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Some reactions of azides with diyne-bis(phosphine)ruthenium-cyclopentadienyl complexes

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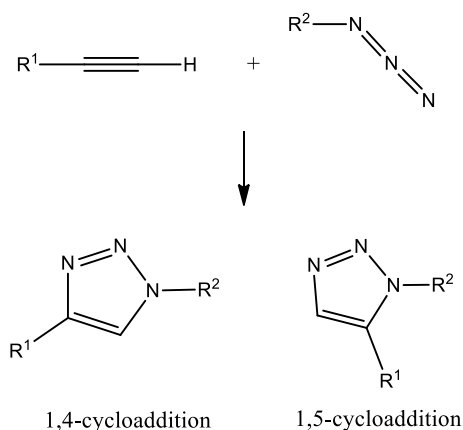
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Abstract

Reactions of $\text{SiMe}_3(\text{N}_3)$ with $\text{Ru}(\text{C}\equiv\text{CH})(\text{PP})\text{Cp}'$ [$\text{PP} = (\text{PPh}_3)_2$, $\text{Cp}' = \text{Cp}$; $\text{PP} = \text{dppe}$, $\text{Cp}' = \text{Cp}^*$] afford $\text{Ru}(\text{N}_3)(\text{PP})\text{Cp}'$. Reactions of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CR})(\text{dppe})\text{Cp}^*$ with $\text{SiMe}_3(\text{N}_3)$ give $\text{Ru}\{\text{N}_3\text{C}(\text{CN})\text{CH}_2\text{R}\}(\text{dppe})\text{Cp}^*$ ($\text{R} = \text{H}$ **2**, Ph **3**). With $\text{RuCl}(\text{dppe})\text{Cp}^*$ in the presence of $[\text{NH}_4]\text{PF}_6$, **2** gives binuclear $[\text{Cp}^*(\text{dppe})\text{Ru}\{\text{N}_3\text{C}\{[(\text{CN})\text{Ru}(\text{dppe})\text{Cp}^*]\text{CMe}\}}]\text{PF}_6$ **4**. The reaction between TsN_3 and $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})\text{Cp}^*$ gives $\text{Ru}\{(\text{NC})\text{C}=\text{NNTs}=\text{CHC}(=\text{NTs})\}(\text{dppe})\text{Cp}^*$ **5**, with a small amount of $\text{TsN}=\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2=\text{NTs}$ **6** being obtained from some reactions. X-ray determined structures of $\text{Ru}(\text{N}_3)(\text{dppe})\text{Cp}^*$ and **2-5** are reported, together with plausible routes to **2** and **3**.

Introduction

A much used synthetic approach to a variety of molecular building blocks is the Cu(I)-catalysed [3 + 2]-cycloaddition of azides with alkynes (CuAAC reaction) [1,2], a common example of a "click" reaction (Scheme 1) [3]. Several reviews are available [4-8], including themed issues of at least two journals [9]. This reaction can also be catalysed by Ag(I) [10] or Ru(II) (the RuAAC reaction) [11,12]. It is of interest that the latter system affords the 1,5-substituted triazole, while the Cu(I)-catalysed reaction generally gives the 1,4-isomer (Scheme 1).



Scheme 1. 1,4- and 1,5-cycloaddition products from [3 + 2]-cycloaddition of 1-alkynes to azides.

While applications to organic synthesis are legion, relatively few examples have involved organometallic substrates. Many electroactive ferrocene-containing products have been obtained [13], with reactions involving both azidoferrocenes [14] or alkynylferrocenes [15,16]. Redox-active triazole derivatives of $M(CO)_3Cp$ were obtained from $M(CO)_3(\eta-C_5H_4N_3)$ and $HC\equiv CAr$ ($Ar = Ph, C_6H_4NH_2-4$) [17], while similar additions of azides to Cr(0)-alkynylcarbene complexes [18] and to Ru_2 complexes containing alkynylphenyl-amidinate ligands [19], and functionalisation of Pd_2L_4 metallo-supramolecular systems [20] have been described.

Several [3 + 2]-cycloaddition reactions of azido or alkynyl ligands directly bonded to transition metal centres have been reported recently. These include addition of a masked alkyne to $Mn(N_3)(CO)_3(bpy)$ [21], of $C_2(CO_2Me)_2$ to $Mo(N_3)(CO)_2(en)(\eta-C_3H_5)$ [22], and of several alkynes to neutral and cationic Ru(II) azido complexes [23,24].

Unsymmetric Pt(bipy) alkynyls formed by mono-addition of azides to bis(alkynyl) complexes show enhanced emission and were incorporated into organic light-emitting diodes (OLEDs) [25]. Reactions of alkynyl-silver(I) compounds with azides afford metal-free triazoles [26], while many reports describe reactions involving phosphine-gold(I) alkynyl or azide derivatives such as those applied to the

synthesis of cytotoxic Au dendrimers [27], the Cu-catalysed click reactions of Au-alkynyls with PhCH₂N₃ [28], and the interesting inorganic click reaction between Au(N₃)(PPh₃) and Au(C≡CPh)(PPh₃) [29]. Similar reactions were later used to prepare multi-metallic derivatives [30,31].

More relevant to the work to be presented below are reactions of platinum(II) poly-ynyl complexes with benzyl azide, later extended to the preparation of permethylated compounds [32].

Results and Discussion

As mentioned above, cycloaddition of activated alkynes HC≡CCO₂Me and C₂(CO₂Me)₂ to Ru(N₃)(dppe)Cp has been reported to give triazolates Ru{N₃C₂R(CO₂Me)}(dppe)Cp (R = H, CO₂Me, respectively), in which the heterocyclic ligand is bonded to ruthenium by N(2) [23,24]. To our knowledge, there are no reports of the reverse reaction, that of organic azides with alkynyl-ruthenium complexes.

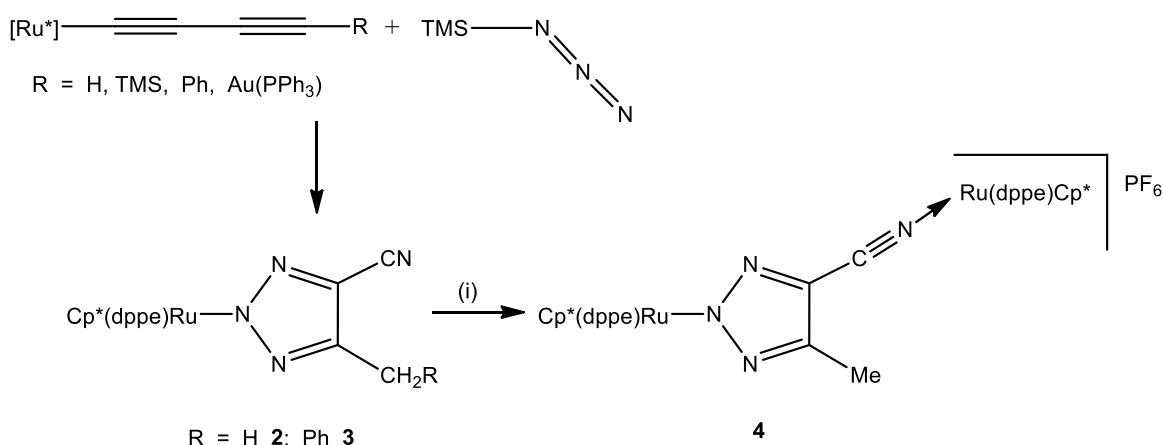
Initial studies showed that reactions of SiMe₃(N₃) with Ru(C≡CH)(PPh₃)₂Cp, Ru(C≡CH)(dppe)Cp* or Ru(C≡CC≡CH)(PPh₃)₂Cp all proceed with metathetic replacement of ethynyl or butadiynyl by azide to give known Ru(N₃)(PP)Cp' complexes [**1a**; PP = (PPh₃)₂, Cp' = Cp (56%); **1b**; PP = dppe, Cp' = Cp* (61%)]. Consequently, we turned our attention to similar reactions of the diyne-ruthenium complexes Ru(C≡CC≡CR)(dppe)Cp* [R = H, Ph, SiMe₃, Au(PPh₃)]. The chemistry described below is summarised in Schemes 2-4, full details being given in the Experimental Section.

