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Ruthenium cluster carbonyls containing ligands derived from ferrocenylalkynes

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Abstract

Reactions of FcC≡CH (**a**), HC≡CC≡CFc (**b**) and FcC≡CC≡CFc (**c**) with $Ru_3(CO)_{10}(NCMe)_2$ (all) and $Ru_3(\mu\text{-dppm})(CO)_{10}$ (**b** and **c** only) are described. Among the products, the complexes $Ru_3(\mu_3\text{-}RC_2R')(\mu\text{-}CO)(CO)_9$ (R = H, R′ = Fc **1**, C≡CFc **2**; R = R′ = Fc **5**), $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2C{\equiv}CFc)(\mu\text{-dppm})(CO)_7$ **3**, $Ru_3(\mu_3\text{-}FcC_2C{\equiv}CFc)(\mu\text{-dppm})(\mu\text{-}CO)(CO)_7$ **6** and $Ru_3\{\mu_3\text{-}C_4Fc_2(C{\equiv}CFc)_2\}(\mu\text{-dppm})(\mu\text{-}CO)(CO)_5$ **7** were characterised, including single-crystal structure determinations for **1**, **3**, **5** and **7**; that of **7** did not differ significantly from an earlier study of a mixed CH_2Cl_2–C_6H_6 solvate. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ruthenium; Ferrocene; Alkyne; Diyne; X-ray structures

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1. Introduction

During the last few years, there has been much interest in the reactions between ruthenium cluster carbonyls and alkynes or poly-ynes containing redox centres, such as the ferrocenyl group. First reported in 1992, reactions between $Ru_3(CO)_{12}$ and HC≡CFc afforded $Ru_2\{\mu\text{-}C_4H_2Fc_2)(CO)_6$, $Ru_2\{\mu\text{-}(HC_2Fc)_2CO\}(CO)_6$, $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Fc)(CO)_9$ and $Ru_3(\mu\text{-}H)(\mu_3\text{-}CFc)(CO)_{10}$ [1], while further reaction of the hydrido-alkynyl clusters $M_3(\mu\text{-}H)(\mu_3\text{-}C_2Fc)(CO)_9$ (M = Ru, Os) with $Ru_3(CO)_{12}$ afforded $RuM_3(\mu\text{-}H)(\mu_4\text{-}C_2Fc)(CO)_{12}$ in which the alkynyl ligand is fluxional [2]. The redox behaviour of some of these complexes has also been reported [3]. Other examples of reactions of ferrocenyl-substituted alkynes have employed FcC≡CCHO [4] and 1,1′-(RC≡C)$_2$-ferrocenes (R = Ph. SiMe$_3$) [5]. Extension of these reactions to the 1,3-diyne FcC≡CC≡CFc resulted in the isolation of isomers of the binuclear complexes $Ru_2\{\mu\text{-}C_4Fc_2(C{\equiv}CFc)_2\}(CO)_6$ and $Ru_2\{\mu\text{-}[CFcC(C{\equiv}CFc)]_2CO\}(CO)_6$ [6], while with Fc(C≡C)$_4$Fc, a low yield of the dehydroannulene derivative $\{Ru_2(CO)_6\}_2\{\mu{:}\mu\text{-}C_4Fc_2(C{\equiv}CC{\equiv}C)_2C_4Fc_2\}$ was obtained [7]. The reaction between FcC≡CC≡CFc and $Ru_3(\mu\text{-dppm})(CO)_{10}$ gave the unusual complex $Ru_3\{\mu_3\text{-}C_4Fc_2\text{-}(C{\equiv}CFc)_2\}(\mu\text{-dppm})(\mu\text{-}CO)(CO)_5$ [8]. This paper describes related studies of HC≡CFc, HC≡CC≡CFc and FcC≡CC≡CFc, which have afforded novel examples of clusters containing ferrocenyl centres. Some electrochemical results are also reported.

2. Results and discussion

The Russian work mentioned above is derived from the reactions of $Ru_3(CO)_{12}$ with the alkynes carried out in refluxing hexane (69 °C) [1]. There is no mention therein of the supposed precursor to the hydrido-alkynyl cluster, namely $Ru_3(\mu_3\text{-}HC_2Fc)(\mu\text{-}CO)(CO)_9$, which under these reaction conditions would be expected to undergo hydrogen migration from the alkyne to the cluster with concomitant expulsion of a CO molecule from the latter. We have used the activated cluster $Ru_3(CO)_{10}(NCMe)_2$, which reacted at room temperature, in similar reactions, and succeeded in isolating the alkyne-Ru_3 precursor. Noting the fragmentation of the Ru_3 cluster that occurs, we have also employed $Ru_3(\mu\text{-dppm})(CO)_{10}$, which we have found gives cleaner reactions at lower temperatures, the bis-phosphine serving to prevent fragmentation of the cluster.

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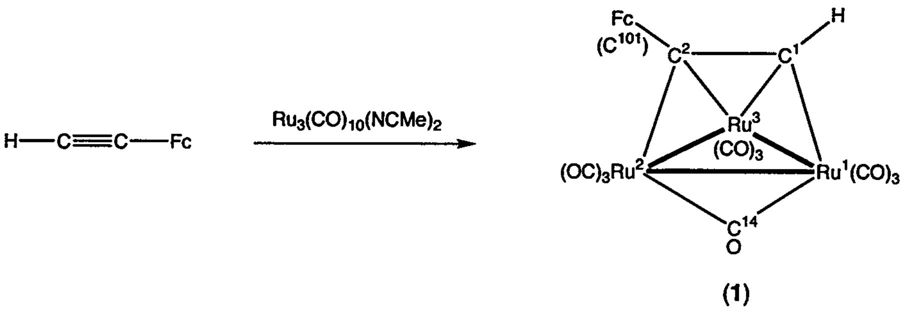
2.1. Reaction of $HC\equiv CFc$ (Scheme 1)

A reaction between $Ru_3(CO)_{10}(NCMe)_2$ and $HC\equiv CFc$ was carried out at room temperature for 1 h, after which conventional work-up gave $Ru_3(\mu_3\text{-}HC_2Fc)(\mu\text{-}CO)(CO)_9$ (**1**) in 52% yield as dark red crystals. This complex was characterised from its IR $\nu(CO)$ spectra, which was similar to that of the parent complex $Ru_3(\mu_3\text{-}HC_2H)(\mu\text{-}CO)(CO)_9$ [4], containing a band at 1876 cm^{-1} assigned to the bridging CO group. The ^1H-NMR spectrum has singlets at δ 4.18 and 8.09 for the Cp and $\equiv CH$ protons, respectively, and multiplets between δ 4.20 and 4.29 for the C_5H_4 ring. The electrospray (ES) mass spectrum of solutions containing NaOMe contained $[M + OMe - nCO]^-$ ($n = 0$, 1) at m/z 826 and 798, respectively, The identity of **1** was confirmed by a single-crystal X-ray structure determination as another example of the familiar μ_3-alkyne-Ru_3 clusters.

