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Journal of Organometallic Chemistry 604 (2000) 150–156

Journal of Organometallic Chemistry

Syntheses and reactions of ruthenium complexes containing C_6 and C_8 chains

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Received 21 February 2000; received in revised form 13 March 2000

Abstract

Reactions of $\{Cp(Ph_3P)_2Ru\}_2\{\mu\text{-}(C{\equiv}C)_n\}$ ($n = 3, 4$) with $C_2(CN)_4$, dicobalt carbonyls and $Fe_2(CO)_9$ are described. For $n = 3$, the central C≡C triple bond is attacked by the metal carbonyls, giving $\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}C{\equiv}CC_2[Co_2(CO)_6]C{\equiv}C\}$ (**4**), $\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}C{\equiv}CC_2[Co_2(\mu\text{-dppm})(CO)_4]C{\equiv}C\}$ (**5**) and $Fe_3\{\mu_3\text{-}CC{\equiv}C[Ru(PPh_3)_2Cp]\}_2(CO)_9$ (**7**). For $n = 4$, the first bis-adduct with tcne is described, while the metal carbonyls gave $\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}C{\equiv}CC_2[Co_2(\mu\text{-dppm})(CO)_4]C{\equiv}CC{\equiv}C\}$ (**6**) and $Fe_3\{\mu_3\text{-}CC{\equiv}C[Ru(PPh_3)_2Cp]\}\{\mu_3\text{-}CC{\equiv}CC{\equiv}C[Ru(PPh_3)_2Cp]\}(CO)_9$ (**8**). While the usual bending of the carbon chain is found in the dicobalt complexes, reactions with the iron carbonyl result in cleavage of a C≡C triple bond to give CFe_3C clusters. The molecular structures of **4** and **7** have been determined. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Cobalt; Tcne; Iron; C_6,C_8 chains

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1. Introduction

The chemistry of metal complexes containing alkynyl, diynyl and higher poly-ynyl ligands is the scene of intense interest at present, one reason being the unusual electronic, magnetic and optical properties and reasonable non-linear optical properties which have been demonstrated for some of these compounds [1,2]. While the synthetic challenge associated with the preparation of compounds containing long chains of sp-hybridised carbon atoms joining two metal centres has been approached by several groups [3–7], there are still relatively few examples of complexes containing C_6 or C_8 chains [8]. Recently, we described a method for preparing compounds of this type containing ruthenium centres, in which silylated poly-ynes react with $RuCl(PPh_3)_2Cp$ in the presence of KF [9]. The chemistry of the resulting complexes has been explored briefly in their reactions with electrophilic (or ynophilic) reagents, such as tetracyanoethene (tcne) or $Co_2(CO)_8$. This paper describes the synthesis and characterisation of $\{Cp(Ph_3P)_2Ru\}_2\{\mu\text{-}(C{\equiv}C)_n\}$ ($n = 4$) and the reactions of the triyndiyl ($n = 3$) and tetrayndiyl complexes with tetracyanoethene, cobalt carbonyls and $Fe_2(CO)_9$, the latter reactions leading to triiron clusters containing alkynylmethylidyne ligands formed by cleavage of one of the C≡C triple bonds (Schemes 1 and 2). Similar reactions have been described by Akita and co-workers, who used complexes containing the $Fe(CO)_2Cp^*$ end-capping group [10].

2. Results and discussion

2.1. Syntheses of $\{Cp(Ph_3P)_2Ru\}_2\{\mu\text{-}(C{\equiv}C)_n\}$ [$n = 3$ (*1*), 4 (*2*)]

The synthesis of **1** was described in a previous publication [7] and a similar reaction between $Me_3Si(C{\equiv}C)_4$-$SiMe_3$ and $RuCl(PPh_3)_2Cp$ was carried out in refluxing MeOH to give the analogous complex $\{Cp(Ph_3P)_2$-$Ru\}_2\{\mu(C{\equiv}C)_4\}$ (**2**), which was obtained as an orange powder. The compound was characterised by elemental analysis and from its spectroscopic properties. The band due to $\nu(C{\equiv}C)$ is found at 2110 cm^{-1}, while the ^{1}H-NMR spectrum contained a singlet resonance for

