10FO  10FC       H   K   L  10FO  10FC

 -12   4   6   214   203      -1   6   6   564   605      -8  10   6   316   332      -6  15   6   121    92      -2   2   7   293   279
 -11   4   6   282   298       0   6   6  1219  1271      -6  10   6   301   265      -3  15   6   177   186      -1   2   7   908   827
 -10   4   6   566   527     -11   7   6   287   288      -5  10   6   371   364      -1  15   6   234   237       0   2   7    66    51
  -9   4   6   338   349     -10   7   6   364   361      -4  10   6   537   506       0  15   6   213   200     -12   3   7   330   329
  -8   4   6   569   587      -9   7   6   528   555      -3  10   6   255   293      -4  16   6   169   166      -9   3   7   316   287
  -7   4   6   314   291      -8   7   6   361   347      -2  10   6   493   551      -2  16   6   224   203      -8   3   7   449   440
  -6   4   6   435   447      -7   7   6   468   443      -1  10   6   614   611       0  16   6   228   181      -7   3   7   626   624
  -5   4   6   506   505      -6   7   6   374   398       0  10   6   855   859      -1  17   6   287   268      -6   3   7   379   395
  -4   4   6   260   269      -5   7   6   217   192     -10  11   6   141   132       0  17   6   224   210      -5   3   7   168   172
  -3   4   6   293   300      -3   7   6   474   478      -9  11   6   358   341       1   0   7   870   823      -4   3   7  1301  1296
  -2   4   6   973   937      -2   7   6   679   702      -7  11   6   277   277       3   0   7  1425  1504      -3   3   7   270   296
  -1   4   6   355   388      -1   7   6   810   816      -5  11   6   199   246       5   0   7  1026   982      -2   3   7  1169  1130
   0   4   6  1236  1287       0   7   6  1107  1156      -4  11   6   498   502       6   0   7   721   712      -1   3   7   172   146
 -11   5   6   274   282     -10   8   6   403   417      -3  11   6   490   539       7   0   7   849   892       0   3   7    80    57
 -10   5   6   530   537      -9   8   6   345   328      -1  11   6   518   555       9   0   7   123    96     -13   4   7   272   282
  -9   5   6   656   673      -8   8   6   456   462       0  11   6   180   187      11   0   7   442   423     -10   4   7   239   240
  -8   5   6   327   328      -7   8   6   479   453      -8  12   6   287   264      13   0   7   430   437      -8   4   7   323   341
  -7   5   6   590   606      -6   8   6   494   495      -6  12   6   252   225     -12   1   7   306   293      -7   4   7   533   499
  -6   5   6   591   577      -5   8   6   290   303      -4  12   6   234   217     -10   1   7   407   417      -6   4   7   340   322
  -5   5   6   612   587      -4   8   6   305   292      -3  12   6   252   250      -8   1   7   281   271      -5   4   7  1007  1091
  -4   5   6   352   347      -3   8   6   403   366      -2  12   6   420   422      -7   1   7   191   194      -4   4   7   502   458
  -3   5   6   979   979      -2   8   6   653   681      -1  12   6   234   253      -6   1   7  1259  1321      -3   4   7   789   800
  -2   5   6   622   638      -1   8   6   515   516       0  12   6   549   565      -5   1   7   258   239      -2   4   7   364   322
  -1   5   6  1314  1329       0   8   6   646   658      -9  13   6   216   205      -4   1   7  1573  1545      -1   4   7   499   482
   0   5   6   311   271     -11   9   6   161   199      -7  13   6   128   172      -3   1   7   461   498     -12   5   7   209   207
 -12   6   6   230   214      -9   9   6   393   373      -6  13   6   160   155      -2   1   7   968   943      -9   5   7   344   355
 -11   6   6   308   297      -8   9   6   421   416      -5  13   6   211   181      -1   1   7   243   243      -8   5   7   302   320
 -10   6   6   399   414      -7   9   6   413   432      -3  13   6   263   277       0   1   7   162   133      -7   5   7   173   179
  -9   6   6   436   420      -6   9   6   258   268      -2  13   6   251   248     -13   2   7   316   325      -6   5   7   596   587
  -8   6   6   612   621      -4   9   6   176   162      -1  13   6   410   418     -12   2   7   124    99      -5   5   7   252   256
  -7   6   6   430   405      -3   9   6   460   488      -8  14   6   197   192     -11   2   7   375   380      -4   5   7   963  1009
  -6   6   6   615   601      -2   9   6   370   408      -5  14   6   197   202     -10   2   7   174   183      -3   5   7   205   188
  -5   6   6   185   209      -1   9   6   736   733      -3  14   6   290   300      -7   2   7   652   678      -2   5   7   457   490
  -4   6   6   312   324       0   9   6   955   970      -2  14   6   225   194      -6   2   7   417   398      -1   5   7   522   552
  -3   6   6   508   563     -10  10   6   294   287      -1  14   6   159   172      -5   2   7  1283  1317       0   5   7   628   553
  -2   6   6  1009  1022      -9  10   6   313   319       0  14   6   365   344      -3   2   7   725   762     -11   6   7   196   202
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR   CPRU(PPH3)2[C(OME)CH3] 4/112                                          PAGE 10
   H   K   L  10FO  10FC       H   K   L  10FO  10FC       H   K   L  10FO  10FC       H   K   L  10FO  10FC       H   K   L  10FO  10FC

  -9   6   7   159   161      -1   9   7   288   280      -1  15   7   186   183       0   2   8  1650  1615     -12   6   8   208   205
  -8   6   7   114   148     -11  10   7   147   164      -3  16   7   282   293     -13   3   8   169   147     -11   6   8   147   124
  -7   6   7   382   401      -7  10   7   336   355       0  16   7   310   314     -11   3   8   293   292     -10   6   8   516   498
  -6   6   7   247   242      -6  10   7   176   202       0   0   8  2401  2314     -10   3   8   184   212      -9   6   8   368   390
  -5   6   7   728   747      -5  10   7   600   576       1   0   8   604   514      -9   3   8   411   414      -8   6   8   647   661
  -4   6   7   425   394      -3  10   7   459   478       2   0   8   384   368      -8   3   8   133   144      -7   6   8   350   336
  -3   6   7   841   840      -2  10   7   266   273       3   0   8  1051   998      -7   3   8   725   715      -6   6   8   613   625
  -2   6   7   163   178      -1  10   7   295   286       4   0   8   254   253      -6   3   8   511   522      -5   6   8   270   298
  -1   6   7   356   335     -10  11   7   152   150       7   0   8   117   112      -5   3   8   404   435      -4   6   8   179   163
   0   6   7   331   274      -8  11   7   322   304       8   0   8   643   642      -4   3   8   394   365      -3   6   8   255   265
  -8   7   7   284   265      -6  11   7   389   413       9   0   8   213   205      -3   3   8   902   876      -2   6   8   864   880
  -7   7   7   188   192      -4  11   7   626   668      10   0   8   153   132      -2   3   8   743   723      -1   6   8   837   843
  -6   7   7   554   529      -3  11   7   120   113     -12   1   8   101    44      -1   3   8   695   704       0   6   8   981   987
  -4   7   7   756   773      -2  11   7   668   653     -11   1   8   147   150       0   3   8   230   257     -11   7   8   330   321
  -3   7   7   252   277      -1  11   7   127   107     -10   1   8   182   170     -12   4   8   239   227     -10   7   8   348   353
  -2   7   7   268   252       0  11   7   370   374      -9   1   8   486   486     -11   4   8   183   158      -9   7   8   632   645
  -1   7   7   386   386      -9  12   7   115   102      -8   1   8   234   207     -10   4   8   578   567      -8   7   8   318   312
   0   7   7   231   229      -7  12   7   372   358      -7   1   8   326   300      -9   4   8   354   355      -7   7   8   520   511
 -11   8   7   112   147      -5  12   7   697   700      -6   1   8   308   297      -8   4   8   442   409      -6   7   8   276   288
 -10   8   7   235   228      -3  12   7   645   673      -5   1   8   354   336      -6   4   8   398   406      -5   7   8   343   344
  -9   8   7   132   153      -1  12   7   233   246      -4   1   8   373   370      -4   4   8   332   332      -3   7   8   430   449
  -7   8   7   269   240      -8  13   7   153   141      -3   1   8   541   492      -3   4   8   109    97      -2   7   8   212   194
  -6   8   7   345   332      -6  13   7   406   419      -2   1   8   739   749      -2   4   8  1175  1142      -1   7   8  1237  1312
  -5   8   7   232   268      -4  13   7   595   613      -1   1   8   327   309      -1   4   8   500   483       0   7   8   456   486
  -3   8   7   611   601      -3  13   7   233   211       0   1   8   417   397       0   4   8   749   785     -11   8   8   176   162
  -2   8   7   373   419      -2  13   7   457   450     -12   2   8   366   313     -11   5   8   370   361     -10   8   8   382   375
  -1   8   7   574   585      -1  13   7   236   226     -10   2   8   361   356     -10   5   8   191   194      -9   8   8   277   268
   0   8   7   311   342       0  13   7   143   145      -9   2   8   426   406      -9   5   8   569   520      -8   8   8   665   668
  -9   9   7   230   229      -7  14   7   259   249      -8   2   8   470   460      -8   5   8   465   479      -7   8   8   225   223
  -8   9   7   222   196      -5  14   7   402   375      -7   2   8   326   354      -7   5   8   788   813      -6   8   8   414   417
  -7   9   7   155   161      -4  14   7   238   211      -6   2   8   343   333      -6   5   8   252   232      -5   8   8   322   337
  -6   9   7   664   657      -3  14   7   449   460      -5   2   8   317   310      -4   5   8    84   102      -4   8   8   414   382
  -5   9   7   199   199      -1  14   7   307   298      -4   2   8   343   370      -3   5   8   623   633      -3   8   8   599   590
  -4   9   7   386   398      -6  15   7   291   307      -3   2   8   925   886      -2   5   8   610   631      -2   8   8   748   734
  -3   9   7   176   166      -4  15   7   437   450      -2   2   8   608   624      -1   5   8   746   802      -1   8   8   266   271
  -2   9   7   388   403      -2  15   7   197   201      -1   2   8   694   631       0   5   8   932   853       0   8   8   803   832
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Table 1.5 (continued)

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CPRU(PPH3)2[C(OME)CH3] 4/112

PAGE 11

H	K	L	10FO	10FC
-11	9	8	223	222
-10	9	8	157	142
-9	9	8	439	446
-8	9	8	176	150
-7	9	8	508	503
-6	9	8	224	207
-4	9	8	191	192
-2	9	8	341	317
-1	9	8	881	898
0	9	8	190	190
-10	10	8	393	361
-8	10	8	429	439
-6	10	8	195	204
-5	10	8	291	273
-3	10	8	393	379
-2	10	8	330	321
-1	10	8	363	361
0	10	8	878	894
-10	11	8	119	143
-9	11	8	352	329
-7	11	8	331	323
-6	11	8	170	195
-4	11	8	333	318
-3	11	8	345	329
-2	11	8	291	307
-1	11	8	496	482
0	11	8	153	138
-9	12	8	157	133
-8	12	8	246	258
-6	12	8	188	171
-3	12	8	244	226
-2	12	8	408	394
-1	12	8	246	241
0	12	8	366	343
-6	13	8	141	146
-4	13	8	211	191
-3	13	8	296	281
-1	13	8	336	334
0	13	8	250	253
-5	14	8	151	116
-2	14	8	307	299
-1	14	8	159	155
0	14	8	265	259
-3	15	8	185	205
-1	15	8	287	283
-2	16	8	227	222
0	16	8	342	337
1	0	9	884	851
2	0	9	1685	1666
3	0	9	612	543
4	0	9	794	764
6	0	9	430	418
7	0	9	434	480
11	0	9	146	161
12	0	9	405	405
-13	1	9	304	313
-11	1	9	327	343
-9	1	9	216	211
-8	1	9	240	222
-7	1	9	523	465
-6	1	9	709	671
-5	1	9	1281	1405
-4	1	9	498	483
-3	1	9	1231	1137
-2	1	9	618	638
-1	1	9	289	245
0	1	9	434	404
-13	2	9	201	196
-12	2	9	293	300
-11	2	9	238	232
-10	2	9	219	240
-9	2	9	294	299
-7	2	9	492	497
-6	2	9	557	559
-5	2	9	536	589
-4	2	9	1270	1293
-3	2	9	690	657
-2	2	9	651	631
-1	2	9	290	246
0	2	9	167	167
-13	3	9	232	263
-12	3	9	384	347
-11	3	9	265	249
-8	3	9	525	524
-7	3	9	459	441
-6	3	9	833	784
-5	3	9	660	648
-4	3	9	931	922
-3	3	9	888	878
-2	3	9	385	379
-1	3	9	496	500
0	3	9	505	478
-9	4	9	263	268
-8	4	9	121	99
-7	4	9	445	439
-6	4	9	679	681
-5	4	9	668	671
-4	4	9	552	569
-3	4	9	582	589
-2	4	9	489	448
-1	4	9	415	429
0	4	9	410	371
-12	5	9	278	253
-11	5	9	153	159
-10	5	9	141	170
-9	5	9	110	140
-8	5	9	268	242
-7	5	9	361	374
-6	5	9	484	446
-5	5	9	313	296
-4	5	9	905	921
-3	5	9	260	294
-2	5	9	439	425
-1	5	9	484	493
0	5	9	671	641
-11	6	9	110	133
-8	6	9	288	284
-7	6	9	275	310
-6	6	9	275	265
-5	6	9	501	485
-4	6	9	237	231
-3	6	9	839	844
-2	6	9	310	295
-1	6	9	310	278
0	6	9	217	231
-12	7	9	122	135
-8	7	9	266	227
-7	7	9	236	246
-6	7	9	383	419
-5	7	9	387	398
-4	7	9	211	198
-2	7	9	578	605
-1	7	9	141	139
0	7	9	200	176
-11	8	9	154	174
-8	8	9	206	184
-7	8	9	441	454
-5	8	9	373	352
-4	8	9	239	216
-3	8	9	225	251
-2	8	9	318	324
-1	8	9	184	176
0	8	9	147	135
-8	9	9	275	265
-6	9	9	544	507
-5	9	9	451	450
-4	9	9	368	369
-3	9	9	306	325
-2	9	9	364	376
-1	9	9	143	126
0	9	9	261	275
-8	10	9	114	87
-7	10	9	327	342
-5	10	9	279	289
-4	10	9	527	520
-3	10	9	397	372
-2	10	9	107	107
-1	10	9	302	305
-6	11	9	422	417
-5	11	9	401	404
-4	11	9	495	542
-3	11	9	605	636
-2	11	9	343	376
-1	11	9	348	364
-7	12	9	154	164
-6	12	9	327	333
-5	12	9	355	361
-4	12	9	452	451
-3	12	9	474	486
-2	12	9	283	284
0	12	9	111	110
-8	13	9	123	146
-7	13	9	227	217
-6	13	9	256	254
-5	13	9	372	355
-4	13	9	458	458
-3	13	9	394	415
-1	13	9	263	252
0	13	9	284	274
-7	14	9	182	191