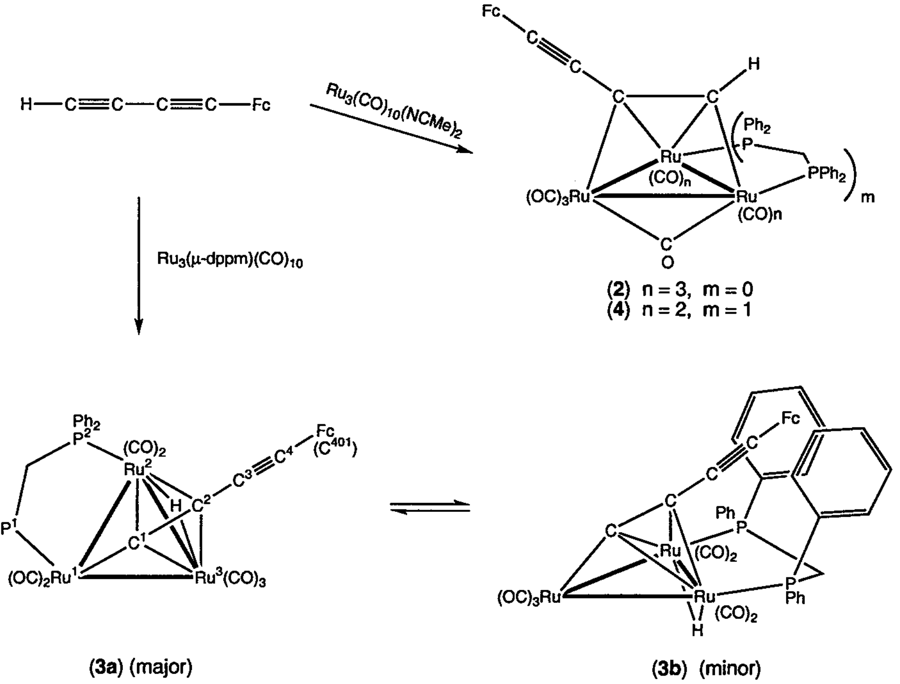
2.2. Reactions of $HC\equiv CC\equiv CFc$ (Scheme 2)

A similar reaction between the diyne and $Ru_3(CO)_{10}(NCMe)_2$ afforded dark red $Ru_3(\mu_3\text{-}HC_2C\equiv CFc)(\mu\text{-}CO)(CO)_9$ (**2**), identified only from its IR $\nu(CO)$ spectrum, which is essentially identical with that of **1** above, major bands being some 3 cm^{-1} to higher energy. The bridging carbonyl absorption is at 1882 cm^{-1}, while the $\nu(CC)$ absorption of the uncoordinated $C\equiv C$ triple bond is at 2183 cm^{-1}. In the ^1H-NMR spectrum, singlet resonances for the Cp and $\equiv CH$ protons were at δ 4.19 and 8.26, accompanied by a multiplet between δ 4.29 and 4.36 for the C_5H_4 group. The complex decomposed before full characterisation could be obtained.

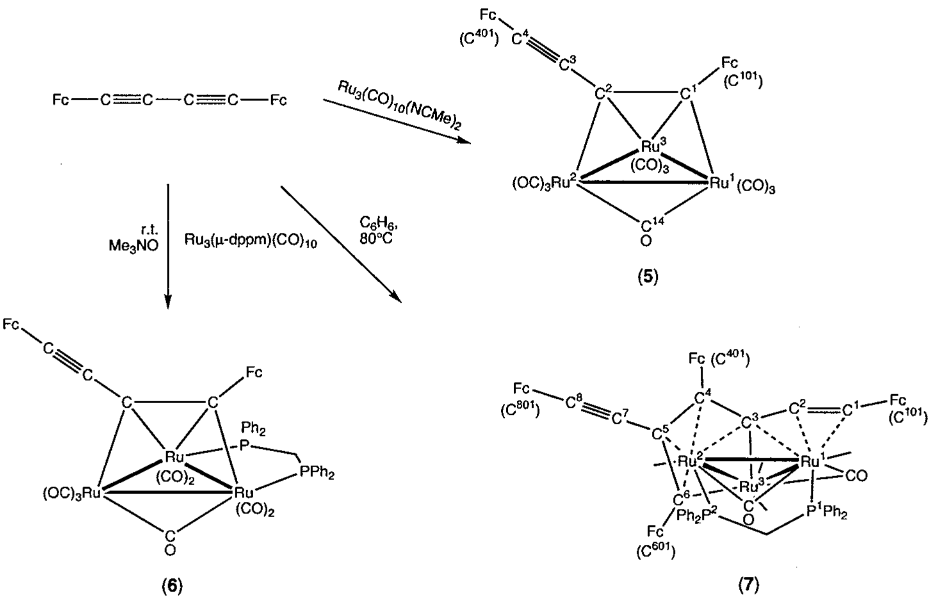
A room temperature reaction between $HC\equiv CC\equiv CFc$ and $Ru_3(\mu\text{-}dppm)(CO)_{10}$ gave a 43% yield of the orange hydrido-alkynyl derivative $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2C\equiv CFc)(\mu\text{-}dppm)(CO)_7$ (**3**); the expected μ_3-alkyne complex **4** was



Scheme 1.



Scheme 2.



Scheme 3.

observed in trace amounts by IR spectroscopy, but not fully characterised. Complex **3** exists as two isomers in solution, as indicated by the presence of two Ru–H resonances at δ −19.44 and −19.81, and two Cp singlets at δ 4.22 and 4.13, both in the ratio 2.5:1, in the ^{1}H-NMR spectrum. Other resonances arising from the C_5H_4 group and the dppm ligand were also present. In the ES mass spectrum, the ions $[M - n\text{CO}]^+$ ($n = 0$–4) were found.

The NMR data suggest that the two forms of the complex are related by windscreen-wiper motion of the alkynyl group relative to the μ-dppm ligand, as has been found previously on several occasions, e.g. with $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2R)(\mu\text{-dppm})(CO)_7$ (R = Bu^t [9], C≡C[W(CO)$_3$Cp] [10]). In the present case, the Ru–H resonance of the major isomer shows a doublet coupling to one of the phosphorus nuclei, whereas in the minor isomer, the corresponding resonance is a double doublet. In the ^{31}P-NMR spectrum, the major isomer gives rise to two doublets at δ 31.54 and 36.94, whereas, there is only a singlet at δ 27.70 in the spectrum of the minor isomer. We interpret these data in terms of the two structures shown in Scheme 2, in which the major isomer corresponds to the solid-state structure, whereas in the minor isomer, with equivalent ^{31}P nuclei, the H and alkynyl groups bridge the same Ru–Ru vector as the dppm ligand, the C≡CFc moiety being aligned between one phenyl group from each PPh_2 group.

