# Tri- and Tetra-nuclear $\mu$-Alkyne Clusters from $[Ru_2(\mu\text{-}CO)(\mu\text{-}C_2R_2)(\eta\text{-}C_5H_5)_2]$ (R = Ph or $CF_3$)†

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The unsaturated Ru=Ru double-bonded complexes $[Ru_2(\mu\text{-}CO)(\mu\text{-}C_2R_2)(\eta\text{-}C_5H_5)_2]$ (R = Ph **1a** or $CF_3$ **1b**) react at room temperature with $[Fe_2(CO)_9]$ to produce the new mixed-metal trinuclear complexes $[Ru_2Fe(CO)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(\mu_3\text{-}C_2R_2)(\eta\text{-}C_5H_5)_2]$ (R = Ph **2** or $CF_3$ **3**) in good yield. Similarly, complexes **1a** and **1b** react with $[Ru(CO)_4(C_2H_4)]$ at room temperature to afford the analogous triruthenium complexes $[Ru_3(CO)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(\mu_3\text{-}C_2R_2)(\eta\text{-}C_5H_5)_2]$ (R = Ph **4** or $CF_3$ **5**). The new complexes exist in two geometric forms which can be regarded as 'rotamers', differing only in the metal atom to which the alkyne ligand is π bound. The structure of complex **2** has been determined by X-ray diffraction and shows a triangular metal core with a triply bridging alkyne ligand bonding parallel to the $(C_5H_5)Ru\text{-}Ru(C_5H_5)$ edge, π bound to the $Fe(CO)_3$ unit, giving the molecule a plane of symmetry. The major isomers of **3** and **4** and the minor isomer of **5** also have this structure. An X-ray diffraction study on the major isomer of the latter, **5b**, revealed that this adopts the other geometric form which has the alkyne π bound to a $Ru(C_5H_5)$ unit, with no plane of symmetry. The rotation of the alkyne relative to the $\{M(C_5H_5)\}_2M(CO)_3$ triangle is accompanied by a shift of the μ-CO ligand to bridge a $\{M(C_5H_5)\}M(CO)_3$ edge of the $M_3$ triangle, *i.e.* as in the other isomer, the edge opposite the π-bound metal is bridged. A similar structure is observed for the minor isomers of **3** and **4**. Fluxional interconversion was observed for the isomers of **4** at elevated temperatures. Reaction of **1a** with $[Co_2(CO)_8]$ at room temperature gives the tetranuclear cluster $[Ru_2Co_2(CO)_4(\mu_3\text{-}CO)_2(\mu_4\text{-}C_2Ph_2)(\eta\text{-}C_5H_5)_2]$ **6** as one of the products. An X-ray diffraction study showed that this 60-electron complex has a *closo*-$Co_2Ru_2C_2$ octahedral core with each $CoRu_2$ face capped by a $\mu_3$-CO ligand. Complex **6** can also be regarded as a 'butterfly' type structure with the Co atoms at the wing-tips and the diphenylethyne ligand bridging all four metal atoms.

Following the study of alkyne oligomerisation at dimolybdenum[1] and diruthenium centres[2,3] in this Laboratory, we have sought to extend this work to trinuclear metal centres. We report here the initial steps; namely the synthesis of some new trinuclear transition metal $\mu_3$-alkyne complexes. The fact that methylene can be added to the Ru=Ru double bonded complexes $[Ru_2(\mu\text{-}CO)(\mu\text{-}C_2R_2)(\eta\text{-}C_5H_5)_2]$ (R = Ph **1a** or $CF_3$ **1b**),[4,5] taken with the isolobal relationship between $CH_2$ and $d^8$ $M(CO)_4$ fragments, led us to treat the complexes **1a** and **1b** with $M(CO)_4$ fragments (M = Fe or Ru), affording new $\mu_3$-alkyne species in high yield. This paper also describes the reaction of **1a** with $[Co_2(CO)_8]$ to form a new mixed-metal tetranuclear cluster.