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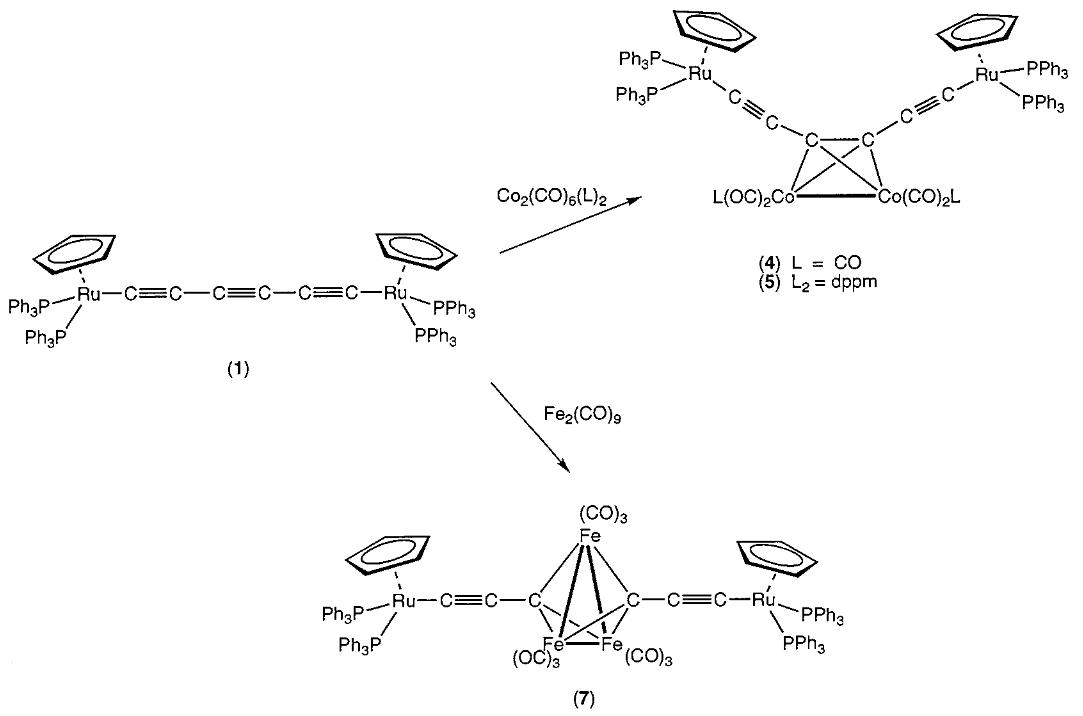
PII: S0022-328X(00)00191-1



Scheme 1.

the Cp protons at δ 4.30 (cf. δ 4.29 in **1**) and the Ph multiplet between δ 7.12 and 7.40. The electrospray (ES) mass spectrum contains M^+ at *m*/*z* 1478 and fragment ions formed loss of PPh_3 groups at *m*/*z* 1216 and 954.

