

Preparation, structure and some chemistry of $\text{FcC}\equiv\text{CC}\equiv\text{CC}\equiv\text{CRu}(\text{dppe})\text{Cp}$

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Abstract

The synthesis of $\text{Fc}(\text{C}\equiv\text{C})_3\text{Ru}(\text{dppe})\text{Cp}$ (**2**) from $\text{Fc}(\text{C}\equiv\text{C})_3\text{SiMe}_3$ and $\text{RuCl}(\text{dppe})\text{Cp}$ is described, together with its reactions with tene to give the tetracyano-dienyl $\text{FcC}\equiv\text{CC}\equiv\text{C}\{\text{C}[\text{C}(\text{CN})_2]\}_2\text{Ru}(\text{dppe})\text{Cp}$ (**3**) and -cyclobutenyl $\text{FcC}\equiv\text{CC}\equiv\text{C}\{\text{C}=\text{CC}(\text{CN})_2\text{C}(\text{CN})_2\}-\text{Ru}(\text{dppe})\text{Cp}$ (**4**), with $\text{Co}_2(\mu\text{-dppm})_n(\text{CO})_{8-2n}$ ($n = 0, 1$) to give $\text{FcC}_2\{\text{Co}_2(\text{CO})_6\}\text{C}_2\{\text{Co}_2(\text{CO})_6\}\text{C}\equiv\text{CRu}(\text{dppe})\text{Cp}$ (**5**) and $\text{FcC}\equiv\text{CC}\equiv\text{CC}_2\{\text{Co}_2(\mu\text{-dppm})(\text{CO})_4\}\text{Ru}(\text{dppe})\text{Cp}$ (**6**), respectively, and with $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ to give $\text{Os}_3\{\mu_3\text{-C}_2\text{C}\equiv\text{CC}\equiv\text{C}[\text{Ru}(\text{dppe})\text{Cp}]\}-\text{C}(\text{CO})_{10}$ (**7**). On standing in solution, the latter isomerises to the cyclo-metallated derivative $\text{Os}_3(\mu\text{-H})\{\mu_3\text{-C}[\text{Ru}(\text{dppe})\text{Cp}]\text{CCC}[(\eta\text{-C}_5\text{H}_3)\text{FeCp}]\}(\text{CO})_8$ (**8**). X-ray structural determinations of **1**, **2**, **6** and **7** are reported.
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Keywords: Ferrocene; Ruthenium; Triyne; Cyanoalkene; Dicobalt; Triosmium cluster; X-ray structures

1. Introduction

Poly-unsaturated carbon chains have evinced much interest as models for molecular wires for the design and construction of molecular-scale electronic devices [1–3]. To function in this way, there must be evidence for electronic communication through such “wires” and to this effect, several groups have studied compounds wherein the poly-yne chains are end-capped with redox-active groups. Examples containing manganese [4], rhenium [5], iron [6,7], ruthenium [8,9], rhodium [10] and platinum [11] have been studied extensively, many of these being summarised in recent reviews [12].

A well-known redox-active organometallic fragment is the ferrocenyl group (Fc). The few accounts of ferrocenyl-poly-ynes end-capped with σ -bonded transition metal fragments available include studies of $\text{TiX}(\text{C}\equiv\text{CC}\equiv\text{CFc})\text{Cp}^{\text{Si}}$ ($\text{X} = \text{Cl}, \text{C}\equiv\text{CFc}, \text{C}\equiv\text{CRc}, \text{C}\equiv\text{CC}\equiv\text{CFc}$); $\text{Cp}^{\text{Si}} = \eta\text{-}$

$\text{C}_5\text{H}_4(\text{SiMe}_3)$ [13] and *trans*- $\text{RuX}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{dppe})_2$ ($\text{X} = \text{Cl}, \text{C}\equiv\text{CC}_6\text{H}_4\text{NO}_2\text{-4}, \text{C}\equiv\text{CFc}, \text{C}\equiv\text{CC}\equiv\text{CFc}$) [14]. An early approach of ours involved the syntheses of $\text{Fc}(\text{C}\equiv\text{C})_n\text{W}(\text{CO})_3\text{Cp}$ ($n = 1\text{--}4$), but the lack of any measurable electrochemical response of the tungsten end-cap precluded assessment of any electronic communication between the two centres [15]. Detailed studies of the reactions of $\text{FcC}\equiv\text{CC}\equiv\text{CFc}$ with ruthenium cluster carbonyls have been reported [16], while the syntheses and structures of a series of osmium cluster carbonyls derived from $\text{Fc}(\text{C}\equiv\text{C})_n\text{Fc}$ ($n = 2, 4, 6$) together with some of their electrochemical properties have also been described [17]. Other cluster-bonded poly-ynylferrocene ligands include complexes obtained from the triosmium cluster and 1,1'-($\text{Me}_3\text{SiC}\equiv\text{C}$) $_2\text{Fc}'$ [$\text{Fc}' = \text{ferrocene-1,1'-diyl}, \text{Fe}(\eta\text{-C}_5\text{H}_4\text{-})_2$] [18]. We and others have described some of the chemistry associated with complexes $\text{Fc}(\text{C}\equiv\text{C})_n\text{Ru}(\text{PP})\text{Cp}'$ [$n = 1, 2$; $\text{PP} = \text{dppe}, \text{Cp}' = \text{Cp}, \text{Cp}^*$; $\text{PP} = (\text{PPh}_3)_3, \text{Cp}' = \text{Cp}$] and the 1,1'-bis(ethynyl)ferrocene complexes of the type $\text{Fc}'\text{-1,1'-}\{\text{C}\equiv\text{CRu}(\text{PP})\text{Cp}\}_2$ [19,20]. The present account is devoted to the third member of this series, of

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which we have studied the molecule $\text{Fc}(\text{C}\equiv\text{C})_3\text{-Ru}(\text{dppe})\text{Cp}$.

2. Results and discussion

The triyne $\text{Fc}(\text{C}\equiv\text{C})_3\text{SiMe}_3$ (**1**; Scheme 1) was obtained in 78% yield by dehydrochlorination of *cis*- $\text{FcC}\equiv\text{CC}\equiv\text{CCH}=\text{CHCl}$ with LiN^iPr_2 , followed by quenching of the resulting lithiated triyne with SiClMe_3 . It formed a dark orange oil which was not fully characterised on account of its instability. Nevertheless, the ^1H [singlets at δ 0.22 (SiMe_3), 4.26 (Cp) and multiplets at δ 4.29–4.30, 4.54–4.56 (C_5H_4)] and ^{13}C NMR spectra [δ -0.48 (SiMe_3), 70.35 (Cp) and several signals between δ 61.69 and 88.54 arising from the C_5H_4 and $\equiv\text{C}$ carbons], together with ions at m/z 330 and 258, assigned to M^+ and $[\text{M}-\text{SiMe}_3]^+$, respectively, are consistent with its formulation.