## Results and Discussion

*Synthesis and Characterisation of* $[Ru_2Fe(CO)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(\mu_3\text{-}C_2R_2)(\eta\text{-}C_5H_5)_2]$ (R = Ph **2** *or* $CF_3$ **3**).—The species $[Fe(CO)_4(thf)]$ is generated when $[Fe_2(CO)_9]$ is dissolved in tetrahydrofuran (thf),[6] and on stirring with $[Ru_2(\mu\text{-}CO)(\mu\text{-}C_2Ph_2)(\eta\text{-}C_5H_5)_2]$ **1a** for *ca.* 5 h at room temperature gave the new trinuclear complex $[Ru_2Fe(CO)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(\mu_3\text{-}C_2R_2)(\eta\text{-}C_5H_5)_2]$ **2** in 85% yield as a dark purple crystalline solid after purification by column chromatography on alumina. The IR spectrum of **2** in hexane shows three terminal carbonyl stretching vibrations at 2028, 1974 and 1963 $cm^{-1}$, a doubly bridging CO band at 1812 $cm^{-1}$ and a band at 1759 $cm^{-1}$ indicative of a carbonyl ligand with some triply bridging character. The $^1H$ NMR spectrum of **2** shows a single signal for the two cyclopentadienyl rings (δ 4.91), suggesting a plane of symmetry in the molecule. The signals for the phenyl protons appear in the region δ 7.24–6.99. The $^{13}C$ NMR spectrum shows a typical lowfield resonance (δ 243.6) for a triply bridging carbonyl carbon and single resonances for terminal CO, cyclopentadienyl and alkyne carbon atoms, at δ 215.2, 96.4 and 181.0 respectively, emphasising the symmetry of the molecule. The characterisation was completed by fast atom bombardment (FAB) mass spectrometry, showing the parent ion $M^+$ at $m/z$ 707, and a satisfactory elemental analysis. These spectroscopic data are consistent with the structure shown in Scheme 1, which was confirmed by an X-ray diffraction study.

Crystals of complex **2** consisted of dark purple diamond shaped plates grown from dichloromethane–hexane. The molecular structure of complex **2** is shown in Fig. 1, and selected bond lengths and angles are given in Table 1. The three metal atoms form a closed near-equilateral triangular skeleton with the Ru(1)–Fe bond equal in length to the Ru(1)–Ru(2) bond at 2.676(1), and the Ru(2)–Fe distance being 2.672(1) Å. The diphenylethyne moiety is σ bound to the two ruthenium atoms and lies parallel to this edge of the $M_3$ triangle. It is π bound to the iron atom with Fe–C(16) 2.048(5) and Fe–C(17) 2.033(5) Å. This parallel mode of bonding is the most stable for alkynes in trimetallic complexes with 48 electrons[7] and many similar complexes have been reported.[8] The alkyne C–C bond is substantially lengthened [C(16)–C(17) 1.412(7) Å] upon coordination to the three metal atoms when compared to the free alkyne (1.20 Å). The asymmetric $\mu_3$-carbonyl ligand is bound more closely to the ruthenium atoms [Ru(1)–C(4) 2.041(6), Ru(2)–C(4) 2.040(6) Å] than to the iron atom [Fe–C(4) 2.503(6) Å]. The μ-carbonyl ligand is elevated from the trinuclear plane by 41.8° and bridges the Ru–Ru edge symmetrically [Ru(1)–C(5) 2.035(5), Ru(2)–C(5) 2.039(6) Å].

The hexafluorobut-2-yne analogue of **2**, $[Ru_2Fe(CO)_3(\mu\text{-}CO)(\mu_3\text{-}CO)\{\mu_3\text{-}C_2(CF_3)_2\}(\eta\text{-}C_5H_5)_2]$ **3**, was prepared in *ca.*

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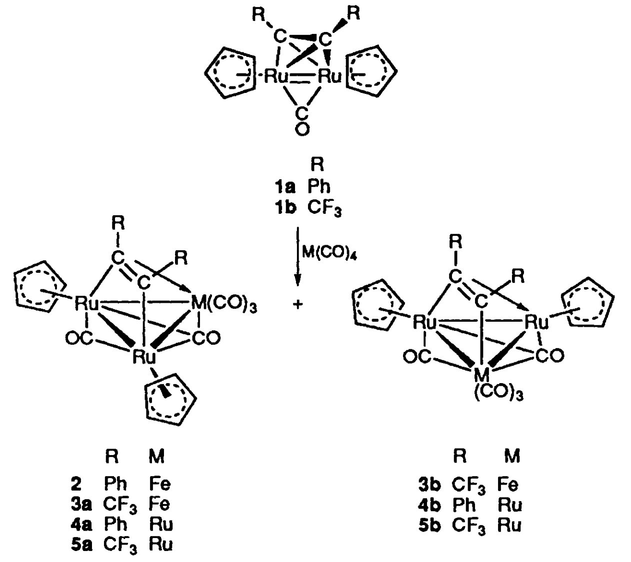
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