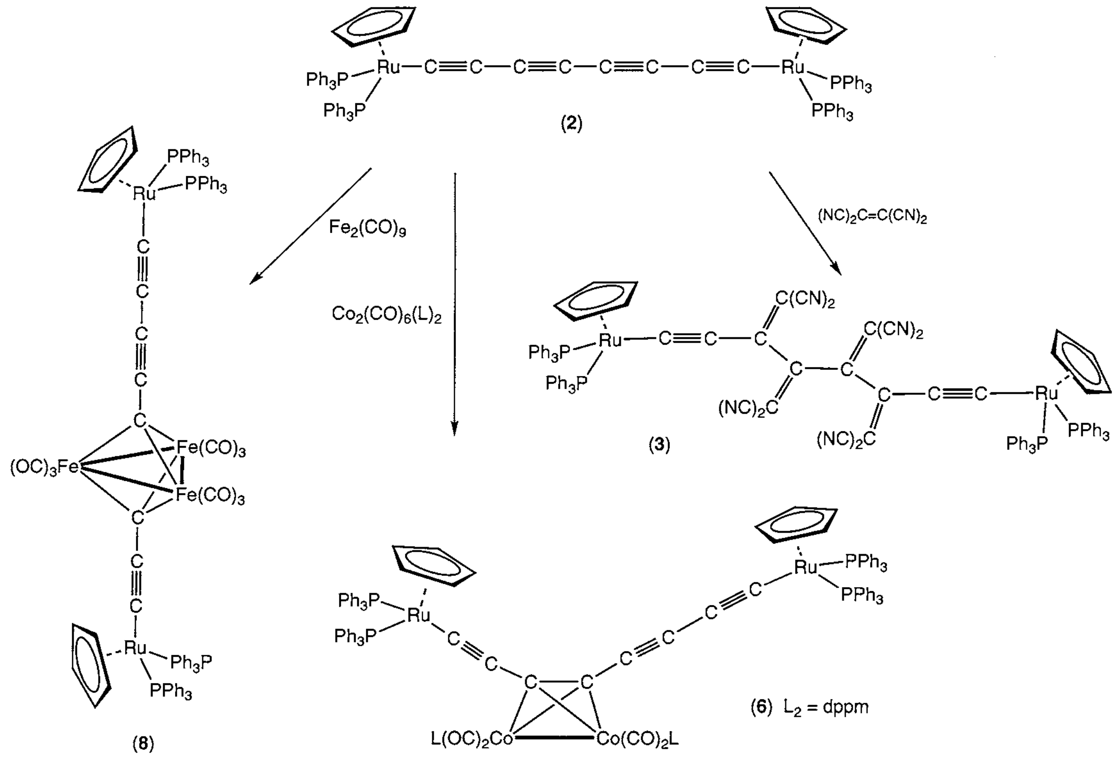
2.2. Reaction of **2** with $C_2(CN)_4$

Complex **2** reacts readily with tcne to give a dark red–brown crystalline compound characterised by elemental analysis and spectroscopy as the bis-adduct, which we formulate as $\{Cp(Ph_3P)_2Ru\}_2\{\mu\text{-}C{\equiv}CC[{=}C(CN)_2]C[{=}C(CN)_2]C[{=}C(CN)_2]C[{=}C(CN)_2]C{\equiv}C\}$ (**3**). In the IR spectrum single ν(CN) and ν(C≡C) bands are found at 2215 and 1954 cm^{-1}, respectively, while the ^1H-NMR spectrum contains only a singlet at δ 4.74 for the Cp protons and the Ph multiplet at δ 7.18–7.37. The ^{13}C-NMR spectrum contained resonances assigned to Cp (δ 89.20), CN (δ 109.83, 110.78, 115.24, 115.78) and the dicyanomethylene carbons (δ 81.57, 93.30). No resonances were observed for C_α. In the ES mass spectrum, the molecular ion is at *m*/*z* 1734. This is the first example of a bis-tcne adduct of a $M–C_n–M$ complex. That the bis-adduct is formed by addition to the C≡C triple bonds far from the ruthenium atoms is supported by a single ν(C≡C) band and the lack of further reaction to form the η^3-dienyl complex, and is favoured on steric grounds.

2.3. Reactions with cobalt carbonyls

Reactions of **1** with $Co_2(CO)_8$ or $Co_2(\mu\text{-dppm})(CO)_6$ afforded green $\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}C{\equiv}CC_2[Co_2(CO)_6]\text{-}C{\equiv}C\}$ (**4**) and brown $\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}C{\equiv}CC_2[Co_2(\mu\text{-dppm})(CO)_4]C{\equiv}C\}$ (**5**), respectively. While **4** was identified by elemental analyses and spectroscopically, a satisfactory microanalysis could not be obtained for **5**. The ES mass spectra contained ions at *m*/*z* 1763 (**4**; $[M+Na]^+$) and 2068 (**5**; M^+), while the ^1H-NMR spectra contained singlets at δ 4.35 (**4**) and 4.10 (**5**), together with two CH_2 multiplets at δ 3.49 and 4.28 for the dppm ligand in **5**. The single Cp resonance observed each case indicates that the dicobalt carbonyl is attached to the central C≡C triple bond. The molecular structure of **4** has been confirmed by, a single-crystal X-ray study.

With **2**, a reaction with $Co_2(\mu\text{-dppm})(CO)_6$ gave black crystals of $\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}C{\equiv}CC_2[Co_2(\mu\text{-dppm})(CO)_4]C{\equiv}CC{\equiv}C\}$ (**6**), whose asymmetric structure is suggested by the appearance of two Cp singlets at δ 4.33 and 4.44, together with the CH_2 multiplets at δ 3.20 and 3.85. The ES mass spectrum contains the molecular ion at *m*/*z* 2092, while in addition to a weak ν(C≡C) band at 2119 cm^{-1}, several terminal ν(CO) absorptions are found between 2040 and 1946 cm^{-1} in the IR spectrum. The choice of the C≡C triple bond for coordination of the dicobalt moiety is probably governed by steric factors and we propose that **6** has the structure shown.



Scheme 2.

2.4. Reactions with $Fe_2(CO)_9$

Reactions of **1** and **2** with $Fe_2(CO)_9$, were carried out in refluxing THF for a short period. Conventional work-up by TLC. (silica gel) gave cherry-red solids in both cases, characterised as $Fe_3\{\mu_3\text{-CC}{\equiv}\text{C[Ru(PPh}_3\text{),Cp]}\}_2(CO)_9$ (**7**) and $Fe_3\{\mu_3\text{-CC}{\equiv}\text{C[Ru(PPh}_3)_2\text{Cp]}\}$ $\{\mu_3\text{-CC}{\equiv}\text{CC}{\equiv}\text{C[Ru(PPh}_3)_2\text{Cp]}\}(CO)_9$ (**8**), respectively. The molecular structure of **7** has been determined from an X-ray study. Both complexes give molecular ions in their ES mass spectra at *m/z* 1874 and 1898, respectively; fragmentation occurs by stepwise loss of up to nine CO groups. For **7**, singlet resonances for the Cp groups are found at δ_H 4.49 and δ_C 86.84, whereas for **8**, two pairs of Cp singlets are at δ_H 4.67 and 4.78 and at δ_C 86.27 and 87.09. In the ^{13}C-NMR spectra, the Fe–CO resonances are at δ 212.89 (**7**) and 211.56 (**8**). Other resonances are assigned to the carbons of the C_n chain: C_α at δ 178.94 (**7**) and at 160.21 and 191.50 (**8**) show triplet *J*(CP) couplings. Of the others, low-field resonances at δ 266.29 (**7**) and 260.06 and 275.35 (**8**) can be assigned to the alkylidyne carbons attached to the Fe_3 clusters.

Cleavage of C≡C triple bonds by organometallic centres of varying nuclearity is a well known reaction, several examples involving polynuclear complexes of iron [11], cobalt [12], rhodium [13] and iridium [13] having been described. In some cases, the reactions can be reversed [11a]. In the case of trinuclear metal clusters, the reaction appears to proceed either directly on the cluster or by pre-assembly of such a cluster from mononuclear fragments. A theoretical analysis suggests that any intermediate unsaturated alkyne complex, such as Cp_3M(alkyne) (M = Co, Rh, Ir), has a higher energy than similar saturated intermediates. As has been pointed out earlier [10], the present reaction possibly proceeds via an unsaturated tetrahedral intermediate formed by addition of the iron carbonyl to the C≡C triple bond, so that the presence of electron-rich metal fragments at each end of the carbon chain serves to stabilise the postulated intermediate.