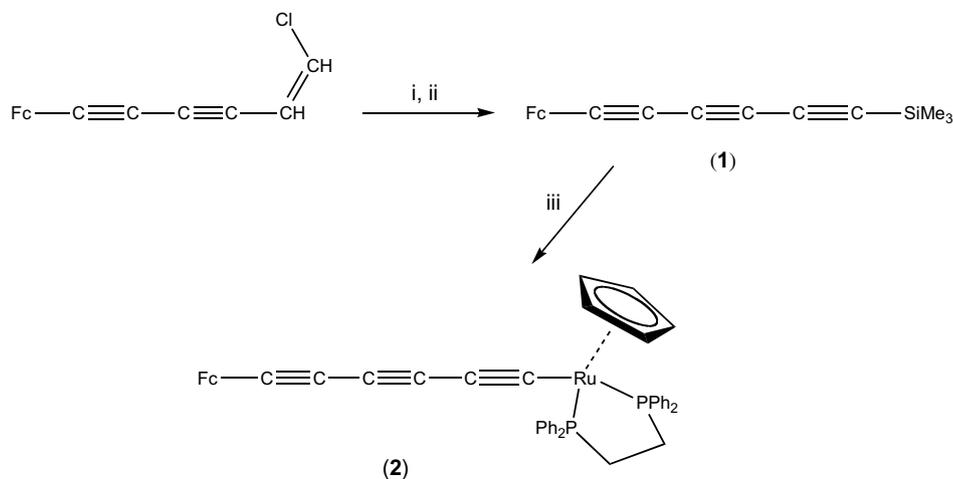
Coupling of **1** with $\text{RuCl}(\text{dppe})\text{Cp}$ in MeOH containing a small amount of water, a drop of dbu and KF afforded $\text{Fc}(\text{C}\equiv\text{C})_3\text{Ru}(\text{dppe})\text{Cp}$ (**2**) in 53% yield as a dark orange solid. This complex was fully characterised by elemental analyses, its spectroscopic properties and by a single-crystal X-ray structure determination (see below). The IR spectrum contains two $\nu(\text{C}\equiv\text{C})$ bands at 2108 and 1992 cm^{-1} , while the ES-MS, obtained from a MeOH solution containing NaOMe, contains $[\text{M}+\text{Na}]^+$ at m/z 845. The ^1H NMR spectrum contains resonances characteristic of the Fc [δ 3.93 (Fe–Cp), multiplets at δ 3.76 and 4.23 (C_5H_4)], dppe (CH₂ and Ph multiplets at δ 1.80–2.00 and 2.30–2.50, and 6.85–7.87) and the Ru–Cp singlet at δ 4.58, and the dppe ligands give rise to a ^{31}P resonance at δ 85.2 (cf. δ 86.0 in $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{dppe})\text{Cp}$ [19a], δ 79.4 in $\{\text{Cp}^*(\text{dppe})\text{Ru}\}_2\{\mu-(\text{C}\equiv\text{C})_3\}$ [21]).

In the ^{13}C NMR spectrum, resonances at δ 69.69 and 83.13 (for the Fe–Cp and Ru–Cp groups, respectively), multiplet signals at δ 27.4–28.3 (dppe–CH₂), 65.9 and 68.2 (C_5H_4) and between 129 and 142 (Ph) were accompanied by a triplet at δ 123.13 [$J(\text{CP}) = 22$ Hz], which we

assign to C_α attached to Ru. Other resonances at δ 65.91, 69.34, 70.71, 74.85 and 94.40 are tentatively assigned to the other atoms of the C_6 chain. The assignment of carbon resonances in poly-yne chains end-capped by various groups has been a matter of debate for some time. In an account of the poly-ynes $\text{Ar}(\text{C}\equiv\text{C})_n\text{Ar}$ [$\text{Ar} = 3,5\text{-}(\text{TBDMS-O})_2\text{C}_6\text{H}_3$, $n = 2, 4, 6, 8, 10$], it was pointed out that elongation of the chain resulted in new signals appearing in the range δ 62–65, whilst an earlier suggestion by the same group was that the expected chemical shift of carbyne $[-(\text{C}\equiv\text{C})_n-]$ would be a broad signal at δ 63–64 [22]. The C_6 chain resonances for $\text{Fc}(\text{C}\equiv\text{C})_3\text{Fc}$ occur at δ 65.8, 79.3 and 72.1, which have been assigned to C(1,2,3), respectively [numbering is from the Fc–C(1) atom] [23]. For $\{\text{Cp}^*(\text{dppe})\text{Ru}\}_2\{\mu-(\text{C}\equiv\text{C})_4\}$ (the C_6 complex is not soluble enough to give a resolved ^{13}C NMR spectrum) the C_4 chain carbons are found at δ 51.12, 63.60, 92.54 and 94.58t [$J(\text{CP}) = 22$ Hz] and have been assigned to C(1,2,3,4), respectively [20a]. For $\text{Ru}\{(\text{C}\equiv\text{C})_n\text{Fc}\}(\text{dppe})\text{Cp}^*$, we have reported the chain carbon resonances at δ 69.81, 77.77, 95.19 and 115.75t [$J(\text{CP}) = 25.2$ Hz] ($n = 2$) [19a] and at δ 65.91, 69.34, 70.71, 74.85, 94.40 and 123.13t [$J(\text{CP}) = 22.0$ Hz] ($n = 3$, **2**). On the basis of these values, we are inclined to assign the resonance of the carbon atom attached to Ru as being at lowest field and showing coupling to ^{31}P , other carbons in the chain being found at progressively higher field. The resonance for the carbon attached the Fc group is likely to be one of the signals found between δ 65.9 and 74.85.

2.1. Electrochemistry

The series $\text{Ru}\{(\text{C}\equiv\text{C})_n\text{Fc}\}(\text{dppe})\text{Cp}$ ($n = 1\text{--}3$) have now been prepared and it is of interest to compare their electrochemical responses. Under similar conditions (see Section 4) all three complexes show two oxidation processes, one irreversible at +0.14, +0.32 and +0.50 V (for $n = 1, 2, 3$, respectively) and a reversible process at +0.72, +0.76 and



Scheme 1. Reagents: (i) LiN^iPr_2 ; (ii) SiClMe_3 ; (iii) $\text{RuCl}(\text{dppe})\text{Cp}$, KF, dbu.

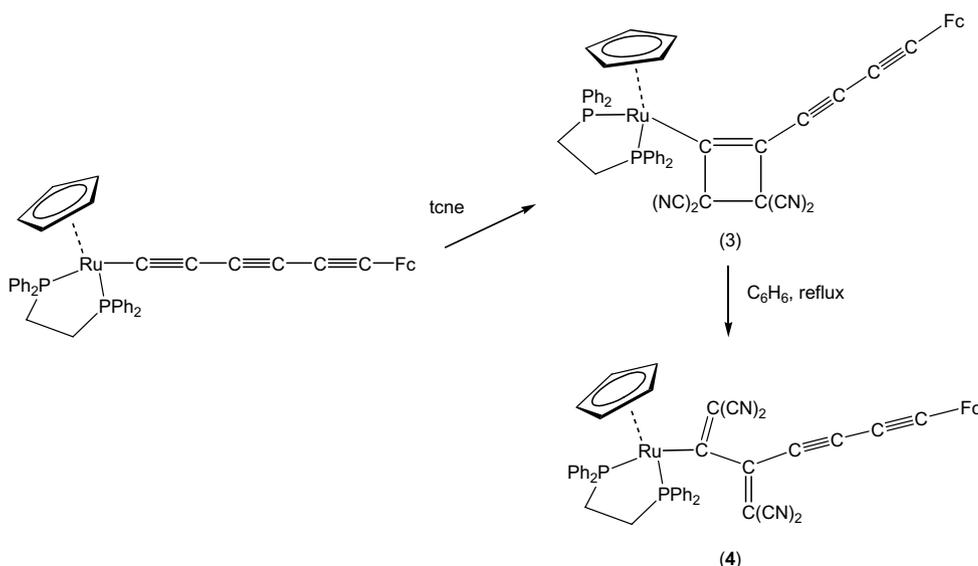
+0.73 V (for $n = 1, 2, 3$, respectively). The diyne ($n = 2$) also shows a quasi-reversible oxidation at +0.94 V. The relative insensitivity of the higher oxidation to the carbon chain length suggests that it is associated with the ferrocene moiety, whereas the increase in oxidation potential of the lower energy process with increasing chain length suggests that it is associated with the ruthenium centre, reflecting an increase in transfer of electron density to the carbon chain. We note that a previous study of the complexes $W\{(C\equiv C)_nFc\}(CO)_3Cp$ ($n = 1-4$) showed a similar increase in oxidation potential with increasing chain length, each added $C\equiv C$ unit resulting in an approximate 0.06 V increase in oxidation potential [15b]. However, in this case, the processes are reversible and the changes result from partial electron transfer to the carbon chain from the ferrocene centre.