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CPRU(PPH3)2[C(OME)CH3] 4/112

PAGE 12

H	K	L	10FO	10FC
-6	14	9	291	322
-5	14	9	258	273
-4	14	9	222	225
-3	14	9	318	321
-2	14	9	438	445
-5	15	9	288	283
-4	15	9	283	284
-3	15	9	266	278
-2	15	9	233	230
-1	15	9	183	177
-2	16	9	229	220
-1	16	9	196	193
0	0	10	2112	2010
1	0	10	912	915
3	0	10	351	394
6	0	10	281	273
7	0	10	546	602
8	0	10	644	618
9	0	10	360	366
10	0	10	363	332
11	0	10	344	322
-12	1	10	302	294
-11	1	10	164	142
-10	1	10	360	374
-9	1	10	277	283
-8	1	10	524	527
-7	1	10	482	507
-5	1	10	203	226
-4	1	10	280	284
-3	1	10	378	345
-2	1	10	337	323
-1	1	10	713	666
0	1	10	599	613
-11	2	10	321	321
-10	2	10	230	221
-9	2	10	563	547
-8	2	10	502	498
-7	2	10	605	586
-6	2	10	156	161
-5	2	10	134	121
-4	2	10	350	312
-3	2	10	356	389
-2	2	10	230	227
-1	2	10	1103	1106
0	2	10	906	878
-12	3	10	293	304
-11	3	10	143	154
-10	3	10	375	376
-8	3	10	605	617
-7	3	10	246	234
-6	3	10	661	649
-5	3	10	301	305
-4	3	10	710	647
-2	3	10	853	867
-1	3	10	369	371
0	3	10	1201	1222
-12	4	10	223	204
-11	4	10	330	343
-10	4	10	217	225
-9	4	10	564	538
-8	4	10	143	154
-7	4	10	665	668
-6	4	10	279	291
-5	4	10	311	320
-4	4	10	155	149
-3	4	10	560	569
-2	4	10	556	526
-1	4	10	1440	1410
0	4	10	125	128
-10	5	10	375	380
-8	5	10	767	775
-7	5	10	211	187
-6	5	10	400	382
-5	5	10	90	56
-4	5	10	344	365
-3	5	10	205	224
-2	5	10	1149	1134
-1	5	10	183	198
0	5	10	1351	1345
-11	6	10	260	242
-9	6	10	466	488
-8	6	10	92	60
-7	6	10	714	727
-6	6	10	204	194
-5	6	10	193	154
-4	6	10	210	232
-3	6	10	510	521
-2	6	10	293	258
-1	6	10	983	1007
0	6	10	323	339
-10	7	10	476	498
-8	7	10	411	416
-6	7	10	292	291
-5	7	10	325	310
-4	7	10	283	281
-3	7	10	230	231
-2	7	10	800	830
-1	7	10	279	267
0	7	10	1104	1120
-11	8	10	338	341
-9	8	10	420	400
-8	8	10	109	74
-7	8	10	476	522
-5	8	10	204	209
-4	8	10	334	331
-3	8	10	492	494
-1	8	10	717	723
0	8	10	578	656
-10	9	10	346	331
-9	9	10	155	163
-8	9	10	478	479
-6	9	10	231	242
-5	9	10	281	297
-3	9	10	249	269
-2	9	10	602	624
-1	9	10	185	183
0	9	10	710	722
-9	10	10	336	361
-8	10	10	234	222
-7	10	10	273	268
-4	10	10	228	194
-3	10	10	309	322
-1	10	10	597	619
0	10	10	140	151
-9	11	10	130	147
-8	11	10	240	218
-7	11	10	218	233
-6	11	10	303	345
-4	11	10	119	107
-2	11	10	469	484
-1	11	10	280	277
0	11	10	356	354
-8	12	10	176	178
-7	12	10	160	185
-6	12	10	285	260
-3	12	10	180	182
-2	12	10	240	222
-1	12	10	321	332
-8	13	10	226	205
-3	13	10	323	346
-2	13	10	196	199
0	13	10	431	452
-2	14	10	240	223
-1	14	10	343	371
0	14	10	124	138
-3	15	10	159	173
-2	15	10	258	250
0	15	10	323	314
-2	16	10	120	133
-1	16	10	300	276
1	0	11	623	559
2	0	11	668	644
3	0	11	542	570
4	0	11	669	650
6	0	11	903	880
9	0	11	186	140
10	0	11	211	192
12	0	11	369	360
-11	1	11	267	270
-9	1	11	229	210
-8	1	11	280	268
-7	1	11	360	368
-6	1	11	250	294
-5	1	11	628	607
-4	1	11	388	418
-3	1	11	1150	1181
-2	1	11	312	293
-1	1	11	602	561
-12	2	11	436	397
-11	2	11	179	198
-10	2	11	230	216
-9	2	11	168	148
-8	2	11	411	396
-6	2	11	672	687
-5	2	11	594	599
-4	2	11	930	915
-3	2	11	197	206
-2	2	11	427	420
-1	2	11	303	264
0	2	11	1052	949

Table 1.5 (continued)

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CPRU(PPH3)2[C(OME)CH3] 4/112

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H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-11	3	11	328	332	-11	7	11	242	239	-3	12	11	181	206	0	1	12	1419	1437	-11	5	12	146	133
-10	3	11	153	161	-10	7	11	110	119	-2	12	11	245	265	-11	2	12	225	247	-10	5	12	360	342
-7	3	11	480	496	-7	7	11	422	416	-1	12	11	140	127	-9	2	12	443	466	-9	5	12	270	270
-5	3	11	785	827	-5	7	11	408	409	-7	13	11	206	223	-8	2	12	293	291	-8	5	12	386	389
-3	3	11	802	827	-4	7	11	264	281	-5	13	11	374	371	-7	2	12	566	561	-7	5	12	465	491
-2	3	11	451	443	-3	7	11	471	451	-4	13	11	126	103	-6	2	12	320	291	-6	5	12	242	290
-1	3	11	775	692	-2	7	11	596	585	-3	13	11	411	410	-5	2	12	182	167	-5	5	12	407	410
0	3	11	317	293	-1	7	11	404	435	-2	13	11	253	247	-4	2	12	214	221	-4	5	12	433	412
-12	4	11	306	305	-9	8	11	205	223	-1	13	11	202	183	-3	2	12	352	365	-3	5	12	593	566
-9	4	11	448	438	-8	8	11	171	175	-6	14	11	344	328	-2	2	12	233	221	-2	5	12	424	411
-8	4	11	280	280	-7	8	11	188	146	-4	14	11	400	414	-1	2	12	1101	1079	-1	5	12	619	634
-7	4	11	231	194	-6	8	11	672	642	-3	14	11	216	232	0	2	12	573	525	0	5	12	887	869
-6	4	11	611	610	-5	8	11	156	115	-2	14	11	295	317	-12	3	12	260	246	-11	6	12	193	187
-5	4	11	266	292	-4	8	11	438	443	-1	14	11	203	192	-10	3	12	326	338	-10	6	12	249	225
-4	4	11	663	659	-3	8	11	326	322	-3	15	11	374	367	-9	3	12	246	260	-9	6	12	426	419
-3	4	11	259	279	-2	8	11	380	378	0	0	12	487	474	-8	3	12	394	393	-8	6	12	403	402
-2	4	11	598	618	0	8	11	213	242	1	0	12	1179	1191	-7	3	12	337	353	-7	6	12	270	281
-1	4	11	230	212	-10	9	11	176	194	2	0	12	123	110	-6	3	12	301	270	-5	6	12	203	233
0	4	11	182	187	-7	9	11	372	358	3	0	12	283	275	-5	3	12	359	369	-4	6	12	240	217
-8	5	11	198	207	-5	9	11	580	575	4	0	12	420	391	-4	3	12	387	363	-3	6	12	273	247
-7	5	11	325	350	-3	9	11	526	556	5	0	12	168	118	-3	3	12	326	277	-2	6	12	401	398
-5	5	11	804	794	-1	9	11	335	342	6	0	12	495	505	-2	3	12	493	488	-1	6	12	534	555
-4	5	11	580	538	-9	10	11	132	139	7	0	12	393	402	-1	3	12	813	804	0	6	12	495	511
-3	5	11	630	617	-6	10	11	398	392	9	0	12	578	571	0	3	12	1380	1382	-11	7	12	251	220
-2	5	11	257	287	-5	10	11	253	219	11	0	12	323	296	-11	4	12	285	278	-10	7	12	226	230
-1	5	11	419	422	-4	10	11	619	609	12	0	12	203	224	-10	4	12	124	143	-9	7	12	313	308
-12	6	11	290	268	-3	10	11	258	252	-12	1	12	141	161	-9	4	12	364	344	-8	7	12	296	229
-10	6	11	128	136	-2	10	11	475	486	-11	1	12	266	255	-8	4	12	528	534	-7	7	12	299	304
-8	6	11	235	195	-7	11	11	272	283	-10	1	12	508	494	-7	4	12	260	263	-6	7	12	154	169
-6	6	11	583	570	-5	11	11	596	583	-8	1	12	693	682	-6	4	12	212	195	-5	7	12	283	271
-5	6	11	483	458	-3	11	11	407	439	-7	1	12	236	238	-5	4	12	504	491	-4	7	12	486	454
-4	6	11	726	758	-2	11	11	236	230	-6	1	12	243	249	-4	4	12	265	291	-3	7	12	251	257
-3	6	11	286	299	-1	11	11	135	155	-5	1	12	173	197	-3	4	12	689	691	-2	7	12	500	494
-2	6	11	487	512	-8	12	11	176	170	-4	1	12	366	376	-2	4	12	437	453	-1	7	12	690	680
-1	6	11	207	224	-6	12	11	329	328	-2	1	12	1065	1010	-1	4	12	622	604	0	7	12	247	243
0	6	11	684	645	-4	12	11	531	543	-1	1	12	628	611	0	4	12	968	954	-10	8	12	278	269

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CPRU(PPH3)2[C(OME)CH3] 4/112

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H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-9	8	12	237	218	-7	12	12	339	353	-6	2	13	136	153	-10	6	13	164	177	-3	9	13	225	221
-8	8	12	239	197	-5	12	12	168	166	-5	2	13	838	807	-8	6	13	234	236	-2	9	13	233	265
-7	8	12	222	222	-3	12	12	326	317	-4	2	13	420	399	-7	6	13	339	346	-1	9	13	132	148
-6	8	12	406	404	-2	12	12	136	130	-3	2	13	880	813	-6	6	13	436	433	0	9	13	487	492
-5	8	12	182	195	-1	12	12	432	426	-2	2	13	373	360	-5	6	13	609	564	-8	10	13	175	153
-4	8	12	186	176	-6	13	12	250	259	-1	2	13	257	280	-4	6	13	701	703	-7	10	13	274	270
-3	8	12	232	223	-5	13	12	135	99	0	2	13	340	390	-3	6	13	613	635	-6	10	13	290	285
-2	8	12	500	480	-4	13	12	118	125	-11	3	13	149	152	-2	6	13	251	266	-5	10	13	327	362
-1	8	12	581	624	-2	13	12	386	386	-10	3	13	162	169	-1	6	13	533	520	-4	10	13	133	149
0	8	12	325	351	-1	13	12	191	165	-8	3	13	481	456	-11	7	13	193	211	-3	10	13	508	538
-10	9	12	219	211	0	13	12	490	493	-7	3	13	208	186	-8	7	13	129	138	-2	10	13	290	322
-9	9	12	176	169	-3	14	12	198	193	-6	3	13	660	680	-7	7	13	352	374	-1	10	13	262	301
-8	9	12	345	349	-1	14	12	396	410	-5	3	13	554	571	-6	7	13	371	363	0	10	13	99	60
-7	9	12	316	325	0	14	12	212	207	-4	3	13	444	470	-5	7	13	259	256	-6	11	13	270	261
-6	9	12	173	174	-2	15	12	320	296	-3	3	13	618	567	-4	7	13	764	772	-5	11	13	250	248
-5	9	12	209	218	-1	15	12	139	152	-2	3	13	459	432	-3	7	13	597	564	-4	11	13	376	360
-3	9	12	310	306	0	15	12	285	281	-1	3	13	80	74	-2	7	13	482	484	-2	11	13	274	274
-2	9	12	370	387	1	0	13	507	489	-11	4	13	191	199	-1	7	13	300	316	-1	11	13	217	192
-1	9	12	383	389	3	0	13	575	534	-9	4	13	143	154	0	7	13	427	404	-7	12	13	233	211
0	9	12	456	482	4	0	13	463	454	-8	4	13	276	284	-10	8	13	186	190	-5	12	13	340	339
-9	10	12	323	294	5	0	13	977	945	-7	4	13	566	560	-9	8	13	114	72	-4	12	13	176	177
-7	10	12	360	352	9	0	13	249	268	-6	4	13	218	190	-8	8	13	213	210	-3	12	13	413	421
-6	10	12	219	218	-12	1	13	321	317	-5	4	13	352	343	-7	8	13	303	324	-2	12	13	186	176
-4	10	12	184	185	-8	1	13	306	298	-4	4	13	575	571	-6	8	13	543	523	-6	13	13	310	302
-3	10	12	362	349	-7	1	13	305	292	-3	4	13	625	621	-5	8	13	758	753	-4	13	13	230	233
-2	10	12	215	208	-6	1	13	271	257	-2	4	13	634	629	-4	8	13	358	350	-3	13	13	124	88
-1	10	12	408	397	-5	1	13	127	131	-1	4	13	559	568	-3	8	13	338	334	-2	13	13	277	253
0	10	12	233	252	-4	1	13	894	905	-10	5	13	162	159	-1	8	13	277	290	-1	13	13	130	113
-9	11	12	169	146	-3	1	13	277	289	-7	5	13	174	141	0	8	13	208	201	-5	14	13	255	259
-8	11	12	314	321	-2	1	13	396	346	-6	5	13	690	693	-10	9	13	114	140	-4	14	13	196	195
-6	11	12	281	260	-1	1	13	412	402	-5	5	13	671	678	-9	9	13	164	155	-3	14	13	209	211
-5	11	12	143	142	0	1	13	359	333	-4	5	13	354	312	-8	9	13	107	96	-1	14	13	112	115
-3	11	12	189	228	-11	2	13	204	198	-3	5	13	650	647	-7	9	13	179	169	-2	15	13	231	238
-2	11	12	455	466	-9	2	13	159	163	-2	5	13	556	563	-6	9	13	251	238	0	0	14	779	707
0	11	12	534	555	-8	2	13	266	269	-1	5	13	110	98	-5	9	13	302	286	2	0	14	544	670
-8	12	12	173	157	-7	2	13	226	227	-11	6	13	189	183	-4	9	13	665	665	3	0	14	192	212

