CYCLOPENTADIENYL RUTHENIUM CHEMISTRY

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by

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SUMMARY

Section A of this thesis discusses the chemistry of the carbonyl-free complex $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$, detailing reactions involving (i) reactions of the metal-halogen bond (ii) ligand exchange reactions and (iii) reactions affording cationic complexes.

A variety of other cationic complexes are obtained with nitriles, isonitriles, tertiary phosphines and phosphites, together with some observations on the relation between ease of addition and replacement of ligands in the formation of these cations.

Reactions between terminal acetylenes HC_2R and $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ afford the monosubstituted vinylidene complexes $\{Ru(C{=}CHR)(PPh_3)_2(\eta\text{-}C_5H_5)\}^+$ (I), which are readily deprotonated by bases to give the corresponding σ-acetylides, $Ru(C{\equiv}CR)(PPh_3)_2(\eta\text{-}C_5H_5)$ {R = Me, Pr, Ph, C_6H_4F-4, C_6F_5, CO_2Me}. The σ-acetylides react with strong non-coordinating acids, such as HBF_4 or HPF_6, and also with trialkyloxonium salts, such as $\{Me_3O\}PF_6$, to give the complexes (I), and $\{Ru(C{=}CRR')(PPh_3)_2(\eta\text{-}C_5H_5)\}^+$ (II; R' = Me, Et), respectively. The structure of (II; R = R' = Me) has been determined. Ligand exchange reactions of the σ-acetylides afford complexes $Ru(C{\equiv}CR)(L)(PPh_3)(\eta\text{-}C_5H_5)$, $Ru(C{\equiv}CR)(L)_2(\eta\text{-}C_5H_5)$ {L = PR_3, $P(OR)_3$} and $Ru(C{\equiv}CR)(L_2)(\eta\text{-}C_5H_5)$ {L_2 = dppe, dppm}, which can also be converted to the analogous vinylidene complexes. The reaction between $HC_2CH_2CHMeOH$ and $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ does not afford a vinylidene complex; instead intramolecular cyclisation to a complex containing the methyl substituted oxacyclopentylidene ligand occurs spontaneously. This carbene is very reactive, undergoing a rapid base-catalysed H-D exchange at the carbon adjacent to the metal-bonded carbon.

The reactions of several cyanocarbon and cyanonitrogen anions with the complex $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ are reported, in which the chloride is exchanged for the cyano-substituted group. We are not aware of any other compounds containing these anions and organometallic residues.

The last chapter in Section A discusses the ^{13}C spectra of the products obtained above. We had envisaged a relationship between the ^{13}C and ^{1}H resonances of the cyclopentadienyl ligand and wanted to note the chemical shift values of various Ru-C carbons.

Section B of this thesis discusses the chemistry of the cluster carbonyl $Ru_3(CO)_{12}$. With few exceptions, substitution of $Ru_3(CO)_{12}$ by Group V donor ligands, L, affords the trisubstituted complexes $Ru_3(CO)_9L_3$, in which one CO group on each metal atom has been displaced by the ligand molecule. Triruthenium dodecacarbonyl reacts with Bu^tNC under mild conditions to give $Ru_3(CO)_{11}(CNBu^t)$ (III), a fluxional molecule which adopts the axially substituted structure in the solid state. The unusual twisting of the $Ru_2(CO)_8$ fragment in (III) has relevance to the current theories of fluxionality in cluster carbonyls. Di- and tri-substituted products are obtained using more vigorous reaction conditions. Tetranuclear hydrido complexes $H_4Ru_4(CO)_{12-n}(CNBu^t)_n$ {n = 1-4} are formed from $H_4Ru_4(CO)_{12}$. Complex (III) reacts with dihydrogen in inert solvents to give mixtures of $HRu_3(CO)_9(\mu\text{-}HC{=}NBu^t)$, $HRu_3(CO)_8(CNBu^t)$-$(\mu\text{-}HC{=}NBu^t)$, and an intermediate which reacts to give $H_4Ru_4(CO)_{12-n}(CNBu^t)_n$ {n = 0-2}. Similar complexes were formed in reactions between $Ru_3(CO)_{10}(CNBu^t)_2$ and H_2. Complex (III) reacts with Group V donor ligands to give the monosubstituted $Ru_3(CO)_{11}L$ complexes and mixed ligand complexes, $Ru_3(CO)_{10}(CNBu^t)L$. Pyrolysis of $Ru_3(CO)_{11}(CNBu^t)$ affords $Ru_5(CO)_{14}(CNBu^t)_2$, which contains an open 'swallow' cluster, with one isocyanide ligand acting as a six-electron donor, and bonded to four of the five metal atoms.

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.

R. C. WALLIS

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ABBREVIATIONS

In Experimental Section:

Infrared Spectroscopy (I.R.)

m	medium
s	strong
w	weak
vs, etc.	very strong, ...
sh	shoulder

Nuclear Magnetic Resonance Spectroscopy (N.M.R.)

d	doublet
m	multiplet
q	quartet
qu	quintet
s	singlet
se	sextet
t	triplet
d of t, etc.	doublet of triplets, ...

Mass Spectrometry

M	molecular weight or ion
m/e	molecular ion

Others

c.	approximately
h	hour
min	minute
mg	milligram
ml	millilitre
m.p.	melting point
s	second

Chemical Abbreviations throughout Text

Bu^t	tertiary butyl
Cp	cyclopentadienyl
Cy	cyclohexyl
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
Et	ethyl
Pr	propyl
Ph	phenyl
R	alkyl and/or aryl
tosmic	*para*-toluenesulphonylmethyl isocyanide
X	halogen

CHAPTER 1

A SUMMARY OF THE CHEMISTRY OF CARBONYL-FREE COMPLEXES OF THE TYPE $RuX(PR_3)_2(\eta-C_5H_5)$

Studies [1,2] on ruthenium complexes containing both η-cyclopentadienyl and carbonyl ligands have shown that there is surprisingly little difference in reactivity between these complexes and the analogous iron-containing compounds. However, the increased reactivity towards small molecules of phosphine complexes compared with those containing carbonyl groups, together with the usefulness of some ruthenium(II) complexes in many catalytic reactions, [3] suggested that a study of the chemistry of carbonyl-free complexes of the type $RuX(PR_3)_2(\eta\text{-}C_5H_5)$ would be worthwhile.

Although $RuCl(CO)_2(\eta\text{-}C_5H_5)$ can be readily obtained [2] it is unlikely to be a useful precursor for compounds containing the $Ru(PR_3)_2(\eta\text{-}C_5H_5)$ moiety in view of work with the iron compounds $FeX(CO)_2(\eta\text{-}C_5H_5)$ which has shown that monodentate phosphines react to give only monocarbonyl complexes $FeX(CO)(PR_3)(\eta\text{-}C_5H_5)$.[4-6] Only with triphenyl phosphite under forcing conditions have any fully substituted complexes of the type $FeX\{P(OPh)_3\}_2(\eta\text{-}C_5H_5)$ been obtained.[7] Treatment of $RuI(CO)_2(\eta\text{-}C_5H_5)$ with phosphites yield only the monocarbonyl derivatives $RuI(CO)\{P(OR)_3\}(\eta\text{-}C_5H_5)$.[8] It is thought that the stability of the intermediate monocarbonyl results from a delicate balance of steric and electronic effects. Clearly the preparation of fully substituted phosphine complexes $RuX(PR_3)_2(\eta\text{-}C_5H_5)$ by displacement of both CO groups of the $Ru(CO)_2(\eta\text{-}C_5H_5)$ moiety by tertiary phosphines or phosphites has only limited scope.

The synthesis of compounds containing the $Ru(PR_3)_2(\eta\text{-}C_5H_5)$ group involves treating carbonyl-free ruthenium halide complexes with cyclopentadiene or the derived anion, cyclopentadienide. Thus, the reaction between cyclopentadiene and $RuCl_2(PPh_3)_3$ proceeds in about two days to give the yellow-orange $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$,[9] which has proved to have an interesting chemistry quite distinct from that of the analogous dicarbonyl. This reaction has afforded related compounds containing other tertiary phosphines, phosphites and arsines, for example, $RuCl(L)_2(\eta\text{-}C_5H_5)$

{L = PPh_2Me, $P(OMe)_3$, $AsPh_3$}, by reacting compounds related to $RuCl_2(PPh_3)_3$ with cyclopentadiene; methylcyclopentadiene reacts similarly. With PPh_2Me and $AsPh_3$ the initial compounds from reactions with ruthenium trichloride are the complex salt $\{Ru_2Cl_3(PPh_2Me)_6\}Cl$,[10] and the adduct $RuCl_3(AsPh_3)_2(MeOH)$,[11] respectively. The former did not react with cyclopentadiene until an amine was added to the mixture. With the triphenylarsine complex, addition of zinc as a halogen acceptor was necessary. The osmium complex $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$ can be obtained from $OsBr_2(PPh_3)_3$ and cyclopentadiene.[12] Reaction between $RuCl_2(PPh_3)_3$ and thallium cyclopentadienide proceeds in about thirty minutes to give $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$,[11] a reaction which becomes experimentally difficult to scale up when large quantities of the chloride are required. Variable yields are encountered in the original reaction with cyclopentadiene, probably arising out of the tendency for $RuCl_2(PPh_3)_3$ to form the unreactive dimeric $\{RuCl_2(PPh_3)_2\}_2$ on standing in benzene solution particularly at ambient temperatures prevailing in Australia. The synthetic method of choice is a simple three-component reaction between hydrated ruthenium trichloride, cyclopentadiene and triphenylphosphine in refluxing ethanol for a period of thirty minutes, from which high yields of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ may be obtained.[13] The osmium complex $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$ can also be obtained from H_2OsBr_6, cyclopentadiene and triphenylphosphine in refluxing ethanol for a period of two hours.[13] This general reaction is of limited scope, separation of product being governed by solubility considerations and other factors. The reaction between H_2OsBr_6, cyclopentadiene and triphenylphosphine in refluxing methanol affords a high yield of the complex $OsBr_3(PPh_3)_2$ and only low yields of $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$.[14]

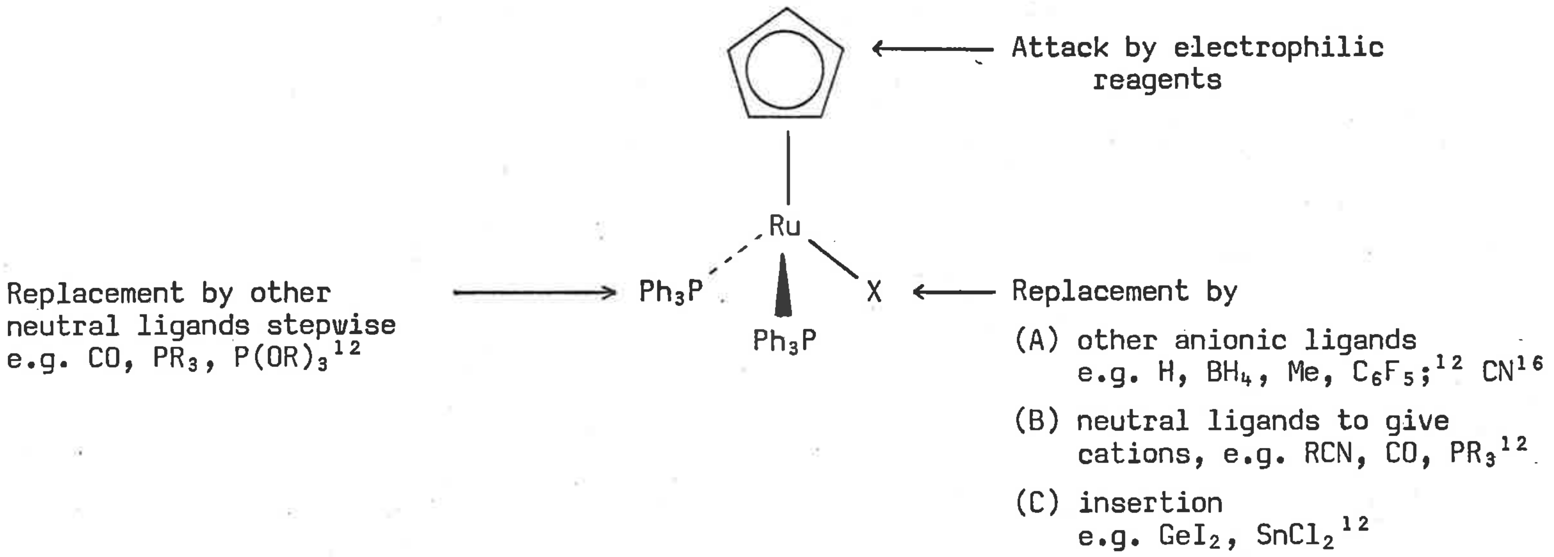
The halides $RuX(PPh_3)_2(\eta\text{-}C_5H_5)$ {X = F, Cl, Br or I} are pale yellow to dark orange in colour, stable in air, and monomeric in solvents such as benzene. The iodide is the major product from reactions between the chloride and MeMgI.[12] Ammonium fluoride reacts with the chloride in the presence of sodium bicarbonate to give $RuF(PPh_3)_2(\eta\text{-}C_5H_5)$ as an unstable yellow compound.[15]

Although both $RuCl(CO)_2(\eta\text{-}C_5H_5)$ and $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ are non-electrolytes in acetone, the phosphine derivative shows ionic behaviour in methanol:

$$RuCl(PPh_3)_2(\eta\text{-}C_5H_5) + MeOH \rightleftharpoons \{Ru(MeOH)(PPh_3)_2(\eta\text{-}C_5H_5)\}^+ + Cl^-$$

The solvento cation can be isolated in low yields by addition of large anions such as tetraphenylborate.[16] The phosphine complex exhibits a tendency to coordinate other donor ligands to give cationic complexes $\{Ru(L)(PPh_3)_2(\eta\text{-}C_5H_5)\}^+$ (see below), and also to lose one or both of the phosphine ligands in reactions affording neutral compounds. The properties and reactions of these two complexes have been compared in detail. Some reactions of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ are summarised in Scheme 1.I.

SOME REACTIONS



SCHEME 1.I

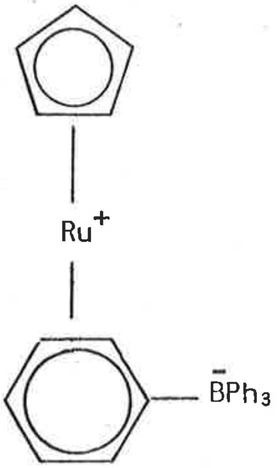
Reactions of the Metal-halogen Bond

The metal-halogen bond is readily cleaved in reactions with a variety of nucleophilic reagents. Both $LiAlH_4$[12] and NaOMe[17] afford the yellow, air-unstable hydride $RuH(PPh_3)_2(\eta\text{-}C_5H_5)$, which is thermally very stable, and can be recovered unchanged after prolonged heating in refluxing di-*n*-butyl ether.[12] Reaction with sodium borohydride gives white crystalline $Ru(H_2BH_2)(PPh_3)_2(\eta\text{-}C_5H_5)$.[12] Infrared and proton n.m.r. data indicate bridging hydrogen atoms between the metal and boron atoms.[18] The structure of this complex may be considered as five-coordinate, with the cyclopentadienyl, two phosphine ligands, and two hydrogen atoms attached to the metal atom. Sodium cyanoborohydride reacts to give the nitrile complex $Ru(NCBH_3)(PPh_3)_2(\eta\text{-}C_5H_5)$ which readily rearranges to give either the metal cyanide or the isonitrile species $Ru(CNBH_3)(PPh_3)_2(\eta\text{-}C_5H_5)$.[16] The cyanide is also formed by decomposition of the corresponding cyanotriphenylborate. The pseudohalides $RuX(PPh_3)_2(\eta\text{-}C_5H_5)$ {X = CN, NCS} have been prepared by metathetical reactions.[16]

Alkyl complexes are best prepared from the appropriate organolithium derivative. Thus, reaction between $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and methyl-lithium afforded $RuMe(PPh_3)_2(\eta\text{-}C_5H_5)$.[12] Reaction with methylmagnesium iodide, as mentioned above, gave a brick-red solid, identified as the iodide, $RuI(PPh_3)_2(\eta\text{-}C_5H_5)$. The failure of the Grignard reagent to give methyl-metal compounds has been noted previously, for example, in the case of $FeCl(CO)_2(\eta\text{-}C_5H_5)$.[19] The pentafluorophenyl complex was similarly obtained from pentafluorophenyl-lithium.[12] The benzyl complex was obtained using $PhCH_2MgBr$.[20]

The chloride undergoes a conventional 'insertion' reaction with stannous chloride to give yellow crystals of the trichlorotin compound, $Ru(SnCl_3)(PPh_3)_2(\eta\text{-}C_5H_5)$.[12] The complex $Ru(SnCl_3)(AsPh_3)_2(\eta\text{-}C_5H_5)$ was obtained similarly. Although related reactions have not been described, it is likely that similar derivatives can be obtained with other Group IV compounds containing the divalent metals.[12]

A phosphine-free product, $Ru(\eta-C_5H_5)(\eta-PhBPh_3)$, is formed in the reaction between $RuCl(PPh_3)_2(\eta-C_5H_5)$ and sodium tetraphenylborate, after refluxing in methanol, in 20% yield.[21] Heating the complex $\{Ru\{P(OMe)_3\}(PPh_3)_2(\eta-C_5H_5)\}BPh_4$ in methanol also affords the phosphine-free product in quantitative yield.[22] This compound has the zwitterionic structure (1.1), in which one of the phenyl rings of the tetraphenylborate group has displaced both triphenylphosphine and chloride (or phosphite) groups, and is bonded in the η^6-mode.[23]



(1.1)

Ligand Exchange Reactions

The tendency for loss or exchange of one of the triphenylphosphine ligands was early recognised in studies of $RuCl(PPh_3)_2(\eta-C_5H_5)$. The mass spectra[24] of some of the complexes described in the previous section show ions formed by ready loss of the phosphine ligands. That this reaction occurs readily in solution, in the presence of other donor ligands, was shown by several reactions. Ready substitution of one triphenylphosphine ligand by carbon monoxide occurs in the reaction between tetrahydrofuran solutions of $RuCl(PPh_3)_2(\eta-C_5H_5)$ and enneacarbonyldi-iron at room temperature overnight, when the compound $RuCl(CO)(PPh_3)(\eta-C_5H_5)$ can be isolated in high yield.[12] The displaced triphenylphosphine can also be isolated in the form of the complex $Fe(CO)_4(PPh_3)$. This monocarbonyl complex is also formed by carbonylating the chloride under pressure.[12] Similarly, carbonylation of $OsBr(PPh_3)_2(\eta-C_5H_5)$ gave the monocarbonyl complex $OsBr(CO)(PPh_3)(\eta-C_5H_5)$.[12]

Relatively few reactions are known in which triphenylphosphine or related ligands are displaced by carbon monoxide. The complexes $Pt(PPh_3)_4$, $RhCl(PPh_3)_3$, and $RuCl_2(PPh_3)_n$ {n = 3 or 4} react with carbon monoxide to give $Pt(PPh_3)_3(CO)$,[25,26] $RhCl(CO)(PPh_3)_2$,[27] and *trans*-$Ru(CO)_2(PPh_3)_2Cl_2$,[11] respectively. Another example is a displacement reaction involving $Co(PPh_3)_2(\eta-C_5H_5)$.[23] However, all these reactions depend to a large degree on the dissociation of a phosphine ligand, which can be shown to occur in solution.[29]

There is no evidence for the dissociation of any of the PPh_3 ligands in $RuCl(PPh_3)_2(\eta-C_5H_5)$ in solution. As mentioned earlier, the replacement of the remaining carbonyl group in complexes of the type $MX(CO)(PR_3)(\eta-C_5H_5)$ {M = Fe, Ru} requires drastic conditions. Thus a reasonable interpretation of the replacement reactions may involve the stability of the resulting complexes, rationalised in terms of electronic effects of the various ligands, that is, in terms of the relative amounts of σ-donor and π-acceptor properties. The most stable complex retains one molecule each of a good σ-donor (phosphine) and a good π-acceptor (CO).

Steric arguments may be considered, but these would appear to be relatively unimportant, for two reasons. Firstly, fairly large groups can be accommodated in complexes such as $RuX(PPh_3)_2(\eta-C_5H_5)$ {X = I, C_6F_5, $SnCl_3$} and secondly, stable cations can be prepared which contain two phosphine ligands and one carbonyl group; in these, the lability of the second phosphine in the neutral complex is reduced by formation of a positively charged complex.

The molecule $RuCl(PPh_3)_2(\eta-C_5H_5)$ is considerably distorted from the ideal $(C_5H_5)ML_3$ case as a result of the presence of two bulky tertiary phosphine ligands.[30] The steric strain induced by the two PPh_3 ligands is relieved in three ways: (i) all substituents are bent away from the C_5H_5 group by markedly more than the tetrahedral angle, *c*. 121-122°; (ii) inter-ring repulsion between the aromatic rings on both phosphines opens out the Ru-P-C angles to 126° for the two rings nearest each other; the other rings are bent back to a lesser degree (107-118°); (iii) the P-Ru-Cl angles close to *c*. 90°. Opening of the angle Cp-Ru-X {X = Cl, P} from the tetrahedral angle to *c*. 121° probably results from interactions of the Cp hydrogens with those of the PPh_3 rings.

Comparison with $RuCl(PMe_3)_2(\eta-C_5H_5)$[30] shows that both molecules have the same long Ru-Cl bonds (2.45 Å), which is reflected in the ready loss of Cl^- in polar solvents. The smaller PMe_3 ligands (cone angle 118°) result in the coordination about ruthenium tending towards octahedral, with a markedly shorter Ru-P bond. These changes provide a dramatic illustration of the steric effect of coordination of two bulky ligands *cis* to one another.

Several exchange reactions with other tertiary phosphines and phosphites have been described. The mixed complex $RuCl(PMePh_2)(PPh_3)(\eta-C_5H_5)$ was detected spectroscopically in the products from the $PMePh_2$.[12] Complete exchange of triphenylphosphine with the phosphites $P(OR)_3$ {R = Me, Ph} require the reasonably vigorous conditions of heating in decalin for short periods.[15] Some dehydrochlorination of the $P(OPh)_3$ complex occurs to give the cyclometallated complex (see below).

Where they have been studied, similar reactions have been found with

$OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$, but the usual reduced reactivity of the third-row element, compared to its second-row cogener, is found.[31]

Cationic Complexes

The chloride is prone to form solvento cations in donor solvents. The methanol cation has been mentioned above, and the acetone derivative is also known. A solution of the chloride in tetrahydrofuran has a deeper colour than the solid, but no cation of the type $\{Ru(thf)(PPh_3)_2(\eta\text{-}C_5H_5)\}^+$ has been isolated. These cations are best prepared from reactions between the chloride and $AgSbF_6$ carried out in the solvent.

Salts of the acetonitrile cation $\{Ru(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)\}^+$ can be obtained readily by dissolution of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ in acetonitrile. Addition of large anions gave tetraphenylborate, hexafluorophosphate, or hexafluoroarsenate salts as yellow crystalline solids.[12] Reactions between the chloride and zinc or mercury (II) chlorides in acetonitrile gave rapid colour changes from orange to yellow, and stable yellow complexes, $\{Ru(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)\}_2Zn_2Cl_6$ and $\{Ru(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)\}HgCl_3$, respectively, were isolated.[12]

Carbonylation of the chloride in ethanol solution,[12,16] in the presence of sodium tetraphenylborate, affords $\{Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)\}BPh_4$ as pale yellow crystals. In this case, no displacement of phosphine and carbonyl ligands by the BPh_4 occurs. With dinitrogen, the infrared spectrum shows bands attributed to $\nu(NN)$, but no complex containing coordinated dinitrogen could be isloated.[16] Small phosphines, PR_3, can also displace chloride to give $\{Ru(PR_3)(PPh_3)_2(\eta\text{-}C_5H_5)\}^+$, although it has not yet been possible to coordinate three triphenylphosphine ligands around a ruthenium atom.

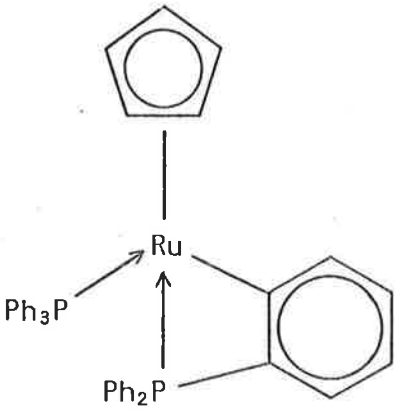
The reactivity of the chloride in these reactions can be ascribed to both steric and electronic effects. In particular, the size of the tertiary phosphine ligand, as recognised by the 'cone angle', is of obvious importance.[32] It is possible to draw up empirical relationships involving total cone angle, etc., but these take no account of the possibilty of 'interleaving' the various groups attached to the phosphorus atom.

Reactions of $RuR(PPh_3)_2(\eta\text{-}C_5H_5)$ *{R=H,Alkyl}*

The reactions of the hydride and alkyl complexes containing the $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$ group have been studied in some detail, and will be described under the headings of cyclometallation and reactions with activated olefins and alkynes.

(A) *Cyclometallation Reactions*

Although the hydride is stable towards the elimination of dihydrogen on heating, when the methyl complex, $RuMe(PPh_3)_2(\eta\text{-}C_5H_5)$, or the benzyl complex, $Ru(CH_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$, are heated under reflux in decalin, for a brief period, the *ortho*-metallated derivative $\overline{Ru(C_6H_4PPh_2}(PPh_3)(\eta\text{-}C_5H_5)$ (1.2) is formed, by elimination of methane or toluene, respectively.[15,33] The reaction of hexafluorobut-2-yne with (1.2) afforded the bis-insertion product (1.3), the structure of which is analogous to that of $\overline{Rh(CPh{=}CPhCPh{=}CPhC_6H_4PPh_2})(PPh_3)$, obtained from $\overline{Rh(C_6H_4PPh_2})(PPh_3)_2$ and diphenylacetylene.[34,35]



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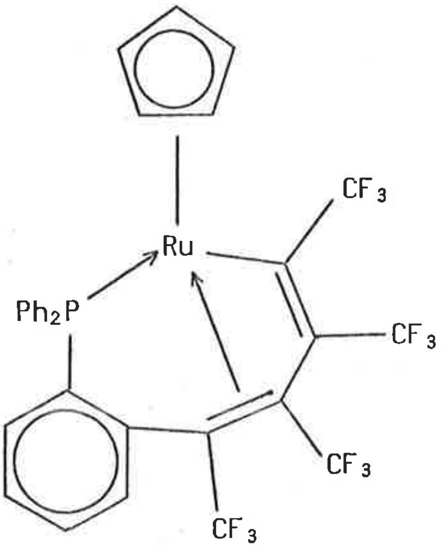
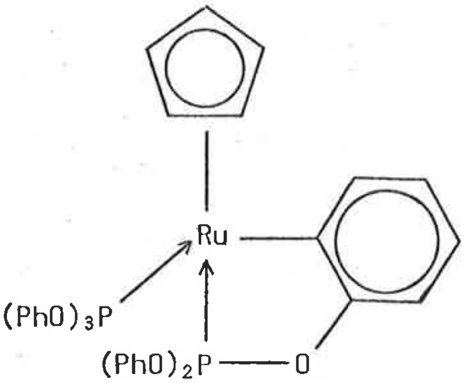


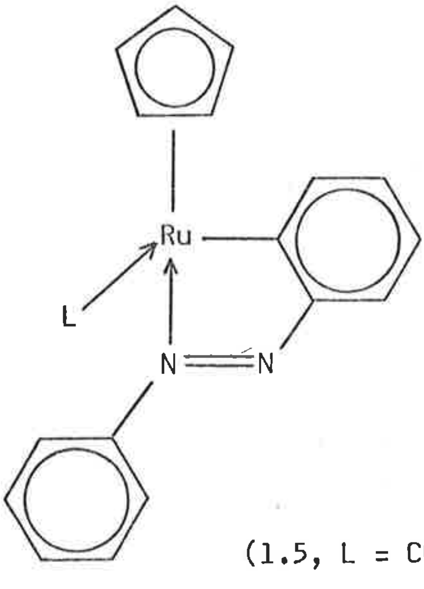
(1.3)

Ligand exchange between $\text{RuCl(PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ and P(OPh)_3 in refluxing decalin afforded a mixture of $\text{RuCl\{P(OPh)}_3\}_2(\eta\text{-C}_5\text{H}_5)$ and $\overline{\text{Ru\{C}_6\text{H}_4\text{OP}}\text{(OPh)}_2\}\{\text{P(OPh)}_3\}(\eta\text{-C}_5\text{H}_5)$ (1.4), the latter also being obtained from $\text{RuCl\{P(OPh)}_3\}_2(\eta\text{-C}_5\text{H}_5)$ and dicyclohexylethylamine, by elimination of HCl.[15] The cyclometallated derivative contains the relatively unreactive five-membered $\overline{\text{RuCCOP}}$ ring and does not react with hexafluorobut-2-yne, even at 100° for one week.



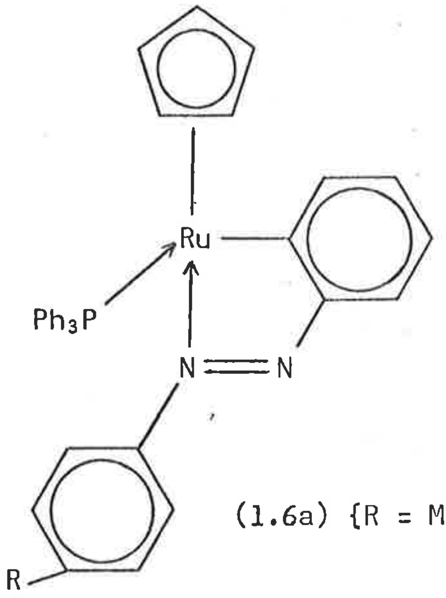
(1.4)

Chelating 2-(phenylazo)phenyl complexes $\overline{\text{Ru(C}_6\text{H}_4\text{N=N}}\text{Ph)(L)}(\eta\text{-C}_5\text{H}_5)$ (1.5, L = CO, PPh_3) have been obtained from reactions between azobenzene and $\{\text{Ru(CO)}_2(\eta\text{-C}_5\text{H}_5)\}_2$ [36] or $\text{RuMe(PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ [15], respectively, or from $\{\overline{\text{Ru(C}_6\text{H}_4\text{N=N}}\text{Ph)(CO)}_2\text{Cl}\}_2$ and NaC_5H_5.[37] The carbonyl group is readily displaced by triphenylphosphine.

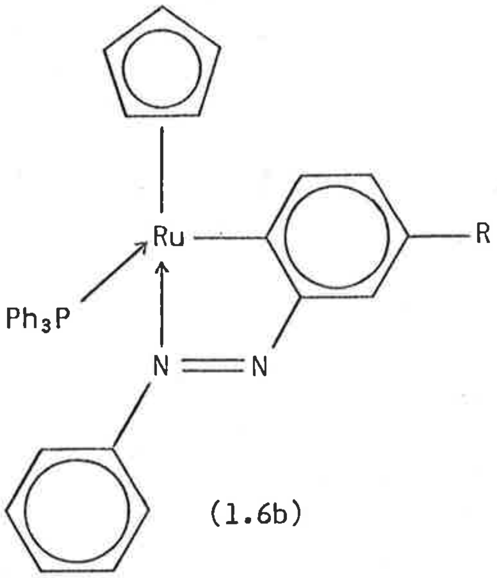


(1.5, L = CO or PPh_3)

This reaction was repeated with a series of *meta*-substituted azobenzenes in order to investigate the mechanism and the effect of the substituent. Inseparable mixtures of isomeric products (1.6a) and (1.6b) were obtained in reactions of the substituted azobenzenes with $RuMe(PPh_3)_2(\eta-C_5H_5)$.[15]



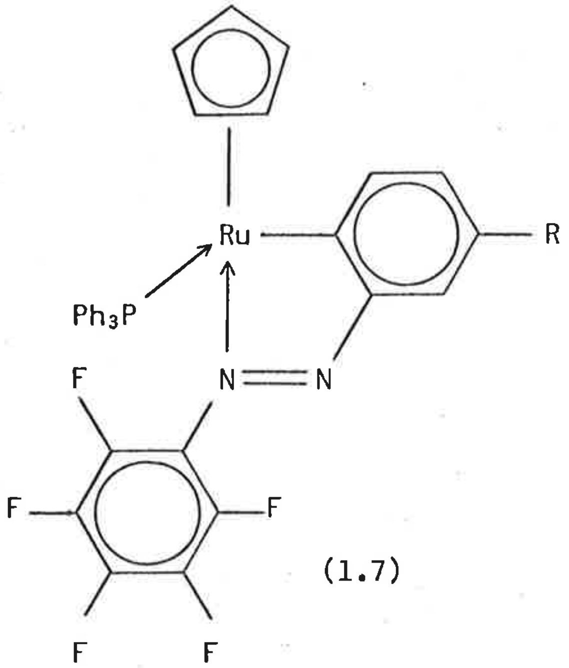
(1.6a) {R = Me, OMe, CO_2Et, or CF_3}



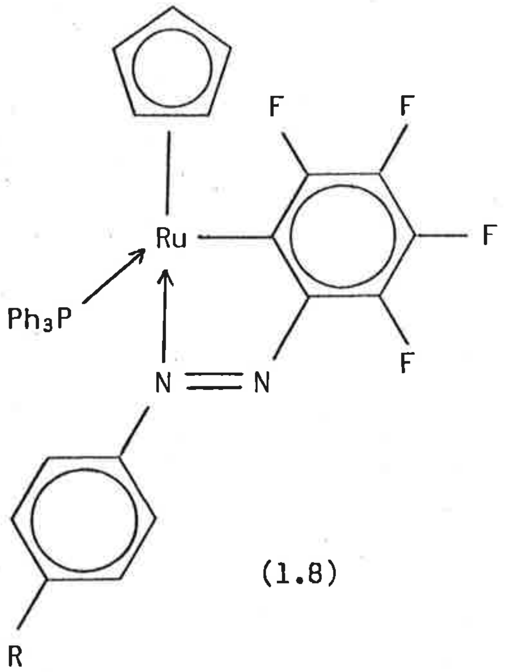
(1.6b)

Similar products were obtained with $3,5-(MeCO_2)_2C_6H_3N{=}NPh$, but in this case the isomeric complexes could be separated by chromatography, the major product (43%) was metallated in the phenyl group, while the isomer corresponding to (1.6b) was formed in only 7% yield. Steric hinderance by the CO_2Me groups may explain low yields of the latter compound.

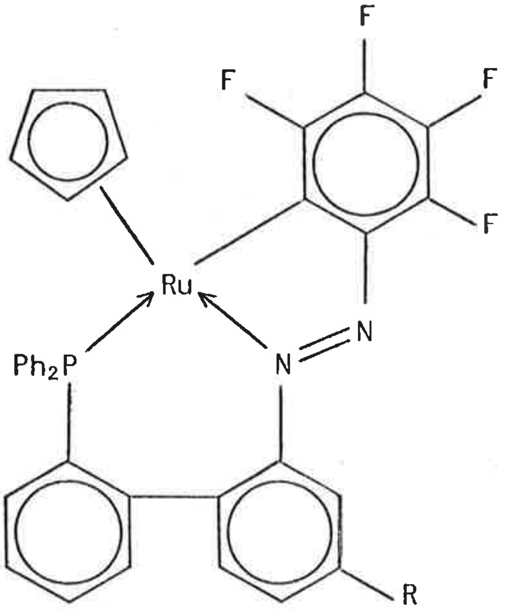
This general behaviour can be related to the strongly nucleophilic character of the ruthenium atom, and suggested that fluorinated azobenzenes might react with the methyl complex. A series of dark green products were obtained from the fluorinated azobenzenes $3-RC_6H_4N{=}NC_6F_5$, corresponding to the two compounds (1.7) and (1.8), and a third containing a phenyl-linked triphenylphosphine-azobenzene ligand (1.9).[15] Complexes (1.8) are unusual in being metallated in the fluorinated ring, and a complex of this type, from the reaction with $3,5-(MeCO_2)_2C_6H_3N{=}NC_6F_5$, is the sole product isolated.



(1.7)

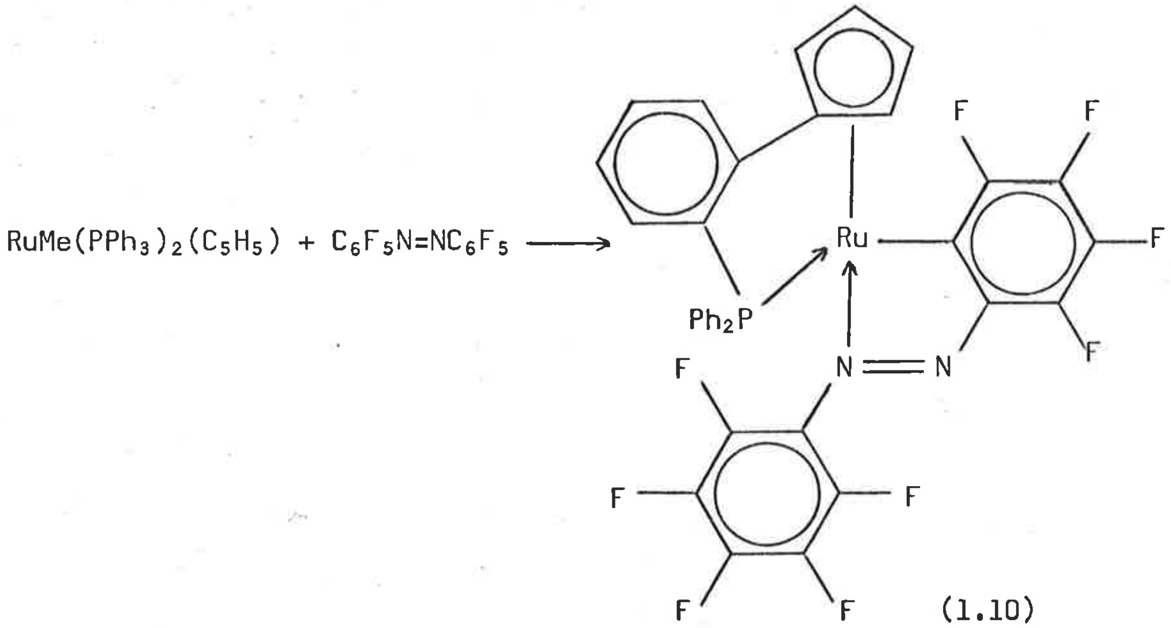


(1.8)



(1.9) {R = H, Me, CF_3}

A single product was also obtained from $RuMe(PPh_3)_2(\eta\text{-}C_5H_5)$ and decafluoroazobenzene, the dark green (1.10). This reaction was one of the first examples of cyclometallation involving elimination of a halide from the arene ring.[15,38] The unusual structural features in this complex include the metallated polyfluorophenyl ring, and the $Ph_2PC_6H_4C_5H_4$ ligand, presumably formed by phenyl migration to the ring.[39] The azo ligand is non-planar, and reflects the non-bonding interactions that are occurring in the ruthenium coordination sphere.


$RuMe(PPh_3)_2(C_5H_5) + C_6F_5N{=}NC_6F_5 \longrightarrow$

(1.10)

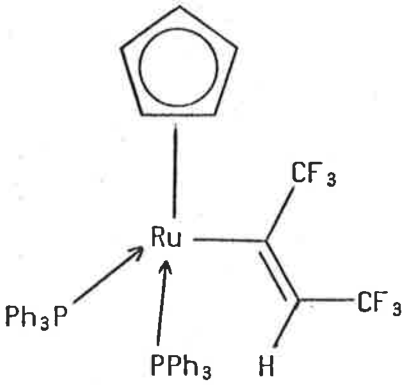
These reactions illustrate a number of possibilities for the formation of metallated complexes. The methyl complex readily metallates phenyl groups by elimination of methane; the elimination of a variety of alkanes has been studied with $MnR(CO)_5$.[40] The exact mode of elimination of fluorine from the polyfluorophenyl derivatives has not been determined: a possibility is as MeF, the electron-rich $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$ moiety readily attacking the C_6F_5 ring by a nucleophilic route. The ready substitution of C_5H_5 by other ligands in these complexes has been noted earlier, and a suggested route to the $C_5H_4C_6H_4$ ligand is mentioned later.

(B) Reactions with Electron-deficient Olefins and Alkynes

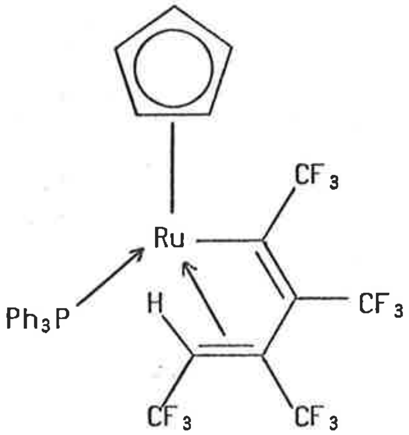
The reaction between $RuH(PPh_3)_2(\eta\text{-}C_5H_5)$ and $(CF_3)_2C{=}C(CN)_2$ affords the substituted ethyl derivative $Ru\{C(CN)_2CH(CF_3)_2\}(PPh_3)_2(\eta\text{-}C_5H_5)$ by a formal 'insertion' reaction, the cyano-substituted carbon becoming attached to the metal.[41]

Reactions of the alkyl ruthenium complexes $RuR(PPh_3)_2(\eta\text{-}C_5H_5)$ $\{R = H, Me, CH_2Ph\}$ with disubstituted acetylenes bearing electronegative substituents have afforded vinyl, butadienyl, hexatrienyl, or cumulenyl groups σ-bonded to ruthenium.[41-43] Where the organic substituent contains four or more carbon atoms, cyclisation occurs through η^2-bonding of one of the double bonds of the chain to ruthenium. Formation of many of these unusual products has been rationalised by postulating ready dissociation of one of the triphenylphosphine ligands from the metal, thereby providing a site for coordination of an acetylene molecule, and subsequent involvement of dipolar intermediates.

Hexafluorobut-2-yne reacts with the hydridoruthenium complex to give the *cis*-vinyl complex (1.11), and a butadienyl derivative (1.12), in which a triphenylphosphine ligand has been displaced; the phosphine reacts with excess alkyne to give a cyclic phosphorane.[41]

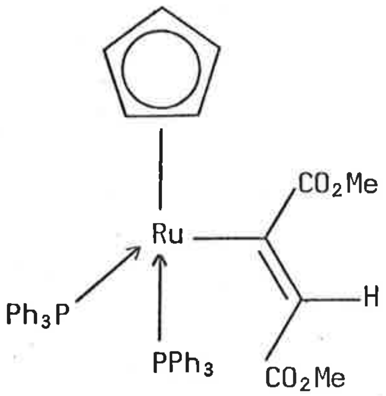


(1.11)

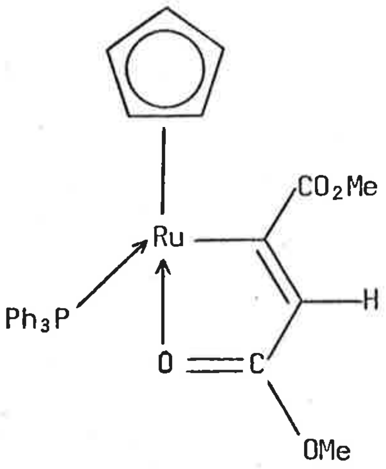


(1.12)

Dimethyl acetylenedicarboxylate affords the *trans*-vinyl complex (1.13) in high yield, which on heating cyclises to give the red-monophosphine complex (1.14), where the ester carbonyl group has displaced the triphenylphosphine ligand.[41]

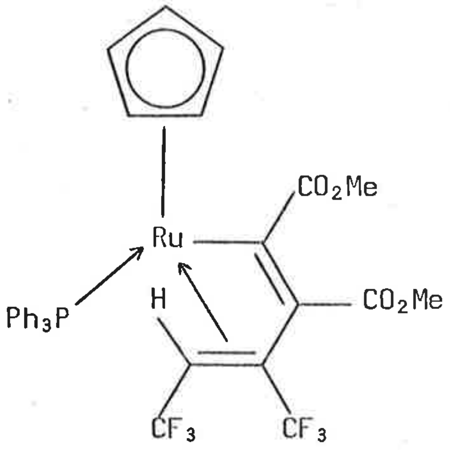


(1.13)

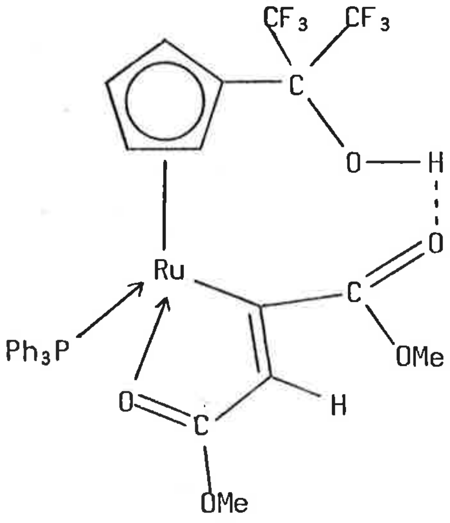


(1.14)

In only one case do both *cis* or *trans* isomers appear to have been obtained from reactions of this type. The reaction between ReH(η-C_5H_5)$_2$ and the acetylenic diester[44] affords this *cis* adduct which was subsequently isomerised to the *trans* complex on heating. Although no bis-insertion product analogous to (1.12) was obtained with $C_2(CO_2Me)_2$, the reaction of complex (1.13) with hexafluorobut-2-yne afforded the mixed butadienyl complex (1.15), in which the fluorinated alkyne has apparently inserted into a vinylic C-H bond.[41,45] Another type of reactive fluorocarbon molecule, hexafluoroacetone, reacts with (1.13) to form the unusual substituted cyclopentadienyl complex (1.16), in which the hydroxy group is hydrogen-bonded to one of the ester carbonyl groups.[46]

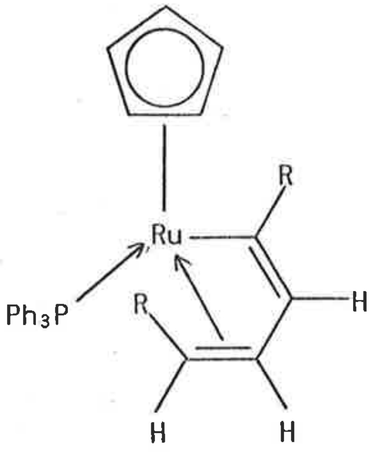


(1.15)



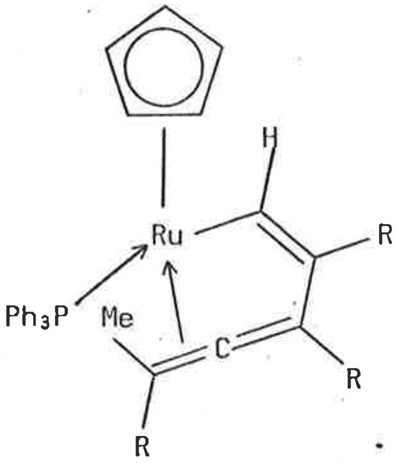
(1.16)

Reactions of the hydride with terminal alkynes[20] generally give oligomeric products, and are complicated by the formation of η^1-acetylide derivatives. Methyl propiolate gives the σ-acetylide $Ru(C_2CO_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)$, a bis-adduct formulated as the butadienyl complex (1.17), and a tris-adduct (1.18) in which trimerisation of the alkyne has accurred. The latter complex is the first example of a complex containing the 1,4,5-η^3-penta-1,3,4-trien-1-yl group.



(1.17)

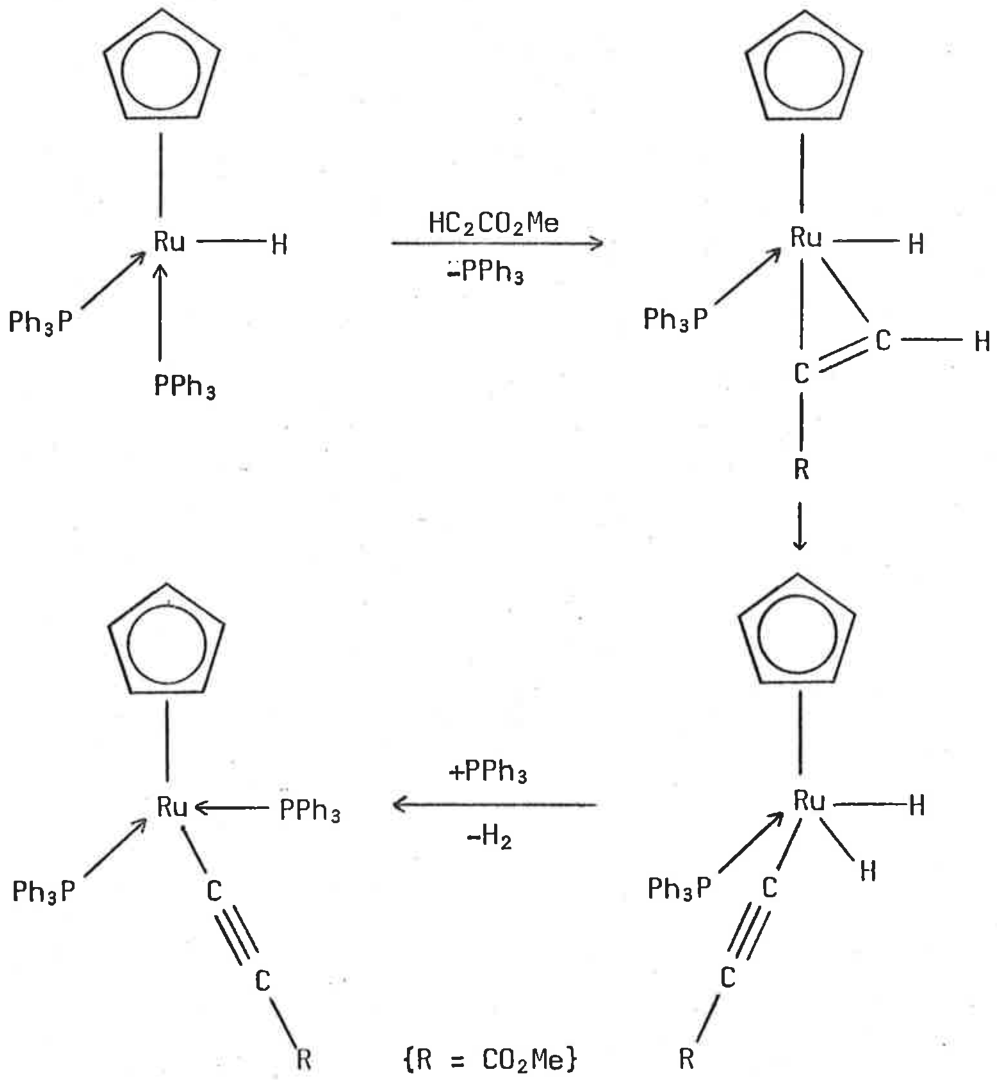
{R = CO_2Me}



(1.18)

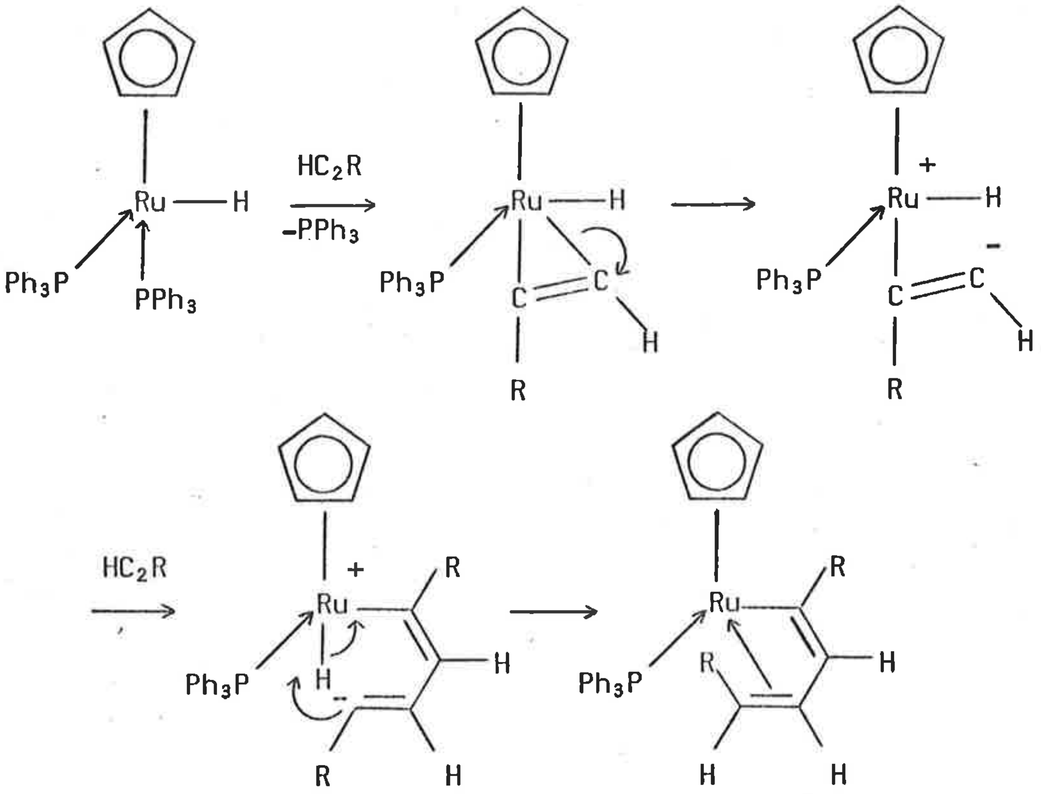
The mechanism for the formation of the acetylide complex probably involves oxidative addition of the acetylene to the ruthenium(II) complex to afford the ruthenium(IV) derivative. Elimination of dihydrogen would then afford the ruthenium(II) acetylide complex (Scheme 1.II). The lability of the tertiary phosphine ligand is an important feature in the proposed mechanism. Oxidative addition to Os(0) species to give Os(II) derivatives is well characterised. Addition of HPF_6 or Cl_2 to the osmium derivative $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$ affords two complexes which may be considered to contain square-pyramidal Os(IV).[47] The corresponding ruthenium complexes are formed in similar reactions, but are too unstable to isolate. The Ru(IV) compounds are stabilised by using PMe_3, a more basic phosphine.[48]

SCHEME 1.II

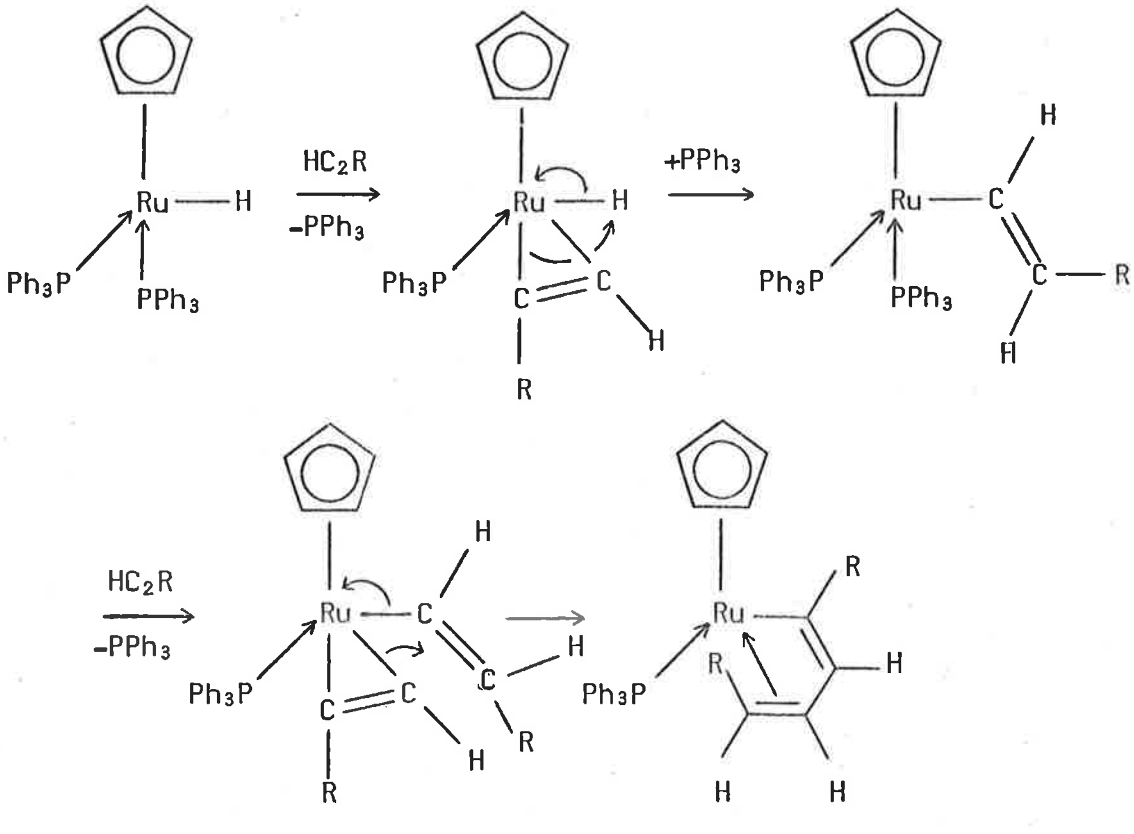


A proposed mechanism for the formation of the butadienyl complex (1.17) (Scheme 1.III) involves the formation of a dipolar intermediate which can subsequently attack another alkyne molecule. Another mechanism for the formation of (1.17) (Scheme 1.IV) involves initial formation of a vinyl complex, subsequent oxidative addition of another alkyne molecule followed by an 'elimination reaction'. A proposed mechanism for the formation of (1.18) is shown in Scheme 1.V. The complex is unusual as it contains a methyl group attached to the hydrocarbon chain, in which an allenyl group is incorporated. In none of these complexes is the hydrocarbon chain chelated via the ester carbonyl group.

