

Heterometallic complexes containing 1,1'-(C≡C)₂Fc' units linking two different metal centres

Michael I. Bruce^{a,*}, Paul A. Humphrey^a, Martyn Jevric^a, Gary J. Perkins^a,
Brian W. Skelton^b, Allan H. White^b

^a School of Chemistry and Physics, University of Adelaide, Adelaide, South Australia 5005, Australia

^b Chemistry M313, SBBCS, University of Western Australia, Crawley, Western Australia 6009, Australia

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Abstract

Proto-desilylation of 1-(Me₃SiC≡C)-1'-{Cp*(dppe)RuC≡C}Fc' (**1**) afforded the corresponding ethynyl derivative **2**, from which the green Co₂(μ-dppm)_n(CO)_{8-2n} (*n* = 0, 1) adducts **3** and **4** were obtained. Replacement of the ethynyl proton in reactions between **2** and AuCl(PPh₃), Hg(OAc)₂ or FeCl(dppe)Cp* gave complexes 1-(RC≡C)-1'-{Cp*(dppe)RuC≡C}Fc' [R = Au(PPh₃) **5**, 1/2Hg **6**, Fe(dppe)Cp* **8**]; the latter gave bis-vinylidene **9** with MeI, characterised (as was **2**) by a single crystal X-ray study. Oxidative coupling of **2** (CuCl/tmeda/acetone, air) gave diyne **10**, while coupling of **5** with Co₃(μ₃-CBr)(μ-dppm)(CO)₇ afforded 1-{Cp*(dppe)RuC≡C}-1'-{(OC)₇(μ-dppm)Co₃(μ₃-CC≡C)}Fc' (**11**). Cyclic voltammetric measurements indicated that there was no significant electronic coupling between the end-groups through the ferrocene centre in any of these compounds.

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1. Introduction

There is continuing interest in complexes containing ethynylferrocene moieties attached to transition metal centres as a result of the well-known redox properties associated with the ferrocenyl (Fc) centre. Of the thirty crystallographically characterised compounds containing σ-bonded FcC≡C- ligands [1], several contain a second redox-active metal group, and it has been of interest to examine the degree of electronic communication between the two metal-containing groups. A series of papers by Sato and coworkers [2,3] have described the properties of ethynylferrocene complexes containing M(PP)Cp' fragments [M = Fe, Ru; PP = (PPh₃)₂, dppe, dmpe; Cp' = Cp, Cp*; not all combinations]. In addition to the ready oxidation

of these derivatives, including isolation of the stable 17-e cation in [Fe(C≡CFc)(PPh₃)₂Cp]PF₆ [2b], unusual involvement of the alkynyl group in formation of fulvalenyl-ruthenium derivatives occurs [3]. A further subset of related compounds contains two FcC≡C groups attached to a single metal centre, such as Ru(C≡CFc)₂(dppx)₂ (*x* = m, e) [4,5]. However, there are few examples of complexes derived from 1,1'-bis(ethynyl)ferrocene, Fc'(C≡CH)₂, and related compounds [6–8].

Recently, we have reported several complexes containing Ru(PP)Cp' groups end-capping the 1,1'-Fc'(C≡C-)₂ nucleus [9]. Similar ruthenocene complexes, and compounds of the type Ru{(C≡C)_nFc}(PP)Cp' [PP = (PPh₃)₂, dppm, dppe, dpff; Cp' = Cp, Cp*] (*n* = 1, 2, 3) have also been made [10]. In the course of our studies on the ferrocene complexes, we discovered a route to the monometallated derivative 1-(Me₃SiC≡C)-1'-{Cp*(dppe)RuC≡C}Fc' (**1**), which we have subsequently used to make a series of asymmetric 1,1'-bis(alkynyl)ferrocenes containing at least two

* Corresponding author. Tel./fax: +61 8 8303 4358.

E-mail address: michael.bruce@adelaide.edu.au (M.I. Bruce).

redox-active centres. This allowed a study of the interactions of two or more metal centres through the ferrocene group. These syntheses and preliminary electrochemical studies of the resulting complexes are reported herein.

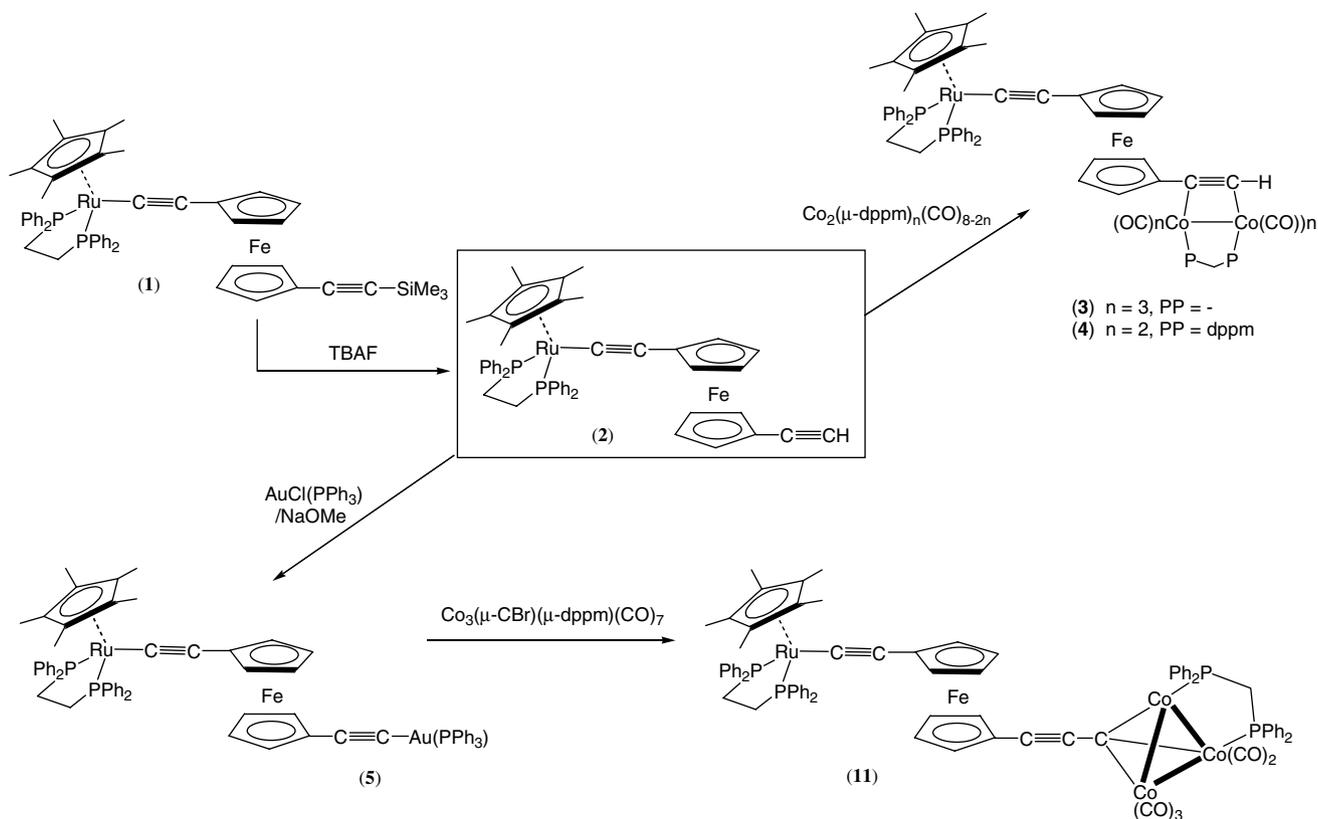
2. Results and discussion

Precursor **1** (Scheme 1) was prepared in 46% yield as described earlier [9], from 1,1'-(Me₃SiC≡C)₂Fc' and one equivalent of RuCl(dppe)Cp* in the presence of KF. Treatment of **1** with [NBu₄]F in thf containing a small amount of water resulted in ready proto-desilylation and formation of orange 1-(HC≡C)-1'-{Cp*(dppe)RuC≡C}Fc' (**2**). Characterisation was by elemental microanalysis (as with all complexes described subsequently) and spectroscopy. The IR spectrum contained $\nu(\text{C}\equiv\text{CH})$ at 3305 and 3281 cm⁻¹ along with $\nu(\text{C}\equiv\text{C})$ at 2109 and 2073 cm⁻¹, while the acetylenic proton appears as a singlet at δ 2.54 in the ¹H NMR spectrum. Other resonances are characteristic of the Fc' and Ru(dppe)Cp* groups. Further discussion of the NMR spectra is given below.