**Table 1** Selected bond lengths (Å) and angles (°) for complex **2**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ru(1)–Ru(2) | 2.676(1) | Fe–C(17) | 2.033(5) | Ru(2)–C(14) | 2.271(6) | Ru(2)–C(4) | 2.040(6) |
| Ru(1)–C(5) | 2.035(5) | C(3)–O(3) | 1.146(8) | Fe–C(1) | 1.792(7) | Ru(2)–C(12) | 2.232(6) |
| Ru(1)–C(8) | 2.271(7) | C(16)–C(17) | 1.412(7) | Fe–C(4) | 2.503(6) | Ru(2)–C(15) | 2.248(7) |
| Ru(1)–C(16) | 2.063(5) | Ru(1)–Fe | 2.676(1) | C(1)–O(1) | 1.146(9) | Fe–C(2) | 1.763(7) |
| Ru(2)–C(5) | 2.039(6) | Ru(1)–C(6) | 2.239(7) | C(4)–O(4) | 1.173(7) | Fe–C(16) | 2.048(5) |
| Ru(2)–C(13) | 2.245(7) | Ru(1)–C(9) | 2.232(6) | Ru(1)–C(4) | 2.041(6) | C(2)–O(2) | 1.148(9) |
| Ru(2)–C(17) | 2.066(5) | Ru(2)–Fe | 2.672(1) | Ru(1)–C(7) | 2.265(7) | C(5)–O(5) | 1.173(7) |
| Fe–C(3) | 1.785(7) | Ru(2)–C(11) | 2.208(7) | Ru(1)–C(10) | 2.202(6) | | |
| | | | | | | | |
| Ru(2)–Ru(1)–Fe | 59.9(1) | C(1)–Fe–C(4) | 84.5(3) | Ru(2)–Ru(1)–C(4) | 49.0(2) | C(2)–Fe–C(4) | 175.3(2) |
| Fe–Ru(1)–C(4) | 62.4(2) | C(3)–Fe–C(4) | 80.7(3) | Ru(2)–Ru(1)–C(5) | 49.0(2) | Ru(1)–Fe–C(16) | 49.6(1) |
| Fe–Ru(1)–C(5) | 99.1(2) | Ru(2)–Fe–C(16) | 72.5(1) | C(4)–Ru(1)–C(5) | 91.6(2) | C(1)–Fe–C(16) | 109.9(3) |
| Ru(2)–Ru(1)–C(16) | 72.2(1) | C(2)–Fe–C(16) | 93.4(2) | Fe–Ru(1)–C(16) | 49.1(1) | C(3)–Fe–C(16) | 151.1(3) |
| C(4)–Ru(1)–C(16) | 105.5(2) | C(4)–Fe–C(16) | 91.2(2) | C(5)–Ru(1)–C(16) | 75.2(2) | Ru(1)–Fe–C(17) | 72.6(1) |
| C(6)–Ru(1)–C(16) | 102.6(2) | Ru(2)–Fe–C(17) | 49.9(1) | C(7)–Ru(1)–C(16) | 131.1(2) | C(1)–Fe–C(17) | 150.2(3) |
| C(8)–Ru(1)–C(16) | 162.9(2) | C(2)–Fe–C(17) | 91.4(3) | C(9)–Ru(1)–C(16) | 135.2(3) | C(3)–Fe–C(17) | 111.6(3) |
| C(10)–Ru(1)–C(16) | 103.7(2) | C(4)–Fe–C(17) | 91.4(2) | Ru(1)–Ru(2)–Fe | 60.1(1) | C(16)–Fe–C(17) | 40.5(2) |
| Ru(1)–Ru(2)–C(4) | 49.0(2) | Fe–C(1)–O(1) | 177.3(7) | Fe–Ru(2)–C(4) | 62.5(2) | Fe–C(2)–O(2) | 178.9(6) |
| Ru(1)–Ru(2)–C(5) | 48.9(2) | Fe–C(3)–O(3) | 177.9(6) | Fe–Ru(2)–C(5) | 99.1(2) | Ru(1)–C(4)–Ru(2) | 82.0(2) |
| C(4)–Ru(2)–C(5) | 91.5(2) | Ru(1)–C(4)–Fe | 71.4(2) | Ru(1)–Ru(2)–C(17) | 72.2(1) | Ru(2)–C(4)–Fe | 71.2(2) |
| Fe–Ru(2)–C(17) | 48.8(1) | Ru(1)–C(4)–O(4) | 137.1(5) | C(4)–Ru(2)–C(17) | 105.3(2) | Ru(2)–C(4)–O(4) | 139.0(5) |
| C(5)–Ru(2)–C(17) | 75.5(2) | Fe–C(4)–O(4) | 125.0(4) | C(11)–Ru(2)–C(17) | 107.0(2) | Ru(1)–C(5)–Ru(2) | 82.1(2) |
| C(12)–Ru(2)–C(17) | 100.0(2) | Ru(1)–C(5)–O(5) | 138.7(5) | C(13)–Ru(2)–C(17) | 125.6(2) | Ru(2)–C(5)–O(5) | 139.2(4) |
| C(14)–Ru(2)–C(17) | 160.2(2) | Ru(1)–C(16)–Fe | 81.2(2) | C(15)–Ru(2)–C(17) | 140.3(2) | Ru(1)–C(16)–C(17) | 107.9(4) |
| Ru(1)–Fe–Ru(2) | 60.0(1) | Fe–C(16)–C(17) | 69.2(3) | Ru(1)–Fe–C(1) | 83.6(2) | Ru(1)–C(16)–C(18) | 118.9(4) |
| Ru(2)–Fe–C(1) | 130.5(3) | Fe–C(16)–C(18) | 130.7(4) | Ru(1)–Fe-C(2) | 138.3(2) | C(17)–C(16)–C(18) | 130.5(5) |
| Ru(2)–Fe–C(2) | 134.6(2) | Ru(2)–C(17)–Fe | 81.4(2) | C(1)–Fe–C(2) | 94.9(3) | Ru(2)–C(17)–C(16) | 107.7(4) |
| Ru(1)–Fe–C(3) | 126.8(2) | Fe–C(17)–C(16) | 70.3(3) | Ru(2)–Fe–C(3) | 82.2(2) | Ru(2)–C(17)–C(24) | 120.7(4) |
| C(1)–Fe–C(3) | 96.9(3) | Fe–C(17)–C(24) | 129.8(4) | C(2)–Fe–C(3) | 94.8(3) | C(16)–C(17)–C(24) | 128.7(5) |
| Ru(1)–Fe–C(4) | 46.3(1) | | | Ru(2)–Fe–C(4) | 46.3(1) | | |



