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Syntheses and Structural Studies of Several Diynyl-Ruthenium Complexes and their Adducts with Cyano-Alkenes

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Abstract. Herein are described some continuing investigations into the reactions of cyano-alkenes with diynyl-ruthenium complexes which have resulted in the preparation and characterisation of diynyl-ruthenium compounds Ru(C≡CC≡C*R*)(PP)Cp [*R* = Ph, PP = dppe; *R* = Fc, PP = dppf; *R* = CPh=CBr$_2$, PP = (PPh$_3$)$_2$], together with the polycyanobutadienyls Ru{C≡CC[=C(CN)$_2$]C*R*=C*R*'(CN)}(PP)Cp' [*R* = Fc, (PP)Cp' = (dppf)Cp; *R* = H, SiMe$_3$, (PP)Cp' = (dppe)Cp*] formed by [2 + 2]-cycloaddition of the cyano-alkenes to the outer C≡C triple bonds and subsequent ring-opening reactions. Single-crystal XRD molecular structure determinations of six complexes are reported.

Introduction

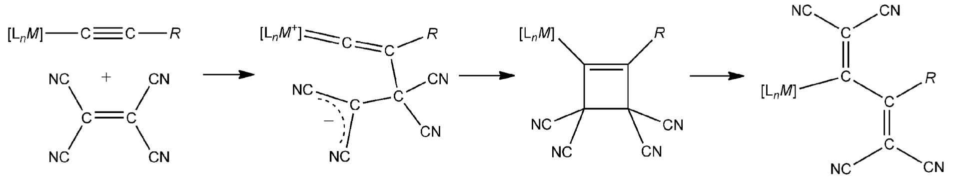
Over the past couple of decades, we have described the extensive chemistry of poly-ynyl-ruthenium complexes containing the Ru(PP)Cp' [PP = (PPh$_3$)$_2$, Cp' = Cp; PP = dppe, Cp' = Cp, Cp*] end-groups.[1] One point of interest has been the reactions of diynyl complexes with electrophilic alkenes, such as tetracyanoethene (tcne). These reactions proceed by initial [2 + 2]-cycloaddition to give (often unobserved) cyclobutenes which then undergo rapid ring-opening to form tetracyanobutadienes (Scheme 1).[2] The site of addition is often the outer (from the metal atom) C≡C triple bond, although in one instance we have obtained two isomers of the adduct from tcne and Ru(C≡CC≡CFc)(dppe)Cp, namely Ru{C[=C(CN)$_2$]C[=C(CN)$_2$]C≡CFc}(dppe)Cp and Ru{C≡CC[=C(CN)$_2$CFc=C(CN)$_2$}(dppe)Cp.[3]

In order to further enhance our understanding of this chemistry, we have prepared further examples of related diynyl- and polycyanobutadienyl- ruthenium complexes. The syntheses and characterisation of six complexes and their X-ray determined-structures are reported below.

Results

Syntheses and Properties

Most compounds described herein have been characterised by elemental microanalyses and from their spectroscopic properties, including IR and NMR spectroscopy and electro-spray mass spectrometry (ES-MS), together with single-crystal X-ray studies. The *M*(PP)Cp' moieties give characteristic NMR resonances for the Cp or Cp* groups and the tertiary phosphine ligands. Details are listed in the Experimental Section and only specific data relating to the organic fragment will be the subject of further comment.



Scheme 1. Reaction of tcne with alkynyl-metal complexes.

(i) Ru(C≡CC≡CPh)(dppe)Cp (1) and Ru(C≡CC≡CFc)(dppf)Cp (2)

These two compounds were made by a modified route from Me$_3$SiC≡CC≡C*R* (*R* = Ph, Fc, respectively), RuCl(PP)Cp (PP = dppe, dppf), KF and dbu in MeOH containing a drop of water.[4,5] Compound **1** has been described previously,[5]

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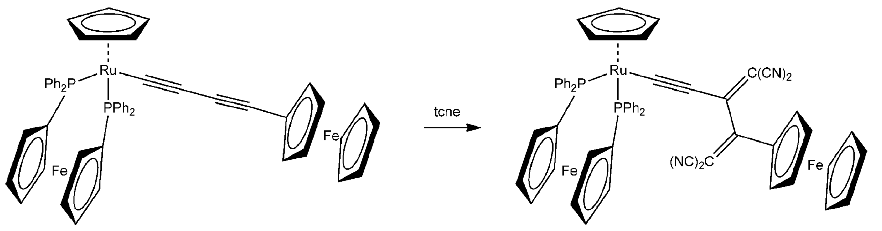
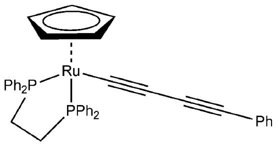


2 **4**

Scheme 2. Synthesis of Ru{C≡CC[=C(CN)$_2$]CFc=C(CN)$_2$}(dppf)Cp (**4**).

whereas **2** (Scheme 2) was characterised by a high resolution ES-MS spectrum from solutions containing NaOMe: strong ions at *m*/*z* 954 and 977 correspond to M$^+$ and [M + Na]$^+$, respectively.