SCHEME 1.III

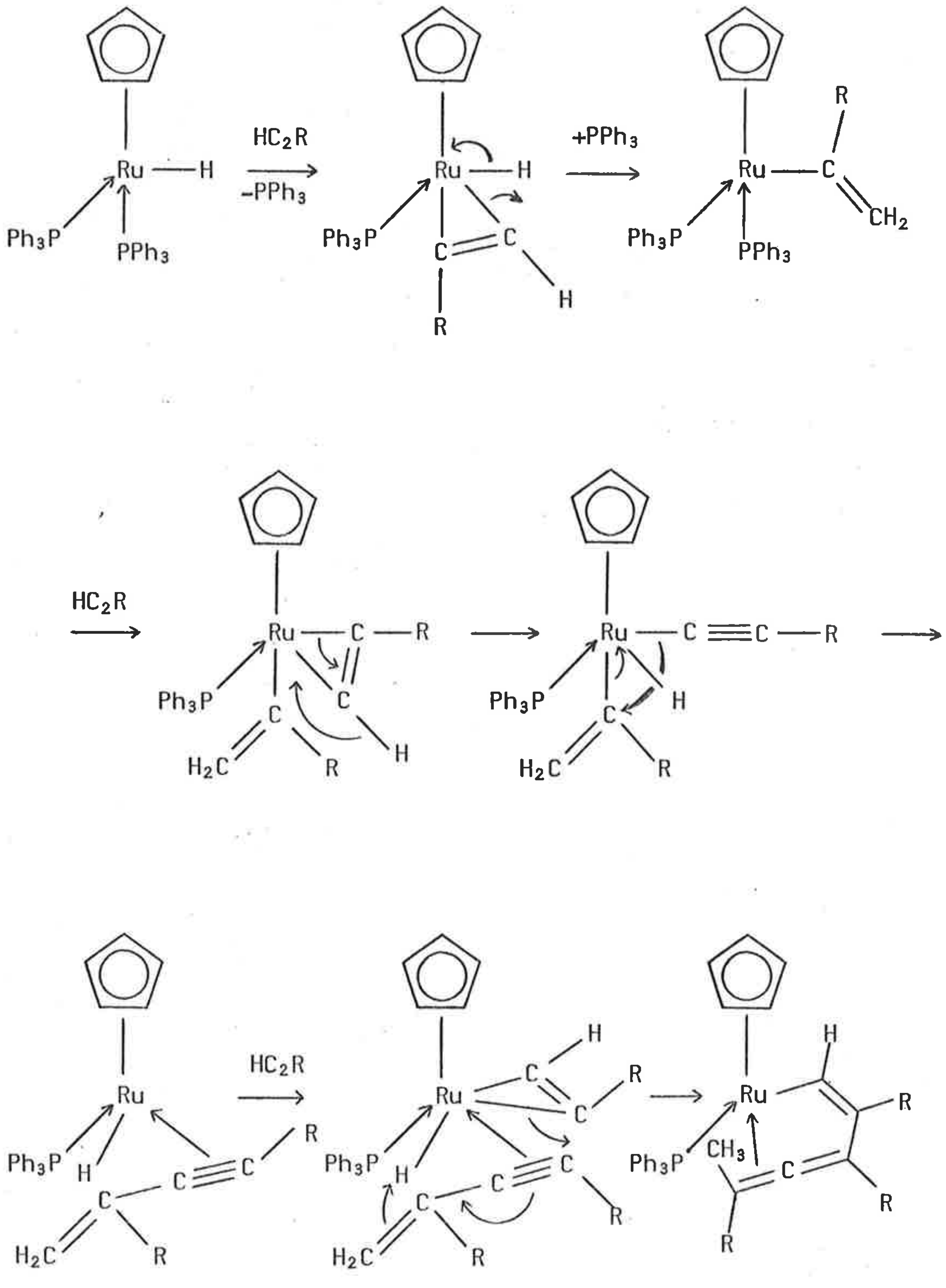


SCHEME 1.IV



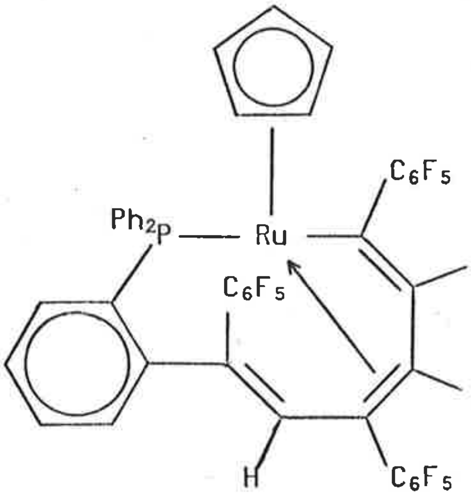
{R = CO_2Me}

SCHEME 1.V



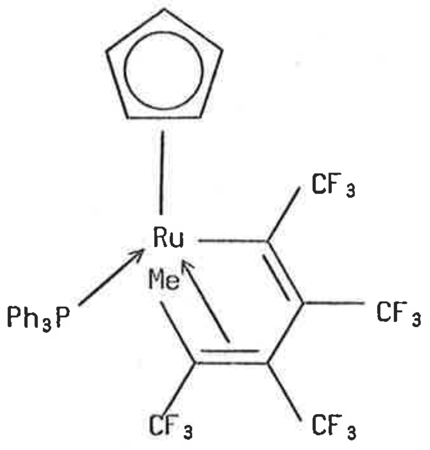
{R = CO$_2$Me}

Pentafluorophenylacetylene also reacts with the hydride to give a tris-adduct, for which the structure (1.19) has been proposed. This complex contains an *ortho*-substituted $C_6H_4PPh_2$ group, and is perhaps formed either by successive insertions of the alkyne into the cyclometallated phosphine complex (1.2), similar to the bis-insertion product (1.3) (although none of the cyclometallated complex was isolated) or less likely, via a trimeric dipolar intermediate which subsequently attacks the *ortho*-phenyl carbon with elimination of dihydrogen.

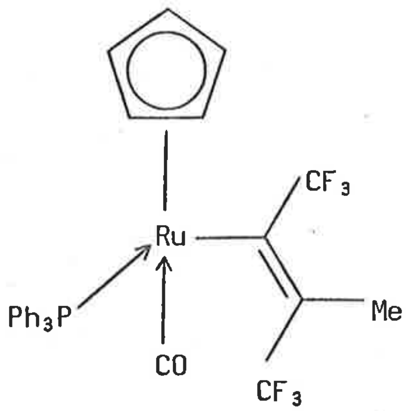


(1.19)

The ruthenium alkyl complexes $RuR(PPh_3)_2(\eta-C_5H_5)$ {*R* = Me, CH_2Ph} react with alkynes to give an equally diverse range of products. Hexafluorobut-2-yne reacts with the methyl complex in benzene to afford the butadienyl complex (1.20), the methyl analogue of one of the products obtained from $RuH(PPh_3)_2(\eta-C_5H_5)$ and hexafluorobut-2-yne. In contrast to the hydride, no mono-insertion product was observed in the methyl case. When the reaction was carried out in 1,2-dimethoxyethane, a monocarbonylruthenium complex (1.21) was obtained.

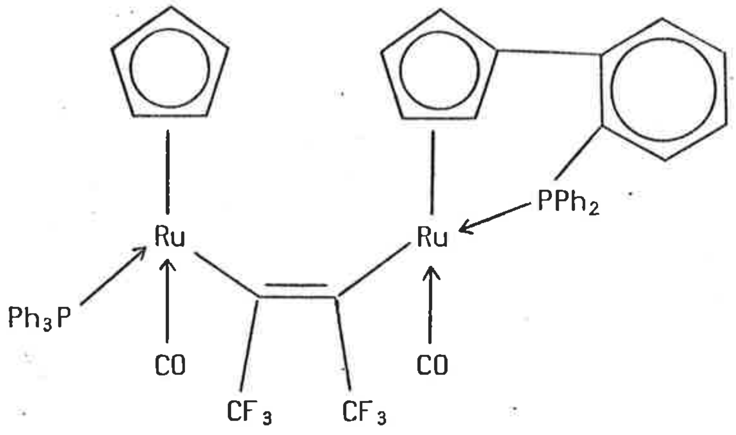


(1.20)



(1.21)

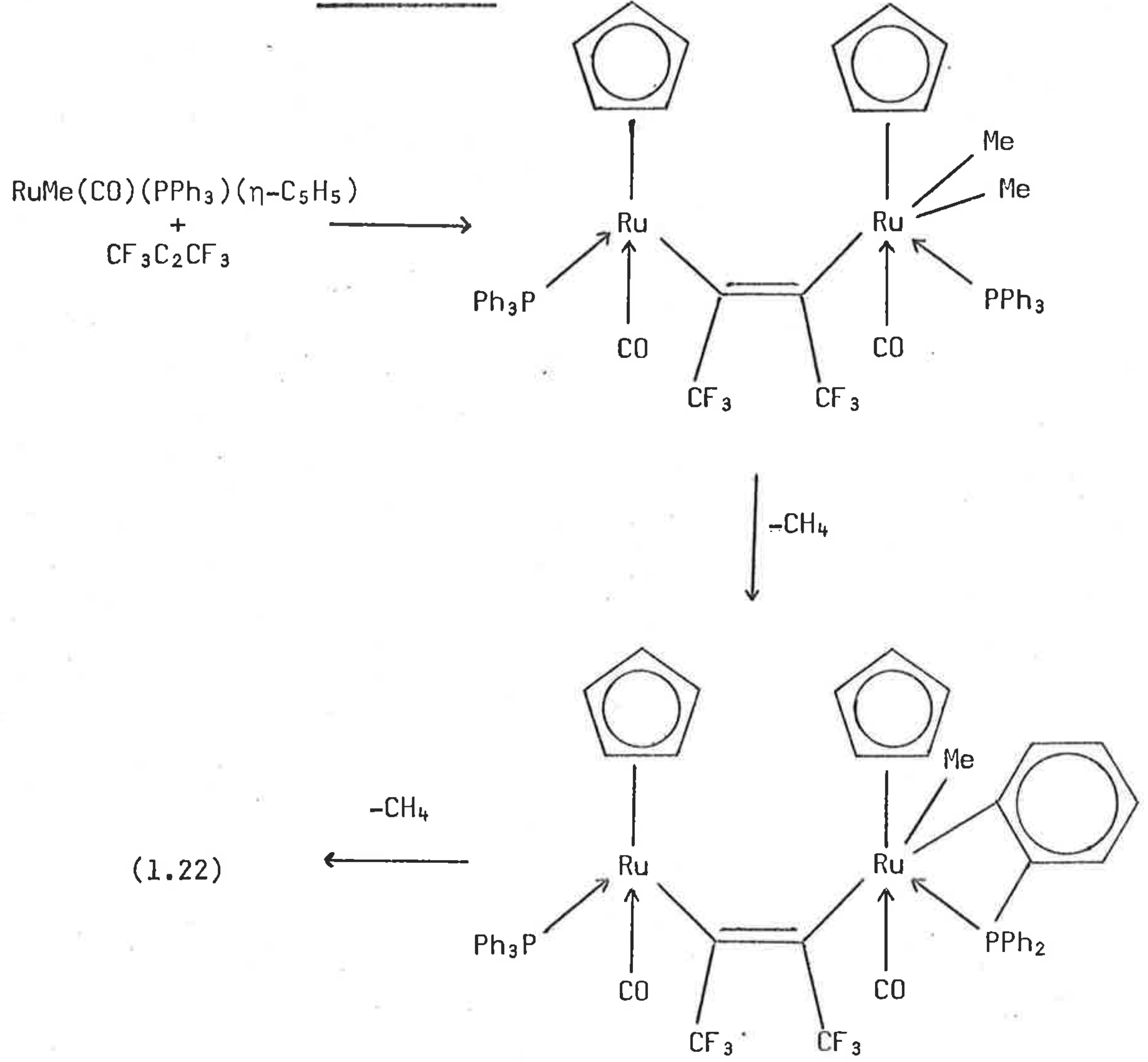
The formation of a *trans*-adduct in this reaction contrasts with other reactions of related complexes with hexafluorobut-2-yne, which have afforded the *cis*-vinyl complexes, and suggests that a different reaction pathway is followed. The monocarbonyl complex RuMe(CO)(PPh$_3$)(η-C$_5$H$_5$) does not react with hexafluorobut-2-yne to give (1.21). However, at 100^0 a yellow crystalline diruthenium complex (1.22) was formed.



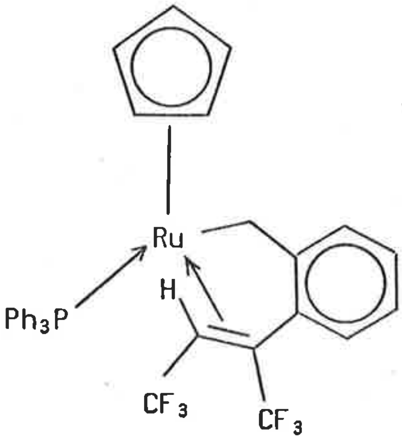
(1.22)

Addition of metal alkyls to hexafluorobut-2-yne to afford dimetal complexes such as (1.22) has been described previously for the gold complexes AuMe(PPh$_2$R) {R = Me, Ph}. For R = Ph, the complex *cis*-$(Ph_3P)Au\{C(CF_3)=C(CF_3)\}Au(PPh_3)$ was isolated.[49] However, with R = Me, an intermediate Au(1)-Au(111) complex was characterised and it was established[50] that formation of the final Au(1)-Au(1) product involved transfer of a methyl group from one gold atom to the other, followed by reductive elimination from the Au(111) centre. Formation of (1.22) probably proceeds via an unstable Ru(11)-Ru(1V) intermediate (methyl migration), subsequent elimination of methane causing cyclometallation through a well established pathway.[51] This could be followed by phenyl-group migration from the Ru(1V) centre to the cyclopentadienyl ring with concomitant loss of a second molecule of methane (Scheme 1.V1). Migration of aryl groups from metal to dienyl ligands[52,53] and linkage[38,39] of $C_6H_4PPh_2$ and η-C_5H_5 moieties has been previously observed.

SCHEME 1.VI

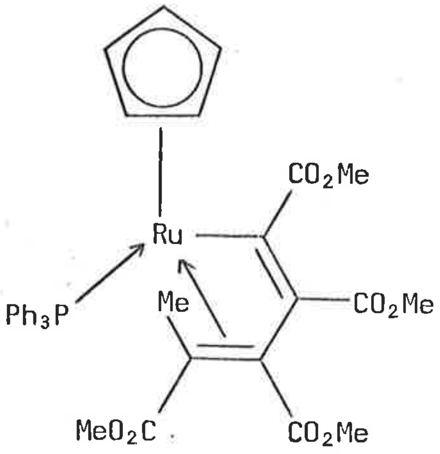


Attack of the ruthenium benzyl derivative by $C_2(CF_3)_2$ gave the *ortho*-substituted vinylbenzyl derivative (1.23),[33] a new reaction type involving activation of the σ-benzyl group, and is akin to metallation followed by insertion of hexafluorobut-2-yne.

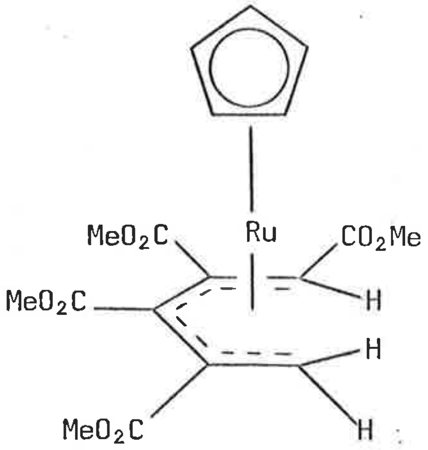


(1.23)

Excess acetylenic diester $C_2(CO_2Me)_2$ reacts with the methyl complex to give the butadienyl complex (1.24), which loses triphenylphosphine forming the acyclic η^5-pentadienyl structure (1.25),[54] the first example of a complex containing the 1,5-η^5-pentadienyl group.



(1.24)

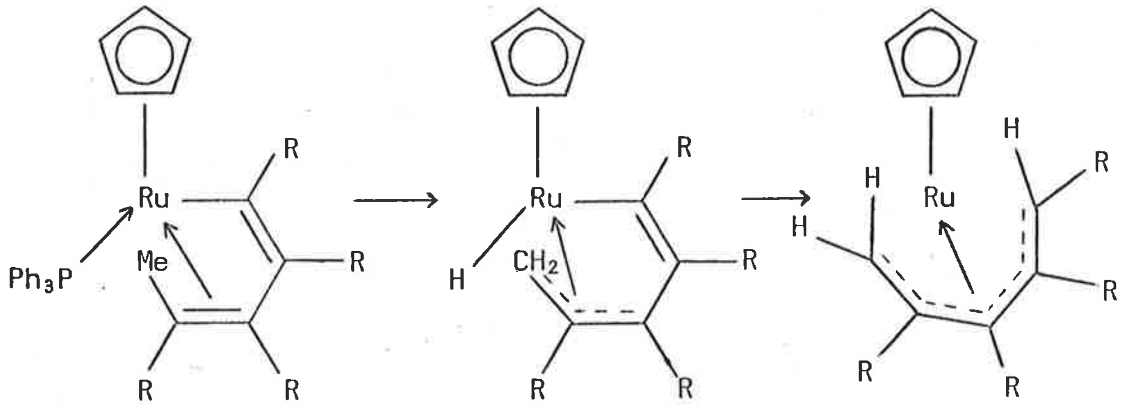


(1.25)

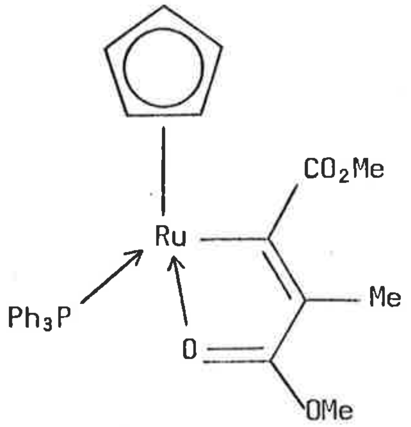
The most likely route to (1.25) via (1.24) is through an (η^3-allyl) hydridoruthenium(IV) species (Scheme 1.VII). The structure of (1.25) has recently been confirmed by an X-ray crystallographic study.[55]

SCHEME 1.VII

{R = CO_2Me}

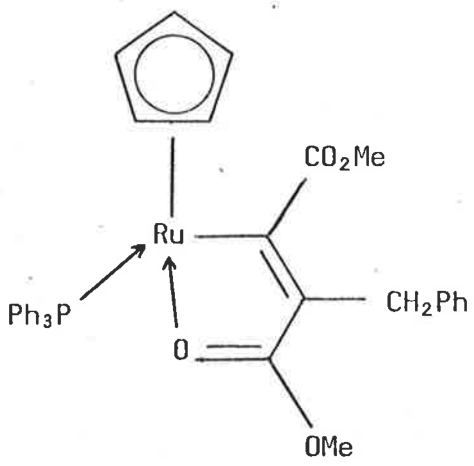


When 1,2-dimethoxyethane at reflux is used as solvent, instead of diethyl ether, a third ruthenium complex (1.26) was isolated in low yield, a vinyl derivative in which coordination of the carbonyl group occurs.

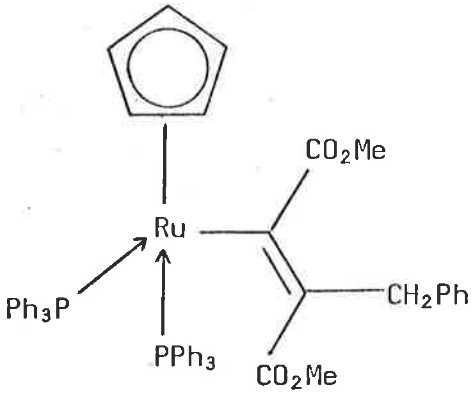


(1.26)

The benzyl complex $Ru(CH_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ reacts with $C_2(CO_2Me)_2$ to give the yellow crystalline complex (1.27), together with small amounts of its precursor (1.28), which readily loses triphenylphosphine to afford the chelate complex.

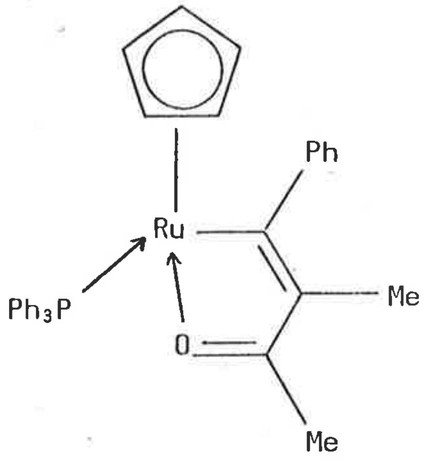


(1.27)

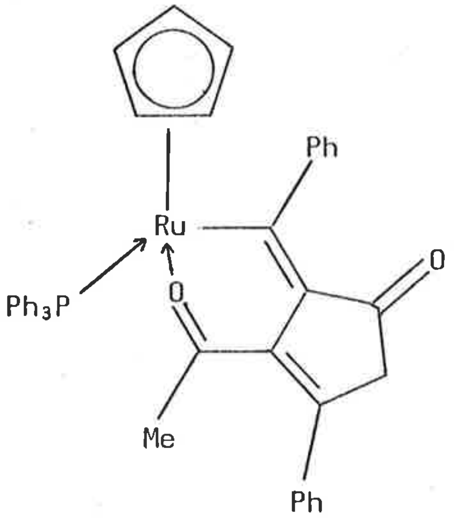


(1.28)

The reaction between 4-phenylbut-3-yn-2-one and $RuMe(PPh_3)_2(\eta\text{-}C_5H_5)$ affords a bright red complex (1.29) and a dark red compound (1.30)



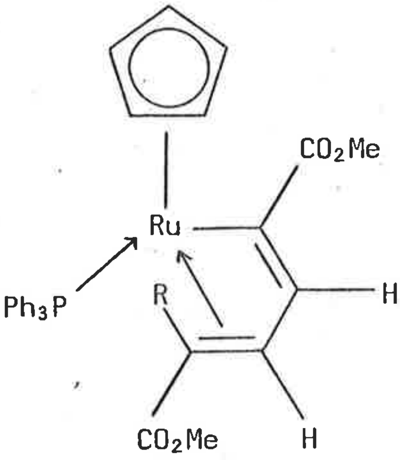
(1.29)



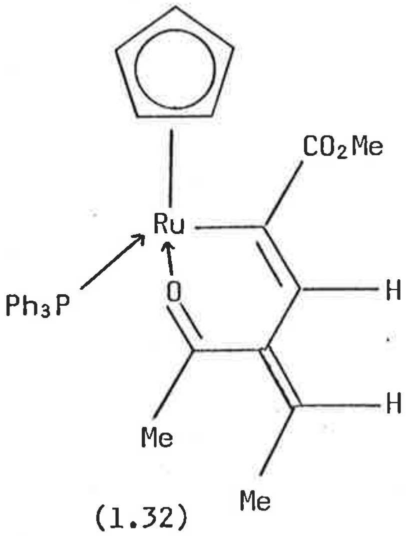
(1.30)

Formation of (1.29) is readily explicable via a conventional insertion reaction involving one mole of the alkynyl ketone. The substituted methylenecyclopentenone complex (1.30) is formed via an insertion reaction involving two moles of the alkynyl ketone with elimination of methane.

As in the case of the hydride, reactions of the methyl complex with terminal acetylenes afford η^1-acetylides in low yield. The methyl and benzyl complexes $RuR(PPh_3)_2(\eta-C_5H_5)$ {R = Me, CH_2Ph} react with methyl propriolate to give yellow microcrystalline bis-insertion products (1.31). Reaction of 3-butyne-2-one with $RuMe(PPh_3)_2(\eta-C_5H_5)$ affords the bis-insertion product (1.32)[20] containing a six-membered ring formed by chelation of one of the keto groups.

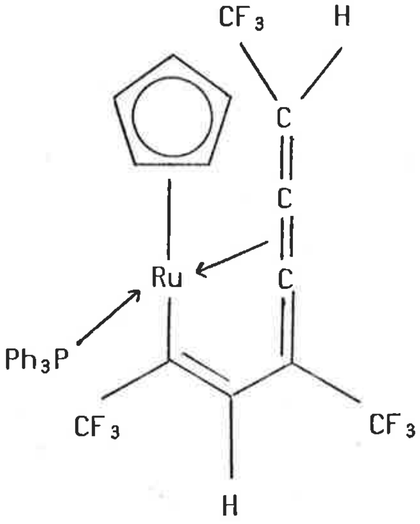


{R = Me, CH_2Ph; 1.31}



(1.32)

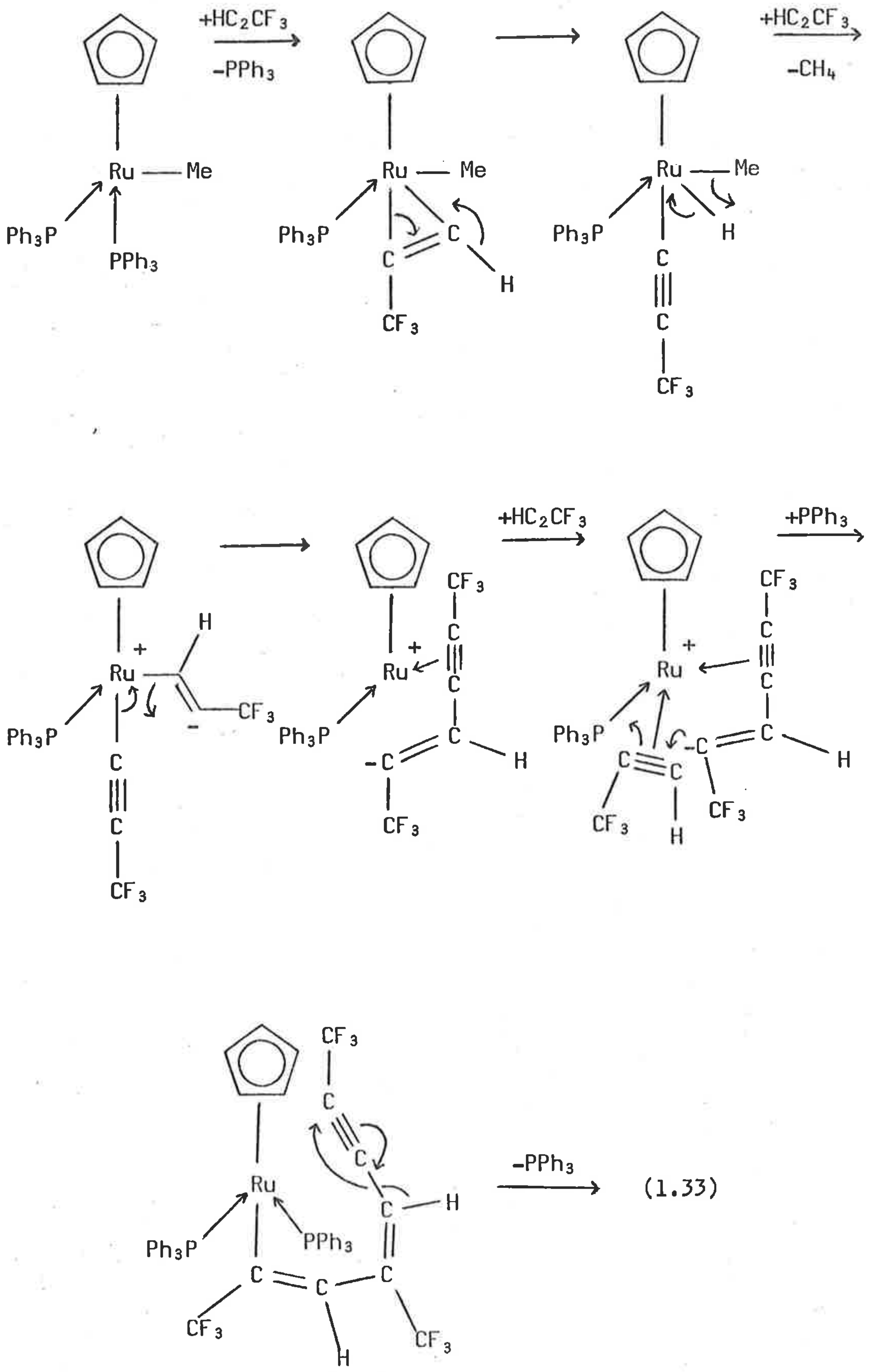
Reaction of 3,3,3-trifluoropropyne with $RuMe(PPh_3)_2(\eta-C_5H_5)$ affords the unusual cumulene derivative (1.33) (a tris-insertion product) which has been structurally characterised. This 1,4,5-η^3-hexa-1,3,4,5,tetraen-1-yl group is a new type of alkyne trimer, and has an unusually high degree of unsaturation.



(1.33)

The proposed mechanism for the formation of (1.33) is shown in Scheme 1.VIII.

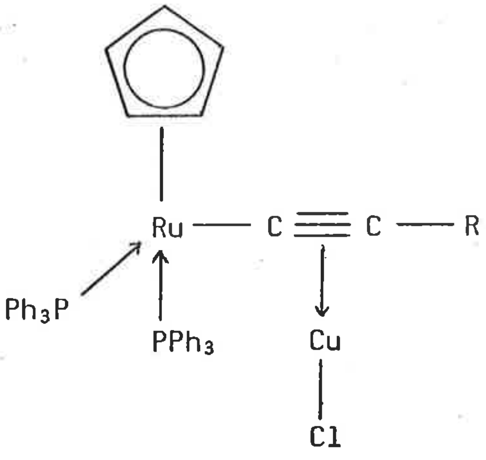
SCHEME 1.VIII



Oligomerisation of alkynes with transition-metal complexes is generally considered to proceed via initial formation of the η^2-alkynemetal complexes or alternatively, 'metallacyclopropenes '. Further reactions with alkyne molecules bearing electronegative substituents have been rationalised on the basis of the initial complex acting as a 1,3-dopole which may react with a second molecule of alkyne.[41,56] The formation of many of the compounds described above can be accounted for, on the basis of these ideas (Scheme 1.III).

Acetylide Complexes

Reactions between $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and subsituted copper(I) acetylides have given several copper-containing complexes.[57] With copper phenylacetylide, two forms of $\{Ru(C_2PhCuCl)(PPh_3)_2(\eta\text{-}C_5H_5)\}_n$ were isolated, one which was shown[58] to be the monomeric 1:1 adduct (1.34). The other form may be the dimer corresponding to that obtained from similar reactions of $FeCl(CO)_2(\eta\text{-}C_5H_5)$. A monomeric 1:1 adduct was also obtained using copper methylacetylide.

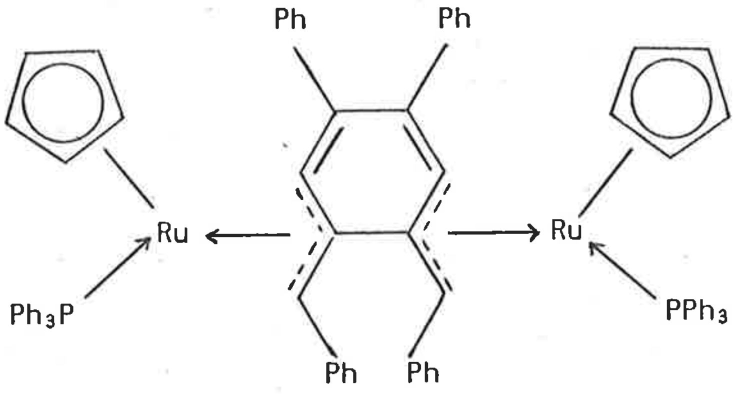


{R = Me, Ph; 1.34}

The major product obtained from copper 4-tolylphenylacetylide $CuC_2C_6H_4Me\text{-}4$ was the complex $RuCu(C_2C_6H_4Me\text{-}4)_2(PPh_3)(\eta\text{-}C_5H_5)$; a similar compound was formed with 4-fluorophenylacetylide $CuC_2C_6H_4F\text{-}4$. The crimson-red tetranuclear $\{RuCu(C_2C_6F_5)_2(PPh_3)(\eta-C_5H_5)\}_2$ was isolated from reactions with copper pentafluorophenylacetylide $CuC_2C_6F_5$.

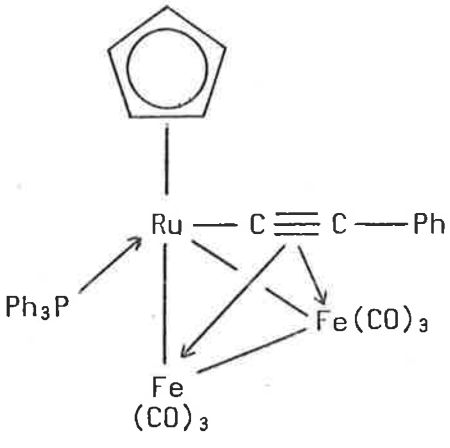
The η-complexed copper(I) chloride may be removed from $Ru(C_2PhCuCl)(PPh_3)_2(\eta-C_5H_5)$ (1.34) by addition of triphos, to form CuCl-(triphos) and the free acetylide $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$, which was recovered in approximately 60% yield. Non-chelating tertiary phosphines, such as triphenylphosphine, did not react.

The reaction between $RuCl(PPh_3)_2(\eta-C_5H_5)$ and silver phenylacetylide afforded the dark blue (1.35), the structure of which has been determined.[59]

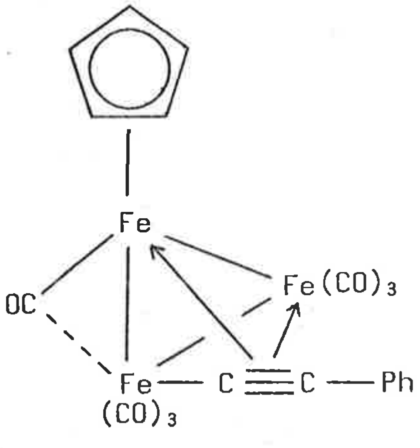


(1.35)

The reaction between $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ and $Fe_2(CO)_9$ has given the mixed metal cluster complex $(\eta-C_5H_5)RuFe_2(CO)_6(C_2Ph)(PPh_3)$ (1.36).[57,58] The iron carbonyl analogue $Fe(C_2Ph)(CO)_2(\eta-C_5H_5)$ has the structure (1.37).[60]



(1.36)



(1.37)

CHAPTER 2

CYCLOPENTADIENYL-RUTHENIUM AND -OSMIUM CHEMISTRY.

COMPLEXES CONTAINING NITRILES, ISONITRILES, TERTIARY PHOSPHINES OR PHOSPHITES FORMED BY ADDITION OR DISPLACEMENT REACTIONS

Introduction

As described in Chapter 1, the chemistry of $RuCl(PPh_3)_2(\eta-C_5H_5)$ and its derivatives is characterised by the ready displacement of one or both triphenylphosphine ligands, which reaction generally occurs under mild conditions.[12] Thus direct carbonylation of the chloride affords the monocarbonyl derivative $RuCl(CO)(PPh_3)(\eta-C_5H_5)$,[12] and the mass spectra of many of these complexes contain an abundant ion $\{Ru(PPh_3)(C_5H_5)\}^+$ centred on m/e 429.[24] In many reactions of the related hydride of alkyl complexes $RuR(PPh_3)_2(C_5H_5)$ $\{R = H$, or Me, $CH_2Ph\}$ with alkynes, new ligands are formed which chelate via an Ru-C σ bond, and a π-type bond from an unsaturated centre, as in the 1,3,4-η^3-butadienyl complexes.[41,42] Chelation occurs by displacement of a tertiary phosphine ligand. There is no evidence for dissociation of $RuCl(PPh_3)_2(\eta-C_5H_5)$ in solution, however, and we have previously interpreted these terms of the relative σ-donor and π-acceptor powers of the various ligands present, together with the pronounced steric effect of the bulky tertiary phosphine ligands.

Much of the chemistry of the $RuCl(PPh_3)_2(\eta-C_5H_5)$ has centred around reactions of the Ru-Cl bond, resulting in replacement of Cl either by other anions, or by neutral ligands, L, to give cationic complexes of the type $\{RuL(PPh_3)_2(\eta-C_5H_5)\}^+$.[12] Stable cations containing the two tertiary phosphine ligands together with a third donor ligand, such as carbon monoxide or acetonitrile, could be obtained in the presence of a suitable large, non-coordinating anion, such as tetraphenylborate, tetrafluoroborate or hexafluorophosphate.[12] Descriptions of complexes containing tertiary phosphines (other than PPh_3), phosphites or arsines are limited to the $PMePh_2$, $P(OMe)_3$ and $AsPh_3$ derivatives mentioned in the initial paper,[12] and the synthesis and internal metallation of the $P(OPh)_3$ complex.[15]

This chapter considers a variety of other cationic complexes obtained from nitriles, isonitriles, tertiary phosphines or phosphites, with some observations on the relation between ease of addition and replacement of ligands in the formation of these cations. We have noted previously that other tertiary phosphine ligands can replace triphenylphosphine in thermal reactions. It was also of interest to look at related complexes containing bidentate phosphines. Herein we describe the synthesis and some reactions of complexes containing bis(diphenylphosphino)methane {dppm, $CH_2(PPh_2)_2$} and 1,2-bis(diphenylphosphino)ethane {dppe, $Ph_2P(CH_2)_2PPh_2$}. Our improved synthesis of $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$ has made this complex readily available,[13] and we have briefly examined some ligand exchange and addition reactions of this complex.

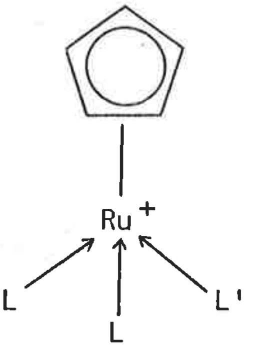
Some chemistry of related iron complexes, $FeX(L_2)(\eta\text{-}C_5H_5)$ {L = $P(OPh)_3$; L_2 = $Me_2P(CH_2)_2PMe_2$, dppe, or (-)-2,3-*O*-isopropylidene-2,3dihydroxy-1,4-bis(diphenylphosphino)butane} and their cationic derivatives, has been reported.[7,61,62] (For Fe-$P(OPh)_3$ complexes see[7,61]; for Fe-L_2 complexes see[62].)

Reaction with Nitriles

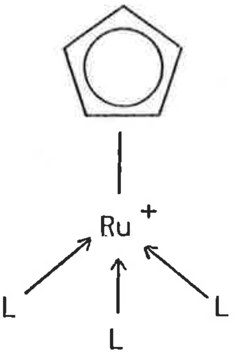
Dissolution of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ in acetonitrile affords $\{Ru(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)\}^+$ directly, and this cation may be isolated in high yield in the form of its salts with large anions.[12] Off-white needles of $\{Os(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)\}BPh_4$ (2.1) were obtained likewise from the reaction between $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$ and $NaBPh_4$ in acetonitrile. Other nitriles behave similarly, although for convenience we have preferred to use methanol as solvent for these reactions. In general, reactions between equimolar amounts of chloride and the appropriate nitrile, carried out in refluxing methanol in the presence of ammonium hexafluorophosphate, afforded good yields of the corresponding cationic nitrile complexes. In no case did we isolate a complex in which a molecule of triphenylphosphine had been displaced, even in reactions using a large excess of the nitrile.

A list of the compounds formed is shown in Diagram 2.I.

Diagram 2.I

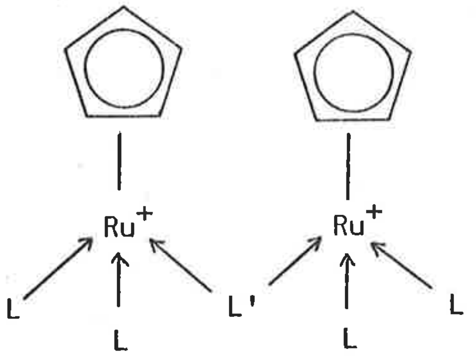


	M	L	L'
(2.1)	Os	PPh_3	MeCN
(2.2)	Ru	PPh_3	$ClCH_2CN$
(2.3)	Ru	PPh_3	$CH_2{=}CHCN$
(2.4)	Ru	PPh_3	$CH_2{=}CClCN$
(2.5)	Ru	PPh_3	PhCN
(2.6)	Ru	PPh_3	C_6F_5CN
(2.7)	Ru	PPh_3	$CH_2(CN)_2$
(2.8)	Ru	PPh_3	EtO_2CCH_2CN
(2.10)	Ru	PPh_3	$C_6H_4(CN)_2$-1,2
(2.11)	Ru	PPh_3	$C_6F_4(CN)_2$-1,2
(2.14)	Ru	PPh_3	$NH_2C_6H_4CN$-1,4
(2.15)	Ru	PPh_3	CF_3CN
(2.22)	Ru	PPh_3	*t*-BuNC
(2.23)	Ru	PPh_3	$C_6H_{11}NC$
(2.24)	Ru	PPh_3	4-$MeC_6H_4SO_2CH_2NC$
(2.26)	Ru	*t*-BuNC	PPh_3
(2.27)	Ru	PPh_3	HNC
(2.28)	Ru	PPh_3	MeNC
(2.29)	Ru	PPh_3	EtNC
(2.30)	Ru	PPh_3	$P(OMe)_3$
(2.34)	Ru	PPh_3	PMe_3
(2.35)	Ru	PPh_3	$PMePh_2$

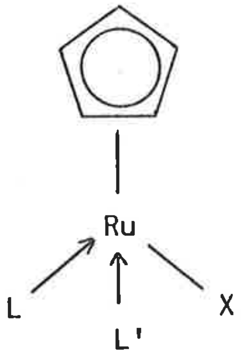


	M	L
(2.33)	Ru	$P(OMe)_3$

Diagram 2.I (cont.)

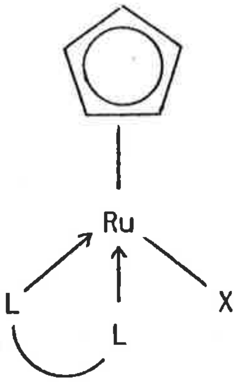


	M	L	L'
(2.9)	Ru	PPh_3	$NC(CH_2)_2CN$
(2.12)	Ru	PPh_3	NCC_6H_4CN-1,3
(2.13)	Ru	PPh_3	NCC_6F_4CN-1,4
(2.48)	Os	PPh_3	$Ph_2P(CH_2)_2PPh_2$
(2.49)	Ru	PPh_3	$Ph_2PC{\equiv}CPPh_2$

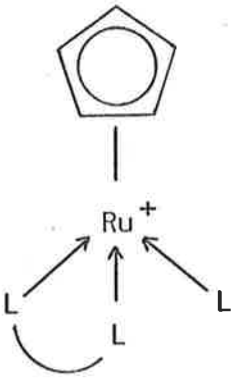


	M	X	L	L'
(2.18)	Ru	Cl	PPh_3	*t*-BuNC
(2.19)	Ru	Cl	PPh_3	$C_6H_{11}NC$
(2.20)	Ru	Cl	PPh_3	4-$MeC_6H_4SO_2CH_2NC$
(2.21)	Ru	Cl	PPh_3	4-$MeOC_6H_4NC$
(2.25)	Ru	Cl	*t*-BuNC	*t*-BuNC
(2.31)	Ru	Cl	PPh_3	$P(OMe)_3$
(2.32)	Ru	Cl	$P(OMe)_3$	$P(OMe)_3$
(2.42)	Os	Br	PPh_3	$P(OMe)_3$
(2.43)	Os	Br	PPh_3	$P(OPh)_3$
(2.44)	Os	Br	$P(OMe)_3$	$P(OMe)_3$
(2.45)	Os	Br	$P(OPh)_3$	$P(OPh)_3$

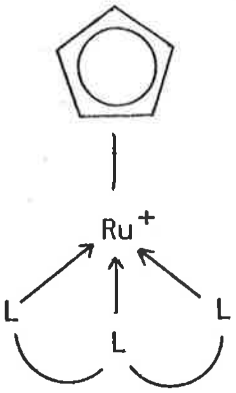
Diagram 2.1 (cont.)



	M	X	L_2
(2.36)	Ru	Cl	$CH_2(PPh_2)_2$
(2.37)	Ru	Cl	$Ph_2P(CH_2)_2PPh_2$
(2.46)	Os	Br	$CH_2(PPh_2)_2$
(2.47)	Os	Br	$Ph_2P(CH_2)_2PPh_2$



	M	L	L_2
(2.38)	Ru	PPh_3	$CH_2(PPh_2)_2$
(2.39)	Ru	PPh_3	$Ph_2P(CH_2)_2PPh_2$
(2.40)	Ru	MeCN	$CH_2(PPh_2)_2$
(2.41)	Ru	MeCN	$Ph_2P(CH_2)_2PPh_2$



	M	L_3
(2.50)	Ru	$MeC(CH_2PPh_2)_3$
(2.51)	Ru	$EtC(CH_2PPh_2)_3$

The chloroacetonitrile complex $\{Ru(NCCH_2Cl)(PPh_3)_2(\eta-C_5H_5)\}PF_6$ (2.2) was obtained as a lime-green crystalline solid, which could be recrystallized readily from dichloromethane/diethyl ether mixtures. Most of the other nitrile derivatives were similar. They were characterised by analysis and from their spectroscopic properties, including the $\nu(CN)$ band in their infrared spectra, and the characteristic sharp singlet for the C_5H_5 protons in their ^1H n.m.r. spectra. In the case of (2.2), for example, $\nu(CN)$ occurs at 2278 cm^{-1}, compared to 2240 cm^{-1} for the free ligand, and this shift confirmed the presence of the N-bonded nitriles. Similarly, the yellow acrylonitrile (2.3) and 2-chloroacrylonitrile (2.4) complexes had $\nu(CN)$ bands at 2265 and 2216 cm^{-1}, respectively, compared with bands in the spectra of the free ligands at 2240 and 2243 cm^{-1}. Unfortunately, the $\nu(C{=}C)$ bands in these complexes were obscured by aromatic absorptions, but it is likely that the ligands are N-bonded, rather than as an η^2-alkene.

Several aromatic nitriles afforded cationic complexes similar to those described above. Benzonitrile gave the yellow salt (2.5), while the pentafluoro analogue (2.6) was obtained with C_6F_5CN. Both complexes showed strong $\nu(CN)$ absorptions (at 2232 and 2230 cm^{-1}, respectively), and in the ^{19}F n.m.r. spectrum of (2.6), the characteristic 2:1:2 intensity pattern of resonances for a C_6F_5 group was observed. The small change in chemical shift of the *ortho* fluorines from the value found in the free ligand agrees with the small change in $\nu(CN)$ also found. This spectrum is discussed further below.

The complex (2.7) obtained from malonitrile contains only one $Ru(PPh_3)_2(\eta-C_5H_5)$ group, and no evidence was obtained for the formation of a dication even when excess of the ruthenium chloro complex was used. Conductivity measurements confirmed that complex (2.7) is a 1:1 electrolyte.63 A similar complex (2.8) was obtained from ethyl cyanoacetate as the benzene solvate.

A binuclear complex (2.9) was formed with succinonitrile, the formulation being confirmed by analytical, spectroscopic and conductometric methods. The ^{1}H n.m.r. spectrum contained Ph, C_5H_5 and CH_2 resonances of the appropriate relative intensities, and in solution the complex behaved as a 1:2 electrolyte. The ^{13}C n.m.r. spectrum showed only a single resonance for the methylene groups at 15.7 ppm, indicating equivalent carbons, and thus confirming the binuclear formulation.

This difference in complexing behaviour of the homologous dinitriles in (2.7) and (2.9) can be ascribed to the lower steric hindrance between the two metal-containing groups resulting from the extra CH_2 group in the ligand in (2.9).

Various phthalodinitriles were examined, and as expected, the 1,2-isomers of $C_6H_4(CN)_2$ and $C_6F_4(CN)_2$ formed only the mononuclear complexes (2.10) and (2.11). Both 1,3-$C_6H_4(CN)_2$ and 1,4-$C_6F_4(CN)_2$ afforded binuclear complexes, (2.12) and (2.13) respectively, the two bulky $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$ moieties being able to bond to the linear CN groups without any appreciable steric interaction in these cases.

In the ^{19}F n.m.r. spectra, the chemical shifts of the fluorinated nitrile complexes can be compared with those of the free ligands (Table 2.I).

Table 2.I ^{19}F chemical shifts (ppm upfield from $CFCl_3$)

Compound	Fluorine	Free ligand*	Complex	Δ
C_6F_5CN	F2,6	132.2	132.8	0.6
	F3,5	158.9	159.25	0.35
	F4	143.1	142.5	-0.6
1,2-$C_6F_4(CN)_2$	F3 F6	127.9	126.35 127.5	-1.55 -0.4
	F4 F5	143.5	141.2 142.1	-2.3 -1.4
1,4-$C_6F_4(CN)_2$		130.6	132.0	1.4

*From Bruce, M.I., *J. Chem. Soc. A*, 1968, 1459.

The resonances of the *ortho* and *meta* fluorines in the C_6F_5CN complex are shifted upfield by a small amount, while that of the *para* fluorine moves downfield by 0.6 ppm. In the symmetrical 1,4-$C_6F_4(CN)_2$ derivative, the fluorines shift upfield by 1.4 ppm or about twice that of the mono-substituted C_6F_5CN complex. The most interesting spectra were obtained with the 1,2-$(CN)_2C_6F_4$ complex, where the asymmetry resulting from coordination of only one of the CN groups results in a small but definite separation of the A and A^1, and X and X^1 resonances. The separation is not large enough for first-order spectra to be obtained. The centres of gravity of each of the two signals is shifted downfield by 1.0 or 1.8 ppm from the corresponding resonances in the free ligand, i.e. in the opposite direction from the other shifts found. The changes are too small for any definite conclusions to be drawn concerning the effect of coordination on the ^{19}F chemical shifts.

4-Aminobenzonitrile also gives a cationic complex (2.14), which we believe contains the ruthenium moiety attached to the cyano group for the following reasons: (i) the $\nu(CN)$ bands of the complex, and of the free ligand, are found at 2230 and 2210 cm^{-1}, respectively, with $\Delta\nu(CN)$ somewhat larger than that found for benzonitrile in complex (2.5); (ii) the $\nu(NH)$ bands of the ligand are essentially unaltered on complex formation; (iii) the chemical shift of the C_5H_5 protons in (2.14) is close to that found in (2.5) (δ 4.51 as against 4.58).

Reaction with Trifluoroacetonitrile

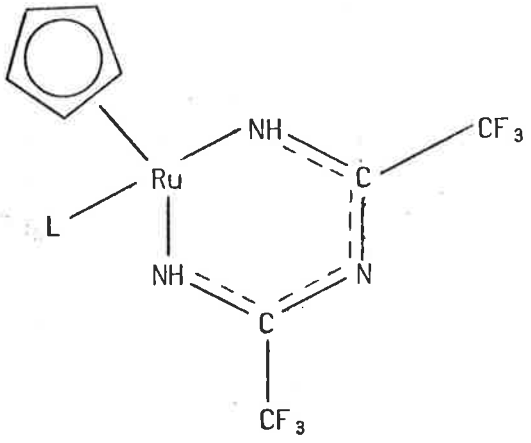
The reaction between trifluoroacetonitrile and $RuCl(PPh_3)_2(\eta-C_5H_5)$ takes a somewhat different course. On passing a stream of the gas through a suspension of the chloride, in the presence of NH_4PF_6, a red-orange solution formed, and chromatography afforded two products which were removed from the column using light petroleum/diethyl ether and acetone, respectively. The latter fraction was identified spectroscopically as the cationic complex $\{Ru(NCCF_3)(PPh_3)_2(\eta-C_5H_5)\}PF_6$ (2.15), the minor product of this reaction. Crystals from the former fraction are red-orange in colour, and an infrared spectrum showed no bands due to a hexafluorophosphate anion. Analysis was consistent with the formulation $Ru\{(NCCF_3)_2N\}(PPh_3)(\eta\text{-}C_5H_5)$, and in the mass spectrum, a molecular ion cluster centred on *m/e* 635 showed that an extra two hydrogen atoms had been incorporated into the molecule. A band in the infrared spectrum at 3351 cm^{-1} confirms the presence of an NH group. The ^{19}F n.m.r. spectrum contained one sharp singlet at 87.5 ppm downfield from perfluorobenzene. The ^{13}C n.m.r. spectrum indicated the complex to be uncharged, containing a single triphenylphosphine molecule (see Chapter 5). Two quartets at 154.1 ppm and 117.8 ppm, are assigned to the C=N and CF_3 carbons, respectively.

Previous studies of the reactions of trifluoroacetonitrile with transition metal substrates have been reported by King,[64] who reacted it with $FeMe(CO)_2(\eta\text{-}C_5H_5)$, by Kemmitt[65] who described the reaction with $Pt(PPh_3)_4$, and more recently by Green[66] who has examined several reactions in detail and fully characterised the King product by X-ray crystallography. These studies have shown a tendency for the trifluoroacetonitrile to dimerise, forming a five-membered chelate ring. Compounds containing a six-membered chelate ring are formed in the reactions of trifluoroacetonitrile with $Pt(PPh_3)_4$ and with $Ir(\eta\text{-}C_3H_5)(CO)(PPh_3)_2$, and in our case, the same type of product has been formed. The iridium complex, $Ir\{NH{=}C(CF_3)N{=}C(CF_3)NH\}(CO)(PPh_3)_2$, exhibits two singlet resonances in the ^{19}F n.m.r. spectrum, indicating an asymmetric *cis*-configuration, whereas our product exhibits one single resonance, indicating a symmetrical arrangement of ligands about the ruthenium atom.

The formation of (2.16) in the reaction of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ with CF_3CN is difficult to explain. Kemmitt *et al*[65] have attributed the source of additional nitrogen atom in the chelate ring of the platinum complex

$\overline{\mathrm{Pt\{N{=}C(CF_3)N{=}C(CF_3)NH}}\mathrm{\}(PPh_3)_2}$ to the *in situ* hydrolytic degradation of CF_3CN by traces of water present in the reaction mixture. A similar assumption may account for the formation of (2.16), and this supposition is supported by the lack of reaction when tetrahydrofuran was used in place of methanol. The presence of the strongly electronegative CF_3 group undoubtedly results in the markedly different behaviour exhibited by this nitrile, the C≡N bond being similar to a C≡C bond in its behaviour. During reaction, addition of two protons to the metallocyclic system occurs, presumably originating from the solvent.

Substitution of the triphenylphosphine by trimethyl phosphite afforded the complex $\overline{\mathrm{Ru\{NH{=}C(CF_3)N{=}C(CF_3)NH}}\mathrm{\}\{P(OMe)_3\}(\eta\text{-}C_5H_5)}$, for which structure (2.17) was determined by a single-crystal *X*-ray diffraction study.[67]



(2.16, L = PPh_3)

(2.17, L = $P(OMe)_3$)

The *X*-ray analysis (Table 2.II) establishes that the 'molecule' (2.17) (the unit cell contains two crystallographically different molecules) has the overall configuration shown in Figure 2.I. The central feature of the molecule (the $\overline{\mathrm{Ru{-}N{-}C{-}N{-}C{-}N}}$ ring, together with the C atoms of the two CF_3 groups) is substantially planar, and the ruthenium atom forms approximately tetrahedral bonds if the C_5H_5 is considered to occupy one site. Interest centres on the geometry of the $\overline{\mathrm{Ru{-}N,1{-}C,1{-}N,2{-}C,2{-}N,3}}$ ring; the planarity of the ring leads to extensive delocalisation. The ring is symmetrical through Ru-N,2.

Table 2.II[*]

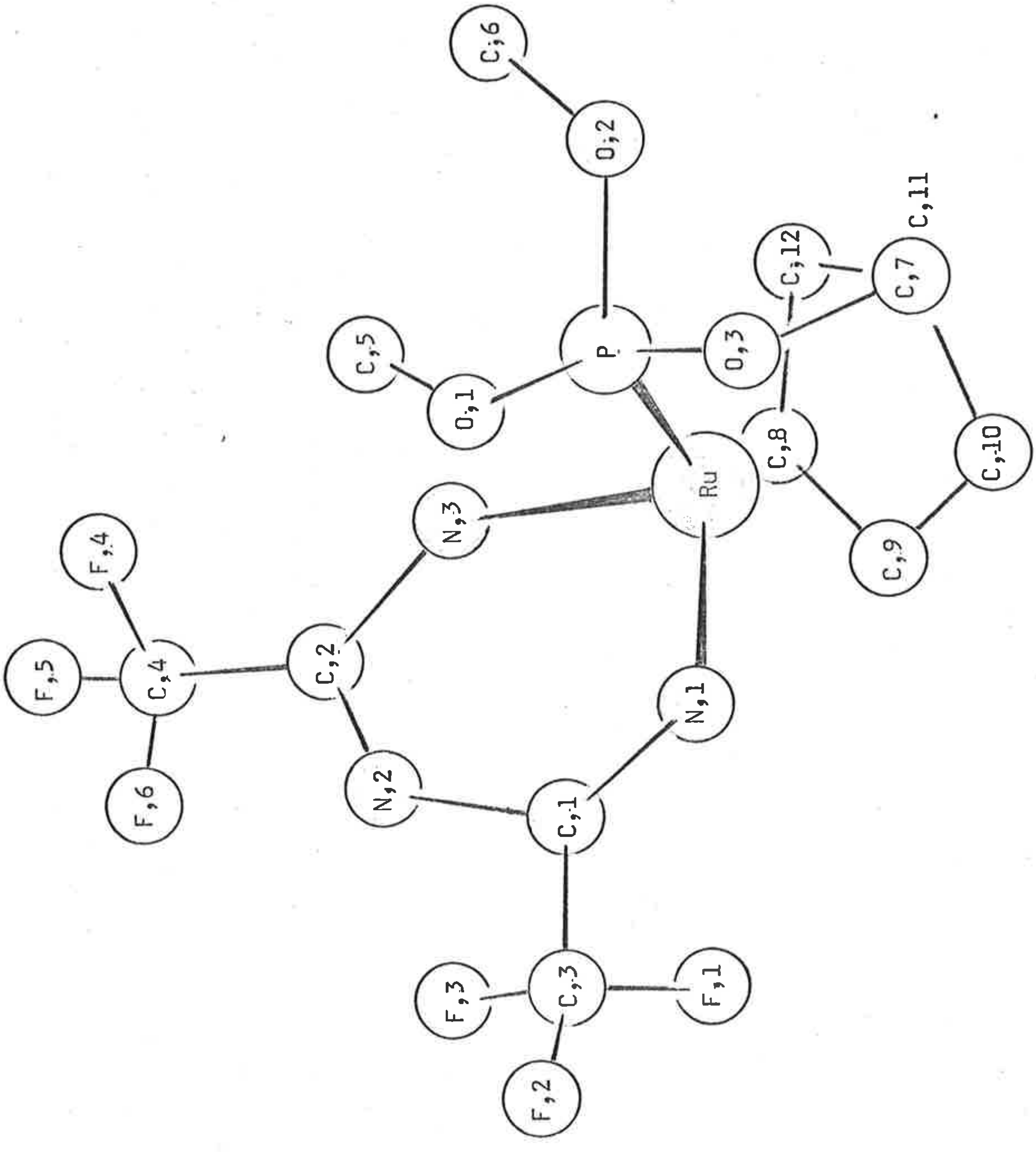
Interatomic distances (Å) and bond angles (°)

	Molecule 1	Molecule 2
Distances		
Ru-Cp	2.153-2.273	2.159-2.248
Ru-P	2.229(1)	2.219(2)
P-O,1	1.573(5)	1.605(5)
P-O,2	1.570(5)	1.587(6)
P-O,3	1.618(5)	1.582(5)
O,1-C,5	1.470(7)	1.432(12)
O,2-C,6	1.457(9)	1.489(13)
O,3-C,7	1.419(10)	1.392(9)
Ru-N,1	2.078(4)	2.070(5)
N,1-C,1	1.276(7)	1.294(8)
C,1-N,2	1.345(9)	1.320(6)
N,2-C,2	1.331(7)	1.362(6)
C,2-N,3	1.295(6)	1.286(8)
N,3-Ru	2.089(5)	2.075(4)
C,1-C,3	1.514(8)	1.519(11)
C,3-F,1	1.314(10)	1.280(7)
C,3-F,2	1.322(8)	1.302(10)
C,3-F,3	1.303(8)	1.281(9)
C,2-C,4	1.510(9)	1.535(7)
C,4-F,4	1.319(8)	1.297(10)
C,4-F,5	1.299(8)	1.320(10)
C,4-F,6	1.324(7)	1.275(10)
Angles		
P-O,1-C,5	123.7(4)	129.5(9)
P-O,2-C,5	121.0(4)	120.6(5)
P-O,3-C,7	121.2(4)	127.8(6)
P-Ru-N,1	87.1(2)	90.3(2)
P-Ru-N,3	89.8(1)	91.2(1)
N,1-Ru-N,3	83.6(2)	84.4(2)
Ru-N,1-C,1	128.1(4)	127.1(4)
N,1-C,1-N,2	130.7(5)	131.4(6)
C,1-N,2-C,2	119.5(5)	119.5(5)
N,2-C,2-N,3	130.6(6)	130.5(4)
C,2-N,3-Ru	127.3(4)	127.2(3)
N,1-C,1-C,3	118.1(6)	117.4(5)
C,1-C,3-F,1	113.5(6)	113.5(6)
C,3-C,1-N,2	111.1(5)	111.2(5)
N,2-C,2-C,4	110.9(5)	110.4(6)
C,2-C,4-F,4	113.6(5)	112.9(6)
C,4-C,2-N,3	118.4(5)	119.1(5)

---

[*] *Data by P. Woodward*

Figure 2.I


C;6
O;2
C,11
C,12
C,7
C,5
P
O,3
O,1
C,8
C,10
Ru
N,3
C,9
F,4
F,5
C,4
C,2
N,1
F,6
N,2
C,1
F,3
C,3
F,1
F,2

The two sets of C-N bonds are different because of their different chemical environments, and while the lengths of C,1-N,2 and N,2-C,2 lie close to the range expected in heterocyclic rings,[68] bonds N,1-C,1 and C,2-N,3 are especially short. It is also noteworthy that the C-CF_3 bonds are shorter than single bonds (Table 2.II), that the C-F mean bond length is 1.303 Å compared with a mean for many fluorocarbons of 1.333(5) Å[69] (though the shortening of the bond length may be apparent rather than real because of the high thermal amplitudes of the fluorine atoms). Several compounds have now been examined in which an abnormally short bond occurs in a metallocyclic system between an electronegative element attached to the metal and an adjacent carbon atom.[70]

Reactions affording Isonitrile Complexes

Generally, isocyanides RNC {R = Bu^t, Cy, $CH_2SO_2C_6H_4Me$-4, anisyl} react with $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$[71] in refluxing inert solvents according to equation (2.I):

$$RuCl(PPh_3)_2(\eta\text{-}C_5H_5) + RNC \longrightarrow RuCl(CNR)(PPh_3)(\eta\text{-}C_5H_5) + PPh_3 \qquad (2.I)$$

The chloro complexes $RuCl(CNR)(PPh_3)(\eta\text{-}C_5H_5)$ {R = Bu^t (2.18), Cy (2.19), $CH_2SO_2C_6H_4Me$-4 (2.20) and C_6H_4OMe-4 (2.21)} were obtained as yellow to orange crystalline solids. In the presence of ammonium hexafluorophosphate in methanol, the reaction takes a different course, with replacement of chloride by the isocyanide ligand in the methanol cation (equation 2.II):

$$\{Ru(MeOH)(PPh_3)_2(\eta\text{-}C_5H_5)\}^+ + RNC \longrightarrow \{Ru(CNR)(PPh_3)_2(\eta\text{-}C_5H_5)\}^+ + Cl^- \qquad (2.II)$$

The cationic derivatives $\{Ru(CNR)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ {R = Bu^t (2.22), Cy (2.23), and $CH_2SO_2C_6H_4Me$-4 (2.24)} so obtained were generally lighter in colour, and both series of compounds were stable in air. The complexes were characterised by elemental analyses, and by the usual spectroscopic techniques. For example, the infrared spectra include sharp ν(CN) bands in the 2000-2200 cm^{-1} region, with broad ν(PF) bands also present for the hexafluorophosphates. The expected resonances for the CMe_3 protons {in (2.18) and (2.22)} the CH_2 and Me groups {in (2.20) and (2.24)}, and the OMe group in (2.21), are observed; the cyclohexyl protons give rise to broad resonances between δ1.1-1.8. The chlorides give well defined mass spectra, and the parent ions fragment by loss of Cl, RNC and PPh_3 groups. The metal-bonded carbons were not detected in the ^{13}C n.m.r. spectra, except in the neutral chloro complex $RuCl(CNBu^t)(PPh_3)(\eta-C_5H_5)$ (2.18), where a low intensity doublet was observed at 156.6 ppm. However, to observe this signal, a concentrated solution in $CDCl_3$ (*c.* 1 *M*) and an extended accumulation time were required.