2.5. Molecular structures of $\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-C}{\equiv}\text{CC}_2[Co_2(CO)_6]\text{C}{\equiv}\text{C}\}$ (4) and $Fe_3\{\mu\text{-CC}{\equiv}\text{C[Ru(PPh}_3)_2\text{Cp]}\}_2(CO)_9$ (7)

Plots of molecules of **4** and **7** are given in Figs. 1 and 2 with selected bond parameters for both complexes summarised in Table 1. The $Ru(PPh_3)_2Cp$ fragments are broadly similar and resemble those found in many other related derivatives, with Ru–P distances between 2.282(4) and 2.304(3) Å, average Ru–C(Cp) distances of 2.23–2.25 Å, with angles at Ru subtended by the P atoms between 97.6(1) and 102.02(3)° and P–Ru–C angles of 85.7–94.9(4)°. The Ru–C bonds are 1.99(1) and 2.009(9) Å. Similarly, the $Co_2(CO)_6$ fragment in **4** has a Co–Co separation of 2.4850(7) Å and Co–C bonds of 1.986 and 2.006(3) Å. Coordination of the

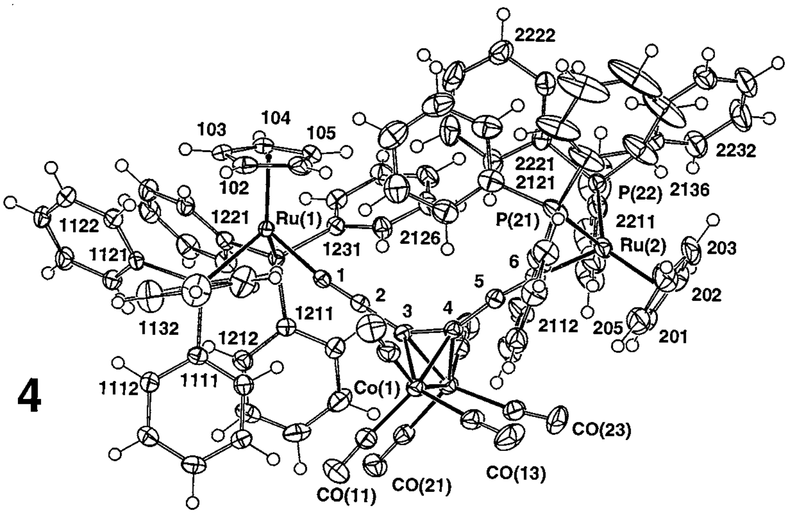


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Fig. 1. Plot of a molecule of $\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}C{\equiv}CC_2[Co_2(CO)_6]C{\equiv}C\}$ (**4**), showing atom numbering scheme. Carbon atoms are denoted by number only. In this and Fig. 2, non-hydrogen atoms are shown as 50% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0 1 Å.

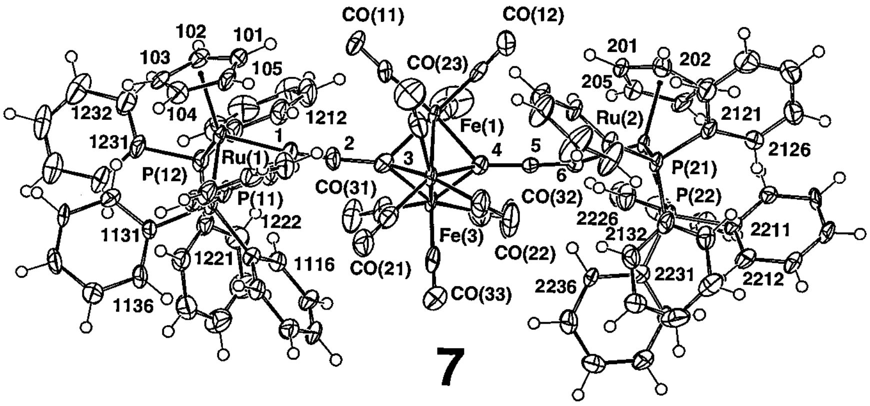

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Fig. 2. Plot of a molecule of $Fe_3\{\mu_3\text{-}CC{\equiv}C[Ru(PPh_3)_2Cp]\}_2(CO)_9$ (**7**), showing atom numbering scheme.

$Co_2(CO)_6$ fragment causes the expected bending of the carbon chain, with angles C(2)–C(3)–C(4) and C(3)–C(4)–C(5) being 144.1 and 148.3(3)°, respectively. The other parts of the chain are close to linear, with angles at the carbon atoms of between 171.8 and 177.5(3)°. The C–C distances alternate between conjugated single [C(2)–C(3) 1.402(4), C(4)–C(5) 1.391(4) Å] and triple bonds [C(1)–C(2) 1.217(4), C(5)–C(6) 1.214(4) Å].