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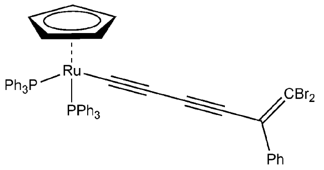

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(ii) Ru(C≡CC≡CPh=CBr$_2$)(PPh$_3$)$_2$Cp (3)

This complex was obtained from RuCl(PPh$_3$)$_2$Cp and Me$_3$SiC≡CC≡CCPh=CBr$_2$ following the established procedure using KF as a desilylating reagent.[4] The dibromovinyl compound was formed from Me$_3$SiC≡CC≡CSiMe$_3$ by a conventional sequence of reactions with PhC(O)Cl/AlCl$_3$ and CBr$_4$/PPh$_3$.[6] Characterisation was routine (see Experimental Section) and included observation of IR ν(C≡C) bands at 2136 and 2008 cm^{-1}, C$_\alpha$ as a triplet at δ_C 102.64 [*J*(P,C) = 28 Hz] and M$^+$, [M + Na]$^+$ and [2M + Na]$^+$ at *m*/*z* 1000, 1023 and 2023, respectively, in the ES-MS, confirmed by high resolution measurements.

(iii) Ru{C≡CC[=(CN)$_2$]CFc=C(CN)$_2$}(dppf)Cp (4)

Addition of tcne to Ru(C≡CC≡CFc)(dppf)Cp, obtained from RuCl(dppf)Cp and FcC≡CC≡CSiMe$_3$ in the presence of KF and dbu,[4] afforded orange crystals of the ring-opened adduct Ru{C≡CC[=(CN)$_2$]CFc=C(CN)$_2$}(dppf)Cp **4** (Scheme 2) for which only high resolution ES-MS data have been obtained. Solutions containing NaOMe show no obvious M$^+$ ion, but a strong [M + Na]$^+$ ion is found at *m*/*z* 1105, resulting from the strong coordination of Na$^+$ to the CN groups. The X-ray structure determination showed that addition had occurred to the outer C≡C triple bond, probably as a result of steric protection of the metal-bonded C≡C fragment by the phosphine ligand. No evidence was found for the formation of any other product.

(iv) Ru{C≡CC[=C(CN)$_2$]CR=CFc(CN)}(dppe)Cp (R = H **5**, SiMe$_3$ **6**).*

Tricyanovinylferrocene, Fc(CN)=C(CN)$_2$, has been described on several occasions.[7,8] In the present study we used the recently described synthesis from ferrocene and tcne in sulfolane.[8] Addition of FcC(CN)=C(CN)$_2$ to Ru(C≡CC≡CSiMe$_3$)(dppe)Cp*, followed by separation of the products by TLC, afforded two complexes identified as Ru{C≡CC[=C(CN)$_2$]C*R*=CFc(CN)}(dppe)Cp* (*R* = H **5**, SiMe$_3$ **6**) (Scheme 3). The former could be obtained pure from an analogous reaction of FcC(CN)=C(CN)$_2$ with Ru(C≡CC≡CH)(dppe)Cp* and likely results from ready protodesilylation of **6**. The IR spectra contained ν(CN) bands at 2209 and 2193 (for **5**) or 2213 and 2202 cm^{-1} (for **6**) and ν(C≡C) bands at 1987 or 1992 cm^{-1}, respectively. The ^{1}H NMR spectra contained resonances at δ_H 6.53 (CH in **5**) and 0.10 (SiMe$_3$ in **6**). Both complexes gave [M + H]$^+$ at *m*/*z* 972 and 1044, respectively.

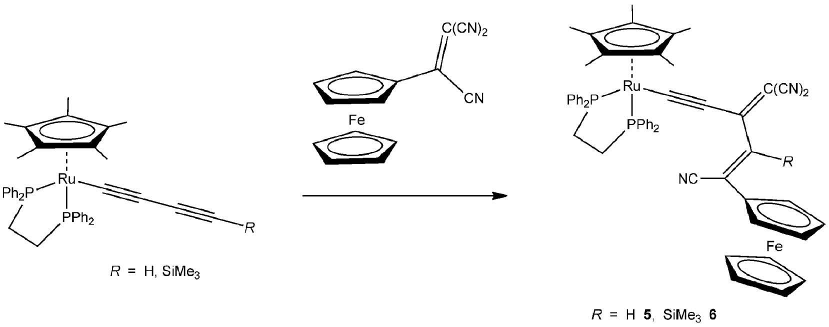
In the reactions which afforded **4**–**6**, there was no indication of the formation of the isomer in which the cyano-alkene had added to the C≡C triple bond adjacent to the metal, although both structurally characterised isomers were obtained from the analogous reaction between tcne and Ru(C≡CC≡CFc)(dppe)Cp.[3] This difference may be ascribed to the greater steric protection of the C(1)≡C(2) triple bond in the complexes used here. For **5** and **6**, the tricyanobutadienyl compounds are formed regioselectively, with the Fc group being *cis* to *R*.

Molecular Structures

Figures 1–3 show plots of single molecules of each of the complexes **1**–**3**, selected bond parameters being presented in Table 1. For the Ru(PP)Cp' centres in all complexes described below, the geometries are pseudo-octahedral and resemble those of many other complexes containing the same *M*(PP)Cp' fragments. For these fragments, Ru–P(1,2) are 2.2515(6) to 2.311(3) Å, Ru–C(cp) are 2.22(4) to 2.282(3) Å, with angles P(1)–Ru–P(2) between 82.80(2) and 102.54(3),the increase from **1**–**3** paralleling the increase in the Ru–P distances. The angles P(1,2)–Ru–C(1) lie between 84.90(6) and 89.4(1)°.