2.3. Reactions of FcC≡CC≡CFc (Scheme 3)

The major product isolated from the reaction between $Ru_3(CO)_{10}(NCMe)_2$ and FcC≡CC≡CFc was isolated in 37% yield and identified as the expected μ_3-alkyne complex $Ru_3(\mu_3\text{-FcC}_2\text{C≡CFc})(\mu\text{-CO})(CO)_9$ (**5**). The IR ν(CO) spectrum is similar to that of **2**, with the bridging carbonyl giving rise to a band at 1871 cm^{-1}. The only peaks in the ^{1}H-NMR spectrum are the singlets (δ 4.26, 4.31) and multiplets (between δ 4.28 and 4.73) arising from the two Fc groups. The ES mass spectrum from a solution containing NaOMe contained $[M - H + OMe]^-$ (m/z 1033) and fragment ions formed by stepwise loss of up to nine CO groups.

The reaction between FcC≡CC≡CFc and $Ru_3(\mu\text{-dppm})(CO)_{10}$ was carried out at room temperature using Me_3NO to further activate the cluster. After 2 h, the major product was $Ru_3(\mu_3\text{-FcC}_2\text{C≡CFc})(\mu\text{-dppm})(\mu\text{-CO})(CO)_7$ (**6**), isolated in 45% yield. In addition to the terminal CO absorptions, the bridging CO gave rise to a band at 1836 cm^{-1}. In the ^{1}H-NMR spectrum, two singlets at δ 4.26 and 4.41 are assigned to the Cp groups, with two multiplets centred on δ 4.23 and 4.32 for the C_5H_4 rings. Other signals at δ 4.75 and 5.72 (CH_2) and between δ 7.02 and 7.43 (Ph) arise from the dppm ligands. Two closely spaced singlets at δ 35.85 and 36.17 are found in the ^{31}P-NMR spectrum. The ES mass spectrum contains M^+ at m/z 1331. These data are consistent with the structure shown, in which the alkyne C–C bond is ca. parallel to one Ru–Ru vector and the dppm ligand bridges one of the other Ru–Ru bonds, although, the isomeric structure in which the Fc–C≡C– group lies over the dppm ligand cannot be ruled out.

If the two reactants are heated together in refluxing benzene for 3 h, about 40% of the starting cluster is recovered, together with 28% of **6**. A third complex, obtained in 8%yield, was identified as $Ru_3\{\mu_3\text{-FcCC(C≡CFc)CFcC(C≡CFc)}\}(\mu\text{-dppm})(\mu\text{-CO})_2(CO)_4$ (**7**), previously described by Koridze and his co-workers [9], and also identified here by a single-crystal X-ray structure determination, the results of which do not differ significantly from the earlier study, which was carried out with a mixed CH_2Cl_2–C_6H_6 solvate. Spectroscopic data not previously recorded include four Cp singlets between δ 4.11 and 4.37, six C_5H_4 multiplets between δ 3.90 and 4.58, and multiplets from the dppm ligand at δ 5.21 and 5.39 (CH_2) and between 6.62 and 7.57 (Ph). The ^{31}P-NMR spectrum contains doublets at δ 8.42 and 32.41, while the ions $[M-n\text{CO}]^+$ ($n=0$–4) are found in the ES mass spectrum.

2.3.1. Molecular structures

Single-crystal X-ray structure determinations have been carried out on complexes **1**, **3**, **5** (as two polymorphs), and **7**. Plots of each structure are given in Figs. 1–4, while selected structural data are listed in Tables 1 and 2. Complexes **1** and **5** are further examples of Ru_3 clusters containing μ_3-alkyne ligands and a μ-CO group with geometrical parameters similar to previously reported examples, including $Ru_3(\mu_3\text{-}HC_2H)(\mu\text{-}CO)(CO)_9$ [11]. The two polymorphs of **5** differ only in the orientation of the Fc group attached to C(4): in one, the C(01)–Fe(1)–C(01′) axis is ca. orthogonal to the C(04)–Fe(4)–C(04′) axis, while in the other, the two axes are ca. parallel [C(0*n*), C(0*n*′) are the mid-points of the respective Cp rings]. Values for

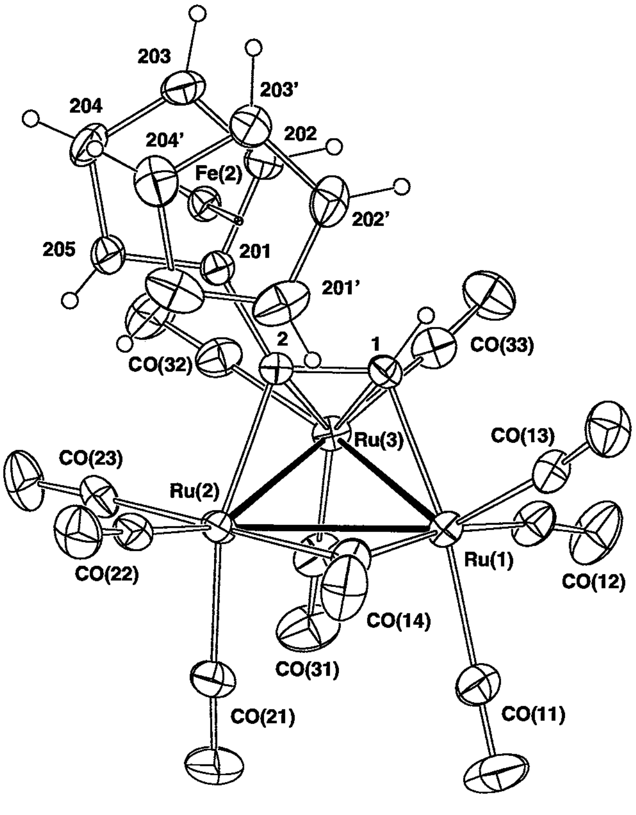


Fig. 1. Plot of a molecule of $Ru_3(\mu_3\text{-}HC_2Fc)(\mu\text{-}CO)(CO)_9$ (**1**).