The molecular structure of **2** has been determined by a single-crystal X-ray diffraction study. The unit cell contains two independent molecules, which differ in the disposition of the C₅H₄C≡CH group around the Fe-C₅ axis with respect to the Cp*(dppe)RuC≡CC₅H₄ group (Fig. 1, Table 1).

The Ru(dppe)Cp* fragment is similar to many others which have been reported, with Ru–P distances ranging between 2.2625 and 2.2673(8) and Ru–C(cp*) between 2.213 and 2.275(3) Å, with angles about the ruthenium consistent with pseudo-octahedral coordination [P(1)–Ru–P(2) 84.77, 83.46(3); P(1,2)–Ru–C(1) range 83.07–85.52(8)°]. The separations Ru–C(1), C(1)–C(2), C(2)–C(201), C(204')–C(206') and C(206')–C(207') [2.012(3), 1.220(5), 1.433(5), 1.429(5), 1.188(5) Å, respectively; values for molecule 1 given] confirm the presence of the alkynyl groups, with the C≡CH triple bond being significantly shorter than the ruthenium-bonded group, as a result of back-bonding from the metal into the latter. The values may be compared with those determined earlier for Ru(C≡CFc)(dppe)Cp* which has Ru–P 2.2482(7), 2.2746(7), Ru–C(1) 2.013(2) and C(1)–C(2) 1.206(4) Å. The ferrocene-1,1'-diyl moiety has no anomalous structural features, the two independent molecules differing by the torsion angles between the two C≡C bonds about the Fe–C(0) axis, which are –159.9 and 64.3°. The two alkynyl groups approach linearity, with angles at C(1), C(2), C(1206') and C(2206') being 177.3(3), 174.9(3), 177.1(4) and 177.6(4)°, respectively.

Further derivatisation of **2** has been carried out and these reactions are summarised in Schemes 1 and 2. As expected, **2** reacts with Co₂(μ-dppm)_n(CO)_{8–2n} (n = 0, 1) to give the corresponding adducts **3** (as a non-crystallisable green oil) and **4**, respectively, in which the dicobalt



Scheme 1.

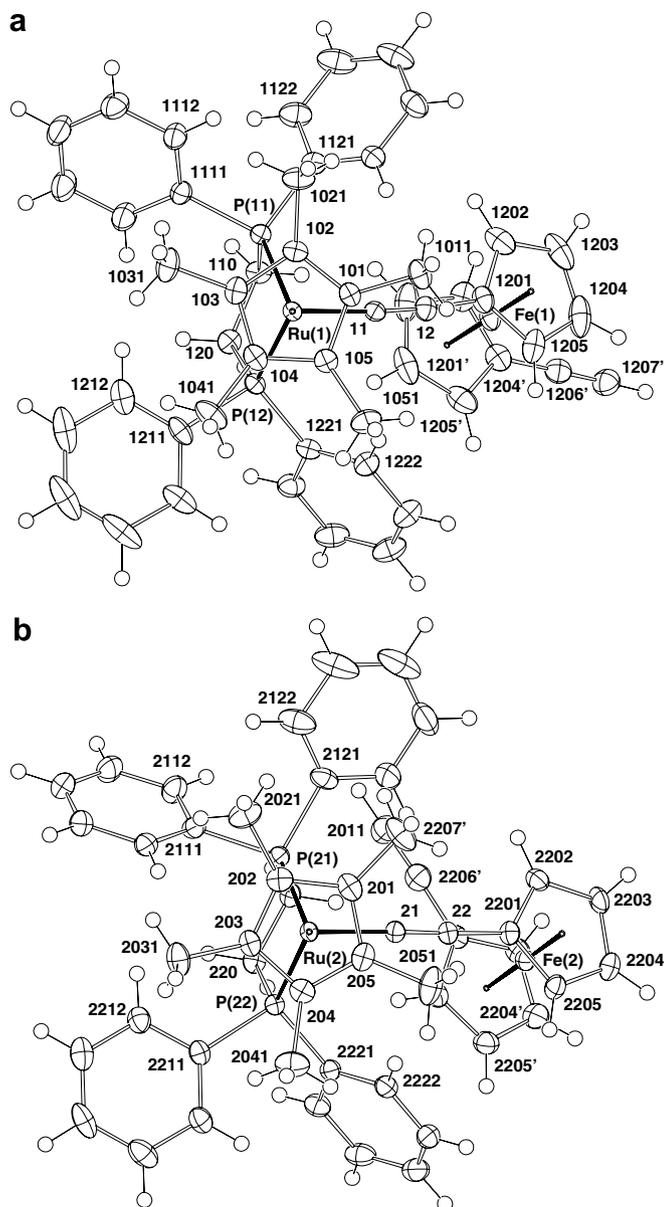


Fig. 1. Plots of the two molecules of 1-(HC≡C)-1'-{Cp*(dppe)RuC≡C}Fc' (**2**), showing the differing dispositions of the $\text{C}\equiv\text{CH}$ substituents.

carbonyl fragment is attached to the less hindered of the two $\text{C}\equiv\text{C}$ triple bonds. This is shown most clearly in the ^{13}C NMR spectra, in which the chemical shifts of the carbons of the $\text{C}\equiv\text{CH}$ fragment show a down-field shift [from δ 74.0 and 84.2 to 75.3 and 83.9 (for **3**), 76.9 and 89.7 (for **4**)], while the resonances for the $\text{C}\equiv\text{C}-\text{Ru}$ group remain close to the values found for **2**. Other data are also consistent with this structural interpretation, detailed assignments being given in Section 4.

Treatment of **2** with $\text{AuCl}(\text{PPh}_3)$ in the presence of NaOH in methanol resulted in the formation of 1-((Ph_3P) $\text{AuC}\equiv\text{C}$)-1'-{Cp*(dppe)RuC≡C}Fc' (**5**) as a light orange solid. The IR spectrum of **5** contained two $\nu(\text{C}\equiv\text{C})$ bands at 2105 and 2077 cm^{-1} , while the NMR spectra contained the resonances anticipated from the three major fragments present. In the ^{31}P NMR spectrum, two reso-

Table 1
Selected bond distances (\AA) and angles ($^\circ$)