In **7**, the triangular Fe_3 core has Fe–Fe separations between 2.500 and 2.535(13) Å. There is rotational disorder of the core with a minor component [occupancy 0.138(2)] being refined, although associated light atoms could not be resolved. Each face of the Fe_3 cluster is capped by a μ_3-C atom, with Fe–C separations being between 1.96 and 1.99(1) Å. The reaction of **2** with $Fe_2(CO)_9$ has resulted in cleavage of the C(3)–C(4) bond [separation through the cluster 2.67(1) Å] while present in the C≡C triple bonds between atoms C(1) and C(2) [1.21(1) Å] and between C(5) and C(6) [1.22(1) Å]. Conjugated single bonds separate atoms C(2)–C(3) and C(4)–C(5) [both 1.41(1) Å]. Angles at the sp-carbons range between 165 and 177(1)°, the greatest deviations from linearity being found in the Ru–C≡C moieties.

3. Conclusions

The results described above encompass the synthesis of a new example of a C_8 chain capped by two ruthenium fragments and the reactions of this complex and its C_6 analogue with tcne, dicobalt carbonyls and $Fe_2(CO)_9$. The products show that addition to the carbon chain is controlled sterically, with the product from **2** and tcne being the first example of such a chain adding two tcne molecules. Addition of dicobalt carbonyls occurs at the central C≡C triple bonds, as confirmed by the structural determination of **4**. Reaction with $Fe_2(CO)_9$ generates a CFe_3C cluster by cleavage of one of the central C≡C triple bonds, as also found recently, with related complexes $\{Cp^*(OC)_2Fe\}_2\{\mu$-

Table 1
Selected bond parameters for $\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}C{\equiv}CC_2[Co_2(CO)_6]\text{-}C{\equiv}C\}$ (**4**) and $Fe_3\{\mu_3\text{-}CC{\equiv}C[Ru(PPh_3)_2Cp]\}_2(CO)_9$ (**7**)

	4	**7**
Bond distances (Å)		
Ru(1)–P(11,12)	2.2894, 2.2928(9)	2.286, 2.282(4)
Ru(2)–P(21,22)	2.299, 2.282(1)	2.304, 2.294(3)
Ru–C(Cp)	2.227–2.279(3)	2.20–2.26(1)
(av.)	2.246	2.24
Ru(1)–C1)	2.001 (3)	2.009(9)
Ru(2)–C(6)	1.995 (3)	1.99(1)
Co(1)–Co(2)	2.4850(7)	
Co(1)–C(3,4)	2.006, 1.986 (3)	
Co(2)–C(3,4)	1.992, 1.991 (3)	
Fe(1)–Fe(2)		2.535(3)
Fe(1)–Fe(3)		2.508(3)
Fe(2)–Fe(3)		2.500(3)
Fe(1)–C(3,4)		1.99, 1.96(1)
Fe(2)–C(3,4)		1.97, 1.96(1)
Fe(3)–C(3,4)		1.96, 1.98(1)
C(1)–C(2)	1.217(4)	1.21(1)
C(2)–C(3)	1.402(4)	1.41(1)
C(3)–C(4)	1.350(4)	[2.67(1)]
C(4)–C(5)	1.391(4)	1.41(1)
C(5)–C(6)	1.214(4)	1.22(1)
Bond angles (°)		
P(11)–Ru(1)–P(12)	102.02(3)	101.3(1)
P(21)–Ru(2)–P(22)	100.53(4)	97.6(1)
P(11, 12)–Ru(l)–C(I)	91.46, 89.44(9)	85.7, 94.9(4)
P(21, 22)–Ru(2)–C(6)	86.6, 88.5(1)	92.9, 94.3(4)
Ru(1)–C(1)–C(2)	171.7(2)	172(1)
C(1)–C(2)–C(3)	177.5(3)	177(2)
C(2)–C(3)–C(4)	144.1(3)	
C(3)–C(4)–C(5)	148.3(3)	
C(4)–C(5)–C(6)	171.8(3)	177(1)
C(5)–C(6)–Ru(2)	174.9(3)	165(1)

$(C{\equiv}C)_n\}$ ($n = 3$, 4) [10]. While in the latter series, complexes with shorter carbon chains ($n = 1$, 2) react with $Fe_2(CO)_9$ in different ways, we have found that similar reactions do not occur with the ruthenium series. In addition, the complex $\{Cp(OC)_3W\}_2\{\mu\text{-}(C{\equiv}C)_4\}$ does not react with $Fe_2(CO)_9$ under similar conditions to those described here, suggesting that the presence of an electron-rich metal centre is necessary for C≡C bond cleavage to occur. Akita and co-workers [8] have attributed this feature to the necessity to stabilise a first-formed electron-deficient C_2Fe_2 intermediate.

4. Experimental

General experimental and instrumental facilities have been described in [7].

$RuCl(PPh_3)_2Cp$ [14], $\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}(C{\equiv}C)_3\}$ (**1**) [9], and $Me_3Si(C{\equiv}C)_nSiMe_3$ ($n = 3$ [15], 4 [16]) were made by the cited methods.