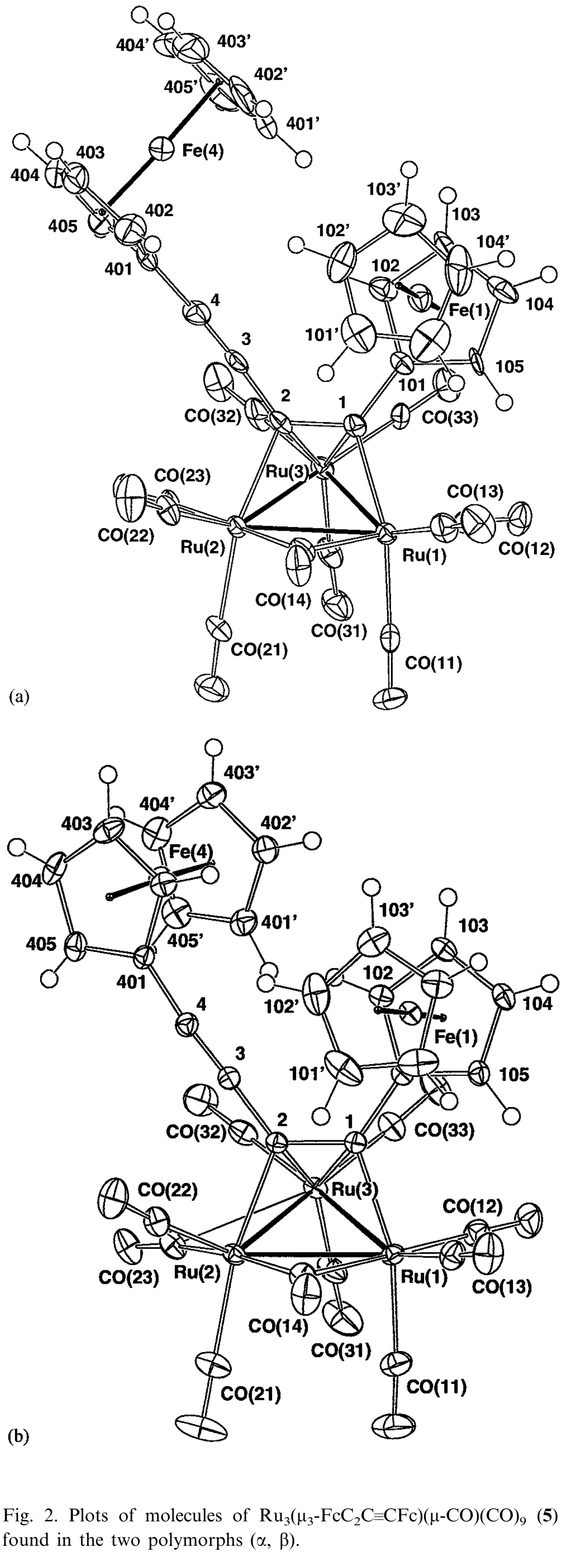


Fig. 2. Plots of molecules of $Ru_3(\mu_3\text{-}FcC_2C{\equiv}CFc)(\mu\text{-}CO)(CO)_9$ (**5**) found in the two polymorphs (α, β).

the more precise determination of the latter are quoted in the following.

There are one long [2.8412(5) in **1**, 2.8174(2) Å in **5**] and two short Ru–Ru separations [2.7535, 2.7165(6) in **1**, 2.7313, 2.7652(2) Å in **5**], the former being bridged by the CO ligand and ca. parallel to the C(1)–C(2) vector. The alkyne is attached in the 2σ,π mode [Ru(1,2)–C(1,2) between 2.092(3) and 2.121(1) Å, Ru(3)–C(1,2) between 2.180(4) and 2.338(3) Å]. The asymmetries in the Ru–Ru and Ru–C distances are also reflected in the Ru–CO(14) bonds [2.008, 2.329(4) for **1**, 2.042, 2.291(2) Å for **5**] and are similar to those found in the symmetrical ethyne complex [11]. This phenomenon has been discussed before, attention being given to the correlations between M–M separations, the precise arrangement of the μ_3-alkyne and the geometry of the μ-CO group [12]. The C(1)–C(2) distances differ significantly [1.378(5) in **1**, 1.412(2) Å in **5**] and can be compared with the free C≡C separation in **5** [1.207(2) Å]. Bend-back angles for the substituents on the com-

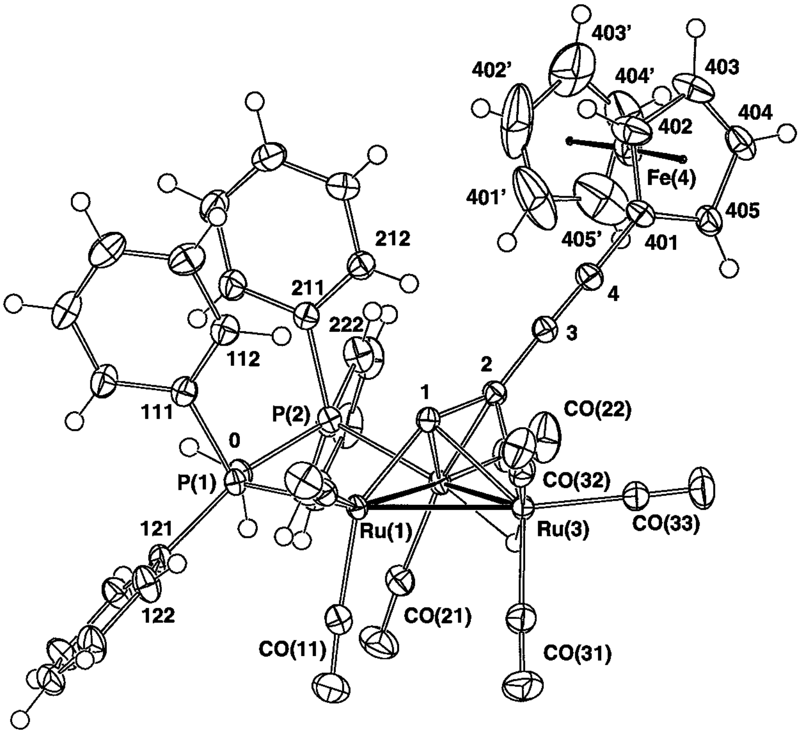


Fig. 3. Plot of a molecule of $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2C{\equiv}CFc)(\mu\text{-dppm})(CO)_7$ (**3**).

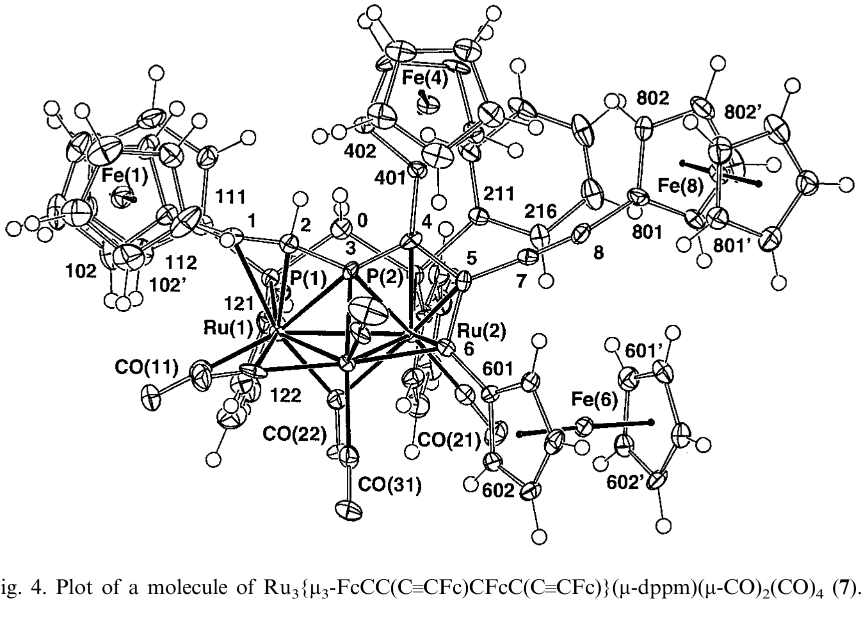


Fig. 4. Plot of a molecule of $Ru_3\{\mu_3\text{-}FcCC(C{\equiv}CFc)CFcC(C{\equiv}CFc)\}(\mu\text{-dppm})(\mu\text{-}CO)_2(CO)_4$ (**7**).