Only with Bu^t under forcing conditions (180°/12 h), was evidence obtained for replacement of the second PPh_3 ligand. The complex $RuCl(CNBu^t)_2(\eta-C_5H_5)$ (2.25) was obtained as a very unstable white solid. Complex (2.25) was readily identified spectroscopically, although no satisfactory analyses were obtained. Neither the infrared and n.m.r. spectra contained any bands characteristic of aromatic groups, confirming the absence of PPh_3; the relative intensities of the sharp CMe_3 and C_5H_5 resonances (18:5) showed that there were two Bu^tNC ligands present.

A cationic complex containing two Bu^tNC ligands could not be formed directly from the chloride and excess ligand, but further reaction of complex (2.18) with Bu^tNC in the presence of NH_4PF_6 gave $\{Ru(CNBu^t)_2(PPh_3)(\eta-C_5H_5)\}PF_6$ (2.26). The identity of this derivative was confirmed by the ^{1}H n.m.r. spectrum which contained signals of the correct relative intensities for the three types of protons present.

An alternative and well-known route to isocyanide complexes is by alkylation of the corresponding cyano complexes. In rare instances, protonation has afforded complexes containing the hydrogen isocyanide

(HNC) ligand stabilised by complexation to the metal.[72]

We have reacted $Ru(CN)(PPh_3)_2(\eta\text{-}C_5H_5)$[16] with hexafluorophosphoric acid, and with trialkyloxonium hexafluorophosphates, to give the pale green $\{Ru(CNR)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ {R = H (2.27), Me (2.28), and Et (2.29)}.[71] These complexes have been identified by elemental analysis, and by characteristic spectral features. In the infrared, sharp ν(CN) bands at *c.* 2025 cm^{-1} {for (2.27)}, and *c.* 2150 cm^{-1} {for (2.28) and (2.29)} showed the presence of the isonitrile ligands, while the n.m.r. spectra contained the appropriate resonances for the Me or Et groups in (2.28) and (2.29), respectively. The metal-bonded carbons were not detected in the ^{13}C n.m.r. spectra, even with extended accumulation times. Conductivity measurements showed that (2.24) and (2.28) behaved as 1:1 electrolytes.

Reactions with Tertiary Phosphines and Phosphites

Replacement of chloride in $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ by trimethyl phosphite in the presence of sodium tetraphenylborate or ammonium hexafluorophosphate occurred readily to give the salts $[Ru\{P(OMe)_3\}(PPh_3)_2(\eta\text{-}C_5H_5)]X$ (2.30a; X = BPh_4) or (2.30b; X = PF_6), respectively. The ^1H n.m.r. spectrum of the cation exhibits a characteristic doublet in the methoxy region at δ 3.17, but no coupling of the phosphite ^{31}P nucleus to the cyclopentadienyl protons was observed. In the absence of NH_4PF_6, under mild conditions (refluxing cyclohexane), one triphenylphosphine was displaced by the phosphite affording $RuCl\{P(OMe)_3\}(PPh_3)(\eta\text{-}C_5H_5)$ (2.31). In this case, the ^1H n.m.r. spectrum contained signals for the OMe and C_5H_5 protons both of which showed coupling to the phosphite ^{31}P nucleus.

A high yield of $RuCl\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (2.32) was obtained from the reaction between $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and $P(OMe)_3$ in refluxing decalin for one hour. Previously, this complex was isolated in only 3% yield from a reaction between hydrated ruthenium trichloride and $P(OMe)_3$ followed by addition of cyclopentadiene.[12] The present method allows this complex to be obtained in amounts sufficient for further study. This result prompted us to repeat the initial reaction which gave complex (2.30) using a considerable excess of trimethyl phosphite. Under similar conditions, the fully substituted complex $[Ru\{P(OMe)_3\}_3(\eta\text{-}C_5H_5)]PF_6$ (2.33) was then obtained as cream crystals. This compound can also be prepared by reacting $RuCl\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ with trimethyl phosphite in the presence of ammonium hexafluorophosphate. In this case, the ^1H n.m.r. spectrum contained signals for the OMe and C_5H_5 protons, both of which showed coupling to the two ^{31}P nuclei.

Replacement of chloride in $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ by trimethylphosphine in the presence of ammonium hexafluorophosphate gave the salt $\{Ru(PMe_3)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (2.34). The ^1H n.m.r. spectrum of the cation exhibits the characteristic doublet in the methyl region at δ 1.37, but no coupling of the trimethylphosphine ^{31}P nucleus to the cyclopentadienyl protons was observed.

A similar reaction with diphenylmethylphosphine gives the salt $\{Ru(PMePh_2)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (2.35). This complex was characterised by n.m.r. spectroscopy.[73]

The two triphenylphosphine ligands in $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ were readily displaced on heating the complex with an equivalent amount of the chelating bis-tertiary phosphines, $CH_2(PPh_2)_2$ {dppm} or $Ph_2P(CH_2)_2PPh_2$ {dppe}, in benzene. The products, $RuCl(dppm)(\eta\text{-}C_5H_5)$ (2.36) and $RuCl(dppe)(\eta\text{-}C_5H_5)$ (2.37) were obtained as dark-red and orange crystalline solids, respectively. Both complexes were readily characterised by analysis and spectroscopy, the ^1H n.m.r. spectra being most useful in this respect (see below). In both cases, product yields were 75-80%, and these reactions are superior to ones involving cyclopentadiene or thallium cyclopentadienide and the corresponding ruthenium (II) chloro complexes.

These chelating bis-tertiary phosphines afforded directly the salts $\{Ru(PPh_3)(dppm)(\eta\text{-}C_5H_5)\}PF_6$ (2.38) and $\{Ru(PPh_3)(dppe)(\eta\text{-}C_5H_5)\}PF_6$ (2.39), respectively, when heated with $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and ammonium hexafluorophosphate in methanol. The latter complex was also obtained from $RuCl(dppe)(\eta\text{-}C_5H_5)$, triphenylphosphine and NH_4PF_6. In these complexes, the dppm or dppe ligands chelate one metal atom, and displace one of the triphenylphosphine ligands. In no case were we able to obtain any evidence for the formation of a complex of the type $\{Ru(PPh_3)_2(dppe)(\eta\text{-}C_5H_5)\}^+$ in which the dppe ligand would be monodentate.

Reactions of complexes (2.36) or (2.37) with sodium tetraphenylborate in acetonitrile afforded the cationic complexes $\{Ru(MeCN)(L_2)(\eta\text{-}C_5H_5)\}BPh_4$ (2.40; L_2 = dppm) or (2.41; L_2 = dppe) as yellow crystals. Both complexes are entirely analogous to $\{Ru(MeCN)(PPh_3)_2(\eta\text{-}C_5H_5)\}BPh_4$ described earlier.[12]

Extension of these reactions to osmium gives evidence for considerably lower lability on the part of ligands attached to this third-row metal. For example, heating $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$ with a tertiary phosphite in decalin for short periods afforded the mono-substituted products $OsBr(PPh_3)\{P(OR)_3\}(\eta\text{-}C_5H_5)$ (2.42; R = Me) or (2.43; R = Ph). Extended heating with excess phosphite in refluxing decalin was required to form the PPh_3-free complexes $OsBr\{P(OR)_3\}_2(\eta\text{-}C_5H_5)$ (2.44; R = Me) or (2.45; R = Ph). Complexes (2.42) and (2.43), each containing one tertiary phosphine and one tertiary phosphite ligand, contained only one C_5H_5 resonance, in contrast to equimolar mixtures of $OsBrL_2(\eta\text{-}C_5H_5)$ {L = tertiary phosphine or phosphite}, which showed two C_5H_5 resonances, one for each component.

Similar reactions with the chelating bis-tertiary phosphines dppm or dppe gave the disubstituted complexes $OsBr(L_2)(\eta\text{-}C_5H_5)$ (2.46; L_2 = dppm) or (2.47; L_2 = dppe) directly. When the reaction with dppe was followed by ^1H n.m.r., an intermediate was detected after 2 h reaction time, but was converted into the product (2.47) after 6 h. The C_5H_5 resonance of the initial triphenylphosphine complex (at δ 4.32) diminished in intensity as the reaction proceeded, with a second peak at δ 4.36 growing in intensity during the initial stages of the reaction. After 6 h, both peaks had been replaced by a third, at δ 4.60, shown to be that of complex (2.47). The intermediate could not be isolated, but we suggest that it may contain monodentate dppe. All these complexes form yellow crystals, generally somewhat less soluble than the analogous ruthenium derivatives.

The reaction between $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$ and dppe in the presence of ammonium hexafluorophosphate gives a white crystalline complex, which is soluble in chloroform. Integration of appropriate peaks in the ^1H n.m.r. spectrum showed that the cation was binuclear, and the formulation $[\{Os(PPh_3)_2(\eta\text{-}C_5H_5)\}_2(dppe)](PF_6)_2$ (2.48) was confirmed by analysis and conductivity measurements.

The acetylenic bis-tertiary phosphine, $Ph_2PC{\equiv}CPPh_2$, contains a linear P-C-C-P sequence, and is unable to chelate a single metal atom; it may be termed an *exo*-bidentate ligand. Accordingly, a reaction between this phosphine, $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$, and NH_4PF_6 gave the binuclear complex $[C_2\{(Ph_2P)Ru(PPh_3)_2(\eta\text{-}C_5H_5)\}_2](PF_6)_2$ (2.49), no intermediate monoruthenium complex being detected. No ν(CC) band was found in the 1900-2000 cm^{-1} region, and the ^1H n.m.r. spectrum was consistent with the binuclear formulation. Conductivity measurements also showed that (2.49) behaved as a 1:2 electrolyte.

Reactions between $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and the tridentate tertiary phosphines $RC(CH_2PPh_2)_3$ {R = Me or Et} under fairly vigorous conditions (refluxing decalin, 30 minutes) afforded reasonable yields of the yellow complexes $[Ru\{(Ph_2PCH_2)_3CR\}(\eta\text{-}C_5H_5)]PF_6$ (2.50; R = Me) or (2.51; R = Et). Both triphenylphosphine ligands have been displaced from the starting material in these reactions. The products were identified in the usual way, their spectroscopic properties being entirely in agreement with the proposed structures.

Discussion

An extensive series of cationic complexes derived from $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$ by displacement of halide by neutral ligands {RCN, RNC, PR_3, $P(OR)_3$, dppm or dppe} has been described. The X-ray crystallographic study[30] of the complex $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ shows that the molecule has a long Ru-Cl bond (2.45 Å), which is reflected in the ready loss of Cl^- in polar solvents. The formation of these complexes occurs by facile displacement of the weakly bound methanol from the cation $\{Ru(MeOH)(PPh_3)_2(\eta\text{-}C_5H_5)\}^+$, which other workers[16] have demonstrated to exist in methanol solutions of the precursor (equation 2.III):

$$RuCl(PPh_3)_2(\eta\text{-}C_5H_5) + MeOH \rightleftarrows \{Ru(MeOH)(PPh_3)_2(\eta\text{-}C_5H_5)\}^+ + Cl^- \qquad (2.III)$$

Where the entering ligand has one donor site, displacement of one or more triphenylphosphine ligands does not occur, except in the case of complex (2.33). If the entering ligand is a potential chelating ligand, displacement of one or more triphenylphosphine ligands may occur {complexes (2.38), (2.39), (2.50) and (2.51)}; *exo*-bidentate ligands may coordinate two $M(PPh_3)_2(\eta\text{-}C_5H_5)$ moieties {complexes (2.9), (2.12), (2.13), (2.48) and (2.49)}, although the large size of the metal and associated ligands apparently prevents formation of complexes of this type in some instances {complexes (2.7), (2.10) and (2.11)}. Interestingly, we have been unable to isolate the cation $\{Ru(PPh_3)_3(\eta\text{-}C_5H_5)\}^+$ from any reactions involving excess PPh_3, and we ascribe this to the difficulty of fitting three bulky PPh_3 molecules (cone angle[32] 145°) and the cyclopentadienyl group (136°) around the central metal atom. In principle, such steric strain may be relieved by 'interleaving' the substituent groups, as found recently for the stable *trans*-$\{PtH(PPh_3)(PCy_3)_2\}^+$ cation.[74] We have succeeded in isolating analogous complexes containing one PPh_3 and the bidentate dppm or dppe ligands (cone angles at each phosphorus 121° and 125°, respectively) from similar reactions.

The steric strain induced by the presence of two bulky tertiary phosphine ligands[30] results in the facile displacement of triphenylphosphine by neutral ligands in non-polar solvents, affording uncharged complexes (equation 2.IV):

$$RuCl(PPh_3)_2(\eta\text{-}C_5H_5) + L \longrightarrow RuCl(L)(PPh_3)(\eta\text{-}C_5H_5) + PPh_3 \qquad (2.IV)$$

Where the entering ligand has only one donor site, vigorous conditions (refluxing decalin) are required to displace both triphenylphosphine ligands {complex (2.25) and (2.32)}. If the entering ligand is a potential chelating ligand, displacement of both triphenylphosphine ligands occurs under milder conditions (refluxing benzene) {complexes (2.36), (2.37), (2.46) and (2.47)}.

The direct comparison of the ruthenium and osmium complexes that we have described above demonstrates the usual reduced reactivity of complexes of third-row elements. This is most convincingly shown in the reactions with tertiary phosphites, in which the ruthenium complex $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ substitutes both triphenylphosphine ligands, while the osmium complex $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$, reacting under the same conditions, forms only the mixed derivatives $OsBr(PPh_3)\{P(OR)_3\}(\eta\text{-}C_5H_5)$ {R = Me or Ph}. Much more vigorous conditions and excess tertiary phosphite, are required to form the disubstituted complexes.

It is also interesting to note that while internal metallation of the ruthenium complex $RuCl\{P(OPh)_3\}_2(\eta\text{-}C_5H_5)$ occurs readily in refluxing decalin,[15] we have obtained no evidence for similar dehydrobromination of the osmium complex.

The mixed complexes $OsBr(PPh_3)\{P(OR)_3\}(\eta\text{-}C_5H_5)$ have a pseudotetrahedral structure, if the $\eta\text{-}C_5H_5$ ligand is considered to occupy one coordination position, and are therefore potentially able to be resolved into optical isomers. However, we have not attempted to resolve these complexes.

In a reaction leading to the formation of complex (2.47), ^{1}H n.m.r. evidence suggests the intermediacy of the monodentate dppe derivative $OsBr(PPh_3)_2(\eta^1\text{-}Ph_2PCH_2CH_2PPh_2)(\eta\text{-}C_5H_5)$.

The ruthenium complexes {except (2.2), which is lime-green, and (2.33), which is cream}, form yellow to orange crystals, soluble in the more polar solvents. The osmium complexes are generally white or pale yellow, and are considerably less soluble than the ruthenium analogues. Their other physical properties are consistent with their formulation, and appropiate spectroscopic data are listed in the experimental section.

The reaction between CF_3CN and $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ afforded low yields of cationic complex (2.15), the major product (2.16) containing a six-membered $\overline{\text{Ru-N-C-N-C-N}}$ ring. The mechanism for the formation of this complex is difficult to explain and requires further investigation.

The cationic isocyanide complexes $\{Ru(CNR)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ {R = Me (2.28) and Et (2.29)} were formed by an alternative route, the alkylation of the cyano complex $Ru(CN)(PPh_3)(\eta\text{-}C_5H_5)$. A complex presumably containing the hydrogen isocyanide (HNC) ligand was formed by protonation of the cyano complex; spectroscopic evidence does not ascertain whether isomerisation of isonitrile to nitrile has taken place. It is interesting that these complexes form light-green crystals rather than yellow.

The ^{1}H n.m.r. spectra of all complexes show sharp resonances in the region δ 5.5 - 4.0 for the $\eta\text{-}C_5H_5$ protons. Complexes containing aromatic groups on the donor ligand(s) showed broad complex resonances in the usual region (from δ 8 to *c.* 7) for the C_6H_5 protons.

Coupling between the cyclopentadienyl protons and ^{31}P atoms of the tertiary phosphite ligands is found in the spectra of $OsBr(L)\{P(OPh)_3\}(\eta\text{-}C_5H_5)$, but it was not detectable in

$OsBr(PPh_3)\{P(OMe)_3\}(\eta-C_5H_5)$. The ruthenium complex $RuCl\{P(OMe)_3\}_2(\eta-C_5H_5)$ also exhibits this coupling. Similar couplings between C_5H_5 protons and the phosphorus atom(s) in a series of complexes $\{Fe(L)(CO)(PPh_3)(\eta-C_5H_5)\}^+$ {L = CO, PPh_3, MeCN} have been reported,[5] but are not found in the corresponding ruthenium and osmium derivatives. The second and third row elements are poorer transmitters of nuclear spin-spin coupling effects than is iron.

In the spectra of the acetonitrile complexes (2.1) and (2.41), the methyl resonance exhibits a small coupling to phosphorus, of about 1 Hz.

It should be noted that this research was undertaken when there were only a few examples of carbonyl-free cyclopentadienyl-ruthenium complexes.[31] We have demonstrated above that a wide range of these compounds can be prepared from the parent complex $RuCl(PPh_3)_2(\eta-C_5H_5)$ by addition or displacement reactions involving a variety of ligands.

EXPERIMENTAL: *General experimental conditions are described in Appendix I.*

PREPARATION OF NITRILE COMPLEXES

From $RuCl(PPh_3)_2(\eta-C_5H_5)$

(A) *Chloroacetonitrile, $ClCH_2CN$.* — The complex $RuCl(PPh_3)_2(\eta-C_5H_5)$ (300 mg, 0.41 mmol) was dissolved in a mixture of $ClCH_2CN$ (20 ml) and tetrahydrofuran (30 ml). KPF_6 (400 mg, 2.17 mmol) was added, and the mixture was refluxed for 2 h. Chromatography (alumina) gave a yellow band which was eluted with dichloromethane/acetone (20:1). Crystallization from a dichloromethane/hexane mixture afforded lime-green *crystals* of $\{Ru(NCCH_2Cl)(PPh_3)_2(\eta-C_5H_5)\}PF_6$ (2.2) (95 mg, 25%), m.p. 175-180° (dec.) (Found: C, 56.9; H, 4.1; N, 1.8. $C_{43}H_{37}ClF_6NP_3Ru$ requires C, 56.6; H, 4.1; N, 1.6%). Infrared (Nujol): $\nu(CN)$ 2278 cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.33, m, 30H, PPh_3; 4.50, s, 5H, C_5H_5; 4.40, t, 2H, CH_2.

(B) *Acrylonitrile, $CH_2=CHCN$.* — A mixture of $RuCl(PPh_3)_2(\eta-C_5H_5)$ (450 mg, 0.62 mmol) and KPF_6 (250 mg, 1.36 mmol) was heated in refluxing acrylonitrile (40 ml) for 3 h. Using chromatography (alumina), a yellow band was eluted with CH_2Cl_2/acetone (20:1). Purification by dissolving in CH_2Cl_2, and addition of hexane, afforded pure $\{Ru(NCCH=CH_2)(PPh_3)_2(\eta-C_5H_5)\}PF$ (2.3) (375 mg, 68%) as a yellow flocculent *precipitate*, m.p. 220-224° (dec.) (Found: C, 59.4; H, 4.4; N, 1.8. $C_{44}H_{38}F_6NP_3Ru$ requires C, 59.4; H, 4.3; N, 1.6%). Infrared (Nujol): $\nu(CN)$ 2265 cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.28, m, 30H, PPh_3; 5.90, m, 3H, $CH_2=CH$; 4.53, s, 5H, C_5H_5.

(C) *2-Chloroacrylonitrile, $CH_2=CClCN$.* — A mixture of $RuCl(PPh_3)_2(\eta-C_5H_5)$ (285 mg, 0.39 mmol), NH_4PF_6 (100 mg, 0.61 mmol) and 2-chloroacrylonitrile (60 mg, 0.69 mmol) was heated in refluxing methanol (30 ml) for 40 min. Removal of solvent and crystallization of the residue from dichloromethane/hexane gave fine yellow *crystals* of

$\{Ru(NCCCl{=}CH_2)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (2.4) (300 mg, 83%), m.p. 95-101° (dec.) (Found: C, 56.8; H, 4.2; Cl 4.6; N, 1.7. $C_{44}H_{37}ClF_6NP_3Ru$ requires C, 57.2; H, 4.0; Cl, 3.9; N, 1.5%). Infrared (Nujol): ν(CN) 2216 cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.31, m, 30H, PPh_3; 6.45, and 6.12, m, 2H, CH_2; 4.60, s, 5H, C_5H_5.

(*D*) *Benzonitrile, PhCN*. — A mixture of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (250 mg, 0.34 mmol), NH_4PF_6 (200 mg, 1.22 mmol) and benzonitrile (100 mg, 0.97 mmol) was heated in refluxing methanol for 1 h. Filtration, evaporation and recrystallization (dichloromethane/ether) gave yellow *crystals* of $\{Ru(NCPh)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (2.5) (245 mg, 77%), m.p. 190-200° (dec.) (Found: C, 61.1; H, 4.3; N, 1.7. $C_{48}H_{40}F_6NP_3Ru$ requires C, 61.3; H, 4.3; N, 1.5%). Infrared (Nujol): ν(CN) 2232 cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.31, m, and 7.26, m, 35H, PPh_3+Ph; 4.56, s, 5H, C_5H_5. ^{13}C n.m.r. ($CDCl_3$): δ 135.9-128.8, m, PPh_3; 132.7, 129.5, and 111.5, s, Ph; 84.2, s, C_5H_5.

(*E*) *Pentafluorobenzontirile, C_6F_5CN*. — The complex $\{Ru(NCC_6F_5)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (2.6) (160 mg, 74%) was obtained as yellow *crystals*, m.p. 168-174° (dec.), from a reaction between $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (150 mg, 0.21 mmol), NH_4PF_6 (100 mg, 0.61 mmol) and C_6F_5CN (60 mg, 0.52 mmol), carried out as described in (*D*) above (Found: C, 56.8; H, 3.5; N, 1.6. $C_{48}H_{35}F_{11}NP_3Ru$ requires C, 56.0; H, 3.4; N, 1.4%). Infrared (Nujol): ν(CN) 2230 cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.30, m, 30H, PPh_3; 4.62, s, 5H, C_5H_5. ^{19}F n.m.r. ($CDCl_3$): δ 159.3, s, F3,5, C_6F_5; 142.5, s, F4, C_6F_5; 132.8, s, F2,6, C_6F_5. Conductivity (acetone): Λ_M 90 S cm^{-2} mol^{-1}.

(*F*) *Malononitrile, $CH_2(CN)_2$*. — Fine yellow *crystals*, m.p. 180-183 (dec.), of $[NCCH_2\{CNRu(PPh_3)_2(\eta\text{-}C_5H_5)\}]PF_6$ (2.7) (210 mg, 86%) separated after heating a mixture of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.28 mmol), NH_4PF_6 (100 mg, 0.61 mmol) and malononitrile (40 mg, 0.61 mmol) in refluxing MeOH (30 ml) for 40 min, and allowing to cool to room temperature (Found: C, 58.6; H, 4.2; N, 2.9. $C_{44}H_{37}F_6N_2P_3Ru$ requires C, 58.6; H, 4.2; N, 3.1%).

Infrared (Nujol): ν(CN) 2267 cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.33, m, 30H, PPh_3; 4.56, s, 5H, C_5H_5; 3.96, m, 2H, CH_2.

(G) *Ethyl cyanoacetate, $NCCH_2CO_2Et$.* — Addition of NH_4PF_6 (300 mg, 1.84 mmol) and ethyl cyanoacetate (150 mg, 1.33 mmol) to a suspension of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (500 mg, 0.69 mmol) in methanol (40 ml), followed by heating for 2 h at reflux, gave a yellow solution. Filtration, evaporation and recrystallization from benzene gave yellow *crystals* of $\{Ru(NCCH_2CO_2Et)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6,C_6H_6$ (2.8) (460 mg, 69%), m.p. 135-137^0 (Found: C, 60.8; H, 4.8; N, 1.4. $C_{46}H_{42}F_6NO_2P_3Ru,C_6H_6$ requires C, 60.8; H, 4.7; N, 1.4%). Infrared (Nujol): ν(CN) 2267w; ν(CO) 1741m cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.36, s, 6H, C_6H_6; 7.26, m, 30H, PPh_3; 4.48, s, 5H, C_5H_5; 4.09, q, J(HH) 7.2 Hz, 2H, CH_2Me; 3.83, m, 2H, CH_2CN; 1.17, t, J(HH) 7.1 Hz, 3H, Me. ^{13}C n.m.r. ($CDCl_3$): δ 136.0-128.5, m, PPh_3; 84.0, s, C_5H_5; 62.9, s, CH_2CN; 27.2, s, CH_2Me; 13.9, s, Me. Conductivity (acetone): Λ_M 100 S cm^{-2} mol^{-1}.

(H) *Succinonitrile, $NC(CH_2)_2CN$.* — In a similar reaction to (F) above, $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.28 mmol) and succinonitrile (40 mg, 0.5 mmol) gave yellow *crystals* of $[C_2H_4\{CNRu(PPh_3)_2(\eta\text{-}C_5H_5)\}_2](PF_6)_2$ (2.9) (190 mg, 77%), m.p. 205-210^0 (dec.) (Found: C, 58.5; H, 4.3; N, 1.7. $C_{86}H_{74}F_{12}N_2P_6Ru_2$ requires C, 58.9; H, 4.2; N, 1.6%). Infrared (Nujol): ν(CN) 2264 cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.32, and 7.12, m, 60H, PPh_3; 4.46, s, 10H, C_5H_5; 2.73, m, 4H, CH_2. ^{13}C n.m.r. ($CDCl_3$): δ 136.1-128.6, m, PPh_3; 84.1, s, C_5H_5; 15.7, s, CH_2. Conductivity (acetone): Λ_M 163 S cm^{-2} mol^{-1}.

(I) *Phthalodinitrile, 1,2 -$C_6H_4(CN)_2$.* — A mixture of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (400 mg, 0.55 mmol), the dinitrile (150 mg, 1.17 mmol) and NH_4PF_6 (400 mg, 2.45 mmol) was heated for 2 h in refluxing methanol (40 ml). The solution was evaporated, and the residue chromatographed (alumina) to give a yellow band eluted with dichloromethane/acetone (4:1). Recrystallization from a dichloromethane/ether mixture gave yellow *crystals* of $[NCC_6H_4\{CNRu(PPh_3)_2(\eta\text{-}C_5H_5)\}]PF_6$ (2.10) (451 mg, 85%), m.p. 195-200° (dec.) (Found: C, 60.4; H, 4.2; N, 2.8. $C_{49}H_{39}F_6N_2P_3Ru$ requires C, 61.0; H, 4.1; N, 2.9%). Infrared (Nujol): $\nu(CN)$ 2220 cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.84, m, 4H, C_6H_4; 7.34, m, 30H, PPh_3; 4.65, s, 5H, C_5H_5.

(*J*) *Tetrafluorophthalodinitrile, 1,2-$C_6F_4(CN)_2$.* — A mixture of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (230 mg, 0.32 mmol), NH_4PF_6 (150 mg, 0.92 mmol) and tetrafluorophthalodinitrile (100 mg, 0.5 mmol) was heated in refluxing methanol (30 ml) for 1 h. Evaporating and recrystallization (dichloromethane/ether) afforded fine yellow-orange *crystals* of $[NCC_6F_4\{CNRu(PPh_3)_2(\eta\text{-}C_5H_5)\}]PF_6$ (2.11) (310 mg, 94%), m.p. 127-132° (Found: C, 56.1; H, 3.4; N, 3.2. $C_{49}H_{35}F_{10}N_2P_3Ru$ requires C, 56.75; H, 3.4; N, 2.7%). Infrared (Nujol): $\nu(CN)$ 2214 cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 142.1, and 141.2, m, F4,5, C_6F_4; 127.5, and 126.4, m, F3,6, C_6F_4. Conductivity (acetone): Λ_M 103 S cm^{-2} mol^{-1}.

(*K*) *Isophthalonitrile, 1,3-$C_6H_4(CN)_2$.* — A reaction similar to (*I*) above between $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$, NH_4PF_6 and the dinitrile, on the same scale, afforded yellow *microcrystals* of $[1,3\text{-}C_6H_4\{CNRu(PPh_3)_2(\eta\text{-}C_5H_5)\}_2](PF_6)_2$ (2.12) (371 mg, 75%), m.p. 195-200° (dec.) (Found: C, 60.1; H, 4.2; N, 1.7. $C_{90}H_{74}F_{12}N_2P_6Ru_2$ requires C, 60.0; H, 4.1; N, 1.6%). Infrared (Nujol): $\nu(CN)$ 2231 cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.90, m, 4H, C_6H_4; 7.35, m, 60H, PPh_3; 4.70, s, 5H, C_5H_5. Conductivity (acetone): Λ_M 148 S cm^{-2} mol^{-1}.

(*L*) *Tetrafluoroterephthalodinitrle, 1,4-$C_6F_4(CN)_2$.* — Addition of tetrafluoroterephthalodinitrile (100 mg, 0.5 mmol) to a warm solution of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (250 mg, 0.34 mmol) and NH_4PF_6 (150 mg, 0.92 mmol) in methanol (30 ml), followed by heating for 30 min under reflux, gave an orange precipitate. Recrystallization of this material from dichloromethane/methanol gave fine orange *crystals* of $[1,4\text{-}C_6F_4\{CNRu(PPh_3)_2(\eta\text{-}C_5H_5)\}_2](PF_6)_2$ (2.13) (270 mg, 85%), m.p. 218-

224° (Found: C, 57.3; H, 3.8; N, 1.5. $C_{90}H_{70}F_{16}N_2P_6Ru_2$ requires C, 57.7; H, 3.8; N, 1.5%). Infrared (Nujol): ν(CN) 2247 cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.33, m, 60H, PPh_3; 4.68, s, 10H, C_5H_5. ^{19}F n.m.r. ($CDCl_3$): δ 132.0, s, C_6F_4. Conductivity (acetone): Λ_M 151 S cm^{-2} mol^{-1}.

(M) 4-Aminobenzonitrile, 4-$NCC_6H_4NH_2$. — A reaction between $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (500 mg, 0.69 mmol), NH_4PF_6 (380 mg, 2.33 mmol) and 4-aminobenzonitrile (130 mg, 1.1 mmol) in refluxing methanol (40 ml), followed by chromatography (alumina), and crystallization (dichloromethane/ether) of the band eluted with dichloromethane/acetone (3:1) gave yellow *crystals* of $\{Ru(NCC_6H_4NH_2)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (2.14) (330 mg, 50%), m.p. 185-190° (dec.) (Found: C, 59.9; H, 4.3; N, 2.9. $C_{48}H_{41}F_6N_2P_3Ru$ requires C, 60.4; H, 4.3; N, 3.0%). Infrared (Nujol): ν(CN) 2230w; ν(NH) 3385m, and 3470m cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.33, m, 30H, PPh_3; 6.82, m, 4H, C_6H_4; 4.58, m, 2H, NH_2; 4.51, s, 5H, C_5H_5.

From $RuCl(L_2)(\eta\text{-}C_5H_5)$ $\{L_2$ = dppm or dppe$\}$ and Acetonitrile

(A) Sodium tetraphenyloborate (86 mg, 0.25 mmol) was added to a solution of complex (2.36) (140 mg, 0.24 mmol) in acetonitrile (25 ml), and the mixture was refluxed for 5 min. The yellow solution was filtered, concentrated to *ca.* 5 ml, and diethyl ether was added. The yellow *crystals* which formed were collected, washed with diethyl ether and dried under vacuum, to give pure $\{Ru(MeCN)(dppm)(\eta\text{-}C_5H_5)\}BPh_4$ (2.40) (91 mg, 42%), m.p. 162-163° (Found: C, 72.3; H, 5.5; P, 6.6. $C_{56}H_{50}BNP_2Ru$ requires C, 73.8; H, 5.5; P, 6.8%). Infrared (Nujol): ν(CN) 2258 cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.30, m, 40H, PPh_3+BPh_4; 4.70, s, 5H, C_5H_5; 1.30, m, 3H, MeCN.

(B) Using complex (2.37) (140 mg, 0.23 mmol), a similar reaction afforded yellow *crystals* of $\{Ru(MeCN)(dppe)(\eta\text{-}C_5H_5)\}BPh_4$ (2.41) (98 mg, 45%), m.p. 195-197° (Found: C, 72.3; H, 5.7; P, 6.5. $C_{57}H_{52}BNP_2Ru$ requires C, 73.9; H, 5.6; P, 6.7%). Infrared (Nujol): ν(CN) 2258 cm^{-1}.

^{1}H n.m.r. ($CDCl_3$): δ 7.44, and 6.98, m, 40H, PPh_3+BPh_4; 4.69, s, 5H, C_5H_5; 2.30, m, 4H, PCH_2; 1.95, m, 3H, MeCN.

From $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$ and Acetonitrile

The reaction between $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$ (83 mg, 0.096 mmol) and sodium tetraphenylborate (50 mg, 0.145 mmol) was carried out as described above for the preparation of $\{Ru(MeCN)(dppm)(\eta\text{-}C_5H_5)\}BPh_4$, and afforded off-white *needles* of $\{Os(MeCN)(PPh_3)_2(\eta\text{-}C_5H_5)\}BPh_4$ (2.1) (85 mg, 77%), m.p. 170-173° (dec.) (Found: C, 70.6; H, 5.2; N, 1.2. $C_{67}H_{58}BNOsP_2$ requires C, 70.6; H, 5.1; N, 1.2%). Infrared (Nujol): ν(CN) 2257 cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.42, m, 50H, PPh_3+BPh_4; 4.63, s, 5H, C_5H_5; 1.33, t, J(HH) 1 Hz, 3H, MeCN.

Reaction Between $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and Trifluoroacetonitrile

(i) Trifluoroacetonitrile was introduced into a mixture of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.28 mmol) and NH_4PF_6 (150 mg, 0.92 mmol) in methanol (40 ml), for 2 min, and the mixture was heated under reflux for 1 h. The reaction mixture was filtered, to recover unreacted $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (100 mg, 50%). The orange filtrate was evaporated, the residue extracted with dichloromethane (5 ml) and chromatographed (Florisil). Two fractions were eluted, an orange band with light petroleum, and a yellow band with acetone. The latter fraction, the minor product, was not isolated but identified spectroscopically as the trifluoroacetonitrile cation $\{Ru(NCCF_3)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (2.15). ^{1}H n.m.r. ($CDCl_3$): δ 7.37, m, 30H, PPh_3; 4.55, s, 5H, C_5H_5. Crystallization of the former fraction (light petroleum) gave red-orange flaky *crystals* of $\overline{Ru\{NHC(CF_3)NC(CF_3)NH}\}(PPh_3)(\eta\text{-}C_5H_5)$ (2.16), m.p. 146-147° (Found: C, 51.4; H, 3.6; N, 6.6%; *M* (mass spectrometry), 635. $C_{27}H_{22}F_6N_3PRu$ requires C, 51.4; H, 3.5; N, 6.7%; *M*, 635). Infrared (Nujol): ν(NH) 3387m, and 3371m;

ν(C=N) 1585ms, 1550m, and 1520m; ν(CF) 1260s, and 1175s cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.36, m, 15H, PPh_3; 4.24, s, 5H, C_5H_5. ^{13}C n.m.r. ($CDCl_3$): δ 154.1, q, *J*(CF) 33 Hz, $C(CF_3)$; 136.2-128.5, m, PPh_3; 117.8, q, *J*(CF) 280 Hz, CF_3; 76.6, s, C_5H_5. ^{19}F n.m.r. ($CDCl_3$): -87.5 ppm. (relative to internal C_6F_6), s, CF_3.

(ii) Trifluoroacetonitrile (197 mg, 2.07 mmol) was condensed into an ampoule containing $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (500 mg, 0.69 mmol) in methanol (40 ml). The sealed ampoule was placed in an oven at 100^0 for 24 h. The solvent was removed and the residue chromatographed (alumina). An orange band was eluted with diethyl ether. Crystallization (light petroleum) then afforded red-orange flaky crystals of (2.16) (370 mg, 85%).

(iii) A mixture of (2.16) (250 mg, 0.39 mmol) and $P(OMe)_3$ (250 mg, 2.01 mmol) was heated in refluxing decalin (50 ml) for 60 min. The cooled solution was chromatographed (alumina), the decalin and excess $P(OMe)_3$ being washed out with light petroleum. A yellow band was eluted with diethyl ether. Crystallization (light petroleum) then afforded red *crystals* of $Ru\overline{\{NHC(CF_3)NC(CF_3)NH\}}\{P(OMe)_3\}(\eta\text{-}C_5H_5)$ (2.17), m.p. 105-107^0 (Found: C, 29.3; H, 3.2; N, 8.3%; *M* (mass spectrometry), 497. $C_{12}H_{16}F_6O_3N_3PRu$ requires C, 29.0; H, 3.3; N, 8.5%; *M*, 497). Infrared (Nujol): ν(NH) 3355w, and 3290w; ν(CN) 1586m, and 1546m; ν(CF) 1274s, and 1125s; ν(PO) 1125s; ν(C_5H_5) 833w cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 4.52, d, *J*(HP) 1.2 Hz, 5H, C_5H_5; 3.53, d, *J*(HP) 11.5 Hz, 9H, $P(OMe)_3$. ^{13}C n.m.r. ($CDCl_3$): δ 154.7, q, *J*(CF) 33 Hz, N=C; 117.9, q, *J*(CF) 281 Hz, CF_3; 77.4, d, *J*(CP) 4 Hz, C_5H_5; 51.1, d, *J*(CP) 4 Hz, $P(OMe)_3$.

PREPARATION OF ISONITRILE COMPLEXES

From $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$

(A) t-*Butyl isocyanide*, Bu^tNC. — (i) A suspension of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (250 mg, 0.34 mmol) and Bu^tNC (60 mg, 0.72 mmol) was heated in refluxing decalin (40 ml) for 5 h. The cooled solution was chromatographed (alumina), the decalin and excess *t*-butyl isocyanide being washed out with light petroleum. A yellow band was eluted with diethyl ether/dichloromethane (20:1). Crystallization (light petroleum) then afforded orange *crystals* of $RuCl(CNBu^t)(PPh_3)(\eta\text{-}C_5H_5)$ (2.18) (168 mg, 89%), m.p. 172-174° (Found: C, 61.5; H, 5.4; N, 2.6%; *M* (mass spectrometry), 547. $C_{28}H_{29}ClNPRu$ requires C, 61.5; H, 5.3; N, 2.6%; *M*, 547). Infrared (Nujol): $\nu(CN)$ 2108, 2071 cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.56, and 7.36, m, 15H, PPh_3; 4.53, s, 5H, C_5H_5; 1.17, s, 9H, CMe_3. ^{13}C n.m.r. ($CDCl_3$): δ 156.6, d, *J*(CP) 24Hz, CN; 137.3-128.1, m, PPh_3; 81.6, d, *J*(CP) 2 Hz, C_5H_5; 56.1, s, CMe_3; 31.0, s, CMe_3.

(ii) A mixture of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.28 mmol), NH_4PF_6 (100 mg, 0.61 mmol) and Bu^tNC (60 mg, 0.72 mmol) was heated in refluxing MeOH (45 ml) for 20 min. Evaporation and recrystallization of the residue from chloroform/diethyl ether afforded pale yellow *crystals* of $\{Ru(CNBu^t)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (2.22) (205 mg, 80%), m.p. 222-224° (dec.) (Found: C, 59.3; H, 4.8; N, 1.6. $C_{46}H_{44}F_6NP_3Ru$ requires C, 60.1; H, 4.8; N, 1.5%). Infrared (Nujol): $\nu(CN)$ 2136 cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.38, 7.26, 7.20, and 7.06, m, 30H, PPh_3; 4.68, s, 5H, C_5H_5; 1.36, s, 9H, CMe_3. ^{13}C n.m.r. ($CDCl_3$): δ 136.2-128.6, m, PPh_3; 87.8, s, C_5H_5; 59.0, t, *J*(CP) 3 Hz, CMe_3; 30.4, s, CMe_3.

(iii) A sealed ampoule containing $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (250 mg, 0.34 mmol) and Bu^tNC (120 mg, 1.4 mmol) in petroleum spirit (100-120°, 5 ml) was heated at 180° for 12 h. The brown residue was extracted with diethyl ether (3 x 20 ml) and combined with the petroleum spirit fraction. Evaporation, followed by trituration of the residue with light petroleum, afforded a white *precipitate* which was tentatively identified as $RuCl(CNBu^t)_2(\eta-C_5H_5)$ (2.25) from its n.m.r. spectra. ^1H n.m.r. ($CDCl_3$): δ 4.73, s, 5H, C_5H_5; 1.10, s, 18H, CMe_3. ^{13}C n.m.r. ($CDCl_3$): δ 83.9, s, C_5H_5; 56.4, s, CMe_3; 30.7, s, CMe_3.

(iv) The complex $RuCl(CNBu^t)(PPh_3)(\eta-C_5H_5)$ (140 mg, 0.26 mmol) NH_4PF_6 (100 mg, 0.61 mmol) and Bu^tNC (60 mg, 0.72 mmol) were heated in refluxing methanol (40 ml) for 15 min. Evaporation and recrystallization (chloroform/light petroleum) gave pale yellow *crystals* of $\{Ru(CNBu^t)_2(PPh_3)(\eta-C_5H_5)\}PF_6$ (2.26) (175 mg, 92%), m.p. 212-215^0 (dec.) (Found: C, 52.8; H, 5.1; N, 3.8. $C_{33}H_{38}F_6N_2P_2Ru$ requires C, 53.6; H, 5.2; N, 3.8%). Infrared (Nujol): ν(CN) 2172, and 2140 cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.45, m, 15H, PPh_3; 4.97, s, 5H, C_5H_5; 1.21, s, 18H, CMe_3. ^{13}C n.m.r. ($CDCl_3$): δ 136.2-129.0, m, PPh_3; 85.8, s, C_5H_5; 52.2, s, CMe_3; 30.4, s, CMe_3.

(*B*) *Cyclohexyl isocyanide, CyNC*. — (i) A suspension of $RuCl(PPh_3)_2(\eta-C_5H_5)$ (312 mg, 0.43 mmol) and cyclohexyl isocyanide (47 mg, 0.43 mmol) was heated in refluxing decalin (40 ml) for 1 h. The cooled solution was chromatographed (alumina), washing out the decalin with light petroleum. A yellow band was eluted with diethyl ether/dichloromethane (20:1); evaporation and recrystallization (diethyl ether/light petroleum) afforded orange *crystals* of $RuCl(CNCy)(PPh_3)(\eta-C_5H_5)$ (2.19) (192 mg, 78%), m.p. 147-148^0 (Found: C, 62.7; H, 5.5; N, 2.5%; *M* (mass spectrometry), 573. $C_{30}H_{31}NPClRu$ requires C, 62.9; H, 5.5; N, 2.4%; *M* 573). Infrared (Nujol): ν(CN) 2130s, and 2116s cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.56, and 7.35, m, 30H, PPh_3; 4.53, s, 5H, C_5H_5; 1.8-1.1, m, 11H, Cy. ^{13}C n.m.r. ($CDCl_3$): δ 137.2-128.1, m, PPh_3; 81.6, d, *J*(CP) 2 Hz, C_5H_5; 54.7, s, C1, Cy; 33.3, m, C2,6, Cy; 25.1, s, C4, Cy; 23.2, s, C3,5, Cy.

(ii) A mixture of $RuCl(CNCy)(PPh_3)(\eta-C_5H_5)$ (150 mg, 0.26 mmol), NH_4PF_6

(100 mg, 0.61 mmol) and PPh_3 (100 mg, 0.38 mmol) was heated in refluxing MeOH (40 ml) for 30 min. Evaporation and recrystallization (chloroform/light petroleum) gave pale yellow *crystals* of $\{Ru(CNCy)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (2.23) (230 mg, 93%), m.p. 242-243^0 (Found: C, 59.9; H, 4.8; N, 1.4. $C_{48}H_{46}F_6NP_3Ru$ requires C, 61.0; H, 4.9; N, 1.5%). Infrared (Nujol): ν(CN) 2143m, ν(PF) 840vs cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.57, and 7.27, m, 30H, PPh_3; 4.68, s, 5H, C_5H_5; 1.8-1.1, m, 11H, Cy. ^{13}C n.m.r. ($CDCl_3$): δ 136.1-128.6, m, PPh_3; 87.7, s, C_5H_5; 56.1, s, C1, Cy; 32.9, s, C2,6, Cy; 24.9, s, C4, Cy; 23.6, s, C3,5, Cy.

(C) *4-Toluenesulphonylmethyl isocyanide tosmic , 4-MeC$_6$H$_4$SO$_2$CH$_2$NC.* — (i) A suspension of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (363 mg, 0.5 mmol) and tosmic (98 mg, 0.5 mmol) was heated in refluxing cyclohexane (40 ml) for 40 min. The yellow-orange precipitate that formed was collected, washed with warm light petroleum (2 x 30 ml), and recrystallized (diethyl ether/light petroleum) to give orange *crystals* of $RuCl(CNCH_2SO_2C_6H_4Me\text{-}4)(PPh_3)(\eta\text{-}C_5H_5)$ (2.20) (305 mg, 95%), m.p. 186-187^0 (Found: C, 57.9; H, 4.4; N, 2.1%; *M* (mass spectrometry), 659. $C_{32}H_{29}ClNO_2PRuS$ requires C, 58.3; H, 4.4; N, 2.1%; *M*, 659). Infrared (Nujol): ν(CN) 2028m (br); ν(SO) 1138m cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.86, 7.75, 7.52, 7.39, and 7.35, 19H, PPh_3+C_6H_4; 4.69, s, 5H, C_5H_5; 4.37, m, 2H, CH_2; 2.45, s, CH_2.

(ii) A mixture of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.28 mmol), NH_4PF_6 (100 mg, 0.61 mmol) and tosmic (100 mg, 0.51 mmol) in refluxing methanol (35 ml) for 40 min readily afforded a light yellow *precipitate*, which was purified using a chloroform/diethyl ether mixture to give $\{Ru(CNCH_2SO_2C_6H_4Me\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (2.24) (230 mg, 80%), m.p. 207-212^0 (dec.) (Found: C, 57.3; H, 4.4; N, 1.5. $C_{50}H_{44}F_6NO_2P_3RuS$ requires C, 58.2; H, 4.3; N, 1.4%). Infrared (Nujol): ν(CN) 2115s, and 2047m; ν(PF) 834s cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.80, 7.69, and 7.26, m, 34H, PPh_3+C_6H_4; 5.04, m, 2H, CH_2; 4.78, s, 5H, C_5H_5; 2.45, s, 3H, Me. ^{13}C n.m.r. ($CDCl_3$):

δ 146.5, and 137.4, s, C_6H_4; 135.6-128.8, m, PPh_3; 89.0, s, C_5H_5; 64.7, s, CH_2; 21.9, s, Me. Conductivity (acetone): Λ_M 138 S cm^{-2} mol^{-1}.

(*D*) *4-Methoxyphenyl isocyanide, 4-MeOC$_6$H$_4$NC.* — A mixture of $RuCl(PPh_3)_2(\eta-C_5H_5)$ (363 mg, 0.5 mmol) and 4-$MeOC_6H_4NC$ (47 mg, 0.43 mmol) was heated in refluxing cyclohexane (40 ml) for 40 min affording a yellow-orange precipitate, which was recrystallized (dichloromethane/light petroleum) to give orange *crystals* of $RuCl(CNC_6H_4OMe\text{-}4)(PPh_3)(\eta-C_5H_5)$ (2.21) (275 mg, 92%), m.p. 198-199° (Found: C, 62.2; H, 4.5; N, 2.3%; *M* (mass spectrometry), 597. $C_{31}H_{27}ClNOPRu$ requires C, 62.4; H, 4.6; N, 2.3%; *M*, 597). Infrared (Nujol): ν(CN) 2068m (br); ν(CO) 1242m cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.60, and 7.36, m, 15H, PPh_3; 6.67, s, 4H, C_6H_4; 4.68, s, 5H, C_5H_5; 3.75, s, 3H, OMe. ^{13}C n.m.r. ($CDCl_3$): δ 136.7-126.9, m, PPh_3; 158.4, 126.9, 123.8, and 114.4, s, C_6H_4; 82.8, d, *J*(CP) 2 Hz, C_5H_5; 55.6, s, OMe.

From Ru(CN)(PPh$_3$)$_2$(η-C$_5$H$_5$)

(A) *With HPF$_6$,OEt$_2$* — A solution of $Ru(CN)(PPh_3)_2(\eta-C_5H_5)$ (150 mg, 0.21 mmol) and HPF_6,OEt_2 (110 mg, 0.5 mmol) in dichloromethane (40 ml) was stirred for 30 min at 25°. Evaporation gave a light green oil, which was triturated several times with hot diethyl ether. Crystallization of the residue (dichloromethane/diethyl ether) gave light green *crystals* of $\{Ru(CNH)(PPh_3)_2(\eta-C_5H_5)\}PF_6$ (2.27) (120 mg, 67%), m.p. 186-189° (dec.) (Found: C, 57.7; H, 4.3; N, 1.6. $C_{42}H_{36}F_6NP_3Ru$ requires C, 58.5; H, 4.2; N, 1.6%). Infrared (Nujol): ν(CN) 2024w; ν(PF) 834s cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.24, m, 30H, PPh_3; 4.63, s, 5H, C_5H_5. ^{13}C n.m.r. ($CDCl_3$): δ 136.0-128.5, m, PPh_3; 87.5, s, C_5H_5.

(B) *With {Me$_3$O}PF$_6$* — The reaction between $Ru(CN)(PPh_3)_2(\eta-C_5H_5)$ (494 mg, 0.69 mmol) and $\{Me_3O\}PF_6$ (142 mg, 0.69 mmol) was carried out in a similar manner to (A) above, to give light green *crystals* of $\{Ru(CNMe)(PPh_3)(\eta-C_5H_5)\}PF_6$ (2.28) (510 mg, 84%), m.p. 236-240° (Found:

C, 58.7; H, 4.7; N, 1.7; P, 10.8. $C_{43}H_{38}F_6NP_3Ru$ requires C, 58.9; H, 4.4; N, 1.6; P, 10.6%). Infrared (Nujol); ν(CN) 2162m; ν(PF) 839s cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.33, 7.27, 7.17, and 7.06, m, 30H, PPh_3; 4.69, s, 5H, C_5H_5; 3.39, t, J(HP) 1.6 Hz, 3H, Me. ^{13}C n.m.r. ($CDCl_3$): δ 136.0-128.6, m, PPh_3; 87.5, s, C_5H_5; 30.9, s, Me. Conductivity (acetone): Λ_M 144 S cm^{-2}mol^{-}

(C) *With {Et_3O}PF_6* — Similarly, Ru(CN)(PPh_3)$_2$(η-C_5H_5) (100 mg, 0.14 mmol) and {Et_3O}PF_6 (35 mg, 0.14 mmol) afforded {Ru(CNEt)(PPh_3)$_2$(η-C_5H_5)}PF_6 (2.29) (110 mg, 88%), m.p. >250° (Found: C, 59.2; H, 4.5; N, 1.6. $C_{44}H_{40}F_6NP_3Ru$ requires C, 59.3; H, 4.5; N, 1.6%). Infrared (Nujol): ν(CN) 2150s; ν(PF) 832s cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.34, 7.26, 7.18, and 7.05, m, 30H, PPh_3; 4.68, s, 5H, C_5H_5; 3.73, q, J(HH) 7.5 Hz, 3H, Me. ^{13}C n.m.r. ($CDCl_3$): δ 136.0-128.6, m, PPh_3; 87.5, s, C_5H_5; 40.7, s, CH_2; 14.8, s, Me.

COMPLEXES CONTAINING TERTIARY PHOSPHINES AND PHOSPHITES

The Phosphites

(A) *Trimethyl phosphite*, $P(OMe)_3$. — (i) The phosphite (980 mg, 7.9 mmol) was added to a suspension of $RuCl(PPh_3)_2(\eta-C_5H_5)$ (726 mg, 1 mmol) in MeOH (20 ml), and the mixture was heated for 15 min to give a yellow solution. To this was added $NaBPh_4$ (342 mg, 1 mmol) in MeOH (10 ml), whereupon a light yellow product precipitated. Recrystallization (CH_2Cl_2/MeOH) afforded fine yellow *crystals* of $[Ru(PPh_3)_2\{P(OMe)_3\}(\eta-C_5H_5)]BPh_4$ (2.30a) (910 mg, 80%), m.p. 197-199° (Found: C, 70.6; H, 5.9; P, 7.8. $C_{68}H_{64}BO_3P_3Ru$ requires C, 72.0; H, 5.7; P, 8.2%). Infrared (Nujol): ν(PO) 1040 cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.37, m, 30H, PPh_3; 7.0, m, 20H, BPh_4; 4.50, s, 5H, C_5H_5; 3.17, d, *J*(HP) 11 Hz, 9H, $P(OMe)_3$.

(ii) The yellow hexafluorophosphate salt (2.30b), m.p. 212-213° (dec.), was obtained in a similar reaction carried out in the presence of NH_4PF_6 (Found: C, 54.7; H, 4.6; F, 11.3. $C_{44}H_{44}F_6O_3P_4Ru$ requires C,55.0; H, 4.6; F, 11.9%). Infrared (Nujol): ν(PO) 1040 cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.40, m, 30H, PPh_3; 4.61, s, 5H, C_5H_5; 3.49, d, *J*(HP) 11 Hz, 9H, $P(OMe)_3$.

(iii) The complex $RuCl\{P(OMe)_3\}_2(\eta-C_5H_5)$ (100 mg, 0.22 mmol) {previously prepared from $RuCl(PPh_3)_2(\eta-C_5H_5)$ and excess $P(OMe)_3$ in decalin (see below)}, NH_4PF_6 (200 mg, 1.23 mmol) and $P(OMe)_3$ (60 mg, 0.48 mmol) were heated in refluxing tetrahydrofuran (30 ml) for 2 h, after which time the solution was almost colourless. Evaporation and recrystallization (chloroform/light petroleum) gave cream *crystals* of $[Ru\{P(OMe)_3\}_3(\eta-C_5H_5)]PF_6$ (2.33) (60 mg, 40%) (Found: C, 24.2; H, 4.8. $C_{14}H_{32}F_6O_9P_4Ru$ requires C, 24.6; H, 4.7%). Infrared (Nujol): ν(PO) 1040 cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 5.23, m, 5H, C_5H_5; 3.69, m, 27H, $P(OMe)_3$.

(iv) A suspension of $RuCl(PPh_3)_2(\eta-C_5H_5)$ (500 mg, 0.69 mmol), NH_4PF_6

(337 mg, 2.07 mmol) and $P(OMe)_3$ (1000 mg, 8.06 mmol) was heated in refluxing diglyme (50 ml) for 4 h. The solvent was removed, and the yellow oil was triturated several times with hot light petroleum. The residue was recrystallized from CH_2Cl_2/Et_2O to give cream *crystals* of complex (2.33) (190 mg, 40%), identical with the product prepared in reaction (iii) above.

(v) A mixture of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (100 mg, 0.14 mmol) and $P(OMe)_3$ (250 mg, 2.0 mmol) was heated in refluxing cyclohexane (25 ml) for 10 min. The cooled solution was chromatographed (alumina), the decalin and excess $P(OMe)_3$ being washed out with light petroleum. A yellow band was eluted with diethyl ether/dichloromethane (4:1). Crystallization (dichloromethane/light petroleum) then afforded yellow *crystals* of $RuCl(PPh_3)\{P(OMe)_3\}(\eta\text{-}C_5H_5)$ (2.31) (74 mg, 91%). ^1H n.m.r. ($CDCl_3$): δ 7.62, and 7.33, m, 15H, PPh_3; 4.49, d, $J(HP)$ 1.0 Hz, 5H, C_5H_5; 3.47, d, $J(HP)$ 11.2 Hz, 9H, $P(OMe)_3$. ^{13}C n.m.r. ($CDCl_3$): δ 138.4-127.6, m, PPh_3; 81.6, t, $J(CP)$ 3 Hz, C_5H_5; 52.2, d, $J(CP)$ 7 Hz, $P(OMe)_3$.

(vi) A mixture of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (1.0 g, 1.38 mmol) and $P(OMe)_3$ (0.5 g, 4.03 mmol) was heated in refluxing decalin (50 ml) for 60 min. The cooled solution was chromatographed (alumina), the decalin and excess $P(OMe)_3$ being washed out with light petroleum. A yellow band was eluted with diethyl ether/dichloromethane (20:1). Crystallization (light petroleum) then afforded yellow *crystals* of $RuCl\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (2.32) (520 mg, 84%), m.p. 126-129^0 (Found: C, 29.6; H, 5.1%; M (C_6H_6), 443. $C_{11}H_{23}ClO_6P_2Ru$ requires C, 29.3; H, 5.1%; M 450.5). Infrared (Nujol): ν(PO) 1040 cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 4.84, t, $J(HP)$ 1.2 Hz, C_5H_5; 3.69, t, $J(HP)^*$ 11.8 Hz, 18H, $P(OMe)_3$. ^{13}C n.m.r. ($CDCl_3$): δ 81.6, t, $J(CP)$ 3 Hz, C_5H_5; 52.2, t, $J(CP)$ 2 Hz, $P(OMe)_3$.