Complex	2 ^a	9 ^b
<i>Bond distances (\AA)</i>		
Ru–P(1)	2.2673(8), 2.2653(8)	2.279(1)
Ru–P(2)	2.2625(7), 2.2666(7)	2.250(1)
Ru–C(cp)	2.240–2.268(3), 2.217–2.275(3)	2.187–2.255(5)
(Av.)	2.255(6), 2.25(2)	2.22(3)
Ru–C(1)	2.012(3), 2.022(3)	1.799(5)
C(1)–C(2)	1.220(5), 1.212(4)	1.329(7)
C(2)–C(3)		1.502(8)
C(2)–C(201)	1.433(5), 1.438(5)	1.479(7)
Fe–C(cp)	2.027–2.067(3), 2.036–2.076(3)	2.036–2.076(3), 2.040–2.056(3)
(Av.)	2.052(15), 2.046(6)	2.046(15)
C(204')–C(206')	1.429(5), 1.428(5) [C(202')]	
C(206')–C(207')	1.188(5), 1.183(6)	
<i>Bond angles ($^\circ$)</i>		
P(1)–Ru–P(2)	84.77(3), 83.46(3)	83.43(4)
P(1)–Ru–C(1)	83.07(9), 83.57(9)	94.9(2)
P(2)–Ru–C(1)	85.14(8), 85.52(8)	82.3(2)
Ru–C(1)–C(2)	177.3(3), 177.6(3)	178.3(4)
C(1)–C(2)–C(3)		119.6(5)
C(1)–C(2)–C(201)	174.9(3), 178.5(3)	125.4(4)
C(3)–C(2)–C(201)		114.8(4)
C(204')–C(206')–C(207')	177.1(4), 177.6(4) [C(202')]	

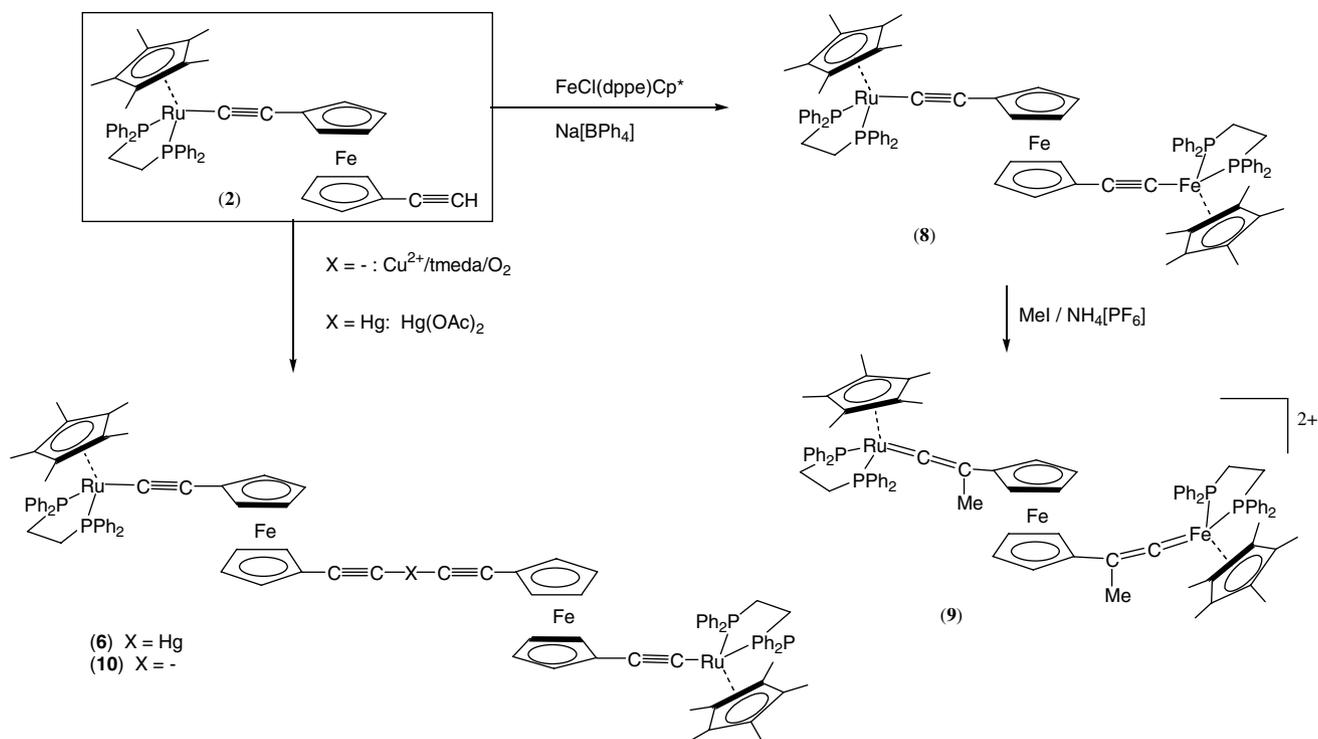
^a Values for two independent molecules given.

^b For Ru, read M (disordered Fe, Ru).

nances at δ 43.4 and 82.3 (ratio 1/2) were assigned to the PPh_3 and dppe ligands, respectively. Of interest are the metal-bonded C(sp) atoms, which resonate at δ 102.07 ($\equiv\text{CAu}$) and 119.45 ($\equiv\text{CRu}$) as a doublet [$J(\text{CP}) = 28.3$ Hz] and triplet [$J(\text{CP}) = 25.5$ Hz], respectively; only one of the other C(sp) atoms is found, at δ 104.36.

The mercury(II) derivative $\text{Hg}\{1\text{-C}\equiv\text{C}-1'\text{-[C}\equiv\text{CRu}(\text{dppe})\text{Cp}^*\text{]Fc}'\}_2$ (**6**) was obtained from a reaction carried out between **2** and $\text{Hg}(\text{OAc})_2$ in refluxing thf overnight. The IR spectrum of **6** contained four $\nu(\text{C}\equiv\text{C})$ bands between 2145 and 2075 cm^{-1} , while the NMR spectra contained resonances anticipated from the component groups. In particular, proton resonances at δ 1.65 and ^{13}C signals at δ 10.79 and 92.93 confirmed the presence of the Cp* groups, and resonances at δ_{C} 103.84, 106.08, 119.60 and 122.02 [triplet, $J(\text{CP}) = 24.1$ Hz] were assigned to carbons of the $\text{C}\equiv\text{C}$ triple bonds, the latter to the $\equiv\text{CRu}$ atoms.

Previously we have described the synthesis, characterisation and electrochemical behaviour of the symmetrical derivative, 1,1'-{Cp*(dppe)RuC≡C} $_2$ Fc' (**7**) [7]. The availability of **2** enabled us to prepare the related asymmetric complex 1-{Cp*(dppe)FeC≡C}-1'-{Cp*(dppe)RuC≡C}Fc' (**8**), which was obtained from **2** and $\text{FeCl}(\text{dppe})\text{Cp}^*$ in the presence of $\text{Na}[\text{BPh}_4]$. This complex contained strong $\nu(\text{C}\equiv\text{C})$ bands at 2100, 2074 and 2057 cm^{-1} (cf. 2107, 2082 cm^{-1} for the Ru_2 analogue [9]) and resonances in the ^1H NMR spectrum at δ 1.56 and 1.69, assigned by comparison with **7** to the Fe- and Ru-bonded Cp* Me



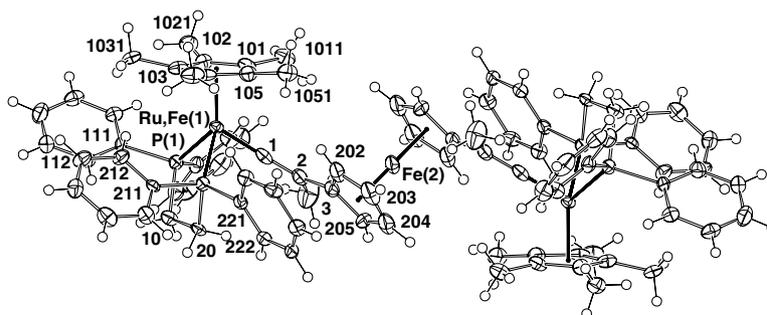
Scheme 2.

groups, respectively. The ³¹P NMR spectrum contained resonances at δ 82.11 and 101.45, similarly assigned to the Ru- and Fe-bonded dppe ligands. The solubility of this complex was not high enough for a ¹³C NMR spectrum to be measured.