(i) Ru(C≡CC≡CPh)(dppe)Cp (1)

Figure 1 is a plot of a molecule of Ru(C≡CC≡CPh)(dppe)Cp (**1**), from which it can be seen that the phenylbutadiynyl ligand is attached to the metal atom through C(1) [Ru–C(1) 1.987(2) Å]. The C(1–4) chain shows the alternating short-long-short-long C-C separations consistent with the diynyl for-



Scheme 3. Reactions of FcC(CN)=C(CN)$_2$ with Ru(C≡CC≡C*R*)(dppe)Cp* (*R* = H, SiMe$_3$) to give **5** and **6**.

Table 1. Structure parameters for Ru(C≡C*R*)(PP)Cp' groups in **1**–**3**.

Complex	**1**	**2**	**3**
PP	dppe	dppf	(PPh$_3$)$_2$
R	C≡CPh	C≡CFc	C≡CCPh=CBr$_2$
Bond lengths /Å			
Ru–P(1)	2.2576(6)	2.2788(9)	2.2959(8)
Ru–P(2)	2.2515(6)	2.2692(9)	2.2914(8)
Ru–C(cp)	2.239–2.250(2)	2.223–2.255(4)	2.228–2.254(3)
(av.)	*2.244*	*2.237*	*2.241*
Ru–C(1)	1.987(2)	1.999(3)	1.988(3)
C(1)–C(2)	1.227(3)	1.202(5)	1.215(5)
C(2)–C(3)	1.367(3)	1.388(5)	1.367(5)
C(3)–C(4)	1.147(7)	1.203(5)	1.222(5)
C(4)–C(41)	1.439(8)	1.438(5)	
Bond angles /°			
P(1)–Ru–P(2)	82.80(2)	96.14(3)	102.54(3)
P(1)–Ru–C(1)	84.90(6)	89.4(1)	87.59(9)
P(2)–Ru–C(1)	88.74(6)	89.4(1)	87.49(9)
Ru–C(1)–C(2)	174.5(2)	174.4(3)	178.7(3)
C(1)–C(2)–C(3)	172.5(2)	176.4(4)	173.9(3)
C(2)–C(3)–C(4)	167.4(3)	178.8(4)	176.7(3)

For **1**: C(3)–C(4') 1.302(7), C(4')–C(41') 1.433(8) Å; C(2)–C(3)–C(4') 167.8(3), C(3)–C(4)–C(41) 172.4(6), C(3)–C(4')–C(41') 176.1(7)°. For **2**: Fe(1)–C(Cp) 2.019–2.050 / 2.022–2.048(4), (av.) 2.038 / 2.036, Fe(4)–C(Cp) 2.026–2.054(4), (av.) 2.043, P(1)–C(131) 1.830(4), P(2)–C(231) 1.836(4) Å; C(3)–C(4)–C(401) 177.3(4)°. For **3**: C(4)–C(5) 1.409(5), C(5)–C(6) 1.337(5), C(5)–C(51) 1.500(5), C(6)–Br(1,2) 1.885, 1.880(3) Å; C(3)–C(4)–C(5) 177.4(3), C(4)–C(5)–C(6) 121.2(3), C(4)–C(5)–C(51) 117.3(3), C(5)–C(6)–Br(1,2) 122.4(3), 124.1(2)°.

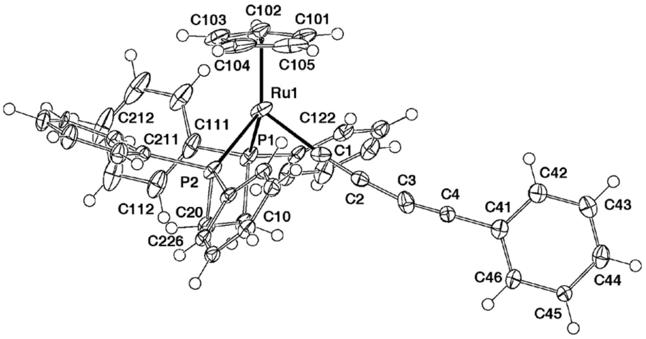


Figure 1. Plot of a molecule of Ru(C≡CC≡CPh)(dppe)Cp (**1**).

mulation, the outer C≡C triple bond being considerably shorter than that involving C(1). The usual non-linearity of the C$_4$ chain is found [angles at individual carbons 167.4(3)–174.5(2)°], ascribed to "crystal packing forces" and the low bending moment about a C(sp) carbon atom.[9]

(ii) Ru(C≡CC≡CFc)(dppf)Cp (2)

The molecule of **2** (Figure 2, Table 1) differs from the dppe analogue[4a] by replacement of dppe with dppf, the parameters of the Ru(dppf)Cp fragment being similar to those found earlier in RuH(dppf)Cp.[10] The diynyl nature of the C(1–4) chain is confirmed by the alternating short-long-short-long C–C separations and angles at the individual carbon atoms range between 174.4(2) and 178.8(2)°, the deviations from linearity being somewhat less marked than those found for **1**.

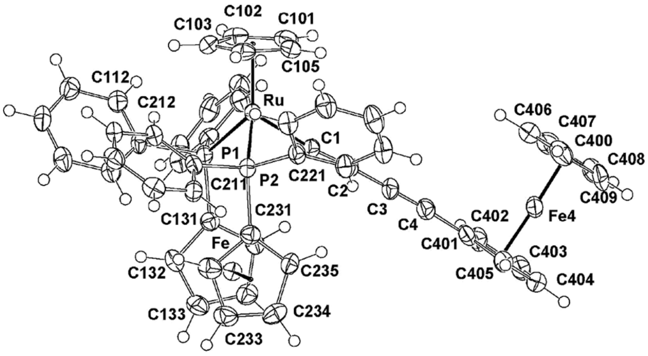


Figure 2. Plot of a molecule of Ru(C≡CC≡CFc)(dppf)Cp (**2**).

