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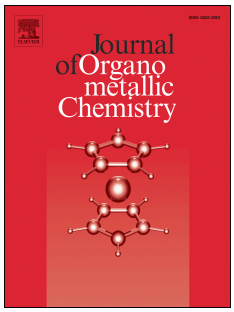


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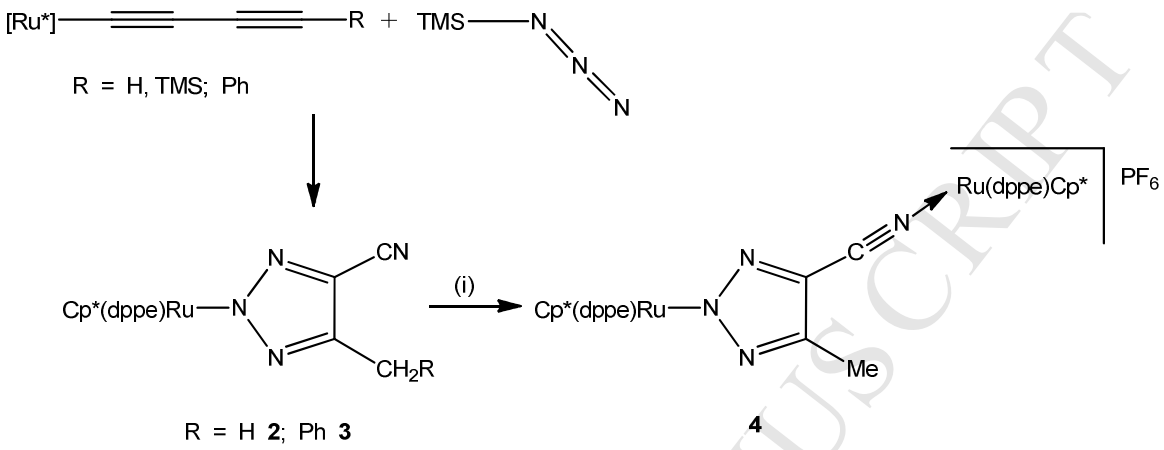
Graphical abstract

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

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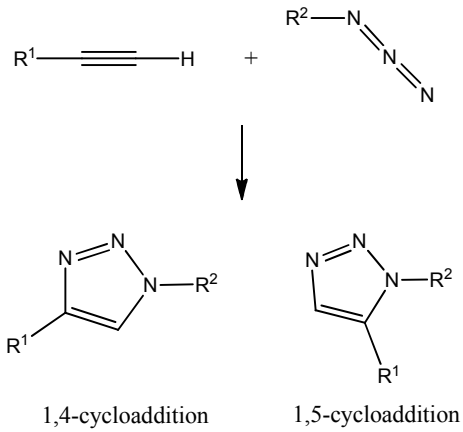
**Abstract**
Reactions of $SiMe_3(N_3)$ with Ru(C≡CH)(PP)Cp' [PP = $(PPh_3)_2$, Cp' = Cp; PP = dppe, Cp' = Cp*] afford $Ru(N_3)$(PP)Cp'. Reactions of Ru(C≡CC≡CR)(dppe)Cp* with $SiMe_3(N_3)$ give $Ru\{N_3C(CN)CH_2R\}$(dppe)Cp* (R = H **2**, Ph **3**). With RuCl(dppe)Cp* in the presence of $[NH_4]PF_6$, **2** gives binuclear $[Cp^*(dppe)Ru\{N_3C[\{(CN)Ru(dppe)Cp^*\}CMe\}]PF_6$ **4**. The reaction between $TsN_3$ and Ru(C≡CC≡CH)(dppe)Cp* gives Ru{(NC)C=NNTs=CHC(=NTs)}(dppe)Cp* **5**, with a small amount of $TsN{=}PPh_2CH_2CH_2PPh_2{=}NTs$ **6** being obtained from some reactions. X-ray determined structures of $Ru(N_3)$(dppe)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 $M(CO)_3(\eta\text{-}C_5H_4N_3)$ and HC≡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 $Mo(N_3)(CO)_2(en)(\eta\text{-}C_3H_5)$ [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 $PhCH_2N_3$ [28], and the interesting inorganic click reaction between $Au(N_3)(PPh_3)$ and $Au(C{\equiv}CPh)(PPh_3)$ [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 permetallated compounds [32].

**Results and Discussion**

As mentioned above, cycloaddition of activated alkynes $HC{\equiv}CCO_2Me$ and $C_2(CO_2Me)_2$ to $Ru(N_3)(dppe)Cp$ has been reported to give triazolates $Ru\{N_3C_2R(CO_2Me)\}(dppe)Cp$ (R = H, $CO_2Me$, 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.