However, treatment of **8** with MeI in the presence of Na[BPh₄] afforded the bis-vinylidene [1-{Cp*(dppe)Fe=C=CMe}-1'-{Cp*(dppe)Ru=C=CMe}Fc']₂(BPh₄)₂ (**9**) as red-brown crystals. The ¹H NMR spectrum contained Cp* Me signals at δ 1.40 and 1.57 together with the vinylidene Me groups at δ 1.16 and 1.45. The Cp* Me and ring carbons are found at δ 10.19 and 10.25 (FeCp*), and 99.43 and 102.52 (RuCp*), with the =CMe groups resonating at δ 9.79 and 12.67. The Fe=C and Ru=C signals are downfield at δ 349.13 and 359.53, showing triplet *J*(CP) couplings of 17.4 and 33.4 Hz, respectively. In the ³¹P NMR spectrum, the dppe ligands give signals at δ 75.8 (Ru) and 90.1 (Fe). The ES mass spectrum contains a strong M²⁺ ion at *m/z* 743.

The structure of the cation of **9** found in the single-crystal X-ray determination of the tetraphenylborate salt is shown in Fig. 2. Selected bond distances and angles are listed in Table 1.

The centrosymmetric cation is isostructural with the Ru₂ analogue and the iron and ruthenium atoms are fully scrambled, as is now customary with complexes of this type, particularly [Cp*(dppe)Fe]CC-CC[Ru(dppe)Cp*]_n²⁺ (*n* = 0, 1, 2) [5]. The structure itself offers no surprises, confirming the formulation proposed on the basis of the chemistry and spectroscopy. Only average M–P [2.250, 2.279(1) Å] and M–C distances [1.799(5) Å] can be measured, but these approximate to the average of similar distances found in related complexes, such as the diruthenium analogue [Ru–P 2.298(1), 2.298(1), Ru–C 1.859(4) Å [9]] and [Fe(=C=CHPh)(dppe)Cp*]₂PF₆ [Fe–P, 2.222(2), 2.219(2), Fe–C 1.763(7) [11]. Geometries around the metal atoms are pseudo-octahedral, with P(1)–M–P(2) 83.43(4) and P(1,2)–M–C(1) 82.3, 94.9(2)°.

Fig. 2. Plot of the cation in [1-{Cp*(dppe)Fe=C=CMe}-1'-{Cp*(dppe)Ru=C=CMe}Fc']₂(BPh₄)₂ (**9**).

The C(1)–C(2) separation of 1.329(7) Å indicates a bond order approaching 2, while C(2)–C(3) [1.502(8) Å] and C(2)–C(201) [1.479(7) Å] are in accord with the expected C(sp²)–C(sp³) and C(sp²)–C(sp²) separations. The angle at atom C(1) [178.3(4)°] confirms its sp hybridisation, while the three angles at C(2) [range 114.8–125.4(4)°] are consistent with the expected sp² hybridisation of this atom. With a centre of symmetry in the molecule, the two substituents necessarily have a torsion angle of 180° about the C(0)–Fe–C(0') axis.

Oxidative dimerisation of **8** under Hay conditions (CuCl/tmeda/acetone/air) afforded the expected diyne 1-{Cp*(dppe)RuC≡C}Fc'-1',1''-C≡CC≡C-Fc'{C≡CRu(dppe)Cp*}-1''' (**10**) as an orange solid in 78% yield. The ν(C≡C) bands were at 2144m, 2108 w and 2072s cm⁻¹, while the Cp* Me resonance is at δ 1.66. In the ¹³C NMR spectrum, the Cp* Me and ring carbons resonate at δ 10.78 and 92.91, respectively, with the ≡C atoms at δ 72.88, 80.97, 103.60 and 122.70t [*J*(CP) 24.1 Hz], the latter being assigned to the ≡CRu atoms. The molecular ion is found in the ES MS at *m/z* 1734.

We were able to utilise the phosphine-gold halide elimination reaction [6] to prepare a complex in which the ferrocene-1,1'-bis(ethynediyl) nucleus bridges mononuclear ruthenium and carbon-tricobalt cluster centres. Treatment of the gold derivative **5** with Co₃(μ₃-CBr)(μ-dppm)(CO)₇ in a Pd(0)/Cu(I)-catalysed reaction gave 1-{Cp*(dppe)RuC≡C}-1'-{(μ-dppm)(OC)₇Co₃(μ₃-CC≡C)}Fc' (**11**) as a dark red powder in 60% yield. The IR spectrum contains a weak ν(C≡C) band at 2114 cm⁻¹ and terminal ν(CO) bands between 2068 and 1966 cm⁻¹. The ¹H NMR spectrum contained a signal for the Cp* Me groups at δ 1.70, while resonances for the Cp* Me and ring carbons are at δ 10.78 and 92.94 in the ¹³C NMR spectrum. Other signals assigned to the ≡C atoms occur at δ 103.84, 108.74 and 114.46. Both NMR spectra contain resonances for the dppm and dppe ligands in the usual regions, while signals at δ 34.3 and 82.1 in the ³¹P NMR spectrum arise from the dppm and dppe ligands, respectively. In the ES MS, the peak at *m/z* 1636 is assigned to M⁺.

NMR spectra. The ¹³C NMR spectra of these complexes contain resonances characteristic of the ligands present, minor variations being ascribed to the different metal centres. Thus, the Ru(dppe)Cp* group gives rise to resonances at δ 10.7–10.8 and 92.8–93.0 (Cp* Me and ring carbons), 29.5–31.0 (dppe CH₂), and 128.0–140.8 (Ph), while the Fc' resonances are found as four signals for the two different C₃H₄ groups (δ 69.4–70.1, 70.2–72.0, 71.6–72.5 and 73.2–74.0; exceptions to the latter are found with **3** and **4**, where the lowest field resonances are at δ 72.5 and 71.8, respectively) and the two *ipso* carbons (δ 64.3–69.7 and 78.2–79.4, the latter assigned to the ring bearing the Ru group because of its constancy). The ³¹P NMR spectra contain resonances for the Ru-dppe ligand (δ 82.1–82.4) and for other phosphine ligands if present [δ 41.0 (dppm in **4**), 43.4 (PPh₃ in **5**), 101.5 (Fe-dppe in **8**), 34.3 (dppm

in **11**]. In the cation of **8**, the resonances are shifted to lower field, at δ 75.8 (Ru-dppe) and 90.1 (Fe-dppe).

Electrochemistry. One of the reasons for preparing this set of compounds was to measure the extent of any electronic interaction between the two metal centres bridged by the ferrocene-1,1'-diethynyl moiety. In previous studies, we and others have concluded that, while there is extensive delocalisation (strong interaction) in oxidised complexes derived from M(C≡CFc)(dppe)Cp' (M = Fe, Ru; PP = (PPh₃)₂, dppe; Cp' = Cp, Cp*), the ferrocene group acts as an insulator when inserted into the C₄ chain of complexes {Ru(PP)Cp'}₂(μ-C≡CC≡C) [9].

The electrochemical responses of each complex described herein were examined by cyclic voltammetry (Table 2). All potentials were referenced against an internal ferrocene standard and converted to the saturated calomel electrode (SCE) scale. With scan rates *v* ≥ 100 mV s⁻¹, waves representing one-electron redox processes were found. For **1**, **2**, **5** and **6**, two potentials, separated by 600–670 mV, can be assigned to oxidations at the ruthenium and ferrocene centres, respectively. The shift from corresponding values for model compounds Ru(C≡CPh)(dppe)Cp* (+0.245 V) and FcC≡CH reflect the interactions between both redox centres through the C₂ link. In the case of **5**, a third process, at +1.25 V, may be associated with the gold centre.