(iii) Ru(C≡CC≡CCPh=CBr$_2$)(PPh$_3$)$_2$Cp (3)

The plot of a molecule of **3** (Figure 3) clearly shows the alkenyl substituent on C(4) of the diynyl chain. The C–C separations are those expected for C(sp)≡C(sp) [C(1)–C(2) 1.215(5), C(3)–C(4) 1.222(5) Å] and C(sp^2)=C(sp^2) bonds [C(5)–C(6) 1.337(5) Å], with a closely linear Ru–C(1–5) chain [angles at individual carbons are between 173.9(3) to 178.7(3)°]. Angles at the C(sp^2) atoms C(5) and C(6) are between 117.3(3) and 124.1(2)°.

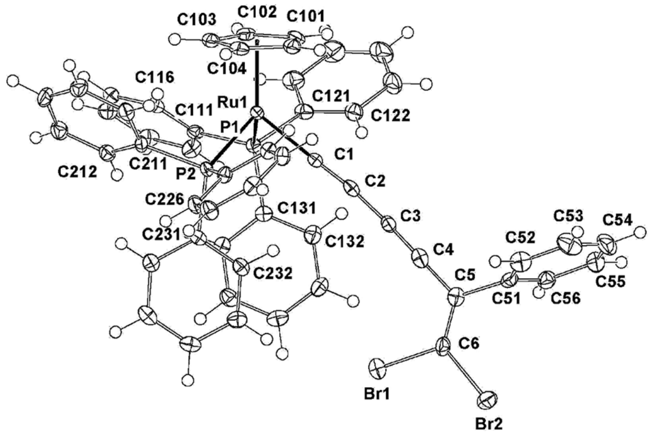


Figure 3. Plot of a molecule of Ru(C≡CC≡CCPh=CBr$_2$)(PPh$_3$)$_2$Cp (**3**).

*(iv) Ru{C≡CC[=C(CN)$_2$]CFc=C(CN)$_2$}(dppf)Cp (**4**), Ru{C≡CC[=C(CN)$_2$]CR=CFc(CN)}(dppe)Cp* (R = H **5**, SiMe$_3$ **6**)*

Plots of molecules of **4**–**6** are presented in Figure 4, Figure 5, and Figure 6, with selected structural parameters collected in Table 2. For **6**, two polymorphs **6a** (monoclinic, solvated) and **6b** (orthorhombic, unsolvated) were studied: the structures are similar, but that in **6b** is less precise. The cyanocarbon ligands in these three compounds are closely similar to those found in many complexes formed by addition of tcne to other diynyl-ruthenium complexes.[2] The Ru–C(1) distances in this group are somewhat shorter than those in **1**–**3**, with the Ru–P distances in similar ligands also being shorter. This feature probably arises from the strong electron-withdrawing power of the cyanocarbon groups, which in turn results in a contribution from the allenylidene tautomer. The different substituents on C(3) result in small changes in the dihedrals of the two C=C(CN)$_2$ groups of the butadienyl cores, which have the *s-trans* conformation in all three complexes. In **4**, the C(3)–C(4) bond is long [1.51(2) Å] with a C$_2$C–C / C–CC$_2$ interplanar dihedral angle of 79.8(6)°. In **5**, the bonds C(3)–C(4), C(4)–C(5) are 1.466(4), 1.340(4) Å, with the C$_2$C–C / C–CC$_2$ interplanar dihedral angle at C(4) being 35.1(4)°. In **6a**, C(3)–C(4) is again long [1.499(2) Å] with an associated C$_2$C–C / C–CCSi interplanar dihedral angle of 88.8(1)°. In **5**, the C(3)–C(4)–C(5) angle [128.5(3)°] is enlarged well above the trigonal value. Together, these data for **5** are indicative of a substantial contribution from the allenylidene tautomer, as suggested earlier for Ru{C≡CC[=C(CN)$_2$CFc=C(CN)$_2$}(dppe)Cp, where the bond length data suggest a major contribution from the allenylidene structure Ru$^+${=C=C=C[C(CN)$_2$]CFc=C(CN)$_2^-$}(dppe)Cp.[3] For example, the Ru–C(1) bond [1.915(4) Å] is shorter than those found in **4**–**6** [1.948(2)–1.96(1) Å], although the C-C distances are comparable.

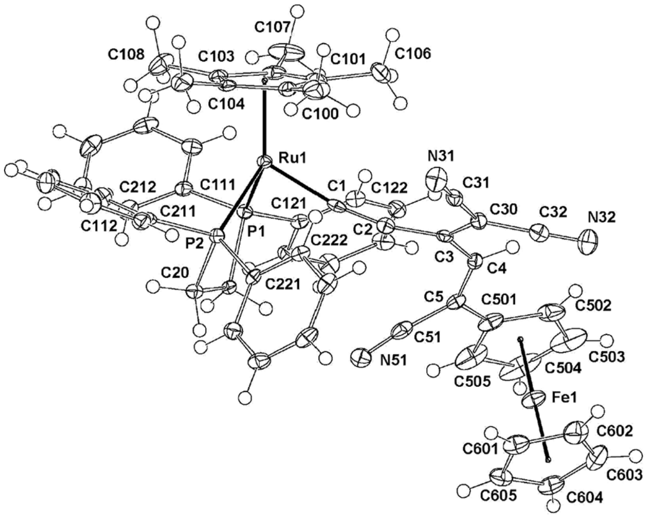


Figure 5. Plot of a molecule of Ru{C≡CC[=C(CN)$_2$]CH=CFc(CN)}(dppe)Cp* (**5**).