Table 1.5 (continued)

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR   CPRU(PPH3)2[C(OME)CH3] 4/112                                              PAGE 15

  H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC

  6  0 14  490  496      0  3 14  198  202     -2  8 14  361  351      8  0 15  116  149     -7  5 15  247  255
  8  0 14  283  287    -11  4 14  171  168      0  8 14  562  585     -6  1 15  192  200     -6  5 15  514  533
 10  0 14  560  551    -10  4 14  298  279     -9  9 14  321  285     -5  1 15  327  294     -5  5 15  293  281
 12  0 14  185  196     -9  4 14  107   94     -7  9 14  213  211     -4  1 15  557  564     -4  5 15  759  780
-11  1 14  348  361     -8  4 14  521  530     -5  9 14  182  196     -3  1 15  340  321     -3  5 15  274  262
-10  1 14  238  200     -6  4 14  225  242     -3  9 14  431  420     -2  1 15  494  501     -2  5 15  407  389
 -9  1 14  560  564     -5  4 14  336  323     -1  9 14  424  432     -1  1 15  200  207     -1  5 15  468  503
 -7  1 14  579  560     -3  4 14  423  434      0  9 14  247  247     -8  2 15  180  193      0  5 15  245  282
 -6  1 14  297  297     -2  4 14  470  450     -8 10 14  276  265     -7  2 15  380  394     -8  6 15  161  154
 -5  1 14  378  338     -1  4 14  359  326     -6 10 14  262  233     -6  2 15  230  215     -7  6 15  437  439
 -4  1 14  144  117      0  4 14  823  863     -5 10 14  143  147     -5  2 15  463  478     -6  6 15  176  196
 -3  1 14  745  720     -9  5 14  499  512     -4 10 14  271  273     -4  2 15  189  212     -5  6 15  691  715
 -2  1 14  405  402     -8  5 14  264  265     -2 10 14  609  626     -3  2 15  618  603     -4  6 15  368  378
 -1  1 14  868  906     -7  5 14  367  367     -1 10 14  183  216     -1  2 15  177  179     -3  6 15  742  770
  0  1 14  657  621     -4  5 14  225  214      0 10 14  444  437    -11  3 15  137   94     -2  6 15  423  443
-10  2 14  441  444     -2  5 14  491  475     -7 11 14  256  249     -8  3 15  275  265     -1  6 15  189  192
 -9  2 14  257  253     -1  5 14  630  628     -5 11 14  102   84     -7  3 15  279  293      0  6 15  161  177
 -8  2 14  579  584      0  5 14  211  173     -3 11 14  300  315     -6  3 15  486  498     -8  7 15  266  243
 -7  2 14  406  392    -10  6 14  214  264     -1 11 14  617  636     -5  3 15  299  296     -6  7 15  571  558
 -6  2 14  362  369     -9  6 14  131  121     -6 12 14  233  234     -4  3 15  603  609     -5  7 15  234  256
 -5  2 14  155  164     -8  6 14  481  457     -4 12 14  167  174     -3  3 15  336  315     -4  7 15  580  597
 -4  2 14  237  224     -7  6 14  186  187     -3 12 14  105  119     -2  3 15  496  482     -3  7 15  447  468
 -3  2 14  482  461     -6  6 14  222  200     -2 12 14  492  522     -1  3 15  309  283     -2  7 15  636  661
 -2  2 14  624  648     -2  6 14  349  356     -1 12 14  151  155      0  3 15  455  406     -7  8 15  290  296
 -1  2 14  214  207     -1  6 14  242  252      0 12 14  644  639    -11  4 15  256  254     -5  8 15  816  821
  0  2 14  756  763      0  6 14  706  742     -3 13 14  202  215    -10  4 15  124  123     -4  8 15  305  296
-11  3 14  303  272     -9  7 14  249  244     -2 13 14  235  224     -8  4 15  185  219     -3  8 15  568  591
-10  3 14  254  255     -7  7 14  258  274     -1 13 14  516  515     -7  4 15  501  548      0  8 15  203  216
 -9  3 14  572  569     -5  7 14  236  273     -3 14 14  192  197     -6  4 15  207  211     -7  9 15  131  122
 -7  3 14  333  350     -3  7 14  482  477     -2 14 14  264  265     -5  4 15  272  290     -6  9 15  395  412
 -6  3 14  287  282     -2  7 14  166  172      0 14 14  503  509     -3  4 15  674  715     -5  9 15  263  259
 -5  3 14  251  242     -1  7 14  529  540      2  0 15  186  203     -2  4 15  521  500     -4  9 15  739  718
 -4  3 14  177  163      0  7 14  139  109      3  0 15  297  284     -1  4 15  581  587     -3  9 15  284  302
 -3  3 14  193  180    -10  8 14  271  249      4  0 15  543  520    -10  5 15  197  184     -2  9 15  385  379
 -2  3 14  611  584     -5  8 14  195  214      5  0 15  755  770     -9  5 15  197  197     -8 10 15  220  237
 -1  3 14  883  894     -4  8 14  109  119      7  0 15  142  129     -8  5 15  233  246     -7 10 15  278  291
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR   CPRU(PPH3)2[C(OME)CH3] 4/112                                              PAGE 16

  H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC

 -5 10 15  364  390     -1  1 16  468  448     -4  5 16  181  188     -7 11 16  248  244     -2  2 17  306  301
 -4 10 15  228  245      0  1 16  197  226     -3  5 16  365  369     -6 11 16  178  161     -1  2 17  231  228
 -3 10 15  533  531    -11  2 16  247  248     -2  5 16  188  177     -3 11 16  137  140      0  2 17  205  159
 -2 10 15  142  120    -10  2 16  287  305     -1  5 16  435  448     -2 11 16  275  302     -7  3 17  317  310
 -1 10 15  283  287     -9  2 16  410  424      0  5 16  661  636     -1 11 16  290  289     -6  3 17  258  244
  0 10 15  201  180     -8  2 16  305  312    -10  6 16  190  197      0 11 16  314  313     -5  3 17  646  611
 -6 11 15  342  342     -7  2 16  281  248     -9  6 16  229  251     -3 12 16  170  162     -4  3 17  136  152
 -5 11 15  240  220     -6  2 16  357  353     -8  6 16  209  203     -2 12 16  233  232     -3  3 17  515  508
 -4 11 15  375  381     -3  2 16  411  415     -4  6 16  274  268     -1 12 16  253  274     -2  3 17  527  466
 -2 11 15  255  263     -2  2 16  691  665     -2  6 16  385  376      0 12 16  296  274      0  3 17  318  301
 -1 11 15  182  213     -1  2 16  649  627     -1  6 16  277  290     -1 13 16  263  275    -10  4 17  204  191
 -5 12 15  250  241      0  2 16  507  525      0  6 16  417  436      0 13 16  387  382     -8  4 17  237  257
 -3 12 15  321  324    -11  3 16  227  208     -8  7 16  181  186     -1 14 16  329  323     -7  4 17  194  175
 -1 12 15  225  210     -9  3 16  321  333     -7  7 16  228  231      0 14 16  236  240     -6  4 17  448  420
  0 12 15  247  241     -8  3 16  217  203     -3  7 16  253  254      2  0 17  219  220     -5  4 17  256  275
 -1 13 15  130  138     -7  3 16  344  335     -2  7 16  243  228      3  0 17  565  541     -4  4 17  314  322
  0  0 16  265  275     -6  3 16  150  135     -1  7 16  356  371      4  0 17  457  477     -3  4 17  160  155
  1  0 16  977  887     -5  3 16  183  172     -7  8 16  107   90      5  0 17  265  261     -2  4 17  796  801
  2  0 16  682  622     -4  3 16  192  169     -6  8 16  176  151      6  0 17  244  237     -1  4 17  279  283
  3  0 16  413  428     -3  3 16  176  195     -5  8 16  244  298      7  0 17  215  205     -8  5 17  111  103
  5  0 16  316  302     -2  3 16  341  333     -2  8 16  208  232      8  0 17  206  178     -7  5 17  448  427
  6  0 16  299  253     -1  3 16  638  649     -1  8 16  311  332     -9  1 17  185  173     -6  5 17  263  247
  7  0 16  379  369      0  3 16  832  818      0  8 16  254  231     -7  1 17  287  273     -5  5 17  558  555
  8  0 16  244  237    -10  4 16  281  294     -8  9 16  148  140     -6  1 17  499  505     -4  5 17  377  353
  9  0 16  468  451     -9  4 16  340  339     -7  9 16  246  251     -5  1 17  387  389     -3  5 17  537  518
 10  0 16  452  462     -8  4 16  201  208     -6  9 16  234  218     -4  1 17  306  281     -1  5 17  497  475
 11  0 16  302  298     -6  4 16  314  325     -5  9 16  153  163     -3  1 17  504  509      0  5 17  379  363
-11  1 16  285  298     -5  4 16  182  160     -4  9 16  184  160     -2  1 17  207  200     -8  6 17  121  107
-10  1 16  291  325     -3  4 16  146  159     -2  9 16  263  250      0  1 17  247  224     -7  6 17  131  138
 -9  1 16  368  358     -2  4 16  731  715     -1  9 16  377  380    -10  2 17  122   72     -6  6 17  470  473
 -8  1 16  261  286     -1  4 16  390  387     -7 10 16  213  213     -8  2 17  184  192     -5  6 17  255  246
 -7  1 16  263  267      0  4 16  548  507     -6 10 16  187  204     -7  2 17  201  237     -4  6 17  662  649
 -6  1 16  513  517    -10  5 16  129  110     -3 10 16  377  370     -6  2 17  388  384     -2  6 17  568  565
 -5  1 16  317  305     -9  5 16  290  273     -2 10 16  338  354     -5  2 17  234  241      0  6 17  222  242
 -3  1 16  585  559     -8  5 16  409  397     -1 10 16  248  257     -4  2 17  435  418     -7  7 17  399  387
 -2  1 16  877  803     -5  5 16  118  116      0 10 16  260  256     -3  2 17  255  268     -6  7 17  323  313
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Table 1.5 (continued)

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR   CPRU(PPH3)2[C(OME)CH3] 4/112                                PAGE 17