Table 1
Selected bond parameters for **1** and **5**

	1	**5** (α)	**5** (β) [a]
Bond distances (Å)			
Ru(1)–Ru(2)	2.8412(5)	2.8144(9)	2.8174(2)
Ru(1)–Ru(3)	2.7535(5)	2.7255(8)	2.7313(2)
Ru(2)–Ru(3)	2.7165(6)	2.7246(9)	2.7652(2)
Ru(1)–C(1)	2.101(4)	2.103(7)	2.095(1)
Ru(2)–C(2)	2.092(3)	2.114(8)	2.121(1)
Ru(3)–C(1)	2.180(4)	2.274(7)	2.330(1)
Ru(3)–C(2)	2.338(3)	2.256(7)	2.218(1)
Ru(1)–C(14)	2.008(4)	2.163(9)	2.291(2)
Ru(2)–C(14)	2.329(4)	2.107(8)	2.042(1)
C(1)–C(2)	1.378(5)	1.41(1)	1.412(2)
C(2)–C(3)		1.42(1)	1.425(2)
C(3)–C(4)		1.20(1)	1.207(2)
C(*x*)–C(*x*01)	1.475(5) [*x* = 2]	1.46(1) [*x* = 1]	1.472(2) [*x* = 1]
		1.42(1) [*x* = 4]	1.423(2) [*x* = 3]
Bond angles (°)			
Ru(1)–C(14)–O(14)	147.6(4)	136.3(7)	132.4(1)
Ru(2)–C(14)–O(14)	130.6(3)	141.3(7)	146.6(1)
C(101)–C(1)–C(2)		124.6(7)	124.8(1)
C(1)–C(2)–C(3)		127.5(7)	126.2(1)
C(2)–C(3)–C(4)		173.2(9)	176.4(1)
C(*x*–1)–C(*x*)–C(*x*01)	122.4(3) [*x* = 2]	177(1) [*x* = 4]	173.8(2) [*x* = 4]

[a] Ru(3)···C(23) is 3.513(2) Å; Ru(2)–C(23)–O(23) is 167.9(2)°.

plexed C≡C triple bond are between 53.8(1) and 57.6(3)°.

The structure of **3** is similar to those of the related complexes mentioned above [8,9]. The three Ru–Ru separations are similar [2.8012–2.8172(2) Å], the presence of the bridging ligands [dppm on Ru(1)–Ru(2), H on Ru(2)–Ru(3)] seemingly having little influence on the lengthening induced by the μ$_3$-alkynyl ligand. The μ$_3$-alkynyl ligand is σ-bonded to Ru(1) [Ru(1)–C(1) 1.962(1) Å] and π-bonded to the other two Ru atoms [Ru–C 2.194, 2.242(1) Å]. Within the C_4Fc ligand, C(1)–C(2) is lengthened to 1.325(2) Å by complexation to the cluster, while C(2)–C(3) [1.396(2) Å] and C(3)–C(4) [1.210(2) Å] have normal values for C(sp)–C(sp) single and triple bonds, respectively. While C(2)–C(3)–C(4) and C(3)–C(4)–C(401) [176.2, 178.9(2)°] are ca. linear, the bending at C(2) amounts to 30.7(1)° away from the cluster.

The structure of **7** has been reported briefly before, being determined from a solvate containing $2CH_2Cl_2$ and $2.5C_6H_6$ molecules [8]. Comparison with the data obtained from the Cambridge Data Base indicates that there are few significant differences between the two determinations, so that little further discussion is warranted. While the ideal structure of the diyne dimer is best described as the usual Ru-complexed ruthenacyclopentadiene moiety, i.e. Ru(3)–C(3–6), with C(3) bearing a ferrocenylethynyl substituent which interacts via the C(1)–C(2) triple bond with Ru(2), some individual distances are unusual. The σ-type Ru(3)–C(3,6) bonds [2.101, 2.126(7) Å] are shorter than those found for the π-type interactions between Ru(2) and atoms C(3)–C(5) [2.315–2.371(8) Å], while atom C(6) is much closer, at 2.145(8) Å. The bonding of C(1)–C(3) to Ru(1) must be considered to be π-type, with long and hence weak interactions of the outer carbons of the C$_3$ unit [Ru(1)–C(1,3) 2.499, 2.519(8) Å]; in contrast, the

Table 2
Selected bond parameters for **3** and **7**

	3	**7**	**7** [8]
Bond distances (Å)			
Ru(1)–Ru(2)	2.8012(2)	2.796(1)	2.8083(5)
Ru(1)–Ru(3)	2.8172(2)	2.851(1)	2.8241(4)
Ru(2)–Ru(3)	2.8029(2)	2.7372(9)	2.7243(5)
Ru(1)–P(1)	2.3053(6)	2.273(2)	2.263(1)
Ru(2)–P(2)	2.3272(6)	2.333(2)	2.322(1)
Ru(1)–C(1)	1.962(1)	2.499(8)	2.510(4)
Ru(1)–C(2)		2.284(8)	2.312(4)
Ru(1)–C(3)		2.519(8)	2.519(4)
Ru(2)–C(1)	2.194(1)		
Ru(2)–C(2)	2.241(1)		
Ru(2)–C(3)		2.345(7)	2.337(3)
Ru(2)–C(4)		2.371(8)	2.379(4)
Ru(2)–C(5)		2.315(8)	2.308(3)
Ru(2)–C(6)		2.145(8)	2.134(3)
Ru(3)–C(1)	2.242(2)		
Ru(3)–C(2)	2.222(2)		
Ru(3)–C(3)		2.101(8)	2.089(5)
Ru(3)–C(6)		2.126(7)	2.126(4)
Ru(2,3)–H	1.78(3), 1.80(2)		
P(1,2)–C(0)	1.847, 1.844(2)	1.815, 1.837(8)	
C(1)–C(2)	1.325(2)	1.21(1)	1.230(5)
C(1)–C(101)		1.43(1)	1.425(5)
C(2)–C(3)	1.396(2)	1.42(1)	1.430(5)
C(3)–C(4)	1.210(2)	1.41(1)	1.427(6)
C(4)–C(5)		1.44(1)	1.448(5)
C(5)–C(6)		1.45(1)	1.450(7)
C(5)–C(7)		1.44(1)	1.429(5)
C(7)–C(8)		1.21(1)	1.198(5)
C(*x*)–C(*x*01)	1.424(2) [*x* = 4]	1.43(1) [*x* = 1]	1.425(5)
		1.50(1) [*x* = 4]	1.471(7)
		1.47(1) [*x* = 6]	1.483(5)
		1.44(1) [*x* = 8]	1.429(5)
Bond angles (°)			
Ru(1)–C(1)–C(2)	150.6(1)		
Ru(3)–C(3)–C(4)		118.4(6)	118.4(3)
Ru(3)–C(6)–C(5)		114.8(5)	114.6(2)
C(3)–Ru(3)–C(6)		76.4(3)	76.8(2)
C(1)–C(2)–C(3)	149.3(1)	163.4(8)	162.1(5)
C(2)–C(3)–C(4)	176.2(1)	128.0(7)	126.1(5)
C(3)–C(4)–C(5)		113.6(7)	112.9(4)
C(4)–C(5)–C(6)		114.4(7)	115.0(3)
C(4)–C(5)–C(7)		121.1(7)	123.4(4)
C(6)–C(5)–C(7)		124.4(7)	121.6(3)
C(5)–C(7)–C(8)		176.0(9)	176.7(4)
C(*x*–1)–C(*x*)–C(*x*01)	178.9(2) [*x* = 4]	121.8(7) [*x* = 4]	123.0(3)
		122.6(7) [*x* = 6]	121.8(3)
		167.5(9) [*x* = 8]	177.6(4)
C(*x* + 1)–C(*x*)–C(*x*01)		164.1(8) [*x* = 1]	162.0(4)
		124.1(7) [*x* = 4]	124.0(4)