2.2. Reactions of $Fc(C\equiv C)_3Ru(dppe)Cp$ (**2**)

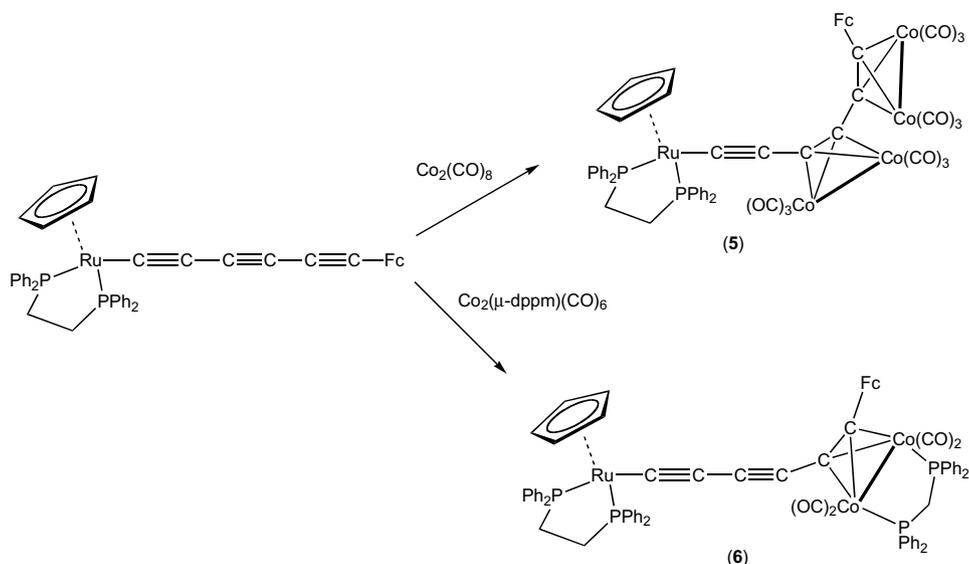
The triyne **2** showed the expected reactivity towards the electron-deficient alkene $C_2(CN)_4$ (tcne), binuclear cobalt carbonyls and $Os_3(CO)_{10}(NCMe)_2$ (Schemes 2–4). With the cyanoalkene, a mixture of green cyclobutenyl (**3**) and dark blue dienyl (**4**) complexes was successfully separated, the latter being shown to have formed by addition to the $C\equiv C$ triple bond adjacent to the ruthenium centre by an X-ray structural determination (Scheme 2). The cyclobutenyl **3** was converted into **4** by heating in benzene for several hours, there being no evidence for the formation of any other product. The IR spectrum of **3** contains bands assigned to $\nu(CN)$ at 2226 and 2207 and to $\nu(C\equiv C)$ at 2181 and 2135 cm^{-1} , while that of **4** has $\nu(CN)$ at 2208 and $\nu(C\equiv C)$ at rather lower frequencies than **3**, at 2163 and 1978 cm^{-1} . The 1H NMR spectra of both isomers are similar and contain no distinguishing features. The ^{31}P NMR spectra contain a singlet resonance at δ 85.4

for **3**, while that of **4** has an AB quartet at δ 66.4/81.8 from the different P nuclei which result from the asymmetry of the cyanocarbon ligand. In their ^{13}C NMR spectra, two multiplets are similarly found for the dppe CH_2 groups in **4**, compared with only one in **3**. Other major differences relate the presence of resonances assigned to the cyclobutenyl sp^3 carbons in **3** at δ 84.43 and 86.57, and one of the sp^2 carbons at δ 148.92; other skeletal carbons of the cyanocarbon ligand were not resolved. In contrast, the spectrum of **4** contained several signals between δ 70.0 and 97.39, of which those at δ 71.24, 73.45d, 77.20, 81.27, 95.72d, 96.87, 97.39 are assigned to skeletal carbons (by comparison with the spectra of related complexes obtained from $FcC\equiv CC\equiv CRu(PP)Cp'$ [19]), and at δ 163.63, which is assigned to C–Ru.

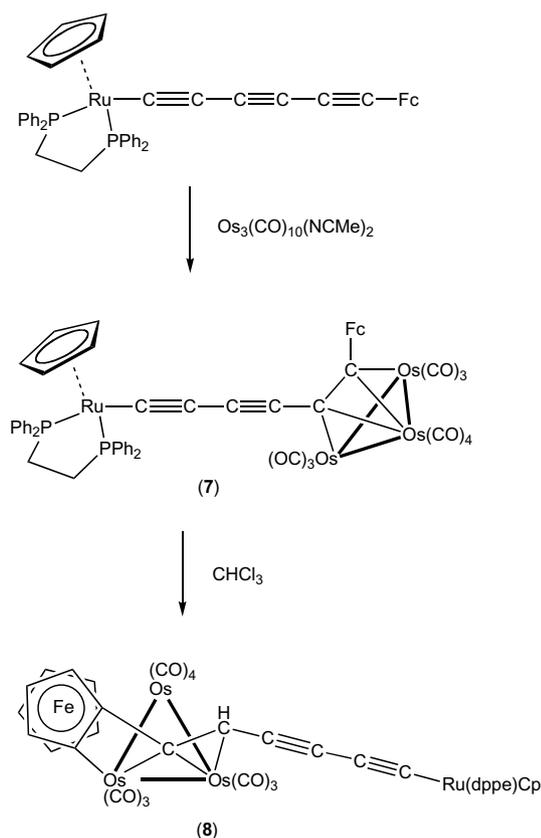
Addition of $Co_2(CO)_8$ to the triyne **2** afforded the bis-adduct $FcC_2\{Co_2(CO)_6\}C_2\{Co_2(CO)_6\}C\equiv CRu(dppe)Cp$ (**5**) as a dark purple solid in 65% yield (Scheme 3). There was no evidence for the presence of either the mono- or tris-adduct, although formation of the latter is not anticipated, since similar complexes of other poly-yne complexes contain a maximum of two adjacent $C_2Co_2(CO)_6$ fragments in the chains [24]. Characterisation of **5** included elemental analyses and the ES-MS of a solution containing NaOMe, which has ions at m/z 1417 and 1391, assigned to $[M+Na]^+$ and M^+ , respectively. Only terminal $\nu(CO)$ bands are present in the IR spectrum between 2091 and 2011 cm^{-1} , while the 1H NMR spectrum contains singlet resonances at δ 4.22 (Cp–Fe) and 4.80 (Cp–Ru), together with other signals arising from the C_5H_4 (δ 4.40, 4.66) and dppe groups (δ 2.56, 2.78 and 7.02–7.76). In the ^{13}C NMR spectrum, signals at δ 69.74 (Cp–Fe) and 83.68 (Cp–Ru) are accompanied by several others in the region δ 68.35–108.87 (assigned collectively to the C_5H_4 and carbon chain nuclei), multiplets from the dppe- CH_2 and Ph groups (δ 26.90–28.12 and 127.90–142.40, respectively) and a triplet



Scheme 2.



Scheme 3.



Scheme 4.

$[J(\text{CP}) = 24.0 \text{ Hz}]$ at $\delta 156.74$, assigned to C(1) attached to the ruthenium centre and indicating that this carbon is not attached to a $\text{Co}_2(\text{CO})_6$ group. The Co–CO groups give a broad signal at $\delta 199.57$.

In contrast, only mono-adduct **6** was obtained from the reaction between **2** and $\text{Co}_2(\mu\text{-dppm})(\text{CO})_6$. The composition is indicated by the elemental analysis and the

ES-MS, which contains M^+ at m/z 1436. The IR spectrum contains a $\nu(\text{C}\equiv\text{C})$ band at 2113 cm^{-1} together with terminal $\nu(\text{CO})$ absorptions between 2009 and 1945 cm^{-1} . In the NMR spectra, characteristic signals for the Cp–Fe ($\delta_{\text{H}} 4.41$, $\delta_{\text{C}} 69.30$) and Cp–Ru ($\delta_{\text{H}} 4.71$, $\delta_{\text{C}} 83.25$) were accompanied by several multiplets arising from the dppe, dppm and C_5H_4 ligands. Also present were peaks at $\delta 91.74$, 125.99, 134.37 and 138.60 all showing triplet couplings to phosphorus, together with two Co–CO multiplet resonances at $\delta 202.22$ and 206.68.