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*Separation of two outer peaks of A part of $A_9XX'A'_9$ system.

(vii) A mixture of $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$ (150 mg, 0.174 mmol) and $P(OMe)_3$ (90 mg, 0.72 mmol) was heated in refluxing toluene (25 ml) for 2 h. After removal of solvent, a dichloromethane extract of the residue was chromatographed (Florisil). Excess $P(OMe)_3$ was washed out with light petroleum, and a pale yellow band was eluted with dichloromethane. Crystallization form light petroleum afforded pale yellow *crystals* of pure $OsBr(PPh_3)\{P(OMe)_3\}(\eta\text{-}C_5H_5)$ (2.42) (108 mg, 86%), m.p. 172° (Found: C, 43.4; H, 4.1; Br, 11.3; P, 9.5. $C_{26}H_{29}BrO_3OsP_2$ requires C, 43.3; H, 4.0; Br, 11.1; P, 8.6%). ^1H n.m.r. ($CDCl_3$): δ 7.50, m, 15H, PPh_3; 4.65, s, 5H, C_5H_5; 3.57, d, $J(HP)$ 11 Hz, 9H, $P(OMe)_3$.

(viii) Heating a mixture of $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$ (100 mg, 0.12 mmol) and $P(OMe)_3$ (100 mg, 0.81 mmol) in refluxing decalin (30 ml) for 1.5 h was followed by chromatography (alumina). Decalin and excess $P(OMe)_3$ were washed out with light petroleum. A pale yellow band was eluted with diethyl ether/dichloromethane (4:1), from which yellow *crystals* of $OsBr\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (2.44) (50 mg, 74%), m.p. 132-135°, were obtained after evaporation and crystallization (diethyl ether/light petroleum) (Found: C, 22.8; H, 3.9%; *M* (C_6H_6), 594. $C_{11}H_{23}BrO_6OsP_2$ requires C, 22.6; H, 4.0%; *M*, 583). ^1H n.m.r. ($CDCl_3$): δ 5.03, t, $J(HP)$ 1 Hz, 5H, C_5H_5; 3.67, t, $J(HP)^*$ 11 Hz, 18H, $P(OMe)_3$.

(B) *Triphenyl phosphite*, $P(OPh)_3$. — A mixture of $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$ (150 mg, 0.174 mmol) and $P(OPh)_3$ (143 mg, 0.46 mmol) was heated in refluxing decalin (15 ml) for 15 min. The cooled solution was chromatographed (Florisil), the decalin being washed out with light petroleum. Chloroform then eluted a yellow band, shown by n.m.r. to contain two products. Crystallization from a dichloromethane/light petroleum mixture gave a mixture of large orange crystals and a yellow powder, which could be separated by a rapid extraction into toluene. The orange *crystals*

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*Separation of two outer peaks of A part of $A_9XX'A'_9$ system remaining were recrystallized from dichloromethane/light petroleum to give pure $OsBr(PPh_3)\{P(OPh)_3\}(\eta\text{-}C_5H_5)$ (2.43) (43 mg, 30%), m.p. 198° (Found: C, 54.2; Br, 8.8; P, 6.7. $C_{41}H_{35}BrO_3OsP_2$ requires C, 54.2; Br, 8.8; P, 6.8%). ^1H n.m.r. ($CDCl_3$): δ 7.92-6.72, m, 30H, PPh_3+$P(OPh)_3$; 4.43, t, J(HP) 1 Hz, 5H, C_5H_5. Addition of light petroleum to the extract afforded yellow *crystals* of $OsBr\{P(OPh)_3\}_2(\eta\text{-}C_5H_5)$ (2.45) (75 mg, 45%), m.p. 155° (Found: C, 52.1; Br, 8.4; P, 6.4. $C_{41}H_{35}BrO_6OsP_2$ requires C, 51.5; Br, 8.4; P, 6.5%). ^1H n.m.r. ($CDCl_3$): δ 7.06, m, 30H, $P(OPh)_3$; 4.2, t, J(HP) 1.5 Hz, 5H, C_5H_5.

The Phosphines

(A) *Trimethylphosphine, PMe_3.* — Trimethylphosphine (*c.* 1 mmol) (obtained by heating $\{PMe_3.AgI\}_4$ to 200°) was condensed into an ampoule containing $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (550 mg, 0.76 mmol) and NH_4PF_6 (300 mg, 1.84 mmol) in tetrahydrofuran (20 ml). The sealed ampoule was stirred at room temperature for two days and then heated at 50° for 5 min. The solvent and excess phosphine were removed and the residue extracted with benzene. Filtration, evaporation and recrystallization (dichloromethane/light petroleum) afforded yellow *crystals* of $\{Ru(PMe_3)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (2.34). ^1H n.m.r. ($CDCl_3$): δ 7.48, and 7.06, m, 30H, PPh_3; 4.73, s, 5H, C_5H_5; 1.37, d, J(HP) 9 Hz, 9H, PMe_3.

(B) *Diphenylmethylphosphine, PPh_2Me.* — A mixture of $\{Ru(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (142 mg, 0.16 mmol) and diphenylmethylphosphine (32 mg, 0.16 mmol) was heated in refluxing dichloromethane (10 ml) for 10 min. Recrystallization (dichloromethane/light petroleum) afforded yellow *crystals* of $\{Ru(PPh_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (2.35). ^1H n.m.r. ($CDCl_3$): δ 7.40, m, 40H, PPh_3; 4.63, s, 5H, C_5H_5; 1.83, t, J(HP) 7 Hz, 3H, PMe.

(C) *Bis(diphenylphosphino)methane, $CH_2(PPh_2)_2$(dppm).* — (i) A mixture of $RuCl(PPh_3)_2(\eta-C_5H_5)$ (370 mg, 0.51 mmol) and dppm (200 mg, 0.52 mmol) was heated in refluxing benzene (100 ml) for 8 h. The volume was reduced to *ca.* 15 ml and a diethyl ether/hexane mixture (4:1) was added until a light yellow precipitate formed. After filtration, further addition of hexane to the filtrate afforded dark red *crystals* of $RuCl(dppm)(\eta-C_5H_5)$ (2.36) (230 mg, 76%), m.p. 140-143^0 (dec.) (Found: C, 61.4; H, 5.0; P, 10.6%; *M* (C_6H_6), 603. $C_{30}H_{27}ClP_2Ru$ requires C, 61.4; H, 4.6; P, 10.6%; *M*, 586). ^1H n.m.r. ($CDCl_3$): δ 7.8, and 7.3, m, 20H, PPh_3; 4.70, s, 5H, C_5H_5; 2.4, m, 2H, PCH_2 (?).

(ii) A mixture of $RuCl(PPh_3)_2(\eta-C_5H_5)$ (250 mg, 0.34 mmol), NH_4PF_6 (150 mg, 0.92 mmol) and dppm (132 mg, 0.34 mmol) was heated in refluxing methanol (40 ml) for 30 min. The yellow crystalline *product* which separated was recrystallized (CH_2Cl_2/MeOH) to give pure $\{Ru(PPh_3)(dppm)(\eta-C_5H_5)\}PF_6$ (2.38) (210 mg, 62%), m.p. > 225^0 (dec.) (Found: C, 59.7; H, 4.3. $C_{48}H_{42}F_6P_4Ru$ requires C, 60.1; H, 4.4%). ^1H n.m.r. (CD_2Cl_2): δ 7.34, m, 35H, PPh_3; 4.92, s, 5H, C_5H_5; 1.54, m, 2H, PCH_2 (?). Conductivity (acetone): Λ_M 126 S $cm^{-2} mol^{-1}$.

(iii) A mixture of $OsBr(PPh_3)_2(\eta-C_5H_5)$ (100 mg, 0.12 mmol) and dppm (47 mg, 0.12 mmol) was heated in refluxing benzene (40 ml) for 4 h, after which time the solvent was evaporated, decalin (30 ml) added, and the solution heated under reflux for a further 6 h. Chromatography (Florisil) of the cooled solution, after washing out the decalin with light petroleum, and eluting with diethyl ether, afforded a light yellow fraction. Crystallization (dichloromethane/light petroleum) afforded yellow *crystals* of $OsBr(dppm)(\eta-C_5H_5),CH_2Cl_2$ (2.46) (65 mg, 78%), m.p. > 210^0 (dec.) (Found: C, 45.6; H, 3.5%; *M* (C_6H_6), 763. $C_{30}H_{27}BrOsP_2CH_2Cl_2$ requires C, 46.3; H, 3.6%; *M*, 720). ^1H n.m.r. ($CDCl_3$): δ 7.7, and 7.3, m, 20H, PPh_3; 5.30, s, 2H, CH_2Cl_2; 4.80, s, 5H, C_5H_5; 2.3, m, 2H, PCH_2.

(*D*) *1,2-Bis(diphenylphosphino)ethane*, $C_2H_4(PPh_2)_2$ (*dppe*). — (i) A reaction with dppe (215 mg, 0.54 mmol) was carried out as in (*B*) (i) above to give orange *crystals* of RuCl(dppe)(η-C_5H_5) (2.37) (245 mg, 80%), m.p. 232-234° (Found: C, 62.1; H, 5.4; P, 10.2%; *M* (C_6H_6), 617. $C_{31}H_{29}ClP_2Ru$ requires C, 62.0; H, 4.5; P, 10.3%; *M*, 600). ^{1}H n.m.r. ($CDCl_3$): δ 7.9, and 7.3, m, 20H, PPh_3; 4.55, s, 5H, C_5H_5; 2.5, m, 4H, PCH_2.

(ii) A similar reaction to (*C*) (ii) above, using dppe (137 mg, 0.34 mmol) in place of dppm, afforded a solution which was evaporated and recrystallized ($CHCl_3$/light petroleum) to give pure yellow *crystals* of {Ru(PPh_3)(dppe)(η-C_5H_5)}PF_6 (2.39) (280 mg, 82%), m.p. 160-165° (dec.) (Found: C, 60.2; H, 4.6. $C_{49}H_{44}F_6P_4Ru$ requires C, 60.5; H, 4.6%). ^{1}H n.m.r. ($CDCl_3$): δ 7.35, 6.90, and 6.73, m, 35H, PPh_3; 4.92, s, 5H, C_5H_5; 2.39, and 2.15, m, 4H, PCH_2.

(iii) A mixture of RuCl(dppe)(η-C_5H_5) (200 mg, 0.33 mmol), NH_4PF_6 (150 mg, 0.92 mmol) and PPh_3 (87 mg, 0.33 mmol) was heated in refluxing methanol (40 ml) for 2 h. Cooling overnight afforded yellow *needles* of complex (2.39) (270 mg, 80%).

(iv) A reaction with OsBr$(PPh_3)_2$(η-C_5H_5) (100 mg, 0.12 mmol) and dppe (47 mg, 0.12 mmol) was carried out as described in (*C*) (iii) above to give yellow *crystals* of OsBr(dppe)(η-C_5H_5),CH_2Cl_2 (2.47) (70 mg, 82%), m.p. > 205° (dec.) (Found: C, 46.4; H, 3.8%; *M* (C_6H_6), 703. $C_{31}H_{29}BrOsP_2CH_2Cl_2$ requires C, 46.9; H, 3.8%; *M*, 734). ^{1}H n.m.r. ($CDCl_3$): δ 7.9, and 7.3, m, 20H, PPh_3; 5.30, s, 2H, CH_2Cl_2; 4.60, s, 5H, C_5H_5; 2.5, m, 2H, PCH_2.

(v) A similar reaction was followed by ^{1}H n.m.r. spectroscopy. After 2 h, two C_5H_5 resonances at δ 4.32 (the bis-PPh_3 complex) and 4.36 (assigned to the η^1-dppe intermediate) were present, which gradually diminished in intensity, with development of a third signal at δ 4.60. After 6 h, the latter signal only was present, and workup as in (iv) afforded complex (2.47).

(vi) A mixture of $OsBr(PPh_3)_2(\eta-C_5H_5)$ (83 mg, 0.1 mmol), NH_4PF_6 (150 mg, 0.92 mmol) and dppe (39 mg, 0.1 mmol) was heated in refluxing methanol (30 ml) for 2 h. Evaporation of solvent, and crystallization of the residue ($CHCl_3$/light petroleum) afforded white *crystals* of $[\{Os(PPh_3)_2(\eta-C_5H_5)\}_2(dppe)](PF_6)_2$ (2.48) (95 mg, 85%), m.p. 161-162° (Found: C, 59.0; H, 4.3. $C_{108}H_{94}F_{12}Os_2P_8$ requires C, 57.7; H, 4.2%). ^1H n.m.r. ($CDCl_3$): δ 7.2, and 6.65, m, 80H, PPh_3; 4.65, s, 10H, C_5H_5; 2.5, m, 4H, PCH_2. Conductivity (acetone): Λ_M 171 S cm^{-2} mol^{-1}.

(E) *1,2-Bis(diphenylphosphino)acetylene,* $Ph_2PC{\equiv}CPPh_2$. — A mixture of $RuCl(PPh_3)_2(\eta-C_5H_5)$ (125 mg, 0.17 mmol), NH_4PF_6 (100 mg, 0.61 mmol) and $Ph_2PC{\equiv}CPPh_2$ (68 mg, 0.17 mmol) was heated in refluxing methanol (40 ml) for 15 min. The solvent was removed, and the residue was recrystallized ($CHCl_3$/light petroleum) to give $[C_2\{(Ph_2P)Ru(PPh_3)_2(\eta-C_5H_5)\}_2](PF_6)_2$ (2.49) as a light-yellow *solid* (161 mg, 91%), m.p. 140-144° (Found: C, 63.8; H, 4.6; P, 11.1. $C_{108}H_{90}F_{12}P_8Ru_2$ requires C, 62.8; H, 4.4; P, 12.0%). Conductivity (acetone): Λ_M 152 S cm^{-2} mol^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.32, m, 80H, PPh_3; 4.62, s, 10H, C_5H_5.

(F) *1,1,1-Tris{(diphenylphosphino)methyl}ethane,* $MeC(CH_2PPh_2)_3$. — Addition of NH_4PF_6 (150 mg, 0.92 mmol) and $MeC(CH_2PPh_2)_3$ (172 mg, 0.28 mmol) to a suspension of $RuCl(PPh_3)_2(\eta-C_5H_5)$ (200 mg, 0.28 mmol) in decalin (30 ml), followed by brief heating under reflux, gave a yellow solution. The solvent was evaporated, and the residue triturated three times with light petroleum. Crystallization from a dichloromethane/light petroleum mixture gave $[Ru\{(Ph_2PCH_2)_3CMe\}(\eta-C_5H_5)]PF_6$ (2.50) as a yellow *powder* (190 mg, 73%), m.p. 155-160° (dec.) (Found: C, 59.8; H, 5.0. $C_{46}H_{44}F_6P_4Ru$ requires C, 59.0; H, 4.7%). ^1H n.m.r. ($CDCl_3$): δ 7.15, m, 30H, PPh_3; 5.39, s, 5H, C_5H_5; 2.40, m, 6H, CH_2; 1.05, s, 3H, Me.

(G) *1,1,1-Tris{(diphenylphosphino)methyl}propane,* $EtC(CH_2PPh_2)_3$. — A mixture of $RuCl(PPh_3)_2(\eta-C_5H_5)$ (200 mg, 0.28 mmol), $EtC(CH_2PPh_2)_3$

(176 mg, 0.28 mmol) and NH_4PF_6 (100 mg, 0.61 mmol) was heated in refluxing decalin (30 ml) for 30 min. On cooling the solution overnight a yellow precipitate separated. This was recrystallized (dichloromethane/hexane) to give pale yellow *crystals* of $[Ru\{(Ph_2PCH_2)_3CEt\}(\eta\text{-}C_5H_5)]PF_6$ (2.51) (130 mg, 49%), m.p. 325-327° (dec.) (Found: C, 59.0; H, 4.8. $C_{47}H_{46}F_6P_4Ru$ requires C, 59.4; H, 4.7%). ^1H n.m.r. ($CDCl_3$): δ 7.08, m, 30H, PPh_3; 5.38, s, 5H, C_5H_5; 2.40, m, 6H, PCH_2; 2.0, m, 2H, CH_2Me; 1.21, t, 3H, Me.

Reaction of $OsBr(PPh_3)\{P(OMe)_3\}(\eta\text{-}C_5H_5)$ *with Trimethyl Phosphite*

A mixture of $OsBr(PPh_3)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ and $P(OMe)_3$ (40 mg, 0.322 mmol) was heated in refluxing decalin (15 ml) for 1 h. The cooled solution was chromatographed (Florisil), the decalin and excess $P(OMe)_3$ being washed out with light petroleum. A pale yellow band was eluted with dichloromethane/acetone (1:1). Crystallization (light petroleum) then afforded light yellow *crystals* of $OsBr\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (2.44) (25 mg, 77%).

CHAPTER 3

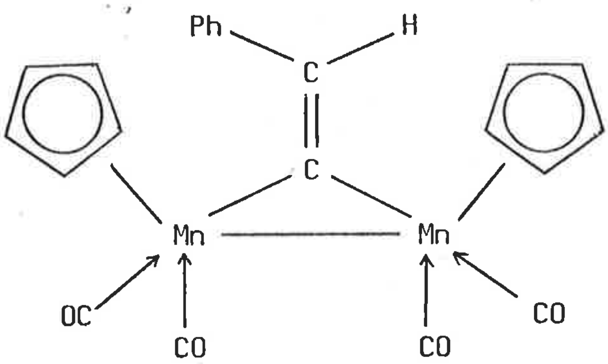
CYCLOPENTADIENYL-RUTHENIUM AND -OSMIUM CHEMISTRY. COMPLEXES CONTAINING SOME SUBSTITUTED η^1-VINYLIDENE, η^1-ACETYLIDE AND CARBENE LIGANDS

Introduction

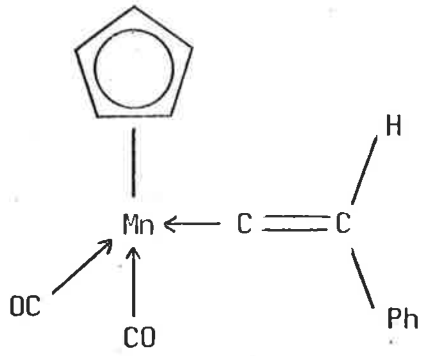
The reations between terminal acetylenes (alk-1-ynes, HC_2R) and the hydride or alkyl complexes $RuR(PPh_3)_2(\eta\text{-}C_5H_5)$ {R = H, Me or CH_2Ph} have given a variety of unusual products containing unsaturated ligands formed by oligomerisation of the alkyne (see Chapter 1). Up to three alkyne units have been incorporated in these complexes. It has been widely accepted[56] that the initial stage of reactions between alkynes and transition metal complexes is coordination of the alkyne to form an η^2-alkyne-metal complex. This then undergoes further reaction, either with a second molecule of alkyne, or with another ligand, such as CO, bonded to the metal. The ways in which these further reactions may occur are of obvious interest and importance in formulating reaction patterns for the various complexes. The reactions may be influenced by subtle changes within the coordination sphere of the metal, as evidenced by the different stereochemistries of products obtained from $C_2(CF_3)_2$ and $RuH(L)_2(\eta\text{-}C_5H_5)$ {L = CO[76] or PPh_3[41]}, and the former account suggests the possibility of a concerted ($\sigma^2s + \pi^2a$) reaction occurring with the dicarbonyl,[76] in contrast with the step wise reaction demonstrated with the triphenylphosphine complex.[41]

We have sought a route to complexes containing η^2-alkynes so that their reactions might be studied further. The pronounced tendency of the $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$ moiety to form cationic complexes by addition of a molecule of a neutral ligand, L,[31] suggested that cationic η^2-alkyne complexes might be obtained in this way. Accordingly, we have reacted the readily available complex $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$[13] with several alk-1-ynes in methanol, in the presence of a large anion (BPh_4^-, BF_4^- or PF_6^-). A deep red reaction mixture was formed, and afforded complexes containing cations with the empirical composition $\{Ru(HC_2R)(PPh_3)_2(\eta\text{-}C_5H_5)\}^+$. This chapter describes the synthesis and characterisation of these complexes as substituted η^1-vinylidene derivatives, and their ready deprotonation to η^1-ethynyl complexes.

The vinylidene ligand* may act as a terminal or bridging group. Complexes in which two metal atoms are bridged by $C{=}CR_2$ groups (and also by a metal-metal bond) include $\{Fe(CO)_4\}_2(\mu\text{-}C{=}CPh_2)$ {obtained from $Fe(CO)_5$ and $Ph_2C{=}C{=}O$},[80] the *cis* and *trans* isomers of $\{Fe(CO)(\eta\text{-}C_5H_5)\}_2(\mu\text{-}CO)\text{-}\{\mu\text{-}C{=}C(CN)_2\}$ (from $CCl_2{=}C(CN)_2$ and $\{Fe(CO)_2(\eta\text{-}C_5H_5)\}^-$),[81] and the complex $\{Mn(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C{=}CHPh)$ (3.1).[82,83,84] The manganese complex was obtained in c. 2% yield from the reaction between $Mn(CO)_2(thf)(\eta\text{-}C_5H_5)$ and phenylacetylene, and was accompanied by the complex $Mn(CO)_2(C{=}CHPh)\text{-}(\eta\text{-}C_5H_5)$ (3.2), formed in c. 7% yield.[83,85]



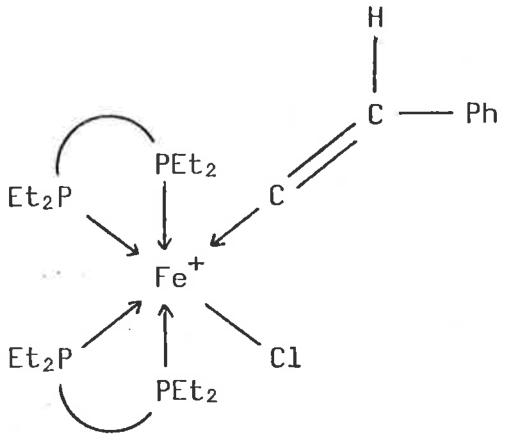
(3.1)



(3.2)

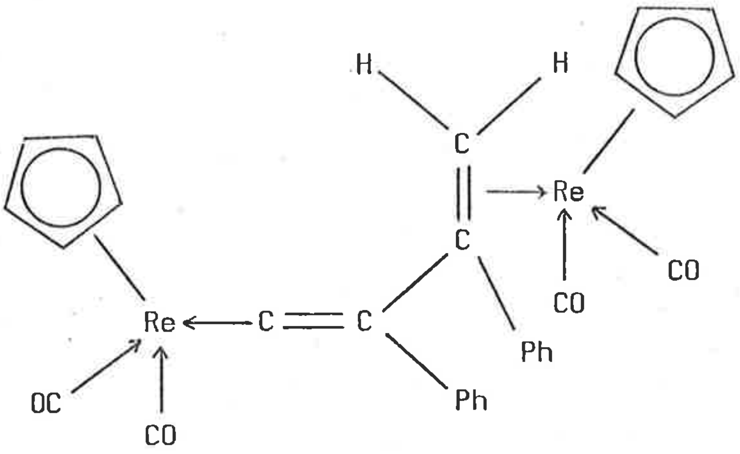
*There exists some confusion in the recent literature concerning the nomenclature of these complexes. A recent review[77] has termed $C{=}CR_2$ groups 'unsaturated carbenes' or 'alkylidenes', reserving the term 'vinylidene' for the group $C{=}C{=}CR_2$. We prefer to follow established usage, using the term 'vinylidene' for $C{=}CR_2$ ligands, e.g. $C{=}CHPh$ is phenylvinylidene. Ligands with further unsaturation, e.g. $C{=}C{=}CR_2$, are termed 'allenylidenes'. The terms 'alkylidene' should be used for the ligand $\equiv CR$, as found in $RCCo_3(CO)_9$[78] or $Ta(CR)Cl(PMe_3)_2(\eta\text{-}C_5Me_5)$,[79] for example.

The structures of all these complexes have been confirmed by X-ray analysis. Other complexes containing terminal vinylidene ligands include the rhenium analogue of (3.2),[86] and several dicyanovinylidene complexes formed from σ-1-chloro-2,2-dicyanovinyl compounds by an unusual chlorine migration induced by reaction of precursor complexes with tertiary phosphites.[81,87] The reaction between $FeCl_2(depe)_2$ {depe = $Et_2P(CH_2)_2PEt_2$} and phenylacetylene affords the cationic complex (3.3), the ^1H n.m.r. data for which closely resemble those for $\{Ru(PPh_3)_2(\eta\text{-}C_5H_5)(\eta^1\text{-}C{=}CHPh)\}^+$,[88] while the interaction of 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT) and an iron (II) porphyrin affords a bis(4-chlorophenyl)vinylidene-iron complex.[89] Related complexes containing $C{=}C{=}CPh(NMe_2)$[90] and $C{=}C{=}CBu^t_2$ ligands[91] have also been described.



(3.3)

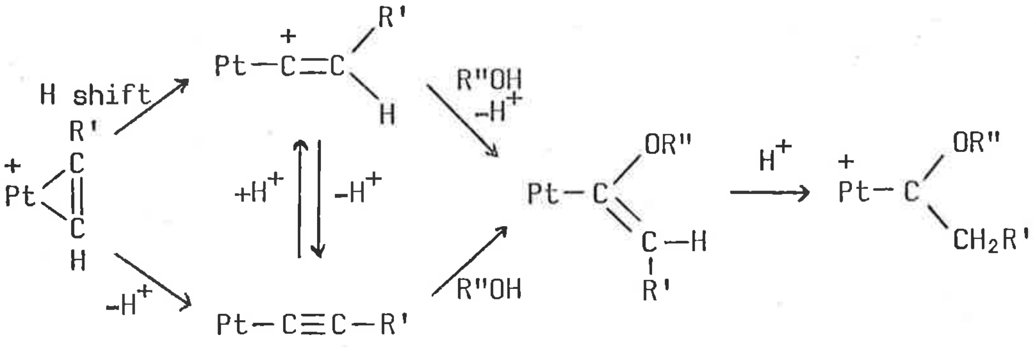
Vinylidene complexes have been implicated in several reactions. The synthesis of $(OC)_5Cr\{CCH_2C(=NCy)NCy\}$ from $(OC)_5Cr\{C(OH)Me\}$ and dicyclohexylcarbodiimide is thought to proceed through the intermediate $(OC)_5Cr(C{=}CH_2)$,[92] while intramolecular coupling of two *t*-butylvinylidene ligands has been proposed as a mechanism for the stereospecific dimerisation of *t*-butylacetylene to *trans*-1,4-di-*t*-butylbutatriene.[93] The latter reaction may be related to the formation of the unusual bridging ligand found in (3.4).[86]



(3.4)

Of more interest in connection with the present work are the extensive studies of Clark, Chisholm and coworkers[94] which implicate cationic platinum vinylidene complexes (alternatively considered to be metal-stabilized vinyl carbonium ions, MC^+=CHR, or metalloallene cations, M^+=C=CHR) as *intermediates* in:

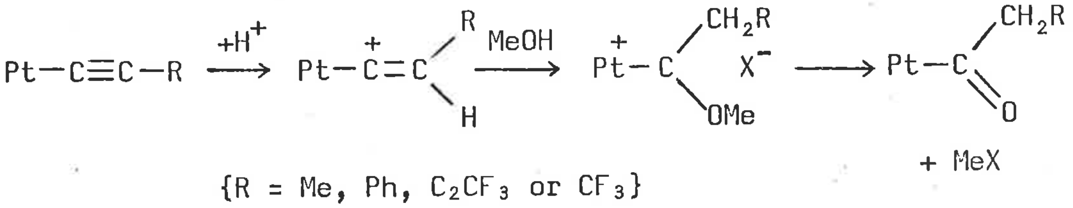
(i) certain reactions of cationic π-acetylenic-platinum(II) complexes, particularly the formation of cationic organoplatinum alkoxycarbene complexes in reactions between alk-1-ynes and *trans*-$PtRClL_2$ {L = PMe_2Ph or $AsMe_3$} in the presence of $AgPF_6$ (Scheme 3.I).



{R' = H, alkyl or Ph; R" = Me or Et}

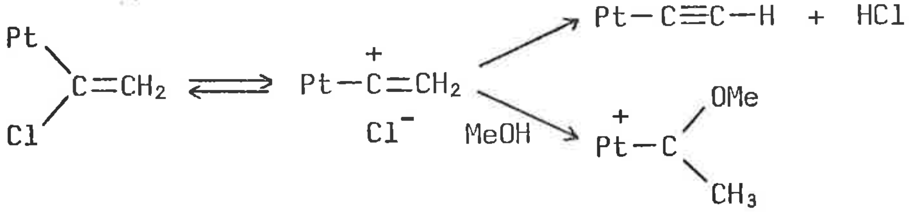
Scheme 3.I

(ii) the protonation of alkynylplatinum(II) complexes in alcohols to give instantaneously cationic alkoxycarbene complexes (which can be isolated as hexafluorophosphate salts), which with HCl or CF_3CO_2H, are slowly converted to an acyl complex as the ultimate product[95] (Scheme 3.II).



Scheme 3.II

(iii) reactions of α-chlorovinylplatinum(II) compounds, including the elimination of HCl to form the acetylide, and addition of methanol to give a methoxymethylcarbene complex, which proceed via a platinum-vinylidene complex[96] (Scheme 3.III); this interpretation is supported by the abnormally long C_α-Cl distance found in *trans*-$Pt(CCl{=}CH_2)_2(PMe_2Ph)_2$.

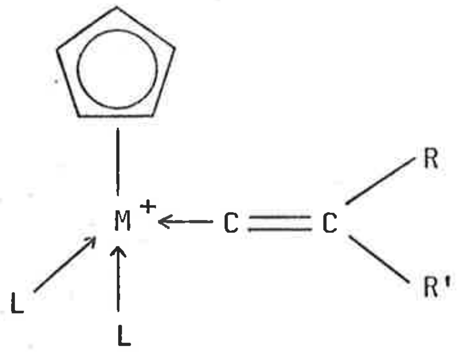


Scheme 3.III

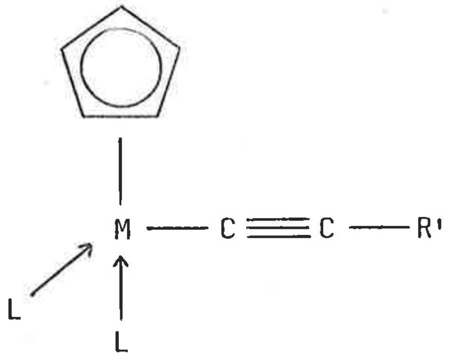
In none of the reactions studied, however, was a vinylidene-metal complex isolated or detected, the presumed intermediate being converted rapidly into the products mentioned above. The merit of the present work lies in the formation of a variety of vinylidene complexes[97] in essentially quantitative yield, free of other products.

A list of the compounds formed is shown in Diagram 3.I.

Diagram 3.1

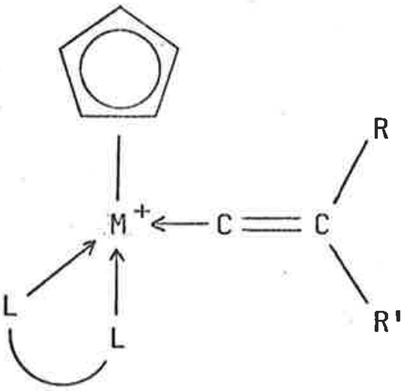


	M	L	R	R'
(3.5)	Ru	PPh$_3$	H	Ph
(3.6)	Ru	PPh$_3$	H	Me
(3.7)	Ru	PPh$_3$	H	Pr
(3.8)	Ru	PPh$_3$	H	CO$_2$Me
(3.9)	Ru	PPh$_3$	H	C$_6$H$_4$F-4
(3.10)	Ru	PPh$_3$	H	C$_6$F$_5$
(3.13)	Os	PPh$_3$	H	Ph
(3.24)	Ru	PPh$_3$	Me	Ph
(3.25)	Ru	PPh$_3$	Et	Ph
(3.26)	Ru	PPh$_3$	Me	Me
(3.27)	Ru	PPh$_3$	Me	Pr
(3.28)	Ru	PPh$_3$	Me	C$_6$F$_5$
(3.32)	Ru	P(OMe)$_3$	H	Ph
(3.33)	Ru	P(OMe)$_3$	Me	Ph

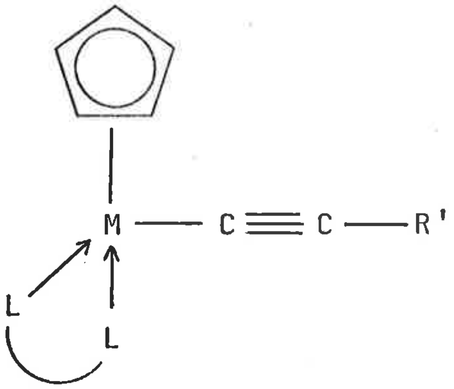


	M	L	R'
(3.14)	Ru	PPh$_3$	Ph
(3.15)	Ru	PPh$_3$	Me
(3.16)	Ru	PPh$_3$	Pr
(3.17)	Ru	PPh$_3$	CO$_2$Me
(3.18)	Ru	PPh$_3$	C$_6$H$_4$F-4
(3.19)	Ru	PPh$_3$	C$_6$F$_5$
(3.22)	Os	PPh$_3$	Ph
(3.23)	Ru	PPh$_3$	CH$_2$Br
(3.30)	Ru	P(OMe)$_3$	Ph
(3.25)	Ru	PPh$_3$	CH$_2$CHMeO(thp)

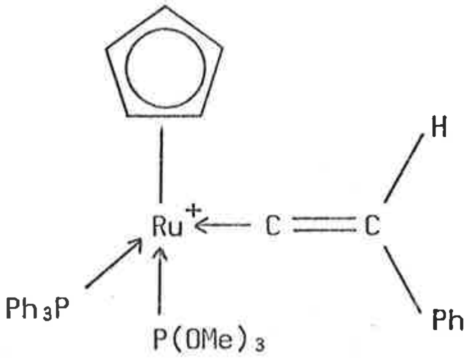
Diagram 3.I (cont.)



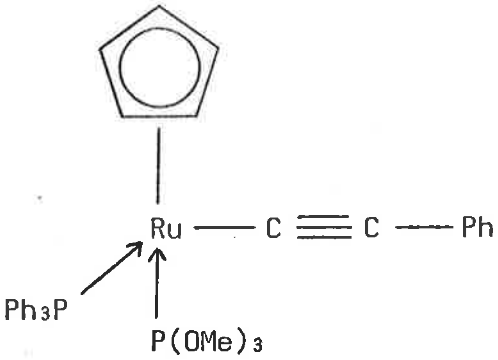
	M	L_2	R	R'
(3.11)	Ru	dppm	H	Ph
(3.12)	Ru	dppe	H	Ph



	M	L_2	R'
(3.20)	Ru	dppm	Ph
(3.21)	Ru	dppe	Ph



(3.31)



(3.29)

Monosubstituted η^1-Vinylidene Complexes

The dark red crystalline salts obtained from alk-1-ynes and $RuCl(PPh_3)_2(\eta-C_5H_5)$ in the presence of NH_4PF_6 are soluble in methanol, dichloromethane, acetone or tetrahydrofuran, and moderately soluble in benzene, but insoluble in light petroleum and diethyl ether. The infrared spectrum of the complex (3.5) derived from phenylacetylene does not contain any bands in the region 2000 - 1700 cm^{-1}, although two medium intensity bands are found at 1640 and 1622 cm^{-1}. One of these may arise from the phenyl group, since the spectrum of the corresponding propyne derivative (3.6) (see below) contains only one band in this region, assigned to a ν(CC) vibration. Strong absorptions at *c.* 840 cm^{-1} (or *c.* 1050 cm^{-1}) are characteristic of the PF_6 (or BF_4) anion. The ^1H n.m.r. spectrum of (3.5) contains the expected sharp singlet for the C_5H_5 protons, and broad multiplets in the aromatic region, which can be assigned to the PPh_3 and C_2Ph protons (see Experimental). In addition to these bands, a triplet at δ 5.40 is assigned to the single proton of the alkyne, coupled to the two ^{31}P nuclei of the tertiary phosphine ligands. We have previously noted[41] the coupling of olefinic protons with the ^{31}P nucleus in $Ru\{\overline{C(CF_3)=C(CF_3)C(CF_3)=CH(CF_3)\}}(PPh_3)(\eta-C_5H_5)$, so that this would not have been inconsistent with the anticipated η^2-alkyne formulation.

The ^{13}C n.m.r. spectrum contains several resonances, which can be assigned to the carbons of the C_5H_5 and Ph groups (see Experimental), together with a low-intensity triplet at very low field (*c.* 360 ppm). Signals in this region are usually associated with metal-bonded carbene or carbyne ligands. Thus, in $Cr(CO)_5\{CPh(OEt)\}$[98] and *trans*- $PtMe\{CMe(OMe)\}(AsMe_3)_2$,[99] the carbene carbons resonate at 351 and 321 ppm, respectively. In $MoH(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta-C_5H_5)$, the carbyne carbon resonance occurs at 346.7 ppm.[100] In contrast, η^2-alkyne carbons in $Pt(C_2Me_2)(PPh_3)_2$ and in *trans*-$\{PtMe(C_2Me_2)(PEt_2Ph)_2\}^+$ resonate at

69.5 and 112.8 ppm, respectively.[101] This result immediately suggested reformulation of complex (3.5) as the phenylvinylidene derivative, containing the C=CHPh ligand. Support for this interpretation comes from the ^{13}C n.m.r. spectra of the complexes $M(CO)_2(C{=}CHPh)(\eta\text{-}C_5H_5)$ {M = Mn[82] or Re[86]}, described during the course of this work, wherein the vinylidene carbons resonate at 379.5 and 329.5 ppm, respectively. The infrared data also support the existence of a C=C double bond in these complexes.

Related reactions occur with several alk-1-ynes and we have obtained the compounds $\{Ru(C{=}CHR)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ {R = Me (3.6), Pr (3.7), CO_2Me (3.8), C_6H_4F-4 (3.9), and C_6F_5 (3.10)} using the appropriately substituted acetylene. All these complexes form dark red crystals, which are soluble in the more polar solvents, to give more or less air-sensitive solutions. The majority of these complexes are stable for short periods (days) in air in the solid state, but it is noteworthy that the complexes derived from alkynes bearing electron-withdrawing groups are considerably less stable. For this reason, we were unable to obtain satisfactory analyses for some complexes. Their infrared spectra contain the ν(CC) band at *c.* 1650 cm^{-1}, and that of complex (3.8) contains the characteristic ν(ester CO) bands at 1727, 1263 and 1241 cm^{-1}. The ^1H n.m.r. spectra contain sharp singlets for the C_5H_5 resonances, and characteristic triplet or multiplet resonances for the =CHR proton. The vinylidene formulation is further confirmed in the case of (3.6) by the large *gem* coupling (*c.* 7 Hz) between the vinylidene proton and the methyl group. Such a coupling is entirely in accord with the presence of a group C=CHMe, but is difficult to reconcile with the alternative HC≡CMe formulation. The C*H*Me resonance in this case is a multiplet, with each line of the usual triplet being further split into a quartet by the methyl group. A similar coupling with protons in the alkyl chain of the pent-1-yne derivative was found.

The metal-bonded carbons resonate *c.* 360 ppm downfield from the TMS reference, and show a coupling of *c.* 20 Hz to the ^{31}P nuclei. The β-carbons of the vinylidene ligands resonate at *c.* 120 ppm, while other signals in the ^{13}C n.m.r. spectra are characteristic of the C_5H_5 and PPh_3 ligands.

The vinylidene complexes may also be obtained by replacement of a weak donor molecule, such as acetonitrile in the cation $\{Ru(MeCN)(PPh_3)_2(\eta\text{-}C_5H_5)\}^+$, by the alk-1-ynes. In several cases, the tetraphenylborate or tetrafluoroborate salts were also obtained by carrying out the reaction in the presence of $NaBPh_4$ or NH_4BF_4, respectively, in place of NH_4PF_6.

The previous chapter described the preparation of cyclopentadienylruthenium complexes containing the chelating bis-tertiary phosphine ligands dppm or dppe. The respective chlorides react readily with phenylacetylene, under similar conditions to those employed for the synthesis of (3.5), to give the corresponding phenylvinylidene complexes, $\{Ru(C{=}CHPh)(L_2)(\eta\text{-}C_5H_5)\}PF_6$ $\{L_2$ = dppm (3.11), or dppe (3.12)$\}$. These complexes were obtained as buff-coloured solids, which had similar spectral properties to those of complex (3.5). The osmium derivative $\{Os(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (3.13) was similarly obtained from $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$ as a light purple solid, entirely analogous to (3.5) in its properties.

Substituted η^1-Ethynyl Complexes

The vinylidene complexes are readily deprotonated on treatment with base. This reaction was originally discovered while attempting to purify complex (3.5) by column chromatography on alumina. Elution with diethyl ether afforded a bright yellow fraction, shown to contain the neutral phenylacetylide complex, $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (3.14). This compound is best obtained by addition of sodium methoxide to the cationic complex formed *in situ*, when conversion is almost quantitative. The vinylidene complex is also deprotonated, with formation of (3.14), on treatment with methyllithium, Grignard reagents, sodium borohydride, lithium aluminium hydride or sodium bicarbonate.

Complex (3.14) has been obtained on previous occasions,[57] and is characterised by a medium intensity ν(CC) band at 2068 cm^{-1} in its infrared spectrum, bands at δ 4.32 (C_5H_5) and 7.1 - 7.5 (PPh_3) in the ^1H n.m.r. spectrum, and a parent ion cluster centred on *m/e* 792 in the mass spectrum.

Other substituted acetylides, $Ru(C_2R)(PPh_3)_2(\eta\text{-}C_5H_5)$ {R = Me (3.15), Pr (3.16), CO_2Me (3.17), $C_6H_4F\text{-}4$ (3.18), or C_6F_5 (3.19)}, $Ru(C_2Ph)(L_2)(\eta\text{-}C_5H_5)$ {L = dppm (3.20), or dppe (3.21)} and $Os(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (3.22), were obtained similarly. The reaction between $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and propargyl bromide, followed by addition of sodium methoxide, afforded $Ru(C_2CH_2Br)(PPh_3)_2(\eta\text{-}C_5H_5)$ (3.23). The low yield obtained for this η^1-ethynyl complex is probably due to cyclisation of the η^1-vinylidene intermediate (see below). All form yellow crystals, the infrared spectra of which contain a sharp ν(CC) band between 2055 - 2100 cm^{-1}, which was not present in the spectra of the precursor vinylidene complexes. Their ^1H n.m.r. spectra contain the expected bands, but not the characteristic triplet or multiplet resonances arising from the vinylidene proton. The mass spectra contained parent ion clusters centred on the appropriate *m/e* values; these ions fragment by loss of an intact PPh_3 molecule, in the case of the PPh_3 complexes, or by loss of C_5H_5 and HC_2Ph when dppm or dppe is present.

Synthesis of η^1-Vinylidene Derivatives from η^1-Ethynyl Complexes

The relative stability of the cationic vinylidene complexes suggested that the neutral η^1-ethynyl derivatives might be protonated to reform the cations. Addition of HBF_4 or HPF_6 to a solution of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$

in dichloromethane resulted in an immediate change in colour from yellow to deep red. Addition of diethyl ether resulted in precipitation of a salt which was identical in all respects to complex (3.5). Similar protonation of the substituted acetylides (3.15) - (3.22) readily afforded the cationic vinylidene complexes (3.6) - (3.13). This deprotonation-protonation cycle could be repeated many times without apparent loss of complex. Addition of trifluoroacetic acid to solutions of the ethynyl derivatives also resulted in the same colour change, but no solid trifluoroacetate salts were isolated from these reactions. Formation of the vinylidene complexes was confirmed by examination of the ^{1}H n.m.r. spectra, for example, of the complex $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ dissolved in $CDCl_3$ both before and after the addition of a drop of CF_3CO_2H.

We were unable to obtain any cationic complexes from reactions between disubstituted alkynes, such as C_2Me_2, MeC_2Ph or C_2Ph_2, and $RuCl(PPh_3)_2(\eta-C_5H_5)$ in methanol or acetonitrile in the presence of NH_4PF_6. This is perhaps not surprising when the nature of the rearrangement is considered, in conjunction with the tendency of say, a methyl or a phenyl group, to migrate. Steric congestion about the ruthenium in the $Ru(PPh_3)_2(\eta-C_5H_5)$ moiety apparently makes it difficult for an alkyne to bond in the η^2 mode. However, the phenylethynyl complex reacts with trialkyloxonium salts to form the cationic complexes $\{Ru(C{=}CRPh)(PPh_3)_2(\eta-C_5H_5)\}PF_6$ {R = Me (3.24), or Et (3.25)}. These complexes form dark red crystals, similar in appearance and general physical properties to the phenylvinylidene complex (3.5). Their infrared spectra contain a ν(CC) band between 1655 - 1665 cm^{-1}, as well as the phenyl band, and the ^{1}H n.m.r. spectra contain resonances at δ c. 7.35 (PPh_3) and c. 5.15 (C_5H_5), together with a singlet at δ 1.93 {for (3.24)} or multiplets at δ 0.9 and 2.3 {for (3.25)}. Similar complexes (3.26) -

(3.28) were prepared from reactions between $\{Me_3O\}PF_6$ and $Ru(C_2R)(PPh_3)_2(\eta\text{-}C_5H_5)$ {R = Me, Pr, or C_6F_5}, and these derivatives have properties similar to those described for the alkyl(phenyl)vinylidene complexes (3.24) and (3.25). These complexes are stable towards weak bases.

Reactions Between $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ and Trimethyl Phosphite

The metal-carbon resonance could not be located in the ^{13}C n.m.r. spectra of the η^1-ethynyl complexes. To simplify the spectrum of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (3.14), simple ligand-exchange reactions with trimethyl phosphite were carried out,[102] affording complexes $Ru(C_2Ph)\{P(OMe)_3\}(PPh_3)(\eta\text{-}C_5H_5)$ (3.29) and $Ru(C_2Ph)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (3.30). Reaction between these complexes and HPF_6 or $\{Me_3O\}PF_6$ afforded the vinylidene complexes $\{Ru(C{=}CHPh)(L)(L')(\eta\text{-}C_5H_5)\}PF_6$ {L = PPh_3, L' = $P(OMe)_3$, R = H (3.31); L = L' = $P(OMe)_3$, R = H (3.32), or Me (3.33), respectively}.[102] These compounds were characterised in the usual way. However, we were not successful in locating the Ru-C resonance in the η^1-ethynyl complexes (3.29) or (3.30). This implied a long relaxation time for this Ru-C carbon and subsequently, we repeated the ^{13}C n.m.r. spectrum with a concentrated solution of (3.14) in $CDCl_3$ (*c.* 1 *M*) for an extended accumulation time, observing a low intensity triplet at 116.1 ppm.

Reaction Between 4-Hydroxypent-1-yne and $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$

Reaction between 3-butyn-1-ol and $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ in the presence of NH_4PF_6 gave the cationic cyclic carbene complex $\left[Ru\{\overline{C(CH_2)_3O}\}(PPh_3)_2(\eta\text{-}C_5H_5)\right]PF_6$.[103]

The first complex containing the 2-oxacyclopentylidene ligand was reported in 1963,[104] but not recognised as such until seven years later.[105] Since that time, intramolecular cyclisation reactions of ω-chlorobutyryl complexes have given cyclic carbene complexes of molybdenum,[106] and manganese, iron and ruthenium;[107] other syntheses include the $BF_3.OEt_2$-promoted cyclisation of a β-diethylacetal acyl ligand on molybdenum,[108] and the alkylation of $Cr(CO)_5\{C(OMe)CH_2R\}$ {R = H or Me} with $LiBu^n$, followed by reaction with ethylene oxide.[109] Of more interest to us was the report of the reaction between $PtIMe_2(CF_3)(PMe_2Ph)_2$ and 3-butyn-1-ol in the presence of $AgPF_6$ to give $[PtMe_2(CF_3)\{\overline{C(CH_2)_3O}\}(PMe_2Ph)_2]PF_6$; its formation by intramolecular cyclisation of an intermediate vinylidene-platinum complex was proposed.[110]

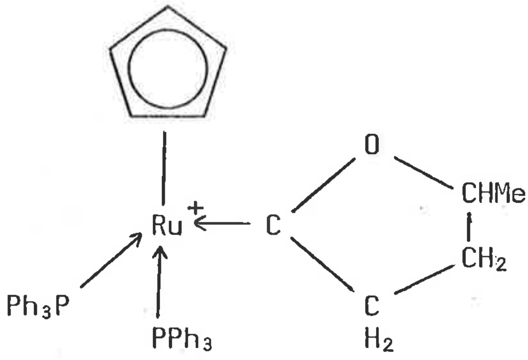
Intramolecular cyclisation reactions occur with other ω-hydroxyalk-1-ynes, $HC_2(CH_2)_3OH$ and $HC_2CH_2CHMeOH$.[103] While the present work was in progress, Japanese workers reported similar reactions of nickel(II) complexes,[111] and a brief account of reactions of ω-hydroxyalk-1-ynes with $\{Fe(CH_2{=}CMe_2)(CO)_2(\eta\text{-}C_5H_5)\}^+$ appeared;[112] both systems show significant differences from the chemistry of the analogous $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$ complexes, and is discussed below.

The ^1H and ^{13}C n.m.r. spectra of $[Ru\{\overline{C(CH_2)_3O}\}(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ contained the usual resonances arising from the C_5H_5 and PPh_3 ligands, together with several signals which can be assigned to the cyclic carbene ligand. In particular, the ^1H n.m.r. spectrum contained well-resolved multiplets assigned to a $-CH_2CH_2CH_2-$ group, while the carbenic nature of the metal-bonded carbon is shown by its very low ^{13}C chemical shift of *c.* 300 ppm. The latter signal is a triplet, by coupling to the two ^{31}P nuclei. Complex (3.34) was prepared to assist with the interpretation of the n.m.r. spectra of the 2-oxacyclopentylidene complex. These complexes are yellow crystalline solids, stable in air, and soluble in the more polar solvents.

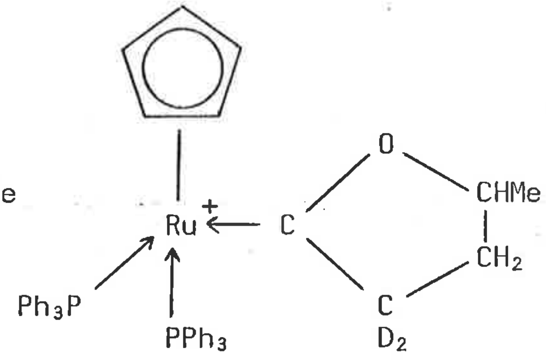
In attempt to isolate intermediate complexes, the reaction of the tetrahydropyranyl (thp) ether of $HC_2CH_2CHMeOH$ with $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ was investigated. In the presence of NH_4PF_6, a methanol solution of the reactants developed a red-purple colour, characteristic of the cationic vinylidene complexes.[97] Addition of sodium methoxide resulted in the separation of yellow crystals of the neutral acetylide complex $Ru\{C_2CH_2CHMeO(thp)\}(PPh_3)_2(\eta\text{-}C_5H_5)$ (3.35), readily identified by elemental analysis and from its mass and n.m.r. spectra (see Experimental).

By addition of acid, we hoped to detect either the vinylidene complex corresponding to (3.35), or a related intermediate formed by loss of the thp group. In the event, the only product detected or isolated was the cyclic carbene derivative (3.34).

During attempts to assign the ^1H resonances to specific CH_2 groups in the 2-oxacyclopentylidene complex, we studied the base-catalysed H-D exchange. This occurred readily and specifically on warming a pyridine solution of this complex with D_2O, when one of the CH_2 multiplets disappeared, with concomitant reduction in multiplicity of the other CH_2 resonances. The site of exchange was finally confirmed by deuteration of the methyl-substituted complex (3.34), to give (3.36), in which the CHMe resonances remain unchanged, while the resonances assigned to the methylene group adjacent to the carbene carbon disappear.



(3.34)



(3.36)

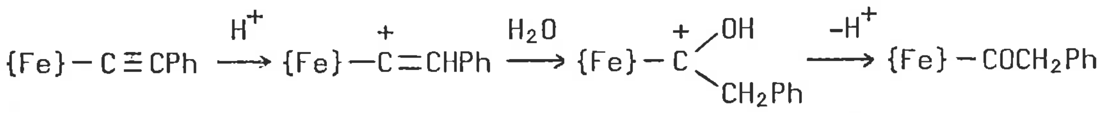
The Reaction Between $\{Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)\}^+$ and Dioxygen

The electrophilic nature of the η^1-vinylidene ligand was demonstrated by the reaction of $\{Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ with dioxygen.[113] In a preparation of (3.5), a band in the infrared spectrum at 1984 cm^{-1} was observed, indicating the presence of a second product. If dioxygen was bubbled through a solution of (3.5) in deuterochloroform, conversion to the second product was complete after 1 h, the reaction being monitored by ^1H n.m.r. spectroscopy. The cyclopentadienyl resonance at δ 5.27 gradually diminished with concomitant growth of a signal at δ 4.97. The product of this reaction (3.37) was isolated in quantitative yield as the hexafluorophosphate salt of the carbonyl cation $\{Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)\}^+$, the identity being confirmed by the usual methods and by comparison (infrared and ^1H n.m.r.) with an authentic sample, prepared according to the published method.[12] Benzoic acid was isolated as the organic product, identified by mass spectroscopy and by mixed melting point using an authentic sample.

Discussion

We have described above the formation of monosubstituted vinylidene complexes of ruthenium and osmium from direct reactions between alk-1-ynes and appropriate chloro-ruthenium or bromo-osmium precursors, in the presence of a large, non-coordinating anion. These new complexes are generally obtained in high yield, and have been characterised principally by the ν(CC) bands around 1650 cm^{-1}, and, in the case of compounds containing the C=CHR group, by the triplet or multiplet resonance of the single vinylidene proton, at δ c. 5. In addition, the ^{13}C n.m.r. spectra contain triplet resonances at c. 360 ppm, characteristic of carbon multiply bonded to a transition metal.

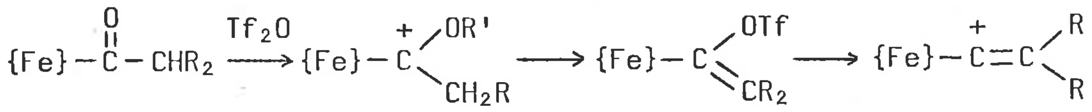
It is of interest that we are able to prepare the complexes described above in methanol solution; that is, addition of methanol to the vinylidene complex does not occur during their preparation, forming the alkoxycarbene derivatives. There are many reports describing the formation of alkoxycarbene complexes from 1-alkynes and suitable transition metal complexes.[94,114-117] Mentioned in the introduction to this chapter are the prolonged reactions of some platinum(II) acetylides with HX {X = Cl or PF_6} in methanol, affording the acylplatinum(II) derivatives via intermediate alkoxycarbene complexes.[95] The addition of water to $Fe(C_2Ph)(CO)_2(\eta-C_5H_5)$ in the presence of acid [118] may also proceed through an intermediate vinylidene-iron complex (Scheme 3.IV).



$\{Fe\} \equiv Fe(CO)_2(\eta-C_5H_5)$

Scheme 3.IV

It is interesting to find that all of these reactions can be reversed to give a general synthesis of vinylidene complexes (Scheme 3.V).[119]



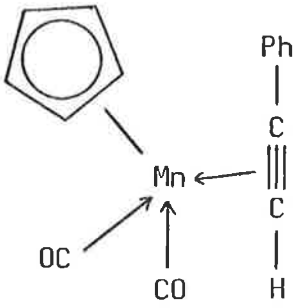
$\{Fe\} \equiv Fe(CO)(PPh_3)(\eta-C_5H_5)$ $Tf \equiv CF_3SO_2$

Scheme 3.V

The reasons for this intriguing difference in behaviour are not clear at present, although one may speculate that it is the bulky PPh_3 ligands that shield the vinylidene ligand from further attack. Some support for this is found in the reactions of the corresponding mono-carbonyl complex,

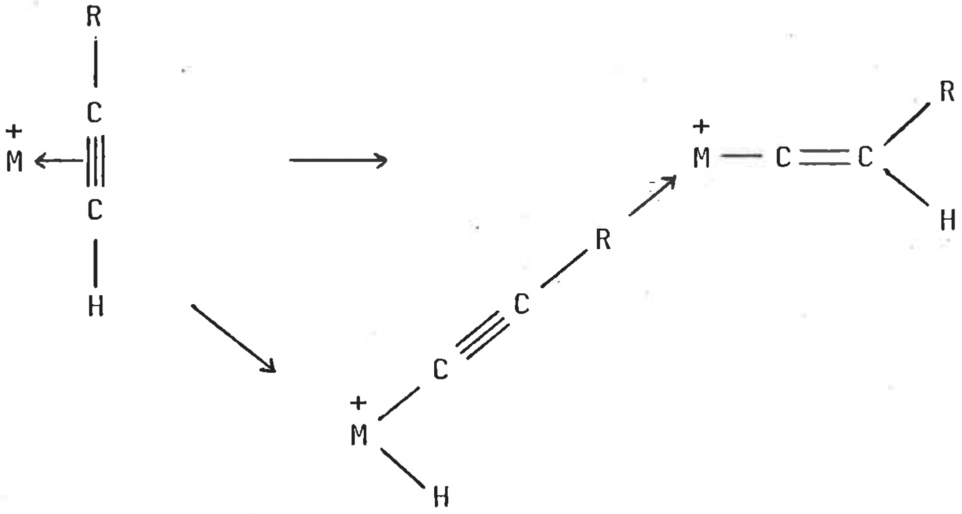
$\{Fe(C{=}CHPh)(CO)(PPh_3)(\eta\text{-}C_5H_5)\}BF_4$, formed as an unstable pink solid by protonation of the corresponding σ-phenylethynyl complex. Davison and Solar,[120] who reported this reaction a few weeks before our own communication,[121] also found ready deprotonation by base ($NHEt_2$), and a *rapid* reaction with methanol to give $[Fe\{C(OMe)CH_2Ph\}(CO)(PPh_3)(\eta\text{-}C_5H_5)]$-$BF_4$.[122] Unfortunately, the analogous reactions of other isolated vinylidene complexes, such as $Mn(C{=}CHPh)(CO)_2(\eta\text{-}C_5H_5)$ or $\{FeCl(C{=}CHPh)(depe)_2\}^+$, have not been reported.

We have not yet been able to obtain any evidence which points to the mechanism of formation of the vinylidene complexes. Clark and coworkers[94] have suggested the intermediate formation of η^2-alkyne complexes in this synthesis of alkoxycarbene complexes, and the Russian workers[82,83] have isolated the complex (3.38) as one of the products from the reaction which also affords the corresponding phenylvinylidene complex. The formal



(3.38)

1,2-shift of the proton may then occur directly along the C_2 chain. Alternatively the alkyne may oxidatively add to the metal centre to give an intermediate hydrido-ruthenium(IV) complex, which isomerizes to the phenylvinylidene complex (Scheme 3.VI).