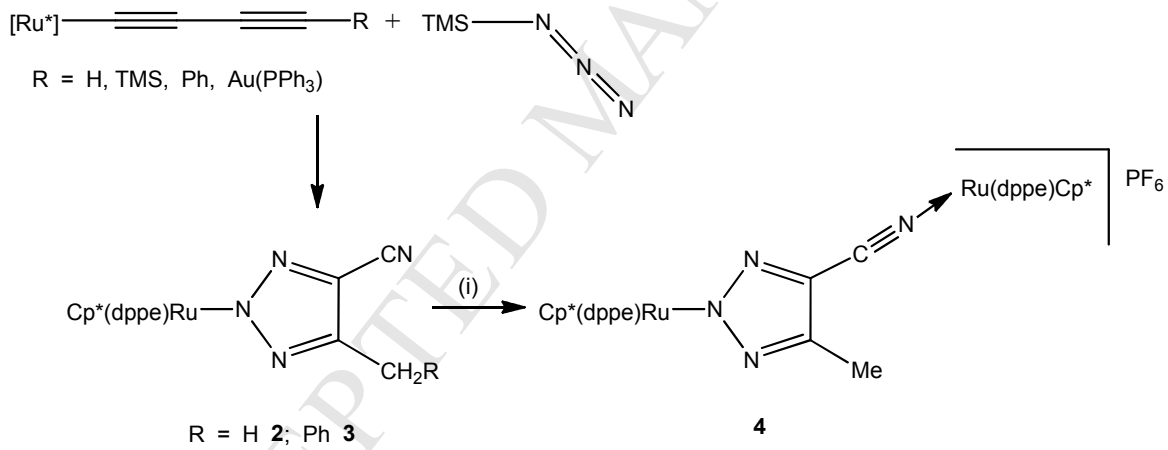
Initial studies showed that reactions of $SiMe_3(N_3)$ with $Ru(C{\equiv}CH)(PPh_3)_2Cp$, $Ru(C{\equiv}CH)(dppe)Cp^*$ or $Ru(C{\equiv}CC{\equiv}CH)(PPh_3)_2Cp$ all proceed with metathetic replacement of ethynyl or butadiynyl by azide to give known $Ru(N_3)(PP)Cp'$ complexes [**1a**; PP = $(PPh_3)_2$, Cp' = Cp (56%); **1b**; PP = dppe, Cp' = Cp* (61%)]. Consequently, we turned our attention to similar reactions of the diynyl-ruthenium complexes $Ru(C{\equiv}CC{\equiv}CR)(dppe)Cp^*$ [R = H, Ph, $SiMe_3$, $Au(PPh_3)$]. The chemistry described below is summarised in Schemes 2-4, full details being given in the Experimental Section.

Addition of $SiMe_3(N_3)$ to solutions of $Ru(C{\equiv}CC{\equiv}CH)(dppe)Cp^*$ in refluxing THF resulted in a rapid reaction which afforded the yellow complex **2** in 67% yield, containing the $N_3C(CN)CMe$ 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 $Ru\{N_3C(CN)CMe\}(dppe)Cp^*$ **2**, the IR spectrum contained bands at 2216 [$\nu$(CN)] and 1724 $cm^{-1}$ [$\nu$(C=N)]. In the $^1H$ and $^{13}C$ NMR spectra, the Cp* and dppe ligands gave resonances at $\delta$ 1.47, 9.88 and 91.70 (Cp*), 2.29, 3.05 and 31.62 (dppe $CH_2$), while the triazole ligand gives rise to $^{13}C$ resonances at $\delta$ 9.57 (Me), 115.42 (CN), 117.71 [C(2)] and 147.10 [C(1)]; the dppe $^{31}P$ resonance is at $\delta$ 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 $Ru(C{\equiv}CC{\equiv}CSiMe_3)(dppe)Cp^*$ and $SiMe_3(N_3)$ in similar yield.

With Ru(C≡CC≡CPh)(dppe)Cp*, a similar reaction with $SiMe_3(N_3)$ afforded the related compound Ru{$N_3C(CN)C(CH_2Ph)$}(dppe)Cp* **3** in 13% yield together with Ru($N_3$)(dppe)Cp* (43%). Pertinent spectroscopic data for **3** include an IR band at 2213 $cm^{-1}$ [ν(C≡N)], $^1$H NMR signals at δ 1.39 (Cp*), 2.19 and 2.85 (dppe $CH_2$), 3.39 ($CH_2$Ph), $^{13}$C NMR resonances at δ 10.47 and 92.37 (Cp*), 31.98 ($CH_2$Ph), 32.37 (dppe $CH_2$), 118.12 [C(2)], 115.83 (CN), 150.85 [C(1)], and a $^{31}$P NMR signal at δ 88.85 (dppe). In the ESI-MS, peaks at *m/z* 841 (weak, $[M + Na]^+$) and 818 (strong, $M^+$) are present.