Purple crystalline $\text{Os}_3\{\mu_3\text{-C}_2\text{C}\equiv\text{CC}\equiv\text{C}[\text{Ru}(\text{dppe})\text{-Cp}]\}(\text{CO})_{10}$ (**7**) was obtained in 25% yield from a reaction between triyne **2** and $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ carried out in thf at r.t. for 1 h (Scheme 4). The molecular structure was determined from a single-crystal X-ray study, both analytical data and the ES-MS ($[\text{M}+\text{OMe}]^-$ at m/z 1704) being consistent with the solid state structure. The IR spectrum contained both terminal $\nu(\text{CO})$ bands (between 2092 and 2000 cm^{-1}) and a bridging $\nu(\text{CO})$ absorption at 1821 cm^{-1} , likely arising from the two semi-bridging CO ligands found in the crystal structure. A single band at 2128 cm^{-1} is assigned to a $\nu(\text{C}\equiv\text{C})$ mode. In the NMR spectra, Cp–Fe ($\delta_{\text{H}} 4.23$, $\delta_{\text{C}} 70.5$) and Cp–Ru ($\delta_{\text{H}} 4.60$, $\delta_{\text{C}} 83.95$) singlets are accompanied by resonances from the dppe and C_5H_4 ligands and a broad singlet at $\delta_{\text{C}} 179.16$ for the Os–CO groups. Several singlets between $\delta 53.7$ and 152.9 arise from the chain carbons, although it has not been possible to assign these with confidence.

On allowing a solution in chloroform to stand for seven days at r.t., complex **7** was transformed into brown crystalline **8** which has only been partially characterised. The presence of terminal ($2092\text{--}1990 \text{ cm}^{-1}$) and bridging (1815 cm^{-1}) $\nu(\text{CO})$ bands indicates the preservation of the Os_3 cluster, also supported by $[\text{M}+\text{H}]^+$ appearing in the ES-MS at m/z 1673. In the absence of an X-ray determination, we can only speculate on the molecular structure,

which we suspect involves further metallation of the C₅H₄ ring of the ferrocenyl moiety. Singlet resonances (δ_{H} 3.78 and 4.72, δ_{C} 69.19 and 82.88) confirm the retention of the Cp–Fe and Cp–Ru moieties, and only three substituted C₅ ring protons are found at δ 3.72, 4.16 and 4.26. Three of the corresponding carbons resonate at δ 64.25, 66.75 and 67.61. The presence of a single proton resonance at δ 6.29 is consistent with the H atom being transferred to the carbon chain rather than to the cluster (there is no high-field resonance characteristic of a cluster-bonded proton). The separation of the ³¹P NMR resonance of **8** into an AB quartet suggests that a degree of asymmetry has arisen near to the ruthenium centre. Considering the above data, we are inclined to suggest a structure similar to **9** (Chart 1), proposed as an intermediate on the way to one of the products isolated from the reaction of Fc(C≡C)₄Fc with Os₃(μ-H)₂(CO)₁₀ [17e]. The complex may also be related to Os₃(μ-H){μ₃-C(SiMe₃)CMeCHC[(η-C₅H₃)-FeCp]}(CO)₈ (**10**), containing a cyclometalated ferrocenyl group, recently described as being obtained by thermolysis of Os₃{μ₃-C(SiMe₃)CMeCHCFC}(CO)₉ in refluxing benzene [25]. In the present case, if migration of the proton occurs first to the Os₃ cluster, further migration of this proton to the C₆ chain then takes place.

Molecular structures. Molecules of **2**, **4**, **6** and **7** are depicted in Figs. 1–4, while significant bond parameters are collected in Table 1; in all cases, one formula unit of the substrate, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. All contain the familiar Ru(dppe)Cp end-cap, the geometries of which resemble those of the many other examples recorded in the Cambridge Data Base. In the present compounds, the Ru–P distances range between 2.260 and 2.309(3) Å, the Ru–C(cp) distances are between 2.185 and 2.273(6) Å (averages 2.23–2.25 Å) and the P(1)–Ru–P(2) and P(1,2)–Ru–C(1) angles are between 82.7° and 84.03(8)°, and 83.8° and 102.4(3)°, respectively. Similarly, the ferrocenyl moieties show no unusual features, with average Fe–C(cp) distances of between 2.01 and 2.05 Å, with the C(6)–C(601) bonds being between 1.40 and 1.47(2) Å.

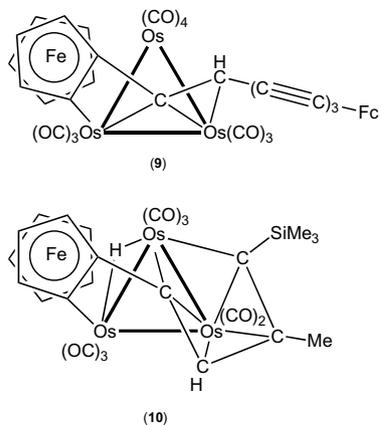
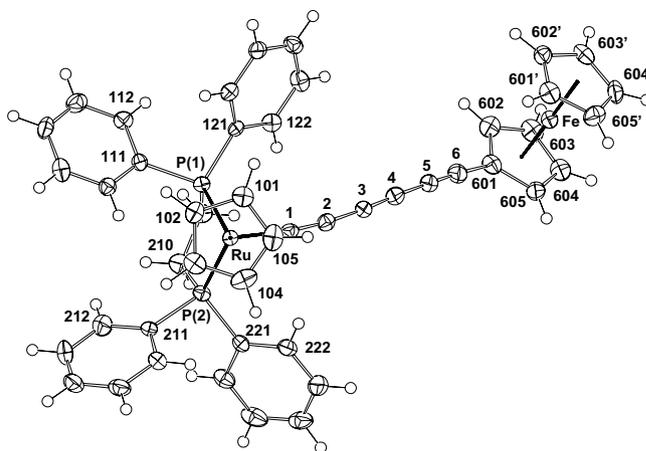
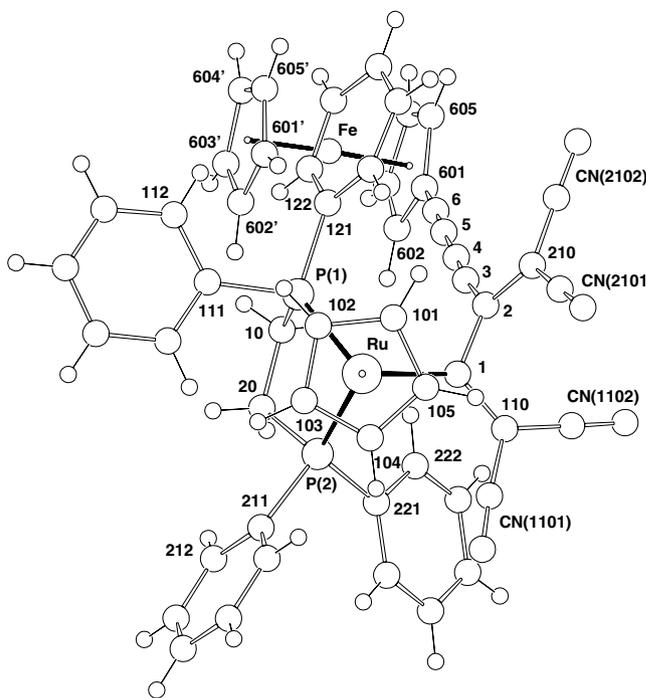


Chart 1.

Fig. 1. Projection of a molecule of Ru(C≡C≡C≡CFc)(dppe)Cp (**2**).Fig. 2. Projection of a molecule of Ru{C≡C(CN)₂}C[C≡C(CN)₂]C≡C≡CFc)(dppe)Cp (**4**).

In **2**, the Ru–C≡C–C≡C–C≡C–Fc chain shows an alternating short–long–short–long–short C–C bond pattern [short, 1.212–1.217(7), long 1.371, 1.374(7) Å], with an Ru–C(1) separation of 1.986(4) Å. Angles at the individual carbons range between 173.1° and 177.0 (5)°. Since there are no intermolecular contacts between these carbons and other atoms, the usual explanation of a weak bending moment for the C–C bonds affected by the crystal environment probably applies in this case also [26]. Comparison with the recently reported structure of Fc(C≡C)₃Fc [23] shows little difference in the C–C bond lengths [short, 1.211(1), 1.215(1), long

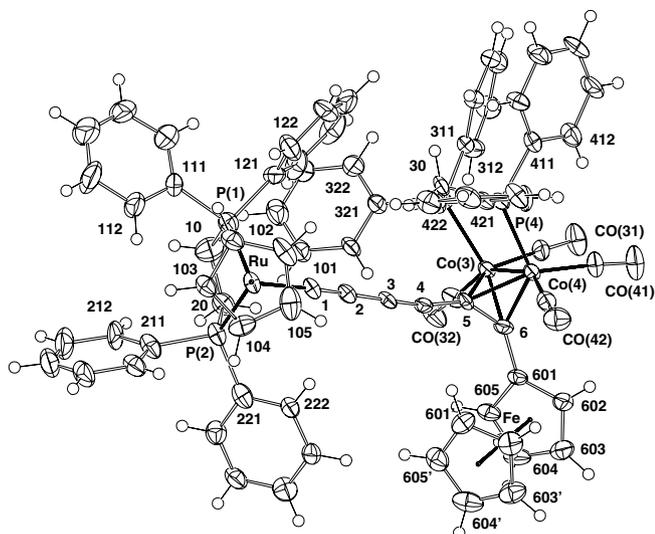


Fig. 3. Projection of a molecule of $\text{Ru}\{\text{C}\equiv\text{CC}\equiv\text{CC}_2\text{Fc}[\text{Co}_2(\mu\text{-dppm})(\text{CO})_4]\}(\text{dppe})\text{Cp}$ (**6**).