(3.39)

Scheme 3.VI

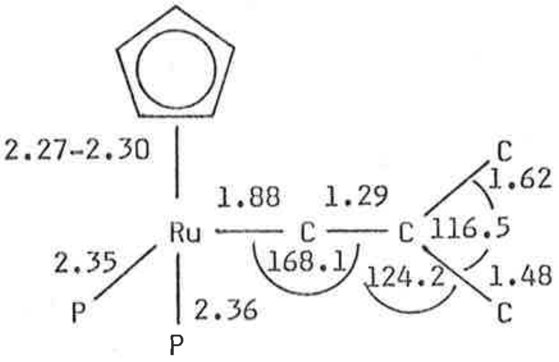
The intermediacy of species such as (3.39) in some oligomerisation reactions of 1-alkynes on ruthenium has been suggested,[42] and cationic osmium(IV) complexes of the type $\{OsHBr(PPh_3)_2(\eta-C_5H_5)\}^+$ have been isolated.[47] The surprisingly ready deprotonation of the monosubstituted vinylidene complexes to the corresponding acetylide complexes affords these compounds in high yield, and is the synthetic method of choice. Reactions between the halide $RuCl(PPh_3)_2(\eta-C_5H_5)$ and lithium or Grignard reagents derived from alk-1-ynes afford the acetylides in yields ranging from 25 to 40%. Metathesis between the chloride and substituted copper(I) acetylides gives the ruthenium acetylides containing copper(I) chloride π-complexed to the C≡C triple bond; it proved difficult to remove the copper halide without simultaneously breaking the Ru-C bond.[57]

Much more important is our demonstration that the acetylides may themselves be protonated readily to form the vinylidene complexes, and that this reaction can be extended to alkylation by cationic alkylating agents. We have used the commercially available reagents $HBF_4.Me_2O$, $HPF_6.Et_2O$, $\{Me_3O\}PF_6$, and $\{Et_3O\}PF_6$ as giving readily isolable products, but we have also shown that protonation occurs with other strong acids such as trifluoroacetic acid, and it is likely that other strong alkylating agents will achieve similar results. The alkylated complexes are not available from the appropriate disubstituted alkynes. In principle, protonation or alkylation of the appropriate η^1-alkynyl complex should be a source of new vinylidene complexes, which may either be isolable, or undergo further reaction. In contrast, however, Chisholm[95] has reported that similar attempted protonation of some alkynylplatinum(II) complexes is a general route to alkoxycarbene complexes (see above), but that no reaction occurs between *trans*-$Pt(C_2CF_3)_2(PMe_2PH)_2$ and HPF_6 in methanol over 1 h.

A key datum in the confirmation of the vinylidene formulation of the cationic complexes described in this chapter was the chemical shift of the metal-bonded carbon, which resonates at *c*. 360 ppm downfield from TMS. These fall in the same region as those found for other carbene-metal complexes, and also for carbonium ions, suggesting that the carbons are very electron deficient. As a result, efficient back-bond from suitable metal *d* orbitals gives a significant amount of multiple-bond character to the metal-carbon bond, and effectively shields the carbon nuclei.

We have been able to confirm the vinylidene structure of $\{Ru(C{=}CMe_2)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (3.26) by crystal structure analysis.* The approximate bond distances and angles are shown below (Figure 3.I), the small size of the crystal resulting in poor intensity statistics.

Figure 3.I

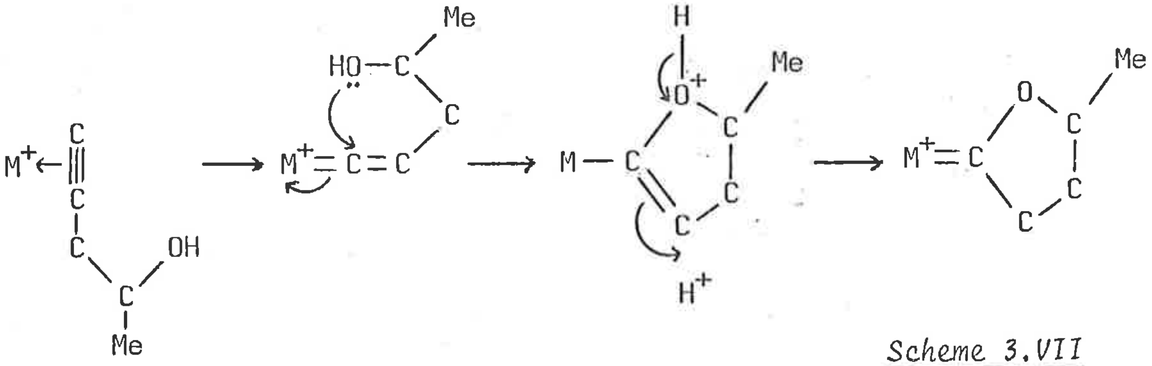


*Data by R. E. Davis

Some indication of the importance of the metal-to-carbon multiple bonding is shown by the Ru-C bond length (1.88 Å) which may be compared to the Mn-C and Mn-CO bond lengths in complex (3.2),[84] 1.68 Å and 1.67 Å, respectively; these bond lengths are considerably shorter than the Mn-C(alkyl) bond in $MnMe(CO)_5$ (2.185 Å).[123]

Simple ligand-exchange reactions between $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (3.14) and $P(OMe)_3$ afford the η^1-ethynyl complexes $Ru(C_2Ph)(L)(L')(\eta\text{-}C_5H_5)$ {L = PPh_3, L' = $P(OMe)_3$ (3.29); L = L' = $P(OMe)_3$ (3.30)}. These exchange reactions are analogous to those described in Chapter 2. The η^1-ethynyl complexes are protonated and alkylated affording η^1-vinylidene complexes (as described above).

Reactions between $HC_2CH_2CHMeOH$ and $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ in the presence of NH_4PF_6 gave the cationic complex (3.34) containing the five-membered $\overline{CCH_2CH_2CHMeO}$ cyclic carbene (substituted 2-oxacyclopentylidene) ligand. The formation of this complex presumably proceeds via an intermediate vinylidene complex, which, however, was not detected. A facile intramolecular attack of the hydroxyl function on the vinylidene α-carbon, accompanied by a proton shift, results in formation of the cyclic carbene ligand (Scheme 3.VII).



Scheme 3.VII

Protection of the hydroxyl group by formation of the corresponding tetrahydropyranyl (thp) ether enables the acetylide complex (3.35) to be isolated; the formation of a red-purple colour in the solution prior to addition of sodium methoxide suggests the initial formation of the analogous vinylidene cation. Addition of acid, which normally cleaves thp ethers to regenerate the alcohol, to the complex, results in immediate cyclisation to form complex (3.34); no intermediates could be detected either visually or by ^{1}H n.m.r.

The related reaction between $HC_2CH_2CH_2OH$ and $\{Fe(\eta^2\text{-}CH_2{:}CMe_2)(CO)_2(\eta\text{-}C_5H_5)\}^+$ also gives the η^2-2,3-dihydrofuran complex, formed by a competing nuclephilic attack on the η^2-alkyne-iron complex before rearrangement to the η^1-vinylidene isomer.[112] In the studies reported here, we have found no evidence for the formation of any η^2-vinyl ether complexes; it may be significant that we have not been able to deprotonate our cyclic carbene complexes to the derived η^1-dihydrofuryl complex, although addition of hydride to the carbene carbon affords the η^1-tetrahydrofuryl complex.[103] In this respect the reactivity of our complexes also differs markedly from that of *trans*-$[Ni(C_6Cl_5)\{\overline{C(CH_2)_3O}\}\text{-}(PMe_2Ph)_2]^+$, which is readily deprotonated by NEt_3.[111]

Complex (3.34) undergoes facile base-catalysed H-D exchange, e.g. by addition of D_2O to a solution of (3.34) in pyridine. Analysis of the ^{1}H and ^{13}C n.m.r. spectra show that it is the two protons attached to C(5) which exchange. Similar observations have been made with cyclic carbene complexes of manganese.[105,107]

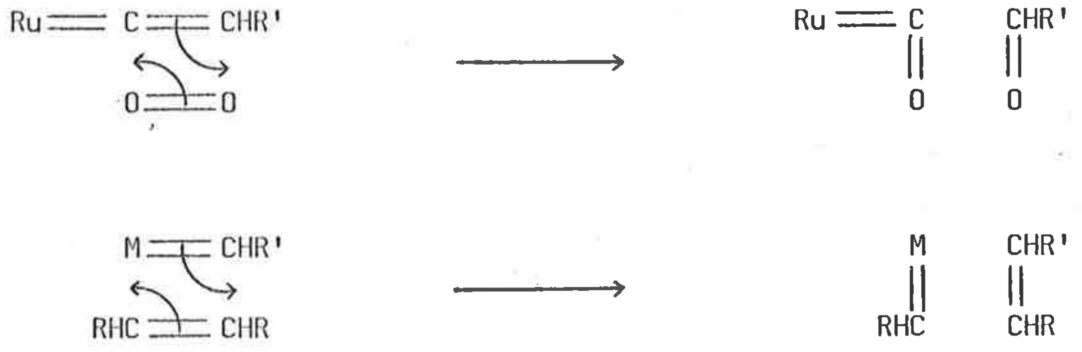
The facile intramolecular attack of the hydroxyl function on the vinylidene α-carbon suggested that reaction of $\{Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)\}^+$ with methanol should occur. Indeed, the slow reaction (24 h) of (3.5) with methanol gave the methoxy(benzyl)carbene complex $[Ru\{C(OMe)CH_2Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$,[102] a conventional Fischer-type carbene complex.

Oxidation of $\{Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (3.5) gives the carbonyl complex $\{Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (3.37), together with benzoic acid as the isolated organic product. This reaction is an interesting example of the oxidative cleavage of a C≡C triple bond to CO (which remains coordinated to the metal) and an organic carbonyl product (Scheme 3.VIII).

$$HC{\equiv}CR \longrightarrow C{=}CHR \xrightarrow{(O)} CO + HC(O)R \xrightarrow{(O)} HO(CO)R$$

Scheme 3.VIII

The similarity to olefin metathesis[124] can be seen, although it is not the carbene-bearing metal that interacts with incoming dioxygen but the carbene carbon of the vinylidene ligand (Scheme 3.IX).



Scheme 3.IX

EXPERIMENTAL: *General experimental conditions are described in Appendix I.*

PREPARATION OF VINYLIDENE COMPLEXES FROM ALK-1-YNES

From $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$

(A) *Phenylacetylene*, HC_2Ph. — (i) *Method A*. Addition of NH_4PF_6 (337 mg, 2.07 mmol) and phenylacetylene (102 mg, 1.0 mmol) to a suspension of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (500 mg, 0.69 mmol) in methanol (40 ml), followed by a brief period under reflux, gave a deep red solution, which was then filtered and evaporated. The residue was extracted with CH_2Cl_2 (5 ml), and the extract filtered into Et_2O (50 ml), to give a reddish tan *precipitate* of $\{Ru(C{=}CH)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (3.5a) (570 mg, 88%), m.p. 105-110° (dec.) (Found: C, 62.1; H, 4.4; F, 10.9. $C_{49}H_{41}F_6P_3Ru$ requires C, 62.7; H, 4.4; F, 12.1%). Infrared (Nujol): ν(CC) 1640m, and 1622m; ν(PF) 842vs cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.33, 7.24, 7.16, 7.11, and 7.02, m, 35H, PPh_3+Ph; 5.40, t, J(HP) 2.6 Hz, 1H, =CH; 5.27, s, 5H, C_5H_5. ^{13}C n.m.r. ($CDCl_3$): δ 359.0, t, J(CP) 24 Hz, RuC; 135.1-129.0, m, PPh_3; 129.2, 127.5, and 119.8, s, Ph; 95.2, s, C_5H_5. Conductivity (acetone): Λ_M 95 S cm^{-2} mol^{-1}.

(ii) *Method B*. A mixture of $\{Ru(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (400 mg, 0.46 mmol) and phenylacetylene (102 mg, 1.0 mmol) was heated in refluxing CH_2Cl_2 (25 ml) for 30 min. Concentration and addition of Et_2O gave pure (3.5a) (310 mg, 74%), identical with the product obtained by method A.

(iii) The tetrafluoroborate (3.5b) was obtained by method A, from $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (500 mg, 0.69 mmol), phenylacetylene (102 mg, 1.0 mmol) and NH_4BF_4 (217 mg, 2.07 mmol), as a tan *powder* (510 mg, 84%), m.p. 145-150° (dec.). Infrared (Nujol): ν(CC) 1640m, and 1620m; ν(BF) 1050vs; ν(C_5H_5) 842 cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.20, m, 35H, PPh_3+Ph; 5.41, m, 1H, =CH; 5.26, s, 5H, C_5H_5.

(iv) The tetraphenylborate (3.5c) was obtained by method A, from

$RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (500 mg, 0.69 mmol), phenylacetylene (102 mg, 1.0 mmol) and $NaBPh_4$ (300 mg, 0.88 mmol), as a tan *powder* (565 mg, 74%), m.p. 110-115° (dec.) (Found: C, 78.0; H, 5.6. $C_{73}H_{61}BP_2Ru$ requires C, 78.8; H, 5.5%). Infrared (Nujol): ν(CC) 1640m, and 1620m; $\nu(C_5H_5)$ 841m cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.14, m, 55H, PPh_3+Ph; 5.27, t, J(HP) 2.4 Hz, 1H, =CH; 4.94, s, 5H, C_5H_5.

(B) *Propyne, HC_2Me.* — (i) A suspension of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (500 mg, 0.69 mmol) and NH_4PF_6 (300 mg, 1.84 mmol) in methanol (40 ml) was cooled in a dry ice/methanol bath. A rapid stream of propyne was introduced into the mixture for about 30 s, and the stirred mixture was allowed to warm slowly to room temperature. Following the reaction, an isolation procedure similar to that described in method A (above) afforded an orange-red *powder* of $\{Ru(C{=}CHMe)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (3.6a) (535 mg, 89%), m.p. 120-125° (Found: C, 60.4; H, 4.6. $C_{44}H_{39}F_6P_3Ru$ requires C, 60.3; H, 4.5%). Infrared (Nujol): ν(CC) 1655m; ν(PF) 840s cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.35, 7.28, 7.19, and 7.05, m, 30H, PPh_3; 5.10, s, 5H, C_5H_5; 4.68, q of t, J(HH) 7.8 Hz, J(HP) 2.4 Hz, 1H, =CH; 1.86, d, J(HH) 7.8 Hz, 3H, Me. ^{13}C n.m.r. ($CDCl_3$): δ 349.9, t, J(CP) 17 Hz, RuC; 134.5-128.8, m, PPh_3; 109.4, s, =CH; 94.5, s, C_5H_5; 5.5, s, Me.

(ii) The tetrafluoroborate (3.6b) was prepared by a reaction similar to that for (3.6a) above, $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (500 mg, 0.69 mmol), NH_4BF_4 (217 mg, 2.07 mmol) and propyne being used, as an orange-red *solid* (465 mg, 83%), m.p. 120-125° (Found: C, 64.2; H, 4.8. $C_{44}H_{39}BF_4P_2Ru$ requires C, 64.6; H, 4.8%). Infrared (Nujol): ν(CC) 1680-1650m (br); ν(BF) 1050s cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.26, m, PPh_3; 5.10, s, 5H, C_5H_5; 4.67, m, 1H, =CH; 1.86, d, J(HH) 7.5 Hz, 3H, Me.

(C) *Pent-1-yne, HC_2Pr.* — (i) The compound $\{Ru(C{=}CHPr)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (3.7a) was prepared by method A, from $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (500 mg, 0.69 mmol), pent-1-yne (100 mg, 1.49 mmol) and NH_4PF_6 (150 mg, 0.92 mmol), as a tan *powder* (535 mg, 86%), dec. > 98° (Found: C, 60.8; H, 4.6. $C_{46}H_{43}F_6P_3Ru$ requires C, 61.1; H, 4.8%). Infrared (Nujol): ν(CC) 1660s; ν(PF) 840vs cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.35, 7.28, 7.19, and 7.06, m, 30H, PPh_3; 5.10, s, 5H, C_5H_5; 4.66, t of t, *J*(HH) 7.5 Hz, *J*(HP) 2.4 Hz, 1H, =CH; 2.20, q, *J*(HH) 7.5 Hz, 2H, $=CCH_2$; 1.24, m, 2H, CH_2Me; 0.93, t, *J*(HH) 7.5 Hz, 3H, Me. ^{13}C n.m.r. ($CDCl_3$): δ 134.6-128.9, m, PPh_3; 114.7, s, =CH; 94.5, s, C_5H_5; 24.5, and 23.9, s, CH_2; 13.7, s, Me.

(ii) The tetrafluoroborate (3.7b) was prepared by method A, as for (3.7a) above, NH_4BF_4 (200 mg, 1.91 mmol) being used in place of NH_4PF_6, as a tan *powder* (510 mg, 88%), dec. > 92°. Infrared (Nujol): ν(CC) 1660m; ν(BF) 1050s cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.32, m, 30H, PPh_3; 5.13, s, 5H, C_5H_5; 4.84, m, 1H, =CH; 2.27, q, *J*(HH) 7.5 Hz, 2H, $=CCH_2$; 1.26, m, 2H, CH_2Me; 0.93, t, *J*(HH) 7.5 Hz, 3H, Me.

(iii) The tetraphenylborate (3.7c) was also prepared by method A, as for (3.7a) above, using $NaBPh_4$ (300 mg, 0.88 mmol) in place of NH_4PF_6 and refluxing for 1.5 h, as a tan *powder* (669 mg, 90%), m.p. 90-95° (Found: C, 77.5; H, 6.0; P, 6.0. $C_{70}H_{63}BP_2Ru$ requires C, 78.0; H, 5.9; P, 5.8%). Infrared (Nujol): ν(CC) 1660m cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.12, m, 30H, PPh_3; 6.87, m, 20H, BPh_4; 5.08, s, 5H, C_5H_5; 2.14, m, 2H, $=CCH_2$; 1.24, m, 2H, CH_2Me; 0.92, m, 3H, Me.

(D) *Methyl propiolate*, HC_2CO_2Me. — (i) The compound $\{Ru(C{=}CHCO_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (3.8a) was prepared by method A, from $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (500 mg, 0.69 mmol), methyl propiolate (70 mg, 0.83 mmol) and NH_4PF_6 (337 mg, 2.07 mmol), by refluxing for 45 min, as an orange-brown *solid* (580 mg, 92%) (Found: C, 58.4; H, 4.2. $C_{45}H_{39}F_6O_2P_3Ru$ requires C, 58.8; H, 4.3%). Infrared (Nujol): ν(CO) 1727ms, 1263m, and 1241m; ν(CC) 1640m; ν(PF) 840s cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.39, 7.32, 7.21, and 7.06, m, 30H, PPh_3; 5.28, s, 5H, C_5H_5; 5.02, t, *J*(HP) 1.8 Hz, 1H, =CH; 3.49, s, 3H, OMe. ^{13}C n.m.r. ($CDCl_3$): δ 134.6-129.1, m, PPh_3; 96.5, s, C_5H_5; 66.1, s, OMe.

(ii) The tetrafluoroborate (3.8b) was obtained similarly, by using NH_4BF_4 (200 mg, 1.91 mmol) in place of NH_4PF_6, as an orange-brown *solid* (535 mg, 90%). Infrared (Nujol): ν(CO) 1725ms, 1265m, and 1241m; ν(CC) 1640m; ν(BF) 1050vs cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.36, m, 30H, PPh_3; 5.28, s, 5H, C_5H_5; 4.98, t, *J*(HP) 2 Hz, 1H, =CH; 3.43, s, 3H, OMe.

(iii) The tetraphenylborate (3.8c) (695 mg, 92%) was formed by using $NaBPh_4$ (300 mg, 0.88 mmol) in place of NH_4PF_6, and was also an orange-brown *powder*, m.p. 100-105° (dec.) (Found: C, 75.4; H, 5.7. $C_{69}H_{59}BO_2P_2Ru$ requires C, 75.8; H, 5.4%). Infrared (Nujol): ν(CO) 1708ms; ν(CC) 1640m cm^{-1}.

(E) *4-Fluorophenylacetylene, $HC_2C_6H_4F$-4.* — (i) The compound $\{Ru(C{=}CHC_6H_4F\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (3.9a) was prepared by method A, from $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (500 mg, 0.69 mmol), 4-fluorophenylacetylene (85 mg, 0.71 mmol) and NH_4PF_6 (300 mg, 1.84 mmol), by refluxing for 30 min, as a red-brown *powder* (550 mg, 84%), m.p. c. 120° (Found: C, 61.2; H, 4.3. $C_{49}H_{40}F_7P_3Ru$ requires C, 61.6; H, 4.2%). Infrared (Nujol): ν(CC) 1635m; ν(PF) 840vs cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.11, m, 34H, PPh_3+C_6H_4; 5.35, m, 1H, =CH; 5.20, s, 5H, C_5H_5. ^{13}C n.m.r. ($CDCl_3$): δ 134.4-128.7, m, PPh_3; 95.2, s, C_5H_5.

(ii) The tetrafluoroborate (3.9b) was obtained similarly, using NH_4BF_4 (200 mg, 1.91 mmol) in place of NH_4PF_6, as a red-brown *powder* (485 mg, 78%) (Found: C, 65.1; H, 4.7. $C_{49}H_{40}BF_5P_2Ru$ requires C, 65.6; H, 4.5%). Infrared (Nujol): ν(CC) 1635m; ν(BF) 1050s cm^{-1}.

(F) *Pentafluorophenylacetylene, $HC_2C_6F_5$.* — The complex $\{Ru(C{=}CHC_6F_5)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (3.10) was prepared by method A, from $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (500 mg, 0.69 mmol), pentafluorophenylacetylene (150 mg, 0.78 mmol) and NH_4PF_6 (300 mg, 1.84 mmol), as a tan *powder*

(570 mg, 80%), dec. 60-65° (Found: C, 57.0; H, 3.8. $C_{49}H_{36}F_{11}P_3Ru$ requires C, 57.3; H, 3.5%). Infrared (Nujol): ν(CC) 1640m; ν(PF) 840ms cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.36, 7.27, 7.17, 7.13, 7.03, and 6.98, m, 30H, PPh_3; 5.35, s, 5H, C_5H_5; 5.09, t, *J*(HP) 2.1 Hz, 1H, =CH. ^{13}C n.m.r. ($CDCl_3$): δ 134.6 - 129.0, m, PPh_3; 103.0, s, =CH; 96.1, s, C_5H_5.

From $RuCl(L_2)(\eta-C_5H_5)$ $\{L_2$ *= dppm or dppe*$\}$ *and Phenylacetylene.*

(A) A mixture of $RuCl(dppm)(\eta-C_5H_5)$ (150 mg, 0.26 mmol), phenylacetylene (27 mg, 0.26 mmol) and NH_4PF_6 (82 mg, 0.5 mmol) was heated in refluxing methanol (15 ml) for 1 h. The solvent was evaporated, the residue was extracted with dichloromethane (10 ml), and the extract was filtered directly into diethyl ether (50 ml). The buff precipitate was collected, washed with diethyl ether, and dried in a vacuum to give pure $\{Ru(C{=}CHPh)(dppm)(\eta-C_5H_5)\}PF_6$ (3.11) (93 mg, 46%) as a buff coloured *powder*, m.p. 208-210° (Found: C, 57.0; H, 4.3; P. 11.4. $C_{38}H_{33}F_6P_3Ru$ requires C, 57.2; H, 4.2; P, 11.6%). Infrared (Nujol): ν(CC) 1651w; ν(PF) 831s cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.36. 6.87, and 6.39, m, 25H, PPh_2+Ph; 5.57, s, 5H, C_5H_5; 1.52, m, 2H, PCH_2.

(B) The complex $\{Ru(C{=}CHPh)(dppe)(\eta-C_5H_5)\}PF_6$ (3.12) was prepared similarly to (3.11) described above, on the same scale. A pale orange *precipitate* of (3.12) (110 mg, 54%) was obtained, m.p. 210-212° (Found: C, 57.5; H, 4.4; P, 11.5. $C_{39}H_{35}F_6P_3Ru$ requires C, 57.7; H, 4.3; P, 11.4%). Infrared (Nujol): ν(CC) 1646m, and 1621w; ν(PF) 836s cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.41, 6.90, and 6.30, m, 25H, PPh_2+Ph; 5.57, s, 5H, C_5H_5; 2.61, m, 4H, PCH_2. ^{13}C n.m.r. ($CDCl_3$): δ 133.4 - 117.8, m, PPh+Ph; 92.3, s, C_5H_5.

From $OsBr(PPh_3)_2(\eta-C_5H_5)$ *and Phenylacetylene*

A mixture of $OsBr(PPh_3)_2(\eta-C_5H_5)$ (83 mg, 0.10 mmol), phenylacetylene (10 mg, 0.10 mmol) and NH_4PF_6 (25 mg, 0.15 mmol) was heated in refluxing methanol (20 ml) for 1 h. After removal of solvent and extraction of the residue with dichloromethane (10 ml), filtration of the extract into diethyl ether (50 ml) precipitated the product which was filtered off, washed with diethyl ether and dried in a vacuum to give pure {Os(C=CHPh)(PPh_3)$_2$(η-C_5H_5}-PF_6 (3.13) (70 mg, 70%) as a light purple powder, m.p. 136-138^0 (Found: C, 57.5; H, 4.1. $C_{49}H_{41}F_6OsP_3$ requires C, 57.3; H, 4.0%). Infrared (Nujol): ν(CC) 1648m, and 1629m; ν(PF) 833s cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.29, 7.22, 7.15, and 7.05, m, 35H, PPh_3+Ph; 5.42, s, 5H, C_5H_5; 5.08, m, 1H, =CH. ^{13}C n.m.r. ($CDCl_3$): δ 134.8 - 128.8, m, PPh_3; 127.6, 126.9, and 118.0, s, Ph; 108.2, s, =CH; 92.7, s, C_5H_5. Conductivity (acetone): Λ_M 96 S cm^{-2} mol^{-1}.

ETHYNYL COMPLEXES

From $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ or Vinylidene Complexes

(A) *Phenylacetylene, HC_2Ph.* - (i) *Method C.* A solution of $\{Ru(C{=}CHPh)\text{-}(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (3.5a) (470 mg, 0.5 mmol) in dichloromethane (5 ml) was transferred to a short column of chromatographic alumina. On adsorption, the red colour of the cation was discharged, and elution with diethyl ether gave a yellow fraction. Evaporation and recrystallization (dichloromethane/methanol) afforded yellow *crystals* of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (3.14) (320 mg, 81%), m.p. 202-205° (dec.) {lit.[57] m.p. 205° (dec.)} (Found: C, 73.7; H, 5.4; P, 7.6%; *M* (mass spectrometry), 792. $C_{49}H_{40}P_2Ru$ requires C, 74.3; H, 5.1; P, 7.8%; *M*, 792). Infrared (Nujol): ν(CC) 2068s cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.50, and 7.12, m, 35H, PPh_3+Ph; 4.32, s, 5H, C_5H_5. ^{13}C n.m.r. ($CDCl_3$): δ 139.3-127.4, m, PPh_3; 130.7, 127.8, and 123.2, s, Ph; 116.1, t, *J*(CP) 24 Hz, RuC; 114.7, s, $\equiv$CR; 85.4, t, *J*(CP) 2 Hz, C_5H_5.

(ii) *Method D.* A mixture of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (500 mg, 0.69 mmol) and phenylacetylene (102 mg, 1 mmol) was heated in refluxing methanol for 30 min. Sodium methoxide (1 ml of a 1 *M* solution in methanol) was added to the deep red solution, and the yellow *crystals* that were rapidly deposited were recrystallized (dichloromethane/methanol) to give pure (3.14) (475 mg, 87%), identical with the product obtained using method C.

(B) *Propyne, HC_2Me.* - $Ru(C_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)$ (3.15) was obtained as yellow *crystals* (405 mg, 81%), m.p. 209-215° (dec.), by addition of sodium methoxide to the solution formed after passing a rapid stream of propyne into a suspension of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (500 mg, 0.69 mmol) in methanol for about 30 s, followed by stirring at room temperature for 3 h. (Found: C, 72.4; H, 5.7 P, 8.1%; *M* (mass spectrometry), 730. $C_{44}H_{38}P_2Ru$ requires C, 72.4; H, 5.3; P, 8.5%; *M*, 730). Infrared (Nujol): ν(CC) 2100s cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.46, and 7.15, m, 30H, PPh_3; 4.22, s, 5H, C_5H_5; 1.99, t, *J*(HP) 2.2 Hz, 3H, Me. ^{13}C n.m.r. ($CDCl_3$): δ 139.5-127.2, m, PPh_3; 105.3, s, $\equiv$CR; 84.5, s, C_5H_5; 7.8, s, Me.

(C) *Pent-1-yne*, HC_2Pr. - $Ru(C_2Pr)(PPh_3)_2(\eta-C_5H_5)$ (3.16) was prepared by method D, from $RuCl(PPh_3)_2(\eta-C_5H_5)$ (500 mg, 0.69 mmol) and excess pent-1-yne, as yellow *crystals* (380 mg, 73%), m.p. 183-185^0 (dec.) (Found: C, 72.5; H, 5.6; P, 8.3%; *M* (mass spectrometry), 758. $C_{46}H_{42}P_2Ru$ requires C, 72.9; H, 5.6; P, 8.2%; *M*, 758). Infrared (Nujol): ν(CC) 2096s cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.50, and 7.14, m, 30H, PPh_3; 4.22, s, 5H, C_5H_5; 2.38, t, *J*(HH) 7.0 Hz, 2H, $\equiv CCH_2$; 1.38, se, *J*(HH) 7.0 Hz, 1H, CH_2Me; 0.84, t, *J*(HH) 7.0 Hz, 3H, Me. ^{13}C n.m.r. ($CDCl_3$): δ 139.7-127.2, m, PPh_3; 111.4, s, $\equiv CR$; 84.7, s, C_5H_5; 25.5, and 24.3, s, CH_2; 13.9, s, Me.

(D) *Methyl propiolate*, HC_2CO_2Me. - $Ru(C_2CO_2Me)(PPh_3)_2(\eta-C_5H_5)$ (3.17),[42] from RuCl $(PPh_3)_2(\eta-C_5H_5)$ (500 mg, 0.69 mmol) and methyl propiolate (168 mg, 2.0 mmol), was obtaind as yellow *crystals* (250 mg, 47%), m.p. 216-219^0 (dec.) (Found: C, 69.6; H, 5.1; P, 8.3%; *M* (mass spectrometry), 774. $C_{45}H_{38}O_2P_2Ru$ requires C, 69.9; H, 5.0; P, 8.3%; *M*, 774). Infrared (Nujol): ν(CC) 2058s; ν(CO) 1665s, 1192s, and 1181s cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.41, and 7.18, m, 30H, PPh_3; 4.36, s, 5H, C_5H_5; 3.63, s, 34, OMe. ^{13}C n.m.r. ($CDCl_3$): δ 177.4, s, CO; 138.5-127.6, m, PPh_3; 105.3, s, $\equiv CR$; 86.2, s, C_5H_5; 51.4, s, OMe.

(E) *4-Fluorophenylacetylene*, $HC_2C_6H_4F$-4. - $Ru(C_2C_6H_4F\text{-}4)(PPh_3)_2(\eta-C_5H_5)$ (3.18), by method D, from $RuCl(PPh_3)_2(\eta-C_5H_5)$ (500 mg. 0.69 mmol) and *p*-fluorophenylacetylene (120 mg, 1.0 mmol), was obtained as yellow *crystals* (450 mg, 81%), m.p. 195-200^0 (dec.) (lit. [57]m.p. 187-190^0) (Found: C, 72.2; H, 4.8; P, 8.1%; *M* (mass spectrometry), 810. $C_{49}H_{39}FP_2Ru$ requires C, 72.6; H, 4.8; P, 7.7%; *M*, 810). Infrared (Nujol): ν(CC) 2079s cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.49, and 7.13, m, 34H, PPh_3+C_6H_4; 4.31, s, 5H, C_5H_5. ^{13}C n.m.r. ($CDCl_3$): δ 139.3-127.4, m, PPh_3; 131.8, d, *J*(CF) 5 Hz, C4, C_6H_4; 115.1, and 114.1, s, C_6H_4; 85.3, s, C_5H_5.

(F) *Pentafluorophenylacetylene*, $HC_2C_6F_5$. - $Ru(C_2C_6F_5)(PPh_3)_2(\eta-C_5H_5)$ (3.19), by method D, from $RuCl(PPh_3)_2(\eta-C_5H_5)$ (1.8 g, 2.48 mmol) and pentafluorophenylacetylene (500 mg, 2.6 mmol), for 1 h, was obtained as yellow crystals of the ½CH_2Cl_2 solvate (1.75 g, 76%), m.p. 146-149^0 (dec.) {lit.[57]

m.p. 142° (non solvated)} (Found: C, 67.1; H, 4.5%; *M* (mass spectrometry), 882. $C_{49}H_{35}F_5P_2Ru,\frac{1}{2}CH_2Cl_2$ requires C, 66.7; H, 4.0%; *M* (for unsolvated complex 882). Infrared (Nujol): ν(CC) 2064s cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.16, m, 30H, PPh_3; 5.28, s, 1H, CH_2Cl_2; 4.35, s, 5H, C_5H_5. ^{13}C n.m.r. ($CDCl_3$): δ 138.8-127.5, m, PPh_3; 86.0, s, C_5H_5; 53.8, s, CH_2Cl_2.

(G) *Propargyl bromide, HC_2CH_2Br.* — $Ru(C_2CH_2Br)(PPh_3)_2(\eta\text{-}C_5H_5)$ (3.23), by method D, from $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (500 mg, 0.69 mmol) and propargyl bromide (500 mg, 4.20 mmol), was obtained as yellow *crystals* (180 mg, 34%), m.p. 182-187° (dec.) (Found: C, 68.9; H, 5.0; P, 7.6. $C_{44}H_{37}BrP_2Ru$ requires C, 68.6; H, 4.8; P, 8.0%). Infrared (Nujol): ν(CC) 2090m cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.38, and 7.15, m, 30H; PPh_3; 4.27, s, 5H, C_5H_5; 3.22, s, 2H, CH_2.

From $RuCl(L_2)(\eta\text{-}C_5H_5)$ {L_2 = dppm or dppe} and Phenylacetylene

(A) A mixture of $RuCl(dppm)(\eta\text{-}C_5H_5)$ (62 mg, 0.11 mmol) and phenylacetylene (50 mg, 0.49 mmol) was heated in refluxing methanol for 30 min. Sodium methoxide (1 ml of a 1 *M* solution in methanol) was added to the orange solution. Evaporation and recrystallization (dichloromethane/light petroleum) afforded yellow *crystals* of $Ru(C_2Ph)(dppm)(\eta\text{-}C_5H_5)$ (3.20) (42 mg, 61%), m.p. 231-232° (dec.) (Found: C, 67.5; H, 5.2%; *M* (mass spectrometry), 652. $C_{38}H_{32}P_2Ru$ requires C, 70.0; H, 5.0%; *M*, 652). Infrared (Nujol): ν(CC) 2077m cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.72, and 7.25, m, 20H, PPh_2; 6.77, and 6.31, m, 5H, Ph; 4.99, s, 5H, C_5H_5; 1.54, m, 2H, PCH_2.

(B) Using the complex $RuCl(dppe)(\eta\text{-}C_5H_5)$ (100 mg, 0.17 mmol) and phenylacetylene (50 mg, 0.49 mmol), a similar reaction afforded yellow *needles* of $Ru(C_2Ph)(dppe)(\eta\text{-}C_5H_5)$ (3.21) (89 mg, 80%), m.p. 215-216° (dec.) (Found: C, 70.2; H, 5.0%; *M* (mass spectrometry), 666. $C_{39}H_{34}P_2Ru$ requires C, 70.4; H, 5.1%; *M*, 666). Infrared (Nujol): ν(CC) 2082m cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.95, 7.41, 7.29, 6.85, and 6.44, m, 25H, PPh_2+Ph; 4.78, s, 5H, C_5H_5: 2.50, m, 4H, PCH_2. ^{13}C n.m.r. ($CDCl_3$): δ 134.4-123.2, m and s, PPh_2+Ph; 112.0, s, ≡CR; 82.6, m, C_5H_5; 28.2, t, *J*(CP) 23 Hz, PCH_2.

From $OsBr(PPh_3)_2(\eta-C_5H_5)$ and Phenylacetylene

A mixture of $OsBr(PPh_3)_2(\eta-C_5H_5)$ (100 mg, 0.12 mmol) and phenylacetylene (50 mg, 0.49 mmol) was heated in refluxing methanol for 45 min. Sodium methoxide 1 ml of a 1 *M* solution in methanol) was added to the light purple solution. Evaporation and recrystallization (chloroform/methanol) afforded pale yellow *crystals* of $Os(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ (3.22) (96 mg, 94%), m.p. 217-218° (dec.) (Found: C, 66.3; H, 4.7; P, 6.8%; *M* (mass spectrometry), 880. $C_{49}H_{40}OsP_2$ requires C, 66.8; H, 4.6; P, 7.0%; *M*, 882). Infrared (Nujol): $\nu(CC)$ 2066m cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.44, 7.13, and 7.10, m, 35H, PPh_3+Ph; 4.39, s, 5H, C_5H_5. ^{13}C n.m.r. ($CDCl_3$): δ 139.4-127.3, m, PPh_3; 131.2, 127.7, and 122.9, s, Ph; 110.3, s, $\equiv CR$; 81.5, m, C_5H_5.

Preparation of Ethynyl Complexes Containing Trimethyl Phosphite.

(*A*) A mixture of $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ (400 mg, 0.51 mmol) and $P(OMe)_3$ (180 mg, 1.45 mmol) was heated in refluxing 2-methoxyethanol (40 ml) for 4 h. The solvent was removed, and the yellow oil chromatographed (alumina), excess $P(OMe)_3$ being washed out with light petroleum. A yellow band was eluted with light petroleum/diethyl ether (1:1). Crystallization (light petroleum) then afforded yellow *crystals* of $Ru(C_2Ph)(PPh_3)\{P(OMe)_3\}(\eta-C_5H_5)$ (3.29) 315 mg, 95%), m.p. 128-130° (Found: C, 62.4; H, 5.1%; *M* mass spectrometry), 654. $C_{34}H_{34}O_3P_2Ru$ requires C, 62.5; H, 5.2%; *M*, 654). Infrared (Nujol): $\nu(CC)$ 2085m; $\nu(PO)$ 1016s cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.71, 7.30, and 7.00, m, 20H, PPh_3+Ph; 4.68, d, *J*(HP) 1.2 Hz, 5H, C_5H_5; 3.42, d, *J*(HP) 11.2 Hz, 9H, $P(OMe)_3$. ^{13}C n.m.r. ($CDCl_3$): δ 139.3-127.4, m, PPh_3; 130.8, 127.7, and 123.2, s, Ph; 84.3, t, *J*(CP) 3 Hz, C_5H_5; 52.0, d, *J*(CP) 5 Hz, $P(OMe)_3$.

(*B*) A mixture of $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ (500 mg, 0.63 mmol) and $P(OMe)_3$ (400 mg, 3.22 mmol) was heated in refluxing decalin (30 ml) for 4 h. The cooled solution was chromatographed (alumina), the decalin and excess $P(OMe)_3$ being washed out with light petroleum. A yellow band was eluted with diethyl ether. Crystallization (light petroleum) gave yellow crystals of $Ru(C_2Ph)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (3.30) (245 mg, 75%), m.p. 70-72^0 (Found: C, 43.9; H, 5.6%; *M* (mass spectrometry), 516. $C_{19}H_{28}O_6P_2Ru$ requires C, 44.3; H, 5.5%; *M*, 516). Infrared (Nujol): ν(CC) 2083m; ν(PO) 1010m cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.11, m, 5H, Ph; 4.99, t, *J*(HP) 1.1 Hz, 5H, C_5H_5; 3.68, t, *J*(HP)* 11.7 Hz, 18H, $P(OMe)_3$. ^{13}C n.m.r. ($CDCl_3$): δ 130.9, 127.9, and 123.6, s, Ph; 83.6, t, *J*(CP) 3 Hz, C_5H_5; 52.3, s, $P(OMe)_3$.

* Separation of two outer peaks of A part of $A_9XX'A'_9$ system.

PREPARATION OF VINYLIDENE COMPLEXES FROM η^1-ALKYNYL COMPLEXES

From $Ru(C_2R)(PPh_3)_2(\eta\text{-}C_5H_5)$ $\{R = Ph, Me, Pr, CO_2Me, C_6H_4F\text{-}p,$ *or* $C_6F_5\}$

(A) $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$. — (i) *Method* E. Addition of HPF_6,OEt_2 (121 mg, 0.55 mmol) to $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (100 mg, 0.13 mmol) in dichloromethane (2 ml) gave a bright red solution. After stirring at room temperature for a brief period, the solution was filtered into diethyl ether (50 ml), to give a reddish tan *precipitate* of $\{Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (3.5a) (115 mg, 97%), identical with the products obtained by methods A or B above.

(ii) The tetrafluoroborate (3.5b) was obtained by method E, from $Ru(C_2Ph)(PPh_3$ $(\eta\text{-}C_5H_5)$ (100 mg, 0.25 mmol) and HBF_4,OEt_2 (100 mg, 1.14 mmol), as a reddish-tan *precipitate* (107 mg, 97%).

(iii) The trifluoroacetate salt (3.5d), which was not isolated, was formed by adding a drop of trifluoroacetic acid to a solution of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ in deuterochloroform, contained in an n.m.r. tube. The phenylvinylidene cation was identified spectroscopically. ^1H n.m.r. ($CDCl_3$): δ 7.21, m, 35H, PPh_3+Ph; 5.43, t, $J(HP)$ 2.5 Hz, 1H, =CH; 5.27, s, 5H, C_5H_5.

(iv) *Method* F. A mixture of $\{Me_3O\}PF_6$ (300 mg, 1.46 mmol) and $Ru(C_2Ph)(PPh_3)_2$-$(\eta\text{-}C_5H_5)$ (300 mg, 0.38 mmol) in dichloromethane (20 ml) was stirred at room temperature for 2 h. Filtration and addition of diethyl ether to the filtrate resulted in the crystallization of the complex $\{Ru(C{=}CMePh)(PPh_3)_2(\eta\text{-}C_5H_5)\}$-$PF_6,CH_2Cl_2$ (3.24) as red *flakes* of the dichloromethane solvate (335 mg, 93%), m.p. 205-210° (dec.) (Found: C, 59.0; H, 4.4; P, 8.7. $C_{50}H_{43}F_6P_3Ru,CH_2Cl_2$ requires C, 59.1; H, 4.4; P, 9.0%). Infrared (Nujol): $\nu(CC)$ 1687m, and 1665m; $\nu(PF)$ 840s cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.33, 7.25, 7.05, and 6.92, m, 35H, PPh_3+Ph; 5.30, s, 2H, CH_2Cl_2; 5.13, s, 5H, C_5H_5; 1.93, s, 3H, Me. ^{13}C n.m.r. ($CDCl_3$): δ 365.7, m, RuC; 134.6-128.8, m, PPh_3; 129.3, 128.0, and 125.5, s, Ph; 94.5, s, C_5H_5; 53.8, s, CH_2Cl_2; 12.6, s, Me. Conductivity (acetone): Λ_M 110 S cm^{-2} mol^{-1}.

(v) {Ru(C=CEtPh)(PPh$_3$)$_2$(η-C$_5$H$_5$)}PF$_6$ (3.25) was prepared by method F, from Ru(C$_2$Ph)(PPh$_3$)$_2$(η-C$_5$H$_5$) (100 mg, 0.13 mmol) and {Et$_3$O}PF$_6$ (50 mg, 0.2 mmol), as red *flakes* of the ½CH$_2$Cl$_2$ solvate (110 mg, 87%), m.p. 195-200^0 (Found: C, 60.8; H, 4.5. C$_{51}$H$_{45}$F$_6$P$_3$Ru,½CH$_2$Cl$_2$ requires C, 61.3; H, 4.6%). Infrared (Nujol): ν(CC) 1665m; ν(PF) 840s cm^{-1}. ^{1}H n.m.r. (CDCl$_3$): δ 7.34, 7.24, 7.02, and 6.92, m, PPh$_3$+Ph; 5.29, s, 1H, CH$_2$Cl$_2$; 5.09, s, C$_5$H$_5$; 2.26, q, J(HH) 7.5 Hz, 2H, CH$_2$; 0.90, t, J(HH) 7.5 Hz, 3H, Me. ^{13}C n.m.r. (CDCl$_3$): δ 134.6-128.8, m, PPh$_3$; 129.3, 128.3, 127.6, and 125.0, s, Ph; 94.4, s, C$_5$H$_5$; 53.8, s, CH$_2$Cl$_2$; 20.6, s, CH$_2$; 13.4, s, Me.

(B) *Ru(C$_2$Me)(PPh$_3$)$_2$(η-C$_5$H$_5$)*. - (i) {Ru(C=CHMe)(PPh$_3$)$_2$(η-C$_5$H$_5$)}PF$_6$ (3.6a), from Ru(C$_2$Me)(PPh$_3$)$_2$(η-C$_5$H$_5$) (40 mg, 0.06 mmol) and HPF$_6$,OEt$_2$ (12 mg, 0.05 mmol), was obtained as a reddish tan *powder* (35 mg, 73%).

(ii) The trifluoroacetate salt (3.6), which was not isolated, was formed by adding a drop of trifluoroacetic acid to a solution of Ru(C$_2$Me)(PPh$_3$)$_2$(η-C$_5$H$_5$) in deuterochloroform, contained in an n.m.r. tube. The methylvinylidene cation was identified spectroscopically. ^{1}H n.m.r. (CDCl$_3$): δ 7.36-7.04, m, 30H, PPh$_3$; 5.06, s, 5H, C$_5$H$_5$; 4.62, q of t, J(HH) 7.5 Hz, J(HP) 2.4 Hz, 1H, =CH; 1.86, d, J(HH) 7.5 Hz, 3H, Me. ^{13}C n.m.r. (CDCl$_3$): δ 349.4, t, J(CP) 17 Hz, RuC; 1340-128.5, m, PPh$_3$; 109.0, s, =CH; 94.1, s, C$_5$H$_5$; 5.3, s, Me.

(iii) {Ru(C=CMe$_2$)(PPh$_3$)$_2$(η-C$_5$H$_5$)}PF$_6$ (3.26) was prepared by method F, from Ru(C$_2$Me)(PPh$_3$)$_2$(η-C$_5$H$_5$) (500 mg, 0.69 mmol) and {Me$_3$O}PF$_6$ (400 mg, 1.94 mmol) as deep red *crystals* (from dichloromethane/diethyl ether) (410 mg, 67%), m.p. 202-207^0 (Found: C, 60.4; H, 4.6. C$_{45}$H$_{41}$F$_6$P$_3$Ru requires C, 60.7; H, 4.6%). Infrared (Nujol): ν(CC) 1678ms; ν(PF) 840s cm^{-1}. ^{1}H n.m.r. (CDCl$_3$): δ 7.48, m, 30H, PPh; 5.24, s, 5H, C$_5$H$_5$; 1.78, s, 6H, Me.

(C) *Ru(C$_2$Pr)(PPh$_3$)$_2$(η-C$_5$H$_5$)*. - (i) {Ru(C=CHPr)(PPh$_3$)$_2$(η-C$_5$H$_5$)}PF$_6$ (3.7a), by method E, from Ru(C$_2$Pr)(PPh$_3$)$_2$(η-C$_5$H$_5$) (40 mg, 0.05 mmol) and HPF$_6$,OEt$_2$ (15 mg, 0.07 mmol), was obtained as a tan *powder* (40 mg, 84%).

(ii) {Ru(C=CMePr)(PPh$_3$)$_2$(η-C$_5$H$_5$)}PF$_6$ (3.27), by method F, from Ru(C$_2$Pr)(PPh$_3$)$_2$-(η-C$_5$H$_5$) (750 mg, 0.99 mmol) and {Me$_3$O}PF$_6$ (400 mg, 1.94 mmol), formed deep red *crystals* (710 mg, 77%). m.p. 194-196^0 (Found: C, 60.7; H, 4.7. $C_{47}H_{45}F_6P_3Ru$ requires C, 61.5; H, 4.9%). Infrared (Nujol): ν(CC) 1678m; ν(PF) 840s cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.43, m, 30H, PPh_3; 5.19, s, 5H, C_5H_5; 1.77, s, 3H, Me; 1.97, and 0.93, m, 7H, Pr. ^{13}C n.m.r. ($CDCl_3$): δ 352.0, m, RuC; 135-128.4, m, PPh_3; 121.3, s, =C; 93.4, s, C_5H_5; 27.8, s, CH_2Me; 20.9, s, $=CCH_2$; 13.8, s, CH_2Me; 9.3, s, =CMe.

(*D*) $Ru(C_2CO_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)$. — (i) $\{Ru(C{=}CHCO_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (3.8a) was obtained by method E, from $Ru(C_2CO_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)$ (40 mg, 0.05 mmol) and HPF_6,OEt_2 (12 mg, 0.06 mmol), as a tan *powder* (45 mg, 94%). (ii) The trifluoroacetate (3.8d) was formed by adding trifluoroacetic acid to a solution of $Ru(C_2CO_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)$ in deuterochloroform, contained in an n.m.r. tube. The carbomethoxyvinylidene cation was identified spectroscopically. ^{1}H n.m.r. ($CDCl_3$): δ 7.40, and 7.27, m, 30H, PPh; 5.26, s, 5H, C_5H_5; 5.00, t, *J*(HP) 2 Hz, 1H, =CH; 3.47, s, 3H, OMe.

(*E*) $Ru(C_2C_6H_4F\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)$. — $\{Ru(C{=}CHC_6H_4F\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (3.9a) was obtained by method E, from $Ru(C_2C_6H_4F\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)$ (100 mg, 0.12 mmol) and HPF_6,OEt_2 (30 mg, 0.14 mmol), as a red brown *powder* (95 mg, 81%).

(*F*) $Ru(C_2C_6F_5)(PPh_3)_2(\eta\text{-}C_5H_5)$. — (i) $\{Ru(C{=}CHC_6F_5)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (3.10) as obtained by method E, from $Ru(C_2C_6F_5)(PPh_3)_2(\eta\text{-}C_5H_5)$ (100 mg, 0.11 mmol) and HPF_6,OEt_2 (30 mg, 0.14 mmol) as a red-brown *powder* (85 mg, 75%) (ii) $\{Ru(C{=}CMeC_6F_5)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (3.28), by method F, from $Ru(C_2C_6F_5)(PPh_3)_2(\eta\text{-}C_5H_5)$ (650 mg, 0.74 mmol) and $\{Me_3O\}PF_6$ (400 mg, 1.94 mmol), formed red flaky *crystals* (470 mg, 61%), m.p. 191-194^0 (Found: C, 59.3; H, 3.9 $C_{50}H_{38}F_{11}P_3Ru$ requires C, 57.6; H, 3.7%). Infrared (Nujol): ν(CC) 1638m; ν(PF) 834s cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.23, m, 30H, PPh; 5.30, s, 5H, C_5H_5; 1.98, s, 3H, Me.

From $Ru(C_2Ph)(L_2)(\eta\text{-}C_5H_5)$ $\{L_2 = \text{dppm or dppe}\}$

(A) $\{Ru(C{=}CHPh)(dppm)(\eta\text{-}C_5H_5)\}PF_6$ (3.11) was prepared by method E, from $Ru(C_2Ph)(dppm)(\eta\text{-}C_5H_5)$ (25 mg, 0.04 mmol) and HPF_6,OEt_2 (15 mg, 0.07 mmol), as a buff coloured *powder* (28 mg, 92%).

(*B*) $\{Ru(C{=}CHPh)(dppe)(\eta\text{-}C_5H_5)\}PF_6$ (3.12) was prepared by method E, from $Ru(C_2Ph)(dppe)(\eta\text{-}C_5H_5)$ (25 mg, 0.04 mmol) and HPF_6,OEt_2 (15 mg, 0.07 mmol), as a pale orange *powder* (24 mg, 79%).

From $Os(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$

$\{Os(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (3.13) was prepared by method E, from $Os(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (20 mg, 0.02 mmol) and HPF_6,OEt_2 (15 mg, 0.07 mmol), as a light purple *powder* (22 mg, 94%).

From $Ru(C_2Ph)(L)(L')(\eta\text{-}C_5H_5)$ $\{L = PPh_3,\ L = P(OMe)_3;\ L = L' = P(OMe)_3\}$

(*A*) Addition of HPF_6,OEt_2 (60 mg, 0.27 mmol) to $Ru(C_2Ph)(PPh_3)\{P(OMe)_3\}(\eta\text{-}C_5H_5)$ (100 mg, 0.15 mmol) in deuterochloroform (2 ml) gave an orange-red solution of $[Ru(C{=}CHPh)(PPh_3)\{P(OMe)_3\}(\eta\text{-}C_5H_5)]PF_6$ (3.31) which was not isolated but identified spectroscopically. ^1H n.m.r. (CDCl): δ 7.42. and 7.39, m, 15H, PPh_3; 7.05, and 6.98, m, 5H, Ph; 5.05, m, 5H, C_5H_5; 3.44, d, *J*(HP) 12 Hz, 9H, $P(OMe)_3$.

(*B*) Addition of HPF_6,OEt_2 (30 mg, 0.14 mmol) to $Ru(C_2Ph)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (50 mg, 0.10 mmol) in deuterochloroform (2 ml) gave an orange-red solution. The solution was filtered into diethyl ether (50 ml), to give a brown-red *precipitate* of $[Ru(C{=}CHPh)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]PF_6$ (3.32) (40 mg, 62%) (Found: C, 34.7; H, 4.5. $C_{19}H_{29}F_6O_6P_3Ru$ requires C, 34.5; H, 4.4%). Infrared (Nujol): ν(CC) 1660m; ν(PO) 1010s; ν(PF) 840v cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.04, m, 5H, Ph; 5.35, m, 5H, C_5H_5; 5.08, m, 1H, =CH; 3.68, m, 18H, $P(OMe)_3$.

(*C*) A mixture of $\{Me_3O\}PF_6$ (50 mg, 0.24 mmol) and $Ru(C_2Ph)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (50 mg, 0.10 mmol) in dichloromethane (20 ml) was stirred at room temperature for 2 h. Filtration and addition of diethyl ether to the filtrate resulted in the precipitation of the tan complex $[Ru(C{=}CMePh)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]PF_6$ (3.33) (45 mg, 67%) (Found: C, 35.2; H, 4.5. $C_{20}H_{31}F_6O_6P_3Ru$

requires C, 35.6; H, 4.6%). Infrared (Nujol): ν(CC) 1655m; ν(PO) 1010s; ν(PF) 840s. ^{1}H n.m.r. (CDCl$_3$): δ 7.29, m, 5H, Ph; 5.72, m, 5H, C_5H_5; 3.67, t, J(HP)* 11 Hz, 18H, $P(OMe)_3$; 2.20, s, 3H, Me.

* Separation of two outer peaks of A part of $A_9XX'A'_9$ system

Reversibility of the Protonation Reaction of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$

A solution of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.25 mmol) and HPF_6,OEt_2 (100 mg, 0.45 mmol) in deuterochloroform (2 ml) was added to a solution of sodium methoxide (10 ml of a o.1 *M* solution in methanol). The dark red colour of the phenyvinylidene cation was dissipated, and the yellow crystals that were rapidly deposited were recrystallized (dichloromethane/methanol) to give pure $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (195 mg, 98%), m.p. 202-205° (dec.).

The complexes $Ru(C_2R)(PPh_3)_2(\eta\text{-}C_5H_5)$ {R = Me, Pr, CO_2Me, C_6H_4F-*p* or C_6F_5}, $Ru(C_2Ph)(L_2)(\eta\text{-}C_5H_5)$ {L_2 = dppm or dppe} and $Os(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ were similarly treated with HPF_6,OEt_2. Addition to a solution of sodium methoxide in methanol afforded the alkynyl complexes in high yields.

All protonation reactions, monitored by ^{1}H n.m.r. spectroscopy, showed that conversion of the alkynyl complex to the vinylidene complex (as evidenced by the characteristic C_5H_5 singlet) was quantitative after the addition of the hexafluorophosphoric acid.

PREPARATION OF A CYCLIC CARBENE COMPLEX

Reaction between $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and 4-Hydroxypent-1-yne

A mixture of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (500 mg, 0.69 mmol), NH_4PF_6 (150 mg, 0.78 mmol) and 4-hydroxypent-1-yne (60 mg, 0.71 mmol) was heated in refluxing methanol (40 ml) for 1 h. Filtration, evaporation and crystallization (chloroform/light petroleum) afforded pale yellow *crystals* of $[Ru\{\overline{C(CH_2)_2CHMeO}\}(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ (3.34) (550 mg, 87%), m.p. 232-235° (Found: C, 59.6; H, 4.9. $C_{46}H_{43}F_6OP_3Ru$ requires C, 60.1; H, 4.7%). Infrared (Nujol): $\nu(CO)$ 1219s, 1198s, and 1179s; $\nu(PF)$ 837vs cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.37, 7.29, 7.15, and 7.03, m, PPh_3; 4.83, s, 5H, C_5H_5; 4.07, m, 1H, C(3)H; 4.07, and 3.40, m, 2H, $C(5)H_2$; 2.06, and 1.40, m, 2H, $C(4)H_2$; 0.85, d, $J(HH)$ 6.4 Hz, 3H, Me. ^{13}C n.m.r. ($CDCl_3$): δ 299.4, t, $J(CP)$ 14 Hz, RuC; 135.6-128.4, m, PPh_3; 92.4, s, C(3); 91.2, s, C_5H_5; 61.7, s, C(5); 30.1, s, C(4); 19.0, s, Me.

Deuteration of $[Ru\{\overline{C(CH_2)_2CHMeO}\}(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ (3.34)

Complex (3.34) (300 mg, 0.33 mmol) was dissolved in dry pyridine (25 ml), and deuterium oxide (0.5 ml) was added. After 1 h. at 70-80°, the solution was cooled to room temperature, dry diethyl ether (100 ml) was added, and trituration of the resulting oil caused it to solidify. Filtration, washing with diethyl ether until pyridine was completely removed, and drying (0.01 mm) afforded the yellow deuterated complex $[Ru\{\overline{C(CD_2)CH_2CHMeO}\}(PPh_3)_2(\eta\text{-}C_5H_5)]$-$PF_6$ (3.36) (230 mg, 77%), m.p. 212-214°, identified from its n.m.r. spectra. ^1H n.m.r. ($CDCl_3$): δ 7.37, 7.29, 7.15, and 7.03, m, 30H, PPh_3; 4.83, s, 5H, C_5H_5; 4.07, m, 1H, C(3)H; 2.06, and 1.40, m, 2H, $C(4)H_2$; 0.85, d, $J(HH)$ 6.4 Hz, 3H, Me. ^{13}C n.m.r. ($CDCl_3$): δ 299.9, m, RuC; 135.5-128.4, m, PPh_3; 92.6, s, C(3), 91.2, s, C_5H_5; 30.0, s, C(4); 19.2, s, Me.

Preparation of $Ru\{C_2CH_2CHMeO(thp)\}(PPh_3)_2(\eta\text{-}C_5H_5)$ *(3.35)*

A mixture of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (335 mg, 0.46 mmol) and the tetrahydropyranyl derivative of 4-hydroxypent-1-yne (100 mg, 0.6 mmol) was heated in refluxing methanol (25 ml) for 30 min. Concentration and addition of sodium methoxide (1 ml of a 1 *M* solution in methanol) gave yellow *crystals* of $Ru\{C_2CH_2CHMeOCH(CH_2)_4O\}(PPh_3)_2(\eta\text{-}C_5H_5)$ (3.35) (120 mg, 30%) (Found: C, 71.1; H, 5.8%; *M* (mass spectrometry), 858. $C_{51}H_{50}O_2F_2Ru$ requires C, 71.4; H, 5.9%; *M*, 858). ^1H n.m.r. ($CDCl_3$): δ 7.47, and 7.15, m, 30H, PPh_3; 4.69, m, 1H, OCHO; 4.22, s, 5H, C_5H_5; 3.75, m, 3H, OCH_2+CHMe; 1.56-1.11, m, 9H, $\equiv CCH_2$, $CHCH_2CH_2$, and Me.

Protonation of Complex (3.35)

Addition of HPF_6,OEt_2 (20 mg, 0.09 mmol) to the tetrahydropyranyl complex (3.35) (50 mg, 0.06 mmol) in chloroform (2 ml) gave a yellow-orange solution. After stirring at room temperature for 2 min. the solution was filtered into diethyl ether (50 ml), to give a yellow *precipitate* of complex (3.34) (50 mg, 93%), shown to be identical with the product obtained from the reaction of 4-hydroxypent-1-yne with $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$.