Addition of SiMe₃(N₃) to solutions of Ru(C≡CC≡CH)(dppe)Cp* in refluxing THF resulted in a rapid reaction which afforded the yellow complex **2** in 67% yield, containing the N₃C(CN)CMe ligand attached through N(2), as shown by a single crystal X-ray structure determination (see below for details). Azido complex **1b** was also isolated in 8% yield and identified by comparison with an authentic sample and crystallographically. For Ru{N₃C(CN)CMe}(dppe)Cp* **2**, the IR spectrum contained bands at 2216 [ν(CN)] and 1724 cm⁻¹ [ν(C=N)]. In the ¹H and ¹³C NMR spectra, the Cp* and dppe ligands gave resonances at δ 1.47, 9.88 and 91.70 (Cp*), 2.29, 3.05 and 31.62 (dppe CH₂), while the triazole ligand gives rise to ¹³C resonances at δ 9.57 (Me), 115.42 (CN), 117.71 [C(2)] and 147.10 [C(1)]; the dppe ³¹P resonance is at δ 88.11 (dppe). The ESI-MS (from a solution containing NaOMe) contained strong peaks centred on *m/z* 765 ([M + Na]⁺) and 743 ([M + H]⁺).

The same complex was obtained from Ru(C≡CC≡CSiMe₃)(dppe)Cp* and SiMe₃(N₃) in similar yield.

With $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CPh})(\text{dppe})\text{Cp}^*$, a similar reaction with $\text{SiMe}_3(\text{N}_3)$ afforded the related compound $\text{Ru}\{\text{N}_3\text{C}(\text{CN})\text{C}(\text{CH}_2\text{Ph})\}(\text{dppe})\text{Cp}^*$ **3** in 13% yield together with $\text{Ru}(\text{N}_3)(\text{dppe})\text{Cp}^*$ (43%). Pertinent spectroscopic data for **3** include an IR band at 2213 cm^{-1} [$\nu(\text{C}\equiv\text{N})$], ^1H NMR signals at δ 1.39 (Cp^*), 2.19 and 2.85 (dppe CH_2), 3.39 (CH_2Ph), ^{13}C NMR resonances at δ 10.47 and 92.37 (Cp^*), 31.98 (CH_2Ph), 32.37 (dppe CH_2), 118.12 [$\text{C}(2)$], 115.83 (CN), 150.85 [$\text{C}(1)$], and a ^{31}P NMR signal at δ 88.85 (dppe). In the ESI-MS, peaks at m/z 841 (weak, $[\text{M} + \text{Na}]^+$) and 818 (strong, M^+) are present.

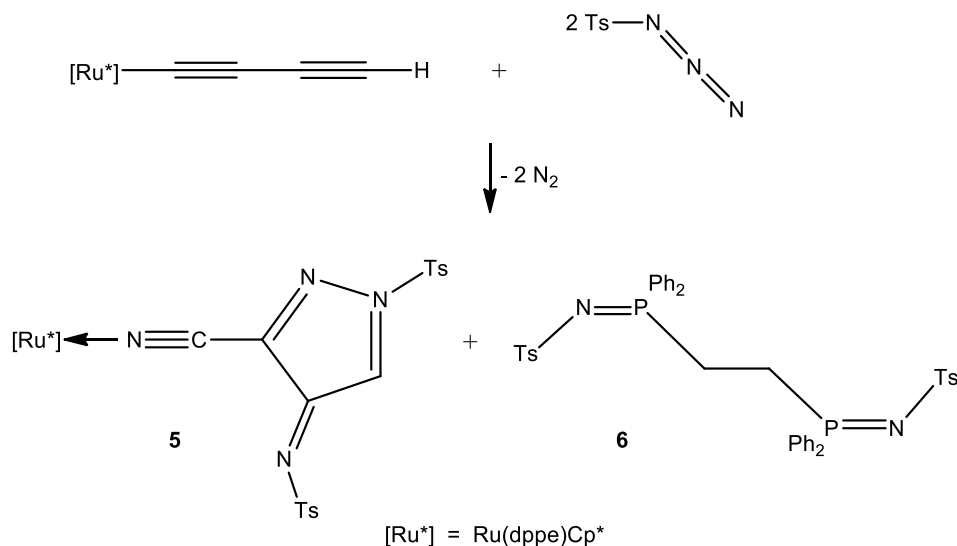
A subsequent reaction of $\text{Ru}\{\text{N}_3\text{C}(\text{CN})\text{CMe}\}(\text{dppe})\text{Cp}^*$ with an equivalent of $\text{RuCl}(\text{dppe})\text{Cp}^*$ in MeOH, in the presence of $[\text{NH}_4]\text{PF}_6$, afforded the yellow binuclear complex $[\text{Cp}^*(\text{dppe})\text{Ru}\{\text{N}_3\text{C}[(\text{CN})\text{Ru}(\text{dppe})\text{Cp}^*]\text{CMe}\}]\text{PF}_6$ **4** in 68% yield. The IR spectra contained bands at 2224 cm^{-1} [$\nu(\text{CN})$] and 840 cm^{-1} [$\nu(\text{PF})$], with duplicated resonances in the ^1H , ^{13}C and ^{31}P NMR spectra arising from the two $\text{Ru}(\text{dppe})\text{Cp}^*$ centres. The $\text{C}(2)$ and $\text{C}(1)$ ^{13}C resonances were at δ 107.50 and 148.12, with the two dppe groups giving ^{31}P signals at δ 73.07 and 86.71, along with the PF_6 signal at δ 143.93. In the ESI-MS, the cation was found at m/z 1377. The structure was confirmed by a single-crystal X-ray study (see below).



Scheme 2. Synthesis of cyano(alkyl)triazoles from $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CR})(\text{dppe})\text{Cp}^*$ ($\text{R} = \text{H}$, SiMe_3 , Ph) and $\text{SiMe}_3(\text{N}_3)$. Reagent: (i) = $\text{RuCl}(\text{dppe})\text{Cp}^* + [\text{NH}_4]\text{PF}_6$.

The reaction between TsN_3 and $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})\text{Cp}^*$, carried out in refluxing THF, gave an intractable mixture of products. However, the major product isolated from a reaction carried out in toluene at r.t. was bright yellow $\text{Ru}\{\text{N}\equiv\text{C}\text{C}_3\text{N}_2\text{Ts}_2\}(\text{dppe})\text{Cp}^*$ **5** (43%) as determined by a single-crystal X-ray structure determination. Spectroscopic data include $\nu(\text{CH})$ at 2977 , $\nu(\text{C}\equiv\text{N})$ at 2229 , $\nu(\text{C}=\text{N})$ at 1703 and $\nu(\text{SO})$ at 1179 cm^{-1} . In addition to characteristic signals for the $\text{Ru}(\text{dppe})\text{Cp}^*$ fragment, the C_6H_4 protons are at δ 6.61 and 7.68 (both d with $J = 8$ Hz) and the Me group a singlet at δ 2.25. The pyrazole ring proton gives a singlet at δ

1.23. The ^{13}C NMR spectrum contains a singlet at δ 21.14 (Me) and pyrazole ring C at δ 58.52, 116.63, 122.85 (not individually assigned), together with several signals between δ 134.9 and 145.2 from the Ts groups. In the ESI-MS, $[\text{M} + \text{Na}]^+$ and $[\text{M} - \text{H}]^+$ are at m/z 1073 and 1051, respectively.



Scheme 3. Reaction of $\text{Ru}(\text{C}\equiv\text{C}\text{C}\equiv\text{CH})(\text{dppe})\text{Cp}^*$ and TsN_3 to give $\text{Ru}\{(\text{N}\equiv\text{C})\text{C}_3\text{N}_2\text{Ts}_2\}(\text{dppe})\text{Cp}^*$ **5** and $\text{TsN}=\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2=\text{NTs}$ **6**.