  H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC

 -5  7 17  422  434    -10  1 18  410  405     -9  6 18  272  283     -5  1 19  696  708     -3  6 19  426  428
 -3  7 17  711  725     -8  1 18  326  338     -3  6 18  158  153     -3  1 19  572  565     -2  6 19  313  306
 -1  7 17  307  303     -7  1 18  122  164     -2  6 18  136  149     -2  1 19  235  255      0  6 19  209  203
 -6  8 17  428  420     -6  1 18  479  494     -1  6 18  573  607     -1  1 19  124  184     -7  7 19  257  268
 -5  8 17  153  175     -5  1 18  114  159      0  6 18  262  264     -8  2 19  136  162     -6  7 19  218  193
 -4  8 17  807  825     -4  1 18  245  262     -8  7 18  266  267     -7  2 19  118  112     -5  7 19  398  371
 -3  8 17  175  175     -3  1 18  281  273     -4  7 18  130  166     -6  2 19  566  589     -4  7 19  297  312
 -2  8 17  255  237     -2  1 18  505  499     -2  7 18  492  479     -5  2 19  193  199     -3  7 19  265  271
 -7  9 17  166  160     -1  1 18  245  259     -1  7 18  215  256     -4  2 19  533  500     -2  7 19  386  364
 -6  9 17  271  260      0  1 18  202  183      0  7 18  455  474     -3  2 19  315  312     -1  7 19  342  353
 -5  9 17  566  569    -10  2 18  151  155     -7  8 18  265  276     -2  2 19  267  249      0  7 19  292  285
 -3  9 17  571  576     -9  2 18  418  412     -5  8 18  105   70     -7  3 19  239  253     -5  8 19  401  408
 -2  9 17  118   74     -7  2 18  409  404     -4  8 18  195  197     -6  3 19  224  231     -4  8 19  448  445
 -7 10 17  263  258     -6  2 18  260  264     -3  8 18  365  375     -5  3 19  452  471     -3  8 19  308  294
 -6 10 17  243  246     -5  2 18  247  240     -1  8 18  370  368     -3  3 19  455  465     -2  8 19  342  335
 -4 10 17  412  416     -4  2 18  122  146     -6  9 18  259  242     -2  3 19  167  151     -6  9 19  139  172
 -2 10 17  274  269     -3  2 18  476  461     -2  9 18  410  404     -1  3 19  304  343     -5  9 19  358  378
 -1 10 17  165  181     -2  2 18  433  421      0  9 18  326  343     -9  4 19  126  130     -4  9 19  228  234
 -5 11 17  355  354     -1  2 18  611  630     -5 10 18  201  220     -7  4 19  249  256     -3  9 19  285  302
 -4 11 17  181  188      0  2 18  124  112     -3 10 18  341  342     -6  4 19  425  456     -1  9 19  143  162
 -3 11 17  288  305    -10  3 18  327  320     -2 10 18  173  193     -4  4 19  311  301     -4 10 19  415  395
 -2 11 17  218  233     -8  3 18  398  406     -1 10 18  353  364     -3  4 19  251  277      0 10 19  187  173
  0 11 17  384  386     -6  3 18  333  319      0 10 18  206  215     -2  4 19  237  243     -4 11 19  116   91
 -5 12 17  246  211     -4  3 18  229  202     -2 11 18  359  367     -1  4 19  297  302     -3 11 19  343  335
 -4 12 17  132  116     -2  3 18  450  472      0 11 18  375  366     -7  5 19  321  333     -1 11 19  240  242
 -3 12 17  227  237     -1  3 18  580  557     -3 12 18  142  175     -5  5 19  324  332      0 12 19  353  349
 -1 12 17  232  257      0  3 18  454  510     -2 12 18  197  192     -4  5 19  272  267      0  0 20  308  319
 -1 13 17  138  146     -9  4 18  358  335     -1 12 18  413  395     -3  5 19  301  322      2  0 20  433  426
  0 13 17  188  203     -7  4 18  291  309      2  0 19  521  468     -2  5 19  290  291      3  0 20  268  237
  0  0 18  152  117     -3  4 18  190  178      4  0 19  718  729     -1  5 19  222  256      4  0 20  229  244
  1  0 18  559  608     -2  4 18  211  208      5  0 19  226  222      0  5 19  266  271      6  0 20  465  469
  3  0 18  361  393     -1  4 18  680  677      6  0 19  367  361     -8  6 19  185  151      8  0 20  273  284
  5  0 18  473  477     -8  5 18  392  387      9  0 19  111   82     -7  6 19  224  196     -9  1 20  269  266
  6  0 18  185  191     -5  5 18  145  166     -9  1 19  109   76     -6  6 19  359  358     -7  1 20  258  249
  7  0 18  331  325     -2  5 18  461  506     -7  1 19  268  277     -5  6 19  274  269     -5  1 20  283  305
  9  0 18  479  475      0  5 18  684  663     -6  1 19  101   98     -4  6 19  287  305     -4  1 20  192  188
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR   CPRU(PPH3)2[C(OME)CH3] 4/112                                PAGE 18

  H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC      H  K  L 10FO 10FC

 -3  1 20  337  316     -6  6 20  147  118      5  0 21  622  604     -7  6 21  291  285     -1  3 22  525  510
 -2  1 20  176  155     -2  6 20  251  249     -8  1 21  163  154     -6  6 21  168  157      0  3 22  198  124
 -1  1 20  666  659     -1  6 20  417  433     -7  1 21  213  206     -5  6 21  294  299     -7  4 22  120  108
  0  1 20  342  296      0  6 20  349  390     -6  1 21  343  362     -4  6 21  134  123     -2  4 22  279  292
 -6  2 20  264  290     -7  7 20  175  186     -5  1 21  263  256     -2  6 21  110  117     -1  4 22  232  207
 -3  2 20  162  166     -6  7 20  177  176     -4  1 21  581  617     -1  6 21  273  271      0  4 22  782  792
 -2  2 20  426  432     -5  7 20  133  130     -2  1 21  277  295     -4  7 21  335  334     -3  5 22  172  213
 -1  2 20  293  290     -4  7 20  178  199      0  1 21  179  127     -3  7 21  210  215     -1  5 22  556  531
  0  2 20  411  417     -3  7 20  174  172     -8  2 21  238  243     -2  7 21  180  181     -6  6 22  167  154
 -9  3 20  297  304     -1  7 20  370  382     -7  2 21  223  231     -5  8 21  260  283     -2  6 22  308  298
 -8  3 20  289  301      0  7 20  541  601     -5  2 21  597  580     -3  8 21  326  332      0  6 22  655  637
 -5  3 20  185  201     -5  8 20  166  164     -4  2 21  313  318     -4  9 21  376  390     -5  7 22  128   96
 -4  3 20  222  216     -4  8 20  248  244     -3  2 21  397  395      0  9 21  225  237     -4  7 22  185  199
 -3  3 20  180  209     -3  8 20  247  259     -2  2 21  184  173     -3 10 21  280  284     -1  7 22  479  488
 -2  3 20  252  259     -2  8 20  244  264      0  2 21  455  444      0  0 22  147  164     -4  8 22  160  157
 -1  3 20  469  509     -1  8 20  383  383     -7  3 21  262  259      1  0 22  157   94     -2  8 22  390  385
  0  3 20  482  466      0  8 20  228  208     -6  3 21  329  317      2  0 22  446  375      0  8 22  321  305
 -8  4 20  326  332     -5  9 20  173  171     -5  3 21  101  100      3  0 22  220  177     -3  9 22  324  317
 -4  4 20  189  206     -3  9 20  236  254     -4  3 21  390  373      6  0 22  286  264     -1  9 22  368  362
 -2  4 20  383  356     -2  9 20  305  329     -2  3 21  472  459     -7  1 22  275  232      2  0 23  400  302
 -1  4 20  396  399     -1  9 20  288  268     -8  4 21  204  186     -1  1 22  542  459      3  0 23  728  514
  0  4 20  495  520      0  9 20  219  203     -7  4 21  266  262     -6  2 22  241  196      4  0 23  531  402
 -8  5 20  335  338     -4 10 20  149  122     -6  4 21  181  156     -4  2 22  211  194      5  0 23  631  498
 -7  5 20  255  265     -3 10 20  204  202     -5  4 21  385  378     -2  2 22  310  294      6  0 23  212  148
 -6  5 20  144  151     -2 10 20  318  333     -4  4 21  130  104     -1  2 22  270  227     -5  1 23  585  402
 -4  5 20  163  196     -1 10 20  185  211     -3  4 21  304  298      0  2 22  428  424     -3  1 23  355  255
 -3  5 20  255  264      0 10 20  201  209     -2  4 21  138  157     -7  3 22  341  341     -2  1 23  315  222
 -2  5 20  234  254     -1 11 20  236  247     -1  4 21  261  268     -4  3 22  197  182     -5  3 23  121  265
 -1  5 20  399  432      1  0 21  130  123     -6  5 21  394  389     -3  3 22  223  206     -2  3 23  111  252
  0  5 20  393  419      3  0 21  564  560     -4  5 21  239  206     -2  3 22  113   61     -2  5 23  134  236
 -7  6 20  316  327      4  0 21  200  215     -2  5 21  335  343
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APPENDIX 2. Supplementary data for $Au_2Fe_2Ir(\mu_4-\eta^2-C_2Ph)(CO)_7(PPh_3)_3$ (39) (Chapter 4).

Table 2.1	Fractional atomic coordinates and thermal parameters for non-hydrogen atoms
Table 2.2	Positional and thermal parameters for hydrogen atoms
Table 2.3	Interatomic distances
Table 2.4	Interatomic angles
Table 2.5	Observed and calculated structure factors

Table 2.1. Fractional atomic coordinates (X 10^5 for Au, Ir and Fe; X 10^4 for remaining non-hydrogen atoms) and thermal parameters (X 10^4 for Au, Ir and Fe; X 10^3 for remaining non-hydrogen atoms)

Atom	x	y	z	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Au(1)	22385(10)	64626(3)	29031(6)	476(6)	352(5)	331(5)	-56(4)	-38(5)	39(4)
Au(2)	7270(10)	66169(3)	38390(7)	438(5)	403(5)	363(5)	15(4)	-28(5)	-64(4)
Au(1a)	25908(5)	64282(6)	23775(5)	119(26)					
Au(1b)	16966(9)	64347(2)	32091(3)	119(26)					
Au(2a)	11376(6)	66411(2)	33205(0)	119(26)					
Au(2b)	1793(2)	66452(6)	41674(3)	119(26)					
Ir(1)	24600(-)	71966(3)	38300(-)	388(5)	290(5)	282(5)	5(4)	-66(4)	11(4)
Ir(1a)	28593(0)	71995(4)	33520(8)	119(26)					
Ir(1b)	19637(9)	71920(4)	41327(3)	119(26)					
Fe(1)	1271(3)	7805(1)	2926(2)	52(2)	35(2)	34(2)	6(1)	-6(2)	5(1)
Fe(1a)	1681(54)	7835(35)	2319(45)	12(3)					
Fe(1b)	555(53)	7751(35)	3235(46)	12(3)					
Fe(2)	1904(3)	8165(1)	4106(2)	62(2)	32(2)	42(2)	-6(2)	-4(2)	-3(2)
Fe(2a)	2212(53)	8135(36)	3655(49)	12(3)					
Fe(2b)	1737(60)	8105(51)	4298(55)	12(3)					
P(1)	3113(5)	6805(2)	4851(3)	45(3)	41(3)	36(3)	3(2)	-7(3)	-6(2)
P(2)	-532(5)	6045(2)	3973(3)	44(3)	32(3)	45(3)	2(3)	-2(3)	1(2)
P(3)	2282(5)	5955(2)	1957(3)	61(3)	36(3)	33(3)	-8(2)	-5(3)	4(3)
C(1)	3733(22)	7156(10)	3495(15)	62(6)	50(6)	52(6)	-5(6)	-20(6)	-8(6)
O(1)	4540(16)	7182(7)	3299(12)	72(4)					
C(2)	498(18)	7401(9)	2337(13)	46(4)					
O(2)	-1(17)	7139(8)	1961(12)	77(4)					
C(3)	2371(17)	7816(8)	2514(12)	49(4)					
C(4)	759(22)	8368(11)	2551(16)	61(5)					
O(4)	429(20)	8742(10)	2292(15)	105(5)					
C(5)	1569(23)	8770(13)	4003(18)	75(5)					
O(5)	1276(23)	9216(12)	3946(17)	123(5)					
C(6)	2149(24)	8181(13)	5060(18)	76(5)					
O(6)	2315(17)	8242(9)	5638(13)	86(5)					
C(7)	3215(19)	8244(10)	3944(14)	50(5)					
O(7)	4013(17)	8323(8)	3821(12)	73(4)					
C(8)	1096(18)	7496(8)	3896(11)	57(6)	34(6)	33(6)	4(6)	-33(6)	8(6)
C(9)	431(18)	7883(8)	3812(10)	63(6)	38(6)	11(5)	-1(5)	-9(6)	-7(6)
C(10)	-1012(10)	8481(5)	3852(8)	73(5)					
C(11)	-2068(10)	8576(5)	3871(8)	84(5)					
C(12)	-2762(10)	8176(5)	3885(8)	68(5)					

Table 2.1 (continued)

Atom	x	y	z	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
C(13)	-2401(10)	7682(5)	3879(8)	70(5)					
C(14)	-1346(10)	7588(5)	3860(8)	49(4)					
C(15)	-651(10)	7988(5)	3847(8)	41(4)					
C(16)	3190(9)	6940(5)	6300(7)	55(5)					
C(17)	2761(9)	7037(5)	6918(7)	84(5)					
C(18)	1699(9)	7137(5)	6891(7)	68(5)					
C(19)	1068(9)	7139(5)	6247(7)	79(5)					
C(20)	1497(9)	7041(5)	5630(7)	67(5)					
C(21)	2558(9)	6941(5)	5656(7)	45(4)					
C(22)	5238(11)	6562(5)	5357(8)	74(5)					
C(23)	6275(11)	6696(5)	5555(8)	79(5)					
C(24)	6574(11)	7199(5)	5544(8)	77(5)					
C(25)	5836(11)	7569(5)	5335(8)	86(5)					
C(26)	4800(11)	7435(5)	5137(8)	58(5)					
C(27)	4501(11)	6932(5)	5149(8)	52(5)					
C(28)	3703(11)	5887(5)	4328(7)	57(5)					
C(29)	3739(11)	5364(5)	4300(7)	79(5)					
C(30)	3183(11)	5077(5)	4735(7)	105(6)					
C(31)	2592(11)	5314(5)	5198(7)	116(6)					
C(32)	2556(11)	5838(5)	5227(7)	60(5)					
C(33)	3112(11)	6124(5)	4792(7)	47(4)					
C(34)	-1830(10)	6424(5)	2853(8)	58(5)					
C(35)	-2786(10)	6525(5)	2458(8)	74(5)					
C(36)	-3709(10)	6418(5)	2731(8)	81(5)					
C(37)	-3678(10)	6208(5)	3400(8)	89(6)					
C(38)	-2723(10)	6107(5)	3795(8)	65(5)					
C(39)	-1799(10)	6215(5)	3522(8)	45(4)					
C(40)	-914(11)	6393(5)	5250(8)	88(6)					
C(41)	-1048(11)	6356(5)	5958(8)	83(5)					
C(42)	-981(11)	5889(5)	6291(8)	82(5)					
C(43)	-778(11)	5459(5)	5916(8)	98(6)					
C(44)	-644(11)	5495(5)	5207(8)	72(5)					
C(45)	-712(11)	5963(5)	4874(8)	42(4)					
C(46)	763(10)	5272(5)	3636(7)	54(5)					
C(47)	992(10)	4786(5)	3431(7)	80(5)					
C(48)	190(10)	4442(5)	3253(7)	92(6)					

Table 2.1 (continued)

Atom	x	y	z	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
C(49)	-841(10)	4584(5)	3280(7)	74(5)					
C(50)	-1070(10)	5070(5)	3485(7)	78(5)					
C(51)	-268(10)	5414(5)	3664(7)	46(4)					
C(52)	129(11)	5928(5)	1646(7)	66(5)					
C(53)	-804(11)	5923(5)	1197(7)	81(5)					
C(54)	-792(11)	5913(5)	471(7)	92(6)					
C(55)	154(11)	5909(5)	194(7)	89(6)					
C(56)	1088(11)	5915(5)	643(7)	68(5)					
C(57)	1075(11)	5924(5)	1369(7)	47(4)					
C(58)	3226(12)	6716(6)	1344(9)	81(5)					
C(59)	3926(12)	6933(6)	936(9)	106(6)					
C(60)	4626(12)	6631(6)	630(9)	89(6)					
C(61)	4626(12)	6112(6)	732(9)	99(6)					
C(62)	3926(12)	5894(6)	1140(9)	85(5)					
C(63)	3226(12)	6196(6)	1446(9)	52(5)					
C(64)	3618(11)	5183(6)	2467(8)	85(5)					
C(65)	3902(11)	4682(6)	2589(8)	94(6)					
C(66)	3204(11)	4299(6)	2365(8)	103(6)					
C(67)	2222(11)	4416(6)	2019(8)	66(5)					
C(68)	1939(11)	4918(6)	1897(8)	58(5)					
C(69)	2637(11)	5301(6)	2121(8)	56(5)					
O(108)	6362(28)	4892(16)	465(21)	172(6)					
C(100)	6325(45)	4811(23)	1201(19)	236(6)					
C(101)	6608(25)	5128(14)	1862(18)	90(6)					

Where the anisotropic thermal parameter is given by the following expression:

$$T_{aniso} = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})].$$

Table 2.2. Positional (X 10^4) and thermal parameters (X 10^3) for hydrogen atoms.