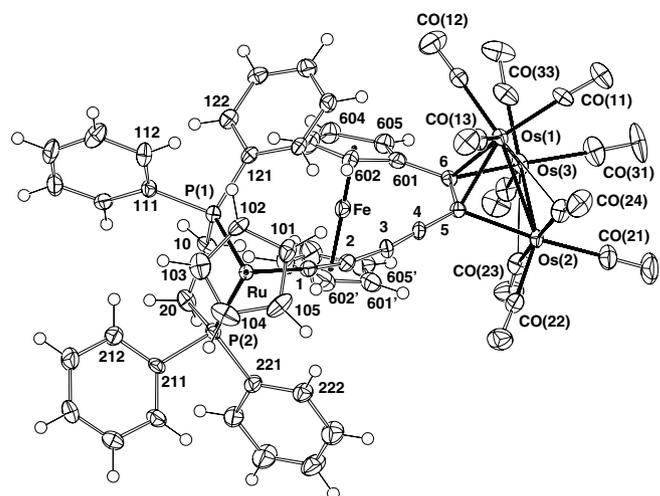


Fig. 4. Projection of a molecule of $\text{Os}_3\{\mu_3\text{-C}_2\text{C}\equiv\text{CC}\equiv\text{C}[\text{Ru}(\text{dppe})\text{Cp}]\}(\text{CO})_{10}$ (**7**).

Table 1
Selected bond distances (Å) and angles (°)

Complex	2	4	6	7
<i>Bond distances (Å)</i>				
Ru(1)–P(1)	2.260(1)	2.266(3)	2.244(2)	2.264(2)
Ru(1)–P(2)	2.262(1)	2.309(3)	2.250(2)	2.261(2)
Ru(1)–C(cp)	2.229(5)–2.252(5)	2.185(13)–2.263(12)	2.222(6)–2.263(8)	2.237(11)–2.273(6)
Ru(1)–C(cp) (av.)	2.242(9)	2.23(3)	2.247(17)	2.251(15)
Ru(1)–C(1)	1.986(4)	2.018(11)	1.989(5)	1.983(8)
C(1)–C(2)	1.212(6)	1.49(2)	1.222(7)	1.24(1)
C(2)–C(3)	1.371(6)	1.37(2)	1.363(6)	1.37(1)
C(3)–C(4)	1.217(7)	1.20(2)	1.232(6)	1.22(1)
C(4)–C(5)	1.374(7)	1.34(2)	1.390(6)	1.43(1)
C(5)–C(6)	1.214(7)	1.20(2)	1.359(6)	1.44(1)
C(6)–C(601)	1.415(7)	1.40(2)	1.452(6)	1.47(1)
Fe–C(cp)	2.024(5)–2.045(5), 2.026(5)– 2.046(5)	1.978(14)–2.035(14), 1.999(17)– 2.013(15)	2.026(6)–2.061(5), 2.004(6)– 2.048(6)	2.033(7)–2.055(9), 2.032(8)– 2.049(14)
Fe–C(cp) (av.)	2.036(9), 2.038(7)	2.01(2), 2.007(6)	2.046(12), 2.03(2)	2.045(11), 2.040(7)
<i>Bond angles (°)</i>				
P(1)–Ru(1)– P(2)	83.66(4)	82.7(1)	83.86(5)	84.03(8)
P(1)–Ru(1)– C(1)	81.8(1)	102.4(3)	85.2(2)	83.8(2)
P(2)–Ru(1)– C(1)	90.1(1)	90.0(3)	84.6(2)	87.7(2)
Ru(1)–C(1)– C(2)	174.3(4)	118.6(8)	175.8(5)	175.7(7)
C(1)–C(2)–C(3)	173.1(5)	121.7(11)	177.1(6)	171.1(9)
C(2)–C(3)–C(4)	176.5(5)	172.6(13)	177.7(6)	172.4(9)
C(3)–C(4)–C(5)	175.3(5)	178.4(14)	168.5(4)	178.2(8)
C(4)–C(5)–C(6)	176.3(5)	176.8(15)	144.6(4)	125.9(7)
C(5)–C(6)– C(601)	177.0(5)	178.0(15)	140.5(4)	122.9(7)

For **4**: C(1)–C(110) 1.35(2), C(2)–C(210) 1.40(2), C(n10)–CN 1.37(2)–1.42(2), C–N 1.14(2)–1.16(2) Å; Ru, C(2)–C(1)–C(110) 126.9(9)°, 114.0(10)°, C(1,3)–C(2)–C(210) 117.8(10)°, 120.4(11)°, C(n101)–C(n10)–C(n102) 114.1(10)°, 116.4(11)° (only Ru, Fe, Cl, P were refined with anisotropic U_{ij}).

For **6**: Co(3)–Co(4) 2.458(1), Co(3)–P(3) 2.202(1), Co(4)–P(4) 2.217(1), Co(3)–C(5,6) 1.978(5), 1.958(5), Co(4)–C(5,6) 1.997(4), 1.943(5) Å.

For **7**: Os(1)–Os(2,3) 2.8281(11), 2.7307(8), Os(2)–Os(3) 2.8689(11), Os(1)–C(5,6) 2.209(8), 2.343(7), Os(2)–C(5) 2.158(7), Os(3)–C(6) 2.108(8) Å.

1.362(1) Å], although the bending of the chain is considerably less [angles at C(2,3) 178.9(1)°, 179.7(1)°, respectively]. The C(6)–C(601) distance is 1.415(7) Å [cf.

1.4182(13) Å for C(1)–C(11) in $\text{Fc}(\text{C}\equiv\text{C})_3\text{Fc}$ [23]]. The solvation comprises columns of centrosymmetric benzene molecules stacked face-to-edge up *a*.

The molecule of **4** contains a tetracyanobuta-1,3-dienyl ligand attached to Ru [Ru–C(1) 2.018(11) Å], in which the two C=C(CN)₂ groups have taken up an *s-trans* conformation, in common with the majority of other structurally determined examples of this class of compound, such as Ru{C[=C(CN)₂]CPh=C(CN)₂}(dppe)Cp [27], but with the notable exceptions of PtCl{C[=C(CN)₂]CPh=C(CN)₂}(PEt₃)₂ and {PtCl(PMe₃)₂}₂{μ-C[=C(CN)₂]C[=C(CN)₂]}, in which the cyano-diene ligands adopt the *s-cis* conformation [28]. Atom C(2) is attached to the diyne chain in which the C≡C triple bonds are localised [C(2)···C(6) separations 1.37, 1.20, 1.34, 1.20(2) Å]. Angles at C(1) and C(2) [118.6(8), 121.7(11)°] are consistent with their sp² hybridisation, while those at C(3)–C(6) [172.6–178.4(14)°] reflect the C(sp) constituents. The structure confirms the site of addition of the cyanoalkene at the C≡C triple bond adjacent to the Ru centre, suggesting that this bond is more activated than that adjacent to the Fc nucleus. Many examples of addition of cyano-alkenes to alkynyl-metal complexes containing a σ-bonded alkynyl ligand have been described [27,29,30], but it is only recently that similar reactions with a diyne-ferrocene have been reported [31].