Coordination of the dicobalt carbonyl fragments to one of the C≡C triple bonds results in little change in these potentials for **3**, but three waves, at -0.02, +0.58 and +0.87 V, are found for **4**, indicating that considerable electronic interaction occurs between the three metal centres. Also found are reduction waves at -1.40 and -1.57 V for **3** and **4**, respectively, which are associated with processes taking place at the dicobalt centres.

The trinuclear complex **8** shows three processes, at -0.29, +0.17 and +0.71 V, potentials which lie between

Table 2
Electrochemistry of some disubstituted ferrocene complexes

Complex ^a	<i>E</i> ₁ /V	<i>E</i> ₂ /V	Δ <i>E</i> /mV	<i>E</i> ₃ /V
1	+0.09	+0.75	660	
2	+0.09	+0.76	670	
3 ^b	+0.11	+0.72	610	
4 ^c	-0.02	+0.58	600	+0.87
5	+0.04	+0.69	650	+1.25 ^d
6	+0.10	+0.72	620	
8	-0.29	+0.17		+0.71
8' [Fe ₂]	-0.31	-0.13		+0.64
8' [Ru ₂]	+0.04	+0.68		+1.29
9	+0.44	+0.87 ^d		
9' [Ru ₂]	+0.44	+0.89 ^d		
10	+0.11	+0.77		+0.97

Measured as 1 mM solutions in CH₂Cl₂ containing 0.5 M [NBu₄]BF₄ at 100 mV s⁻¹, referenced to internal FeCp₂/[FeCp₂]⁺ = 0.46 V.

^a For **8** and **9**, primed complexes are the symmetrical Fe₂ and Ru₂ complexes.

^b Reduction process at -1.40 V (irrev.).

^c Reduction process at -1.57 V (irrev.).

^d Irreversible.

those found for the corresponding di-iron (−0.31, −0.13, +0.64 V) and diruthenium complexes (+0.04, +0.68, +1.29 V), suggesting that all three compounds have very similar interactions between the metal centres, again through the C₂ links. The related bis(methylvinylidene) complex shows two waves, at +0.44 and +0.89 V.

Diyne **10** gives three waves at +0.11, +0.77 and +0.97 V, suggesting that the extended unsaturated system linking the two ruthenium centres similarly allows a degree of communication between them. Of interest in this connection are the redox properties of Os₃(μ₃-η²-FcC₂C≡CFc)(μ-CO)(CO)₉ and Os₃(μ₃-η⁴-FcC₄Fc)(CO)₁₁ [12]. In the former, there are two closely spaced oxidation waves (Δ*E*_p = 57 mV) for the non-equivalent Fc groups. The latter complex gives two resolved 1-e processes separated by Δ*E*_p = 184 mV, suggesting that there is significant electronic communication between the two formally equivalent Fc groups here.

3. Conclusions

The serendipitous discovery of a route to the asymmetric dialkynylferrocene 1-(Me₃SiC≡C)-1'-{Cp*(dppe)RuC≡C}Fc' **1** has allowed the subsequent preparation of several related compounds, including the protodesilylated complex **2**, and others in which the acetylenic hydrogen in **2** has been replaced by Au(PPh₃) **5**, Hg/2 **6** or Fe(dppe)Cp* **7**, while the (μ₃-C)Co₃(μ-dppm)(CO)₇ derivative **11** was obtained from **5** and Co₃(μ₃-CBr)(μ-dppm)(CO)₇. In addition, complexes containing Co₂(μ-dppm)_n(CO)_{6-2n} (*n* = 0, 1) groups attached to one of the C≡C triple bonds of **2**, and the novel diyne 1-{Cp*(dppe)RuC≡C}Fc'-1'',1''-C≡CC≡C-Fc'{C≡CRu(dppe)Cp*}-1''' **10** have also been prepared and characterised. Some electrochemical studies of these complexes are also reported.

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 [13].

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 ferrocene as internal calibrant (FeCp₂/[FeCp₂]⁺ = +0.46 V). The cell contained a Pt-mesh working electrode, Pt wire counter and pseudo-reference electrodes. Elemental analyses were by CMAS, Belmont, Vic., Australia.

4.3. Reagents

1-(Me₃SiC≡C)-1'-{Cp*(dppe)RuC≡C}Fc' (**1**) was obtained as previously described [9].

4.4. Preparation of 1-(HC≡C)-1'-{Cp*(dppe)RuC≡C}Fc' (**2**)

TBAF (1.0 M solution in thf, 3 ml, 3.0 mmol) was added to a solution of 1-(Me₃SiC≡C)-1'-{Cp*(dppe)RuC≡C}Fc' (**1**) (1700 mg, 1.81 mmol) in thf (100 ml) and the mixture was stirred for 16 h at r.t. After removal of solvent in vacuum, a diethyl ether extract of the residue was filtered through a pad of neutral alumina. Evaporation of the filtrate afforded pure 1-(HC≡C)-1'-{Cp*(dppe)RuC≡C}Fc' (**2**) as an orange solid (1320 mg, 84%). Anal. Found: C, 69.32; H, 5.59. Calcd (C₅₀H₄₈FeP₂Ru): C, 69.20; H, 5.58; *M*, 868. IR (nujol, cm⁻¹): 3305 m, 3281 m [ν(≡CH)], 2109w, 2073s [ν(C≡C)], 1585w 1571w. ¹H NMR (C₆D₆): δ 1.63 (s, 15 H, C₅Me₅), 1.90-2.05, 2.70-2.90 (2 × m, 2 × 2 H, CH₂), 2.54 (s, 1H, ≡CH), 3.90-3.92, 4.03-4.05, 4.17-4.19, 4.30-4.32 (4 × m, 4 × 2H, C₅H₄), 7.07-7.32, 7.90-7.96 (2 × m, 16H + 4H, Ph). ¹³C NMR (C₆D₆): δ 10.75 (C₅Me₅), 29.78-30.69 (m, CH₂), 64.49 (Fc *ipso*), 69.39 (C₅H₄), 71.11 (C₅H₄), 72.02 (C₅H₄), 73.53 (C₅H₄), 74.01 (C≡C), 79.05 (Fc *ipso*), 84.19 (C≡C), 92.94 (C₅Me₅), 103.68 (C_β), 122.09 [t, *J*(CP) 25.6 Hz, Ru-C≡], 128.67-140.44 (m, Ph). ³¹P NMR (C₆D₆): δ 82.1 (dppe). ES MS (MeOH, positive ion, *m/z*): 868, M⁺.