Atom	x	y	z	U(11)
H(10)	-530(10)	8759(5)	3842(8)	117(6)
H(11)	-2319(10)	8919(5)	3874(8)	117(6)
H(12)	-3496(10)	8242(5)	3898(8)	117(6)
H(13)	-2884(10)	7404(5)	3889(8)	117(6)
H(14)	-1095(10)	7245(5)	3857(8)	117(6)
H(16)	3928(9)	6870(5)	6319(7)	117(6)
H(17)	3200(9)	7036(5)	7366(7)	117(6)
H(18)	1401(9)	7204(5)	7321(7)	117(6)
H(19)	330(9)	7208(5)	6229(7)	117(6)
H(20)	1058(9)	7042(5)	5182(7)	117(6)
H(22)	5030(11)	6212(5)	5365(8)	117(6)
H(23)	6787(11)	6438(5)	5700(8)	117(6)
H(24)	7294(11)	7292(5)	5681(8)	117(6)
H(25)	6044(11)	7919(5)	5327(8)	117(6)
H(26)	4287(11)	7692(5)	4992(8)	117(6)
H(28)	4090(11)	6086(5)	4026(7)	117(6)
H(29)	4151(11)	5199(5)	3977(7)	117(6)
H(30)	3208(11)	4713(5)	4715(7)	117(6)
H(31)	2205(11)	5115(5)	5501(7)	117(6)
H(32)	2144(11)	6002(5)	5549(7)	117(6)
H(34)	-1188(10)	6499(5)	2663(8)	117(6)
H(35)	-2807(10)	6671(5)	1992(8)	117(6)
H(36)	-4373(10)	6488(5)	2456(8)	117(6)
H(37)	-4320(10)	6133(5)	3590(8)	117(6)
H(38)	-2701(10)	5961(5)	4260(8)	117(6)
H(40)	-961(11)	6718(5)	5018(8)	117(6)
H(41)	-1189(11)	6656(5)	6219(8)	117(6)
H(42)	-1074(11)	5864(5)	6783(8)	117(6)
H(43)	-731(11)	5134(5)	6147(8)	117(6)
H(44)	-503(11)	5196(5)	4946(8)	117(6)
H(46)	1320(10)	5512(5)	3760(7)	117(6)
H(47)	1708(10)	4687(5)	3412(7)	117(6)
H(48)	349(10)	4104(5)	3110(7)	117(6)
H(49)	-1398(10)	4344(5)	3156(7)	117(6)
H(50)	-1786(10)	5169(5)	3504(7)	117(6)
H(52)	121(11)	5935(5)	2150(7)	117(6)

Table 2.2 (continued)

Atom	x	y	z	U(11)
H(52)	121(11)	5935(5)	2150(7)	117(6)
H(53)	-1462(11)	5926(5)	1389(7)	117(6)
H(54)	-1441(11)	5909(5)	159(7)	117(6)
H(55)	163(11)	5902(5)	-311(7)	117(6)
H(56)	1745(11)	5912(5)	451(7)	117(6)
H(58)	2739(12)	6926(6)	1557(9)	117(6)
H(59)	3925(12)	7294(6)	865(9)	117(6)
H(60)	5112(12)	6782(6)	346(9)	117(6)
H(61)	5113(12)	5902(6)	519(9)	117(6)
H(62)	3926(12)	5533(6)	1211(9)	117(6)
H(64)	4104(11)	5450(6)	2622(8)	117(6)
H(65)	4584(11)	4600(6)	2829(8)	117(6)
H(66)	3401(11)	3950(6)	2450(8)	117(6)
H(67)	1737(11)	4150(6)	1864(8)	117(6)
H(68)	1256(11)	4999(6)	1657(8)	117(6)

Table 2.3. Interatomic distances (Å)

Au(2)	---	Au(1)	2.847(1)	Ir(1)	---	Au(1)	2.633(1)
P(3)	---	Au(1)	2.269(6)	C(1)	---	Au(1)	2.810(25)
Au(1)	---	Au(2)	2.847(1)	Ir(1)	---	Au(2)	2.726(1)
P(2)	---	Au(2)	2.269(6)	C(8)	---	Au(2)	2.387(22)
Au(1)	---	Ir(1)	2.633(1)	Au(2)	---	Ir(1)	2.726(1)
Fe(1)	---	Ir(1)	2.709(3)	Fe(2)	---	Ir(1)	2.744(4)
Ir(1)	---	Fe(1)	2.709(3)	Fe(2)	---	Fe(1)	2.501(5)
C(2)	---	Fe(1)	1.776(25)	C(3)	---	Fe(1)	1.713(25)
C(4)	---	Fe(1)	1.755(30)	Ir(1)	---	Fe(2)	2.744(4)
Fe(1)	---	Fe(2)	2.501(5)	C(5)	---	Fe(2)	1.672(34)
C(6)	---	Fe(2)	1.819(35)	C(7)	---	Fe(2)	1.777(24)
C(8)	---	Fe(2)	2.079(23)	Ir(1)	---	P(1)	2.287(6)
C(21)	---	P(1)	1.819(15)	C(27)	---	P(1)	1.849(16)
C(33)	---	P(1)	1.816(15)	Au(2)	---	P(2)	2.269(6)
C(39)	---	P(2)	1.815(15)	C(45)	---	P(2)	1.787(16)
C(51)	---	P(2)	1.826(15)	Au(1)	---	P(3)	2.269(6)
C(57)	---	P(3)	1.813(16)	C(63)	---	P(3)	1.778(17)
C(69)	---	P(3)	1.818(17)	Au(1)	---	C(1)	2.810(25)
Ir(1)	---	C(1)	1.847(30)	O(1)	---	C(1)	1.156(31)
C(1)	---	O(1)	1.156(31)	Fe(1)	---	C(2)	1.776(25)
O(2)	---	C(2)	1.145(30)	C(2)	---	O(2)	1.145(30)
Fe(1)	---	C(3)	1.713(25)	O(3)	---	C(3)	1.209(30)
C(3)	---	O(3)	1.209(30)	Fe(1)	---	C(4)	1.755(30)
O(4)	---	C(4)	1.169(35)	C(4)	---	O(4)	1.169(35)
Fe(2)	---	C(5)	1.672(34)	O(5)	---	C(5)	1.248(40)
C(5)	---	O(5)	1.248(40)	Fe(2)	---	C(6)	1.819(35)
O(6)	---	C(6)	1.116(36)	C(6)	---	O(6)	1.116(36)
Fe(2)	---	C(7)	1.777(24)	O(7)	---	C(7)	1.109(28)
C(7)	---	O(7)	1.109(28)	Au(2)	---	C(8)	2.387(22)
Ir(1)	---	C(8)	1.957(23)	Fe(1)	---	C(8)	2.074(23)
Fe(2)	---	C(8)	2.079(23)	C(9)	---	C(8)	1.340(31)
Fe(1)	---	C(9)	2.141(22)	Fe(2)	---	C(9)	2.063(23)
C(8)	---	C(9)	1.340(31)	C(15)	---	C(9)	1.439(28)
C(9)	---	C(15)	1.439(28)	P(1)	---	C(21)	1.819(15)
P(1)	---	C(27)	1.849(16)	P(1)	---	C(33)	1.816(15)
P(2)	---	C(39)	1.815(15)	P(2)	---	C(45)	1.787(16)
P(2)	---	C(51)	1.826(15)	P(3)	---	C(57)	1.813(16)
P(3)	---	C(63)	1.778(17)	P(3)	---	C(69)	1.818(17)
C(100)	---	O(108)	1.435(19)	O(108)	---	C(100)	1.435(19)
C(101)	---	C(100)	1.530(19)	C(100)	---	C(101)	1.530(19)

Table 2.4. Interatomic angles (°)

Ir(1)	Au(1)	Au(2)	59.5
P(3)	Au(1)	Ir(1)	166.0(2)
C(1)	Au(1)	Ir(1)	39.5(6)
Ir(1)	Au(2)	Au(1)	56.3
P(2)	Au(2)	Ir(1)	170.0(2)
C(8)	Au(2)	Ir(1)	44.4(6)
Au(2)	Ir(1)	Au(1)	64.1
Fe(1)	Ir(1)	Au(2)	86.5(1)
Fe(2)	Ir(1)	Au(2)	107.1(1)
Fe(2)	Fe(1)	Ir(1)	63.4(1)
C(2)	Fe(1)	Fe(2)	154.6(8)
C(3)	Fe(1)	Fe(2)	102.3(9)
C(4)	Fe(1)	Ir(1)	158.2(10)
C(4)	Fe(1)	C(2)	95.7(12)
Fe(1)	Fe(2)	Ir(1)	62.0(1)
C(5)	Fe(2)	Fe(1)	102.1(11)
C(6)	Fe(2)	Fe(1)	156.5(11)
C(7)	Fe(2)	Ir(1)	78.4(8)
C(7)	Fe(2)	C(5)	96.1(13)
C(8)	Fe(2)	Ir(1)	45.3(6)
C(8)	Fe(2)	C(5)	133.1(12)
C(8)	Fe(2)	C(7)	122.5(11)
C(27)	P(1)	Ir(1)	115.0(5)
C(33)	P(1)	Ir(1)	113.8(6)
C(33)	P(1)	C(27)	101.2(7)
C(45)	P(2)	Au(2)	111.9(5)
C(51)	P(2)	Au(2)	114.4(5)
C(51)	P(2)	C(45)	104.8(7)
C(63)	P(3)	Au(1)	108.3(6)
C(69)	P(3)	Au(1)	117.5(6)
C(69)	P(3)	C(63)	105.3(7)
O(1)	C(1)	Au(1)	120.9(20)
O(2)	C(2)	Fe(1)	179.5(21)
O(4)	C(4)	Fe(1)	178.9(27)
O(6)	C(6)	Fe(2)	172.9(34)
Ir(1)	C(8)	Au(2)	77.0(7)
Fe(1)	C(8)	Ir(1)	84.4(10)
Fe(2)	C(8)	Ir(1)	85.6(9)
C(9)	C(8)	Au(2)	128.7(17)
C(9)	C(8)	Fe(1)	74.2(13)
Fe(2)	C(9)	Fe(1)	73.0(8)
C(8)	C(9)	Fe(2)	71.8(14)
C(15)	C(9)	Fe(2)	142.3(15)
C(10)	C(15)	C(9)	120.8(10)
C(16)	C(21)	P(1)	120.1(4)
C(22)	C(27)	P(1)	124.4(4)
C(28)	C(33)	P(1)	119.7(4)
C(34)	C(39)	P(2)	117.4(5)
C(40)	C(45)	P(2)	117.0(5)
C(46)	C(51)	P(2)	118.7(4)
C(52)	C(57)	P(3)	119.6(5)
C(58)	C(63)	P(3)	116.5(5)
C(64)	C(69)	P(3)	119.5(5)
C(101)	C(100)	O(108)	134.3(50)
P(3)	Au(1)	Au(2)	132.7(2)
C(1)	Au(1)	Au(2)	98.3(6)
C(1)	Au(1)	P(3)	129.0(6)
P(2)	Au(2)	Au(1)	122.4(2)
C(8)	Au(2)	Au(1)	91.2(6)
C(8)	Au(2)	P(2)	142.6(6)
Fe(1)	Ir(1)	Au(1)	90.3(1)
Fe(2)	Ir(1)	Au(1)	144.8(1)
Fe(2)	Ir(1)	Fe(1)	54.6(1)
C(2)	Fe(1)	Ir(1)	106.1(8)
C(3)	Fe(1)	Ir(1)	82.3(9)
C(3)	Fe(1)	C(2)	98.8(12)
C(4)	Fe(1)	Fe(2)	96.3(10)
C(4)	Fe(1)	C(3)	95.2(12)
C(5)	Fe(2)	Ir(1)	162.1(11)
C(6)	Fe(2)	Ir(1)	101.5(11)
C(6)	Fe(2)	C(5)	96.1(16)
C(7)	Fe(2)	Fe(1)	95.7(9)
C(7)	Fe(2)	C(6)	97.0(13)
C(8)	Fe(2)	Fe(1)	52.9(6)
C(8)	Fe(2)	C(6)	103.7(12)
C(21)	P(1)	Ir(1)	119.6(5)
C(27)	P(1)	C(21)	100.0(7)
C(33)	P(1)	C(21)	104.8(7)
C(39)	P(2)	Au(2)	113.5(5)
C(45)	P(2)	C(39)	105.9(7)
C(51)	P(2)	C(39)	105.6(7)
C(57)	P(3)	Au(1)	114.8(5)
C(63)	P(3)	C(57)	105.8(7)
C(69)	P(3)	C(57)	104.1(7)
Ir(1)	C(1)	Au(1)	65.1(7)
O(1)	C(1)	Ir(1)	173.1(23)
O(3)	C(3)	Fe(1)	175.2(22)
O(5)	C(5)	Fe(2)	176.8(29)
O(7)	C(7)	Fe(2)	175.3(25)
Fe(1)	C(8)	Au(2)	113.0(10)
Fe(2)	C(8)	Au(2)	160.2(10)
Fe(2)	C(8)	Fe(1)	74.1(8)
C(9)	C(8)	Ir(1)	151.4(19)
C(9)	C(8)	Fe(2)	70.5(13)
C(8)	C(9)	Fe(1)	68.7(14)
C(15)	C(9)	Fe(1)	130.5(14)
C(15)	C(9)	C(8)	139.4(20)
C(14)	C(15)	C(9)	119.2(10)
C(20)	C(21)	P(1)	119.9(4)
C(26)	C(27)	P(1)	115.6(4)
C(32)	C(33)	P(1)	120.3(4)
C(38)	C(39)	P(2)	122.4(5)
C(44)	C(45)	P(2)	122.9(5)
C(50)	C(51)	P(2)	121.3(4)
C(56)	C(57)	P(3)	120.4(5)
C(62)	C(63)	P(3)	123.5(5)
C(68)	C(69)	P(3)	120.4(5)