Reaction between $\{Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ *and Dioxygen*

The complex $\{Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (500 mg, 0.53 mmol) was dissolved in deuterochloroform (3 ml). Dioxygen was bubbled through the solution, at room temperature, for a period of 60 min. Examination of the ^1H n.m.r. spectrum showed that conversion of the vinylidene complex to another product(s) (as evidenced by the characteristic C_5H_5 singlet) was quantitative after this period of time. The deuterochloroform solution was extracted with aqueous sodium bicarbonate, the aqueous layer neutralized with hydrochloric acid and then extracted with diethyl ether. The diethyl ether extract was evaporated to dryness to give white *crystals* of benzoic acid (50 mg, 77%), m.p. 120-121° (Found: *M*-17 (mass spectrometry), 105. $C_7H_6O_2$ requires *M*-17, 105) {Authentic sample of benzoic acid: m.p. 122°; *M*-17, 105}. The deuterochloroform layer was added dropwise to stirred diethyl ether (50 ml) to precipitate a light yellow *powder* of the carbonyl complex $\{Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ (3.37) (430 mg, 93%), m.p. 236-240° (Found: C, 58.1, H, 4.0; P, 10.5. $C_{42}H_{35}F_6OP_3Ru$ requires C, 58.4; H, 4.1; P, 10.8). Infrared (Nujol): $\nu(CO)$ 1984s; $\nu(PF)$ 840s cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.37, 7.30, 7.19, and 7.07, m, 30H, PPh_3; 4.97, s, 5H, C_5H_5. ^{13}C n.m.r. ($CDCl_3$): δ 203.2, s, CO; 135-129.1, m, PPh_3; 91.0, s, C_5H_5.

CHAPTER 4

CYCLOPENTADIENYL-RUTHENIUM AND -OSMIUM CHEMISTRY.

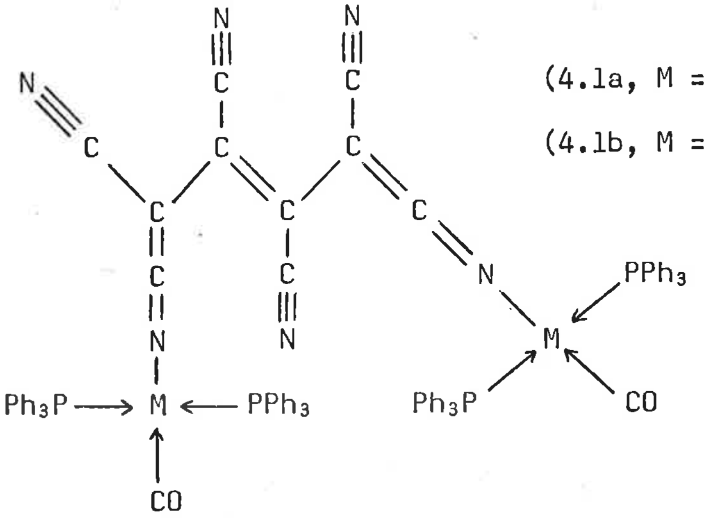
COMPLEXES CONTAINING CYANOCARBON AND CYANONITROGEN LIGANDS

Introduction

Replacement of H by F in transition metal σ-alkyls increases thermal stability, and decreases the M-C bond length;[125] experimental ESCA shifts of $Mn(CH_3)(CO)_5$ and $Mn(CF_3)(CO)_5$ show that the electron density at the C atom is considerably higher in the CH_3 than in the CF_3 compound.[126] Calculations on a series of $Mn(CO)_5$ compounds using an extended CNDO formalism support observations that electron-withdrawing groups decrease reaction rates.[127] The experimental observations are not limited to σ-bonded groups; transition metal complexes containing olefins, dienes, and arenes bearing electron-withdrawing groups, and particularly those containing polysubstituted ligands, show significant differences in structure and reactivity from their hydrocarbon analogues.

The most commonly studied compounds have F or CF_3 groups in place of H in the ligands; a growing number of reports are concerned with poly-CO_2Me-substituted ligands, often derived from $C_2(CO_2Me)_2$, and with ligands containing several cyano groups. Both substituents can conjugate with unsaturated centres also present in the ligand, facilitating electron delocalisation. Many studies of tricyanomethanide, $C(CN)_3$, and tetracyanoethylene, $C_2(CN)_4$, complexes have appeared.[128,129] Without detailing all papers concerned with cyanocarbon-transition metal chemistry, it is nevertheless pertinent to note King's studies of the reactions of chlorocyanocarbons with metal carbonyl anions, which have given polycyanovinyl complexes, and via subsequent reactions and transformations, derivatives containing dicyanomethylene and dicyanovinyldene ligands;[87] various cyano-alkyl complexes obtained by insertion of tetracyanoethylene into M-H or M-C bonds,[130] and also by oxidative addition of chloroacetonitrile and related compounds to suitable electron-rich transition metal complexes;[131] and the work of Köhler and coworkers on the preparation of simple salts containing many simple substituted cyanocarbon, cyanonitrogen and related pseudo-halide ions.[132]

Ligands containing more than two carbons bearing cyano-substituents are rare. Reactions of $MCl(CO)(PPh_3)_2$ {M = Rh or Ir} with the tetracyanoethylene radical anion gives $\{M(CO)(PPh_3)_2\}_2C_4(CN)_6$ (4.1), containing a μ-$(NC)_2CC(CN)C(CN)C(CN)_2$ ligand,[133 134] while pentacyanobutadienyl complexes were obtained from several metal carbonyl anions and $ClC(CN)=C(CN)C(CN)=C(CN)_2$.[135]



(4.1a, M = Rh)

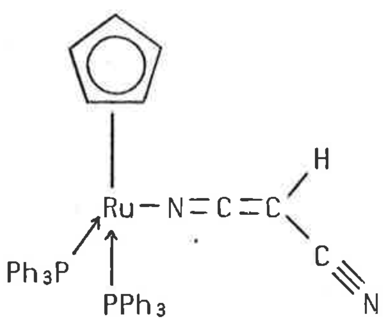
(4.1b, M = Ir)

Complexes containing poly-cyano cyclic ligands appear to be limited to the complexes of $C_5H_{5-n}(CN)_n^-$ {n = 1, 2, 3 and 5} with manganese, rhenium and the silver and iron derivatives of pentacyanocyclopentadienide, $\{C_5(CN)_5\}^-$, obtained by Webster.[137] The iron(II) complex, decacyanoferrocene, is an insoluble brown solid, thought to be polymeric via bridging CN groups.

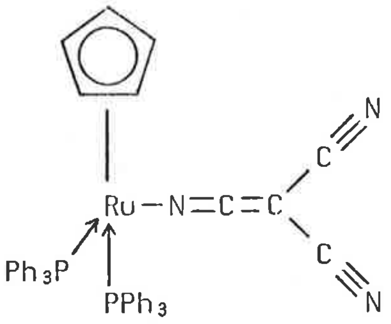
Cyanocarbon acids are among the strongest organic acids, and the original paper describing these intriguing compounds report the preparation of several simple salts of these anions with transition metal cations.[138] However, we are not aware of any compounds containing these anions and organometallic residues, and we have commenced a study of these derivatives with a survey of some reactions with the versatile complex $RuCl(PPh_3)_2$-$(\eta$-$C_5H_5)$.[139] The resulting complexes, together with some related derivatives containing smaller cyanocarbon and cyanonitrogen ligands, and the crystal and molecular structure of $Ru\{C_3(CN)_5\}\{P(OMe)_3\}(PPh_3)_2(\eta$-$C_5H_5)$, are described.

Results

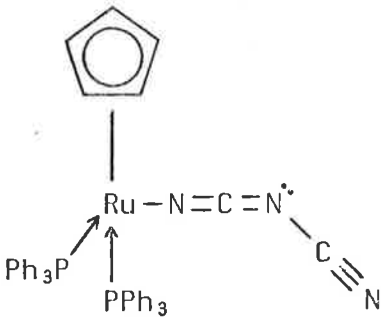
We have described previously the cationic complexes {Ru(MeCN)$(PPh_3)_2$-(η-C_5H_5)}PF_6 and {Ru($NCCH_2CN$)$(PPh_3)_2$(η-C_5H_5)}PF_6, obtained directly from RuCl$(PPh_3)_2$(η-C_5H_5) and the nitrile in the presence of NH_4PF_6.[31] The latter complex is readily deprotonated by strong bases, such as $KOBu^t$, to give the neutral dicyanomethanide complex (4.2). This forms as orange yellow crystals, and is also obtained directly from $NaCH(CN)_2$ and RuCl$(PPh_3)_2$(η-C_5H_5). Yellow crystals of the tricyanomethanide (4.3) and dicyanamide (4.4) complexes were similarly prepared from $KC(CN)_3$ or $NaN(CN)_2$. These complexes were characterised by elemental analyses and spectroscopic methods, although the cyanocarbon ligand was only detected by the characteristic ν(CN) bonds around 2200 cm^{-1} in the infrared spectra.



(4.2)

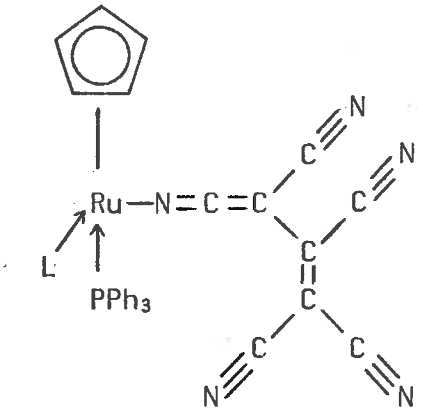


(4.3)

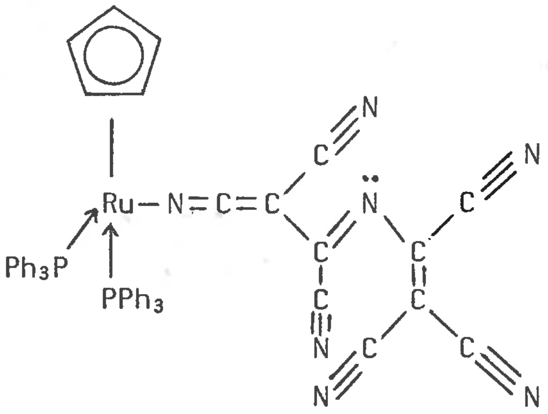


(4.4)

Reactions between RuCl$(PPh_3)_2$(η-C_5H_5) and other cyanocarbon anions such as 1,1,2,3,3-pentacyanopropenide and 1,1,2,4,5,5-hexacyanoazapentadienide afforded the intensely red Ru{$C_3(CN)_5$}$(PPh_3)_2$(η-C_5H_5) (4.5a) and deep purple Ru[N{$C_2(CN)_3$}$_2$]$(PPh_3)_2$(η-C_5H_5) (4.6) complexes. The identity of these complexes was again deduced from the manner of synthesis, elemental analyses, and the presence of ν(CN) bonds in the infrared spectra. We were unable to identify any ^{13}C n.m.r. resonances which might be assigned to the cyanocarbon ligands, in spite of long accumulation times, delayed pulse techniques, or the addition of a variety of paramagnetic relaxation reagents. This contrasts with the results obtained for a series of carbon-bonded derivatives, where resonances in the region 100-120 ppm were observed.[140]



(4.5a, L = PPh_3)
(4.5b, L = $P\{OMe\}_3$)



(4.6)

Finally, orange crystals of the binuclear complex $\{Ru(PPh_3)_2(\eta\text{-}C_5H_5)\}_2\text{-}(C_2N_{10})$ (4.7), were obtained from the chloro complex and sodium azotetrazolate; the precise structure of this complex has not yet been determined. There are no distinctive features in the infrared spectrum, and the ^1H and ^{13}C n.m.r. spectra contain only resonances arising from the C_5H_5 and PPh_3 ligands.

Many organometallic complexes containing cyanocarbon ligands have been shown to contain the ligand attached via the nitrogen of a cyano group; the ligand thus assumes the keteniminato resonance forms. Structurally characterised examples include $Ir\{N{=}C{=}C(CN)CH(CN)_2\}(tcne)(CO)(PPh_3)$,[141] and the hexacyanobutenediide-rhodium complex mentioned above.[134] In several cases, it has been possible to deduce the presence of the N-bonded form of the ligand by the characteristic $\nu(CN)$ bonds which appear between c. 2050-2150 cm^{-1} rather than at the higher frequency of c. 2250 cm^{-1} usually associated with the CN group. Similar structures have been found for complexes obtained from insertion reactions of tetracyanoethylene into metal-carbon bonds, although the products from carbonylmetal anions and chlorocyanoethylenes contain carbon-bonded cyanocarbon ligands.

In the spectra of complexes (4.2)-(4.6), ν(CN) bands occur in the range 2266-2137 cm^{-1}; no well-defined separation of bands which could be due to cyano groups and keteniminato fragments was found, although in the best spectra some fine structure was observed in the ν(CN) bands. Since no examples of metal complexes of the $C_3(CN)_5$ ligand have been described, we decided to determine the structure of the pentacyanopropenide complex to further clarify the mode of attachment of the cyanocarbon ligand. In the event, no suitable crystals of (4.5a) were obtained, but simple exchange of one PPh_3 ligand for $P(OMe)_3$ in decalin afforded $Ru\{C_3(CN)_5\}\{P(OMe)_3\}(PPh_3)(\eta\text{-}C_5H_5)$ (4.5b) whose structure was readily determined by X-ray diffraction methods.

Coordination about ruthenium The structure determination confirms that the pentacyanopropenide group is N-bonded to ruthenium, that is, as the cyano-(tricyanovinyl) keteniminato ligand. Other ligands attached to ruthenium are the η^5-cyclopentadienyl ring, with Ru-Cp distances 2.160(12)-2.236(6) Å, the triphenylphosphine ligand, with Ru-P(1) distance 2.322(2) Å and the trimethyl phosphite ligand, with a Ru-P(2) distance 2.239(2) Å. The angles at ruthenium accord with the more or less distorted octahedral coordination found for other complexes containing the $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$ moiety {e.g. P(1)-Ru-P(2) 91.2(1)°; P(1)-Ru-N(411), 90.1(1)°; P(2)-Ru-N(411), 90.1(1)°}, with the $\eta\text{-}C_5H_5$ group formally occupying three coordination positions.

The triphenylphosphine ligand The Ru-P(1) distance is similar to that found in $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ {2.335(1) Å}.[30] The ligand geometry is also similar to that found in other metal-PPh_3 complexes, with distorted tetrahedral geometry at phosphorus {e.g. C(111)-P(1)-Ru, 112.4(2)°; C(112)-P(1)-Ru, 115.1(2)°; C(113)-P(1)-Ru, 119.9(1)°}, and the slightly opened intra-ring angle at the phenyl carbon which is attached to phosphorus.

The trimethylphosphite ligand Again, the Ru-P(2) distance is close to that found in $\overline{Ru\{NH{=}C(CF_3)N{=}C(CF_3)NH}\}\{P(OMe)_3\}(\eta\text{-}C_5H_5)$ (2.17) {2.219(2) Å}, with other bond parameters also similar.[67]

The cyclopentadienyl ligand Although the C_5 ring is a regular pentagon within experimental error, there is some evidence for differing *trans* influences of the various ligands present as shown by the Ru-Cp distances, e.g. Ru-C(7) 2.236(6) Å, approximately *trans* to P(1); Ru-C(9) 2.160(12) Å, approximately *trans* to N. This is the trend expected if the cyanocarbon ligand is a better π-donor than the P-donor ligands and this phenomenon is also present in $\overline{Ru\{NH{=}C(CF_3)N{=}C(CF_3)NH\}}\{P(OMe)_3\}(\eta\text{-}C_5H_5)\}$.[67]

The $C_3(CN)_5$ ligand The Ru-N distance {2.032(5) Å} is close to that found in complex (2.17), and the bond distances in the ketenimine fragment {C-N, 1.142(9) C-C, 1.423(10) Å} confirm the multiple order of these bonds. The uncoordinated C-N bonds are between 1.106(11) and 1.152(14) Å, with bond angles at the cyano carbon of between 169.3(1.1) and 179.1(9)°, both parameters indicating that these are normal cyano groups. These are attached to the carbon skeleton with C-N distances which are scattered between 1.385(12) and 1.512(13) Å. The C(41)-C(42)-C(43) system shows evidence for considerable multiple bonding between those carbons, with C-C separations of 1.330(10) and 1.366(9) Å.

The overall configuration of complex (4.5b) is shown in Figure 4.I, and important bond distances and angles are listed in Table 4.I.* The crystal structure consists of monomeric molecules, of which one forms the asymmetric unit.

**Data by B. W. Skelton and A. H. White*

Figure 4.I

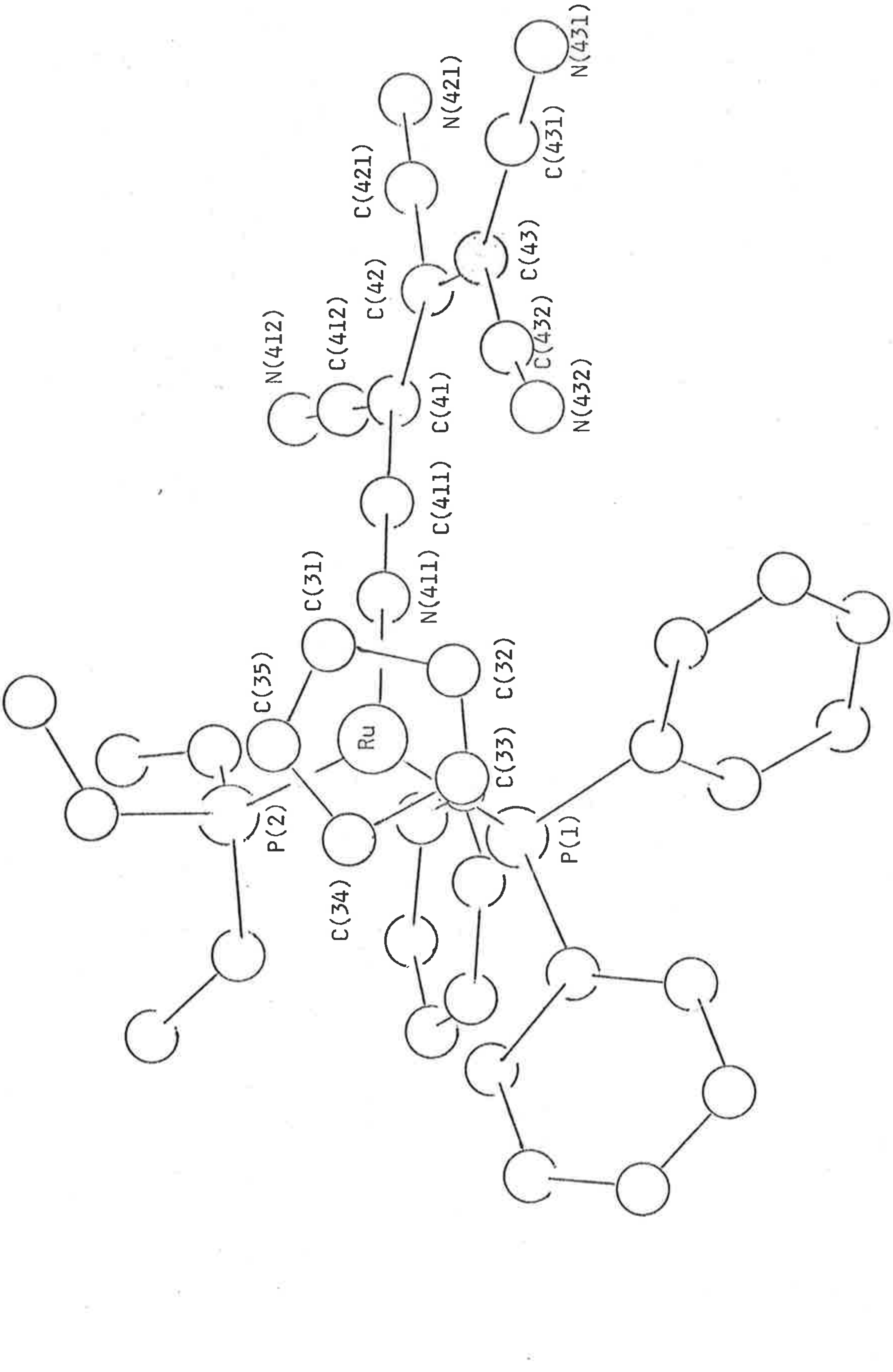

N(431)
N(421)
C(431)
C(421)
C(43)
C(42)
C(432)
N(412)
C(412)
C(41)
N(432)
C(411)
N(411)
C(31)
C(35)
C(32)
Ru
C(33)
P(2)
P(1)
C(34)

Table 4.I

Interatomic distances (Å) and bond angles (°)

Ruthenium geometry

Distances

Ru-P(1)	2.322(2)
Ru-P(2)	2.239(2)
Ru-C(31)	2.220(8)
Ru-C(32)	2.236(6)
Ru-C(33)	-
Ru-C(34)	2.160(12)
Ru-C(35)	-
Ru-N(411)	2.032(5)

Angles

P(1)-Ru-P(2)	91.2(1)
P(1)-Ru-N(411)	90.1(1)
P(2)-Ru-N(411)	90.1(1)

Triphenylphosphine ligand non-hydrogen geometry

	Ring 1	Ring 2	Ring 3
Distances			
P(1)-C(11)	1.831(6)	1.831(6)	1.838(5)
C(11)-C(12)	1.371(7)	1.380(7)	1.376(8)
C(12)-C(13)	1.396(10)	1.379(9)	1.389(9)
C(13)-C(14)	1.366(12)	1.383(9)	1.385(12)
C(14)-C(15)	1.370(8)	1.360(9)	1.358(10)
C(15)-C(16)	1.389(10)	1.390(10)	1.390(9)
C(16)-C(11)	1.402(10)	1.377(8)	1.384(10)
Angles			
Ru-P(1)-C(11)	112.4(2)	115.1(2)	119.9(1)
P(1)-C(11)-C(12)	122.8(5)	120.5(4)	124.1(5)
P(1)-C(11)-C(16)	118.6(3)	121.3(4)	117.4(4)
C(12)-C(11)-C(16)	118.6(6)	118.2(6)	118.5(5)
C(11)-C(12)-C(13)	121.0(7)	120.8(5)	121.2(7)
C(12)-C(13)-C(14)	119.8(5)	120.0(5)	119.4(6)
C(13)-C(14)-C(15)	120.2(7)	120.0(7)	119.8(6)
C(14)-C(15)-C(16)	120.5(8)	119.6(6)	120.7(7)
C(15)-C(16)-C(11)	119.8(5)	121.4(5)	120.3(6)

Other angles

C(111)-P(1)-C(112), 103.2(2); C(112)-P(1)-C(113), 100.4(3);
C(113)-P(1)-C(111), 103.8(2).

Table 4.I (cont.)

Interatomic distances (Å) and bond angles (°)

Trimethylphosphite ligand non-hydrogen geometry

Distances

P(2)-O(21)	1.595(4)
P(2)-O(22)	1.570(6)
P(2)-O(23)	1.583(4)
O(21)-C(21)	1.437(8)
O(22)-C(22)	1.429(8)
O(23)-C(23)	1.435(7)

Angles

Ru-P(2)-O(21)	119.4(2)
Ru-P(2)-O(22)	113.4(2)
Ru-P(2)-O(23)	111.5(1)
O(21)-P(2)-O(22)	104.2(2)
O(21)-P(2)-O(23)	98.0(2)
O(22)-P(2)-O(23)	108.9(2)
P(2)-O(21)-C(21)	120.5(5)
P(2)-O(22)-C(22)	129.6(6)
P(2)-O(23)-C(23)	126.4(4)

Cyclopentadienide ligand non-hydrogen geometry

Distances

C(31)-C(32)	1.401(9)
C(32)-C(33)	1.366(12)
C(33)-C(34)	1.356(12)
C(34)-C(35)	1.342(11)
C(35)-C(31)	1.348(13)

Angles

C(35)-C(31)-C(32)	107.9(7)
C(31)-C(32)-C(33)	106.1(7)
C(32)-C(33)-C(34)	108.4(6)
C(33)-C(34)-C(35)	109.0(8)
C(34)-C(35)-C(31)	108.5(7)

Table 4.1 (cont.)

Interatomic distances (Å) and bond angles (°)

Pentacyanopropenyl ligand non-hydrogen geometry

Distances

C(41)-C(42)	1.366(9)
C(41)-C(411)	1.424(10)
C(41)-C(412)	1.423(9)
C(411)-N(411)	1.142(9)
C(412)-N(412)	1.112(10)
C(42)-C(43)	1.331(10)
C(42)-C(421)	1.511(13)
C(421)-N(411)	1.152(14)
C(43)-C(431)	1.477(12)
C(43)-C(432)	1.335(12)
C(431)-N(431)	1.106(11)
C(432)-N(432)	1.111(11)

Angles

Ru-N(411)-C(411)	176.3(4)
N(411)-C(411)-C(41)	178.5(5)
C(411)-C(41)-C(42)	123.3(6)
C(411)-C(41)-C(412)	116.1(5)
C(42)-C(41)-C(412)	120.6(7)
C(41)-C(42)-C(43)	131.2(8)
C(41)-C(42)-C(421)	115.3(6)
C(43)-C(42)-C(421)	113.5(7)
C(42)-C(421)-N(421)	177.2(9)
C(42)-C(43)-C(431)	120.6(8)
C(42)-C(43)-C(432)	121.9(7)
C(431)-C(43)-C(432)	117.5(7)
C(43)-C(431)-N(431)	169.3(11)
C(43)-C(432)-N(432)	174.3(8)

Discussion

This chapter describes the reactions of several cyanocarbon and cyanonitrogen anions with the complex $RuCl(PPh_3)_2(\eta-C_5H_5)$, in which the chloride is exchanged for the cyano-substituted group, to give the neutral complexes $Ru(R_{CN})(PPh_3)_2(\eta-C_5H_5)$ {(4.2)-(4.6)}. In complexes (4.5) and (4.6), where the organocarbon system is extended, the colours are respectively deep red and deep purple, in accord with the considerable electron delocalisation expected in the cyanocarbon ligands. Other derivatives have the usual yellow colour characteristic of $RuX(PR_3)_2(\eta-C_5H_5)$ complexes.

The structure of these complexes is of interest, since, as mentioned in the introduction to this chapter, examples of both C- and N-bonded cyanocarbon ligands have been described. The $C_3(CN)_5$ ligand in complex (4.5b) is N-bonded through one of the cyano groups attached to a terminal carbon of the propenyl system, that is, as a cyano(tricyanovinyl)ketenimine ligand. Discussion of this structure is facilitated by comparison with those of complex (4.1), and potassium *cis*-hexacyanobutenediide, $K_2(hcbd)$.[142] Although the pentacyanopropenide ion has been structurally characterised in $\{Fe(CO)_2(PPh_3)(\eta-C_5H_5)\}\{C_3(CN)_5\}$, disorder problems prevented an accurate measurement of the bond parameters in the isolated $\{C_3(CN)_5\}^-$ anion.[143] The formal valence bond representations of these cyanocarbon derivatives are shown in Figure 4.II, together with diagrams incorporating significant bond parameters.

Figure 4.II

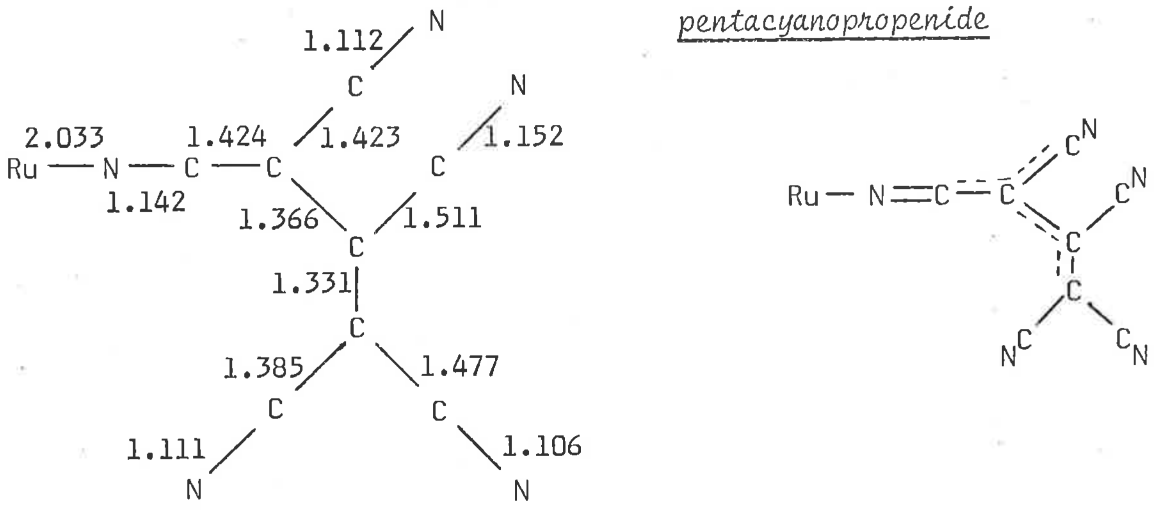
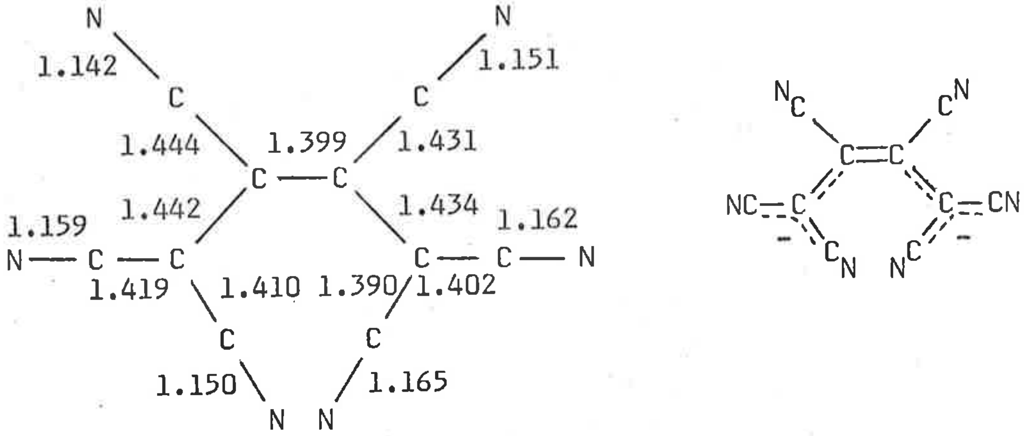
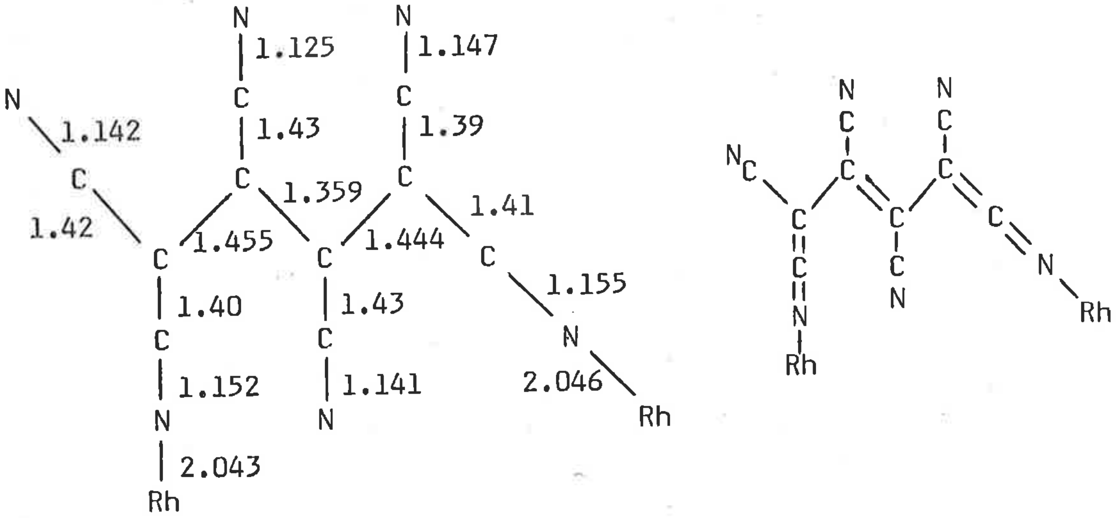

pentacyanopropenide

Figure 4.II (cont)



cis-hexacyanobutenediide [142]



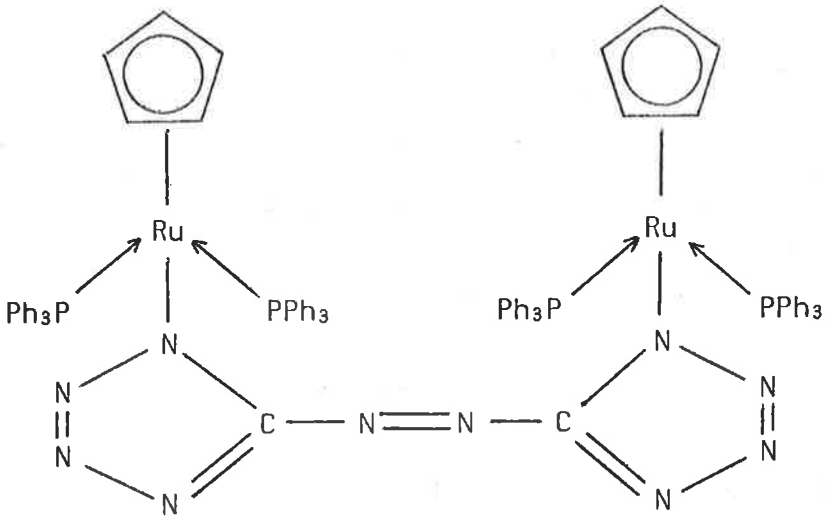
trans-hexacyanobutenediide [134]

The C-CN and C-N bonds of coordinated and uncoordinated cyano groups do not differ significantly; the short Ru-N bond probably reflects a degree of π-bonding to the metal, keteniminato groups being considered to be good π-donors. In complex (4.1), the average Rh-N distance is 2.044(7) Å.

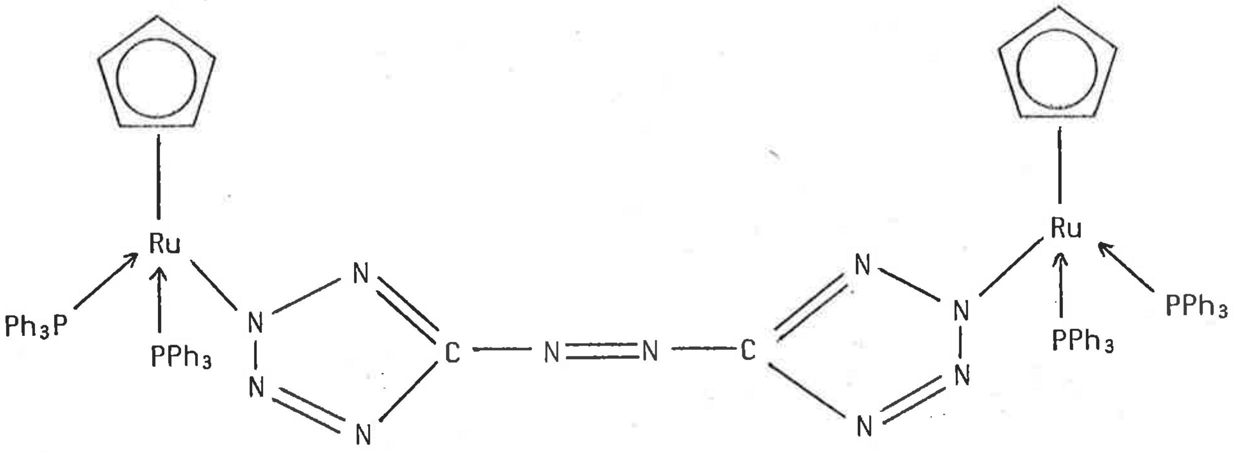
In the hcbd dianion, as in complex (4.1), the 'single' bonds are shorter than those normally found in conjugated systems, while the central C=C double bond in (4.1) is similar to that found in tetracyanoethylene {cubic, 1.344(3);[144] monoclinic, 1.339(9) Å[145]}. That in the hcbd dianion is considerably longer, at 1.399(9) Å, and is in accord with the extensive delocalisation predicted by extended Huckel calculations. In (4.5b), the bond distances within the carbon skeleton suggest a considerable degree of delocalisation over the three carbons, and the slight opening of this system {angle C(41)-C(42)-C(43) 131.2(8)°} supports this tendency to formation of an allenic group.

The results of this structural determination suggest that the degree of conjugation in the cyanocarbon ligand is intermediate between the fully delocalised allylic system, and the formal $(NC)_2C{=}C(CN)C^-(CN)_2$ arrangement. Comparison of the three structures discussed above suggests that delocalisation of charge occurs largely over the dicyanomethylene and carbon skeleton; attachment of a metal atom to one of the terminal cyano nitrogens results in little modification of the system, with the exception of a slight lengthening of the C=C double bond which is conjugated with the M-N=C=C group.

A binuclear complex (4.7) was obtained from the reaction between $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and disodium azotetrazolate, and crystallised as the dichloromethane solvate. Firm conclusions about the structure of (4.7) cannot be drawn at this stage, although a C-bonded ligand would seem to be ruled out on steric grounds; bonding of the metal to one of the ring nitrogens as in (4.7a) or (4.7b) is an obvious alternative.


Ru
Ph3P
PPh3
N
N
N
N
C
N
N
C
N
N
N
N
Ru
Ph3P
PPh3

(4.7a)


Ru
Ph3P
PPh3
N
N
N
N
C
N
N
C
N
N
N
N
Ru
PPh3
PPh3

(4.7b)

EXPERIMENTAL

General experimental conditions are described in Appendix I. Cyanocarbon derivatives were prepared as described in the literature: $NMe_4\{C_3(CN)_5\}$,[138] $NEt_4[N\{C(CN)=C(CN)_2\}_2]$;[138] sodium dicyanamide was purchased from the Aldrich Chemical Company; sodium azotetrazolate from the Department of Inorganic Chemistry, The University of Bristol.

PREPARATION OF CYANOCARBON AND CYANONITROGEN COMPLEXES

From $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$

(A) *Sodium dicyanomethanide,* $NaCH(CN)_2$. — A mixture of sodium dicyanomethanide {prepared *in situ* from malonitrile (33 mg, 0.5 mmol) and sodium (12 mg, 0.5 mmol) in ethanol (40 ml) at 0°} and $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (363 mg, 0.5 mmol) was stirred at room temperature (15h). Removal of solvent and recrystallization of the residue from dichloromethane/diethyl ether gave orange *crystals* of $Ru\{N=C=CH(CN)\}(PPh_3)_2(\eta\text{-}C_5H_5)$ (4.2) (260 mg, 69%), m.p. >110° (dec.) (Found: C, 69.4; H, 4.9; N, 3.9. $C_{44}H_{36}N_2P_2Ru$ requires C, 69.9; H, 4.8; N, 3.7%). Infrared (Nujol): ν(CN) 2231vw, 2161(sh), 2137s cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.24, m, 30H, PPh_3; 4.24, s, 5H, C_5H_5.

(B) *Potassium tricyanomethanide,* $KC(CN)_3$. — A mixture of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (726 mg, 1.0 mmol) and potassium tricyanomethanide (130 mg, 1.0 mmol) was heated in refluxing methanol (40 ml) for 3h. On cooling, fine yellow crystals deposited. Recrystallization (dichloromethane/diethyl ether) afforded yellow *crystals* of the dichloromethane solvate of $Ru\{N=C=C(CN)_2\}(PPh_3)_2(\eta\text{-}C_5H_5)$ (4.3) (680 mg, 79%), m.p. 207-210° (Found: C, 64.1; H, 4.4; N, 5.1; P, 7.3. $C_{45}H_{35}N_3P_2Ru,CH_2Cl_2$ requires C, 63.8; H, 4.3; N, 4.9; P, 7.2%). Infrared (Nujol): ν(CN) 2175vs cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.30, m, and 7.21, m, 30H, PPh_3; 5.30, s, 2H, CH_2Cl_2; 4.29, s, 5H, C_5H_5. ^{13}C N.M.R. ($CDCl_3$): δ 136.4-128.5, m, PPh_3; 82.8, s, C_5H_5; 53.5, s, CH_2Cl_2.

(C) *Sodium dicyanamide*, $NaN(CN)_2$. — A similar reaction to (B) used $\mathrm{RuCl(PPh_3)_2(\eta\text{-}C_5H_5)}$ (726 mg, 1 mmol) and sodium dicyanamide (89 mg, 1.0 mmol) in refluxing 1,2-dimethoxyethane (60 ml) for 14 h. The turbid yellow-brown solution was filtered and evaporated and the residue was chromatographed on alumina, a yellow band being eluted with dichloromethane. Crystallization (dichloromethane/methanol) gave yellow *crystals* of $\mathrm{Ru\{N{=}C{=}N(CN)\}(PPh_3)_2\text{-}(\eta\text{-}C_5H_5)}$ (4.4) (150 mg, 20%), m.p. 160^0 (dec.) (Found: C, 67.4; H, 4.7; N, 5.3. $\mathrm{C_{43}H_{35}N_3P_2Ru}$ requires C, 68.3; H, 4.7; N, 5.6%). Infrared (Nujol): ν(CN) 2266m, 2228m, 2161s cm^{-1}. ^{1}H n.m.r. ($\mathrm{CDCl_3}$): δ 7.23, m, 30H, $\mathrm{PPh_3}$; 4.20, s, 5H, $\mathrm{C_5H_5}$. ^{13}C n.m.r. ($\mathrm{CDCl_3}$): δ 137.0-128.2, m, $\mathrm{PPh_3}$; 82.0, s, $\mathrm{C_5H_5}$.

(D) *Tetramethylammonium 1,1,2,3,3-pentacyanopropenide*, $\mathrm{NMe_4\{C_3(CN)_5\}}$. — (i) A mixture of $\mathrm{RuCl(PPh_3)_2(\eta\text{-}C_5H_5)}$ (500 mg, 0.69 mmol) and $\mathrm{NMe_4\{C_3(CN)_5\}}$ (166 mg, 0.69 mmol) was heated in refluxing methanol (40 ml) for 30 min. A red *precipitate* formed, and was collected, washed with methanol, and dried to give pure $\mathrm{Ru\{C_3(CN)_5\}(PPh_3)_2(\eta\text{-}C_5H_5)}$ (4.5a) (510 mg, 86%), m.p. >225^0 (dec.) (Found: C, 67.8; H, 4.1; N, 7.9. $\mathrm{C_{49}H_{35}N_5P_2Ru}$ requires C, 68.7; H, 4.1; N, 8.2%). Infrared (Nujol): ν(CN) 2199s; ν(C=N) 1500s cm^{-1}. ^{1}H n.m.r. ($\mathrm{CDCl_3}$): δ 7.34-7.07, m, 30H, $\mathrm{PPh_3}$; 4.52, s, 5H, $\mathrm{C_5H_5}$; 4.44, s, c. 2H,

(ii) Complex (4.5a) (216 mg, 0.25 mmol) was heated with $\mathrm{P(OMe)_3}$ (120 mg, 0.97 mmol) in refluxing decalin (40 ml) for 15 min. The cooled solution was then chromatographed directly on alumina, the decalin and excess $\mathrm{P(OMe)_3}$ being washed out with light petroleum. A yellow band was then eluted with diethyl ether. Crystallization (diethyl ether/light petroleum) then afforded red *crystals* of $\mathrm{Ru\{C_3(CN)_5\}(PPh_3)\{P(OMe)_3\}(\eta\text{-}C_5H_5)}$ (4.5b) (105 mg, 72%), m.p. 170-174^0 (Found: C, 56.8; H, 4.0; N, 9.6%; *M* (mass spectrometry), 719. $\mathrm{C_{34}H_{29}N_5P_2O_3Ru}$ requires C, 56.8; H, 4.1; N, 9.8%; *M*, 719). Infrared (Nujol): ν(CN) 2204m, 2193m; ν(C=N) 1502w; ν(PO) 1046m, 1011m cm^{-1}. ^{1}H n.m.r. ($\mathrm{CDCl_3}$): δ 7.55, m, and 7.45, m, 15H, $\mathrm{PPh_3}$; 4.77, d, *J*(HP) 0.7 Hz, 5H, $\mathrm{C_5H_5}$; 4.71, d,

J(HP) 0.7 Hz, c. 1H, ?; 3.53, d, J(HP) 11.5 Hz, 9H, $P(OMe)_3$. ^{13}C n.m.r. ($CDCl_3$): δ 135.3-128.6, m, PPh_3; 83.2, s, C_5H_5; 52.7, d, J(CP) 8 Hz, $P(OMe)_3$.

(E) *Tetraethylammonium 1,1,2,4,5,5-hexacyanoazapentadienide (hcnN)* $NEt_4[N\{C(CN)=C(CN)_2\}_2]$. — A mixture of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (340 mg, 0.47 mmol) and $NEt_4[N\{C(CN)=C(CN)_2\}_2]$ (163 mg, 0.47 mmol) was heated in refluxing methanol (40 ml) for 1 h. Removal of the solvent and recrystallization of the residue from dichloromethane/diethyl ether gave a deep purple *precipitate* of Ru(hcnN)$(PPh_3)_2(\eta\text{-}C_5H_5)$ (4.6) 315 mg, 74%), m.p. >95^0. Satisfactory analyses were not obtained. Infrared (Nujol): ν(CN) 2215s, 2199(sh); ν(C=N) 1500s cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.35-7.07, m, 30H, PPh_3; 4.54, s, 5H, C_5H_5; 4.49, s, c. 2H, ?. ^{13}C n.m.r. ($CDCl_3$): δ 135.4-128.8, m, PPh_3; 84.4, s, C_5H_5.

(F) *Disodium azotetrazolate,* $Na_2\{N(CN_4)\}_2$. — A mixture of $RuCl(PPh_3)_2$-$(\eta\text{-}C_5H_5)$ (250 mg, 0.34 mmol) and disodium azotetrazolate (36 mg, 0.17 mmol) was heated in refluxing methanol (40 ml) for 1 h. On cooling, yellow-brown crystals formed, and were purified by chromatography on alumina. A yellow band was eluted with 9:1 dichloromethane/acetone, and crystallization afforded orange-red *crystals* of the dichloromethane solvate of $\{Ru(PPh_3)_2$-$(\eta\text{-}C_5H_5)\}_2(C_2N_{10})$ (4.7) (210 mg, 75%), m.p. >135^0 (dec.) (Found: C, 62.5; H, 4.6; N, 8.3%; M ($CHCl_3$), 1620. $C_{84}H_{70}N_{10}P_4Ru_2,CH_2Cl_2$ requires C, 62.6; H, 4.5; N, 8.6%; M, 1548). ^{1}H n.m.r. ($CDCl_3$): δ 7.15-7.11, m, 60H, PPh_3; 5.30, s, 2H, CH_2Cl_2; 4.36, s, 10H, C_5H_5. ^{13}C n.m.r. ($CDCl_3$): δ 138.0-127.8, m, PPh_3; 83.3, s, C_5H_5; 53.5, s, CH_2Cl_2.

Acknowledgement We are grateful to Professor M. A. Bennett for a sample of potassium tricyanomethanide.

CHAPTER 5

^{13}C N.M.R. STUDIES OF SOME CYCLOPENTADIENYL-RUTHENIUM AND -OSMIUM COMPLEXES

Introduction

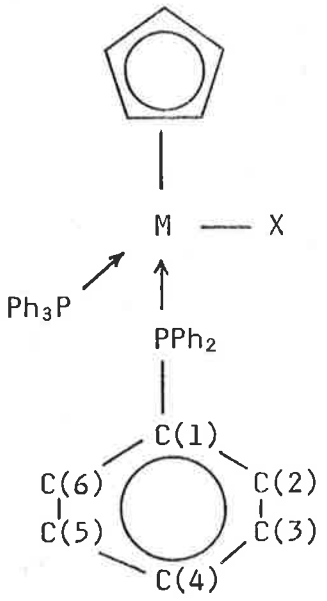
Although the application of ^{13}C nuclear magnetic resonance techniques in organic chemistry is quite common,[146] the value of this technique to the transition metal chemist has only recently become realised.[147,148] A variety of transition metal and metal carbonyl complexes has been examined by ^{13}C techniques.[149-155] It is interesting that the ^{13}C shieldings of some cyclopentadienyl derivatives exhibit a fairly linear correlation with the corresponding proton data,[149] which indicates that both are dominated by similar factors.

During the course of this work, cyclopentadienyl-ruthenium complexes were prepared containing one or two triphenylphosphine ligands and, in a number of cases, no phosphine ligand. Collation of ^{13}C nuclear magnetic resonance spectra was a result of the increasing interest in the application of ^{13}C n.m.r. measurements and the availability of new instrumentation which allowed data to be collected in a routine manner. It was hoped that a correlation between the chemical shifts of the cyclopentadienyl resonances in the ^{13}C and ^{1}H spectra might be observed (for a systematic series). A list of the compounds examined is shown in Table 5.I. together with the ^{1}H and ^{13}C data for the cyclopentadienyl group and ^{13}C data for the triphenylphosphine ligand and/or other ligands.

In order to simplify the ^{13}C spectra and greatly reduce the time required to obtain data with adequate signal-to-noise in the recordings, proton noise decoupling was used in all cases.[156] Thus, splittings due to spin-coupling between ^{13}C and ^{1}H are collapsed, and only ^{13}C chemical shifts and, in some cases, spin-coupling with other nuclei are measured.

Assignments indicated for each spectrum are based upon (i) comparisons with observed peak positions in other similar compounds within the collection, (ii) data reported in the literature, and (iii) results obtained with off-resonance coherent proton spin-decoupling which generally provides indication of the number of protons directly attached to a given carbon atom.

Table 5.I

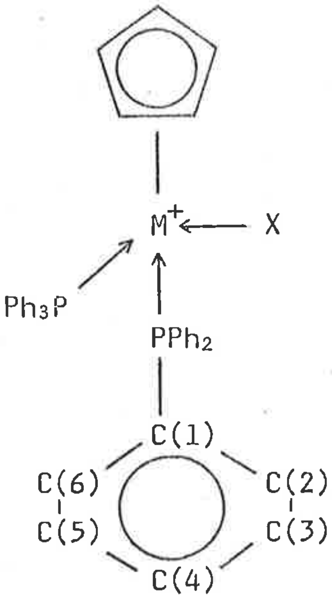


No.	M	X	C_5H_5	C_5H_5	C(1)	C(2,6)	C(3,5)	C(4)	*
1	Ru	H	4.49	82.0	141.7	134.2	127.0	-	
2	Os	H	4.41	77.2	141.9	134.3	127.2	128.4	
3	Ru	Cl	4.10	81.5	138.6	134.0	127.6	128.8	
4	Os	Br	4.31	78.3	-	134.3	127.5	129.0	
5	Ru	I	4.18	81.8	139.1	134.3	127.6	129.0	
6	Ru	CN	4.38	85.3	138.3	133.8	127.8	129.1	
7	Ru	$C(CF_3)=CH(CF_3)$	4.21	84.1	137.9	134.6	127.7	129.3	
8	Ru	C_2Me	4.22	84.5	139.5	134.1	127.2	128.4	
9	Ru	C_2Pr	4.22	84.7	139.7	134.2	127.2	128.3	
10	Ru	C_2Bu^t	4.17	85.2	139.8	134.3	127.1	128.3	
11	Ru	$C_2(CH_2)_2C_2H$	4.22	84.8	139.5	134.1	127.3	128.3	
12	Ru	C_2Ph	4.32	85.4	139.3	134.1	127.4	128.6	
13	Os	C_2Ph	4.39	81.5	139.4	134.1	127.3	128.6	
14	Ru	$C_2C_6H_4F$	4.31	85.3	139.3	134.1	127.4	128.6	
15	Ru	$C_2C_6F_5$	4.35	86.0	138.8	134.0	127.5	128.8	
16	Ru	C_2CO_2Me	4.36	86.2	138.5	134.0	127.6	128.9	
17	Ru	$\overline{CH(CH_2)_3O}$	4.21	86.7	140.5	134.4	127.8	128.8	
18	Ru	$CH(CN)_2$	4.24	82.7	136.2	133.9	128.3	129.9	
19	Ru	$C(CN)_3$	4.29	82.8	136.4	133.5	128.5	130.0	
20	Ru	$C_3(CN)_5$	4.52	83.7	135.7	133.5	128.7	130.4	
21	Ru	hcnN	4 54	84.4	135.4	133.5	128.8	130.5	
22	Ru	$N(CN)_2$	4.20	82.0	137.0	133.5	128.2	129.7	
23	Ru	S_2CH	4.59	83.2	137.8	133.9	128.0	129.4	

hcnN = 1,1,2,4,5,5,-hexacyanoazapentadienide

*Other data in Table 5.II

Table 5.I (cont.)



No.	M	X	C_5H_5	C_5H_5	C(1)	C(2,6)	C(3,5)	C(4)	CO	*
24	Ru	CO	4.97	91.0	135.3	133.2	129.1	131.3	203.2	
25	Ru	CNH	4.63	87.5	136.0	133.4	128.5	130.4		
26	Ru	CNMe	4.69	87.5	136.0	133.4	128.6	130.5		
27	Ru	CNEt	4.68	87.5	136.0	133.3	128.6	130.5		
28	Ru	CNBu*t*	4.68	87.8	136.2	133.4	128.6	130.6		
29	Ru	CNCy	4.68	87.7	136.1	133.4	128.6	130.6		
30	Ru	tosmic	4.78	89.0	135.6	133.4	128.6	130.6		
31	Ru	$C(OMe)CH_2Ph$	4.75	92.0	136.0	133.9	128.6	130.8		
32	Ru	$C(OMe)CD_2Ph$	4.77	91.9	136.0	133.8	128.5	130.7		
33	Ru	$\overline{C(CH_2)_3O}$	4.82	91.2	135.9	133.4	128.3	130.3		
34	Os	$\overline{C(CH_2)_3O}$	4.97	88.4	136.4	133.4	128.4	130.5		
35	Ru	$\overline{CCD_2(CH_2)_2O}$	4.82	91.2	135.9	133.4	128.3	130.3		
36	Ru	$\overline{CCMe_2(CH_2)_2O}$	4.97	89.0	135.7	133.8	128.5	130.8		
37	Ru	$\overline{C(CH_2)_2CHMeO}$	4.83	91.2	135.6	133.5	128.4	130.3		
38	Ru	$\overline{CCD_2CH_2CHMeO}$	4.83	91.2	135.3	133.5	128.4	130.4		
39	Ru	$\overline{C(CH_2)_4O}$	4.76	91.4	136.1	133.7	128.4	130.4		
40	Ru	C_2HMe	5.10	94.5	134.5	133.4	128.8	131.2		
41	Ru	C_2HPr	5.10	94.5	134.6	133.5	128.9	131.3		
42	Ru	C_2MePr	5.19	93.4	134.7	133.2	128.4	130.8		
43	Ru	C_2HPh	5.27	95.2	135.1	133.4	129.0	131.4		
44	Os	C_2HPh	5.42	92.7	134.8	133.5	128.8	131.3		
45	Ru	C_2MePh	5.13	94.5	134.6	133.7	128.8	131.3		
46	Ru	C_2EtPh	5.09	94.5	134.6	133.7	128.8	131.3		
47	Ru	$C_2HC_6H_4F$	5.20	95.2	134.4	133.5	128.7	131.3		
48	Ru	$C_2HC_6F_5$	5.35	96.1	134.6	133.4	129.0	131.6		
49	Ru	C_2HCO_2Me	5.28	96.5	134.6	133.5	129.1	131.7		
50	Ru	NCMe	4.45	83.4	135.9	133.5	128.5	130.3		
51	Ru	$NCCH_2CO_2Et$	4.48	84.0	136.0	133.5	128.5	130.2		
52	Ru	$NC(CH_2)_2CNRu'$	4.46	84.1	136.1	133.5	128.6	130.1		
53	Ru	NCPh	4.56	84.2	135.9	133.5	128.8	130.5		

tosmic = $CNCH_2SO_2C_6H_4Me$-4; Ru' = $Ru(PPh_3)_2(\eta$-$C_5H_5)$

*Other data in Table 5.II

Table 5.I (cont.)

$RuX(PPh_3)L(\eta\text{-}C_5H_5)$

No.	L	X	C_5H_5	C_5H_5	C(1)	C(2,6)	C(3,5)	C(4)	CO	*
54	PMe_3	Cl	4.30	79.4	140.1	134.3	127.9	129.3		
55	PMe_3	C_2Me	4.48	82.2	140.2	134.4	127.4	128.9		
56	PMe_3	C_2Bu^t	4.43	82.5	140.6	134.5	127.3	128.6		
57	PMe_3	C_2Ph	4.52	83.0	140.0	134.4	127.6	129.0		
58	PMe_3	C_2CO_2Me	4.55	84.0	139.1	134.2	127.8	129.4		
59	$P(OMe)_3$	Cl	4.49	81.6	138.4	134.3	127.6	129.2		
60	$P(OMe)_3$	$C_3(CN)_5$	4.77	83.2	135.3	133.9	128.6	130.7		
61	$P(OMe)_3$	C_2Ph	4.68	84.3	139.3	134.4	127.4	128.8		
62	CO	Cl	4.89	86.0	134.9	133.8	128.5	130.5	203.8	
63	CO	CH_2Ph	4.61	88.7	136.8	133.7	128.3	129.9	–	
64	CO	C_2Ph	4.99	87.3	136.3	133.9	128.3	130.2	203.6	
65	CO	$^+C(OMe)CH_2Ph$	5.24	91.3	133.4	133.2	129.5	131.9	201.2	
66	$CNBu^t$	H	4.89	82.2	141.8	134.3	127.9	129.0		
67	$CNBu^t$	Cl	4.53	80.9	136.7	133.5	127.5	129.1		
68	$CNBu^t$	C_2Ph	4.82	84.2	138.1	134.0	127.8	129.3		
69	CNCy	Cl	4.53	81.6	137.2	134.1	128.1	129.6		
70	tosmic	Cl	4.69	84.0	135.9	133.9	128.3	130.0		
71	CNC_6H_4OMe	Cl	4.68	82.8	136.7	133.9	128.2	129.8		

Chelate complexes

72	$C(E)=CH\{C(O)OMe\}$	4.41	76.9	135.1	134.2	127.5	129.2
73	$C(E)=C(CH_2Ph)\{C(O)OMe\}$	4.95	92.2	136.1	134.7	127.8	129.9
74	$CH_2C_6H_4C(CF_3)=CH(CF_3)$	5.11	90.7	–	134.9	127.7	130.2
75	$\{NH=C(CF_3)\}_2N$	4.24	76.6	136.2	133.6	128.5	129.8

$E = CO_2Me$

$MXL_2(\eta\text{-}C_5H_5)$

No.	M	L_2	X	C_5H_5	C_5H_5	PMe_3	$P(OMe)_3$	CO	*
76	Ru	PMe_3	Cl	4.44	77.3	21.5			
77	Os	PMe_3	Br	4.57	72.3	23.4			
78	Ru	PMe_3	C_2Me	4.62	80.2	23.3			
79	Ru	PMe_3	C_2Ph	4.71	81.0	23.3			
80	Ru	PMe_3	C_2CO_2Me	4.72	82.2	23.1			
81	Ru^+	PMe_3	C_2HPh	5.54	92.1	22.9			
82	Ru^+	PMe_3	$\overline{C(CH_2)_3O}$	5.16	88.7	22.7			
83	Ru^+	PMe_3	CO	5.60	87.7	21.5		–	
84	Ru^+	PMe_3	$CNBu^t$	5.20	83.9	21.9			
85	Ru^+	PMe_3	PMe_3	4.82	83.7	23.1			
86	Os^+	PMe_3	PMe_3	5.07	80.0	25.6			
87	Ru^+	PMe_3	$P(OMe)_3$	4.78	82.7	24.2	49.1		
88	Ru^+	PMe_3	MeCN	4.64	77.8	21.4			
89	Ru	$P(OMe)_3$	H	4.73	81.9		52.1		
90	Ru	$P(OMe)_3$	Cl	4.84	81.6		52.2		
91	Ru	$P(OMe)_3$	C_2Ph	4.99	83.6		52.3		

*Other data in Table 5.II

Table 5.I (cont.)