4.5. Reactions of 1-(HC≡C)-1'-{Cp*(dppe)RuC≡C}Fc' (**2**)

(a) With Co₂(CO)₈. Solid Co₂(CO)₈ (100 mg, 0.292 mmol) was added to a solution of 1-(HC≡C)-1'-{Cp*(dppe)RuC≡C}Fc' (**2**) (53 mg, 0.061 mmol) in dry thf (10 ml) and the mixture was stirred at r.t. for 16 h. Chromatography on basic alumina (acetone/hexane 1/9)

afforded adduct 1- $\{\mu\text{-HC}_2[\text{Co}_2(\text{CO})_6]\}$ -1'- $\{\text{Cp}^*(\text{dppe})\text{RuC}\equiv\text{C}\}\text{Fc}'$ (**3**) as a green oil (68 mg, 97%). Anal. Found: C, 58.37; H, 4.15. Calcd ($\text{C}_{56}\text{H}_{48}\text{Co}_2\text{FeO}_6\text{P}_2\text{Ru}$): C, 58.30; H, 4.19; *M*, 1154. IR (cyclohexane, cm^{-1}): $\nu(\text{CO})$ 2087 m, 2048s, 2023s, 2017s (sh), 2005w. ^1H NMR (C_6D_6): δ 1.63 (s, 15H, C_5Me_5), 1.95–2.10, 2.70–2.85 (2 \times m, 2 \times 2H, CH_2), 3.96–3.97, 4.10–4.11, 4.26–4.27 (3m, 2H + 4H + 2H, C_5H_4), 5.78 (s, 1H, m), 7.07 [s (br), Ph], 7.20–7.37, 7.93–7.99 (2 \times m, 10H + 4H, Ph). ^{13}C NMR (C_6D_6): δ 10.72 (C_5Me_5), 30.03–30.95 (m, CH_2), 69.61 (C_5H_4), 71.96 (C_5H_4), 72.04 (C_5H_4), 72.46 (C_5H_4), 75.33 ($\text{C}\equiv\text{C}$), 79.36 (Fc *ipso*), 83.89 ($\text{C}\equiv\text{C}$), 93.03 (C_5Me_5), 103.71 (C_β), 122.78 [t, $J(\text{CP})$ 25.8 Hz, $\text{RuC}\equiv\text{C}$], 128.86–140.48 (m, Ph), 200.74 (CO). ^{31}P NMR (C_6D_6): δ 82.4 (dppe). ES MS (MeOH, positive ion, *m/z*): 1154, M^+ .

(b) *With* $\text{Co}_2(\mu\text{-dppm})(\text{CO})_6$. A mixture of 1-($\text{HC}\equiv\text{C}$)-1'- $\{\text{Cp}^*(\text{dppe})\text{RuC}\equiv\text{C}\}\text{Fc}'$ (**2**) (47 mg, 0.054 mmol) and $\text{Co}_2(\mu\text{-dppm})(\text{CO})_6$ (38 mg, 0.57 mmol) was heated in refluxing thf (20 ml) for 16 h. Purification by chromatography on basic alumina (acetone/hexane 1/9) gave adduct 1- $\{\mu\text{-HC}_2[\text{Co}_2(\mu\text{-dppm})(\text{CO})_4]\}$ -1'- $\{\text{Cp}^*(\text{dppe})\text{RuC}\equiv\text{C}\}\text{Fc}'$ (**4**) as a green solid (61 mg, 76%). Anal. Found: C, 64.02; H, 4.81. Calcd ($\text{C}_{79}\text{H}_{70}\text{Co}_2\text{FeO}_4\text{P}_4\text{Ru}$): C, 64.02; sH, 4.76; *M*, 1482. IR (cyclohexane, cm^{-1}): $\nu(\text{CO})$ 2079w, 2021s, 1994s (sh), 1969s, 1952w. ^1H NMR (C_6D_6): δ 1.68 (s, 15H, C_5Me_5), 2.88–3.01 (m, 4H, CH_2 of dppe), 3.22–3.27 (m, 2H, CH_2 of dppm), 4.16 (m, 2H, C_5H_4), 4.23 (m, 2H, C_5H_4), 4.31 (m, 2H, C_5H_4), 4.57 (m, 2H, C_5H_4), 6.01 (s, 1H, $\equiv\text{CH}$), 6.89, 7.08, 7.27–7.38, 8.00–8.05 (4 \times m, 12H + 6H + 18H + 4H, Ph). ^{13}C NMR (C_6D_6): δ 10.80 (C_5Me_5), 29.84–30.56 (m, CH_2 of dppe), 40.79 [t, $J(\text{CP})$ 20.0 Hz, CH_2 of dppm], 66.25 (Fc *ipso*), 69.64 (C_5H_4), 71.48 (C_5H_4), 71.71 (C_5H_4), 71.83 (C_5H_4), 76.88 ($\text{C}\equiv\text{C}$), 78.37 (Fc *ipso*), 89.71 ($\text{C}\equiv\text{C}$), 92.88 (C_5Me_5), 104.44 (C_β), 120.14 [t, $J(\text{CP})$ 25.5 Hz, $\text{Ru}-\text{C}\equiv$], 127.90–140.58 (m, Ph), 205.35 (CO), 208.05 (CO). ^{31}P NMR (C_6D_6): δ 41.0 (dppm), 82.2 (dppe). ES MS (MeOH, positive ion, *m/z*): 1482, M^+ .

(c) *With* $\text{AuCl}(\text{PPh}_3)$. 1-($\text{HC}\equiv\text{C}$)-1'- $\{\text{Cp}^*(\text{dppe})\text{RuC}\equiv\text{C}\}\text{Fc}'$ (**2**) (203 mg, 0.224 mmol) was added to a solution containing $\text{AuCl}(\text{PPh}_3)$ (113 mg, 0.228 mmol) and NaOH (393 mg, 9.8 mmol) in MeOH (45 ml) and the mixture was stirred at r.t. for 16 h. After this time, the product was filtered off, washed with MeOH and dried to give 1- $\{(\text{Ph}_3\text{P})\text{AuC}\equiv\text{C}\}$ -1'- $\{\text{Cp}^*(\text{dppe})\text{RuC}\equiv\text{C}\}\text{Fc}'$ (**5**) as a light orange solid (255 mg, 86%). Anal. Found: C, 61.61; H, 4.76. Calcd ($\text{C}_{68}\text{H}_{63}\text{AuFeP}_3\text{Ru}$): C, 61.55; H, 4.79; *M*, 1326. IR (nujol, cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2105w, 2077s. ^1H NMR (C_6D_6): δ 1.67 (s, 15H, C_5Me_5), 1.90–2.10, 2.88–3.01 (2 \times m, 2 \times 2H, CH_2 of dppe), 3.97 (m, 2H, C_5H_4), 4.25 (m, 2H, C_5H_4), 4.37 (m, 2H, C_5H_4), 4.51 (m, 2H, C_5H_4), 6.85–6.95, 7.04–7.06, 7.20–7.30, 7.36–7.41, 8.02–8.07 (5 \times m, 10H + 6H + 11H + 4H + 4H, Ph). ^{13}C NMR (C_6D_6): δ 10.82 (C_5Me_5), 30.04–30.66 (m, CH_2 of dppe), 69.58 (C_5H_4), 69.72 (Fc *ipso*), 70.15 (C_5H_4), 72.31 (C_5H_4), 73.66 (C_5H_4), 78.18 (Fc *ipso*), 92.81 [t, $J(\text{CP})$ 2.3 Hz, C_5Me_5], 102.07 [d, $J(\text{CP})$ 28.3 Hz, $\text{Au}-\text{C}\equiv$], 104.36 (C_β),

119.45 [t, $J(\text{CP})$ 25.5 Hz, $\text{Ru}-\text{C}\equiv$], 127.79–140.77 (m, Ph). ^{31}P NMR (C_6D_6): δ 43.4 (PPh₃), 82.3 (dppe). ES MS (MeOH, positive ion, *m/z*): 1326, M^+ ; 1784, $[\text{M} + \text{Au}(\text{PPh}_3)]^+$.