Table 2.5. Observed and calculated structure factors

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR    [IRFE2(CO)7PPH3AU2(PPH3)2C2PH]                        PAGE  1

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  0  0-20 2545 2744      4  8-19 1259 1166     -1  7-18 1052 1070      6  4-17  578  582      7 11-17  834  813
  2  0-20 1355 1428      1  9-19  994 1065      1  7-18 1931 2016     -5  5-17 1571 1725      2 12-17 1039  951
  4  0-20  629  723      3  9-19 1078 1084      3  7-18 2246 2252     -3  5-17 2399 2533      4 12-17  594  541
  0  2-20 1442 1571      2 10-19 1289 1306      5  7-18 1118 1089      1  5-17 1748 1769     -3 13-17  904  998
  4  2-20  952  958      4 10-19 1160 1124      7  7-18 1604 1481      3  5-17 2591 2604      3 13-17  738  781
 -1  3-20 1747 1802      1 11-19 1283 1259     -3  9-18 1270 1294      5  5-17 1487 1486      0 14-17 1007 1056
  1  3-20 1993 2070     -4  0-18 1919 1990      1  9-18 1411 1475      7  5-17 1208 1144      2 14-17  656  727
  2  4-20  937  987      0  0-18 1499 1643      3  9-18 1910 1930     -4  6-17 1303 1428      4 14-17  482  566
  4  4-20  718  753      2  0-18 1019 1062      0 10-18  765  843     -2  6-17 1976 1991      0 16-17 1117 1190
  1  5-20 1152 1211      4  0-18  927 1000      2 10-18 1827 1877      0  6-17 1871 1876     -6  0-16 1767 1801
  3  5-20  675  731      6  0-18 1363 1357      4 10-18  982 1089      2  6-17 1904 1946     -4  0-16 1678 1672
  2  6-20  853  889     -5  1-18  952  950     -2 12-18 1145 1208      4  6-17 1365 1398     -2  0-16  933  947
  1  7-20 1246 1287      3  1-18  860  845      2 12-18 1023 1027      6  6-17  826  863      0  0-16 1271 1307
 -3  1-19 1004 1026     -4  2-18 1047 1196      4 12-18 1113 1092      8  6-17 1408 1253      4  0-16 1249 1267
 -1  1-19 1500 1564      0  2-18 1285 1367      1 13-18 1226 1220     -5  7-17 1107 1107      6  0-16 1957 1914
  1  1-19 1460 1521      4  2-18  823  795     -5  1-17 2049 2044     -3  7-17  968 1056     10  0-16 1608 1418
  5  1-19 1121 1044      6  2-18 1247 1118     -3  1-17 1051 1054      1  7-17  853  889     -5  1-16  741  680
  7  1-19 1134  983     -5  3-18 1827 1992      1  1-17  957  902      3  7-17 1495 1447     -3  1-16  893  912
  0  2-19 1610 1618     -1  3-18 1091 1118      3  1-17  913  983     -4  8-17 2252 2284     -1  1-16  692  691
  2  2-19 1389 1513      1  3-18 1708 1711      5  1-17 1380 1352     -2  8-17 2069 2085      3  1-16  913  977
  6  2-19  815  794      3  3-18 1205 1157     -6  2-17  946 1004      0  8-17 1467 1408     -6  2-16 1460 1572
 -3  3-19 1023 1080      7  3-18 1097 1045     -4  2-17 1396 1435      2  8-17 2801 2870     -4  2-16 1251 1265
  3  3-19 1211 1198     -4  4-18 1617 1695     -2  2-17  876  943      4  8-17 2006 2036      0  2-16 1206 1146
  5  3-19 1164 1146     -2  4-18 1419 1486      2  2-17 1364 1409      6  8-17  977  917      2  2-16  498  513
  0  4-19 1613 1763      0  4-18  845  860      4  2-17 1341 1310      8  8-17 2089 1860      4  2-16 1176 1196
  2  4-19 1307 1311      2  4-18 1787 1884     -3  3-17 1619 1627     -3  9-17 1035 1033      6  2-16 1210 1168
  6  4-19  764  749      4  4-18 1855 1830     -1  3-17  865  877     -1  9-17  654  773     10  2-16 1121 1032
 -3  5-19 1378 1455      6  4-18  882  887      1  3-17 1098 1070      3  9-17 1416 1395     -5  3-16 1297 1354
  1  5-19 1467 1453      8  4-18 1439 1273      3  3-17 1304 1390      5  9-17  927  897     -3  3-16 1314 1301
  3  5-19 1557 1580     -1  5-18 1333 1415      5  3-17 1498 1471     -4 10-17  881  829     -1  3-16 1334 1383
 -2  6-19 1046 1078      1  5-18 1532 1664      7  3-17  965  912     -2 10-17 1123 1043      1  3-16  901  947
  0  6-19 1296 1263      5  5-18 1046  986     -6  4-17 1194 1307      2 10-17 1095 1084      3  3-16 1515 1536
  2  6-19 1589 1602     -4  6-18 1869 1858     -4  4-17  762  835      4 10-17  865  843      5  3-16 1387 1340
  4  6-19 1210 1185      2  6-18 2096 2053     -2  4-17  889  863     -3 11-17 1683 1656      9  3-16  833  843
  0  8-19  861  867      4  6-18 1271 1324      0  4-17 1486 1550      1 11-17 1265 1332     -4  4-16 2159 2153
  2  8-19 2095 2149     -3  7-18 1672 1798      2  4-17 1107 1156      3 11-17 2105 2035     -2  4-16 2045 2046
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR    [IRFE2(CO)7PPH3AU2(PPH3)2C2PH]                        PAGE  2

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  0  4-16 1140 1129      4 10-16 2043 2033      5  3-15 1106 1166     -3  9-15 1547 1533      2 16-15 1197 1150
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Table 2.5 (continued)

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Table 2.5 (continued)

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [IRFE2(CO)7PPH3AU2(PPH3)2C2PH]

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [IRFE2(CO)7PPH3AU2(PPH3)2C2PH]

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Table 2.5 (continued)

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Table 2.5 (continued)

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  0 18 -8 2487 2316     -4 24 -8 1031 1057      3  3 -7 1762 1951     10  6 -7 1629 1690     -6 10 -7 1183 1179
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR    (IRFE2(CO)7PPH3AU2(PPH3)2C2PH)                                PAGE 10

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  4 14 -7 1358 1292      5 19 -7 2555 2427      2 26 -7  800  785    -11  3 -6 2210 2180    -10  6 -6 1767 1809
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Table 2.5 (continued)

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [IRFE2(CO)7PPH3AU2(PPH3)2C2PH] PAGE 11

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [IRFE2(CO)7PPH3AU2(PPH3)2C2PH] PAGE 12

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Table 2.5 (continued)

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [IRFE2(CO)7PPH3AU2(PPH3)2C2PH]

PAGE 13

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4	24	-5	1386	1373
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-1	25	-5	913	947
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Table 2.5 (continued)

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 -9  5 -2 1931 1774    -4  8 -2 1129 1020     5 11 -2 2454 2749    -9 15 -2  897  780     2 18 -2 1385 1508
 -7  5 -2 1440 1340    -2  8 -2  766  638     7 11 -2 1826 1962    -7 15 -2 1407 1315     6 18 -2 1410 1431
 -5  5 -2 3126 2730     0  8 -2 2390 2346     9 11 -2 1402 1426    -5 15 -2 1516 1455    10 18 -2  701  764
 -3  5 -2 1530 1267     2  8 -2 3147 3381    11 11 -2  811  825    -3 15 -2 1410 1365    -9 19 -2  713  719
 -1  5 -2 2119 1952     4  8 -2 1134 1258   -10 12 -2 1255 1177    -1 15 -2 1846 1872    -7 19 -2 1188 1228
  1  5 -2 4094 4013     6  8 -2 1398 1571    -8 12 -2 2166 2067     1 15 -2 2457 2407    -5 19 -2 1123 1091
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Table 2.5 (continued)

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR (IRFE2(CO)7PPH3AU2(PPH3)2C2PH)

PAGE 17

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-1	19	-2	2173	2214	4	24	-2	1156	1200	10	2	-1	1498	1530	13	5	-1	1103	1141	8	8	-1	1440	1538
1	19	-2	1608	1684	-5	25	-2	1201	1195	12	2	-1	1779	1729	-12	6	-1	1475	1354	10	8	-1	674	776
5	19	-2	1405	1393	-3	25	-2	1777	1857	-9	3	-1	1912	1830	-10	6	-1	2258	2063	12	8	-1	990	1038
7	19	-2	1092	1109	-1	25	-2	920	909	-7	3	-1	1639	1435	-8	6	-1	2590	2385	-13	9	-1	788	688
-8	20	-2	1608	1536	1	25	-2	1479	1555	-5	3	-1	3156	2720	-6	6	-1	1073	977	-9	9	-1	986	837
-6	20	-2	1621	1623	3	25	-2	2344	2529	-3	3	-1	1679	1466	-4	6	-1	2573	2420	-7	9	-1	1535	1331
-4	20	-2	1795	1805	5	25	-2	1207	1213	-1	3	-1	2840	2569	-2	6	-1	4569	4093	-5	9	-1	1935	1632
-2	20	-2	2090	2017	-3	27	-2	1542	1529	1	3	-1	2734	3059	0	6	-1	4291	4104	-3	9	-1	1665	1547
0	20	-2	1489	1499	-1	27	-2	649	730	5	3	-1	946	1019	2	6	-1	894	906	-1	9	-1	3151	2887
2	20	-2	2045	2058	1	27	-2	1219	1285	7	3	-1	900	916	4	6	-1	1038	1198	1	9	-1	1124	1151
4	20	-2	1069	1115	3	27	-2	2067	2158	9	3	-1	897	944	6	6	-1	1129	1185	3	9	-1	764	836
-9	21	-2	997	892	-2	28	-2	996	979	-12	4	-1	1595	1418	8	6	-1	905	1018	5	9	-1	1928	2254
-7	21	-2	1322	1312	2	28	-2	1698	1749	-10	4	-1	1057	809	10	6	-1	724	867	7	9	-1	1559	1718
-5	21	-2	2714	2659	-11	1	-1	1138	1110	-8	4	-1	1161	1120	-13	7	-1	614	546	-10	10	-1	1088	1041
-3	21	-2	1215	1267	-9	1	-1	1075	955	-6	4	-1	2565	2391	-11	7	-1	760	666	-8	10	-1	1628	1457
-1	21	-2	1672	1685	-7	1	-1	4205	4102	-4	4	-1	1479	1333	-9	7	-1	1616	1410	-6	10	-1	856	846
1	21	-2	2389	2413	-5	1	-1	3318	3165	-2	4	-1	3151	2752	-7	7	-1	1869	1728	-4	10	-1	5239	4691
3	21	-2	1276	1241	-3	1	-1	1862	1620	0	4	-1	3003	2982	-5	7	-1	1464	1298	-2	10	-1	5092	4690
5	21	-2	647	716	-1	1	-1	9747	8758	2	4	-1	1093	1129	-3	7	-1	2365	2107	0	10	-1	2707	2504
7	21	-2	1066	1080	1	1	-1	7273	9143	4	4	-1	4026	4803	-1	7	-1	2938	2685	2	10	-1	3304	3427
-4	22	-2	1588	1552	3	1	-1	2352	2635	6	4	-1	3740	4205	1	7	-1	2792	2881	4	10	-1	2757	3069
-2	22	-2	1418	1527	5	1	-1	4810	5139	8	4	-1	1616	1668	3	7	-1	1415	1561	6	10	-1	817	952
2	22	-2	2048	2160	7	1	-1	3310	3342	10	4	-1	937	966	5	7	-1	646	680	8	10	-1	1625	1750
4	22	-2	1573	1591	9	1	-1	1052	1138	12	4	-1	1653	1634	7	7	-1	1408	1521	10	10	-1	884	890
6	22	-2	575	633	11	1	-1	2017	2013	-13	5	-1	1330	1321	9	7	-1	1719	1851	-9	11	-1	2107	1729
-7	23	-2	973	985	13	1	-1	1341	1433	-9	5	-1	2891	2586	13	7	-1	720	697	-7	11	-1	2299	2162
-5	23	-2	1128	1183	-12	2	-1	1330	1210	-7	5	-1	4278	3931	-12	8	-1	1211	1106	-5	11	-1	1073	1021
-3	23	-2	1581	1527	-8	2	-1	3388	3304	-5	5	-1	1530	1468	-10	8	-1	1503	1339	-3	11	-1	3420	2971
-1	23	-2	1756	1799	-6	2	-1	3061	2957	-3	5	-1	2498	2218	-8	8	-1	3028	2748	-1	11	-1	2533	2426
1	23	-2	537	490	-4	2	-1	1179	1172	-1	5	-1	4549	4065	-6	8	-1	1066	1038	1	11	-1	1140	1290
3	23	-2	972	1034	-2	2	-1	3380	2925	1	5	-1	1899	2057	-4	8	-1	3811	3248	3	11	-1	2047	2143
5	23	-2	880	953	0	2	-1	6121	6410	3	5	-1	945	980	-2	8	-1	7428	6724	5	11	-1	1752	2015
-6	24	-2	1065	1011	2	2	-1	2064	2433	5	5	-1	2279	2459	0	8	-1	2480	2415	7	11	-1	1550	1717
-4	24	-2	1804	1822	4	2	-1	4313	4647	7	5	-1	2592	2764	2	8	-1	1401	1494	9	11	-1	1342	1488
-2	24	-2	928	958	6	2	-1	4546	4897	9	5	-1	1544	1612	4	8	-1	2741	3282	-8	12	-1	1367	1323
2	24	-2	1870	1910	8	2	-1	2186	2196	11	5	-1	587	589	6	8	-1	648	723	-6	12	-1	3448	3193