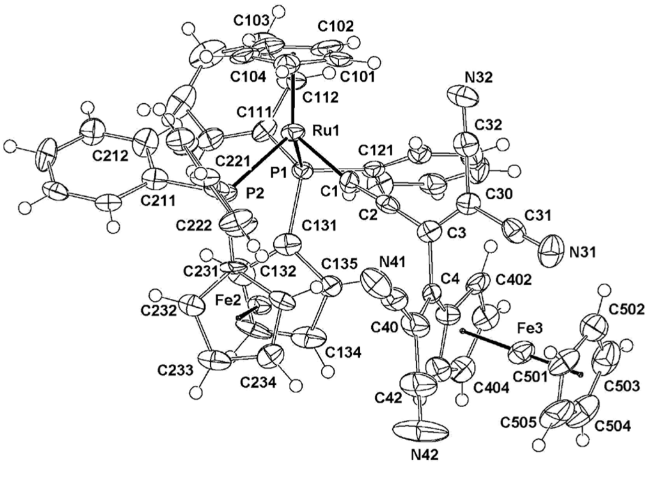


Figure 4. Plot of a molecule of Ru{C≡CC[=C(CN)$_2$]CFc=C(CN)$_2$}(dppf)Cp (**4**).

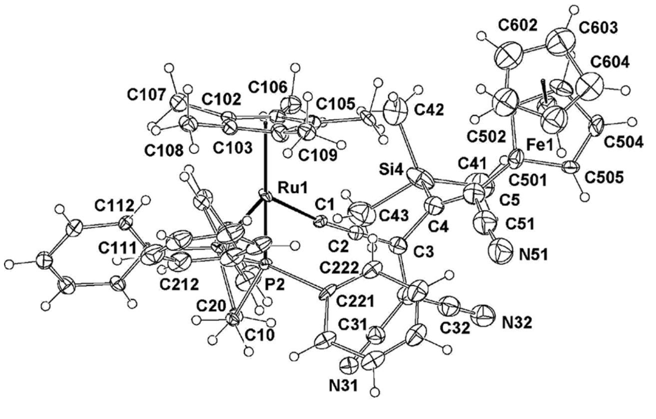


Figure 6. Plot of a molecule of Ru{C≡CC[=C(CN)$_2$]C(SiMe$_3$)=CFc(CN)}(dppe)Cp* (**6a**).

Table 2. Structure parameters for Ru{C[=C(CN)$_2$]C*R*=C*R*'(CN)}(dppe)Cp' in **4**–**6a**.

Complex	**4**	**5**	**6a**
PP	dppf	dppe	dppe
Cp'	Cp	Cp*	Cp*
R	Fc	H	SiMe$_3$
R'	CN	Fc	Fc
Bond lengths /Å			
Ru–P(1)	2.312(3)	2.2853(8)	2.2618(5)
Ru–P(2)	2.311(3)	2.2884(8)	2.2851(5)
Ru-C(cp)	2.237–2.272(2)	2.230–2.282(3)	2.239–2.301(2)
(av.)	*2.26*	*2.257*	*2.270*
Ru–C(1)	1.96(1)	1.951(3)	1.948(2)
C(1)–C(2)	1.24(2)	1.236(4)	1.231(2)
C(2)–C(3)	1.39(2)	1.391(4)	1.391(2)
C(3)–C(4)	1.51(2)	1.466(4)	1.499(2)
C(3)–C(30)	1.40(2)	1.394(4)	1.380(2)
C(30)–C(31,32)	1.44, 1.43(2)	1.424, 1.427(4)	1.428, 1.432(2)
C(4)–C(5)		1.340(4)	1.345(2)
C(5)–C(51)		1.436(5)	1.456(2)
C(5)-C(501)		1.473(4)	1.470(2)
Bond angles /°			
P(1)–Ru–P(2)	96.6(1)	84.41(3)	80.59(2)
P(1)–Ru–C(1)	92.3(4)	88.10(8)	86.92(5)
P(2)–Ru–C(1)	88.7(3)	89.24(9)	85.60(5)
Ru–C(1)–C(2)	167.9(1)	170.5(3)	174.6(1)
C(1)–C(2)–C(3)	177.6(1)	167.4(3)	173.7(2)
C(2)–C(3)–C(4)	116.8(1)	120.7(3)	119.6(1)
C(2)–C(3)–C(30)	122.8(1)	122.5(3)	123.1(2)
C(3)–C(4)–C(5)		128.5(3)	118.1(1)
C(4)–C(5)–C(51)		121.3(3)	119.1(1)
C(4)–C(5)-C(501)		122.6(3)	126.4(1)
C(31)–C(30)–C(32)	117.2(1)	117.2(3)	117.8(1)
C(51)–C(5)–C(501)		116.0(3)	114.4(1)

For **4**: Fe(2)–C(Cp) 2.024–2.077(12), av. 2.053; Fe(3)–C(Cp) 2.042–2.087(15), av. 2.059; C(4)–C(40) 1.39(2), C(4)–C(401) 1.46(2), C(40)–C(41,42) 1.46, 1.45(2) Å; C(3)–C(4)–C(40) 117.4(1), C(3)–C(4)-C(401) 116.4(1), C(41)–C(40)–C(42) 114.5(1)°. For **5**: Fe–C(Cp) 2.023–2.050(3), av. 2.038 Å. For **6a**: Fe–C(Cp) 2.032–2.055(2), av. 2.043; C(4)–Si(4) 1.914(2) Å; C(3)–C(4)–Si(4) 115.3(1)°.