A minor product (3%) was found to be the bis(iminophosphorane) $\text{TsN}=\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2=\text{NTs}$ **6**, evidently formed from a Staudinger reaction between displaced dppe and the azide [33,34]. This material was identified from a single-crystal X-ray structure determination (see below). The ^1H NMR spectrum contained signals at δ 2.33 (Me), 3.12 (dppe) and between δ 7.06 and 7.83 (Ph, C_6H_4). The ESI-MS from MeOH / NaOMe contained $[\text{M} + \text{Na}]^+$ at m/z 759.

Molecular structures

(a) $\text{Ru}(\text{N}_3)(\text{dppe})\text{Cp}^*$ (**1b**; $\text{Cp} = \text{Cp}^*$; $\text{PP} = \text{dppe}$). A molecule of this complex is shown in Fig. 1, significant bond parameters being included in Table 1. The usual coordination within the $\text{Ru}(\text{dppe})\text{Cp}^*$ fragment is found, the almost linear azido ligand [angle $\text{N}(1)-\text{N}(2)-\text{N}(3)$ $175.8(1)^\circ$] being attached via $\text{N}(1)$ [$\text{Ru}-\text{N}(1)$ 2.156(1) Å; $\text{Ru}-\text{N}(1)-\text{N}(2)$ $122.80(8)^\circ$] with the expected bent configuration.

The present structure is similar to that of $\text{Ru}(\text{N}_3)(\text{PPh}_3)_2\text{Cp}$, which has $\text{Ru}-\text{P}$ 2.3292(5), 2.3304(5), $\text{Ru}-\text{N}$ 2.135(3), $\text{N}-\text{N}$ 1.186(3), 1.164(3) Å, and $\text{P}-\text{Ru}-\text{P}$ $105.22(2)$, $\text{P}-\text{Ru}-\text{N}$ $85.39(6)$, $86.65(5)$, $\text{Ru}-\text{N}-\text{N}$ $124.5(2)$ and $\text{N}-\text{N}-\text{N}$ $175.2(3)^\circ$ [35].

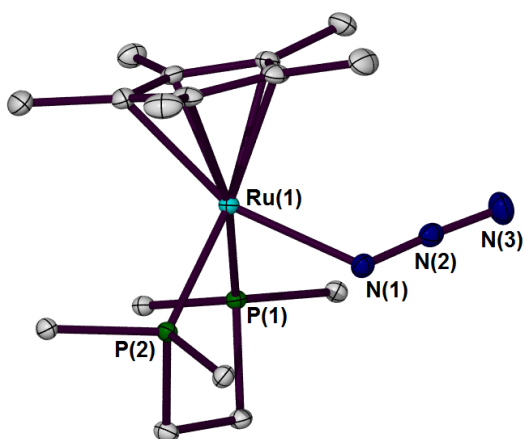


Figure 1. A molecule of $\text{Ru}(\text{N}_3)(\text{dppe})\text{Cp}^*$ **1b**. Selected bond parameters: $\text{Ru-P}(1,2)$ 2.2894, 2.2924(3), $\text{Ru-C}(\text{cp})$ (av.) 2.225 [range 2.2126-2.2402(12)], $\text{Ru-N}(1)$ 2.157(1), $\text{N}(1)\text{-N}(2)$ 1.1917(15), $\text{N}(2)\text{-N}(3)$ 1.1672(16) Å; $\text{P}(1)\text{-Ru-P}(2)$ 83.35(1), $\text{P}(1,2)\text{-Ru-N}(1)$ 79.80, 87.67(3), $\text{Ru-N}(1)\text{-N}(2)$ 122.78(8), $\text{N}(1)\text{-N}(2)\text{-N}(3)$ 175.77(13)°. Ellipsoids have been drawn at the 50% probability level with hydrogen atoms and the phenyl carbons of the dppe ligands (except the *ipso*-carbons) omitted for clarity.

(b) $\text{Ru}\{\text{N}_3\text{CRC}(\text{CN})\}(\text{dppe})\text{Cp}^*$ ($R = \text{Me}$ **2**, CH_2Ph **3**). As shown in Fig. 2 (selected bond parameters are in Table 1), in the molecule of **2** the familiar $\text{Ru}(\text{dppe})\text{Cp}^*$ group is attached to the 1-cyano-2-methyltriazolyl ligand via the central N(1) atom [$\text{Ru-N}(1)$ 2.107(2) Å]. Within the triazolyl group, atom N(1) is bonded asymmetrically to N(2) [$\text{N}(1)\text{-N}(2)$ 1.321(2) Å] and N(5) [$\text{N}(1)\text{-N}(5)$ 1.359(2) Å], with $\text{N}(2)\text{-N}(1)\text{-N}(5)$ 112.4(2)°. Short C-N bonds are consistent with C=N double bonds, while C(3)-C(4) is also short at 1.384(4) Å, suggesting some degree of delocalisation within the ring. The CN and Me groups attached to C(3) and C(4), respectively, have no unusual features. The benzyl complex **3** is similar (selected bond parameters for both molecules are collected in Table 1). Both variants (**2** and **3**) are simply close packed with no significant intermolecular interactions between molecules; in both examples the nitrile moiety protrudes into a pocket surrounded by aromatic hydrogen atoms but makes no notable contacts.

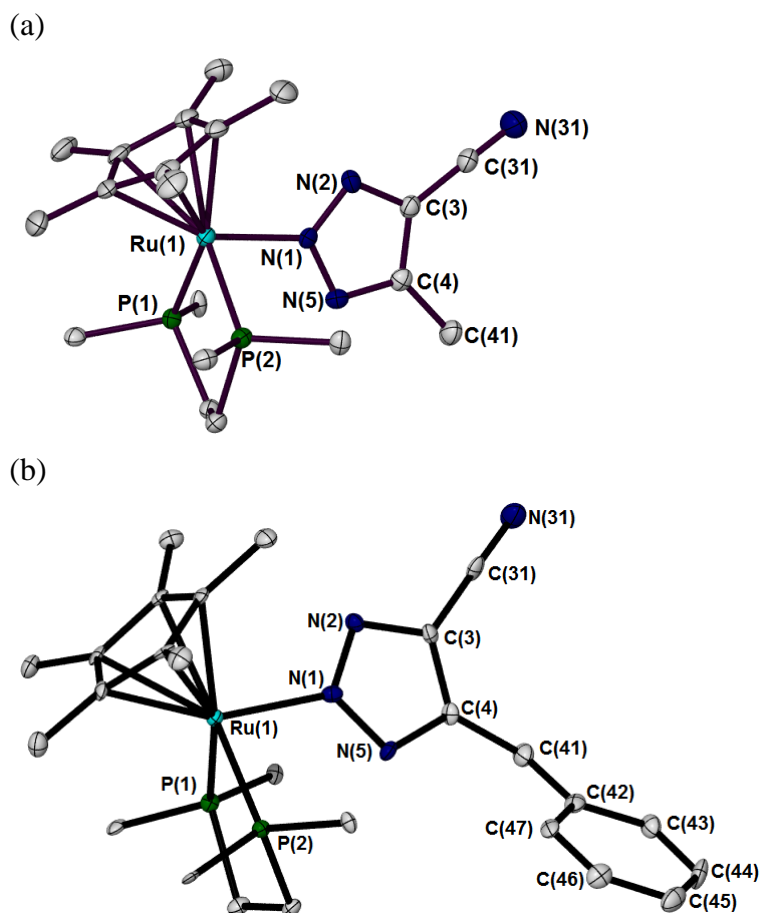


Figure 2. (a) A molecule of $\text{Ru}\{\text{N}_3\text{CMeC}(\text{CN})\}(\text{dppe})\text{Cp}^*$ **2**. (b) The benzyl derivative **3** is similar. Ellipsoids have been drawn at the 50% probability level with hydrogen atoms, the phenyl carbons of the dppe ligands (except the *ipso*-carbons) and the dichloromethane (**2**) and benzene (**3**) solvates omitted for clarity.