(d) *With* $\text{Hg}(\text{OAc})_2$. A solution containing 1-($\text{HC}\equiv\text{C}$)-1'- $\{\text{Cp}^*(\text{dppe})\text{RuC}\equiv\text{C}\}\text{Fc}'$ (**2**) (103 mg, 0.119 mmol) and $\text{Hg}(\text{OAc})_2$ (18 mg, 0.063 mmol) in thf (20 ml) was heated at reflux point for 16 h. Concentration to ca. 3 ml and addition to rapidly stirred hexane (100 ml) gave a precipitate, which after cooling to -20°C overnight was filtered off and washed with hexane to give pure $\text{Hg}\{1-(\text{C}\equiv\text{C})\}$ -1'- $[\text{C}\equiv\text{CRu}(\text{dppe})\text{Cp}^*]\text{Fc}'$ (**6**) (69 mg, 60%). Anal. Found: C, 62.14; H, 4.86. Calcd ($\text{C}_{100}\text{H}_{94}\text{Fe}_2\text{HgP}_4\text{Ru}_2$): C, 62.10; H, 4.90; *M*, 1934. IR (nujol, cm^{-1}): 2145 m, 2123w, 2111w, 2075s [$\nu(\text{C}\equiv\text{C})$], 1585w, 1572w. ^1H NMR (C_6D_6): δ 1.65 (s, 30H, C_5Me_5), 1.95–2.15, 2.75–2.95 (2 \times m, 2 \times 4H, CH_2 of dppe), 3.98–3.99, 4.10–4.11, 4.24–4.25, 4.33–4.34 (4 \times m, 4 \times 4H, C_5H_4), 7.08–7.09, 7.23–7.38, 7.98–8.03 (3 \times m, 12H + 20H + 8H, Ph). ^{13}C NMR (C_6D_6): δ 10.79 (C_5Me_5), 30.18–30.80 (m, CH_2 of dppe), 65.43 (Fc *ipso*), 65.59 (C_5H_4), 70.98 (C_5H_4), 72.47 (C_5H_4), 73.92 (C_5H_4), 78.97 (Fc *ipso*), 92.93 (C_5Me_5), 103.84 (C_β), 106.08 ($\text{C}\equiv\text{C}$), 119.60 ($\text{C}\equiv\text{C}$), 122.02 [t, $J(\text{CP})$ 24.1, $\text{Ru}-\text{C}\equiv$], 128.07–140.30 (m, Ph). ^{31}P NMR (C_6D_6): δ 82.1 (dppe). ES MS (MeOH, positive ion, *m/z*): 1934, M^+ .

(e) *With* $\text{FeCl}(\text{dppe})\text{Cp}^*$. A mixture of 1-($\text{HC}\equiv\text{C}$)-1'- $\{\text{Cp}^*(\text{dppe})\text{RuC}\equiv\text{C}\}\text{Fc}'$ (**2**) (100 mg, 0.115 mmol), $\text{FeCl}(\text{dppe})\text{Cp}^*$ (90 mg, 0.144 mmol) and $\text{Na}[\text{BPh}_4]$ (89 mg, 0.26 mmol) was heated in refluxing MeOH (40 ml) for 1 h. After cooling to r.t., a small piece of sodium (ca 20 mg) was added. The mixture was stirred a further 15 min and the resulting precipitate was collected, washed with MeOH and hexane, and recrystallised (thf/MeOH) to give pure 1- $\{\text{Cp}^*(\text{dppe})\text{FeC}\equiv\text{C}\}$ -1'- $\{\text{C}\equiv\text{CRu}(\text{dppe})\text{Cp}^*\}\text{Fc}'$ (**8**) (112 mg, 67%). Anal. Found: C, 70.29; H, 6.43. Calcd ($\text{C}_{86}\text{H}_{86}\text{Fe}_2\text{P}_4\text{Ru}$): C, 70.93; H, 5.95; *M*, 1456. IR (nujol, cm^{-1}): 2100w, 2074s, 2057s [$\nu(\text{C}\equiv\text{C})$], 1585w, 1572w. ^1H NMR (C_6D_6): δ 1.56 (s, 15H, $\text{Cp}^*\text{-Fe}$), 1.69 (s, 15H, $\text{Cp}^*\text{-Ru}$), 1.80–2.05, 2.70–3.00 [2 \times m (br), 2 \times 4H, CH_2 of dppe], 4.03, 4.13, 4.31–4.35 (3 \times m, 2 \times 2H + 4H, C_5H_4), 7.06–7.36, 7.99–8.04, 8.08–8.14 (3 \times m, 32H + 4H + 4H, Ph). ^{31}P NMR (C_6D_6): δ 82.1 (dppe-Ru), 101.5 (dppe-Fe). ES MS (MeOH, positive ion, *m/z*): 1456, M^+ .

(f) *Reaction of* 1- $\{\text{Cp}^*(\text{dppe})\text{FeC}\equiv\text{C}\}$ -1'- $\{\text{C}\equiv\text{CRu}(\text{dppe})\text{Cp}^*\}\text{Fc}'$ (**8**) *with* MeI. MeI (10 drops, excess) was added to a degassed solution of 1- $\{\text{Cp}^*(\text{dppe})\text{FeC}\equiv\text{C}\}$ -1'- $\{\text{C}\equiv\text{CRu}(\text{dppe})\text{Cp}^*\}\text{Fc}'$ (**8**) (70 mg, 0.48 mmol) and $\text{Na}[\text{BPh}_4]$ (52 mg, 0.15 mmol) in thf (10 ml) and the solution was heated at reflux point for 16 h. After removal of solvent, cautious addition of hexane to a filtered CH_2Cl_2 extract of the residue gave a biphasic system from which bis-vinylidene [1- $\{\text{Cp}^*(\text{dppe})\text{Fe}=\text{C}=\text{CMe}\}$ -1'- $\{\text{Cp}^*(\text{dppe})\text{Ru}=\text{C}=\text{CMe}\}\text{Fc}'$](BPh_4)₂ (**9**) separated as red-brown crystals. Anal. Found: C, 76.40; H, 6.70. Calcd ($\text{C}_{136}\text{H}_{132}\text{B}_2\text{Fe}_2\text{P}_4\text{Ru}$): C, 76.88; H, 6.26; *M*, 1486. IR (nujol, cm^{-1}): 1632 m, 1579w. ^1H NMR (C_6D_6): δ 1.16 (s, 3H, Me), 1.40 (s, 15H, C_5Me_5), 1.45 (s, 3H, Me), 1.57

(s, 15H, Cp*), 2.10–2.40, 2.40–2.70 (2 × m, 2 × 4H, CH₂ of dppe), 3.19, 3.22, 3.70, 3.78 (4 × m, 4 × 2H, C₅H₄), 6.83–7.54 (m, 80H, Ph). ¹³C NMR (C₆D₆): δ 9.79 (Me), 10.19 (C₅Me₅), 10.25 (C₅Me₅), 12.67 (Me), 28.06–29.80 (m, CH₂ of dppe), 66.11 (C₅H₄), 66.41 (C₅H₄), 67.94 (C₅H₄), 77.21 (C₅H₄), 79.95 (Fc *ipso*), 82.40 (Fc *ipso*), 99.43 (C₅Me₅), 102.52 (C₅Me₅), 116.25 (C≡C), 126.90 (C≡C), 121.52–165.07 (m, Ph), 349.13 [t, *J*(CP) 17.4 Hz, Ru=C], 359.53 [t, *J*(CP) 33.4 Hz, Fe=C]. ³¹P NMR (C₆D₆): δ 75.8 (dppe-Ru), 90.1 (dppe-Fe). ES MS (MeOH, positive ion, *m/z*): 743, M²⁺.