Conclusions

The present report describes the structures of the diynyl-ruthenium compounds Ru(C≡CC≡C*R*)(PP)Cp [*R* = Ph, PP = dppe; *R* = Fc, PP = dppf; *R* = CPh=CBr$_2$, PP = (PPh$_3$)$_2$], together with those of the polycyanobutadienyls Ru{C≡CC[=C(CN)$_2$]C*R*=C*R*'(CN)}(PP)Cp' [*R* = Fc, (PP)Cp' = (dppf)Cp; *R* = H, SiMe$_3$, (PP)Cp' = (dppe)Cp*] formed by cycloaddition and subsequent ring-opening reactions of tcne with Ru(C≡CC≡CFc)(dppf)Cp, or of FcC(CN)=C(CN)$_2$ with Ru(C≡CC≡C*R*)(dppe)Cp* (*R* = H, SiMe$_3$). The results confirm the direction of addition of the cyano-alkenes. They are at variance with the isolation of two isomers of the adduct between tcne and Ru(C≡CC≡CFc)(dppe)Cp,[3] probably because of the greater steric protection of the C(1)≡C(2) triple bond in the present diynyl complexes.

Experimental Section

General experimental conditions and instrumentation were similar to those described recently.[11]

Reagents: RuCl(dppf)Cp,[10] Me$_3$SiC≡CC≡CCPh=CBr$_2$[6] and FcC(CN) = C(CN)$_2$[8] were made by the cited methods.

Syntheses of Complexes 1–6

(i) Ru(C≡CC≡CPh)(dppe)Cp (1): A modified procedure was employed for this synthesis.[3] A solution of RuCl(dppe)Cp (895 mg, 1.49 mmol), PhC≡CC≡CSiMe$_3$ (300 mg, 1.51 mmol) in MeOH (25 mL, containing 0.15 mL water) was heated to 50 °C. KF (143 mg, 2.46 mmol) and dbu (1 drop) were added and the mixture was heated at reflux point for 45 min. After cooling to room temp., the precipitate was collected, dried, taken up in a small amount of benzene and purified by column chromatography (basic alumina, Et$_2$O-hexane, 1/1) to give Ru(C≡CC≡CPh)(dppe)Cp **1** (366 mg, 36 %) as a yellow solid, identified by comparison with the literature.[4] X-ray quality crystals were obtained from Et$_2$O / benzene.

(ii) Ru(C≡CC≡CFc)(dppf)Cp (2): As for **1**, solution containing RuCl(dppf)Cp (445 mg, 0.59 mmol), FcC≡CC≡CSiMe$_3$ (183 mg, 0.59 mmol), KF (45 mg, 0.78 mmol) and dbu (1 drop) in MeOH (25 mL, with 0.10 mL water) was heated to reflux point for 1 h. The mixture was cooled to room temperature, filtered and the precipitate washed with methanol. The vacuum dried solid was subsequently purified by column chromatography (basic alumina, benzene) to afford Ru(C≡CC≡CFc)(dppf)Cp (**2**) as an orange solid, which could be crystallised from benzene / hexane. Anal. Calcd ($C_{53}H_{42}Fe_2P_2Ru.2C_6H_6$): C, 70.34; H, 4.90; *M*, 954. Found: C, 70.08; H, 5.05 %. **^{1}H NMR** (C_6D_6): δ3.68 (broad s, 2 H, C_5H_4 of Fc), 3.88–3.39 (m, 2 H, C_5H_4 of Fc), 4.04 (broad s, 2 H, C_5H_4 of Fc), 4.14 (s, 5 H, C_5H_5 of Fc), 4.21 (broad s, 2 H, C_5H_4 of Fc), 4.34 (s, 5 H, C_5H_5Ru), 4.46–4.48 (m, 2 H, C_5H_4 of Fc), 5.87 (broad s, 2 H, C_5H_4 of Fc), 7.00–7.13 (m, 12 H, Ph), 7.44–7.50 (m, 4 H, Ph), 7.98–8.04 (m, 4 H, Ph). **^{31}P NMR** (C_6D_6): δ56.0. **ES-MS** (MeOH + NaOMe, *m/z*): 977.049, [M + Na]$^+$ (calcd. 977.043); 954.055, M$^+$ (calcd. 954.052); 749, [Ru(CO)(dppf)Cp]$^+$; 721, [Ru(dppf)Cp]$^+$.