The structures of **6** and **7** show that the additions of the CO₂ or Os₃ fragments have occurred at the C≡C triple bond adjacent to the Fc group. Along the carbon chain, the bond distances Ru–C(1), C(1)–C(2), C(2)–C(3), C(3)–C(4), C(4)–C(5) are 1.989(5), 1.222(7), 1.363(7), 1.232(6), 1.390(6) Å for **6** and 1.983(8), 1.24(1), 1.37(1), 1.22(1), 1.43(1) Å for **7**, all consistent with preservation of the diyne-ruthenium structure. Lengthening of the C(5)–C(6) bond [to 1.359(6) Å in **6**, 1.44(1) Å for **7**] reflects the usual effect of 2π-coordination to the CO₂ or 2σ,π-coordination to the Os₃ cluster. This is accompanied by bending of the chain at these atoms, which is less for **6** than for **7**, as expected [C(4)–C(5)–C(6) 144.6(4)°, 125.9(7)°; C(5)–C(6)–C(601) 140.5(4)°, 122.9(7)° for **6** and **7**].

3. Conclusions

The synthesis of triyne Fc(C≡C)₃Ru(dppe)Cp (**2**) has been achieved, together with addition of tcne, Co₂(μ-dppm)_n(CO)_{6–2n} (n = 0, 1) and Os₃(CO)₁₀ fragments to the C₆ chain. Whereas the cyanoalkene adds to the C≡C triple bond more activated by the Ru(dppe)Cp group, i.e., in an electronically controlled reaction, the bi- and tri-nuclear metal fragments add to the sterically most accessible C≡C triple bond adjacent to the Fc group. In solution, the Os₃ cluster complex undergoes a still relatively rare metallation of the ferrocenyl group with migration of the H atom to the carbon chain.

4. Experimental

4.1. 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 argon and degassed before use. Separations were carried out by preparative thin-layer chromatography on glass plates (20 × 20 cm²) coated with silica gel (Merck, 0.5 mm thick).

4.2. Instruments

IR spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in CH₂Cl₂ were obtained using a 0.5 mm path-length solution cell with NaCl windows. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra were recorded on a Varian 2000 instrument (¹H at 300.13 MHz, ¹³C at 75.47 MHz, ³¹P at 121.503 MHz). Unless otherwise stated, samples were dissolved in CDCl₃ contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ¹H and ¹³C NMR spectra and external H₃PO₄ for ³¹P NMR spectra. Electrospray-mass spectra (ES-MS) were obtained from samples dissolved in MeOH unless otherwise indicated. Solutions were injected into a Varian Platform II spectrometer via a 10 ml injection loop. Nitrogen was used as the drying and nebulising gas. Chemical aids to ionisation were used [32]. Electrochemical samples (1 mM) were dissolved in CH₂Cl₂ containing 0.5 M [NBu₄]BF₄ as the supporting electrolyte. Cyclic voltammograms were recorded using a PAR model 263 apparatus, with a saturated calomel electrode, with a Pt-mesh working electrode, Pt wire counter and pseudo-reference electrodes. Ferrocene was used as an internal calibrant (FcCp₂/[FcCp₂]⁺ = +0.46 V). Elemental analyses were by CMAS, Belmont, Vic., Australia.

4.3. Reagents

The compounds FcC≡CC≡CCH=CHCl-*cis* [17d], RuCl(dppe)Cp [33], Co₂(μ-dppm)(CO)₆ [34] and Os₃(CO)₁₀(NCMe)₂ [35] were made by the cited methods.

4.4. Fc(C≡C)₃SiMe₃ (**1**)

cis-FcC≡CC≡CCH=CHCl (1320 mg, 4.47 mmol) was added to a solution of LiN^tPr₂ (9.8 mmol) in dry ether at –78 °C and the mixture was stirred for 4 h. After warming briefly to room temperature, the mixture was again cooled to –78 °C and quenched with an excess of SiClMe₃. Solvent was removed under vacuum and a diethyl ether extract was purified by passage through a pad of silica before removing solvent to give Fc(C≡C)₃SiMe₃ (**1**) as an unstable dark orange oil (1150 mg, 78%). No elemental analysis was possible because of its instability.

IR (nujol): ν(C≡C) 2187s, 2165s, 2070s cm⁻¹. ¹H NMR: δ 0.22 (s, 9H, SiMe₃), 4.26 (s, 5H, Cp), 4.29–4.30, 4.54–4.56 (2 × m, 2 × 2H, C₅H₄). ¹³C NMR: δ –0.48 (SiMe₃), 61.69, 62.68, 64.33, 69.79 (C₅H₄), 70.35 (Cp), 70.78, 72.73, 78.18, 87.69, 88.54. ES-MS (MeOH, positive ion, *m/z*): 330, M⁺; 258, [M–SiMe₃]⁺.

4.5. $\text{Fc}(\text{C}\equiv\text{C})_3\text{Ru}(\text{dppe})\text{Cp}$ (**2**)

A degassed solution of $\text{Fc}(\text{C}\equiv\text{C})_3\text{SiMe}_3$ (1011 mg, 3.04 mmol) in MeOH (50 ml) containing water (0.5 ml) and dbu (1 drop) was added to a stirred mixture of $\text{RuCl}(\text{dppe})\text{Cp}$ (1880 mg, 3.13 mmol) and KF (272 mg, 4.70 mmol). After heating at reflux point for 1 h and cooling, the resulting precipitate was collected, dried in vacuum and purified by column chromatography (basic alumina, benzene) to give $\text{Fc}(\text{C}\equiv\text{C})_3\text{Ru}(\text{dppe})\text{Cp}$ (**2**) (1365 mg, 53%) as a dark orange solid. Anal. Calc. for $\text{C}_{47}\text{H}_{38}\text{FeP}_2\text{Ru}$: C, 68.70; H, 4.66. Found: C, 68.67; H, 4.71%. *M*, 822. IR (nujol): $\nu(\text{C}\equiv\text{C})$ 2108s, 1992s; other bands at 1585w, 1571w cm^{-1} . ^1H NMR (C_6D_6): δ 1.80–2.00, 2.30–2.50 (2 \times m, 2 \times 2H, CH_2), 3.76–3.77, 4.23–4.24 (2 \times m, 2 \times 2H, C_5H_4), 3.93 (s, 5H, Cp–Fe), 4.58 (s, 5H, Cp–Ru), 6.85–7.00, 7.05–7.30, 7.81–7.87 (3 \times m, 7H + 8H + 5H, Ph). ^{13}C NMR: δ 27.40–28.32 (m, 2 \times CH_2), 65.91, 68.17 (C_5H_4), 69.34, 69.69 (Cp–Fe), 70.71, 71.82 (C_5H_4), 74.85, 83.13 (Cp–Ru), 94.40, 123.13 [t, $J(\text{CP})$ 22.0 Hz], 129.47, 131.26–131.47, 133.27–134.48, 135.76–136.78, 141.02–141.79 (5 \times m, Ph). ^{31}P : δ 85.23 (dppe). ES-MS (MeOH + NaOMe, positive ion, *m/z*): 845, $[\text{M}+\text{Na}]^+$.

4.6. Reactions of $\text{Fc}(\text{C}\equiv\text{C})_3\text{Ru}(\text{dppe})\text{Cp}$

(a) *With tcne*. A mixture of $\text{Fc}(\text{C}\equiv\text{C})_3\text{Ru}(\text{dppe})\text{Cp}$ (104 mg, 0.127 mmol) and tcne (19 mg, 0.15 mmol) in dry CH_2Cl_2 (5 ml) was sonicated at r.t. for 8 h. Removal of solvent in vacuum and purification by preparative TLC (CH_2Cl_2) gave $\text{FcC}\equiv\text{CC}\equiv\text{C}\{\text{C}[\text{C}(\text{CN})_2]\}_2\text{Ru}(\text{dppe})\text{Cp}$ (**3**) as a dark blue solid ($R_f = 0.3$; 12 mg, 10%). The baseline material was recovered and extracted several times with diethyl ether and purified by a second TLC (5% acetone- CH_2Cl_2) to give the green cyclobutenyl complex $\text{FcC}\equiv\text{CC}\equiv\text{C}\{\text{C}=\text{CC}(\text{CN})_2\text{C}(\text{CN})_2\}\text{Ru}(\text{dppe})\text{Cp}$ (**4**) ($R_f = 0.3$; 50 mg, 41%).