4.6. Oxidative dimerisation of 1-(HC≡C)-1'-{Cp*(dppe)RuC≡C}Fc' (2)

A solution of tmeda (150 mg, 1.29 mmol) and CuCl (103 mg, 1.04 mmol) in acetone (10 ml) was added to a continuously oxygenated solution of 1-(HC≡C)-1'-{Cp*(dppe)RuC≡C}Fc' (2) (99 mg, 0.114 mmol) in acetone (20 ml) over a period of 1 h. After removal of solvent, the residue was purified by chromatography (basic alumina, benzene) to give 1-{Cp*(dppe)RuC≡C}Fc'-1', 1''-C≡CC≡C-Fc' {C≡CRu(dppe)Cp*}-1''' (10) (77 mg, 78%) as an orange solid. Anal. Found: C, 69.14; H, 5.43. Calcd (C₁₀₀H₉₄Fe₂P₄Ru₂): C, 69.28; H, 5.47; *M*, 1734. IR (nujol, cm⁻¹): 2144m, 2108w, 2072s [ν(C≡C)], 1585w, 1571w. ¹H NMR (C₆D₆): δ 1.66 (s, 30H, C₅Me₅), 1.95–2.15, 2.70–2.90 (2 × m, 2 × 4H, CH₂ of dppe), 3.94–3.95, 4.04–4.05, 4.19–4.20, 4.27–4.28 (4 × m, 4 × 4H, C₅H₄), 7.07 [s (br)], 7.25–7.38, 7.94–8.00 (3 × m, 12H + 20H + 8H, Ph). ¹³C NMR (C₆D₆): δ 10.78 (C₅Me₅), 29.89–30.56 (m, CH₂ of dppe), 64.33 (Fc *ipso*), 69.35 (C₅H₄), 71.51 (C₅H₄), 72.14 (C₅H₄), 74.01 (C₅H₄), 72.88 (C≡C), 79.31 (Fc *ipso*), 80.97 (C≡C), 92.91 (C₅Me₅), 103.60 (C_β), 122.70 [t, *J*(CP) 24.1, Ru–C≡], 127.91–140.49 (m, Ph). ³¹P NMR (C₆D₆): δ 82.2 (dppe). ES MS (MeOH, positive ion, *m/z*): 1734, M⁺.

4.7. Preparation of 1-{Cp*(dppe)RuC≡C}-1'-{(μ-dppm)(OC)₇Co₃(μ₃-CC≡C)}Fc' (11)

A mixture of 1-{Cp(dppe)RuC≡C}-1'-{(Ph₃P)Au}Fc' (5) (87 mg, 0.066 mmol), Co₃(μ₃-CBr)(μ-dppm)(CO)₇ (56 mg, 0.066 mmol), Pd(PPh₃)₄ (4 mg, 0.003 mmol) and CuI (1 mg, 0.005 mmol) in thf (15 ml) was stirred at r.t. for 30 min. After removal of solvent, preparative t.l.c. of the residue (acetone/hexane 1/2) gave a major red-purple band (*R_f* 0.35) from which 1-{Cp*(dppe)RuC≡C}-1'-{(μ-dppm)-(OC)₇Co₃(μ₃-CC≡C)}Fc' (11) (64 mg, 60%) was obtained as a dark red powder (CH₂Cl₂/MeOH). Anal. Found: C, 59.70; H, 3.97. Calcd (C₈₃H₆₉Co₃FeO₇.P₄Ru): C, 60.93; H, 4.25; *M*, 1636. IR (nujol, cm⁻¹): 2114vw(br) [ν(C≡C)], 2068(sh), 2056vs, 2005vs, 1991(sh), 1966 (sh) [ν(CO)]. ¹H NMR (C₆D₆): δ 1.70 (s, 15 H, C₅Me₅), 1.98–2.01, 2.74–2.77 (2 × m, 2 × 4H, CH₂ of dppe), 3.07–3.13, 4.42–4.48 (2 × m, 2 × 1H, CH₂ of dppm), 4.23, 4.24, 4.33, 4.58 (4 × m, 4 × 2H, C₅H₄),

6.72–7.36, 7.59–7.62, 7.93–7.96 (3 × m, 32H + 4H + 4H, Ph). ¹³C NMR (C₆D₆): δ 10.78 (C₅Me₅), 29.49–30.46 (m, CH₂ of dppe), 40.78 (CH₂ of dppm), 67.61 (Fc *ipso*), 70.05 (C₅H₄), 71.26 (C₅H₄), 71.61 (C₅H₄), 73.19 (C₅H₄), 79.11 (Fc *ipso*), 92.94 (C₅Me₅), 103.84 (C_β), 108.74 (C≡C), 114.46 (C≡C), 128.25–140.12 (m, Ph), 202.80 (CO). ³¹P NMR (C₆D₆): δ 34.3 [s (br), dppm], 82.1 (dppe). ES MS (MeOH, positive ion, *m/z*): 1636, M⁺.

4.8. 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* > 4σ(*F*) being used in the full matrix least squares refinements. All data were measured using monochromatic Mo Kα radiation, λ = 0.71073 Å. 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: (σ²(*F*²) + *n_wF*²)⁻¹]. Neutral atom complex scattering factors were used; computation used the XTAL 3.7 program system [14].

Pertinent results are given in the Figures (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids and hydrogen atoms with arbitrary radii of 0.1 Å) and in Table 1.

Compound 2 1-(HC≡C)-1'-{Cp*(dppe)RuC≡C}Fc' ≡ C₅₀H₄₈FeP₂Ru, *MW* = 867.80. Triclinic, space group *P*1, bar, *a* = 12.9309(8), *b* = 14.5237(9), *c* = 22.066(1) Å, α = 92.381(2), β = 91.502(2), γ = 100.478 (2)°, *V* = 4069 Å³, *Z* = 4, 2θ_{max} = 60°. *D_c* = 1.416 g cm⁻³, μ = 0.84 mm⁻¹, *T*_{min/max} = 0.93. Crystal 0.56 × 0.41 × 0.12 mm. *N*_{tot} = 93722, *N* = 21058 (*R*_{int} = 0.057), *N*_o = 15363, *R* = 0.044, *R*_w = 0.094, *n_w* = 18.

Compound 9 [1-{Cp*(dppe)Fe=C=CMe}-1'-{Cp*(dppe)Ru=C=CMe}Fc'][(BPh₄)₂ ≡ C₁₃₆H₁₃₂B₂Fe₂P₄Ru, *MW* = 2124.95. Monoclinic, space group *P*2₁/*n*, *a* = 16.139(2), *b* = 18.243(3), *c* = 18.468(3) Å, β = 98.921 (3)°, *V* = 5371 Å³, *Z* = 2. 2θ_{max} = 50°. *D_c* = 1.314 g cm⁻³, μ = 0.52 mm⁻¹, *T*_{min/max} = 0.92. Crystal 0.26 × 0.16 × 0.16 mm. *N*_{tot} = 51324, *N* = 9429 (*R*_{int} = 0.088), *N*_o = 7098, *R* = 0.056, *R*_w = 0.11, *n_w* = 4.5.

Variata. The molecule was modelled as disordered about a crystallographic inversion centre located at the FcFe atom, RuFe(1) being modelled as a composite, with no components of the disorder resolvable further afield.

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Appendix A. Supplementary material

CCDC 619080 and 619081 contain the supplementary crystallographic data for **2** and **9**. 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.2006.11.035](https://doi.org/10.1016/j.jorganchem.2006.11.035).

References

- [1] The Cambridge Crystallographic Data Base (November 2005) contains the following mononuclear complexes which feature an FeCCM fragment (M = transition metal): M = Ti, PULSUK, QAVPOS; M = Zr, YACDOW; M = Hf, JUFPUV; M = Mn, LIFLER, MUJKOR; M = Fe, XAGSUU, ZUJJAP; M = Ru, PIXVOH, PUDNIL, PUTLOF, REQRIO, ULAGUT, ULAHAQ, ULAHEU; M = Os, HERXEH; M = Pt: HAJFON, HEHFAB, MIRVIS, RAMKEV, ZEPNIR, ZITBUZ.
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