(iii) Ru(C≡CC≡CCPh=CBr$_2$)(PPh$_3$)$_2$Cp (3): A suspension of RuCl(PPh$_3$)$_2$Cp (182 mg, 0.25 mmol), Me$_3$SiC≡CC≡CCPh=CBr$_2$ (96 mg, 0.25 mmol), KF (15 mg, 0.25 mmol) in MeOH (10 mL, containing one drop each of water and dbu) was heated at reflux point for 1 h. After cooling to room temp., the yellow precipitate was filtered off and washed with cold MeOH. The residue was then purified on a small basic alumina column eluting with CH$_2$Cl$_2$, a yellow band was collected to give Ru(C≡CC≡CCPh=CBr$_2$)(PPh$_3$)$_2$Cp (134 mg, 54 %) as a yellow solid. Crystals suitable for the X-ray study were obtained from CH$_2$Cl$_2$/hexane. Anal. Calcd ($C_{53}H_{40}Br_2P_2Ru$): C, 63.68; H, 4.03. Found: C, 63.97; H, 4.27 %; *M*, 1000. **IR** (CH$_2$Cl$_2$): ν(C≡C) 2136, 2008;cm^{-1}. **^{1}H NMR** (C_6D_6): δ = 4.36 (s, 5 H, Cp), 6.87–7.60 (m, 35 H, Ph). **^{13}C NMR** (C_6D_6): δ = 64.11 (s), 85.81 (s, Cp), 90.71 [t, ^3J(P,C) = 2.7 Hz, Ru-C≡*C*), 94.48, 97.67, 127.32–133.77 (Ph), 137.99–138.53 (Ph and Ru-*C*≡), 140.07. **^{31}P NMR** (C_6D_6): δ = 49.6. **ES-MS** (MeOH + NaOMe, *m/z*): 1000, M$^+$; 1023, [M + Na]$^+$; 2023, [2M + Na]$^+$. High resolution **MS**: *m/z* 999.997 (calcd. 1000.001), 1022.984 (1022.990), 2022.972 (2022.993).

(iv) Ru{C≡CC[=C(CN)$_2$]CFc=C(CN)$_2$}(dppf)Cp (4): A mixture of Ru(C≡CC≡CFc)(dppf)Cp (100 mg, 0.104 mmol) and tcne (16.1 mg, 0.125 mmol) was heated in refluxing thf (25mL) for 1 h. Solvent was removed in vacuo, and the residue was purified by chromatography (silica, CH$_2$Cl$_2$) to afford Ru{C≡CC[=C(CN)$_2$]CFc=C(CN)$_2$}(dppf)Cp (**4**) as a red solid. High resolution **ES-MS** (MeOH + NaOMe, *m/z*): 1105.059, [M + Na]$^+$ (calcd. 1105.054). This compound was identified by the single-crystal X-ray structure described above.

(v) Ru{C≡CC[=C(CN)$_2$]C*R*=CFc(CN)}(dppe)Cp* (*R* = H 5, SiMe$_3$ 6): *(a)* A solution of Ru(C≡CC≡CSiMe$_3$)(dppe)Cp* (35 mg, 0.043 mmol) and FcC(CN) = C(N)$_2$ (13.3 mg, 0.043 mmol) in thf (7 mL) was stirred at room temp. for 48 h. Separation of the reaction products by preparative TLC (silica gel, acetone-hexane 1/3) gave two major bands. The lower magenta band (R_f = 0.37) yielded Ru{C≡CC[=C(CN)$_2$]CH=CFc(CN)}(dppe)Cp* (**5**) (5.2 mg, 12 %), identified by comparison with an authentic sample (below). The upper orange band (R_f = 0.39) contained Ru{C≡CC[=C(CN)$_2$]C(SiMe$_3$)=CFc(CN)}(dppe)Cp* (**6**) (14 mg, 29 %), which formed orange crystals (C_6H_6 / heptane). Anal. Calcd ($C_{58}H_{57}FeN_3P_2RuSi$): C, 66.80; H, 5.47; N, 4.03; *M*, 1043. Found: C, 67.19; H, 5.85; N, 4.00 %. **IR** (cyclohexane): ν(CN) 2213w, 2202 (sh); ν(C≡C) 1992s cm^{-1}. **^{1}H NMR** (C_6D_6): δ = 0.10 (s, 9 H, SiMe$_3$), 1.58 (s, 15 H, Cp*), 2.17, 3.05 (2 × m, 4 H, dppe), 3.98, 4.52 (2 × m, 4 H, C_5H_4), 4.35 (s, 5 H, Cp), 6.91–7.87 (m, 20 H, Ph). **^{31}P NMR** (C_6D_6): δ = 79.1, 81.2 [2 × d, *J*(P,P) = 14 Hz, dppe]. **ES-MS** (MeOH / NaOMe, *m/z*): 1066, [M + Na]$^+$; 1044, [M + H]$^+$; 994, [M + Na + H - SiMe$_3$]$^+$; 971, [M + H – SiMe$_3$]$^+$. The reaction also gave several unidentified decomposition products and **6** easily underwent protodesilylation during purification.

(b) A similar reaction between Ru(C≡CC≡CH)(dppe)Cp* (25 mg, 0.037 mmol) and FcC(CN) = C(CN)$_2$ (10.5 mg, 0.037 mmol) in thf (5 mL) afforded Ru{C≡CC[= C(CN)$_2$]CH=CFc(CN)}(dppe)Cp* **5** (32.7 mg, 92 %) in the major magenta band, obtained as dark coloured crystals (MeCN / Et$_2$O). Anal. Calcd ($C_{55}H_{49}FeN_3P_2Ru$): C, 68.04; H, 5.09; N, 4.33; *M*, 971. Found: C, 68.46; H, 5.64; N, 4.19 %. **IR** (CH_2Cl_2): ν(CN) 2209w, 2193 (sh); ν(C≡C) 1987 s (br); other bands at 1744w (br), 1595w, 1465m (br), 1437m cm^{-1}. **^{1}H NMR** (C_6D_6): δ = 1.51 (15 H, Cp*), 2.06, 3.11 (2 × m, 4 H, dppe), 4.00, 4.38 [2 × t, *J*(H,H) = 3 Hz, 2 H, C_5H_4], 4.12 (s, 5 H, Cp), 6.53 (s, 1 H, CH), 6.84–7.71 (m, 20 H, Ph). **^{13}C NMR** (C_6D_6): δ = 10.35 (C_5*Me*$_5$), 30.22 [t, *J*(C,P) = 22 Hz, dppe], 67.63, 70.99 (C_5H_4), 70.83 (Cp), 77.34 (C_{ipso} of Fc), 95.93 (*C*$_5$Me$_5$), 115.98, 117.17, 117.36 (3 × CN), other carbon atoms at 80.21, 119.23, 121.45, 125.29, 146.57, 127–138.00 (Ph). **^{31}P NMR** (C_6D_6): δ = 81.7 (dppe). **ES-MS** (MeOH / NaOMe, *m/z*): 1965, [2M + Na]$^+$; 994, [M + Na]$^+$; 972, [M + H]$^+$.