Table 3
Electrochemical data

Complex	$E°$ (V)
1	−0.43 +0.515
2	−0.395 +0.58
3	+0.56 +1.115 (irr.)
5	+0.575
6	+0.43 +0.58 +0.98 (irr.)

Conditions: 1.0 mM in CH_2Cl_2, 0.1 M $[NBu_4]BF_4$, room temperature, Pt electrodes (FcH/$[FcH]^+ = +0.46$ V). irr. = irreversible.

central C(2) atom is 2.284(8) Å removed from Ru(1). These distortions probably result from the presence of the coordinated alkyne unit with resulting steric strain imposed on the overall attachment of the C(1)–C(2)–C(3) moiety dictated by the presence of the Ru(3)–C(3) σ bond. The cluster valence electron count for **7** is 48, if the diyne dimer acts as an 8-electron donor; individual 18-e counts are achieved by each Ru atom if the Ru(2) → Ru(3) bond is considered to be a 2-e donor in the indicated sense.

2.3.2. Electrochemistry

The electrochemistry of some of these complexes has been studied briefly (Table 3). As also reported by others [13], oxidations of HC≡CFc, HC≡CC≡CFc and FcC≡CC≡CFc occur at +0.62, +0.665 and +0.61, 0.70 V (relative to FcH/$[FcH]^+ = +0.46$ V). These data are consistent with the addition of the electron-withdrawing alkyne or diyne fragment, as found earlier for the series $Fc(C{\equiv}C)_nW(CO)_3Cp$ ($n = 1$–4) [14]. Observation of two oxidation waves in the CV of FcC≡CC≡CFc ($\Delta E°$ 90 mV) is consistent with a moderate degree of electronic communication between the two Fc centres. The oxidation potentials for the μ_3-diyne complexes **1**, **2** and **5** are +0.515, +0.58 and +0.575 V, respectively, showing that complexation to the Ru_3 cluster results in an increase in ease of oxidation. For **1** and **2**, reduction waves at −0.43 and −0.395 V were also observed, probably involving the Ru_3 cluster core. Although, there are two inequivalent Fc groups in **5**, we suggest that accidental equivalence of the two oxidation potentials is found resulting from decreased communication as a result of π complexation of one of the C≡C triple bonds to the cluster. In this regard, we recall that the analogous osmium cluster shows two barely resolved oxidation waves, at $E_1 = +0.483$ and $E_2 = +0.54$ V [13]. For the dppm complexes **3** and **6**, two or three oxidation waves, at +0.56 and +1.115 V for **3**, and at +0.43, +0.58 and +0.98 V for **6**, were found. In each case, the highest potential oxidation is irreversible and is assigned to oxidation of the Ru_3(dppm) core. While no direct comparison is available for the diynyl cluster **3**, the well-separated oxidation waves found for **6** ($\Delta E = 150$ mV) suggest that the electron-rich cluster feeds electron density into the complexed C_2 triple bond, and thereby to the adjacent Fc nucleus, resulting in more facile oxidation of this nucleus that found for **5**. The Fc nucleus distant from the cluster shows essentially the same oxidation potential as found for **5**, suggesting that little electronic communication between the two Fc nuclei occurs.

3. Conclusions

This study reports the syntheses of several further examples of complexes obtained from Ru_3 cluster carbonyl precursors and the alkynylferrocenes HC≡CFc, HC≡CC≡CFc and FcC≡CC≡CFc under mild conditions, together with the molecular structures of four of the products. Conventional μ_3-η^2-alkyne complexes $Ru_3(\mu_3\text{-}RC_2R')(\mu\text{-}CO)(CO)_9$ (R = H, R′ = Fc, C≡CFc; R = R′ = Fc) and $Ru_3(\mu_3\text{-}FcC_2C{\equiv}CFc)(\mu\text{-dppm})(\mu\text{-}CO)(CO)_7$, the hydrido-alkynyl $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2C{\equiv}CFc)(CO)_9$ and the diyne dimer derivative $Ru_3\{\mu_3\text{-}C_4Fc_2(C{\equiv}CFc)_2\}(\mu\text{-dppm})(\mu\text{-}CO)_2(CO)_5$ were characterised. In the latter, head-to-tail dimerisation of the 1,3-diyne has occurred on the cluster, one of the free C≡CFc groups coordinating in η^2 fashion to the third Ru atom to generate a rather strained assembly with, e.g. two long Ru–C distances.

4. Experimental

4.1. General reaction conditions

Reactions were carried out under an atmosphere of nitrogen, but no special precautions were taken to exclude oxygen during work-up. Common solvents were dried and distilled under nitrogen before use. Elemental analyses were performed by the Canadian Microanalytical Service, Delta, BC, Canada. Preparative t.l.c. was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thickness).

4.2. Instrumentation

IR: Perkin–Elmer 1720X FTIR (cyclohexane solutions unless otherwise stated). NMR: Bruker CXP300 or ACP300 (^1H at 300.13 MHz, ^{13}C at 75.47 MHz) or Varian Gemini 200 (^1H at 199.8 MHz, ^{13}C at 50.29 MHz) spectrometers. Spectra were recorded using solutions in $CDCl_3$ in 5 mm sample tubes. FAB mass spectra (FABMS): VG ZAB 2HF (using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV. ESMS: Finnigan LCQ. Solutions were directly infused into the instrument. Chemical aids to ionisation were used as required [15]. Electrochemical measurements were carried out with a Maclab 400, using 1.0 mM solutions in dichloromethane, with 0.1 M $[NBu_4]BF_4$ as supporting electrolyte. A three-electrode system was used, consisting of a platinum dot working electrode and platinum counter and reference electrodes.