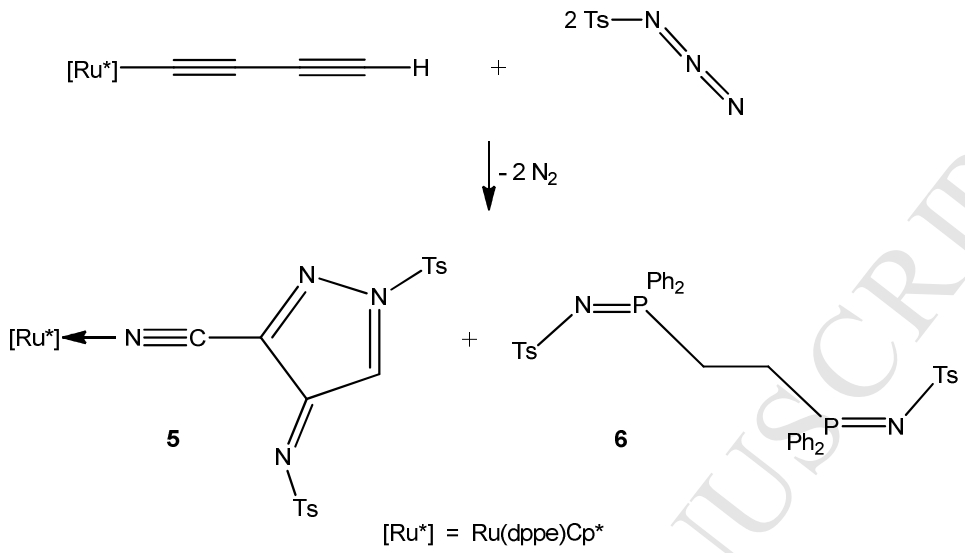
A subsequent reaction of Ru{$N_3C(CN)CMe$}(dppe)Cp* with an equivalent of RuCl(dppe)Cp* in MeOH, in the presence of $[NH_4]PF_6$, afforded the yellow binuclear complex [Cp*(dppe)Ru{$N_3C[(CN)$Ru(dppe)Cp*]CMe}]$PF_6$ **4** in 68% yield. The IR spectra contained bands at 2224 [ν(CN)] and 840 $cm^{-1}$ [ν(PF)], with duplicated resonances in the $^1$H, $^{13}$C and $^{31}$P NMR spectra arising from the two Ru(dppe)Cp* centres. The C(2) and 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 Ru(C≡CC≡CR)(dppe)Cp* (R = H, $SiMe_3$, Ph) and $SiMe_3(N_3)$. Reagent: (i) = RuCl(dppe)Cp* + $[NH_4]PF_6$.

The reaction between $TsN_3$ and Ru(C≡CC≡CH)(dppe)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 Ru{(N≡C)$C_3N_2Ts_2$}(dppe)Cp* **5** (43%) as determined by a single-crystal X-ray structure determination. Spectroscopic data include ν(CH) at 2977, ν(C≡N) at 2229, ν(C=N) at 1703 and ν(SO) at 1179 $cm^{-1}$. In addition to characteristic signals for the Ru(dppe)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, $[M + Na]^+$ and $[M - H]^+$ are at *m/z* 1073 and 1051, respectively.




Scheme 3. Reaction of Ru(C≡CC≡CH)(dppe)Cp* and $TsN_3$ to give Ru{(N≡C)$C_3N_2Ts_2$}(dppe)Cp* **5** and TsN=$PPh_2CH_2CH_2PPh_2$=NTs **6**.

A minor product (3%) was found to be the bis(iminophosphorane) TsN=$PPh_2CH_2CH_2PPh_2$=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 $[M + Na]^+$ at *m/z* 759.

**Molecular structures**

(a) *Ru($N_3$)(dppe)Cp* (**1b**; Cp = Cp*; PP = dppe).* A molecule of this complex is shown in Fig. 1, significant bond parameters being included in Table 1. The usual coordination within the Ru(dppe)Cp* fragment is found, the almost linear azido ligand [angle N(1)-N(2)-N(3) 175.8(1)°] being attached via N(1) [Ru-N(1) 2.156(1) Å; Ru-N(1)-N(2) 122.80(8)°] with the expected bent configuration.

The present structure is similar to that of Ru($N_3$)($PPh_3$)$_2$Cp, which has Ru-P 2.3292(5), 2.3304(5), Ru-N 2.135(3), N-N 1.186(3), 1.164(3) Å, and P-Ru-P 105.22(2), P-Ru-N 85.39(6), 86.65(5), Ru-N-N 124.5(2) and N-N-N 175.2(3)° [35].

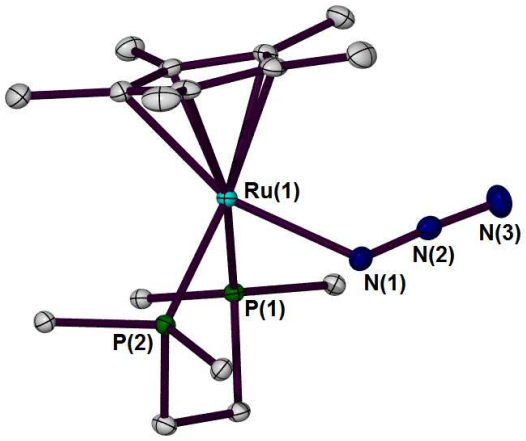



Figure 1. A molecule of Ru($N_3$)(dppe)Cp* **1b**. Selected bond parameters: Ru-P(1,2) 2.2894, 2.2924(3), Ru-C(cp) (av.) 2.225 [range 2.2126-2.2402(12)], Ru-N(1) 2.157(1), N(1)-N(2) 1.1917(15), N(2)-N(3) 1.1672(16) Å; P(1)-Ru-P(2) 83.35(1), P(1,2)-Ru-N(1) 79.80, 87.67(3), Ru-N(1)-N(2) 122.78(8), N(1)-N(2)-N(3) 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) *Ru{$N_3$CRC(CN)}(dppe)Cp* (R = Me **2**, $CH_2$Ph **3**).* As shown in Fig. 2 (selected bond parameters are in Table 1), in the molecule of **2** the familiar Ru(dppe)Cp* group is attached to the 1-cyano-2-methyltriazolyl ligand via the central N(1) atom [Ru-N(1) 2.107(2) Å]. Within the triazolyl group, atom N(1) is bonded asymmetrically to N(2) [N(1)-N(2) 1.321(2) Å] and N(5) [N(1)-N(5) 1.359(2) Å], with N(2)-N(1)-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.