(c) $[\text{Cp}^*(\text{dppe})\text{Ru}\{\text{N}_3\text{C}(\text{CN})[\text{Ru}(\text{dppe})\text{Cp}^*]\text{CMe}\}]\text{PF}_6$ **4**. Fig. 3 shows a plot of the binuclear cation in **4**, with selected bond parameters given in Table 1. The complex is similar to **2**, with an $\text{Ru}(\text{dppe})\text{Cp}^*$ group attached to the nitrogen of the $\text{CN}(31)$ group [$\text{Ru}(2)\text{-N}(31)$ 2.029(3) Å]. The ligands (dppe and Cp^*) of the second $\text{Ru}(\text{dppe})\text{Cp}^*$ group are twisted by approximately 75° to avert a steric clash between the dppe ligands of $\text{Ru}(1)$ and $\text{Ru}(2)$. Bond parameters are overall similar to those found in **2** and in $[\text{Ru}(\text{NCMe})(\text{PPh}_3)_2\text{Cp}^*]\text{PF}_6$ [$\text{Ru}\text{-NC}$ 2.056(2) Å] [36]. Molecules of **4** pack in the triclinic space group $P\bar{1}$ with small solvate-filled channels (ethanol) percolating down the *a*-axis of the crystal. As with the mononuclear complexes above no obvious intermolecular interactions dominate the packing.

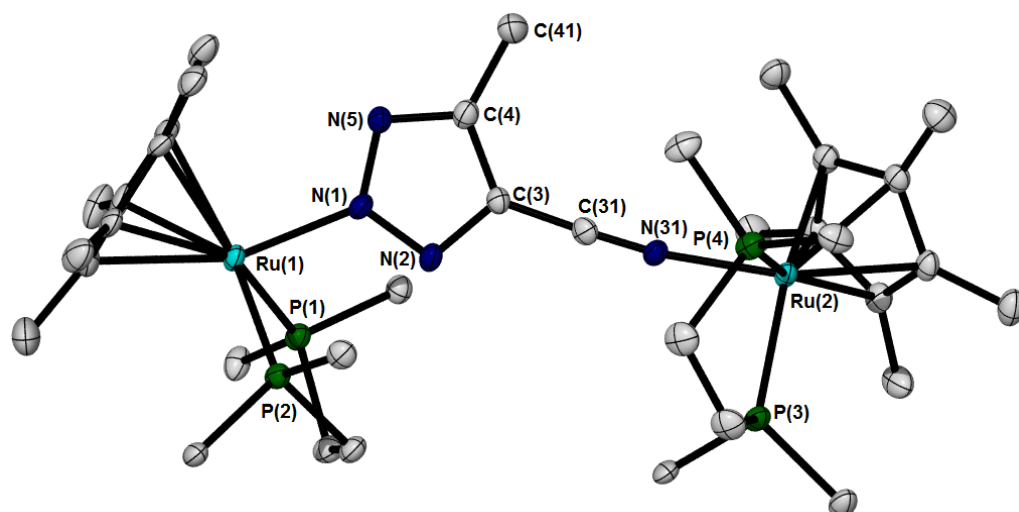


Figure 3. A plot of a molecule of $[\text{Cp}^*(\text{dppe})\text{Ru}\{\text{N}_3\text{C}[\text{CN}\{\text{Ru}(\text{dppe})\text{Cp}^*\}]\text{CMe}\}]\text{PF}_6$ **4**. Ellipsoids have been drawn at the 50% probability level with hydrogen atoms, the phenyl carbons of the dppe ligands (except the *ipso*-carbons) and the hexafluorophosphate anion, which is disordered over three positions, omitted for clarity.

(d) $\text{Ru}[(\text{NC})\text{C}=\text{NNTs}=\text{CC}=\text{NTs}](\text{dppe})\text{Cp}^*$ **5**. A molecule of **5** is shown in Figure 4, from which it can be seen that a $\text{N}=\text{C}_3\text{N}_2$ iminopyrazole ring, bearing tosyl groups on N(4) and N(6), is attached via N(1) of the $\text{N}(1)=\text{C}(2)$ group [$\text{N}(1)-\text{C}(2)$ 1.148(5) Å] to the familiar $\text{Ru}(\text{dppe})\text{Cp}^*$ fragment [$\text{Ru}-\text{N}(1)$ 2.006(3) Å]. The C_3N_2 ring is similar to that found in 3,5-diaminopyrazolone-4-oxime [37].

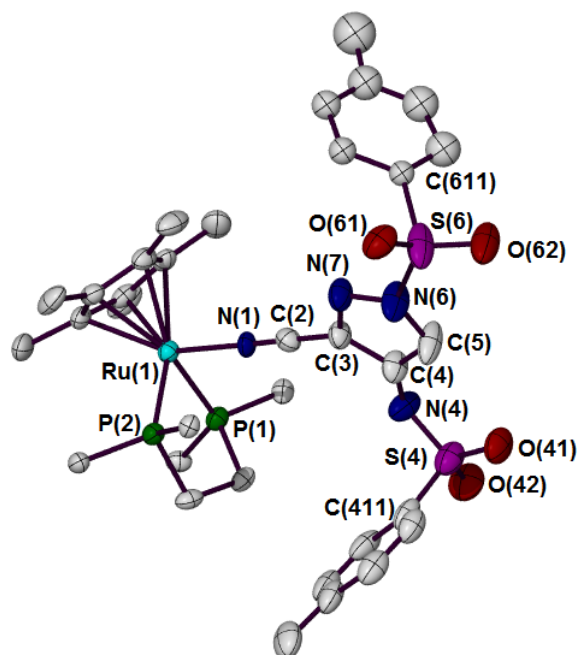


Figure 4. A molecule of $\text{Ru}\{(\text{NC})\text{C}=\text{NNTs}=\text{CC}=\text{NTs}\}(\text{dppe})\text{Cp}^*$ **5**. Ellipsoids have been drawn at the 50% probability level with hydrogen atoms, the phenyl carbons of the dppe ligands (except the *ipso*-carbons) and the disorder of the tolyl ring of the tosyl group attached at N(6) omitted for clarity.

(e) $\text{TsN}=\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2=\text{NTs}$ **6**. This centrosymmetric molecule is depicted in Fig. 5, with selected bond parameters given in the caption thereto. The geometry is similar to that found for $\text{TsN}=\text{PPh}_3$ [cf. N-P 1.579(4), N-S 1.586(4) Å; S-N-P 126.4(2)° [38]] and deserves no further comment.