4.3. Reagents

$Ru_3(CO)_{12}$ [16], $Ru_3(CO)_{10}(NCMe)_2$ [17], $Ru_3(\mu\text{-dppm})(CO)_{10}$ [18], HC≡CFc [19], HC≡CC≡CFc [20] and FcC≡CC≡CFc [20,21] were made according to the cited methods.

4.4. Reactions of $Ru_3(CO)_{10}(NCMe)_2$

4.4.1. With HC≡CFc

HC≡CFc (66 mg, 0.31 mmol) was added to a solution of $Ru_3(CO)_{10}(NCMe)_2$ [prepared from $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) in CH_2Cl_2 (100 ml) and MeCN (20 ml)] at − 10°. On warming slowly to room temperature (r.t.) and stirring for a further 1 h, the colour turned dark red. Preparative t.l.c. (acetone–hexane 1/4) enabled separation of $Ru_3(CO)_{12}$ (R_f 0.77; 12 mg, 6%) from the major product which was contained in a red–orange band (R_f 0.64). This afforded $Ru_3(\mu_3\text{-}HC_2Fc)(\mu\text{-}CO)(CO)_9$ (**1**) (130 mg, 52%) as dark red crystals (CH_2Cl_2–MeOH). Anal. Found: C, 33.36; H, 1.40. $C_{22}H_{10}FeO_{10}Ru_3$ calcd.: C, 33.29; H, 1.26%; *M*, 793. IR: ν (CO) 2093m, 2059vs, 2051s, 2027s, 2011m, 1876w (br) cm^{-1}. ^1H-NMR: δ 4.18 (s, 5H, Cp), 4.20–4.29 (m, 4H, C_5H_4), 8.09 (s, 1H, ≡CH). ES mass spectrum (MeOH, *m/z*): 826, $[M + OMe]^-$; 798, $[M + OMe - CO]^-$. Several other uncharacterised compounds were also present.

4.4.2. With HC≡CC≡CFc

A similar reaction between HC≡CC≡CFc (37 mg, 0.16 mmol) and $Ru_3(CO)_{10}(NCMe)_2$ [from $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol)] gave one major band (R_f 0.57) containing $Ru_3(\mu_3\text{-}HC_2C{\equiv}CFc)(\mu\text{-}CO)(CO)_9$ (**2**) (24 mg, 19%), obtained as a dark red solid. IR: ν (C≡C) 2183w; ν (CO) 2096m, 2062s, 2055vs, 2031s, 2021 (sh), 2011m, 1882m (br) cm^{-1}. ^1H-NMR: δ 4.19 (s, 5H, Cp), 4.29–4.34 (m, 4H, C_5H_4), 8.26 (s, 1H, ≡CH). The complex decomposes rapidly in all solvents tried, so that further purification and characterisation was not possible.

4.4.3. With FcC≡CC≡CFc

This reaction was carried out as described in (a) above, using $Ru_3(CO)_{12}$ (150 mg, 0.24 mmol) and FcC≡CC≡CFc (100 mg, 0.24 mmol). In addition to $Ru_3(CO)_{12}$ (12 mg, 8%), the major product was isolated from a red band (R_f 0.60) as dark red crystals (from C_6H_6) of $Ru_3(\mu_3\text{-}FcC_2C{\equiv}CFc)(\mu\text{-}CO)(CO)_9$ (**5**) (89 mg, 37%). Anal. Found: C, 41.15; H, 1.96. $C_{34}H_{18}Fe_2O_{10}Ru_3$ calcd.: C, 40.76; H, 1.80%; *M*, 1001. IR: ν (CO) 2093m, 2062vs, 2052vs, 2029s, 2011m, 1991 (sh), 1972 (sh), 1871w (br) cm^{-1}. ^1H-NMR: δ 4.26, 4.31 (2 × s, 2 × 5H, 2 × Cp), 4.28–4.73 (m, 8H, C_5H_4). ES–MS (MeOH containing NaOMe, *m/z*): 1033, $[M - H + OMe]^-$ (≡M′), 1005–781, $[M' - nCO]^-$ ($n = 1$–9). Several other products amounted to 42 mg, but were not further investigated.

4.5. Reactions of $Ru_3(\mu\text{-dppm})(CO)_{10}$

4.5.1. With HC≡CC≡CFc

A solution of $Ru_3(\mu\text{-dppm})(CO)_{10}$ (100 mg, 0.1 mmol) and HC≡CC≡CFc (24 mg, 0.1 mmol) in thf (10 ml) was treated with Me_3NO (15 mg, 0.2 mmol) and stirred at r.t. for 3 h. Preparative t.l.c. (acetone–hexane 1/3) separated the reaction products into recovered $Ru_3(\mu\text{-dppm})(CO)_{10}$ (R_f 0.50; 24 mg, 24%) and a red band (R_f 0.42) which gave $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2C{\equiv}CFc)(\mu\text{-dppm})(CO)_7$ (**3**) (47 mg, 43%) as orange crystals (CH_2Cl_2–pentane). Anal. Found: C, 49.02; H, 3.17. $C_{46}H_{32}FeO_7P_2Ru_3$ calcd.: C, 49.43; H, 2.89%; *M*, 1117. IR: ν (CO) 2066s, 2059m, 2018m, 2012s, 2006vs, 1998m, 1990m, 1987 (sh), 1975vw, 1959m (br), 1940w cm^{-1}. ^1H-NMR: δ (major) − 19.44 [d, *J*(HP) 33.3, 1H, RuH], 3.49, 4.37 (2 × m, 2 × 1H, CH_2), 4.22 (s, 5H, Cp), 4.49 (m, 4H, C_5H_4), 7.02–7.55 (m, Ph); δ (minor) − 19.81 [t, *J*(HP) 14.1, 1H, RuH], 3.10, 3.79 (2 × m, 2 × 1H, CH_2), 4.13 (2, 5H, Cp), 4.25 (m, 4H, C_5H_4), 7.02–7.55 (m, Ph). ^{31}P-NMR: δ (major) 31.54 [d, *J*(PP) 55, PPh_2], 36.94 [d, *J*(PP) 55, PPh_2]; (minor) 27.70 (s, PPh_2). ES–MS (MeOH, *m/z*): 1118, $[M - H]^-$; 1090–1006, $[M - H - nCO]^-$ ($n = 1$–4). A third band (R_f 0.25), containing 1.5 mg red solid with ν (CO) 2062s, 2013s, 2000vs (br), 1989 (sh), 1928 (sh), 1834w (br) cm^{-1}, was not investigated further; the IR spectrum suggests that it is $Ru_3(\mu_3\text{-}HC_2C{\equiv}CFc)(\mu\text{-dppm})(\mu\text{-}CO)(CO)_7$ (**4**).