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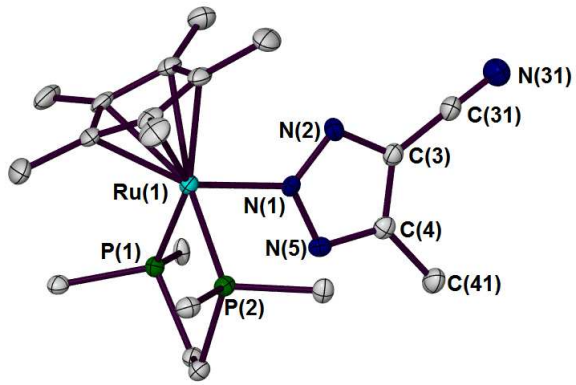
(a)




(b)

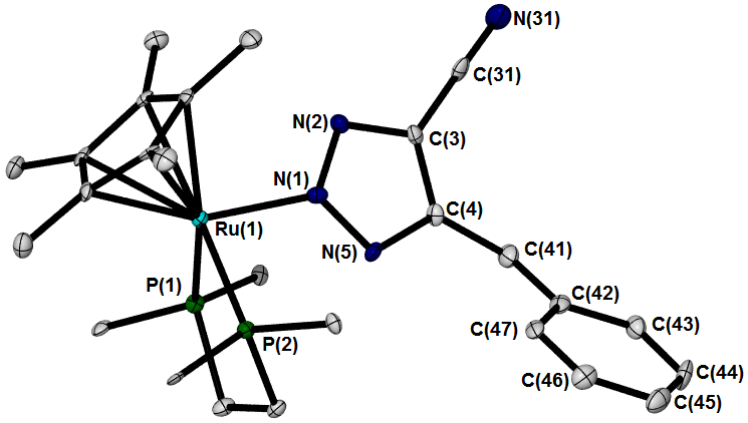



Figure 2. (a) A molecule of Ru{$N_3$CMeC(CN)}(dppe)Cp* **2**. (b) The benzyl derivative **3** is similar. Ellipsoids have been drawn at the 50% probability level with hydrogen atoms, the phenyl carbons of the dppe ligands (except the *ipso*-carbons) and the dichloromethane (**2**) and benzene (**3**) solvates omitted for clarity.

(c) *[Cp*(dppe)Ru{$N_3$C(CN)[Ru(dppe)Cp*]CMe}]$PF_6$* ***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 Ru(dppe)Cp* group attached to the nitrogen of the CN(31) group [Ru(2)-N(31) 2.029(3) Å]. The ligands (dppe and Cp*) of the second Ru(dppe)Cp* group are twisted by approximately 75° to avert a steric clash between the dppe ligands of Ru(1) and Ru(2). Bond parameters are overall similar to those found in **2** and in [Ru(NCMe)($PPh_3$)$_2$Cp*]$PF_6$ [Ru-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.

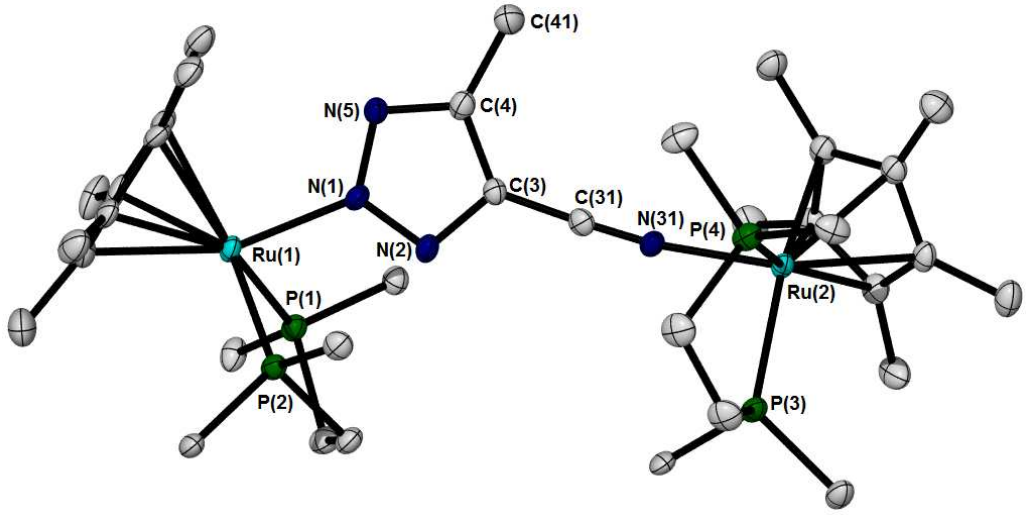



Figure 3. A plot of a molecule of [Cp*(dppe)Ru{$N_3C$[CN{Ru(dppe)Cp*}]CMe}]$PF_6$ **4**. Ellipsoids have been drawn at the 50% probability level with hydrogen atoms, the phenyl carbons of the dppe ligands (except the *ipso*-carbons) and the hexafluorophosphate anion, which is disordered over three positions, omitted for clarity.