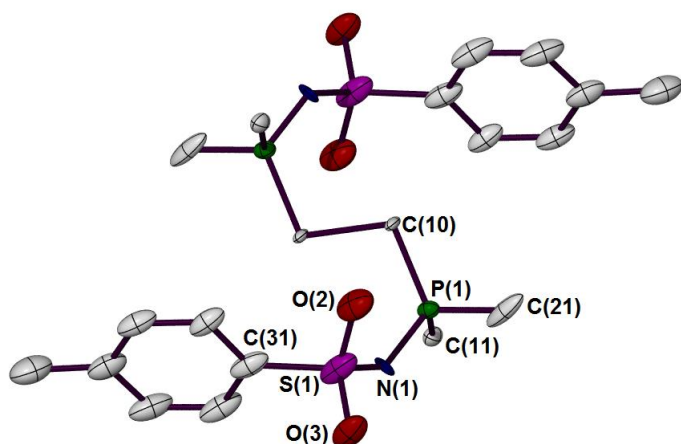


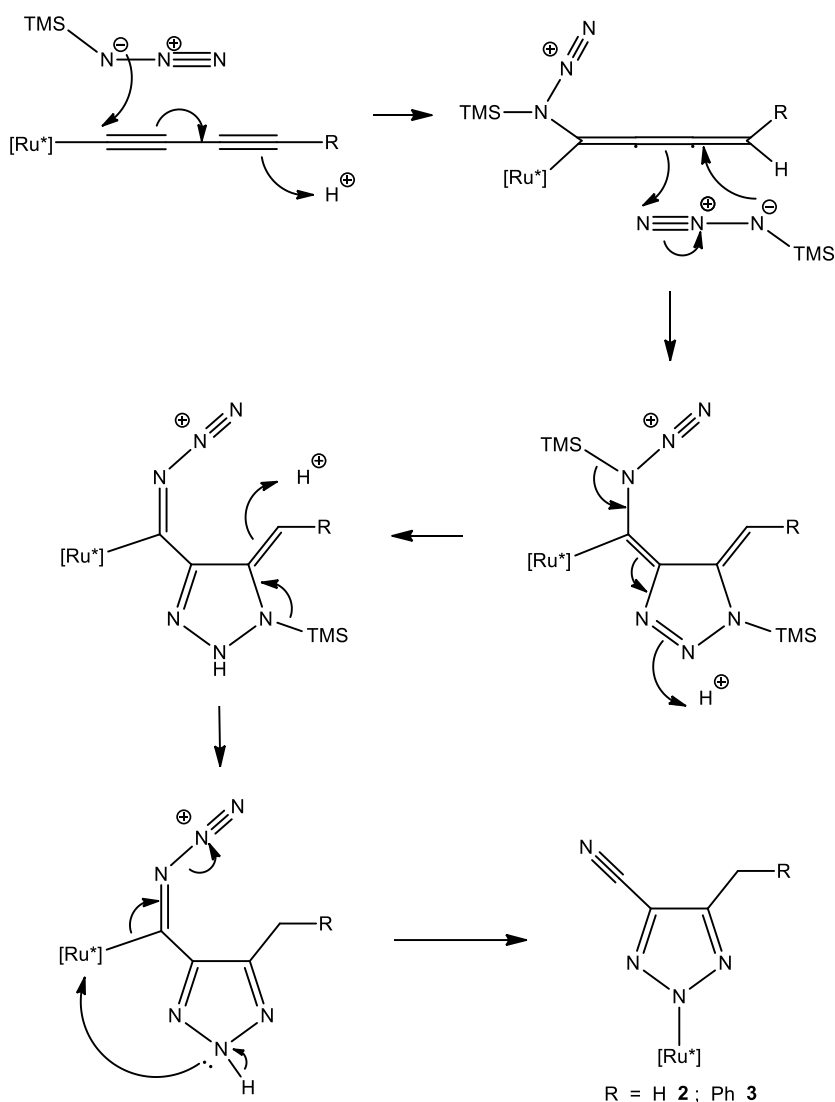
Figure 5. A molecule of $\text{TsN}=\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2=\text{NTs}$ **6**. Selected bond parameters: C(10)-P(1) 1.817(11), P(1)-N(1) 1.575(9), N(1)-S(1) 1.582(10), S(1)-O(2,3) 1.448(3),

1.447(3), C(10)-C(10') 1.510(10) Å; P(1)-C(10)-C(10') 113.1(6), C(10)-P(1)-N(1) 115.1(6), P(1)-N(1)-S(1) 134.7(6), N(1)-S(1)-O(2,3) 104.4(4), 110.8(5), N(1)-S(1)-C(31) 112.2(3), O(2)-S(1)-O(3) 116.2(2)°. Ellipsoids have been drawn at the 50% probability level with hydrogen atoms, the phenyl carbons of the dppe ligands (except the *ipso*-carbons) and the disorder of the N=PPh omitted for clarity.

Discussion

The reactions described above are notable for not producing the expected triazolyl complexes, at least under the conditions employed here (which differ from those commonly employing Cu(I) or Ru(II) catalysts). Further reaction with the free C≡C triple bond has occurred to give the cyano-methyl (or -benzyl) -triazolyl ligands found by the single-crystal X-ray structure determinations.

Of some interest is the course of the reactions described above. A possible mechanism for the formation of **2** and **3** is shown in Scheme 4. Nucleophilic addition of TMS azide to C(1) of the diyne ligand and addition of a proton (from solvent) is followed by cycloaddition of a second TMS azide to C2 and C3. Rearrangement by tandem protodesilylation is then followed by loss of N₂ and of a proton to give the CN group. Migration of the [Ru*] fragment to the central N of the triazole affords the isolated product.



Scheme 4. Formation of **2** or **3** by addition of two molecules of $\text{SiMe}_3(\text{N}_3)$ to precursor diynyl complexes $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CR})(\text{dppe})\text{Cp}^*$ ($\text{R} = \text{H}$ or Ph , respectively).

Derivatisation of **3** was carried out by reaction with $\text{RuCl}(\text{dppe})\text{Cp}^*$ in THF, which afforded binuclear $[\text{Cp}^*(\text{dppe})\text{Ru}\{\text{N}_3\text{C}[\text{CNRu}(\text{dppe})\text{Cp}^*]\text{CMe}\}]\text{PF}_6$ **4**. Coordination of the second $\text{Ru}(\text{dppe})\text{Cp}^*$ moiety to N(31) of the ligand in **3** has occurred.

Reactions of sulfonyl azides with alkynes have been found to give products which depend upon conditions and reagents and may include *N*-sulfonylamidines when amines are present, or *N*-sulfonylamides in the presence of water [40].

From a reaction of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})\text{Cp}^*$ with TsN_3 , triazolyl complex **5** was obtained. The structural study suggests that reaction with the outer $\text{C}\equiv\text{C}$ triple bond has occurred, the resulting iminopyrazolyl ligand bearing a $-\text{C}\equiv\text{N}-\text{Ru}(\text{dppe})\text{Cp}^*$ substituent on C(1). In the course of this reaction, one molecule of N_2 is formally

eliminated, although the precise mechanism of this reaction is unclear. The Staudinger bis(iminophosphorane) $\text{TsN}=\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2=\text{NTs}$ **6** was obtained, although only in minor amount, from this reaction. Combination of dppe (presumably displaced from Ru during the reaction) with nitrene TsN would afford this compound.

Conclusions

Reactions of $\text{SiMe}_3(\text{N}_3)$ with complexes such as $\text{Ru}(\text{C}\equiv\text{CH})(\text{PP})\text{Cp}'$ [PP = $(\text{PPh}_3)_2$, $\text{Cp}' = \text{Cp}$; PP = dppe, $\text{Cp}' = \text{Cp}^*$] result in metathetical displacement of the ethynyl group by azide, rather than the [3 + 2]-cycloaddition to give triazoles expected from “click” reactions. The diyne $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{PPh}_3)_2\text{Cp}$ reacts similarly. However, formation of a substituted triazole occurs when $\text{SiMe}_3(\text{N}_3)$ reacts with $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})\text{Cp}^*$, in which the diyne group is more strongly attached to the metal centre, while not possessing the tendency for the PR_3 ligand to dissociate as is often found with the $(\text{PPh}_3)_2$ analogues. Nevertheless, formation of **6** shows that decoordination of dppe is possible and may occur to a degree.

Formation of the triazole is accompanied by further reaction to give the CN and alkyl substituents (Scheme 2). A related reaction using tosyl azide afforded a cyano-substituted pyrazole, in a reaction involving two molecules of azide (Scheme 4).

It is evident that this chemistry is somewhat removed from the “click” chemistry found by others in the reactions of various azides with alkynyl metal complexes. The relatively low yields of the metal complexes also argues against conventional “click” mechanisms being operative here. While detailed discussion of possible mechanisms is inappropriate at this stage, defining factors may involve the steric hindrance attendant on the approach of reagents to the diyne group, resulting from the presence of relatively bulky dppe and Cp^* ligands on the metal centre.

None of the reactions described above were carried out in the presence of the usual Cu or Ru catalysts used in conventional “click” chemistry. Further work is necessary to determine the effect of the metal centre upon the reactivity of the diyne group towards azide.

Experimental

General. All reactions were carried out under dry nitrogen, although normally no special precautions to exclude air were taken during subsequent work-up. Common solvents were dried, distilled under nitrogen and degassed before use. Separations were carried out by preparative thin-layer chromatography on glass plates (20 x 20 cm²) coated with silica gel (Merck, 0.5 mm thick).