Structure Determinations

Full spheres of CCD area-detector diffraction data were measured using monochromatic Cu-K_α radiation, λ = 1.54184 Å (**2**, **3**) or Mo-K_α radiation, λ = 0.71073 Å (1, 4–6). N_{tot} reflections were merged to N unique (R_{int} cited) after "empirical" / multiscan absorption correction (proprietary software) and used in the full-matrix least-squares refinements on F^2; N_o with $F > 4\sigma(F)$ were considered "observed". Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, hydrogen atom treatment following a riding model. Reflection weights were $(\sigma^2(F_o^2) + (aP)^2\ (+\ bP))^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$. Neutral atom complex scattering factors were used within the SHELXL 97 program.[12] Pertinent results are given in the figures, which show non-hydrogen atoms with 50 % probability amplitude displacement ellipsoids and hydrogen atoms with arbitrary radii of 0.1 Å) and in Table 1, Table 2, and Table 3.

Full details of the structure determinations (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 3. Crystal data and refinement details for complexes **1**–**6**.

Complex	**1**[a)]	**2**	**3**	**4**	**5**	**6a**	**6b**
CCDC #	687320	804926	804932	804927	804928	804929	805355
Formula	$C_{41}H_{34}P_2Ru$	$C_{53}H_{42}Fe_2P_2Ru$ $\cdot 2C_6H_6$	$C_{53}H_{40}Br_2P_2Ru$ $\cdot 2CH_2Cl_2$	$C_{59}H_{42}Fe_2N_4P_2Ru$ $\cdot Me_2CO$	$C_{55}H_{49}FeN_3P_2Ru$	$C_{58}H_{57}FeN_3P_2RuSi$ $\cdot 2C_6H_6$	$C_{58}H_{57}FeN_3P_2RuSi$
MW	689.69	1109.79	1169.53	1139.75	970.83	1199.23	1043.02
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic
Space group	$C2/c$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$Pna2_1$
a /Å	29.6151(5)	13.7621(2)	19.0483(2)	11.268(4)	11.3659(3)	19.2066(3)	29.541(1)
b /Å	9.3742(3)	19.6788(2)	9.8487(1)	14.502(6)	25.9762(5)	9.3523(1)	9.0255(3)
c /Å	27.6709(9)	18.2699(2)	27.1907(4)	16.318(6)	16.0205(4)	33.2458(5)	19.2281(8)
α /deg				99.141(6)			
β /deg	124.885(2)	91.556(1)	106.530(1)	94.524(6)	108.781(3)	92.960(2)	
γ /deg				98.279(6)			
V /Å^3	6301.5(3)	4946.1(1)	4890.2(1)	2591(2)	4478.1(2)	5963.8(1)	5126.6(3)
ρ_c /g·cm^{-3}	1.454	1.490	1.589	1.461	1.440	1.336	1.351
Z (f.u.)	8	4	4	2	4	4	4
μ /mm^{-1}	0.63 [Mo-K_α]	8.0 [Cu-K_α]	7.4 [Cu-K_α]	0.95 [Mo-K_α]	0.78 [Mo-K_α]	0.62 [Mo-K_α]	0.70 [Mo-K_α]
$T_{min/max}$	0.93	0.72	0.68	0.70	0.94	0.92	0.81
Crystal dimensions /mm	0.40 × 0.19 × 0.04	0.09 × 0.06 × 0.03	0.13 × 0.04 × 0.03	0.26 × 0.24 × 0.12	0.25 × 0.12 × 0.022	0.41 × 0.045 × 0.04	0.24 × 0.21 × 0.08
$2\theta_{max}$ /deg.	65	134	134	50	62	64	55
N_{tot}	43507	58439	42835	17734	57381	85128	50811
N (R_{int})	11204 (0.054)	8825 (0.067)	8680 (0.058)	8786 (0.072)	13531 (0.084)	19995 (0.082)	11727 (0.116)
N_o	7201	6289	6820	5205	7654	9226	7512
$R1$ [$I > 2\sigma(I)$]	0.040	0.035	0.032	0.094	0.048	0.044	0.126
$wR2$ (all data)[(a,b)]	0.084 (0.040, –)	0.089 (0.049, –)	0.080 (0.050, –)	0.26 (0.054, 37)	0.086 (0.030, –)	0.082 (0.029, –)	0.27 (0.078, 47)
T /K	100(2)	150(2)	100(2)	150(2)	100(2)	100(2)	100(2)

a) *Variata*. **1**. One phenyl ring of the dppe ligand and the CPh component of the alkyne were modeled as disordered over pairs of sites, occupancies set at 0.5 after trial refinement, and with restrained geometries.

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