For **3**: Anal. Calc. for $\text{C}_{53}\text{H}_{38}\text{FeN}_4\text{P}_2\text{Ru}$: C, 67.02; H, 4.03; N, 5.90. Found: C, 67.08; H, 3.93; N, 5.96%. *M*, 950. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{N})$ 2226w, 2207w; $\nu(\text{C}\equiv\text{C})$ 2181s, 2135w; other bands at 1605m, 1502m cm^{-1} . ^1H NMR: δ 2.30–2.50, 2.50–2.70 (2 \times m, 2 \times 2H, CH_2), 4.31 (s, 5H, Cp–Fe), 4.42 [m (br), 2H, C_5H_4], 4.62, 4.66 (2 \times m, 2 \times 1H, C_5H_4), 4.93 (s, 5H, Cp–Ru), 6.63–6.69, 7.12–7.34, 7.50–7.73, 7.97–8.03 (4 \times m, Ph). ^{13}C NMR: δ 26.28–26.96, 29.02–29.67 (2 \times m, CH_2), 60.75 (C_5H_4 ipso), 70.01, 71.01 (Cp–Fe), 71.24, 72.18, 73.24, 73.45 [d, $J(\text{CP})$ 3.2 Hz], 77.20, 81.27, 86.04 (Cp–Ru), 95.72 [d, $J(\text{CP})$ 6.8 Hz], 96.87, 97.39, 111.93, 112.36, 112.88, 118.12 (4 \times CN), 127.78–128.24, 128.64–128.76, 130.54, 131.26–131.74 (4 \times m, Ph), 134.52, 135.03, 136.13, 136.72, 140.07, 140.49, 163.63 (C=C). ^{31}P NMR: δ 66.4 [d, $J(\text{PP})$ 22.2 Hz], 81.8 [d, $J(\text{PP})$ 22.2 Hz]. ES-MS (MeOH + NaOMe, positive ion, *m/z*): 973, $[\text{M}+\text{Na}]^+$.

For **4**: Anal. Calc. for $\text{C}_{53}\text{H}_{38}\text{FeN}_4\text{P}_2\text{Ru}$: C, 67.02; H, 4.03; N, 5.90. Found: C, 66.94; H, 3.97; N, 6.02%. *M*, 950. IR (nujol): $\nu(\text{C}\equiv\text{N})$ 2208m; $\nu(\text{C}\equiv\text{C})$ 2163s, 1978vs;

other bands at 1584w, 1573w, 1537m (sh), 1531m cm^{-1} . ^1H NMR: δ 2.40–2.65, 2.85–3.10 (2 \times m, 2 \times 2H, 2 \times CH_2), 4.37 (s, 5H, Cp–Fe), 4.60, 4.69 (2 \times m, 2 \times 2H, C_5H_4), 5.02 (s, 5H, Cp–Ru), 7.20–7.26, 7.33–7.43, 7.68–7.72 (3 \times m, 4H + 12H + 4H, Ph). ^{13}C NMR: δ 28.42–28.73 (m, CH_2), 60.56 (Fc ipso), 71.21 (Cp–Fe), 72.25, 73.40 (2 \times C_5H_4), 84.43, 86.57 [2 \times C(sp³) of cyclobutene], 86.26 (Cp–Ru), 112.07, 113.88, 115.42, 116.54, 119.77 (4 \times CN + C), 128.04–128.43, 129.71, 130.29, 130.94–131.08, 133.46–133.60 (6 \times m, Ph), 134.89–134.23, 139.80–140.35 (2 \times m), 148.92 (C=C). ^{31}P NMR: δ 85.4 (dppe). ES-MS (MeOH, positive ion, *m/z*): 973, $[\text{M}+\text{Na}]^+$.

(b) *With $\text{Co}_2(\text{CO})_8$* . A solution of $\text{Fc}(\text{C}\equiv\text{C})_3\text{Ru}(\text{dppe})\text{Cp}$ (35 mg, 0.043 mmol) and $\text{Co}_2(\text{CO})_8$ (135 mg, 0.38 mmol) in dry thf (5 ml) was stirred overnight. After removal of solvent in vacuum, the residue was purified by preparative TLC (hexane/acetone 2/1) to give $\text{Fc}\{\text{C}_2[\text{Co}_2(\text{CO})_6]\}_2\text{C}\equiv\text{CRu}(\text{dppe})\text{Cp}$ (**5**) as a dark purple solid (39 mg, 65%). Anal. Calc. for $\text{C}_{59}\text{H}_{38}\text{Co}_4\text{FeO}_{12}\text{P}_2\text{Ru}$: C, 50.85; H, 2.75. Found: C, 50.96; H, 2.69%. *M*, 1394. IR (CH_2Cl_2): $\nu(\text{CO})$ 2091w, 2070m, 2051s, 2044s (sh), 2023s (sh), 2011s; other band at 1435w cm^{-1} . ^1H NMR: δ 2.56, 2.78 [2 \times s (br), 2 \times 2H, CH_2], 4.22 [s (br), 5H, Cp–Fe], 4.40, 4.66 [2 \times s (br), 2 \times 2H, C_5H_4], 4.80 (br s, 5H, Cp–Ru), 7.02–7.30, 7.76 (2 \times m, 16H + 4H, Ph). ^{13}C NMR: δ 26.90–28.12 (m, CH_2), 68.35, 71.36 (2 \times m, C_5H_4), 69.74 (s, Cp–Fe), 83.68 (s, Cp–Ru), 88.09, 88.64, 89.39, 98.30, 98.88, 108.87, 127.90–128.17, 128.75, 131.06–131.12, 133.58–133.72, 136.19–136.87, 141.87–142.40 (6 \times m, Ph), 156.74 [t, J 24.0 Hz, C_x], 199.57 (CO). ^{31}P NMR: δ 86.79 (dppe). ES-MS (MeOH, positive ion, *m/z*): 1417, $[\text{M}+\text{Na}]^+$; 1394, M^+ .

(c) *With $\text{Co}_2(\mu\text{-dppm})(\text{CO})_6$* . A solution of $\text{Fc}(\text{C}\equiv\text{C})_3\text{Ru}(\text{dppe})\text{Cp}$ (38 mg, 0.046 mmol) and $\text{Co}_2(\mu\text{-dppm})(\text{CO})_6$ (39 mg, 0.58 mmol) in dry thf (20 ml) was heated at reflux point overnight. After removal of solvent under vacuum, preparative TLC of the residue (hexane/acetone 3/2) afforded the mono adduct $\text{FcC}_2\{\text{Co}_2(\mu\text{-dppm})(\text{CO})_4\}\text{C}\equiv\text{CC}\equiv\text{CRu}(\text{dppe})\text{Cp}$ (**6**) as a brown solid (60 mg, 91%). Anal. Calc. for $\text{C}_{76}\text{H}_{60}\text{Co}_2\text{FeO}_4\text{P}_4\text{Ru}$: C, 63.57; H, 4.21. Found: C, 63.41; H, 4.09%. *M*, 1436. IR (CH_2Cl_2): $\nu(\text{CC})$ 2113w; $\nu(\text{CO})$ 2009m, 1992s, 1964m, 1945w; other band at 1435w cm^{-1} . ^1H NMR: δ 1.95–2.15, 2.60–2.80 (2 \times m, 2 \times 2H, 2 \times CH_2 of dppe), 2.95–3.15, 3.70–3.85 (2 \times m, 2 \times 1H, CH_2 of dppm), 4.16 (m, 2H, C_5H_4), 4.41 (s, 5H, Cp–Fe), 4.71 (m, 7H, C_5H_4 + Cp–Ru), 6.77–7.27, 7.53, 7.91–7.97 (3 \times m, 31H + 5H + 4H, Ph). ^{13}C NMR: δ 27.95–28.56 (m, 2 \times CH_2 of dppe), 31.42 [t, $J(\text{CP})$ 21.6 Hz, CH_2 of dppm], 63.48, 67.63, 69.71 (2 \times s, C_5H_4), 69.30 (s, Cp–Fe), 77.21, 83.25 (Cp–Ru), 91.02, 91.74 [t, $J(\text{CP})$ 2.6 Hz], 96.25, 125.99 [t, $J(\text{CP})$ 24.8 Hz, C_a], 127.80–128.13, 128.64, 128.97, 129.46–129.52, 130.98–131.14, 131.41–131.55, 132.71–132.91, 136.11–136.79, 141.62–142.13 (8 \times m, Ph), 134.37 [t, $J(\text{CP})$ 15.9 Hz], 138.60 [t, $J(\text{CP})$ 23.6 Hz], 202.22 (CO), 206.68 (CO). ^{31}P NMR: δ 9.5 (dppm), 85.5 (dppe). ES-MS (MeOH, positive ion, *m/z*): 1436, M^+ .