$RuXL_2(\eta-C_5H_5)$ (cont.)

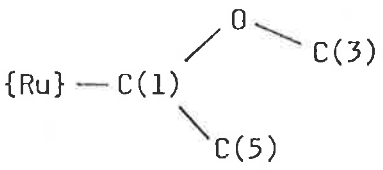
No.	L_2	X	$C_5\mathit{H}_5$	C_5H_5	C(1)	C(2,6)	C(3,5)	C(4)	*
92	$PMePh_2$	Cl	4.32	80.2	136.3	133.1	128.1	129.5	
					135.1	131.7	127.9	128.8	
93	$P(OPh)_3$	Cl	4.05	82.1	152.3	122.2	129.5	124.5	
94	dppe	H	4.76	80.1	145.8	134.0	125.4	131.8	
95	dppe	Cl	4.53	79.8	-	134.2	128.2	129.8	
					-	131.7	128.2	129.2	
96	dppe	C_2Ph	4.78	82.6	142.7	134.2	128.0	129.4	
					137.3	131.7	127.8	129.0	
97	$CNBu^t$	Cl	4.73	83.9					
98	$^+CNBu^t$	PPh_3	4.97	85.8	136.2	133.3	129.0	131.1	

Other $Ru(\eta-C_5H_5)$ complexes

No.	Complex	$C_5\mathit{H}_5$	C_5H_5	PMe_3	$P(OMe)_3$	*
99	$\{HRuCl(PMe_3)_2(\eta-C_5H_5)\}^+$	5.11	84.4	21.7		
100	$\{RuCl_2(PMe_3)_2(\eta-C_5H_5)\}^+$	6.13	94.7	15.2		
101	$Ru(\eta-C_5H_5)_2$	4.55	70.1			
102	$Ru(\eta-C_5H_5)\{C_5(CO_2Me)_5\}$	4.93	78.8			
103	$Ru[\{HN{=}C(CF_3)\}_2N]\{P(OMe)_3\}(\eta-C_5H_5)$	4.52	77.4		51.1	

*Other data in Table 5.II

Table 5.II lists the other resonances for the compounds in Table 5.I. No other data were obtained for compounds (7), (15), (47) and (48) as the solutions were too dilute. Carbons with long relaxation times (vinylidene, alkynyl, carbene and quaternary carbons) were generally observed only under favourable conditions (see below). Those carbons attached to nitrogen were usually not observed even under favourable conditions. Carbon positions for the carbene and cyclic-carbene ligands are shown below.



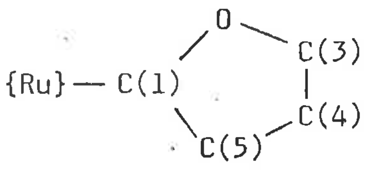


Table 5.II

Alkynyl products

No.	Ru-C	≡C-	Other
8	90.7	105.3	Me 7.8
9	-	111.4	CH_2 24.3, 25.5; Me 13.9
10	-	120.4	CR -; Me 33.0
11	-	109.2	C≡CH 85.4; C≡CH 68.2; CH_2 23.4, 20.9
12	116.1	114.7	Ph 130.7, 127.8, 123.2
13	-	110.3	Ph 131.2, 127.7, 122.9
14	-	113.4	C_6H_4F 132.0, 131.6, 115.1, 114.1
16	-	105.3	CO 177.4; OMe 51.4
55	94.0	101.4	Me 7.3; PMe 21.7
56	89.0	116.5	CR -; Me 33.2; PMe 22.1
57	-	103.0	Ph 130.9, 130.8, 123.0; PMe 23.3
58	-	-	CO -; OMe 51.3; PMe 21.9
61	-	112.9	Ph 134.8, 130.8, 127.7, 123.2; P(OMe) 52.0
64	100.1	112.8	CO 203.6; Ph 131.2, 129.2, 127.6, 124.3
68	111.2	111.8	Ph 131.0, 128.8, 127.5, 123.2; CN 159.6; CR 56.2; Me 30.8
78	-	98.7	Me 7.0
79	-	103.0	Ph 134.2, 131.0, 127.9, 123.0
80	-	-	CO -; OMe 51.3
91	-	112.0	Ph 134.7, 130.9, 127.9, 123.6
96	116.1	112.0	Ph 130.7, 130.3, 123.1; CH_2 28.2

Vinylidene products

No.	Ru-C	=C	Other
40	349.9	109.4	Me 5.5
41	-	114.7	CH_2 23.9, 24.5; Me 13.7
42	352.0	121.3	CH_2 27.8, 20.9; Me 13.8, 13.7
43	359.0	119.8	Ph 129.2, 127.5
44	-	108.2	Ph 127.6, 126.9, 118.0
45	365.7	-	Ph 129.3, 128.0, 125.5
46	-	-	Ph 129.9, 128.3, 127.6, 125.0; CH_2 20.6; Me 13.4
49	-	113.3	CO -; OMe 66.1
81	-	114.7	Ph 132.5, 129.7, 127.2, 126.2

Carbene, cyclic-carbenes and related compounds

No.	Ru-C	C(3)	C(5)	C(4)	Other
17	148.7	62.9	52.4	44.4	
31	308.7	62.8	63.4		Ph 129.6, 127.4, 122.3
32	308.7	62.8	-		Ph 129.6, 127.4, 122.4
33	300.5	81.6	60.8	22.6	
34	263.4	80.8	62.0	23.6	
35	300.5	81.6	60.8*	22.6	
36	310.8	79.5	67.0	38.1	Me 26.9
37	299.4	92.4	61.7	30.1	Me 19.0
38	299.9	92.6	-	30.0	Me 19.2
39	-	73.0	55.3		C(4) 20.3, 16.4
65	318.1	62.9	66.2		Ph 131.2, 129.6, 128.8, 127.8
82	296.9	80.5	59.4	21.9	

*multiplet

Table 5.II (cont.)

Nitrile products

No.	Ru-NC	Other
50	-	Me 4.1
51	-	NCCH$_2$ 62.9; CH$_2$ 27.2; Me 13.9
52	-	CH$_2$ 15.7
53	-	Ph 132.7, 129.5, 111.5
88	-	Me 10.7

Isocyanide products

No.	Ru-CN	Other
25	-	
26	-	Me 30.9
27	-	CH$_2$ 40.7; Me 14.8
28	-	CR -; Me 30.4
29	-	Cy 56.1, 32.9, 24.9, 23.6
30	-	C$_6$H$_4$ 146.5, 137.4; CH$_2$ 64.7; Me 21.9
66	-	CR 55.5; Me 31.3
67	156.6	CR 56.1; Me 30.4
68	159.6	CR 56.2; Me 30.8; Ph 131.0, 128.8, 127.5, 123.2; C≡C 111.2,111.8
69	-	Cy 56.1, 32.9, 24.9, 23.6
70	-	C$_6$H$_4$ 146.2, 130.4,129.3; CH$_2$ 64.0; Me 21.8
71	-	C$_6$H$_4$ 158.4, 126.9, 123.8; OMe 56.6
84	-	CR -; Me 30.2
97	-	CR 56.4; Me 30.7
98	-	CR 52.2; Me 30.4

Other products

No.	Ru-C	Other
6	153.2	
18	104.0	
23		SCH 203.5
63	4.5	Ph 127.8, 127.3, 121.6;
72	-	CO 186.6, 178.7; =CH 116.4; OMe 52.6, 50.6
73	-	CO 177.9, 176.0; Ph 127.5,123.1, 122.4; OMe 52.7, 52.4
74	44.5	CF$_3$ 132.8; C$_6$H$_4$ 128.0, 127.5, 123.5, 121.9
75		N=C 154.1; CF$_3$ 117.8
92		Me 14.9
94		CH$_2$ 31.3
95		CH$_2$ 27.3
102		CO 166.0; Cpp 82.2
103		N=C 154.7; CF$_3$ 117.9

Cpp = C$_5$(CO$_2$Me)

The spectra in this collection were recorded on computer-equipped Bruker HX-90E or WP-80DS spectrometers. The samples were run using 10 mm sample tubes. The standard operating conditions were c. 5000 accumulations at 0.8 sec. per accumulation with an exponential weighting time constant of 1.0 sec. applied to the accumulated free-induction decay before Fourier transformation, and a radio frequency pulse width of 4.0 microseconds which corresponded to a tipping angle of about 45^0. The lock signal was provided by the deuterium resonance from the deuterated solvent. Ten percent TMS was used as the internal reference. Peak positions and calculated chemical shifts (referred to TMS) were obtained from computer listings and the accuracy in calculated chemical shifts is ±0.1 ppm. The probe temperature was c. 30^0.

Discussion

Examination of the data in Table 5.I. shows that *regular* trends between the ^{13}C and ^{1}H resonances of the cyclopentadienyl group are not discernible and the data are not readily interpreted in terms of current shielding theory. The ^{13}C shieldings do exhibit a fairly linear correlation as shown by King,[149] but a simple rationalization of the trend is not evident. The cationic complexes have higher chemical shift values than the neutral complexes and this is to be expected. It can be noted that in all these cases these carbon nuclei are significantly shielded relative to cyclopentadiene itself (δ_C 132.9).[146] The osmium complexes have lower δ_C values than the ruthenium derivatives although the former have higher δ_H values. Information on the number of triphenylphosphine ligands bonded to the metal can be obtained by examining the ^{13}C spectra of mono- and di-substituted phosphine complexes. The phenyl carbons are spin-coupled to the phosphorus atom(s) and examples of the triphenylphosphine and cyclopentadienyl regions of mono- and di-substituted products are shown in Figure 5.II and Figure 5.III respectively, together with the spectrum of free triphenylphosphine (Figure 5.I.).

Figure 5.I

^{13}C spectrum of PPh_3

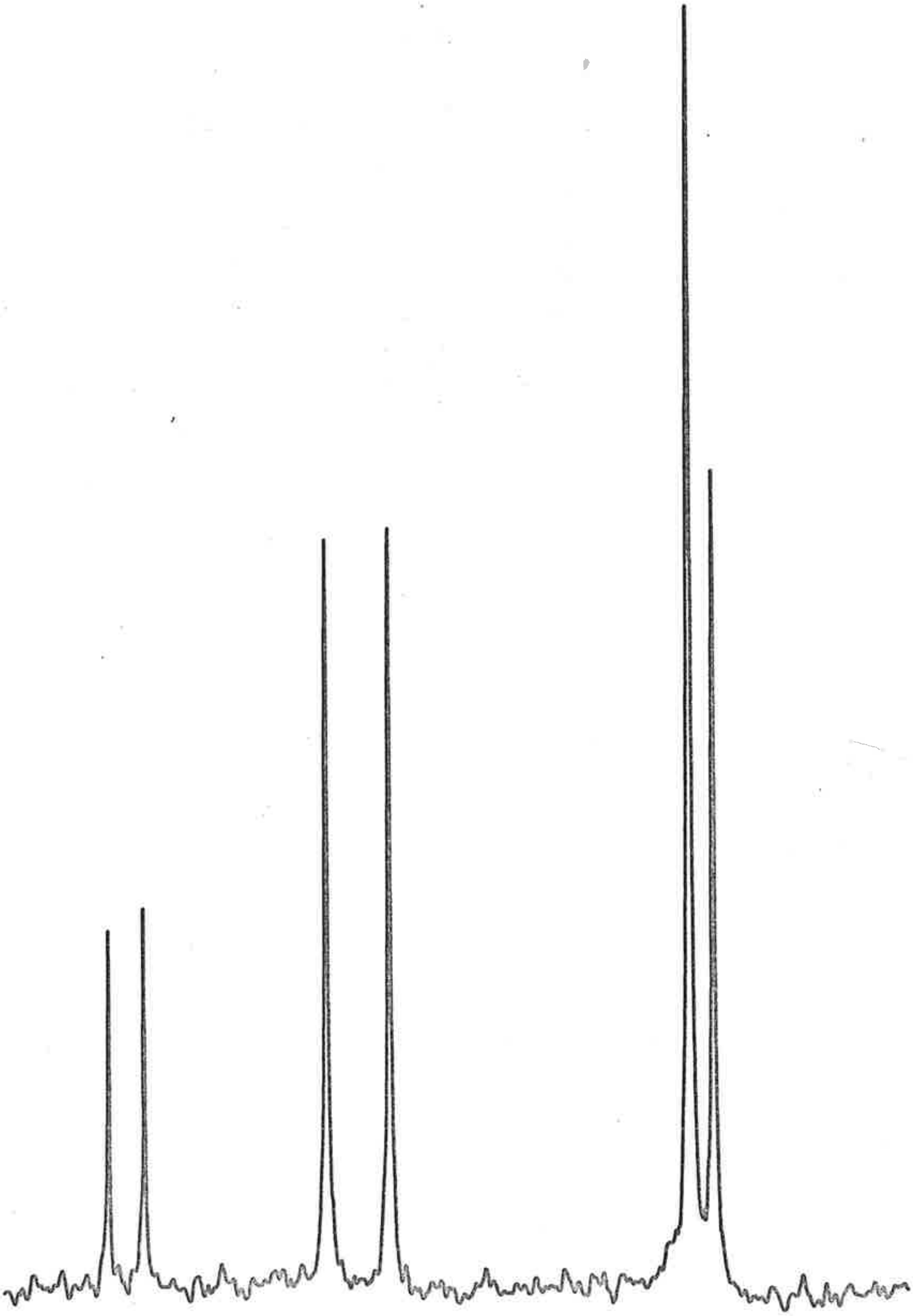


Figure 5.II

^{13}C spectrum of the aromatic and cyclopentadienyl regions for the complex $RuCl(CNBu^{t})(PPh_3)(\eta\text{-}C_5H_5)$

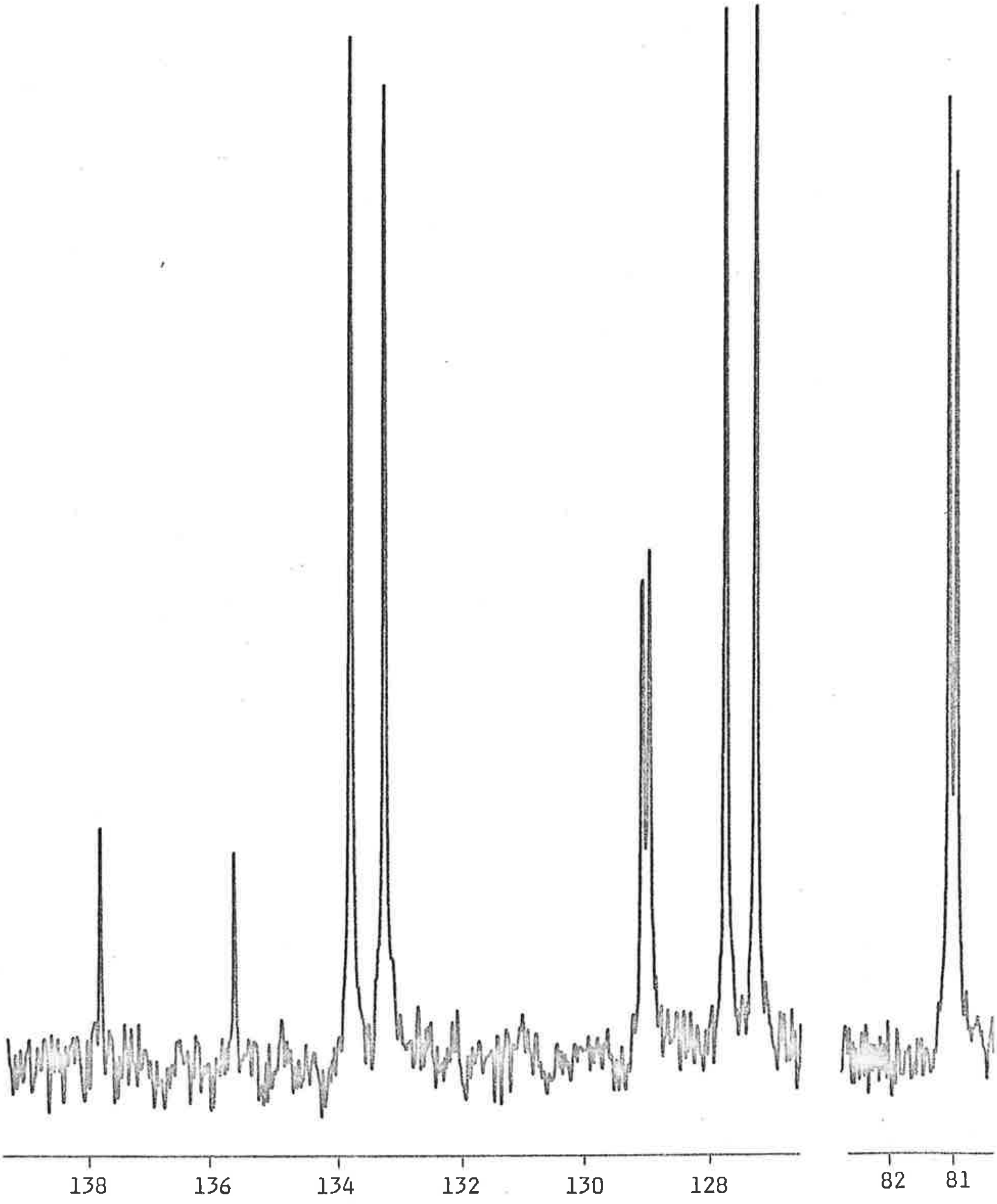


Figure 5.III

^{13}C spectrum of the aromatic and cyclopentadienyl regions for the complex $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$

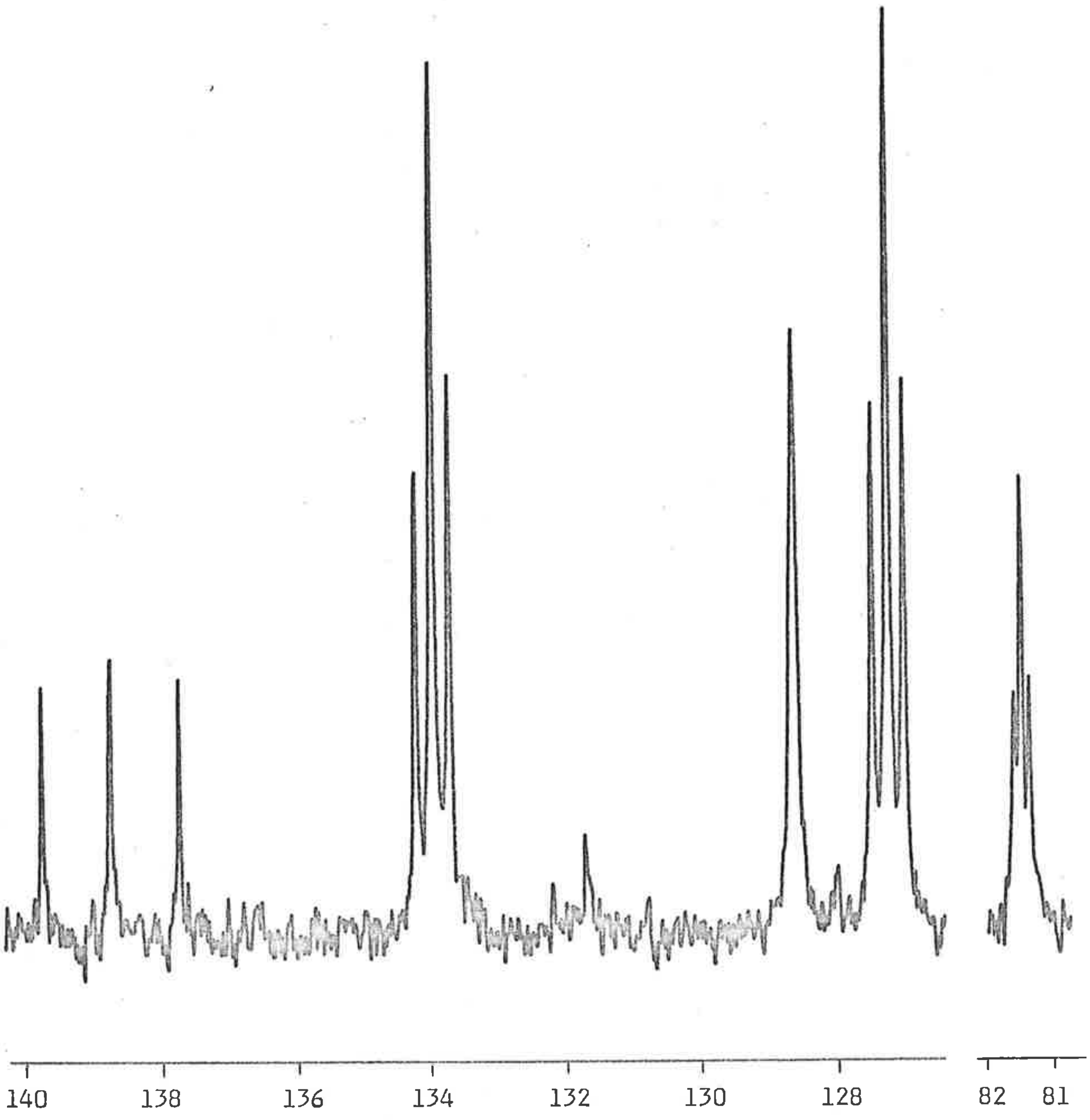
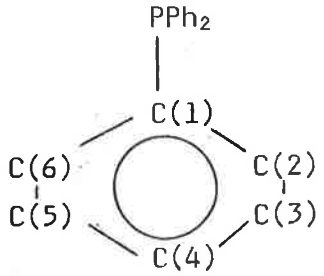
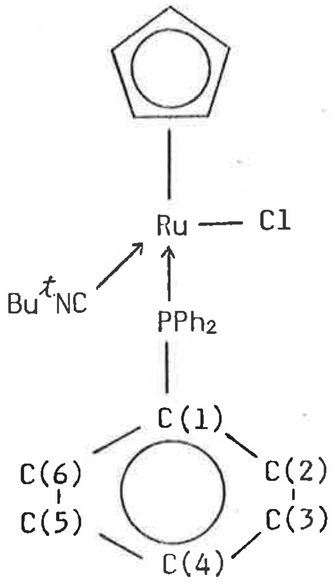


Diagram 5.I shows the chemical shift values (ppm) and the $J(CP)$ coupling constants (hertz) for the phenyl, cyclopentadienyl and isocyanide carbons.

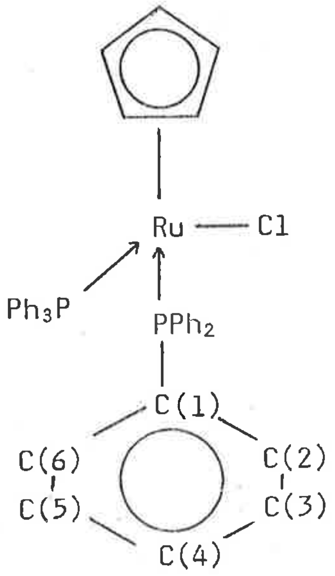
Diagram 5.I



	δ_C	$J(CP)$
C(1)	137.5	11
C(2,6)	133.9	20
C(3,5)	128.6	7
C(4)	128.8	-



(η-C_5H_5)	80.9	2
Ru-C	156.6	24
CR	56.1	-
Me	30.4	-
C(1)	136.7	44
C(2,6)	133.5	11
C(3,5)	127.5	10
C(4)	129.1	2



(η-C_5H_5)	81.5	2
C(1)	138.6	20
C(2,6)	134.0	5
C(3,5)	127.6	5
C(4)	128.8	-

The assignments for the phenyl carbons are based on the data of free triphenylphosphine.[157] The *para* carbon is usually observed as a singlet, the other carbons being either doublets or 'triplets' (doublet of doublets) coupled to either one or two phosphorus atoms, respectively. The cyclopentadienyl resonance also shows coupling to the phosphorus atom(s). In those products containing PPh_3 and PMe_3 or $P\{OMe\}_3$, for example, $RuCl(PPh_3)(PMe_3)(\eta\text{-}C_5H_5)$ or $RuCl(PPh_3)\{P(OMe)_3\}(\eta\text{-}C_5H_5)$, coupling of the phenyl carbons to the second phosphorus is not observed. The methyl appears as a doublet in the above spectra and as a triplet in complexes $RuCl(PMe_3)_2(\eta\text{-}C_5H_5)$ and $RuCl\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$. In the case of complexes containing the bidentate ligands, dppm or dppe, the phenyl carbons are observed as doublets of triplets (for the P-C, *ortho* and *meta* carbons) and a doublet of singlets (for the *para* carbon). Thus, ^{13}C n.m.r. affords specific evidence as to the number and types of tertiary phosphine of phosphite ligands present.

There is a correlation between the chemical shift of the P-C carbon and whether or not the complex being studied was neutral or cationic. The cationic complexes showed resonances at values of *c.* 3 ppm lower than those of the neutral products.

The variation in carbon shieldings in the neutral organometallic compounds is approximately 20-fold greater than that of protons. Examples of the ranges exhibited by carbon nuclei is given in Table 5.I. Carbonyl carbons absorb *c.* 200 ppm downfield from tetramethylsilane while alkane carbons absorb *c.* 10-20 ppm downfield from TMS. In addition to these systems we have noted the electron-deficient carbene carbons in the vinylidene complexes, which resonate at *c.* 360 ppm downfield from TMS. This information enabled characterisation of these complexes as η^1-vinylidene derivatives rather than the η^2-alkyne complexes. Thus, the total range of ^{13}C shieldings is more than 350 ppm. The position of individual spectral bands can readily be measured to a precision of better than 0.1 ppm. Although the detection of ^{13}C absorption bands is inherently much nore difficult than those of protons, the instruments are capable of generating spectra from samples of less than 100 mg containing carbon in natural abundance.

Enhancement of ^{13}C resonance signals upon proton decoupling, "the nuclear Overhauser effect", allowed ready observation of ^{13}C signals of a wide variety of carbons. However, those carbons not bearing hydrogen, such as the vinylidene carbons mentioned above, or the cyclic carbene carbons, the alkynyl carbons of the η^1-alkynyl complexes and the isonitrile carbons were not readily observed and the standard operation conditions had to be altered. Solutions, degassed thoroughly to exclude oxygen, were made as concentrated as possible (*c.* 1 *M* rather than *c.* 0.1 *M*). Approximately 8000 accumulations were collected at 0.8 sec. per accumulation and with a delay of five to ten seconds between scans. This enabled resonance signals for carbon atoms with long relaxation times to be observed.

The η^1-vinylidene carbon resonates as a low intensity multiplet at *c.* 360 ppm. Coupling to the phosphorus atoms of *c.* 20 hertz is observed. In the alkynyl complexes, the metal-bonded carbon resonates at *c.* 90-120 ppm, with the β-carbon appearing in a similar region to that of the vinylidene complexes (100-120 ppm). The β-carbon does not show coupling to the phosphorus atoms. The cyclic-carbene and alkoxy-carbene signals are detected at *c.* 300 ppm. The isocyanide carbon was observed at 156.6 ppm in the complex $RuCl(PPh_3)(CNBu^t)(\eta-C_5H_5)$. All these Ru-C carbons show coupling to phosphorus, if present in the complex.

Off-resonance and single-frequency decoupled ^{13}C spectra were run of hydrogen-bearing carbons, enabling signals in the ^{13}C n.m.r. spectra to be specifically assigned to those signals in the ^1H n.m.r. spectra.

The location of the acidic hydrogens in the cyclic carbene complexes[103] could be made using these techniques, together with the ^{13}C data of the methoxy carbene complex $[Ru\{C(OMe)CH_2Ph\}(PPh_3)_2(\eta-C_5H_5)]PF_6$.

Of course, the double-frequency decoupling technique normally employed means that spin-spin interactions of ^{13}C nuclei with neighbouring magnetic nuclei (^1H) are eliminated. Thus, the spectra normally consist entirely of singlet signals, and the interpretation of the spectra merely involves the assignment of specific signals to various non-equivalent carbons. Spectral analysis in the usual sense is not required, as for interpretations of proton spectra, since the fine structure is eliminated in routine operation. The complex $[C_2H_4\{CNRu(PPh_3)_2(\eta-C_5H_5)\}_2](PF_6)_2$ (2.9) has a ^{13}C spectrum which indicated equivalent methylene carbons thus confirming the dimeric formulation. In the following chapter we describe a complex $Ru_5(CO)_{14}(CNBu^t)_2$ containing seemingly equivalent *t*-butyl groups (^1H n.m.r.). The ^{13}C n.m.r. indicated non-equivalent *t*-butyl groups and the crystal structure of the complex shows one terminal *t*-butyl isocyanide ligand and a bridging isocyanide.

Proton spectroscopy has had an enormous impact on organic chemistry over the past 30 years. It is reasonable to expect that carbon spectroscopy should offer similar promise.

REFERENCES

SECTION A

References

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CHAPTER 6

DODECACARBONYLTRIRUTHENIUM CHEMISTRY.

REACTIONS BETWEEN RUTHENIUM CARBONYL AND ISOCYANIDES

Introduction

Since the discovery of a high-yield route to dodecacarbonyltriruthenium,[1,2] a number of reports have appeared describing reactions between this carbonyl and a variety of Group V donor ligands. The usual product from reactions of $Ru_3(CO)_{12}$ with tertiary phosphines, PR_3, is the trisubstituted complex, $Ru_3(CO)_9(PR_3)_3$, the mono- and di-substituted derivatives normally not being isolated. An early kinetic study of the reaction suggested that formation of $Ru_3(CO)_{11}(PR_3)$ is the rate-determining step, with subsequent reactions to form $Ru_3(CO)_{10}(PR_3)_2$ and $Ru_3(CO)_9(PR_3)_3$ being fast.[3]

In several instances, it has proved possible to isolate the mono- and di-substituted complexes, particularly by the use of chromatographic methods.[4] The yields obtained in these reactions were low. Similar complexes have been isolated as by-products from reactions between $Ru_3(CO)_{12}$ and platinum(0)-tertiary phosphine complexes such as $Pt(PR_3)_4$ or $Pt(C_2H_4)(PPh_3)_2$, and $Ru_3(CO)_{11}(PPh_3)$ has been obtained in low yield by irradiation (>390 nm) of hexane solutions of $Ru_3(CO)_{12}$ and PPh_3; $Ru(CO)_4(PPh_3)$ and $Ru(CO)_3(PPh_3)_2$ are the major products.[5]

In contrast, the phosphonite $PPh(OMe)_2$ reacts to give both di- and tetra-substituted complexes. The tetrasubstituted complex $Ru_3(CO)_8(PH_3)_4$ is a product of the reaction between $\{RuCl_2(CO)_3\}_2$ and phosphine.[6] The stereochemistries of most of these complexes are unknown, attempted structure determinations being thwarted by extensive disorder problems. However, chemical evidence points to substitution occurring at each metal atom.

In contrast to PPh_3, triphenylarsine reacts with $Ru_3(CO)_{12}$ to form $Ru_3(CO)_{10}(AsPh_3)_2$.[7] Preliminary X-ray results from a disordered crystal suggest that a linear AsRuRuAs sequence is present. Other tertiary arsines, such as $AsMe_2Ph$ and $AsMe_2(CH_2Ph)$, react to form the trisubstituted $Ru_3(CO)_9(AsR_3)_3$ complexes.

Only a cursory mention of $Ru_3(CO)_9(SbPh_3)_3$ occurs in the literature;[3] irradiation of mixtures of $Ru_3(CO)_{12}$ and $SbPh_3$ in hexane gives only $Ru(CO)_4(SbPh_3)$.[8]

Bidentate phosphines have been relatively little studied. While an early report suggested the formation of $Ru_3(CO)_6(dppe)_3$, this has not been confirmed, and only complexes of the type $Ru_3(CO)_{10}(P_2)$ $\{P_2$ = dppm, dppe and ffos$\}$ and $Ru_3(CO)_8(ffos)_2$ have been fully characterised.[4]

Other polydentate Group V donor ligands have given only mononuclear complexes, perhaps as a result of the harsh conditions used. Thus the only isolated products from reactions between $Ru_3(CO)_{12}$ and the ligands tp, tas, qp or qas $\{te = PhE(C_6H_4EPh_2\text{-}2)_2$; $qe = E(C_6H_4EPh_2\text{-}2)_3$; E = P or As$\}$ in chlorobenzene (100°/48 h) were $Ru(CO)_2(te)$ or $Ru(CO)(qe)$. The intermediate complex $Ru(CO)_2(qp)$ was detected but not isolated.[9]

It has proved possible to 'cap' the Ru_3 cluster by using the tridentate tertiary phosphine $MeSi(PBu_2)_3$; yellow $Ru_3(CO)_9\{(Bu_2P)_3SiMe\}$ is formed in low yield from a reaction between the ligand and $Ru_3(CO)_{12}$ in benzene.[10] The Ru-Ru edges are longer (2.917 Å) than in other non-bridged cluster complexes of ruthenium.

Many nitrogen-containing ligands react with $Ru_3(CO)_{12}$ to give mono- or bi-nuclear products.[11-21] The trinuclear complex $HRu_3(\mu_2\text{-}NHPh)(CO)_{10}$ is formed from the reaction between aniline and $Ru_3(CO)_{12}$, by oxidative addition of the amino group to the Ru-Ru bond. In the presence of $Ru_3(CO)_{12}$, nitrobenzene is reduced to aniline by high pressures of dihydrogen, and a mechanism involving intermediate nitrene complexes was postulated.[22]

Complexes containing μ_3-NR groups have also been isolated from the reactions of $Ru_3(CO)_{12}$ with several other nitrogen-containing ligands, including phenyl isocyanate,[23] *2H*-hexafluoropropylazide[24] and trimethylsilylazide.[25]

Pyridazine affords deep maroon $Ru_3(CO)_{10}(C_4H_4N_2)$, containing three μ_2-CO groups, which can be considered to be derived from the supposed μ_2-CO intermediate for scrambling CO groups on $Ru_3(CO)_{12}$.[26,27]

The electron-rich olefin $(:\overline{\text{CNEtCH}_2\text{CH}_2\text{N}}\text{Et})_2$ reacts with $Ru_3(CO)_{12}$ in hexane at 65° to give crimson red $Ru_3(CO)_{11}(\overline{\text{CNEtCH}_2\text{CH}_2\text{N}}\text{Et})$ (25%).[28] The ^{13}C n.m.r. spectrum shows all CO groups to be equivalent, scrambling occurring by asymmetric two-carbonyl- or symmetric three-carbonyl-bridged species. No low temperature spectra were recorded.

In a search for new carbene complexes, $Ru_3(CO)_{12}$ was treated with LiPh; acidification gave a low yield (1%) of $HRu_3(CO)_9(C_6H_4CPh)$.[29] The ligand was the first example of the commonly found σ,π-allylic system, and can also be considered as a metallated diphenylcarbene.

The reaction between ethylene and $Ru_3(CO)_{12}$ (65-75°/1 atmosphere) affords $H_2Ru_4(CO)_{13}$ (30%), together with $H_3Ru_3(CMe)(CO)_9$ 12%, as major products.[30] The structure of $H_3Ru_3(CMe)(CO)_9$ is closely related to that of $Co_3(CMe)(CO)_9$; the Ru-Ru distance (2.842 Å), is not significantly lengthened over that in $Ru_3(CO)_{12}$.[31] The normal bond lengthening observed with μ_2-H ligands is counteracted by the presence of the μ_3-CMe group. The complex is not fluxional between -60 and 90°, perhaps because of the high coordination number of the ruthenium.[32] Two CO resonances are found, one of which exhibits coupling to the metal-bonded protons.

Further examples of $H_3Ru_3(\mu_3\text{-CX})(CO)_9$ complexes have been obtained from $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$, itself readily formed by alkylation of $\{HRu_3(\mu_2\text{-CO})(CO)_{10}\}^-$.[33] The ruthenium complexes are less stable, both oxidatively and thermally, than the cobalt analogue.

It is of interest that slow replacement of two hydrogens occurs with $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$ at 100° under CO to give $HRu_3(\mu\text{-COMe})(CO)_{10}$.[34] The reaction between $H_3Ru_3(\mu_3\text{-CBr})(CO)_9$ (formed from the reaction of $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$ with BBr_3) and diethylamine, also under CO, affords orange $HRu_3(\mu\text{-}CNEt_2)(CO)_{10}$ as the only product, none of the trihydro complex being obtained. The tendency to form these complexes probably arises because of the favourable stabilisation via the $\overset{-}{C}=\overset{+}{O}Me$ or $\overset{-}{C}=\overset{+}{N}R_2$ ylid resonance forms.

The dimethyl analogue is among the products obtained from $Ru_3(CO)_{12}$ and $Me_3SnCH_2NMe_2$.[35,36] These complexes contain an Ru_3 triangle, one edge of which is bridged by H and $C{=}NMe_2$ ligands, the latter acting as a 3e donor. The structure provides another example of the normal lengthening of an Ru-H-Ru three-centre bond being counteracted by the shortening effect of a μ_2-ligand.

The merit of the present work is that monosubstituted derivatives of the trinuclear ruthenium carbonyl, $Ru_3(CO)_{12}$, which are not readily obtained (except for those products mentioned above), were formed in high yields from reactions between $Ru_3(CO)_{12}$ and isocyanides.[37] Reaction between $Ru_3(CO)_{12}$ and isocyanides had not been reported at the beginning of this work. Brief reports of the preparation of complexes $Ru_3(CO)_{12-n}(CNR)_n$ {n = 1-4, R = Bu^t, Xy} have appeared;[38,39] catalysis by $CoCl_2{,}2H_2O$ appears to be a promising general route to these derivatives. The preparation of the osmium analogues $Os_3(CO)_{12-n}(CNR)_n$ {n = 1 or 2 for R = Me, C_6H_4OMe, Bu^n, or Bu^t; n = 3 or 4 for R = Bu^n, or Bu^t}, has been reported.[40] Such substituted derivatives are of considerable interest since their pyrolysis provides a valuable route to higher nuclearity clusters which are not readily accessible by other means.[41]

Reactions of $Ru_3(CO)_{12}$ with Isocyanides

In a remarkably facile reaction, *t*-butyl isocyanide reacts with an equimolar amount of the cluster carbonyl $Ru_3(CO)_{12}$ in light petroleum at 50^0 for 1-2 h to give a high yield of red plate-like crystals of the monosubstituted complex $Ru_3(CO)_{11}(CNBu^t)$ (6.1). The complex was readily identified by elemental microanalysis and its spectroscopic properties. In the infrared spectrum a band at 2170 cm^{-1} is readily assigned to $\nu(CN)$, and the six-band $\nu(CO)$ spectrum is different to those observed for the equatorially monosubstituted phosphine derivatives. This evidence suggests that the isonitrile ligand is axially rather than equatorially substituted, and was confirmed by the crystal and molecular structures of (6.1) (discussed below). In the ^1H n.m.r. spectrum, the protons of the CMe_3 group resonate as a sharp singlet at δ 1.53, while in the ^{13}C n.m.r., all CO groups give rise to a singlet at δ 201.1; the CMe_3 carbons are found at δ 30.1 and 59.0, but the isocyanide carbon was not detected. This simple spectrum indicates that (6.1) is fluxional at room temperature, and indeed the CO resonance does not change at -100^0. In this, the complex resembles the parent $Ru_3(CO)_{12}$, which is also fluxional at low temperatures.

Reactions with increasing amounts of *t*-butyl isocyanide have given the deep red complexes $Ru_3(CO)_{12-n}(CNBu^t)_n$ $\{n = 1-3\}$. The disubstituted complex (6.2) shows $\nu(CN)$ at 2155 cm^{-1}, and also has a six-band $\nu(CO)$ spectrum. The ^1H n.m.r. and ^{13}C n.m.r. spectra are similar to those of (6.1), although the isocyanide carbon was also observed as a singlet at δ 144.1; again, the spectra indicate that (6.2) is highly fluxional. The trisubstituted complex (6.3) is much more sensitive to oxidation than the other two derivatives, and we have not been able to obtain satisfactory microanalytical results. The spectral properties are consistent with substitution at all three metal atoms, with a three-band $\nu(CO)$ spectrum, and a singlet for the CO groups in the ^{13}C n.m.r. spectrum.

The mass spectra of these complexes are characterised by parent ions which fragment by initial loss of two carbonyl groups then by competitive loss of CO and $CNBu^t$ ligands; the near-equivalence of three CO groups (84 daltons) and the $CNBu^t$ ligand (83 daltons) results in a series of ion clusters spaced at approximately 28 units, although overlap of the ion clusters corresponding to $\{P-3CO\}^+$ and $\{P-CNBu^t\}$ is apparent from the different intensity pattern compared with those of $\{P-nCO\}^+$ {n = 0 or 2}.

The reaction between $Ru_3(CO)_{12}$ and 4-toluenesulphonylmethyl isocyanide contrasts with the above, in that the only product obtained under a variety of conditions was the purple-brown $Ru_3(CO)_9(CNCH_2SO_2C_6H_4Me\text{-}4)_3$ (6.4), which readily crystallizes from the reaction mixture. Complex (6.4) is also unusual in that the infrared spectrum contains only one broad but strong $\nu(CO)$ band, at 1980 cm^{-1}, in addition to the $\nu(CN)$ absorption at 2168 cm^{-1}.

The complex obtained with cyclohexyl isocyanide $Ru_3(CO)_{11}(CNCy)$ (6.5) has an infrared spectrum which closely resembles that of (6.1), although the frequency of the $\nu(CN)$ band is some 15 cm^{-1} lower.

The nature of the substitution product obtained from $Ru_3(CO)_{12}$ and simple two electron donor ligands will depend on a number of factors, of which two practically important ones are the relative magnitudes of the rate constants for the successive reactions

$$Ru_3(CO)_{12} + L \xrightleftharpoons{K_1} Ru_3(CO)_{11}L + CO \qquad (i)$$

$$Ru_3(CO)_{11}L + L \xrightleftharpoons{K_2} Ru_3(CO)_{10}L_2 + CO \qquad (ii)$$

$$Ru_3(CO)_{10}L_2 + L \xrightleftharpoons{K_3} Ru_3(CO)_9L_3 + CO \text{ ..etc.} \qquad (iii)$$

and the solubility of the various substituted products. In the case of L = tertiary phosphine, K_2 and K_3 appear to be larger than K_1, that is, reaction (i) is the rate-determining step, and even with a deficiency of tertiary phosphine, $Ru_3(CO)_9L_3$ is the usual product. However, if the reaction is carried out in a closed system, the partial pressure of CO may become sufficient to enable the intermediate products to be isolated.[41] We have shown also that solubility of the products is an important factor, and that for L = PPh_3, for example, the complex $Ru_3(CO)_{10}(PPh_3)_2$ may be readily prepared by using hexane as solvent.[42]

Reactions between $Ru_3(CO)_{12}$ and some isocyanides evidently have rate constants for reactions (i) - (iii) which allows successive formation (and isolation) of the three substitution products $Ru_3(CO)_{12-n}L_n$ {n = 1-3}. Indeed, in most cases, reactions (iii) is so slow that forcing conditions are often required. In one of the limited range of reactions studied, a trisubstituted product (6.4) was the only product isolated; in this instance the limited solubility of the complex is probably a factor aiding its formation under the reaction conditions employed.

The ready formation of a mono-substituted derivative of $Ru_3(CO)_{12}$ opened up intriguing possibilities for the preparation of further complexes containing two or more different ligands, and as we shall see below, the isocyanide is a useful reagent for "activating" $Ru_3(CO)_{12}$ in several reactions.

Crystal and Molecular Structure of $Ru_3(CO)_{11}(CNBu^t)$

The unit cell contents comprise discrete molecules of the parent complex with one molecule comprising the asymmetric unit of the structure. The molecule, as expected, comprises an $Ru_3(CO)_{12}$ unit with one of the axial carbonyls replaced by the *t*-butylisocyanide ligand. As reported previously, the model is complicated by disorder;[37] the present more precise data enables a more precise description of this disorder and the refinement model used.

The molecular structure is shown in Figure 6.I. Relevant bond lengths are shown in Table 6.I.* The average Ru-Ru distance of 2.854(2) Å compares favourably with that found in $Ru_3(CO)_{12}$, 2.8515(4) Å.[43] The isocyanide ligand occupies an axial position on one of the ruthenium atoms with an Ru-C(isocyanide) distance of 1.99(2) Å.

The carbonyls on any two $Ru(CO)_4$ units, in $Ru_3(CO)_{12}$, are in an eclipsed arrangement when viewed along an Ru-Ru bond. However, in the isocyanide complex (6.1), the ligands adopt a partially staggered configuration (Figure 6.I). This distortion can be derived from the $Ru_3(CO)_{12}$ structure by twisting each $Ru(CO)_4$ group in turn and in the same direction about the bisectors of the internal angles of the Ru triangle. The twisting, which could be considered to be the first stage of a rotation similar to that proposed by Cotton and Troup as a pathway for complete scrambling of all CO groups in $Fe_3(CO)_{12}$,[44] results in a distortion of the ligand polyhedron from the twinned cuboctahedron of $Ru_3(CO)_{12}$ towards an icosahedral arrangement (Figure 6.II).

**Data by B. W. Skelton and A. H. White*

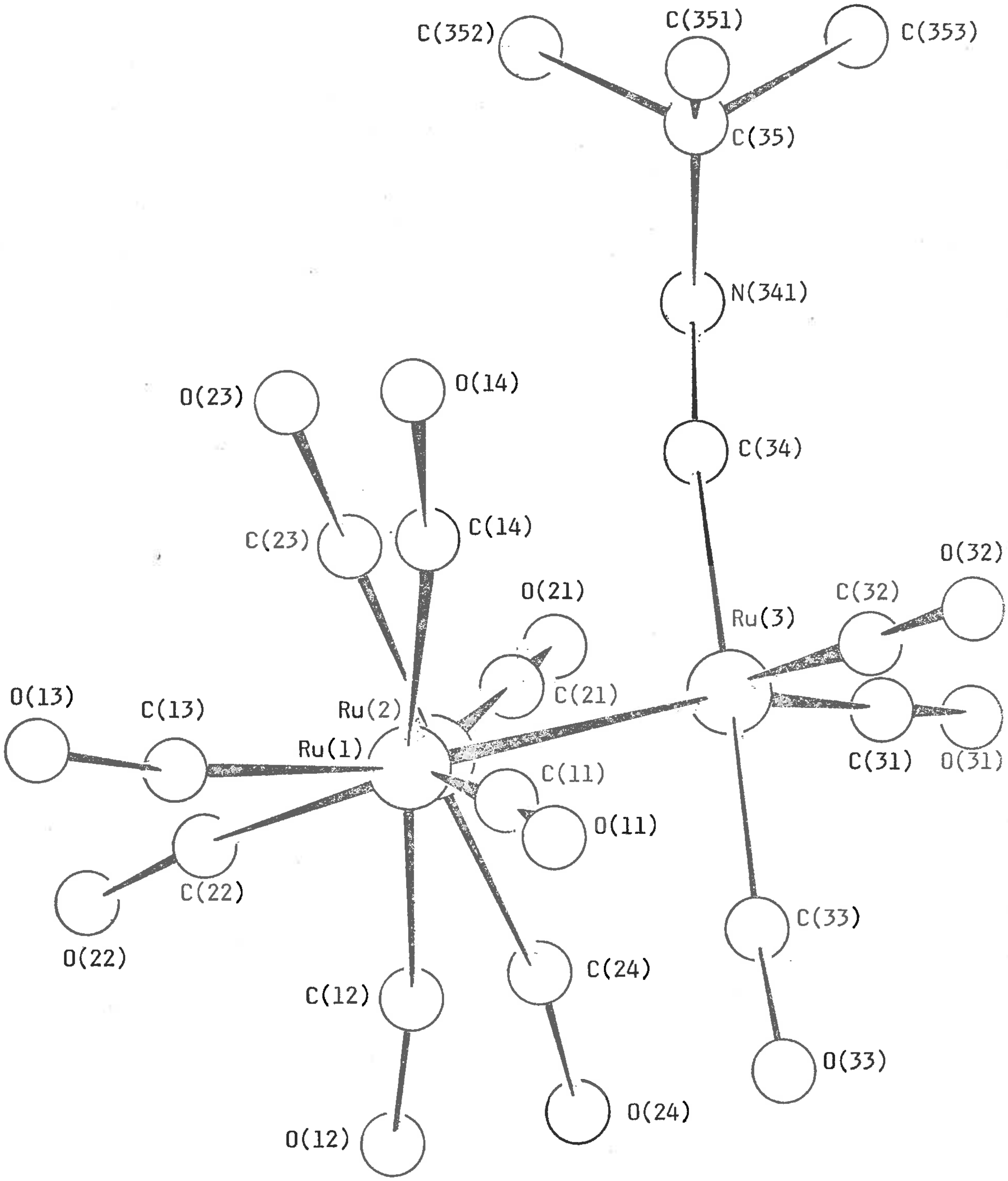

C(352)
C(351)
C(353)
C(35)
N(341)
O(23)
O(14)
C(34)
C(23)
C(14)
O(32)
O(21)
C(32)
Ru(3)
C(21)
O(13)
C(13)
Ru(2)
Ru(1)
C(11)
C(31)
O(31)
O(11)
C(22)
O(22)
C(33)
C(24)
C(12)
O(33)
O(24)
O(12)

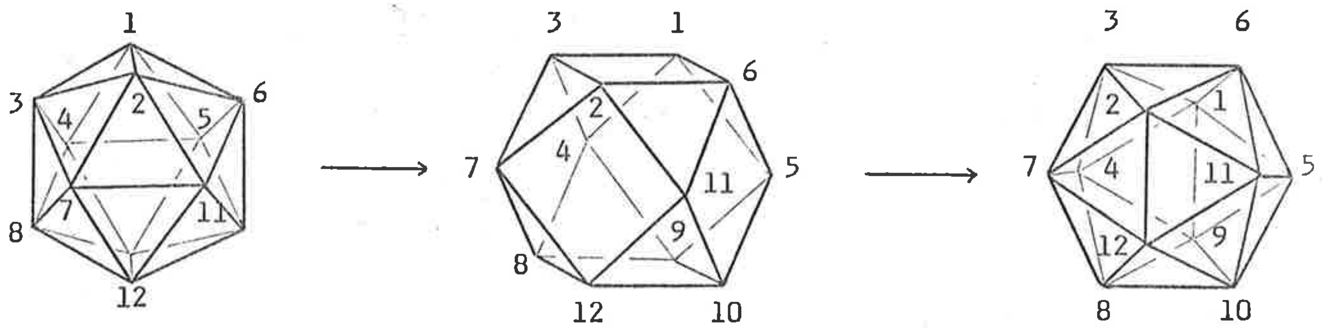
Figure 6.1

TABLE 6.I

Interatomic distances (Å)

Ru(1)-Ru(2)	2.866
Ru(2)-Ru(3)	2.844
Ru(3)-Ru(1)	1.852
Ru(1)-C(11)	1.93
Ru(1)-C(12)	1.93
Ru(1)-C(13)	1.93
Ru(1)-C(14)	1.86
C(11)-O(11)	1.13
C(12)-O(12)	1.13
C(13)-O(13)	1.11
C(14)-O(14)	1.17
Ru(2)-C(21)	1.90
Ru(2)-C(22)	1.93
Ru(2)-C(23)	1.89
Ru(2)-C(24)	1.87
C(21)-O(21)	1.13
C(22)-O(22)	1.12
C(23)-O(23)	1.19
C(24)-O(24)	1.16
Ru(3)-C(31)	1.87
Ru(3)-C(32)	1.83
Ru(3)-C(33)	1.90
Ru(3)-C(34)	1.99
C(31)-O(31)	1.14
C(32)-O(32)	1.15
C(33)-O(33)	1.16
C(34)-N(341)	1.16
N(341)-C(35)	1.51
C(35)-C(351)	1.52
C(35)-C(352)	1.54
C(35)-C(353)	1.58

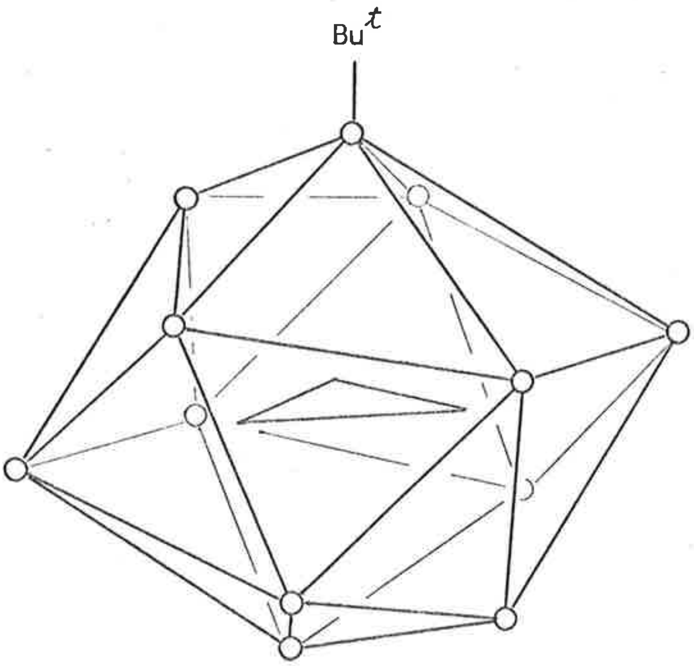
Figure 6.II



Initial icosahedron

cuboctahedron

Final icosahedron



$Ru_3(CO)_{11}(CNBu^t)$

It is evident, from the comparison of the spectral properties of (6.1) and $Os_3(CO)_{11}(CNBu^t)$, that the various ν(CN) and ν(CO) frequencies and ^1H and ^{13}C n.m.r. resonances are not very closely related. The osmium complex exists in two isomeric forms, with axial and equatorial isocyanide substituents.[40] The fluxional process is slowed sufficiently at -60^0 for individual ^{13}C resonances to be assigned, but the weighted mean for the axial isomer is some 20 ppm to lower field than found for (6.1). The ν(CO) spectra of the two complexes have similar patterns, most bands being shifted to higher frequencies by c. 5-7 cm^{-1} in the Os complex Similar comparisons between $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ show that these shifts form part of a general pattern, and indeed are consistent with the replacement of Ru by the heavier Os.

Reactions of $Ru_3(CO)_{11}(CNBu^t)$ (6.1)

A reaction between (6.1) and one equivalent of tosmic gave the trisubstituted complex $Ru_3(CO)_9(CNCH_2SO_2C_6H_4Me\text{-}4)_3$ (6.4) in moderate yield, no mixed isocyanide complexes being isolated. The lability of the *t*-butyl isocyanide ligand was further demonstrated in a reaction between (6.1) and CO (at atmospheric pressure), the complexes $Ru_3(CO)_{12}$, (6.1) and $Ru_3(CO)_{10}(CNBu^t)_2$ being isolated. This latter reaction suggested that the monosubstituted group V derivatives of $Ru_3(CO)_{12}$, which are not readily obtained, might be formed from reactions between (6.1) and these group V ligands.

The reaction between (6.1) and PPh_3 was monitored by n.m.r. spectroscopy (see experimental). The major product of the reaction, $Ru_3(CO)_{10}(CNBu^t)(PPh_3)$ (6.6), was characterized in the normal manner. A low yield of the monosubstituted phosphine complex $Ru_3(CO)_{11}(PPh_3)$ was also obtained. The initial product of the reaction was not characterized but probably is an isomeric form of (6.6). When the reaction was carried out using excess phosphine, the trisubstituted complex $Ru_3(CO)_9(PPh_3)_3$ was obtained. Using tri-4-tolylphosphine, under milder conditions, a reasonable yield (40%) of the monophosphine complex $Ru_3(CO)_{11}\{P(C_6H_4Me\text{-}4)_3\}$ (6.7) was obtained. Under more vigorous conditions a product analogous to (6.6) was isolated, $Ru_3(CO)_{10}(CNBu^t)\text{-}\{P(C_6H_4Me\text{-}4)_3\}$ (6.8). This complex is sensitive to oxidation and we have not been able to obtain satisfactory microanalytical results.

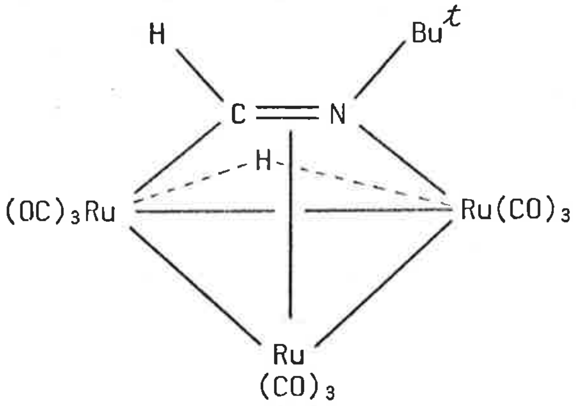
Reaction of $Ru_3(CO)_{11}(CNBu^t)$ and $Ru_3(CO)_{10}(CNBu^t)_2$ with dihydrogen

In a surprisingly easy reaction, dihydrogen reacts directly with $Ru_3(CO)_{12}$ in a boiling hydrocarbon solvent at *c.* 120° to give $H_4Ru_4(CO)_{12}$ in high yield.[45] There have been few reported extensions of this reaction other than those mentioned in the original account, although the reaction is an important example of the activation of molecular hydrogen by metal cluster complexes.

We have studied the reaction of dihydrogen with $Ru_3(CO)_{11}(CNBu^t)$,[46] which occurs under somewhat milder conditions than those employed for $Ru_3(CO)_{12}$. For example, a reaction carried out in refluxing cyclohexane for 90 minutes under dihydrogen (1 atmosphere) afforded five products in a combined yield of *c.* 80%, which have been separated by extensive chromatography on Florisil. Three minor products were readily identified as the tetranuclear hydrido complexes $H_4Ru_4(CO)_{12-n}(CNBu^t)_n$ {n = 0-2} by comparison of their infrared, ^1H n.m.r. and mass spectra with those of authentic samples.[37,45]

The major product isolated from this reaction formed yellow plates, m.p. *c.* 100° (dec.), with ν(CO) at 2093m, 2067s, 2038s, 2020s, 1998s, 1995m and 1986 cm^{-1}, which were identified as $HRu_3(CO)_9(HC{=}NBu^t)$ (6.9) from the following evidence. The infrared spectrum does not contain any ν(CN) absorption between 2100-2200 cm^{-1}, and resonances in the ^1H n.m.r. spectrum occur at δ 9.45 (the formimidoyl hydrogen), 1.16 (the *t*-butyl hydrogens) and -18.01 (metal hydride hydrogen). The mass spectrum contains 13 ion clusters between *m/e* 305-642, the highest ion cluster and microanalytical results confirming the molecular formula.

Consideration of possible structures for this complex suggested that the one shown below represents the best arrangement of non-hydrogen atoms which accords with the spectroscopic evidence. A formimidoyl ligand is bonded to all three metal atoms, acting as a five-electron donor; the absence of a ν(CN) band, and the lowest field ^{1}H resonance are both consistent with the presence of this ligand. The metal-bonded hydrogen must occupy a bridging position (chemical shift), but this cannot be determined at present. An analogous osmium complex, $HOs_3(CO)_9(HC{=}NPh)$ with similar spectral properties, has recently been structurally characterised.[47]



(6.9)

The fifth complex, obtained in very low yield, was shown to be $HRu_3(CO)_8(CNBu^t)(HC{=}NBu^t)$ (6.10) formally derived from (6.9) by replacement of a CO group by the isocyanide ligand.

The reaction of dihydrogen with $Ru_3(CO)_{10}(CNBu^t)_2$ afforded (6.9) and (6.10) in yields of 22% and 56% respectively. A third minor product was identified as $H_4Ru_4(CO)_{10}(CNBu^t)_2$.