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

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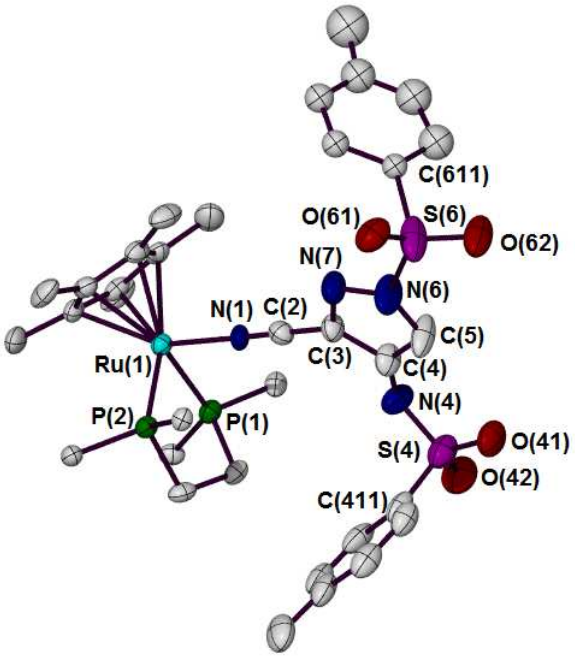


Figure 4. A molecule of Ru{(NC)C=NNTs=CC=NTs}(dppe)Cp* **5**. Ellipsoids have been drawn at the 50% probability level with hydrogen atoms, the phenyl carbons of the dppe ligands (except the *ipso*-carbons) and the disorder of the tolyl ring of the tosyl group attached at N(6) omitted for clarity.

(e) *TsN=PPh$_2$CH$_2$CH$_2$PPh$_2$=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 TsN=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.

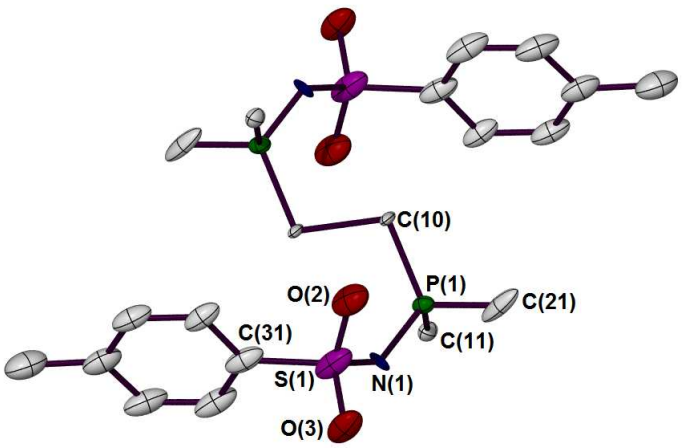


Figure 5. A molecule of TsN=PPh$_2$CH$_2$CH$_2$PPh$_2$=NTs **6**. Selected bond parameters: C(10)-P(1) 1.817(11), P(1)-N(1) 1.575(9), N(1)-S(1) 1.582(10), S(1)-O(2,3) 1.448(3),

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 diynyl 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 $N_2$ 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.

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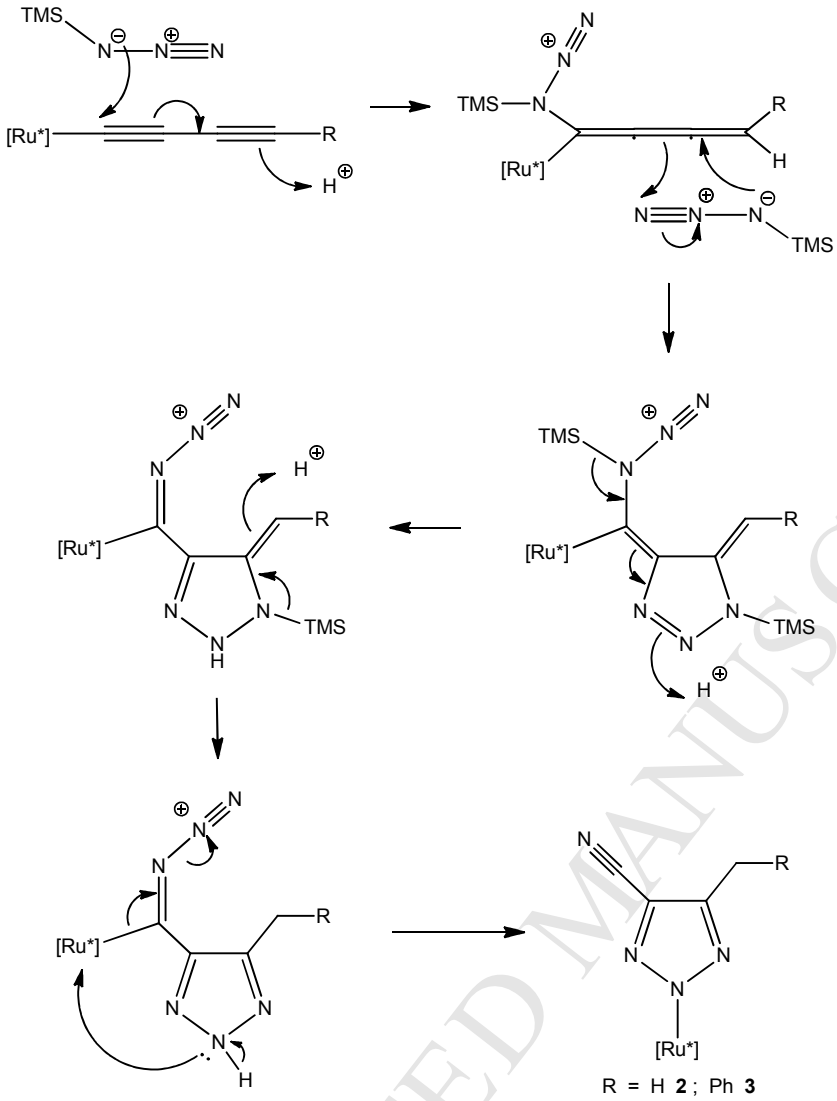


Scheme 4. Formation of **2** or **3** by addition of two molecules of $SiMe_3(N_3)$ to precursor diynyl complexes Ru(C≡CC≡CR)(dppe)Cp* (R = H or Ph, respectively).