(d) With $Os_3(CO)_{10}(NCMe)_2$. A mixture of $Fc(C\equiv C)_3Ru(dppe)Cp$ (50 mg, 0.061 mmol) and $Os_3(CO)_{10}(NCMe)_2$ (57 mg, 0.061 mmol) in dry thf (10 ml) was stirred at r.t. for 1 h. After removal of solvent under vacuum, the residue was purified by preparative TLC (acetone/hexane 2/1) to give the major dark red band ($R_f = 0.63$) containing $Os_3\{\mu_3-FcC_2C\equiv CC\equiv C[Ru(dppe)Cp]\}(CO)_{10}$ (**7**) (25 mg, 25%) as a purple crystalline solid (CH_2Cl_2 /hexane). Anal. Calc. for $C_{57}H_{38}FeO_{10}Os_3P_2Ru$: C, 40.94; H, 2.29. Found: C, 40.97; H, 2.32%. M , 1673. IR (CH_2Cl_2): $\nu(CC)$ 2128w (br); $\nu(CO)$ 2092m, 2062vs, 2050s, 2019m, 2000m, 1821w (br) cm^{-1} . 1H NMR (C_6D_6): δ 1.90–2.10, 2.40–2.60 (2 \times m, 2 \times 2H, CH_2), 4.00, 4.27 (2 \times m, 2 \times 2H, C_5H_4), 4.23 (s, 5H, Cp–Fe), 4.60 (s, 5H, Cp–Ru), 6.94, 7.12–7.16, 7.22–7.27, 7.31–7.36, 7.85–7.90 (5 \times m, 6H + 4H + 2H + 4H + 4H, Ph). ^{13}C NMR (C_6D_6): δ 28.04–28.96 (m, CH_2), 53.66, 70.41, 70.77 [2 \times m (br), C_5H_4], 70.51 (Cp–Fe), 83.95 (Cp–Ru), 90.18, 95.54, 99.09, 104.23, 129.23, 129.52, 132.18–132.32, 134.33–134.47, 135.06–135.29, 136.97–137.65, 142.19–142.83 (7 \times m, Ph), 152.91, 179.16 (br, CO). ^{31}P NMR (C_6D_6): δ 85.6 (dppe). ES-MS (MeOH + NaOMe, negative ion, m/z): 1704, $[M+OMe]^-$.

Isomerisation of 7. A sample of $Os_3\{\mu_3-FcC_2C\equiv CC\equiv C[Ru(dppe)Cp]\}(CO)_{10}$ (45 mg, 0.027 mmol) was dissolved in $CDCl_3$ (3 ml) and stirred for 2 d at r.t. After removal of solvent, the residue was purified by preparative TLC (hexane/acetone 2/1) to give a major brown fraction, tentatively identified as $Os_3(\mu-H)\{\mu_3-CpFe(\eta-C_5H_3)CCHC\equiv CC\equiv C[Ru(dppe)Cp]\}(CO)_8$ (**8**) (27 mg, 60%), obtained as a brown crystalline solid. Anal. Calc. for $C_{56}H_{38}FeO_9Os_3P_2Ru$: C, 40.94; H, 2.29. Found: C, 39.97; H, 1.82%. M , 1645. IR (CH_2Cl_2): $\nu(CO)$ 2092w, 2054vs,

2015m, 1992w, 1990w (sh), 1815 vw (br) cm^{-1} . 1H NMR (C_6D_6): δ 2.14–2.28, 2.61–2.73 (2 \times m, 2 \times 2H, CH_2), 3.72 (dd, J 2.4, 2.4 Hz, 1H, C_5H_3), 3.78 (s, 5H, Cp–Fe), 4.16 (dd, J 2.4, 1.2 Hz, 1H, C_5H_3), 4.26 (dd, J 2.4, 1.2 Hz, C_5H_3), 4.72 (s, 5H, Cp–Ru), 6.29 (s, 1H), 6.93–6.96, 7.12–7.36, 7.96–8.01 (3 \times m, 4H + 12H + 4H, Ph). ^{13}C NMR: δ 27.96–28.76 (m, CH_2), 64.25, 66.75, 67.61 (3 \times m, C_5H_3), 69.19 (Cp–Fe), 77.21, 82.88 [t, $J(CP)$ 2.2, Cp–Ru], 83.78, 101.51, 109.84, 127.88–128.06, 128.39, 128.78, 129.66–129.78, 130.89–131.13, 131.40, 132.38, 134.33–134.67, 136.20, 136.35, 136.86, 141.17, 142.56–143.00 (5 \times m, Ph), 179.39 (CO). ^{31}P NMR: δ 88.3 (d, J 4.6), 88.5 (d, J 4.6) (AB quartet) (dppe). ES-MS (MeOH + NaOMe, m/z): 1645, M^+ .

4.7. Structure determinations

Full spheres of diffraction data were measured at *ca* 153 K using a Bruker AXS CCD area-detector instrument. N_{tot} reflections were merged to N unique (R_{int} cited) after “empirical”/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being used in the full-matrix least-squares refinements. All data were measured using monochromatic Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, (x, y, z, U_{iso})_H being included, constrained at estimates. Conventional residuals R , R_w on F^2 are quoted [weights: $(\sigma^2(F^2) + n_w F^2)^{-1}$]. Neutral atom complex scattering factors were used; computation used the XTAL-3.7 program system [36]. Pertinent results are given in the Figures (which show non-hydrogen atoms with 50% probability amplitude displacement envelopes and hydrogen atoms with arbitrary radii of 0.1 \AA) and in Tables 1

Table 2
Crystal data and refinement details

Complex	2	4	6^a	7
Formula	$C_{47}H_{38}FeP_2Ru \cdot C_6H_6$	$C_{53}H_{38}FeN_4P_2Ru \cdot CH_2Cl_2$	$C_{76}H_{60}Co_2FeO_4P_4Ru$	$C_{57}H_{38}FeO_{10}Os_3P_2Ru \cdot CH_2Cl_2$
Molecular weight	899.80	1034.74	1435.99	1757.34
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a (\AA)	9.964(2)	11.073(4)	18.240(3)	9.282(4)
b (\AA)	15.347(3)	22.688(8)	17.820(1)	16.710(7)
c (\AA)	27.876(4)	17.649(6)	21.315(2)	19.255(8)
α ($^\circ$)				74.878(10)
β ($^\circ$)	96.643(3)	94.581(7)	107.333(6)	89.834(10)
γ ($^\circ$)				74.479(10)
V (\AA^3)	4234	4420	6614	2771
Z	4	4	4	2
ρ_{calc} ($Mg \text{ m}^{-3}$)	1.412	1.555	1.442	2.106
$2\theta_{max}$ ($^\circ$)	53	50	42	65
μ (Mo $K\alpha$) (mm^{-1})	0.81	0.91	0.37	7.6
$T_{min/max}$	0.79	0.78	0.82	0.57
Crystal dimensions (mm)	$0.35 \times 0.24 \times 0.18$	$0.12 \times 0.10 \times 0.04$	$0.11 \times 0.04 \times 0.02$	$0.32 \times 0.10 \times 0.08$
N_{total}	16511	32944	185506	42819
N (R_{int})	7503 (0.047)	7758 (0.17)	22806 (0.079)	20215 (0.046)
N_{total}	5710	5031	15044	13867
R	0.045	0.096	0.075	0.058
R_w	0.055	0.196	0.140	0.094

^a Data were measured using synchrotron radiation, $\lambda = 0.48595 \text{ \AA}$.

and 2. In 7, the CH_2Cl_2 was modelled as disordered over two sets of sites, occupancies refining to 0.703(8) and complement.

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Appendix A. Supplementary material

Full details of the structure determinations (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre. CCDC 620037, 620038, 620039 and 620040 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.02.043](https://doi.org/10.1016/j.jorganchem.2007.02.043).

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