Instruments. IR spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in CH₂Cl₂ were obtained using a 0.5 mm path-length solution cell with NaCl windows. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra were recorded on a Varian Gemini 2000 instrument (¹H at 300.145 MHz, ¹³C at 75.479 MHz, ³¹P at 121.501 MHz). Unless otherwise stated, samples were dissolved in CDCl₃ contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ¹H and ¹³C NMR spectra and external H₃PO₄ for ³¹P NMR spectra. Electrospray mass spectra (ES-MS) were obtained from samples dissolved in MeOH, with added NaOMe to aid ionisation [41]. Solutions were injected into a Fisons VG Platform II spectrometer via a 10 ml injection loop. Nitrogen was used as the drying and nebulising gas. Elemental analyses were by Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand.

Reagents. Ru(C≡CC≡CR)(dppe)Cp* [R = H [42], Ph [43], SiMe₃ [42], Au(PPh₃) [42]], Ru(C≡CH)(PPh₃)₂Cp [44], Au(N₃)(PPh₃) [45] were made by the cited methods. SiMe₃(N₃), (tos)N₃ were commercial samples (Sigma-Aldrich).

Reactions of SiMe₃(N₃)

(a) *With Ru(C≡CC≡CH)(dppe)Cp*.* SiMe₃(N₃) (14 mg, 0.12 mmol) was added to a solution of Ru(C≡CC≡CH)(dppe)Cp* (40 mg, 0.06 mmol) in THF (5 ml) and the mixture was heated at reflux point for 2 h. Removal of THF, dissolution of the residue in CH₂Cl₂ and separation by preparative TLC (silica gel, acetone / hexane = 3/7) gave two bands. The bright yellow fraction (*R_f* = 0.75) gave Ru{N₃C(CN)CMe}(dppe)Cp* **2** (29.1 mg, 67%) as yellow crystals (from benzene / hexane). Anal. Found: C, 65.77; H, 6.25; N, 7.00. Calcd (C₄₀H₄₂N₄P₂Ru.0.5C₆H₆): C, 65.80; H, 6.29; N, 7.14; M, 742. IR (CH₂Cl₂, cm⁻¹): ν(C≡N) 2216m, ν(C=N) 1724m. ¹H NMR (C₆D₆): δ 1.47 (s, 15H, Cp*), 1.67 (s, 3H, Me), 2.29, 3.05 (2 x m, 4H, dppe), 6.99-7.25 (m, 20H, Ph). ¹³C NMR (C₆D₆): δ 9.57 (s, Me), 9.88 (s, C₅Me₅), 31.62 (m, dppe), 91.70 (s, C₅Me₅), 115.42 (s, CN), 117.71 (s, C₂), 127.67-141.78 (m, Ph); 147.10 (s, C₁). ³¹P NMR (C₆D₆): δ 88.1 (s, dppe). ES-MS, MeOH-NaOMe, *m/z*): 765.187, [M + Na]⁺ (calcd 765.183); 743.204, [M + H]⁺ (calcd 743.201); 635, [Ru(dppe)Cp*]⁺.

The second dark yellow band (*R_f* = 0.52) yielded Ru(N₃)(dppe)Cp* (3.3 mg, 8%), identified by comparison with an authentic sample.

Similarly, **2** (21 mg, 38%) was obtained from Ru(C≡CC≡CSiMe₃)(dppe)Cp* (51 mg, 0.07 mmol) and SiMe₃(N₃) (9 μL, 0.07 mmol), and also from Ru{C≡CC≡CAu(PPh₃)}(dppe)Cp* or Ru(C≡CC≡CSiMe₃)(dppe)Cp* and SiMe₃(N₃).

(b) *With Ru(C≡CC≡CPh)(dppe)Cp**. SiMe₃(N₃) (9.1 mg, 0.08 mmol) was added to a solution of Ru(C≡CC≡CPh)(dppe)Cp* (30 mg, 0.04 mmol) in THF (7 ml). After heating at reflux for 6 h, THF was removed, the residue dissolved in acetone and separated by preparative TLC (SiO₂, acetone / hexane = 1/3). The yellow band (*R_f* = 0.58) gave Ru{N₃C(CN)C(CH₂Ph)}(dppe)Cp* **3** (4.1 mg, 13%) as yellow crystals (from benzene / hexane). Anal. Found: C, 68.81; H, 5.81; N, 6.45. Calcd (C₄₆H₄₆N₄P₂·0.5C₆H₆): C, 68.59; H, 5.76; N, 6.53; *M*, 818. IR (CH₂Cl₂, cm⁻¹): ν(CN) 2213 cm⁻¹. ¹H NMR (C₆D₆): δ 1.39 (s, 15H, Cp*), 2.19, 2.85 (2 x m, 4H, dppe), 3.39 (s, 2H, CH₂), 6.65-7.18 (m, 25H, Ph). ¹³C NMR (C₆D₆): δ 10.47 (s, C₅Me₅), 31.98 (s, CH₂), 32.37 (m, dppe), 92.37 (s, C₅Me₅), 115.83 (s, CN), 118.12 (s, C₂), 126.36-142.65 (m, Ph), 150.85 (s, C₁). ³¹P NMR (C₆D₆): δ 88.9 (s, dppe). ES-MS (MeOH-NaOMe, *m/z*): 841.228, w, [M + Na]⁺ (calcd 841.215); 818.238, s, [M]⁺ (calcd 818.225).

The second dark yellow band (*R_f* = 0.47) contained Ru(N₃)(dppe)Cp* (11.6 mg, 43%), identified by comparison with an authentic sample.

(c) *With Ru(C≡CC≡CH)(PPh₃)₂Cp*. SiMe₃(N₃) (0.92 mg, 0.08 mmol) was added to a solution of Ru(C≡CC≡CH)(PPh₃)₂Cp (30 mg, 0.04 mmol) in THF (8 ml) and the mixture was stirred at 65°C (oil bath) for 6 h. Removal of THF, extraction with acetone and purification by preparative TLC (SiO₂, acetone / hexane = 3/7) gave one yellow band (*R_f* = 0.41) containing Ru(N₃)(PPh₃)₂Cp (16.7 mg, 56%) as yellow-orange crystals (from benzene / hexane), identified by comparison with an authentic sample. IR (CH₂Cl₂, cm⁻¹): ν(N₃) 1981 (m). ¹H NMR (CDCl₃): δ 7.70-6.79 (m, 30H, Ph); 4.26 (s, 5H, Cp). ¹³C NMR (CDCl₃): δ 134.04-125.97 (m, Ph); 86.03 (s, C₅H₅). ³¹P NMR (CDCl₃): δ 43.3 (s, PPh₃). ES-MS (MeOH, *m/z*): 733, [M]⁺; 691, [Ru(PPh₃)₂Cp]⁺; 429, [Ru(PPh₃)Cp]⁺.

(d) *With Ru(C≡CH)(PPh₃)₂Cp*. A mixture of Ru(C≡CH)(PPh₃)₂Cp (37 mg, 0.05 mmol) and SiMe₃N₃ (12 mg, 0.1 mmol) in THF (5 ml) was stirred at r.t. for 48 h. Removal of THF, extraction with benzene and purification on a short column of SiO₂ (eluant acetone / hexane = 1/3) gave a single yellow band containing Ru(N₃)(PPh₃)₂Cp (13.7 mg, 36.2 %) as a yellow-orange powder.

(e) *With Ru(C≡CH)(dppe)Cp**. As in (d), a mixture of Ru(C≡CH)(dppe)Cp* (25 mg, 0.04 mmol) and SiMe₃N₃ (9.2 mg, 0.08 mmol) in THF (6 ml) after 72 h at r.t. gave orange Ru(N₃)(dppe)Cp* (15.6 mg, 61%). IR (CH₂Cl₂, cm⁻¹): ν(N₃) 2035 (s). ¹H NMR (C₆D₆): δ 7.25-7.07 (m, 20H, Ph); 2.37-2.35, 1.98-1.85 (2 x m, 2 x 2H,

CH₂CH₂); 1.53 (s, 30H, Cp*). ³¹P NMR (C₆D₆): δ 77.7 (s, dppe). ES-MS (+ve ion, MeOH, *m/z*): 700, [M+ Na]⁺; 635, [Ru(dppe)Cp*]⁺.