Derivatisation of **3** was carried out by reaction with RuCl(dppe)Cp* in THF, which afforded binuclear [Cp*(dppe)Ru{$N_3$C[CNRu(dppe)Cp*]CMe}]$PF_6$ **4**. Coordination of the second Ru(dppe)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 Ru(C≡CC≡CH)(dppe)Cp* with $TsN_3$, triazolyl complex **5** was obtained. The structural study suggests that reaction with the outer C≡C triple bond has occurred, the resulting iminopyrazolyl ligand bearing a -C≡N-Ru(dppe)Cp* substituent on C(1). In the course of this reaction, one molecules of $N_2$ is formally

eliminated, although the precise mechanism of this reaction is unclear. The Staudinger bis(iminophosphorane) TsN=$PPh_2CH_2CH_2PPh_2$=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 $SiMe_3(N_3)$ with complexes such as Ru(C≡CH)(PP)Cp' [PP = $(PPh_3)_2$, Cp' = Cp; PP = dppe, Cp' = 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 diynyl Ru(C≡CC≡CH)$(PPh_3)_2$Cp reacts similarly. However, formation of a substituted triazole occurs when $SiMe_3(N_3)$ reacts with Ru(C≡CC≡CH)(dppe)Cp*, in which the diynyl 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 $(PPh_3)_2$ 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 diynyl 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 diynyl group towards azide.

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## 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 $cm^2$) coated with silica gel (Merck, 0.5 mm thick).

*Instruments*. IR spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in $CH_2Cl_2$ 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, $^{13}C$ at 75.479 MHz, $^{31}P$ at 121.501 MHz). Unless otherwise stated, samples were dissolved in $CDCl_3$ contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for $^1H$ and $^{13}C$ NMR spectra and external $H_3PO_4$ for $^{31}P$ 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] , $SiMe_3$ [42], Au($PPh_3$) [42]], Ru(C≡CH)($PPh_3$)$_2$Cp [44], Au($N_3$)($PPh_3$) [45] were made by the cited methods. $SiMe_3(N_3)$, (tos)$N_3$ were commercial samples (Sigma-Aldrich).

*Reactions of $SiMe_3(N_3)$*

*(a) With Ru(C≡CC≡CH)(dppe)Cp*.* $SiMe_3(N_3)$ (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 $CH_2Cl_2$ and separation by preparative TLC (silica gel, acetone / hexane = 3/7) gave two bands. The bright yellow fraction ($R_f$ = 0.75) gave Ru{$N_3$C(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 ($C_{40}H_{42}N_4P_2Ru.0.5C_6H_6$): C, 65.80; H, 6.29; N, 7.14; M, 742. IR ($CH_2Cl_2$, $cm^{-1}$): ν(C≡N) 2216m, ν(C=N) 1724m. $^1H$ NMR ($C_6D_6$): 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). $^{13}C$ NMR ($C_6D_6$): δ 9.57 (s, Me), 9.88 (s, $C_5\mathit{Me}_5$), 31.62 (m, dppe), 91.70 (s, $\mathit{C}_5Me_5$), 115.42 (s, CN), 117.71 (s, $C_2$), 127.67-141.78 (m, Ph); 147.10 (s, $C_1$). $^{31}P$ NMR ($C_6D_6$): 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($N_3$)(dppe)Cp* (3.3 mg, 8%), identified by comparison with an authentic sample.

Similarly, **2** (21 mg, 38%) was obtained from Ru(C≡CC≡CSiMe$_3$)(dppe)Cp* (51 mg, 0.07 mmol) and SiMe$_3$(N$_3$) (9 μL, 0.07 mmol), and also from Ru{C≡CC≡CAu(PPh$_3$)}(dppe)Cp* or Ru(C≡CC≡CSiMe$_3$)(dppe)Cp* and SiMe$_3$(N$_3$).

*(b) With Ru(C≡CC≡CPh)(dppe)Cp**. SiMe$_3$(N$_3$) (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 (SiO$_2$, acetone / hexane = 1/3). The yellow band ($R_f$ = 0.58) gave Ru{N$_3$C(CN)C(CH$_2$Ph)}(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 (C$_{46}$H$_{46}$N$_4$P$_2$.0.5C$_6$H$_6$): C, 68.59; H, 5.76; N, 6.53; *M*, 818. IR (CH$_2$Cl$_2$, cm$^{-1}$): ν(CN) 2213 cm$^{-1}$. $^1$H NMR (C$_6$D$_6$): δ 1.39 (s, 15H, Cp*), 2.19, 2.85 (2 x m, 4H, dppe), 3.39 (s, 2H, CH$_2$), 6.65-7.18 (m, 25H, Ph). $^{13}$C NMR (C$_6$D$_6$): δ 10.47 (s, C$_5$*Me*$_5$), 31.98 (s, CH$_2$), 32.37 (m, dppe), 92.37 (s, *C*$_5$Me$_5$), 115.83 (s, CN), 118.12 (s, C$_2$), 126.36-142.65 (m, Ph), 150.85 (s, C$_1$). $^{31}$P NMR (C$_6$D$_6$): 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(N$_3$)(dppe)Cp* (11.6 mg, 43%), identified by comparison with an authentic sample.