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR (IRFE2(CO)7PPH3AU2(PPH3)2C2PH)

PAGE 18

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-4	12	-1	3678	3331	-1	15	-1	4120	4093	-3	19	-1	1533	1524	-2	26	-1	1753	1820	-6	2	0	2465	2330
-2	12	-1	4526	4260	1	15	-1	4107	4036	-1	19	-1	1120	1088	2	26	-1	2342	2529	-4	2	0	2920	2791
0	12	-1	3433	3583	3	15	-1	2009	2066	1	19	-1	1406	1382	4	26	-1	2136	2235	-2	2	0	4791	4704
2	12	-1	2856	2983	5	15	-1	3134	3489	3	19	-1	903	970	-3	27	-1	1163	1152	0	2	0	7032	7595
4	12	-1	2545	2808	7	15	-1	2686	2983	5	19	-1	482	485	-1	27	-1	528	648	2	2	0	3770	4633
6	12	-1	2691	3008	9	15	-1	2055	2252	7	19	-1	404	273	1	27	-1	787	853	4	2	0	2697	2875
8	12	-1	1803	1937	11	15	-1	1572	1726	9	19	-1	725	752	3	27	-1	1370	1400	6	2	0	2443	2419
12	12	-1	1276	1297	-10	16	-1	1102	1061	-6	20	-1	1718	1678	-2	28	-1	1079	1110	8	2	0	1405	1373
-9	13	-1	2213	1966	-6	16	-1	1454	1354	-4	20	-1	1389	1235	0	28	-1	553	683	10	2	0	1063	1110
-7	13	-1	1747	1515	-4	16	-1	2037	2059	0	20	-1	1949	1990	2	28	-1	1209	1209	12	2	0	1006	1049
-5	13	-1	1590	1478	-2	16	-1	1821	1798	2	20	-1	1523	1668	-12	0	0	2095	2051	-13	3	0	1712	1555
-3	13	-1	3301	3221	0	16	-1	652	632	4	20	-1	682	766	-10	0	0	1708	1680	-11	3	0	1622	1560
-1	13	-1	2070	1952	2	16	-1	2089	2157	6	20	-1	1101	1140	-8	0	0	2854	2715	-9	3	0	674	615
1	13	-1	1732	1902	4	16	-1	1413	1530	-7	21	-1	1009	898	-6	0	0	5468	5698	-7	3	0	3344	3064
3	13	-1	2731	2907	8	16	-1	1193	1286	-3	21	-1	1126	1057	-4	0	0	2528	2618	-5	3	0	4806	4570
5	13	-1	1813	1983	-11	17	-1	1323	1289	-1	21	-1	1368	1362	-2	0	0	5725	5839	-3	3	0	964	844
7	13	-1	1679	1824	-7	17	-1	2515	2321	1	21	-1	1114	1181	2	0	0	6052	6229	-1	3	0	4681	3772
9	13	-1	2230	2448	-5	17	-1	2666	2455	3	21	-1	1130	1216	4	0	0	2024	2162	1	3	0	3956	4224
11	13	-1	688	814	-1	17	-1	3530	3510	-8	22	-1	930	888	6	0	0	5723	5933	3	3	0	802	941
-10	14	-1	749	666	1	17	-1	2681	2771	-6	22	-1	1255	1134	8	0	0	2752	2707	5	3	0	4359	4809
-8	14	-1	1403	1304	5	17	-1	2029	2136	-4	22	-1	1603	1478	10	0	0	1504	1460	7	3	0	3041	3130
-6	14	-1	2827	2668	7	17	-1	1663	1940	-2	22	-1	1225	1173	12	0	0	1946	1965	9	3	0	545	647
-4	14	-1	1275	1199	9	17	-1	682	821	0	22	-1	908	934	-13	1	0	806	889	11	3	0	1507	1587
-2	14	-1	2191	2066	11	17	-1	1211	1336	-5	23	-1	1650	1681	-9	1	0	539	486	13	3	0	1648	1600
0	14	-1	4010	3863	-8	18	-1	1599	1573	-3	23	-1	2311	2293	-7	1	0	3029	2957	-12	4	0	950	966
2	14	-1	1393	1371	-6	18	-1	1889	1875	-1	23	-1	849	927	-5	1	0	2498	2388	-10	4	0	1141	1023
4	14	-1	1942	2031	-4	18	-1	1960	1828	1	23	-1	1559	1615	-3	1	0	3523	3189	-8	4	0	3020	2772
6	14	-1	2310	2593	-2	18	-1	2234	2143	3	23	-1	2675	2754	-1	1	0	4318	4497	-6	4	0	2326	2173
8	14	-1	872	910	0	18	-1	2983	3027	5	23	-1	882	855	1	1	0	3471	4500	-4	4	0	581	503
10	14	-1	953	1078	2	18	-1	1430	1443	-4	24	-1	1455	1508	3	1	0	3346	3350	-2	4	0	1242	1000
12	14	-1	1000	1058	4	18	-1	1245	1356	-2	24	-1	1732	1752	5	1	0	2502	2571	0	4	0	2319	2518
-11	15	-1	792	651	6	18	-1	1679	1955	2	24	-1	1722	1765	7	1	0	2876	2946	2	4	0	561	639
-9	15	-1	1505	1323	8	18	-1	987	1132	4	24	-1	1251	1375	13	1	0	904	947	6	4	0	1955	2161
-7	15	-1	2756	2536	-9	19	-1	1147	1073	-3	25	-1	1143	1109	-12	2	0	1185	1120	8	4	0	2501	2659
-5	15	-1	2675	2501	-7	19	-1	1344	1333	3	25	-1	1136	1167	-10	2	0	1186	1164	10	4	0	1145	1151
-3	15	-1	2175	2020	-5	19	-1	2491	2422	-4	26	-1	2162	2136	-8	2	0	1479	1400	12	4	0	1004	985

Table 2.5 (continued)

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR (IRFE2(CO)7PPH3AU2(PPH3)2C2PH)

PAGE 19

H	K	L	10FO	10FC
-11	5	0	1793	1595
-7	5	0	1109	977
-5	5	0	3618	3241
-3	5	0	1474	1306
-1	5	0	2983	2638
1	5	0	3053	3042
3	5	0	1313	1534
5	5	0	2898	3258
7	5	0	1170	1163
11	5	0	1586	1671
13	5	0	717	645
-12	6	0	1166	1116
-10	6	0	1141	1055
-8	6	0	3134	2916
-6	6	0	2979	2582
-4	6	0	1541	1314
-2	6	0	3095	2594
0	6	0	4199	3907
2	6	0	2830	3030
4	6	0	1237	1383
6	6	0	2163	2351
8	6	0	2451	2743
10	6	0	1019	1098
12	6	0	1115	1130
-13	7	0	1516	1371
-11	7	0	776	779
-9	7	0	2316	2071
-7	7	0	2664	2356
-3	7	0	2536	2206
-1	7	0	1858	1701
1	7	0	1260	1299
3	7	0	2110	2349
5	7	0	469	484
7	7	0	2033	2273
9	7	0	1867	2041
11	7	0	756	788
13	7	0	1214	1271
-8	8	0	1257	1075
-4	8	0	651	608
-2	8	0	916	732
8	8	0	1076	1120
10	8	0	754	746
-13	9	0	1427	1328
-9	9	0	1948	1716
-7	9	0	1741	1593
-5	9	0	1974	1765
-3	9	0	4624	4073
-1	9	0	2680	2474
1	9	0	2307	2353
3	9	0	3656	4092
5	9	0	1568	1865
7	9	0	1215	1397
9	9	0	1666	1738
13	9	0	1244	1307
-12	10	0	1082	994
-8	10	0	1836	1621
-6	10	0	2878	2683
-4	10	0	1363	1259
-2	10	0	2189	1981
0	10	0	698	686
2	10	0	1646	1733
4	10	0	1179	1369
6	10	0	2203	2643
8	10	0	1511	1668
-9	11	0	1195	1077
-7	11	0	2247	2051
-5	11	0	4021	3641
-3	11	0	4738	4206
-1	11	0	3231	3111
1	11	0	3200	3223
3	11	0	3763	4076
5	11	0	3030	3528
7	11	0	1717	1986
9	11	0	988	1129
-10	12	0	1376	1228
-8	12	0	2252	1955
-6	12	0	1448	1356
-4	12	0	2611	2331
-2	12	0	2845	2684
0	12	0	656	656
2	12	0	2593	2730
4	12	0	2165	2360
6	12	0	1091	1317
8	12	0	1771	2037
10	12	0	1215	1331
-11	13	0	1130	915
-7	13	0	3142	2864
-5	13	0	3864	3575
-3	13	0	1972	1783
-1	13	0	4153	3919
1	13	0	4005	3906
3	13	0	1623	1721
5	13	0	2977	3438
7	13	0	2340	2714
11	13	0	1013	1026
-10	14	0	1488	1376
-8	14	0	2519	2261
-6	14	0	2158	1994
-4	14	0	2563	2255
-2	14	0	3861	3684
0	14	0	2716	2783
2	14	0	3329	3487
4	14	0	2206	2285
6	14	0	1789	2030
8	14	0	2211	2496
10	14	0	1246	1415
-11	15	0	953	798
-9	15	0	1250	1044
-7	15	0	1433	1285
-5	15	0	1738	1569
-3	15	0	1929	1730
-1	15	0	2229	2055
1	15	0	2098	2038
3	15	0	1518	1577
5	15	0	1470	1642
7	15	0	1117	1302
9	15	0	903	964
11	15	0	796	781
-10	16	0	1373	1214
-8	16	0	1816	1713
-6	16	0	4010	3572
-4	16	0	1763	1671
-2	16	0	2253	2038
0	16	0	5500	5365
2	16	0	1829	1876
4	16	0	1469	1593
6	16	0	3301	3692
8	16	0	1589	1893
10	16	0	1015	1178
-9	17	0	1042	916
-7	17	0	1599	1514
-5	17	0	2163	1953
-3	17	0	2285	2218
-1	17	0	2733	2691
1	17	0	2581	2623
3	17	0	1990	2107
5	17	0	1764	1880
7	17	0	1420	1599
9	17	0	870	958
-10	18	0	1497	1285
-6	18	0	1624	1493
-4	18	0	1660	1524
-2	18	0	1033	1084
0	18	0	2013	2144
2	18	0	981	1099
4	18	0	1373	1490
6	18	0	1469	1612
10	18	0	1158	1159
-7	19	0	1609	1537
-5	19	0	1474	1335
-1	19	0	2482	2263
1	19	0	2266	2162
5	19	0	1110	1138
7	19	0	1323	1502
-4	20	0	950	914
4	20	0	914	971
6	20	0	779	800
8	20	0	841	962
-5	21	0	1431	1271
-3	21	0	1092	1145
-1	21	0	413	271
3	21	0	1020	1186
5	21	0	1146	1184
9	21	0	808	947
-8	22	0	948	902
-4	22	0	1934	1898
-2	22	0	2167	2207
0	22	0	724	699
2	22	0	2030	2155
4	22	0	1771	1852
-7	23	0	499	478
-3	23	0	1237	1107
3	23	0	1060	1092
7	23	0	452	464
-4	24	0	2019	2030
-2	24	0	2049	2033
2	24	0	1970	2022
4	24	0	1845	2045
-5	25	0	1209	1185
-3	25	0	2571	2606

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR (IRFE2(CO)7PPH3AU2(PPH3)2C2PH)

PAGE 20

H	K	L	10FO	10FC
-1	25	0	1237	1200
1	25	0	1180	1219
3	25	0	2520	2733
5	25	0	1172	1234
-3	27	0	2025	2022
-1	27	0	1160	1180
1	27	0	1296	1330
3	27	0	2045	2177
-2	28	0	1756	1791
0	28	0	926	968
2	28	0	1715	1774
-9	19	1	894	730
-3	19	1	1025	961
-8	20	1	799	764
-6	20	1	1369	1238
-2	20	1	1750	1743
0	20	1	2031	2099
4	20	1	1107	1123
6	20	1	1457	1628
-9	21	1	607	567
-7	21	1	840	806
-5	21	1	776	793
-3	21	1	1297	1276
-1	21	1	1313	1252
1	21	1	1205	1207
3	21	1	975	1025
-2	22	1	828	788
0	22	1	1052	1044
2	22	1	1091	1064
4	22	1	1367	1429
6	22	1	1011	1068
-3	23	1	2969	2782
-1	23	1	1608	1677
1	23	1	878	884
3	23	1	2246	2315
5	23	1	1416	1606
-4	24	1	1397	1283
-2	24	1	1724	1619
2	24	1	1887	1878
4	24	1	1248	1437
-3	25	1	1183	1180
-1	25	1	705	662
3	25	1	1069	1099
-4	26	1	2181	2128
-2	26	1	2355	2363
0	26	1	874	875
2	26	1	1799	1971
4	26	1	1955	2131
-3	27	1	1364	1340
-1	27	1	965	927
3	27	1	1097	1149
-2	28	1	1042	1142
2	28	1	1235	1244

APPENDIX 3

PUBLICATIONS BY THE AUTHOR ARISING FROM THIS WORK

1. Reactions of transition metal acetylide complexes, Part IV. Synthesis and X-ray structure of a bromovinylidene complex, $[Ru\{C{=}CBr(C_6H_4Br\text{-}4)\}(PPh_3)_2(\eta\text{-}C_5H_5)][Br_3]\cdot CHCl_3$ (with M.I. Bruce, M.G. Humphrey and B.K. Nicholson) *J. Organomet. Chem.*, 1985, 296, C47.