4.5.2. With FcC≡CC≡CFc

Me_3NO (15 mg, 0.2 mmol) was added to a mixture of $Ru_3(\mu\text{-dppm})(CO)_{10}$ (100 mg, 0.1 mmol) and FcC≡CC≡CFc (42 mg, 0.1 mmol) in thf (10 ml). After stirring at r.t. for 2 h, separation by preparative t.l.c. (acetone–hexane 3/7) gave a red–purple band (R_f 0.36), from which $Ru_3(\mu_3\text{-}FcC_2C{\equiv}CFc)(\mu\text{-dppm})(\mu\text{-}CO)(CO)_7$ (**6**) (62 mg, 45%) was obtained as a red solid. Anal. Found: C, 50.41; H, 3.41. $C_{57}H_{40}Fe_2O_8P_2Ru_3$ calcd.: C, 51.48; H, 3.03%; *M*, 1331. IR: ν (CO) 2039s, 2030m, 2001vs, 1996 (sh) 1980w, 1970w, 1946w, 1836w (br) cm^{-1}. ^1H-NMR: δ 4.26, 4.41 (2 × s, 2 × 5H, Cp), 4.23, 4.32 (2 × m, 8H, C_5H_4), 4.75, 5.72 (2 × m, 2H, CH_2),

Table 4
Crystal data and refinement details

Compound	**1** [a]	**3**	**5α** [b]	**5β** [b]	**7** [c]
CCDC #	172517	172518	172519	172520	172521
Formula	$C_{22}H_{10}FeO_{10}Ru_3$	$C_{46}H_{32}FeO_7P_2Ru_3$	$C_{34}H_{18}Fe_2O_{10}Ru_3$	$C_{34}H_{18}Fe_2O_{10}Ru_3$	$C_{79}H_{58}Fe_4O_6P_2Ru_3 \cdot 2C_2H_4Cl_2$
MW	793.37	1117.76	1001.41	1001.41	1890.80
Crystal system	Orthorhombic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$Pbca$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a (Å)	13.155(1)	12.8309(5)	8.2814(7)	8.9603(3)	21.550(3)
b (Å)	11.335(2)	13.3550(5)	43.479(4)	9.3974(4)	11.811(1)
c (Å)	33.385(4)	14.5451(6)	9.2518(8)	19.7978(8)	28.255(3)
α (°)		86.186(1)		86.629(1)	
β (°)		70.092(1)	100.237(1)	83.060(1)	93.355(2)
γ (°)		65.724(1)		81.057(1)	
V (Å^3)	4978	2128	3278	1633	7179
Z	8	2	4	2	4
D_{calc} (g cm^{-3})	2.117	1.744	2.029	2.036	1.749
μ (cm^{-1})	24.1	1.50	22.7	2.28	1.65
Crystal size (mm)	$0.25 \times 0.20 \times 0.12$	$0.45 \times 0.30 \times 0.17$	$0.23 \times 0.12 \times 0.10$	$0.45 \times 0.30 \times 0.17$	$0.14 \times 0.08 \times 0.07$
$T_{min,max}$	0.55, 0.83	0.70, 0.86	0.72, 0.93	0.53, 0.79	0.59, 0.80
$2\theta_{max}$ (°)	58	75	58	75	55
N_t	54 310	44 233	36 386	34 043	66 853
N (R_{int})	6464 (0.027)	21 911 (0.023)	8451 (0.045)	16 881 (0.021)	16 576 (0.12)
N_o	5832	17 283	7897	14 915	9739
R	0.042	0.028	0.074	0.024	0.057
R_w	0.033	0.032	0.104	0.034	0.062

[a] $T \sim 300$ K.

[b] Crystals of poor quality obtained from CH_2Cl_2–pentane (α form) [$(x, y, z, U_{iso})_H$ constrained in refinement] were recrystallised from benzene, giving a different polymorph (β form).

[c] $(x, y, z, U_{iso})_H$ constrained in refinement.

7.02–7.43 (m, 20H, Ph). ^{31}P-NMR: δ 35.85, 36.17 ($2 \times$ s, PPh_2). ES–MS (MeOH, m/z): 1331, M$^+$.

Alternatively, heating $Ru_3(\mu\text{-dppm})(CO)_{10}$ (100 mg, 0.1 mmol) and FcC≡CC≡CFc (42 mg, 0.1 mmol) in refluxing benzene (10 ml) for 3 h afforded recovered $Ru_3(\mu\text{-dppm})(CO)_{10}$ (42 mg, 42%), **6** (38 mg, 28%) and, from a purple band (R_f 0.31), very dark red crystals (from $ClCH_2CH_2Cl$) of $Ru_3\{\mu_3\text{-FcCC(C≡CFc)CFcC(C≡CFc)}\}(\mu\text{-dppm})(\mu\text{-CO})_2(CO)_4$ (**7**) (14 mg, 8%). IR (CH_2Cl_2): ν (CO) 2038s, 1982m, 1944vs, 1908 (sh) cm^{-1}. ^{1}H-NMR: δ 3.90, 3.95, 4.26, 4.35, 4.41, 4.58 ($6 \times$ m, 16H, C_5H_4), 4.11, 4.31, 4.34, 4,.37 ($4 \times$ s, $4 \times$ 5H, Cp), 5.21, 5.39 ($2 \times$ m, $2 \times$ 1H, CH_2), 6.62–7.57 (m, 20H, Ph). ^{31}P-NMR: δ 8.42 [d, J(PP) 35.2, dppm], 32.41 [d, J(PP) 35.2, dppm]. ES mass spectrum (MeOH, m/z): 1693, M$^+$; 1665–1581, $[M - n\text{CO}]^+$ ($n = 1$–4). Satisfactory elemental analyses could not be obtained.

4.6. Structure determinations

Full spheres of low-temperature CCD area detector diffractometer data (T ca. 153 K; ω scans, $2\theta_{max}$ as specified; monochromatic Mo–$K\alpha$ radiation, $\lambda = 0.7107_3$ Å) were measured, N_t reflections being merged after 'empirical'/multiscan absorption correction (proprietary software), to N unique (R_{int} cited where appropriate), N_o with $F > 2\sigma(F)$ being used in the full matrix least squares refinement, minimising $\Sigma w\Delta^2$ and refining anisotropic thermal parameters for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being refined. Conventional residuals R, R_w on $|F|$ [weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$] are quoted at convergence. Neutral atom complex scattering factors were employed, computation using the XTAL 3.7 program system [22]. Pertinent results are given in the tables and figures, the latter showing 20% thermal ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Individual variations in procedures, abnormalities, idiosyncrasies, etc. are cited as footnotes to Table 4.

5. Supplementary material

Crystallographic data for the structure determinations have been deposited with the Cambridge Crystallographic Data Centre as CCDC 172517–172521 for compounds **1**, **3**, **5** (two forms) and **7**, respectively. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, England (Fax: +44-1223-336033, e-mail: support@ccdc.cam.ac.uk, or www: http://www.ccdc.cam.ac.uk).

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