*(c) With Ru(C≡CC≡CH)(PPh$_3$)$_2$Cp*. SiMe$_3$(N$_3$) (0.92 mg, 0.08 mmol) was added to a solution of Ru(C≡CC≡CH)(PPh$_3$)$_2$Cp (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 (SiO$_2$, acetone / hexane = 3/7) gave one yellow band ($R_f$ = 0.41) containing Ru(N$_3$)(PPh$_3$)$_2$Cp (16.7 mg, 56%) as yellow-orange crystals (from benzene / hexane), identified by comparison with an authentic sample. IR (CH$_2$Cl$_2$, cm$^{-1}$): ν(N$_3$) 1981 (m). $^1$H NMR (CDCl$_3$): δ 7.70-6.79 (m, 30H, Ph); 4.26 (s, 5H, Cp). $^{13}$C NMR (CDCl$_3$): δ 134.04-125.97 (m, Ph); 86.03 (s, *C*$_5$H$_5$). $^{31}$P NMR (CDCl$_3$): δ 43.3 (s, PPh$_3$). ES-MS (MeOH, *m/z*): 733, [M]$^+$; 691, [Ru(PPh$_3$)$_2$Cp]$^+$; 429, [Ru(PPh$_3$)Cp]$^+$.

*(d) With Ru(C≡CH)(PPh$_3$)$_2$Cp.* A mixture of Ru(C≡CH)(PPh$_3$)$_2$Cp (37 mg, 0.05 mmol) and SiMe$_3$N$_3$ (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 SiO$_2$ (eluant acetone / hexane = 1/3) gave a single yellow band containing Ru(N$_3$)(PPh$_3$)$_2$Cp (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 SiMe$_3$N$_3$ (9.2 mg, 0.08 mmol) in THF (6 ml) after 72 h at r.t. gave orange Ru(N$_3$)(dppe)Cp* (15.6 mg, 61%). IR (CH$_2$Cl$_2$, cm$^{-1}$): ν(N$_3$) 2035 (s). $^1$H NMR (C$_6$D$_6$): δ 7.25-7.07 (m, 20H, Ph); 2.37-2.35, 1.98-1.85 (2 x m, 2 x 2H,

$CH_2CH_2$); 1.53 (s, 30H, Cp*). $^{31}$P NMR ($C_6D_6$): 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 $NH_4PF_6$ (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 ($SiO_2$, acetone / hexane = 1/2) gave a yellow band ($R_f$ = 0.42) containing [Cp*(dppe)Ru{$N_3C$[CNRu(dppe)Cp*]CMe}]$PF_6$ **4** (35.5 mg, 67.5%), which formed yellow crystals from EtOH. Anal. Found: C, 59.63; H, 5.57; N, 3.62. Calcd ($C_{76}H_{81}F_6N_4P_5Ru_2$): C, 59.91; H, 5.36; N, 3.68; *M* (cation), 1377. IR ($CH_2Cl_2$, $cm^{-1}$): ν(CN) 2224, ν(PF) 840. $^1$H NMR ($CDCl_3$): 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). $^{13}$C NMR ($CDCl_3$): δ 9.09 (s, Me), 9.25 (s, $C_5Me_5$), 9.36 (s, $C_5Me_5$), 28.10 (m, dppe), 31.16 (m, dppe), 91.70 (s, $C_5Me_5$), 92.24 (s, $C_5Me_5$), 107.50 (s, $C_2$), 124.22-140.26 (m, Ph), 148.12 (s, $C_1$). $^{31}$P NMR ($CDCl_3$): 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, $PF_6$]. ES-MS (MeOH, *m/z*): 1377.341, $[M]^+$ (calcd 1377.353).

*Reaction of Ru(C≡CC≡CH)(dppe)Cp* with $TsN_3$.*

*(a)* In toluene. A solution of Ru(C≡CC≡CH)(dppe)Cp* (31 mg, 0.05 mmol) in toluene (10 mL) was treated with $TsN_3$ (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[$C_3N_2H$(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 ($CH_2Cl_2$, $cm^{-1}$): ν(C-H) 2977 (m); ν(C≡N) 2229 (m); ν(C=N) 1703 (m); ν(SO) 1179 (m). $^1$H NMR ($C_6D_6$): δ 7.68 (d, $^2J$(HH) 8 Hz, 2H, $C_6H_4$); 7.23-6.95 (m, 20H, Ph); 6.61 (d, $^2J$(HH) 8 Hz, 2H, $C_6H_4$); 2.25 (s, 3H, $CH_3$); 2.04-1.99, 1.89-1.85 (2 x m, 2 x 2H, $CH_2CH_2$); 1.49 (s, 15H, Cp*); 1.23 (s, 1H, CH). $^{13}$C NMR ($C_6D_6$): δ 145.17, 144.89, 138.84, 134.87 (4 x s, $C_6H_4$); 130.39-127.06 (m, Ph); 116.63 (s, C); 122.85 (s, C); 92.27 (s, $C_5Me_5$); 58.52 (s, C); 28.77-28.18 (m, $CH_2CH_2$); 21.14 (s, $CH_3$); 9.79 (s, $C_5Me_5$). $^{31}$P NMR ($C_6D_6$): 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 $TsN_3$ (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 $CH_2Cl_2$ extract of the residue ($SiO_2$, acetone / hexane = 2/3) gave several minor products together with a pale yellow band ($R_f$ = 0.58), from which $TsN{=}PPh_2CH_2CH_2PPh_2{=}NTs$ **6** (1.8 mg, 3 %) was isolated as colourless crystals