Reaction of 2 with RuCl(dppe)Cp.*

A mixture of **2** (25.5 mg, 0.034 mmol) and RuCl(dppe)Cp* (23 mg, 0.034 mmol) and NH₄PF₆ (22.6 mg, 0.136 mmol) in MeOH (15 ml) was heated at reflux point for 4 h. Evaporation of the yellow solution, extraction of the residue with benzene and purification by TLC (SiO₂, acetone / hexane = 1/2) gave a yellow band (*R_f* = 0.42) containing [Cp*(dppe)Ru{N₃C[CNRu(dppe)Cp*]CMe}]PF₆ **4** (35.5 mg, 67.5%), which formed yellow crystals from EtOH. Anal. Found: C, 59.63; H, 5.57; N, 3.62. Calcd (C₇₆H₈₁F₆N₄P₅Ru₂): C, 59.91; H, 5.36; N, 3.68; *M* (cation), 1377. IR (CH₂Cl₂, cm⁻¹): ν(CN) 2224, ν(PF) 840. ¹H NMR (CDCl₃): δ 1.36 (s, 15H, Cp*), 1.40 (s, 15H, Cp*), 1.64 [s(br), 3h, Me], 2.17 [m, 4H, dppe of CN-Ru(dppe)Cp*], 2.47, 2.88 [2 x m, 4H, N-Ru(dppe)Cp*], 7.08-7.47 (m, 40H, Ph). ¹³C NMR (CDCl₃): δ 9.09 (s, Me), 9.25 (s, C₅Me₅), 9.36 (s, C₅Me₅), 28.10 (m, dppe), 31.16 (m, dppe), 91.70 (s, C₅Me₅), 92.24 (s, C₅Me₅), 107.50 (s, C₂), 124.22-140.26 (m, Ph), 148.12 (s, C₁). ³¹P NMR (CDCl₃): δ 73.07 [s(br), 2P, CN-Ru(dppe)Cp*], 86.71 [s(br), 2P, N-Ru(dppe)Cp*], -143.93 [sept, *J*(PF) 710 Hz, 1P, PF₆]. ES-MS (MeOH, *m/z*): 1377.341, [M]⁺ (calcd 1377.353).

Reaction of Ru(C≡CC≡CH)(dppe)Cp with TsN₃.*

(a) In toluene. A solution of Ru(C≡CC≡CH)(dppe)Cp* (31 mg, 0.05 mmol) in toluene (10 mL) was treated with TsN₃ (28 mg, 0.14 mmol) and stirred at r.t. for 18 h. The solvent was then evaporated to ca 2 mL and hexane (30 mL) was added dropwise. A yellow precipitate formed and was filtered on sintered funnel and washed with hexane to give Ru{CN[C₃N₂H(NTs)(Ts)]}(dppe)Cp* **5** as a bright yellow crystalline powder (33 mg, 43%). Single crystals suitable for X-ray studies were grown from THF/hexane. IR (CH₂Cl₂, cm⁻¹): ν(C-H) 2977 (m); ν(C≡N) 2229 (m); ν(C=N) 1703 (m); ν(SO) 1179 (m). ¹H NMR (C₆D₆): δ 7.68 (d, ²*J*(HH) 8 Hz, 2H, C₆H₄); 7.23-6.95 (m, 20H, Ph); 6.61 (d, ²*J*(HH) 8 Hz, 2H, C₆H₄); 2.25 (s, 3H, CH₃); 2.04-1.99, 1.89-1.85 (2 x m, 2 x 2H, CH₂CH₂); 1.49 (s, 15H, Cp*); 1.23 (s, 1H, CH). ¹³C NMR (C₆D₆): δ 145.17, 144.89, 138.84, 134.87 (4 x s, C₆H₄); 130.39-127.06 (m, Ph); 116.63 (s, C); 122.85 (s, C); 92.27 (s, C₅Me₅); 58.52 (s, C); 28.77-28.18 (m, CH₂CH₂); 21.14 (s, CH₃); 9.79 (s, C₅Me₅). ³¹P NMR (C₆D₆): δ 74.3 (s, dppe). ES-MS (+ve ion, MeOH, *m/z*): 1073, [M + Na]⁺; 1051, [M + H]⁺; 635, [Ru(dppe)Cp*]⁺. High resolution MS (*m/z*): 1051.224, [M + H]⁺.

(b) In THF. A solution of TsN₃ (28.8 mg, 0.146 mmol) in THF (1 ml) was added to one of Ru(C≡CC≡CH)(dppe)Cp* (50 mg, 0.073 mmol) in THF (5 ml), and the mixture was heated at reflux point for 4 h. Removal of THF, and purification of a CH₂Cl₂ extract of the residue (SiO₂, acetone / hexane = 2/3) gave several minor products together with a pale yellow band (*R_f* = 0.58), from which TsN=PPh₂CH₂CH₂PPh₂=NTs **6** (1.8 mg, 3 %) was isolated as colourless crystals

(from benzene). ^1H NMR (CDCl_3): δ 2.33 (s, 6H, 2Me), 3.12 (m, 4H, dppe), 7.06-7.83 (m, 28H, 4Ph + 2 C_6H_4). ^{31}P NMR (CDCl_3): δ 19.68 (s, dppe). ES-MS (MeOH-NaOMe, m/z): 759.177, $[\text{M} + \text{Na}]^+$ (calcd 759.164).

Structure Determinations

Data for the structures were collected at 100K (110K for **3** and **4**) on either an Oxford Diffraction Gemini (for compounds **1b**, **2**, **5** and **6**) or an Xcalibur (for **3** and **4**) diffractometer with Mo $\text{K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ (Cu $\text{K}\alpha$, $\lambda = 1.54178 \text{ \AA}$ for **5**). Data were corrected for absorption [47] and the structures solved by direct methods and refined by full-matrix least squares on F^2 using SHELXL-2014 [46] interfaced through the program X-Seed [48] or WinGX [49]. Unless stated below, anisotropic displacement parameter forms were refined for the non-hydrogen atoms, hydrogen atom treatment following riding models.

Pertinent results are given in the Figures (which in general show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids/ and in captions to the Figures and Table 1; crystal data and refinement details are collected in Tables 2 and 3.

Special refinement details

2. The solvent was modelled as a dichloromethane molecule disordered over two sets of sites with occupancies constrained to 0.5 after trial refinement. Geometries were restrained to ideal values.
3. The crystal was small and relatively weakly diffracting, thus data above $2\theta = 50^\circ$ were omitted from the refinement.
4. The PF_6 anion was modelled with occupancy over three sites (0.4, 0.4, 0.2 occupancy) and the minor occupancy site was refined with isotropic displacement parameters. Two EtOH molecules were modelled (both at 50% occupancy, isotropic displacement parameters) and one of these shares the low occupancy PF_6 site.
5. One tosyl group was modelled as being disordered over two sets of sites with occupancies constrained to 0.5 after trial refinement. The solvent was modelled as a dichloromethane molecule with site occupancies refined to 0.293(4). Partially weighted atoms were refined with isotropic displacement parameters.
6. One phenyl ring, 11n, together with the associated P and N atoms were modelled as being disordered over two sets of sites with site occupancies constrained to 0.5 after trial refinement.

Supplementary Material

CIFs for the X-ray structure determinations of $\text{Ru}(\text{N}_3)(\text{dppe})\text{Cp}^*$ **1b**, $\text{Ru}\{\text{N}_3\text{CRC}(\text{CN})\}(\text{dppe})\text{Cp}^*$ (R = Me **2**, CH_2Ph **3**), $[\text{Ru}\{\text{N}_3\text{CMeC}(\text{CN})[\text{Ru}(\text{dppe})\text{Cp}^*]\}(\text{dppe})\text{Cp}^*$ **4**, $\text{Ru}\{\text{N}\equiv\text{CC}=\text{NNTs}=\text{CC}(=\text{NTs})\}(\text{dppe})\text{Cp}^*$ **5**, $(\text{TsN}=\text{PPh}_2\text{CH}_2)_2$ **6**. CCDC 1409117-1409122, respectively, contain the supplementary crystallographic data for this paper.