2. Reactions of transition metal σ-acetylides, Part VII. Synthesis and properties of complexes containing halovinylidene ligands. X-ray structure of $[Ru(C{=}CIPh)(PPh_3)_2\text{-}(\eta\text{-}C_5H_5)][I_3]$ (with M.I. Bruce, M.J. Liddell and B.K. Nicholson) *J. Organomet. Chem.*, 1987, 326, 247.

3. Cyclopentadienyl-ruthenium and -osmium chemistry, Part XXVIII. Reactions and isomerisation of 1,2-bis(methoxycarbonyl)ethenyl complexes: X-ray structures of
$Ru\{(Z)\text{-}C(CO_2Me){=}CH(CO_2Me)\}(CO)(PPh_3)(\eta\text{-}C_5H_5)\cdot 0.5EtOH$,
$Ru\{(E)\text{-}C(CO_2Me){=}CH(CO_2Me)\}(dppe)(\eta\text{-}C_5H_5)$ and
$\overline{Ru\{C(CO_2Me){=}C(CO_2Me)C(CO_2Me){=}}CH(CO_2Me)\}(PPh_3)(\eta\text{-}C_5H_5)$
(with M.I. Bruce, A. Catlow, M.G. Humphrey, M.R. Snow and E.R.T. Tiekink) *J. Organomet. Chem.*, 1988, 338, 59.

4. (η-Cyclopentadienyl)[methoxy(methyl)carbene]bis(triphenylphosphine)ruthenium(II) Hexafluorophosphate (with M.I. Bruce and E.R.T. Tiekink) *Acta Cryst.*, 1988, C44, 1130.

5. Cyclopentadienyl-ruthenium and -osmium chemistry, Part XXXI. Preparation of some complexes containing 1,1′-Bis(diphenylphosphino)ferrocene (dppf): X-ray structure of RuH(dppf)(η-C_5H_5) (with M.I. Bruce, I.R. Butler, W.R. Cullen, M.R. Snow and E.R.T. Tiekink) *Aust. J. Chem.*, 1988, 41, 963.

Some Organotransition Metal Chemistry of the Carbon-Carbon Triple Bond
by George Anthony Koutsantonis B. Sc.(Hons.)
A Thesis presented for the degree of Doctor of Philosophy.
The Department of Physical and Inorganic Chemistry.
The University of Adelaide.

Addendum/Correction Sheet, March 1990.

The numbered references contained in the following passages can be found at the end of the respective chapters in the thesis proper.

Chapter 1

Corrections.

1. p.16, Paragraph 2. The C(1)-C(2) bond lengths for complexes (1) and (5) are not short for C=C double bonds. Given the error limits, these distances do not differ significantly from the standard C=C bond length of 1.33Å.
2. p.30, line 17. It has been stated that the bromination of complex (17) probably gave 1-bromo-2-phenylethyne as an organic side product, this is obviously not the case. Direct attack of bromine at the Ru-C(sp) bond would give initially (21) and bromoethyne.

Addendum.

1. Discussion on the ring halogenation reaction of $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$.

A great deal of the chemistry of Group 8 acetylide complexes can be attributed to the nucleophilic beta-carbon found in these complexes. If one takes an organic chemist's view point then the complex $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ can be thought of as a substituted benzene ring. The carbon attached to the ipso position of the benzene ring bears a concentration of electron density[14] and bromination at the 4-position can be thought of as simply an example of aromatic electrophilic substitution.

The theoretical study by Kostic and Fenske[14] showed that the ligand π system in phosphine containing transition metal acetylide complexes can be considered to be polarized away from the the metal fragment, which is a π donating substituent. Any π donating tendency of the negative charge on the beta carbon would have the effect of predominantly directing electrophiles to the 2- and 4-positions of the phenyl ring. The reason that bromination at the

2-position of the phenyl ring is not observed in the reaction of $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ with bromine is probably steric.

Kostic and Fenske[14] also concluded that nucleophilic addition to vinylidene ligands is essentially frontier orbital controlled while the addition of electrophiles to acetylide complexes is largely charge controlled. Once a vinylidene is formed from an acetylide complex several significant electronic and energetic changes take place. The HOMO in cationic vinylidene complexes is 25% localised on the beta carbon and this concentration of charge could also direct para substitution of the phenyl ring. Intuitively electrophilic substitution of a cation should be less favoured than substitution of the neutral acetylide.

The use of neat Br_2 to effect the synthesis of the complex (5) could not be extended to the synthesis of an analogous dppe derivative. Attempts at such reactions produced mixtures from which no tractable products could be isolated. The differences between the PPh_3 and dppe derivatives could relate to the respective reactant ratios and reaction conditions. However, as mentioned above comparable conditions did not allow the isolation of a dppe complex analogous to (5).

In the iodination reaction of $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ a two and half times excess of iodine was used and a product analogous to (5) was also not found. This could relate to the fact that iodine is the least reactive of the the halogens in aromatic substitution. It is usually necessary to catalyse the reaction of iodine by oxidation to a better electrophile[J. March in Advanced Organic Chemistry,3rd Edition, Wiley, 1985, p.478.]

The direct introduction of chlorine gas into tetrahydrofuran solutions of $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ was not attempted. Chlorine is more reactive than bromine and it was feared that this would lead to decomposition of the substrate.

It is still unclear whether the ring halogenation of $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ actually precedes or is concurrent with β-carbon attack. However, it is clear that the mechanism of halogenation of these acetylides deserves more detailed study.

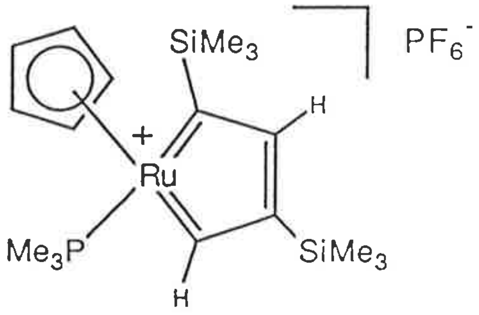
2. The reaction of dioxygen and water with vinylidene complexes.

It is believed that complexes (9) and (10) react with both water and oxygen to form complexes containing carbonyl ligands. The reaction of dioxygen with a ruthenium phenylvinylidene complex to give a cationic carbonyl containing complex has been reported.[6] This result was thought to be a consequence of direct cleavage of the vinylidene C=C double bond by dioxygen. This assumption was supported to some extent by the isolation of the expected organic side product, benzaldehyde, as 2,4-dinitrophenylhydrazine derivative.

The reaction of $[Ru\{C{=}C(Ph)(C_7H_7)\}(dppe)(\eta\text{-}C_5H_5)][PF_6]$ (28) with aqueous tetrahydrofuran also gave a cationic carbonyl complex $[Ru(CO)(dppe)(\eta\text{-}C_5H_5)][PF_6]$[19]. Therefore there is evidence that vinylidene complexes react with water and oxygen to give carbonyl containing complexes. It is also stated(Ch.1, p.28) that the reaction of (9) with water in tetrahydrofuran did indeed give $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ although no experimental details were given. However, it is true that experiments with dry air and deoxgenated water would be necessary to distinguish unambiguously which of the two was reacting with solid vinylidene samples.

3. p.22 Postulated structure of complex (15)

A more reasonable alternative (15a) for the structure postulated for (15) is depicted below.



(15a)

This structure is more consistent with the observation that the SiMe$_3$ groups are magnetically inequivalent. However, the absence of a peak at *ca.* δ 7-8 in the ^{1}H NMR spectrum of (15) due to a ruthenacyclopentatriene =CH[cf. (16)[32]] casts some doubt on both structures. It is conceivable that the peak under the C_5H_5 resonance be assigned to a =CH carbon of a ruthenacyclopentatriene but the chemical shift would seem to be at too high a field.

Chapter2

Corrections.

1. p.96, line 4 & paragraph 2, line 14.

A better explanation of the relatively high field shifts (*ca.* δ 2) of the butadienyl protons and =CH carbons (*ca.* δ 48) of complex (28) is that the ruthenium atom strongly donates electron density into the $\pi*$ orbitals of the diene.

Addendum

1. An important reference on alkyne oligiomerisation was omitted: M.J. Winter in The Chemistry of the Metal-Carbon Bond,Vol. 3, Ed, F.R. Hartley, S. Patai, Wiley, 1985, p. 259-294.

2. The salt NH_4PF_6 was not necessary for the stoichiometry of the reactions in which complexes (27), (28), (29) and (31) were formed(see Scheme 4, p.92). However, the reactions were considerably less clean in its absence.

The Ru-Cl bond of $RuCl(PPh_3)_2(\eta-C_5H_5)$ is highly polarized and is almost completely dissociated in methanol[R.J. Haines and A.L. DuPreez, *J. Organomet. Chem.*,1975, 84, 357]. This allows facile heterolytic cleavage of the chloride ligand and promotes substitution of the ruthenium complex. The equilibrium shown probably also lies somewhat to the right for the iodo complex.

$$RuX(PPh_3)_2(\eta-C_5H_5) + MeOH \rightleftharpoons [Ru(MeOH)(PPh_3)_2(\eta-C_5H_5)] + X$$

X=Cl and I

It is thought that the large non-coordinating PF_6^- ion stabilises the cation to a greater extent than the halide ion. In fact this has allowed Haines and DuPreez to isolate the cation $[Ru(MeOH)(PPh_3)_2(\eta-C_5H_5)][BPh_4]$.

The rate and equilibrium constants for the acetonitrile solvolysis of the halide ligand in the chloro complex, and a range of congeners $RuXL_2(\eta-C_5H_5)$ (L=phosphine, phosphonite, phosphite;L_2=bidentate phosphine;X=Cl,Br) have been determined. [P.M. Treichel and P.J. Vincenti, *Inorg. Chem.*, 1985, 24, 288]

The role of NH_4PF_6 in the synthesis of complexes (27), (28), (29) and (31) is probably to polarize the ruthenium halide bond of the starting material. This provides a situation in which a coordination site on the ruthenium, lightly solvent stabilized, is available for attack by the incoming alkyne. A vacant coordination site can also arise as a result of the substitutional lability of one of the bulky PPh_3 ligands in $RuX(PPh_3)_2(\eta-C_5H_5)$[M.O. Albers, D.J. Robinson and E. Singleton, *Coord. Chem. Rev.*,1987, 79, 1].

3. The essential feature of complexes (28) and (29) is that both complexes contain η5-cyclohexadienyl rings(see Scheme 4). This fact should be mentioned at the beginning of the discussion of the structural characteristics of complexes (28) and (29) and not left to p.102.

Chapter 4

Corrections.

1. P.248 The discussion concerning electron counting.

Trimetallic alkyne clusters have been found to adopt two distinct geometries categorized by their electron counts. The clusters having a 46 cluster valence electrons(CVE's), or 6 SEP's adopt a closo trigonal bipyramidal structure with the alkyne ligand lying perpendicular to one of the metal-metal bonds. The other cluster geometry has 48 CVE's or 7 SEP's and can be described as nido square pyramidal with the acetylenic moiety positioned parallel to a metal-metal bond. In each case the neutral acetylene is counted as a four-electron ligand.

2. p.233 & p234 Scheme 5.

This scheme was intended to depict a hypothetical situation in which the Au-Au vector in complex (39) is cleaved in the presence of carbon monoxide. The dashed arrows indicate a possible vinylidene product while the solid arrows depict a possible alkyne product.

The reaction of several metal cluster complexes with $[O\{Au(PPh_3)\}_3][BF_4]$ in the presence of $[ppn]^+$ salts gave derivatives containing two $Au(PPh_3)$ moieties in which an Au-Au bond may or may not be present[M.I. Bruce, P.E. Corbin, P.A. Humphrey, G.A. Koutsantonis, M.J. Liddell, and E.R.T. Tiekink, *J. Chem. Soc., Chem. Commun.*,1990, in press]. Although no justification was offered for the assumption that the species $Au_2(PPh_3)_2$ is an intermediate in these auration reactions the reagent $[O\{Au(PPh_3)\}_3][BF_4]/[ppn][Co(CO)_4]$ can be considered a formal source of two $Au(PPh_3)$ groups.

Addendum.

1. p.288, paragraph 2. The structure determination of complex (39)

The heavy atom positions were found to be disordered such that about each atom two residual electron density peaks were located approximately 1Å from the parent atom. These were modelled successfully with 2% occupancy factors.

The identity of the disordered solvent molecule was known from ^1H NMR data. However, analytically pure samples of complex (39) could be obtained by subjecting the solvent included complex to high vacuum for thirty six hours at room temperature.