4.1. $\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}(C{\equiv}C)_4\}$ (**2**)

A stirred mixture of $RuCl(PPh_3)_2Cp$ (500 mg, 0.69 mmol), $Me_3Si(C{\equiv}C)_4SiMe_3$ (165 mg, 0.69 mmol) and KF (80 mg, 1.38 mmol) in MeOH (20 ml) was refluxed for 30 min. After cooling, the resulting brown precipitate was filtered, washed with cold hexane, then dried. The solid was dissolved in CH_2Cl_2 (10 ml) and passed through a column of basic alumina, eluting with acetone–hexane (1:5). The orange fraction was concentrated (to ca. 10 ml) and cooled; the resulting precipitate was filtered and washed with cold hexane to give $\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}(C{\equiv}C)_4\}$ as an orange powder (307 mg, 60%). Found: C, 70.14; H, 4.60. $C_{90}H_{70}P_4Ru_2 \cdot CH_2Cl_2$ (one equivalent of CH_2Cl_2 was found by ^{1}H-NMR) requires: C, 69.94; H, 4.64%; M, 1478. IR (CH_2Cl_2): ν(C≡C) 2110 s, 1956 m cm^{-1}. ^{1}H-NMR: δ 4.30 (s, 10H. Cp), 5.29 (s, 2H, CH_2Cl_2) 7.12–7.40 (m, 60H, Ph). ES mass spectrum (CH_2Cl_2–MeOH, with NaOMe, m/z): 1501, $[M + Na]^+$; 1478, $[M]^+$; 1216, $[M - PPh_3]^+$; 954, $[M - 2PPh_3]^+$.

4.2. $\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}C{\equiv}CC[{=}C(CN)_2]C\text{-}[{=}C(CN)_2]C[{=}C(CN)_2]C[{=}C(CN)_2]C{\equiv}C\}$ (**3**)

A mixture of **2** (200 mg, 0.135 mmol) and tcne (43 mg, 0.390 mmol) in CH_2Cl_2, (30 ml) was stirred at room temperature (r.t.) for 3 h. The mixture was then concentrated under reduced pressure and purified by TLC (silica gel; acetone–hexane 4:6, R_f 0.3–0.5). Crystallisation from CH_2Cl_2–pentane afforded $\{Ru(PPh_3)_2\text{-}Cp\}_2\{\mu\text{-}C{\equiv}CC[{=}C(CN)_2]C[{=}C(CN)_2]C[{=}C(CN)_2]C[{=}C\text{-}(CN)_2]C{\equiv}C\}$ (**3**) as dark red–brown crystals (90 mg, 38%). Found: C, 70.64; H, 4.50; N, 6.17. $C_{102}H_{70}N_8\text{-}P_4Ru_2$, requires: C, 70.65; H, 4.07; N, 6.46%; M, 1606. IR (CH_2Cl_2): ν(CN) 2215 w, ν(C≡C) 1954 vs cm^{-1}.^{1}H-NMR: δ 4.14 (s, 10H, Cp), 7.18–7.35 (m, 60H, Ph). ^{13}C-NMR: δ 158.04 (C_β), 127.93–136.81 (m, Ph), 109.83, 110.78, 115.24, 115.78 (CN), 81.57, 93.30 $[C(CN)_2]$, 89.20 (Cp) (C_α was not found). ES mass spectrum (CH_2Cl_2–MeOH, with NaOMe, m/z): 1757, $[M + Na]^+$; 1734, $[M]^+$.

4.3. $\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}C{\equiv}CC_2[Co_2(CO)_6]C{\equiv}C\}$ (**4**)

A mixture of **1** (70 mg, 0.048 mmol) and $Co_2(CO)_8$ (65 mg, 0.190 mmol) in benzene (20 ml) was stirred for 1 h. The mixture was concentrated under reduced pressure and the resulting black residue extracted with CH_2Cl_2 and purified by TLC (silica gel; acetone–hexane 1:4, R_f 0.3–0.6) giving $\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}C{\equiv}CC_2[Co_2(CO)_6]C{\equiv}C\}$ (**4**) as a green solid (47 mg, 56%). X-ray quality crystals were grown from CH_2Cl_2–pentane. Found: C, 62.25; H, 4.08. $C_{94}H_{70}Co_2O_6P_4Ru \cdot CH_2Cl_2$ requires: C, 62.53; H, 3.98%; M, 1740 (CH_2Cl_2 found in ^{1}H-NMR spectrum). IR (cyclohexane):

ν(C≡C) 1983 m, ν(CO) 2072 m, 2030 s, 2002 s (br) cm^{-1}. ^1H-NMR: δ 4.35 (s, 10 H, 2 × Cp), 5.29 (s, 2H, CH_2Cl_2), 7.11–7.50 (m 60H, Ph). ES mass spectrum (CH_2Cl_2–MeOH, with NaOMe, m/z): 1763, $[M + Na]^+$

4.4. $(Ru(PPh_3)_2Cp\}_2\{\mu$-$C{\equiv}CC_2[Co_2(\mu$-dppm)-$(CO)_4]C{\equiv}C\}$ (**5**)