Our results are of interest in relation to the homogeneous reduction of heteronuclear triple bonds. The formation of formimidoyl ligands from isocyanide has been reported in the case of the osmium complex mentioned above, the formation of which is suggested to proceed via an insertion-rearrangement reaction. The stepwise reduction of acetonitrile on an Fe_3 cluster has been demonstrated.[48]

It is interesting to note that the osmium complex containing the $HC{=}NBu^t$ ligand is not formed and this is attributed to the lower tendency of the *t*-butyl isocyanide ligand to engage in insertion reactions.

Comparison of the yields of the products obtained from the reactions of $Ru_3(CO)_{11}(CNBu^t)$ and $Ru_3(CO)_{10}(CNBu^t)_2$ with dihydrogen, suggests that the tetranuclear products are formed only from isocyanide-free compounds. One molecule of dihydrogen displaces either CO or the isocyanide ligand and in the case of $Ru_3(CO)_{11}(CNBu^t)$, $H_2Ru_3(CO)_{10}(CNBu^t)$ and $H_2Ru_3(CO)_{11}$ would be the initial products. The isocyanide complex is then converted via an edge-bridging formimidoyl complex, $HRu_3(CO)_{10}(CH{=}NBu^t)$, to the final product. Presumably $H_2Ru_3(CO)_{11}$ reacts further to give the tetranuclear products. The yield of $H_4Ru_4(CO)_{10}(CNBu^t)_2$ in the reaction of $Ru_3(CO)_{10}(CNBu^t)_2$ with hydrogen was very low and indeed, could be due to $Ru_3(CO)_{11}(CNBu^t)$ impurity in the starting material. The complex $HRu_3(CO)_9(CH{=}NBu^t)$ did not react with dihydrogen, nor did isomerisation take place on heating. In the acetonitrile reduction reaction mentioned above, the complex $HFe_3(CO)_9(MeC{=}NH)$ rearranges on heating to $HFe_3(CO)_9(MeHC{=}N)$ which then undergoes further hydrogenation. Considering the tendency for a *t*-butyl group to undergo a 1,2-shift, compared with a proton, it is not surprising that isomerisation of (6.9) does not occur. The edge-bridging formimidoyl complex, $HRu_3(CO)_{10}(CH{=}NBu^t)$ is indicated as the product in the carbonylation of (6.9), by comparison of infrared data with the Os derivatives.[47]

Thus, examples of partial hydrogenation of the C≡N bond by addition of isocyanide or nitrile to a metal hydride, or of dihydrogen to a coordinated isocyanide, have now been described; there is also one report of formation of a similar ligand from a saturated ligand (NMe_3) on $Os_3(CO)_{12}$.[49]

Pyrolysis of $Ru_3(CO)_{11}(CNBu^t)$

There is currently much interest in reactions which convert one metal cluster into another, and in the extended interactions that are possible between unsaturated ligands and arrays of metal atoms, as one approach to the understanding of the interactions between such molecules and metal surfaces, and hence of heterogeneously catalysed reactions.[50]

On heating powdered $Ru_3(CO)_{11}(CNBu^t)$ at 120°, under a nitrogen atmosphere of c. 0.5 atmospheres, 16 h, a dark brown solid was obtained. Purification by TLC afforded a dark purple pentaruthenium cluster in low yield, later characterised as $Ru_5(CO)_{14}(CNBu^t)_2$ (6.11) by X-ray crystallography.[51] Four other products were isolated from the pyrolysis reaction; ruthenium carbonyl, some residual $Ru_3(CO)_{11}(CNBu^t)$, the disubstituted (6.2) and a purple product (tentatively identified as $Ru_6(CO)_{17}(CNBu^t)$ (6.12) on the basis of mass spectrometric data). Pyrolysis of $Ru_3(CO)_{10}(CNBu^t)_2$ also gave the Ru_5 cluster (6.11) and two other purple fractions which have not been characterised.

The structure of (6.11) is shown in Figure 6.III and relevant bond lengths are shown in Table 6.II. The five metal atoms from an open array of three triangles edge-joined, and bent at these edges to form a 'swallow' cluster. Each metal atom is attached to three two-electron donor ligands (14 CO groups and one $CNBu^t$ ligand), with the second isocyanide ligand being attached to four of the five metal atoms via the N and C atoms. The cluster electron count shows that this ligand acts as a six-electron donor, although a simple account of the attachment is not possible.

Figure 6.III

$Ru_5(CO)_{14}(CNBu^t)_2$

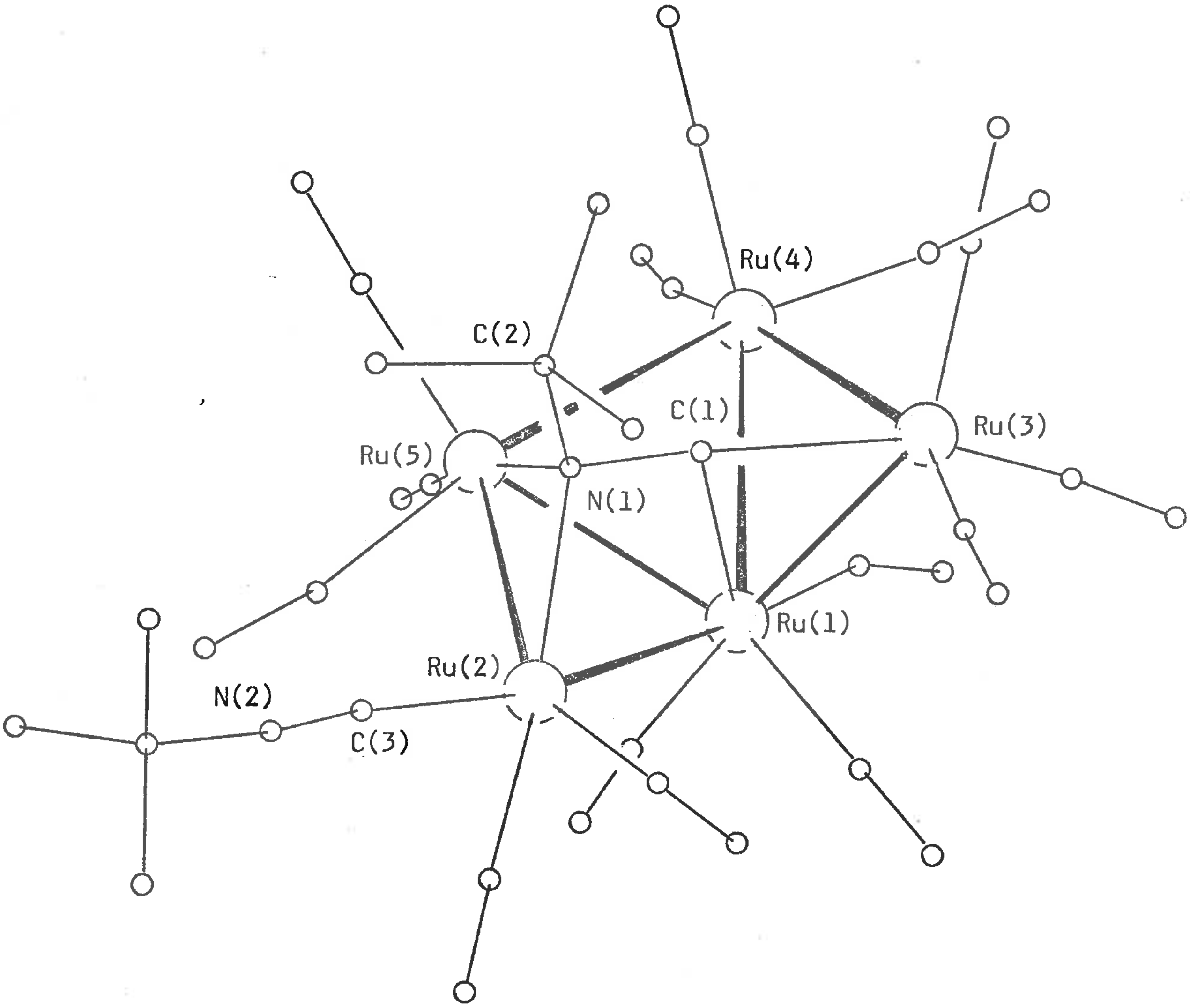
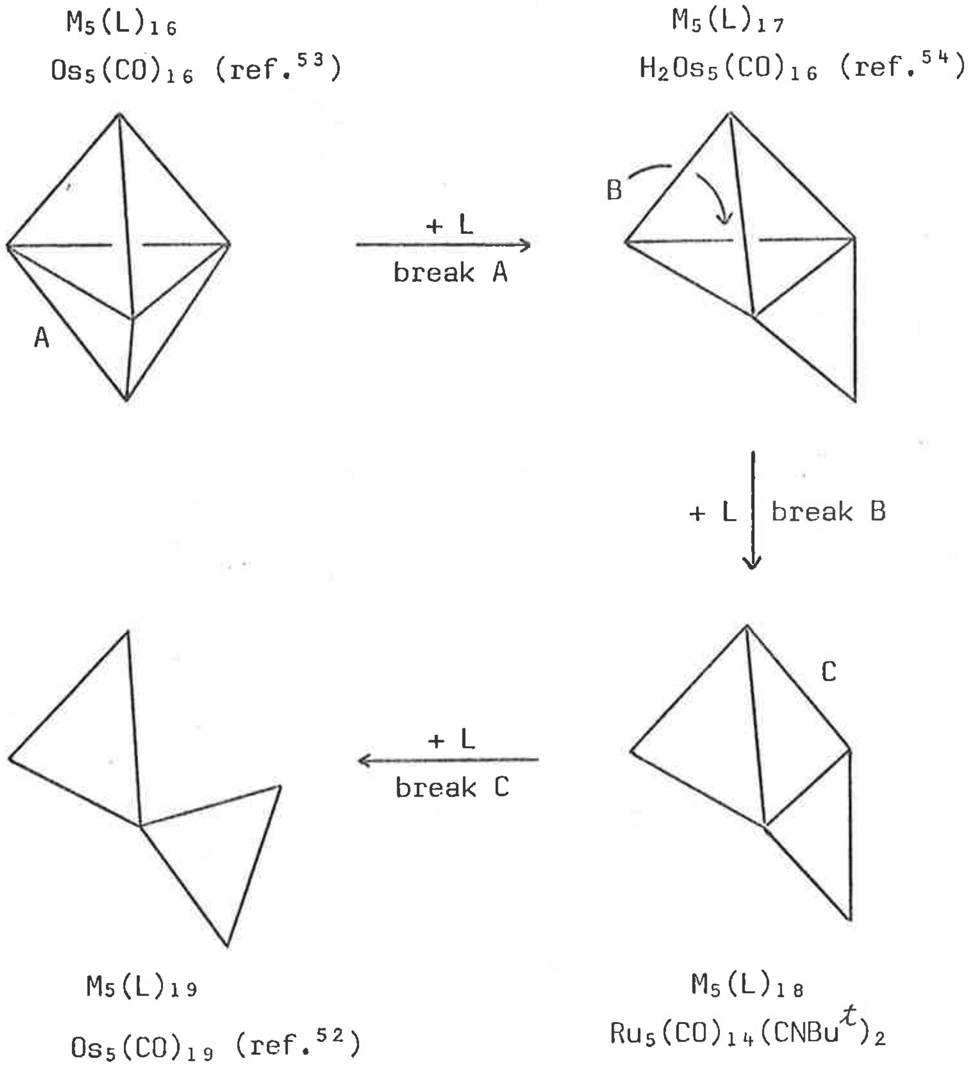


Table 6.II

Interatomic distances (Å)

Ru(1)-Ru(2)	2.78	Ru(3)-C(1)	1.92
Ru(1)-Ru(3)	2.83	C(1)-N(1)	1.38
Ru(1)-Ru(4)	2.78	N(1)-Ru(2)	2.13
Ru(1)-Ru(5)	2.78	N(1)-Ru(5)	2.15
Ru(2)-Ru(5)	2.74	N(1)-C(2)	1.54
Ru(3)-Ru(4)	2.77	Ru(2)-C(3)	2.08
Ru(4)-Ru(5)	2.86	C(3)-N(2)	1.12
Ru(1)-C(1)	2.16		

This cluster is the first Ru_5 system to be crystallographically characterized, although the complex $Ru_5C(CO)_{15}$ is reported as being isostructural with the iron and osmium analogues. More interesting is the open nature of the cluster, which is related to the *closo* polyhedron expected for a M_5 cluster by the opening of two edge bonds. Indeed, with the description of this complex, a complete series of clusters related to each other by successive bond-breaking and addition of two-electron ligands has now been described:[52]



As expected, $Ru_5(CO)_{14}(CNBu^t)_2$ is highly reactive, and readily adds two-electron ligands resulting in a breakdown of the Ru_5 cluster to Ru_3 clusters.

Thus, the trigonal bipyramidal cluster in $Os_5(CO)_{16}$ is converted to the structure in $Os_5(CO)_{19}$ where five Os atoms define triangles sharing a vertex.[52] $H_2Os_5(CO)_{15}$ is isoelectronic with $Os_5(CO)_{16}$ and a similar structure is predicted both by the Wade Theory and the skeletal electron counting scheme. Addition of CO to $H_2Os_5(CO)_{15}$ results in cleavage of an Os-Os bond, followed by an opening out of the structure to yield the edge-bridged tetrahedral arrangement in $H_2Os_5(CO)_{16}$.[54] The cluster in (6.11) is formally derived from the edge-bridged tetrahedron by breaking bond (B), and is related to the $Os_5(CO)_{19}$ structure by further cleavage of bond (C), both processes being accompanied by addition of one two-electron ligand.

It has been established that $Os_5(CO)_{16}$ undergoes reversible addition of CO to give $Os_5(CO)_{19}$[52] and therefore it should be possible to decarbonylate (6.11) to give an edge-bridged tetrahedral or trigonal bipyramidal arrangement.

In contrast, pyrolysis of the related osmium complex, $Os_3(CO)_{11}(CNBu^t)$, affords $Os_6(CO)_{16}(CNBu^t)_2$, which has the same metal skeleton as $Os_6(CO)_{18}$;[56] addition of 4-tolyl isocyanide to the latter affords the complex $Os_6(CO)_{18}(CNC_6H_4CH_3\text{-}4)_2$, containing a bridging isocyanide as a four-electron donor, with a rearranged metal skeleton.[56]

Synthesis of $Ru_3(CO)_{12}$

In the experimental section we describe an improved synthesis of the cluster carbonyl $Ru_3(CO)_{12}$. In the original synthesis,[1] carbonylation of methanol solutions of hydrated ruthenium trichloride under moderate conditions of pressure (less than 10 atmospheres) and temperature (70°), in the presence of zinc as a reducing agent and halogen acceptor, gave the carbonyl in c. 70% yield. However, some workers have experienced difficulty in reproducing this synthesis.

Exploration of the effects of temperature and pressure on the reaction has shown that the conversion of ruthenium trichloride to the carbonyl proceeds efficiently if the reaction is carried out at 125° under carbon monoxide pressure of 50 atmospheres, in the absence of zinc. Under these conditions, essentially quantitative conversion occurs; in general, we recycle the mother liquors, which are pale greenish yellow in colour, often up to five times. The carbon monoxide acts as both reducing and carbonylating agent; by-products of the reaction are presumably hydrogen chloride and methyl formate. We note that under milder conditions (less than 10 atmospheres, 70°) the major product is the carbonyl chloride, $\{RuCl_2(CO)_3\}_2$, but this may be accompanied by up to 18% $Ru_3(CO)_{12}$.

Reactions of $Ru_3(CO)_{12}$ with some Group V Ligands

As mentioned in the introduction to this chapter, the reaction between $Ru_3(CO)_{12}$ and substituted phosphines usually proceeds without the isolation of mono- or di-substituted derivatives. The reaction between $Ru_3(CO)_{12}$ and one equivalent of tricyclohexylphosphine afforded a high yield (41%) of the monosubstituted complex $Ru_3(CO)_{11}\{P(C_6H_{11})_3\}$ (6.13) along with unreacted $Ru_3(CO)_{12}$ (33%). Reaction conditions were varied to maximise the yield of (6.13) and to obtain di- and tri-substituted products. Only in reactions where a large excess (10-fold) of the tertiary phosphine was used were other products obtained; microanalytical results indicated that these were not Ru_3 clusters. Presumably, the ruthenium Ru_3 cluster can accommodate only one bulky $P(C_6H_{11})_3$ ligand; addition of a second ligand results in a breakdown of the cluster.

The reaction $Ru_3(CO)_{12}$ with the bidentate N-donor ligand, 2,2'-dipyridyl, afforded purple crystals of $Ru_3(CO)_{10}(dpy)$ (6.14). The infrared spectrum indicated a bridging carbonyl at 1740 cm^{-1} and is similar to that of the pyridazine complex $Ru_3(CO)_{10}(C_4H_4N_2)$.[26]

Pyridine was found to react with $Ru_3(CO)_{12}$ to give a bridging 2-pyridyl complex $HRu_3(CO)_{10}(NC_5H_4)$ (6.15) in which transfer of an *ortho*-hydrogen to the metal has taken place presumably via the formation of the intermediate $Ru_3(CO)_{11}(py)$. Further reaction with pyridine produced the dihydrido species $H_2Ru_3(NC_5H_4)_2(CO)_8$ (6.16). These products were characterised by mass spectrometric and microanalytical data. Infrared spectra are similar to those of the osmium analogues. Reactions of $Os_3(CO)_{12}$ with pyridine, 4-substituted pyridines, quinoline and isoquinoline, have confirmed that metalation at the α-position is the preferred mode of reaction in all these cases, even where there are β C-H bonds suitable for attack.[57]

Reactions of $H_4Ru_4(CO)_{12}$

The cluster hydride $H_4Ru_4(CO)_{12}$ is the product of the reaction between $Ru_3(CO)_{12}$ and dihydrogen.[45] This complex reacts with a variety of tertiary phosphines and phosphites,[58-63] yielding mono-, di-, tri-, and/or tetra-substituted derivatives depending on the reaction conditions. Bidentate phosphines yield complexes $H_4Ru_4(CO)_{10}L_2$ $\{L_2 = \text{dppe}\}$ where the ligand chelates either one ruthenium,[61] or two ruthenium atoms.[62] Only the trisubstituted product is isolated from the reaction of $H_4Ru_4(CO)_{12}$ with triphenyl phosphite,[60] although all four derivatives are formed with trimethyl phosphite.[59] Hydride mobility has been established for the phosphite derivatives,[59] and the low temperature ^1H n.m.r. studies of the complex $H_4Ru_4(CO)_{10}$(dppe) suggested an edge-terminal-edge pathway for the hydride scrambling for this complex.^{61}

We have found that *t*-butyl isocyanide reacts with the cluster hydride to give the mono-, di-, and tetra-substituted derivatives (6.17), (6.18) and (6.19), respectively. The compounds were characterised in the usual manner and in the mass spectrum of $H_4Ru_4(CO)_{10}(CNBu^t)_2$ (6.18) a very weak signal at *m/e* 911 indicated the presence of the trisubstituted complex. The ^1H n.m.r. spectrum of $H_4Ru_4(CO)_{11}(CNBu^t)$ (6.17) showed a single chemical shift for the metal-hydrogen at δ -17.97 and the disubstituted product, (6.18), contained resonances at δ -17.7 and -18.2, in contrast to the $P(OMe)_3$ derivatives where the hydrogen atoms are in equivalent environments.^{59}

Using an excess of tri-4-tolylphosphine, the tetrasubstituted complex $H_4Ru_4(CO)_8\{P(C_6H_4Me\text{-}4)_3\}_4$ (6.20) was isolated. The ^{13}CO resonance is a singlet, indicating a scrambling of CO groups. The ^1H n.m.r. shows a quintet for the four hydride atoms, indicating the complex to be fluxional. The ^{13}C and ^1H n.m.r. spectra for the monosubstituted complex $H_4Ru_4(CO)_{11}\{P(C_6H_4Me\text{-}4)_3\}$ (6.21) can be interpreted similarly. However, the spectra for the di- and tri-substituted products $H_4Ru_4(CO)_{10}\{P(C_6H_4Me\text{-}4)_3\}_2$ (6.22) and $H_4Ru_4(CO)_9\{P(C_6H_4Me\text{-}4)_3\}_3$ (6.23) show different hydride environments as in complex (6.18). Low temperature n.m.r. studies were not carried out to delineate the hydride exchange mechanism.

EXPERIMENTAL

General experimental conditions are described in Appendix I. Reactions were generally monitored by infrared spectroscopy.

Preparation of $Ru_3(CO)_{12}$

A solution of $RuCl_3,xH_2O$ (4 g) in methanol (300 ml), in an autoclave, was pressurized to 40 atmospheres with CO. The solution was heated at 125° for 20 h, the working CO pressure increasing to approximately 55 atmospheres. The reaction mixture was allowed to cool, the CO vented, and the bright orange *crystals* of $Ru_3(CO)_{12}$ were collected (2.6 g). Hydrated ruthenium trichloride (2.6 g) was added to the mother liquor and the reaction repeated to yield 2.4 g of the ruthenium carbonyl cluster. The latter procedure was followed two more times, total yield of $Ru_3(CO)_{12}$ being 9.84 g (from 11.44 g of ruthenium trichloride), m.p. 154-155° (dec.) (Found: C, 22.4%; *M* (mass spectrometry), 641. $C_{12}O_{12}Ru_3$ requires C, 22.5%; *M*, 641). Infrared (C_6H_{12}): ν(CO) 2062vs, 2030s, and 2004m cm^{-1}. {Lit.[64] 2062, 2032, 2011 cm^{-1}, in CCl_4; m.p. 154-155°}

Reactions of $Ru_3(CO)_{12}$ with isocyanides

(A) t-*Butyl isocyanide*, *$CNBu^t$*. — (i) A mixture of ruthenium carbonyl (706 mg, 1.10 mmol) and *t*-butyl isocyanide (100 mg, 1.20 mmol) was refluxed in cyclohexane (110 ml) for 2 h. Evaporation of solvent and chromatography (Florisil) afforded two fractions. A yellow band was eluted with light petroleum. Crystallization (light petroleum) then afforded orange crystals of $Ru_3(CO)_{12}$ (114 mg, 16%). Infrared (C_6H_{12}): ν(CO) 2062s, 2030s, 2004m cm^{-1}. The second fraction, an orange-red band, was eluted with light petroleum. Crystallization (light petroleum) then afforded red *crystals* of $Ru_3(CO)_{11}(CNBu^t)$ (6.1) (576 mg, 82%), m.p. 114-116° (Found: C, 27.6; H, 1.3; N, 1.9%; *M* (mass spectrometry), 696. $C_{16}H_9NO_{11}Ru_3$ requires C, 27.7;

H, 1.3; N, 2.0%; *M*, 696). Infrared (C_6H_{12}): ν(CN) 2170w; ν(CO) 2093w, 2047s, 2040s, 2016m, 1998m, and 1995m cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 1.53, s, CMe_3. ^{13}C n.m.r. ($CDCl_3$): δ 201.1, s, CO; 59.0, s, CMe_3; 30.1, s, CMe_3.

(ii) A suspension of ruthenium carbonyl (500 mg, 0.78 mmol) and *t*-butyl isocyanide (130 mg, 1.56 mmol) in petroleum spirit (80 ml) was heated under reflux for 30 min. The solvent was removed, and the residue was chromatographed (Florisil). An orange-red band was eluted with petroleum spirit. Crystallization (light petroleum) then afforded red crystals of $Ru_3(CO)_{11}(CNBu^t)$ (6.1) (80 mg, 15%). A second fraction, a red-orange band, was eluted with petroleum spirit. Crystallization from light petroleum gave deep red *crystals* of pure $Ru_3(CO)_{10}(CNBu^t)_2$ (6.2) (410 mg, 70%), m.p. 90-91^0 (Found: C, 31.5; H, 2.4; N, 3.7%; *M* (mass spectrometry), 751. $C_{20}H_{18}N_2O_{10}Ru_3$ requires C, 32.0; H, 2.4; N, 3.7%; *M*, 751). Infrared (C_6H_{12}): ν(CN) 2155w; ν(CO) 2065w, 2020s, 2007m, 1996w, 1990m, and 1986m cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 1.54, s, CMe_3. ^{13}C n.m.r. ($CDCl_3$): δ 204.0, s, CO; 144.1, s, C=N; 58.3, s, CMe_3; 30.2, s, CMe_3.

(iii) A mixture of $Ru_3(CO)_{10}(CNBu^t)_2$ (48 mg, 0.06 mmol) and *t*-butyl isocyanide (5 mg, 0.06 mmol) was warmed in cyclohexane (30 ml) for 10 min. The tri-substituted complex $Ru_3(CO)_9(CNBu^t)_3$ (6.3) was identified spectroscopically. Infrared (C_6H_{12}): ν(CN) 2139m; ν(CO) 2040m, 1998s, and 1971s cm^{-1}. ^{1}H n.m.r. (C_6D_6): δ 1.04, s, CMe_3. ^{13}C n.m.r. (C_6D_6): δ 208.0, s, CO; 57.8, s, CMe_3; 30.0, s, CMe_3.

(*B*) *4-Toluenesulphonylmethylisocyanide* (*tosmic*), $CNCH_2SO_2C_6H_4Me$-4. — (i) A mixture of ruthenium carbonyl (160 mg, 0.25 mmol) and tosmic (49 mg, 0.25 mmol) was refluxed in benzene (40 ml) for 12 h. Chromatography (Florisil) afforded two fractions. An orange band was eluted with light petroleum and crystallization (light petroleum) yielded orange crystals of $Ru_3(CO)_{12}$ (85 mg, 53%). The second band, purple-brown in colour, was eluted with methanol. Crystallization acetone/light petroleum afforded

purple-brown *crystals* of $Ru_3(CO)_9(CNCH_2SO_2C_6H_4Me\text{-}4)_3$ (6.4) (80 mg, 28%) (Found: C, 36.9; H, 2.9; N, 3.8. $C_{36}H_{27}N_3O_{15}Ru_3S_3$ requires C, 37.9; H, 2.4; N, 3.7%). Infrared (Nujol): ν(CN) 2168m; ν(CO) 1980s cm^{-1}.
(ii) A mixture of ruthenium carbonyl (160 mg, 0.25 mmol) and tosmic (147 mg, 0.75 mmol) was refluxed in benzene (40 ml) for 12 h. The solution was allowed to cool, and the purple-brown crystals that deposited were recrystallized (acetone/light petroleum) afforded $Ru_3(CO)_9(CNCH_2SO_2C_6H_4Me\text{-}4)_3$ (6.4) (175 mg, 61%), identical with the product obtained above.

(C) *Cyclohexyl isocyanide, CNCy (by J. Matisons).* — A mixture of ruthenium carbonyl (650 mg, 1.02 mmol) and cyclohexyl isocyanide (130 mg, 1.19 mmol) in tetrahydrofuran (100 ml) at 70°C for 135 min. Evaporation of the solvent and chromatography (Florisil) afforded four fractions. A orange band was eluted with light petroleum. Crystallization (light petroleum) afforded orange crystals of $Ru_3(CO)_{12}$ (320 mg, 49%) identified by infrared spectroscopy. A second fraction, an orange band, was eluted with light petroleum. Crystallization (light petroleum) afforded orange *crystals* of $Ru_3(CO)_{11}(CNCy)$ (6.5) (161 mg, 22%), m.p. 139-141° (Found: C, 30.0; H, 1.5; N, 1.9%; *M* (mass spectrometry), 722. $C_{18}H_{11}NO_{11}Ru$ requires C, 30.0; H, 1.5; N, 1.9%; *M*, 722). Infrared (C_6H_{12}): ν(CN) 2155w; ν(CO) 2092w, 2071vw, 2062w, 2049s, 2041vs, 2019m, 1999m, and 1992m cm^{-1}. ^1H n.m.r. $\{(CD_3)_2CO\}$: δ 1.14, m, Cy. A red fraction, in very low yield, was eluted with light petroleum. The infrared in cyclohexane: ν(CN) 2165m; ν(CO) 2071m, 2046m, 2037sh, 2023vs, 1994s, 1984s, and 1975s cm^{-1}. The fourth fraction eluted with diethyl ether, afforded pink translucent crystals (14 mg), m.p. 80-83° (Found: C, 42.6; H, 5.1; N, 3.4%). Infrared (C_6H_{12}): ν(CN) 2167w; ν(CO) 2073m, 2060w, 2048s, 2040s, 2026vs, 1995s, 1987m, and 1968m cm^{-1}. ^1H n.m.r. $\{(CD_3)_2CO\}$: δ 1.14, m, Cy. The latter two products were not identified.

Reactions of $Ru_3(CO)_{11}(CNBu^t)$

(A) *Tosmic,* $CNCH_2SO_2C_6H_4Me\text{-}4$. — A solution of $Ru_3(CO)_{11}(CNBu^t)$ (6.1) (173 mg, 0.25 mmol) and tosmic (49 mg, 0.25 mmol) in benzene (20 ml) was heated under reflux for 30 min. The solvent was removed, and the residue chromatographed (Florisil). An orange-red band was eluted with petroleum spirit. Crystallization (light petroleum) then afforded red crystals of $Ru_3(CO)_{11}(CNBu^t)$ (6.1) (85 mg, 49%) identified by the infrared spectrum. A purple band was eluted eith light petroleum/diethyl ether (3:1). A second purple fraction was eluted with diethyl ether. The infrared spectra of these two fractions indicated the products were identical to those formed in the pyrolysis of $Ru_3(CO)_{11}(CNBu^t)$ (see below). A fourth purple-brown band was eluted with methanol. Crystallization afforded purple-brown crystals of $Ru_3(CO)_9(CNCH_2SO_2C_6H_4Me\text{-}4)_3$ (6.4) (55 mg, 19%), identical with the product obtained from the reaction of $Ru_3(CO)_{12}$ and tosmic (see above).

(B) *Carbon monoxide,* CO. — Carbon monoxide at atmospheric pressure was bubbled into a refluxing solution of $Ru_3(CO)_{11}(CNBu^t)$ (6.1) (100 mg, 0.14 mmol) in cyclohexane (20 ml) for 75 min. The solution was allowed to cool, the solvent removed, and the residue chromatographed (Florisil). An orange band was eluted with light petroleum. Crystallization (methanol) afforded orange crystals of $Ru_3(CO)_{12}$ (10 mg, 21%) identified by infrared comparison with an authentic sample. A red-orange band was eluted with light petroleum. Crystallization (light petroleum) afforded red crystals of $Ru_3(CO)_{11}(CNBu^t)$ (6.1) (60 mg, 60%) identified by infrared spectroscopy. A red band was eluted with light petroleum. Crystallization (light petroleum) afforded deep red crystals of $Ru_3(CO)_{10}(CNBu^t)_2$ (6.2) (15 mg, 14%), identified by infrared spectroscopy.

(C) *Triphenylphosphine, PPh_3.* — (i) Triphenylphosphine (70 mg, 0.27 mmol) was added to a solution of (6.1) (186 mg, 0.27 mmol) in $CDCl_3$ (2 ml). The reaction was followed by ^1H n.m.r. and ^{13}C n.m.r. spectroscopy, monitoring the Bu^t and CO signals respectively. Resonances at δ 1.54 (starting material) and 1.35 in the ^1H n.m.r. spectrum indicated the presence of at least one new complex. These signals were associated with ^{13}CO resonances at δ 201.3 and 209.9 respectively. Heating for a period of 1 minute at *c.* 45° resulted in a new Bu^t resonance at δ 1.48 in the ^1H n.m.r. spectrum (associated with ^{13}CO resonance at δ 205.4). Heating for a further 4 minutes resulted in the signal at δ 1.48 increasing in intensity, with signals at δ 1.54 and 1.35 decreasing in intensity. After a period of 8 hours at *c.* 35° signal at δ 1.34 was no longer present. Chromatography on a preparative TLC plate (silica gel G adsorbent; light petroleum developer) yielded four bands. Band one, yellow in colour, with R_f *c.* 0.8, afforded yellow-orange crystals of $Ru_3(CO)_{12}$ (5 mg, 3%). Band two, orange in colour, with R_f *c.* 0.7, afforded red crystals of (6.1) (60 mg, 32%). These two compounds were identified by comparison of their infrared spectra with authentic samples. Band three, red-orange in colour and with R_f *c.* 0.5, afforded pink crystals of $Ru_3(CO)_{11}(PPh_3)$ (10 mg, 4%). Infrared (C_6H_{12}): ν(CO) 2092w, 2042s, 2025sh, 2016sh, 2004s, 1993w, and 1988w cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.47, and 7.41, m, PPh_3. This compound was identified by comparison of the infrared spectrum with that of $Ru_3(CO)_{11}(PPh_3)$, prepared by an alternative method. The fourth band, red-brown in colour, with R_f *c.* 0.4, afforded $Ru_3(CO)_{10}(CNBu^t)(PPh_3)$ (6.6) as a burnt-orange powder (75 mg, 30%) (Found: C, 43.6; H, 2.9; N, 1.4. $C_{33}H_{24}NO_{10}PRu_3$ requires C, 42.7; 2.6; N, 1.5%). Infrared (C_6H_{12}): ν(CN) 2161w; (CO) 2064m, 2021s, 1995s, and 1976m cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 7.39, m, 15H, PPh_3; 1.48, s, 9H, CMe_3.

(ii) The reaction of $Ru_3(CO)_{11}(CNBu^t)$ (6.1) (100 mg, 0.14 mmol) with excess triphenylphosphine (150 mg, 0.57 mmol) in refluxing cyclohexane (20 ml) afforded the purple product $Ru_3(CO)_9(PPh_3)_3$ (140 mg, 75%) identified by infrared comparison with an authentic sample.

(*D*) *Tri-4-tolylphosphine*, $P(C_6H_4Me\text{-}4)_3$. — (i) Tri-4-tolylphosphine (110 mg, 0.36 mmol) was added to a solution of $Ru_3(CO)_{11}(CNBu^t)$ (6.1) (250 mg, 0.36 mmol) in light petroleum (60 ml) and the mixture was refluxed for 30 min. The solvent was removed and the residue chromatographed (Florisil). Three fractions were collected. A yellow fraction, eluted with light petroleum, yielded orange crystals of $Ru_3(CO)_{12}$ (15 mg, 7%), identified by infrared spectroscopy. An orange fraction, eluted with light petroleum, yielded red crystals of the starting material $Ru_3(CO)_{11}(CNBu^t)$ (6.1) (110 mg, 44%), identified by infrared spectroscopy. The third fraction, red in colour, eluted with light petroleum, yielded red *crystals* of $Ru_3(CO)_{11}\{P(C_6H_4Me\text{-}4)_3\}$ (6.7) (40 mg, 12%). Infrared (C_6H_{12}): ν(CO) 2093w, 2043s, 2029sh, 2022sh, 2013s, 1987sh, and 1974w cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.32, m, 12H, C_6H_4; 2.39, s, 9H, Me.

(ii) Tri-4-tolylphosphine (100 mg, 0.33 mmol) was added to a solution of $Ru_3(CO)_{11}(CNBu^t)$ (228 mg, 0.33 mmol) in light petroleum (50 ml) and the mixture refluxed for 2 h. Chromatography (Florisil) afforded three fractions. An orange fraction, eluted with light petroleum, afforded red crystals of $Ru_3(CO)_{11}(CNBu^t)$ (6.1) (80 mg, 35%). A second fraction, eluted with light petroleum/diethyl ether (1;20) yielded $Ru_3(CO)_{10}(CNBu^t)$-$\{P(C_6H_4Me\text{-}4)_3\}$ (6.8) (120 mg, 37%) as an orange-red *powder* (Found: *M* (mass spectrometry), 972. $C_{36}H_{30}NO_{10}PRu_3$ requires *M*, 972). Infrared (C_6H_{12}): ν(CN) 2164w; ν(CO) 2066m, 2024s, 1996s, and 1978m cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.26, m, 12H, C_6H_4; 2.36, s, 9H, C_6H_4Me, 1.49, s, 9H, CMe_3. ^{13}C n.m.r. ($CDCl_3$): δ c. 205.5, s, CO; 140.3-128.7, m, C_6H_4; 30.0, s, CMe_3; 21.3, s, C_6H_4Me. The third fraction, purple in colour and a minor product was eluted with light petroleum/diethyl ether (1:1). Infrared (C_6H_{12}): ν(CN) 2148w; ν(CO) 2041w, 1997ms, 1988vs, and 1981sh cm^{-1}. This product was not identified.

(iii) The reaction of $Ru_3(CO)_{11}(CNBu^t)$ (6.1) (100 mg, 0.14 mmol) with three equivalents of tri-4-tolylphosphine (128 mg, 0.42 mmol) in cyclohexane (50 ml) at reflux for 30 minutes afforded purple crystals of $Ru_3(CO)_9\{P(C_6H_4Me\text{-}4)_3\}_3$ (170 mg, 83%), identified by comparison of infrared and ^1H n.m.r. data with an authentic sample.

Reaction of $Ru_3(CO)_{11}(CNBu^t)$ with dihydrogen

Dihydrogen, at atmospheric pressure, was bubbled into a refluxing solution of $Ru_3(CO)_{11}(CNBu^t)$ (300 mg, 0.43 mmol) in cyclohexane (100 ml) for 1 h. The solution was allowed to cool, solvent removed, and the residue chromatographed (Florisil). Five fractions were eluted. A yellow-orange fraction was eluted with light petroleum. Crystallization (light petroleum) afforded yellow crystals of $H_4Ru_4(CO)_{12}$ (40 mg, 12%), identified by infrared and mass spectrometric comparison with an authentic sample. A yellow fraction was eluted with light petroleum. Crystallization (light petroleum) afforded yellow *crystals* of $HRu_3(CO)_9(CHNBu^t)$ (6.9) (145 mg, 52%), m.p. >100° (Found: C, 26.3; H, 1.8; N, 2.2%; *M* (mass spectrometry), 642. $C_{14}H_{11}NO_9Ru_3$ requires C, 26.3; H, 1.7; N, 2.2%; *M* 642). Infrared (C_6H_{12}): ν(CO) 2093m, 2067s, 2038s, 2020s, 1998s, 1995m, and 1986m cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 9.45, s, 1H, CH; 1.16, s, 9H, CMe_3; -18.01, s, 1H, RuH. An orange fraction was eluted with light petroleum. Crystallization (light petroleum) afforded red crystals of $H_4Ru_4(CO)_{11}(CNBu^t)$ (6.17) (45 mg, 13%), identified by infrared and mass spectrometric comparison with the product obtained in the reaction between $H_4Ru_4(CO)_{12}$ and *t*-butyl isocyanide (see below). A fourth band, a yellow fraction, was eluted with light petroleum. Recrystallization (light petroleum) afforded yellow *crystals* of $HRu_3(CO)_8(CNBu^t)(CHNBu^t)$ (6.10) (45 mg, 15%) (Found: *M* (mass spectrometry), 697. $C_{18}H_{20}N_2O_8Ru_3$ requires *M*, 697). Infrared (C_6H_{12}): ν(CN) 2162w; ν(CO) 2075m, 2072m, 2053vw, 2033s, 2013vs, 1996m, 1992s, 1985m, 1971w, and 1963sh cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 9.46, s, 1H, CH; 1.50, s, and 1.14, s, 18H, CMe_3; -17.69, s, and -18.04, s, 1H, RuH. The final band, an orange fraction, was eluted with light petroleum/diethyl ether (1:1). Recrystallization (light petroleum) afforded red crystals of $H_4Ru_4(CO)_{10}(CNBu^t)_2$ (6.18) (17 mg, 5%), identified by infrared and mass spectrometric comparison with the product obtained in the reaction between $H_4Ru_4(CO)_{12}$ and *t*-butyl isocyanide (see below).

Reaction of $Ru_3(CO)_{10}(CNBu^t)_2$ with dihydrogen

Dihydrogen, at atmospheric pressure, was bubbled into a refluxing solution of $Ru_3(CO)_{10}(CNBu^t)_2$ (270 mg, 0.36 mmol) in cyclohexane (100 ml) for 50 min. The solution was allowed to cool, an unidentified brown precipitate (10 mg) was filtered off, the solvent removed, and the residue chromatographed (Florisil). Three fractions were eluted. A yellow fraction was eluted with light petroleum. Crystallization (light petroleum) afforded yellow crystals of $HRu_3(CO)_9(CHNBu^t)$ (6.9) (50 mg, 22%), identified by infrared comparison with the major product obtained in the reaction between $Ru_3(CO)_{11}(CNBu^t)$ and dihydrogen. A second yellow fraction was eluted with light petroleum. Crystallization (light petroleum) afforded yellow crystals of $HRu_3(CO)_8(CNBu^t)(CHNBu^t)$ (6.10) (140 mg, 56%), identified by infrared and mass spectrometric comparison with the minor product obtained in the reaction between $Ru_3(CO)_{11}(CNBu^t)$ and dihydrogen. The final fraction, a yellow-orange band, was eluted with diethyl ether. Crystallization (light petroleum) afforded red crystals of $H_4Ru_4(CO)_{10}(CNBu^t)_2$ (6.18) (40 mg, 12%), identified by infrared comparison with the product obtained in the reaction between $H_4Ru_4(CO)_{12}$ and *t*-butyl isocyanide (see below).

Pyrolysis of $Ru_3(CO)_{11}(CNBu^t)$

A solution of $Ru_3(CO)_{11}(CNBu^t)$ (6.1) (500 mg, 0.72 mmol) in acetone (30 ml), in a 250 ml round-bottomed flask, was evaporated, leaving a film of complex (6.1) on the glass surface. The flask, under a nitrogen pressure *c.* 0.5 atmospheres, was heated in an oil bath, at 120°, for 16 h. The reaction product was extracted with acetone (4x20 ml), leaving a metal-ash residue of *c.* 180 mg. The extracts were combined, concentrated and chromatographed on a preparative TLC plate (silica gel G adsorbent; light petroleum developer). Five bands were obtained. Band one, yellow in colour, with R_f *c.* 0.8, afforded orange crystals of $Ru_3(CO)_{12}$ (10 mg, 2%). Band two, orange in colour, with R_f *c.* 0.7, afforded red crystals of $Ru_3(CO)_{11}(CNBu^t)$ (6.1) (30 mg, 6%). The third band, orange in colour, with R_f *c.* 0.6, afforded red crystals of $Ru_3(CO)_{10}(CNBu^t)_2$ (6.2) (10 mg, 2%). The fourth band was purple in colour with R_f *c.* 0.3. The product was crystallized from light petroleum as purple *crystals* (20 mg, 3%) and identified tentatively as $Ru_5(CO)_{14}$-$(CNBu^t)_2$ (6.11) (Found: C, 27.6; H, 1.5; N, 2.6%; *M* (mass spectrometry), 106 $C_{24}H_{10}N_2O_{14}Ru_5$ requires C, 27.1; H, 1.7; N, 2.6%; *M*, 1068). Infrared (C_6H_{12}) ν(CN) 2158vw; ν(CO) 2073w, 2044s, 2028m, 1999s, and 1995sh cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 1.38, s, CMe_3. ^{13}C n.m.r. ($CDCl_3$): δ 223.0, s, CO; 30.3, and 29.4, s, CMe_3. The fifth band, purple in colour, with R_f *c.* 0.2 was a minor fraction, and we were unable to obtain crystals of the product which was tentatively identified as $Ru_6(CO)_{17}(CNBu^t)$ (6.12) on the basis of mass spectrometric evidence (Found: *M* (mass spectrometry), 1169, $C_{22}H_5NO_{17}Ru_6$ requires *M*, 1169). Infrared (C_6H_{12}): ν(CN) 2149w; ν(CO) 2058w, 2032s, 2022s, 1996vs, 1977w, and 1967sh cm^{-1}.

Reactions of $Ru_3(CO)_{12}$

(A) *Tricyclohexylphosphine, $P(C_6H_{11})_3$.* — A mixture of $Ru_3(CO)_{12}$ (2.00 g, 3.13 mmol) and tricyclohexylphosphine (880 mg, 3.13 mmol) in cyclohexane (350 ml) was heated under reflux for 1 h. Evaporation of the solvent, followed by chromatography (Florisil) afforded two fractions. An orange fraction was eluted with light petroleum. Crystallization (light petroleum) afforded orange crystals of $Ru_3(CO)_{12}$ (650 mg, 33%), identified by infrared comparison with an authentic sample. A second red-orange fraction was eluted with light petroleum. Crystallization (light petroleum) afforded red *crystals* of $Ru_3(CO)_{11}\{P(C_6H_{11})_3\}$ (6.13) (1.15 g, 41%) m.p. 177-178.5^0 (Found: C, 38.9; H, 3.7. $C_{29}H_{33}O_{11}PRu_3$ requires C, 39.1; H, 3.7%). Infrared (C_6H_{12}): ν(CO) 2096w, 2045s, 2024m, 2008vs, 1988w, and 1966vw cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 2.23, 1.58, 1.42, and 0.53, m, 11H, C_6H_{11}.

(B) *2,2'-Dipyridyl, 2,2'-$(C_5H_4N)_2$.* — A mixture of ruthenium carbonyl (300 mg, 0.47 mmol) and 2,2'-dipyridyl (dpy) (73 mg, 0.47 mmol) was refluxed in cyclohexane (100 ml) for 20 min. The purple *crystals* that deposited were collected, washed with light petroleum and dried in air for a short period to give pure $Ru_3(CO)_{10}$(dpy) (6.14) (320 mg, 92%) (Found: C, 31.9; H, 1.4; N, 4.0. $C_{20}H_8N_2O_{10}Ru_3$ requires C, 32.5; H, 1.1; N, 3.8%). Infrared ($CHCl_3$): ν(CO) 2077m, 2034s, 1994s, and 1740vw cm^{-1}.

(C) *Pyridine, C_5H_5N.* — (i) A mixture of ruthenium carbonyl (228 mg, 0.36 mmol) and pyridine (86 mg, 1.09 mmol) was refluxed in cyclohexane (45 ml) for 210 min. Evaporation of solvent and chromatography (Florisil) afforded one fraction, eluted with light petroleum as an orange band. Crystallization (light petroleum) afforded red-orange *crystals* of $HRu_3(CO)_{10}(NC_5H_4)$ (6.15) (Found: C, 26.9; H, 0.7; N, 1.9%; *M* (mass spectrometry), 665. $C_{15}H_5NO_{10}Ru_3$ requires C, 27.2; H, 0.8; N, 2.1%;

M, 665). Infrared (C_6H_{12}): ν(CO) 2100w, 2062vs, 2052vs, 2021s, 2009vs, 2003m, 1995m, and 1989vw cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.97, d, *J*(HH) 5.2 Hz, 1H, H(6), NC_5H_4; 7.26, m, 2H, H(3)+H(4), NC_5H_4; 6.77, m, 1H, H(5), NC_5H_4; -14.43, s, 1H, RuH.

(ii) A mixture of ruthenium carbonyl (388 mg, 0.61 mmol) and pyridine (288 mg, 3.64 mmol) was refluxed in cyclohexane (150 ml) for 4 h. Evaporation of the solvent and chromatography (alumina) afforded two fractions. A yellow-orange band was eluted with light petroleum. Crystallization (light petroleum) afforded red-orange crystals of $HRu_3(CO)_{10}(NC_5H_4)$ (6.15) (385 mg, 96%), identified by infrared comparison with the product obtained in (i) above. A second yellow-orange band was eluted with diethyl ether. The product was identified by mass spectrometry as $H_2Ru_3(CO)_8(NC_5H_4)_2$ (6.16) (Found: *M* (mass spectrometry), 688. $C_{18}H_{10}N_2O_8Ru_3$ requires *M*, 688). Infrared (C_6H_{12}): ν(CO) 2080w, 2047s, 2039s, 1998s, 1992sh, 1990m, and 1986m cm^{-1}.

Preparation of $H_4Ru_4(CO)_{12}$

Hydrogen, at atmospheric pressure, was introduced into a refluxing solution of ruthenium carbonyl (639 mg, 1.0 mmol) in petroleum spirit (100-120^0, 160 ml) for a period of 1 h. The solution was filtered through florisil, the yellow filtrate concentrated (40 ml). The yellow *crystals* that deposited were washed with light petroleum and dried in a vacuum to give pure $H_4Ru_4(CO)_{12}$ (455 mg, 82%). Infrared (C_6H_{12}): ν(CO) 2080m, 2066s, 2028w, 2023m, and 2000vw cm^{-1}. {Lit.[65] 2081s, 2067vs, 2030m, 2024s, and 2009w cm^{-1}, in octane}

Reaction of $H_4Ru_4(CO)_{12}$ with t-*butyl isocyanide*

(i) A solution of $H_4Ru_4(CO)_{12}$ (500 mg, 0.67 mmol) and *t*-butyl isocyanide (112 mg, 1.35 mmol) in cyclohexane (100 ml) was heated under reflux for 1 h. Evaporation of solvent and chromatography (Florisil) afforded three fractions. A yellow band was eluted with light petroleum. Crystallization (light petroleum) afforded yellow crystals of $H_4Ru_4(CO)_{12}$ (60 mg, 12%), identified by infrared comparison with an authentic sample. The major fraction, an orange band, was eluted with light petroleum. Crystallization (light petroleum) afforded red *crystals* of $H_4Ru_4(CO)_{11}(CNBu^t)$ (6.17) (310 mg, 58%), m.p. 122-127^0 (dec.) (Found: C, 24.2; H, 1.6; N, 1.7%; *M* (mass spectrometry), 801. $C_{16}H_{13}NO_{11}Ru_4$ requires C, 24.0; H, 1.6; N, 1.8%; *M*, 801). Infrared (C_6H_{12}): ν(CN) 2168w; ν(CO) 2093m, 2067s, 2059vs, 2032vs, 2012s, 2004s, 1995m, 1992m, and 1988w cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 1.51, s, 9H, CMe_3; -17.97, s, 4H, RuH. The third fraction, an orange band, was eluted with light petroleum/diethyl ether (1:1). Crystallization (light petroleum/diethyl ether) afforded red *crystals* of $H_4Ru_4(CO)_{10}(CNBu^t)_2$(6.18) (80 mg, 14%), m.p. 116-118^0 (dec.) (Found: C, 28.1; H, 2.6; N, 3.2%; *M* (mass spectrometry), 856. $C_{20}H_{22}N_2O_{10}Ru_4$ requires C, 28.1; H, 2.6; N, 3.3%; *M*, 856). Infrared

(C_6H_{12}): ν(CN) 2156w; ν(CO) 2077w, 2048s, 2023vs, 2012s, 1996m, 1992w, 1988m, and 1975vw cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 1.49, s, 18H, CMe$_3$; -17.7, s, and -18.2, s, 4H, RuH.

(ii) A solution of $H_4Ru_4(CO)_{12}$ (400 mg, 0.54 mmol) and *t*-butyl isocyanide (180 mg, 2.17 mmol) in cyclohexane (90 ml) was heated under reflux for 1 h. Infrared (C_6H_{12}): ν(CN) 2142s; ν(CO) 1990vs, 1973s, 1958s, and 1944m cm^{-1}. The tetrasubstituted complex $H_4Ru_4(CO)_8(CNBu^t)_4$ (6.19) is markedly air sensitive, and decomposes rapidly in solution.

Reaction of $H_4Ru_4(CO)_{12}$ with tri-4-tolylphosphine

(i) A mixture of $H_4Ru_4(CO)_{12}$ (400 mg, 0.54 mmol) and $P(C_6H_4Me\text{-}4)_3$ (1.2 g, 3.94 mmol) in petroleum spirit (120 ml, 100-120°) was heated under reflux for 2 h. The solution was allowed to cool, and the red-maroon *crystals* that deposited were washed with hot petroleum spirit (2x40 ml) to give pure $H_4Ru_4(CO)_8\{P(C_6H_4Me\text{-}4)_3\}_4$ (6.20) (720 mg, 72%), m.p. >180° (dec.) (Found: C, 60.1; H, 5.0. $C_{92}H_{88}O_8P_4Ru_4$ requires C, 59.7; H, 4.8%). Infrared (C_6H_{12}): ν(CO) 2008s, 1986m, 1954m, and 1931w cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.22, 6.88, and 6.80, m, 48H, C_6H_4; 2.22, s, 36H, Me; -15.57, quin, *J*(HP) 5.5 Hz, 4H, RuH. ^{13}C n.m.r. ($CDCl_3$): δ 199.4, s, CO; 138.7-128.5, m, C_6H_4; 21.1, s, Me. Concentration of the filtrate afforded more orange-red crystals of (6.20), total yield being 94%.

(ii) A mixture of $H_4Ru_4(CO)_{12}$ (648 mg, 0.87 mmol) and $P(C_6H_4Me\text{-}4)_3$ (265 mg, 0.87 mmol) was heated in refluxing cyclohexane (110 ml) for 1 h. Evaporation of the solvent, followed by chromatography (Florisil) afforded four fractions. A yellow fraction was eluted with light petroleum. Crystallization (light petroleum) afforded yellow crystals of $H_4Ru_4(CO)_{12}$ (120 mg, 19%) identified by infrared comparison with an authentic sample. An orange-yellow fraction was eluted with light petroleum. Crystallization (light petroleum) afforded orange-red *crystals* of $H_4Ru_4(CO)_{11}\{P(C_6H_4Me\text{-}4)_3\}$ (6.21) (150 mg, 17%) (Found: C, 37.3; H, 2.4%; *M* (mass spectrometry),

1024. $C_{32}H_{25}O_{11}PRu_4$ requires C, 37.7; H, 2.5%; *M*, 1024). Infrared (C_6H_{12}): ν(CO) 2093w, 2086vw, 2067vs, 2058vs, 2030m, 2024vs, 2008m, 1998s, 1993w, and 1973w cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.35, 7.26, and 7.24, m, 12H, C_6H_4; 2.39, s, 9H, Me; -17.28, d, *J*(HP) 2.9 Hz, 4H, RuH. ^{13}C n.m.r. ($CDCl_3$): δ 192.2, s, CO; 141.1-129.2, m, C_6H_4; 21.4, s, Me. A third orange fraction was eluted with light petroleum/diethyl ether (99:1). Crystallization (light petroleum) afforded red-brown *crystals* of $H_4Ru_4(CO)_{10}\{P(C_6H_4Me\text{-}4)_3\}_2$ (6.22) (360 mg, 32%) (Found: C, 48.3; H, 3.7. $C_{52}H_{46}O_{10}P_2Ru_4$ requires C, 48.2; H, 3.6%). Infrared (C_6H_{12}): ν(CO) 2076m, 2058vs, 2050m, 2031m, 2012vs, 2000s, 1995m, 1991w, 1979vw, and 1958vw cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.36, 7.27, 7.23, 7.16, 7.12, and 7.09, m, 24H, C_6H_4; 2.34, s, 18H, Me; -16.10, t, *J*(HP) 7.4 Hz, and -16.97, m, 4H, RuH. ^{13}C n.m.r. ($CDCl_3$): δ 198.1, 197.8, 196.8, and 196.5, s, CO; 140.0-128.9, m, C_6H_4; 21.3, s, Me. A final orange fraction was eluted with light petroleum/diethyl ether (7:3). Crystallization (light petroleum) afforded red-orange *crystals* of $H_4Ru_4(CO)_9\{P(C_6H_4Me\text{-}4)_3\}_3$ (6.23) (130 mg, 9%) (Found: C, 54.9; H, 4.4. $C_{72}H_{67}O_9P_3Ru_4$ requires C, 55.0; H, 4.3%). Infrared (C_6H_{12}): ν(CO) 2061s, 2001vs, 1992m, 1987s, 1963m, and 1938vw cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 7.29, 7.26, 7.24, and 7.07, m, 36H, C_6H_4; 2.31, s, 27H, Me; -15.66, and -16.57, m, 4H, RuH. ^{13}C n.m.r. ($CDCl_3$): δ 199.3-194.2, m, CO; 139.4-128.6, m, C_6H_4; 21.3, s, Me.

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SECTION B

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APPENDIX I.

General Experimental Conditions

All preparations and reactions were carried out in an atmosphere of dry nitrogen. All compounds were stored in the dark.

Elemental microanalyses were determined by the Australian Microanalytical Service (Melbourne), the Canadian Microanalytical Service (Vancouver), Pascher (Bonn), or at the South Australian Institute of Technology.

Infrared spectra were recorded using Perkin Elmer 457 or Jasco IRA-2 double-beam Grating Infrared Spectrophotometers in the range 4000-600 cm^{-1} and were calibrated with polystyrene. The Perkin Elmer instrument has incorporated into it a scale changing mechanism at 2000 cm^{-1}, which produces a discontinuity in the spectrum thus interfering with any absorptions near this wavenumber (CO, CN, CC). The Jasco instrument has a smooth scale changing mechanism, which does not interfere with the recording of the spectra. These stretching frequencies were, if possible, recorded in solution between NaCl plates using a standard solution cell. The solvents used were light petroleum, cyclohexane or dichloromethane. Complete spectra were recorded as nujol mulls between NaCl plates (4000-600 cm^{-1}).

Proton n.m.r. spectra were recorded relative to TMS on a Varian T60 spectrometer at 60 MHz. Fourier transformed ^{1}H spectra were recorded on computer-equipped Bruker HX-90E or WP-80DS spectrometers, at 90 and 80 MHz respectively. Broadband proton-decoupled Fourier transformed ^{19}F *and* ^{13}C *n.m.r. spectra* were recorded on the Bruker HX-90E at 84.67 and 22.62 MHz respectively. Carbon n.m.r. spectra were also recorded on the Bruker WP-80DS. The spectra were determined in deuterated solvents, usually deuterochloroform, in 10 mm tubes. Deuterated solvents were required for the deuterium resonance lock. Hexafluorobenzene was used as an internal reference for the ^{19}F spectra and then calibrated against $CFCl_3$.

Concentrations of the samples were in the range 0.01 - 1.0 *M* solutions.

Conductivity measurements were made using a conductivity cell fitted with two taps allowing the cell to be flushed and then filled with an inert gas. Solutions were thermostatted in a water bath at 25.0 ± 0.5°C and the resistance measured using a Philips PR 9500 AC bridge incorporating a cathode ray indicator to detect the balance point. Molar conductances of the complexes were estimated from approximately 1.0×10^{-3} *M* solutions. AR grade solvents dried over molecular sieves were used.

Mass spectra were recorded on an AEI-GEC MS 3074 spectrometer (mass, with 70 eV ionizing energy). *Solution molecular weights* were obtained using a Knauer Vapour Pressure Osmometer with attached Universal Temperature Measuring Instrument.

For conductimetric and osmometric work, samples were weighed on a Cahn Model G2 electrobalance. For routine preparative work, weighings were done on a Mettler H16 balance weighing to 0.01 mg.

Chromatography was on columns of Florisil or alumina (BDH chromatography grade, used as received) initially packed in light petroleum. Thin layer chromatography was carried out using silica gel H (type 60) (Merck).

All solvents, including those used as reagents, were of analytical grade purity and were dried over Linde 4Å molecular sieves before use, except for methanol, which was dried over magnesium turnings and distilled under nitrogen. The light petroleum used in the experiments had a boiling range 40-60°.

High purity nitrogen was obtained from Commonwealth Industrial Gases (CIG) Limited and carbon monoxide from Matheson Gas Products; both were used as received.

Ligands were commercial products and were used as received. *t*-Butyl isocyanide was prepared by a method analogous to that of cyclohexyl isocyanide.[75] The halo complexes, $RuCl(PPh_3)_2(\eta-C_5H_5)$ and $OsBr(PPh_3)_2(\eta-C_5H_5)$ were prepared according to the published method[13] except that ethanol was used in place of methanol in the synthesis of the osmium complex. The cyano complex $Ru(CN)(PPh_3)_2(\eta\text{-}C_5H_5)$ was prepared according to the published procedure.[16] The complex $\{Ru(MeCN)(PPh_3)_2(\eta\text{-}C_5H_5)\}PF_6$ was prepared directly from $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and NH_4PF_6 in refluxing acetonitrile (30 min.), followed by recrystallization from diethyl ether/dichloromethane mixtures (85% yield).