(from benzene). $^{1}$H 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, $[M + Na]^+$ (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 Kα radiation, λ = 0.71073 Å (Cu Kα, λ = 1.54178 Å 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 2θ = 50° 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 an 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 Ru($N_3$)(dppe)Cp* **1b**, Ru{$N_3$CRC(CN)}(dppe)Cp* (R = Me **2**, $CH_2$Ph **3**), [Ru{$N_3$CMeC(CN)[Ru(dppe)Cp*]}(dppe)Cp* **4**, Ru{N≡CC=NNTs=CC(=NTs)}(dppe)Cp* **5,** (TsN=P$Ph_2CH_2$)$_2$ **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<br>[2.220-2.246(3)] | 2.242<br>[2.225-2.266(3)] | 2.236<br>[2.223-2.249(4)] | 2.219<br>[2.210-2.228(4)] |
| Ru(2)-C(cp) (av.) | | | 2.231<br>[2.205-2.250(4)] | |
| N(1)-N(2) | 1.321(2) | 1.325(4) | 1.324(4) | 1.338(5)<br>[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)<br>[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)<br>[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)<br>[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)°.

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

| Compound | **1b** | **2** | **3** | **4** |
|---|---|---|---|---|
| Empirical formula | $C_{36}H_{39}N_3P_2Ru$ | $C_{41}H_{44}Cl_2N_4P_2Ru$ | $C_{49}H_{49}N_4P_2Ru$ | $C_{78}H_{87}F_6N_4OP_5Ru_2$ |
| 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 | $P\bar{1}$ | $P2_1/n$ | $P2_1/c$ | $P\bar{1}$ |
| *a* (Å) | 10.0844(3) | 16.9146(6) | 13.0769(3) | 12.7430(3) |
| *b* (Å) | 11.8343(2) | 11.8508(4) | 13.1142(4) | 15.8051(5) |
| *c* (Å) | 13.1251(4) | 21.1555(5) | 24.1054(8) | 20.3273(7) |
| α (º) | 88.151(2) | | | 89.272(3) |
| β (º) | 82.945(2) | 102.648(3) | 100.105(3) | 72.631(3) |
| γ (º) | 89.216(2) | | | 86.020(2) |
| Volume (Å$^3$) | 1553.63(7) | 4137.7(2) | 4069.8(2) | 3897.8(2) |
| *Z* | 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 (º) | 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 [*R*(int)] | 15475 [0.0254] | 13238 [0.0670] | 8518 [0.0807] | 17527 [0.0327] |
| Completeness (%) [$\theta_{max}$ (°)] | 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 F$^2$ | 0.972 | 0.890 | 1.033 | 1.107 |
| $R_1$ [$I>2\sigma(I)$] | 0.0293 | 0.0425 | 0.0512 | 0.0509 |
| $wR_2$ (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 |

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

| Compound | **5** | **6** |
|---|---|---|
| Empirical formula | $C_{54.29}H_{54.59}Cl_{0.59}N_4O_4P_2RuS_2$ | $C_{40}H_{38}N_2O_4P_2S_2$ |
| Formula weight | 1075.13 | 736.78 |
| Temperature (K) | 100(2) | 100(2) |
| Wavelength (Å) | 1.54178 | 0.71073 |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ |
| $a$ (Å) | 12.1705(3) | 10.5275(9) |
| $b$ (Å) | 14.5774(3) | 9.4570(11) |
| $c$ (Å) | 28.2919(6) | 17.9939(18) |
| β (º) | 98.030(2) | 98.174(9) |
| Volume (Å$^3$) | 4970.17(19) | 1773.2(3) |
| $Z$ | 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 (º) | 3.155 to 67.288 | 2.909 to 25.999 |
| Reflections collected | 37626 | 12563 |
| Independent reflections [$R$(int)] | 8679 [0.0747] | 3484 [0.0558] |
| Completeness (%) [$\theta_{max}$ (°)] | 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 |
| $R_1$ [$I$>2σ($I$)] | 0.0420 | 0.0769 |
| $wR_2$ (all data) | 0.0967 | 0.1598 |
| Largest diff. peak and hole (e.Å$^{-3}$) | 0.962 and -0.675 | 0.333 and -0.434 |

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

(M.I. Bruce et al.)

Highlights

- Alkyl azides (two equiv.) and diynyl-ruthenium complexes give alkyl-cyano-triazolyl complexes
- Tosyl azide and diynyl complex affords a tosylimino-cyano-pyrazolyl-ruthenium complex
- X-ray crystal structures of four ruthenium complexes have been determined

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