A stirred mixture of **1** (80 mg, 0.055 mmol) and Co_2(μ-dppm) $(CO)_6$ (81 mg, 0.121 mmol) in benzene (20 ml) was refluxed for 1 h. The mixture was allowed to cool, concentrated under reduced pressure and the resulting black residue extracted with CH_2Cl_2 and purified by TLC (silica gel; acetone–hexane 2:8, R_f 0.4–0.6) giving $\{Ru(PPh_3)_2Cp\}_2\{\mu$-$C{\equiv}CC_2[Co_2(\mu$-dppm)$(CO)_4]C{\equiv}C\}$ (**5**) as a brown solid (50 mg, 48%). Satisfactory elemental analyses could not be obtained. IR (cyclohexane): ν(CO) 2017 m, 1997 w, 1980 vs, 1952 s, 1935w cm^{-1}. ^1H-NMR ($CDCl_3$): δ 3.49,4.28 (2 m, 2H, CH_2P_2) 4.10 (s, 10H, 2 × Cp), 6.74–7.74 (m, 80H, Ph). ES mass spectrum (CH_2Cl_2–MeOH, m/z): 2068, $[M]^+$ (calc for $C_{117}H_{92}Co_2O_4P_6Ru_2$, 2068).

4.5. $\{Ru(PPh_3)_2Cp\}_2\{\mu$-$C{\equiv}CC_2[Co_2(\mu$-dppm)-$(CO)_4]C{\equiv}CC{\equiv}C\}$ (**6**)

A stirred mixture of **2** (70 mg, 0.047 mmol) and $Co_2(dppm)(CO)_6$ (70 mg, 0.104 mmol) in benzene (20 ml) was refluxed for 1 h. The mixture was allowed to cool, solvent was removed and the resulting black residue extracted with CH_2Cl_2 and purified by TLC (silica gel; acetone–hexane 3:7, R_f 0.4–0.6) to give $\{Ru(PPh_3)_2Cp\}_2\{\mu$-$C{\equiv}CC_2[Co_2(\mu$-dppm)$(CO)_4]C{\equiv}CC{\equiv}C\}$ (**6**) as a black solid (55 mg, 56%). Found: C, 67.24; H, 4.59. $C_{119}H_{92}Co_2O_4P_6Ru_2\cdot0.5CH_2Cl_2$ requires: C, 67.24; H 4.39%; M, 2092. IR (cyclohexane): ν(C≡C), 2119 w, ν(CO) 2040 m, 2012 s, 1993 s (br), 1967 s, 1946 w cm^{-1}. ^1H-NMR: δ 3.20, 3.85 (2 m, 2H, CH_2P_2), 4.33, 4.44 (2 s, 10H, Cp), 6.98–7.63 (m, 80H, Ph). ES mass spectrum (CH_2Cl_2–MeOH, m/z): 2092, $[M]^+$; 2064, $[M - CO]^+$; 2036, $[M - 2CO]^+$.

4.6. $Fe_3\{\mu_3$-$CC{\equiv}C[Ru(PPh_3)_2Cp]\}_2(CO)_9$ (**7**)

A stirred mixture of **1** (50 mg, 0.034 mmol and $Fe_2(CO)_9$ (50 mg, 0.137 mmol) in thf (30 ml) was refluxed for 30 min. The mixture was allowed to cool, concentrated under reduced pressure and purified by TLC (silica gel; acetone–hexane 3:7, R_f 0.5) giving $Fe_3\{\mu_3$-$CC{\equiv}C[Ru(PPh_3)_2Cp]\}_2(CO)_9$ (**5**) as a cherry red solid (10 mg, 16%). X-ray quality crystals were grown from CH_2Cl_2–pentane. Found: C, 61.11; H, 3.95. $C_{97}H_{70}Fe_3O_9P_4Ru_2\cdot0.25CH_2Cl_2$ requires: C, 61.65; H, 3.75%; M, 1874 ($0.25CH_2Cl_2$ found in X-ray structure). IR (CH_2Cl_2): ν(CO) 2015 s, 1998 m, 1939 s cm^{-1}. ^1H-NMR: δ 4.49 (s, 10H, 2 × Cp), 7.14–7.38 (m, 60H, Ph). ^{13}C-NMR: δ 266.29 (s, Fe_3C), 212.89 (s, CO), 178.94 [t, J(CP) = 23 Hz, C_α], 149.12 (s, C_β), 127.36–139.52 (m, Ph), 86.84 (s, Cp). ES mass spectrum (CH_2Cl_2–MeOH, m/z): 1874, $[M] + ^+$; 1846, $[M - CO]^+$; 1790–1622, $[M - nCO]^+$ (n = 3–9).

4.7. $Fe_3\{\mu$-$CC{\equiv}C[Ru(PPh_3)_2Cp]\}\{\mu_3$-$CC{\equiv}CC{\equiv}C$-$[Ru(PPh_3)_2Cp]\}(CO)_9$ (**8**)