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ca.ac.uk/data_request/cif.

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Table 1. Selected bond distances (Å) and angles (deg.)

Parameter	2	3	4	5
Ru(1)-P(1)	2.2908(6)	2.3029(10)	2.2988(10)	2.3011(12)
Ru(1)-P(2)	2.2922(6)	2.2885(10)	2.2961(10)	2.3066(12)
Ru(2)-P(3)			2.2965(10)	
Ru(2)-P(4)			2.2985(10)	
Ru(1)-N(1)	2.107(2)	2.107(3)	2.110(3)	2.006(3)
Ru(2)-N(31)			2.029(3)	
Ru(1)-C(cp) (av.)	2.2362 [2.220-2.246(3)]	2.242 [2.225-2.266(3)]	2.236 [2.223-2.249(4)]	2.219 [2.210-2.228(4)]
Ru(2)-C(cp) (av.)			2.231 [2.205-2.250(4)]	
N(1)-N(2)	1.321(2)	1.325(4)	1.324(4)	1.338(5) [N(6)-N(7)]
N(1)-N(5)	1.359(2)	1.351(4)	1.348(4)	
C(3)-N(2)	1.361(2)	1.363(4)	1.360(5)	1.334(6) [C(3)-N(7)]
C(4)-N(4)				1.373(6)
C(4)-N(5)	1.337(3)	1.340(4)	1.338(5)	1.380(7) [C(5)-N(6)]
C(3)-C(4)	1.384(3)	1.389(5)	1.394(5)	1.436(7)
C(3)-C(31)	1.419(3)	1.420(5)	1.420(5)	
C(31)-N(31)	1.145(3)	1.154(4)	1.146(5)	
C(4)-C(41)	1.498(3)	1.498(4)	1.493(6)	1.368(6) [C(4)-C(5)]
C(41)-C(42)		1.520(5)		
P(1)-Ru(1)-P(2)	83.41(2)	83.55(3)	83.56(3)	
P(1)-Ru(1)-N(1)	86.04(5)	84.42(8)	87.22(8)	85.19(11)

P(2)-Ru(1)-N(1)	87.31(6)	89.40(8)	85.32(9)	85.15(11)
P(3)-Ru(2)-P(4)			83.35(4)	
P(3)-Ru(2)-N(31)			90.83(9)	
Ru(1)-N(1)-N(2)	124.85(17)	122.6(2)	122.8(2)	
Ru(1)-N(1)-N(5)	122.77(18)	124.0(2)	124.5(2)	
Ru(2)-N(31)-C(31)			172.2(3)	173.4(4) [Ru(1)-N(1)-C(2)]
C(3)-N(2)-N(1)	105.0(2)	104.8(3)	105.0(3)	
N(2)-N(1)-N(5)	112.4(2)	112.9(3)	112.7(3)	
C(4)-N(5)-N(1)	106.2(2)	106.0(3)	106.3(3)	
N(5)-C(4)-C(3)	107.3(2)	107.4(3)	107.2(3)	
N(2)-C(3)-C(4)	109.1(2)	108.8(3)	108.7(3)	
C(3)-C(4)-C(41)	130.4(3)	127.5(3)	129.9(4)	
C(4)-C(3)-C(31)	128.9(3)	130.4(3)	129.74	
C(3)-C(31)-N(31)	177.3(3)	178.2(4)	177.4(4)	
C(4)-C(41)-C(42)		119.3(3)		

For 5: C(2)-C(3) 1.435(6) Å; N(1)-C(2)-C(3) 179.0(5), C(4)-C(3)-N(7) 113.7(4), C(3)-C(4)-C(5) 103.1(5), C(3)-C(4)-N(4) 122.3(4), C(4)-C(5)-N(6) 106.3(5), C(5)-N(6)-N(7) 114.4(6), C(3)-N(7)-N(6) 102.4(4)°.

Table 2. Crystal data and structure refinement for **1**, **2**, **3** and **4**.

Compound	1b	2	3	4
Empirical formula	C ₃₆ H ₃₉ N ₃ P ₂ Ru	C ₄₁ H ₄₄ Cl ₂ N ₄ P ₂ Ru	C ₄₉ H ₄₉ N ₄ P ₂ Ru	C ₇₈ H ₈₇ F ₆ N ₄ OP ₅ Ru ₂
Formula weight	676.71	826.71	856.93	1567.50
Temperature (K)	100(2)	100(2)	110(2)	110(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
<i>a</i> (Å)	10.0844(3)	16.9146(6)	13.0769(3)	12.7430(3)
<i>b</i> (Å)	11.8343(2)	11.8508(4)	13.1142(4)	15.8051(5)
<i>c</i> (Å)	13.1251(4)	21.1555(5)	24.1054(8)	20.3273(7)
α (°)	88.151(2)			89.272(3)
β (°)	82.945(2)	102.648(3)	100.105(3)	72.631(3)
γ (°)	89.216(2)			86.020(2)
Volume (Å ³)	1553.63(7)	4137.7(2)	4069.8(2)	3897.8(2)
<i>Z</i>	2	4	4	2
Density (calc.) (Mg/m ³)	1.447	1.327	1.399	1.336
Absorption coefficient (mm ⁻¹)	0.638	0.618	0.504	0.549
Crystal size (mm ³)	0.29 x 0.18 x 0.075	0.36 x 0.18 x 0.04	0.16 x 0.03 x 0.03	0.46 x 0.40 x 0.20
θ range for data collection (°)	2.923 to 37.394	2.617 to 31.773	2.475 to 28.181	2.514 to 29.240
Reflections collected	37660	50423	28470	35337
Independent reflections [<i>R</i> (int)]	15475 [0.0254]	13238 [0.0670]	8518 [0.0807]	17527 [0.0327]
Completeness (%) [θ_{\max} (°)]	99.3 [36.5]	99.9 [30]	98.4 [26]	96.1 [27]
Data / restraints / parameters	15475 / 0 / 384	13238 / 4 / 484	8518 / 0 / 510	17527 / 8 / 967
Goodness-of-fit on <i>F</i> ²	0.972	0.890	1.033	1.107
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0293	0.0425	0.0512	0.0509
<i>wR</i> ₂ (all data)	0.0751	0.1029	0.0913	0.1652
Largest diff. peak and hole (e.Å ⁻³)	1.431 and -0.466	1.211 and -0.807	0.525 and -0.650	1.523 and -0.623

Table 3. Crystal data and structure refinement for **5** and **6**.

Compound	5	6
Empirical formula	C _{54.29} H _{54.59} Cl _{0.59} N ₄ O ₄ P ₂ RuS ₂	C ₄₀ H ₃₈ N ₂ O ₄ P ₂ S ₂
Formula weight	1075.13	736.78
Temperature (K)	100(2)	100(2)
Wavelength (Å)	1.54178	0.71073
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	12.1705(3)	10.5275(9)
<i>b</i> (Å)	14.5774(3)	9.4570(11)
<i>c</i> (Å)	28.2919(6)	17.9939(18)
β (°)	98.030(2)	98.174(9)
Volume (Å ³)	4970.17(19)	1773.2(3)
<i>Z</i>	4	2
Density (calc.) (Mg/m ³)	1.437	1.380
Absorption coefficient (mm ⁻¹)	4.644	0.286
Crystal size (mm ³)	0.17 x 0.07 x 0.015	0.39 x 0.25 x 0.09
θ range for data collection (°)	3.155 to 67.288	2.909 to 25.999
Reflections collected	37626	12563
Independent reflections [<i>R</i> (int)]	8679 [0.0747]	3484 [0.0558]
Completeness (%) [θ _{max} (°)]	98.2 [66.5]	99.9 [25.24]
Data / restraints / parameters	8679 / 21 / 627	3484 / 145 / 308
Goodness-of-fit on F ²	0.849	1.155
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0420	0.0769
<i>wR</i> ₂ (all data)	0.0967	0.1598
Largest diff. peak and hole (e.Å ⁻³)	0.962 and -0.675	0.333 and -0.434