A stirred mixture of **2** (50 mg, 0.030 mmol) and $Fe_2(CO)_9$ (43 mg, 0.118 mmol) in thf (30 ml) was refluxed for 15 min. The mixture was allowed to cool, concentrated under reduced pressure and purified by TLC (silica gel: acetone–hexane 3:7, R_f 0.3–0.5) giving, $Fe_3\{\mu_3$-$CC{\equiv}C[Ru(PPh_3)_2Cp]\}$ $\{\mu_3$-$CC{\equiv}CC{\equiv}C$-$[Ru(PPh_3)_2Cp]\}(CO)_9$ (**8**) as a cherry red solid (25 mg, 39%). Found: C, 62.67; H, 72. $C_{99}H_{70}Fe_3O_9P_4Ru_2$ requires: C, 62.92; H, 4.21%; M, 1898. IR (CH_2Cl_2): ν(C≡C) 2078 w, ν(CO) 2043 m, 2024 s, 1997 s, 1960 m, 1933 s cm^{-1}. ^1H-NMR: δ 4.67, 4.78 (2 s, 10H, 2 × Cp), 7.36–7.72) (m, 60H, Ph). ^{13}C-NMR: δ 275.35, 260.06 [2s, C(3), (4)]. 211.56 (s, CO), 191.50 [t, J(CP) = 23 Hz, C(1) or C(8)], 160.21 [t, J(CP) = 25 Hz, C(1) or C(8)], 152.14 (s), 127.37–138.71 (m, Ph), 116.12 (s), 100.38 (s), 86.27, 87.09 (2s, 2 × Cp), 81.47 (s), 68.02 (s). ES mass spectrum (CH_2Cl_2–MeOH, m/z): 1898, $[M]^+$; 1870, $[M - CO]^+$; 1814–1646, $[M - nCO]^+$ (n = 3–9).

5. Crystallography

Full spheres of data to $2\theta = 58°$ were measured at ca. 153 K using a Bruker AXS CCD area-detector instrument, merged to unique sets after 'empirical' corrections (processing by proprietary software SMART, SAINT, SADABS, XPREP). N_{tot} data gave N unique (R_{int} quoted), N_0 with $F > 4\sigma(F)$ being used in the refinements. All data were measured using monochromatic Mo–K_α radiation, $\lambda = 0.71073$ Å. In the refinements, anisotropic thermal parameter forms were used for the non-hydrogen atoms, $(x, y, z\ U_{iso})_H$ being constrained at estimated values. Conventional residuals R, R_w on $|F|$ are quoted, statistical weights being employed. Neutral atom complex scattering factors were used: computation used the XTAL 3.4 program system [17]. Pertinent results are given in Figs. 1 and 2 (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids) and Table 1.

6. Crystal and refinement data

(**4**) $\{Ru(PPh_3)_2Cp\}_2\{\mu$-$C{\equiv}CC_2[Co_2(CO)_6]C{\equiv}C\}\cdot2CH_2Cl_2 \equiv C_{94}H_{70}Co_2O_6P_4Ru_2\cdot2CH_2Cl_2$, space group $P\bar{1}$, $a = 11.550(1)$, $b = 13.334(2)$, $c = 28.482(3)$ Å, $\alpha = 76.679(2)$, $\beta = 87.316(2)$, $\gamma = 82.006(2)°$, $V = 4226$ Å^3,

$Z = 2$. $D_{\mathrm{calc}} = 1.50_0$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 9.9$ cm^{-1}; specimen: $0.40 \times 0.40 \times 0.40$ mm; $T_{\mathrm{min,\ max}} = 0.67,\ 0.83$. $N_{\mathrm{tot}} = 48712$, $N = 20562$ ($R_{\mathrm{int}} = 0.023$), $N_0 = 16706$, $R = 0.040$, $\mathrm{R_w} = 0.051$. $n_v = 1028$; $|\Delta\rho| = 0.99(5)$ e Å^{-3}.

(**7**) $\mathrm{Fe_3\{\mu_3\text{-}CC{\equiv}C[Ru(PPh_3)_2Cp]\}_2(CO)_9 \cdot 0.25CH_2Cl_2 \equiv C_{97}H_{70}Fe_3O_6P_4Ru_2 \cdot 0.25CH_2Cl_2}$, space group $P\bar{1}$, $a = 12.307(2)$, $b = 20.323(3)$, $c = 20.384(3)$ Å, $\alpha = 60.081(3)$, $\beta = 89.062(3)$, $\gamma = 87.181(3)°$, $V = 4413$ Å^3, $Z = 2$. $D_{\mathrm{calc}} = 1.42_5$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 9.6$ cm^{-1}; specimen: $0.35 \times 0.06 \times 0.05$ mm; $T_{\mathrm{min,\ max}}$ 0.73, 0.94. $N_{\mathrm{tot}} = 52852$, $N = 15463$ ($R_{\mathrm{int}} = 0.052$), $N_0 = 8443$, $R = 0.071$, $R_{\mathrm{w}} = 0.076$. $n = 1067$; $|\Delta\rho| = 2.6(1)$ e Å^{-3}.

Difference map residues near the centre of the cell were modelled in terms of $\mathrm{CH_2Cl_2}$ of solvation, site occupancy set at 0.25 after trial refinement. The $\mathrm{Fe_3}$ core of the central iron carbonyl unit was modelled in terms of a rotationally disordered component, site occupancies of $\mathrm{Fe_3}$, and $\mathrm{Fe'_3}$ refining to 0.862(2) and complement, the Fe...Fe′ displacements ranging between 0.94(2) and 0.97(2) Å. Disordered components, of associated light atoms were not meaningfully resolved.

7. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 140689 (for **4**) and 140690 (for **7**). Copies of the information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Australian Research Council for support of this work and Johnson Matthey plc, Reading, for a generous loan of $\mathrm{RuCl_3 \cdot \mathit{n}H_2O}$.

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