**Scheme 1** Synthesis of $\mu_3$-alkyne complexes

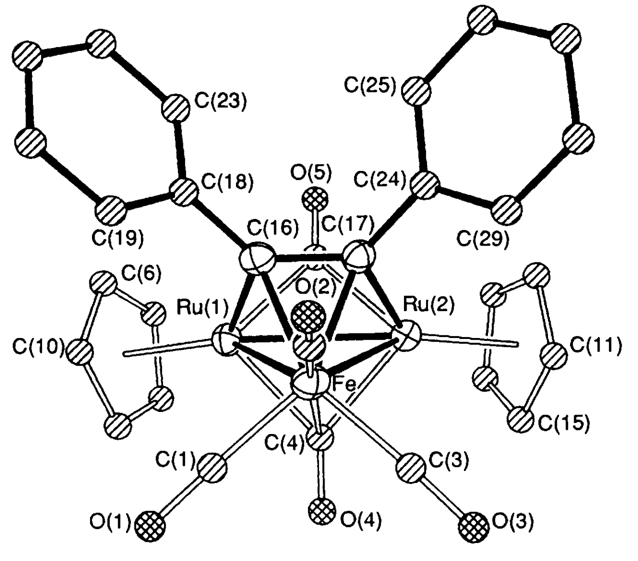


**Fig. 1** Molecular structure of complex **2** showing labelling scheme; all hydrogen atoms have been omitted for clarity

50% yield in the same manner by the room-temperature reaction of complex **1b** with [Fe(CO)$_4$(thf)]. The yields of these reactions have some dependence on the quality of the [Fe(CO)$_4$(thf)] solution prepared, which is unstable and must be used immediately. Unlike **2**, the complex **3** exists as two isomers **3a** and **3b** (ratio 3:1), which are not separable on a chromatographic column. The spectroscopic data (see Experimental section) for the major isomer **3a** are very similar to those for complex **2**. In addition, the $^{19}$F NMR spectrum shows a singlet at δ −51.5 for two equivalent CF$_3$ groups, indicating the alkyne is π bound to the iron atom. This conforms with the expectation that in trinuclear heterometallic complexes it is preferable for the alkyne to be π bound to the least electron-attracting metal fragment.[9] The minor isomer **3b** is less symmetric, illustrated by the NMR spectra which show inequivalent resonances for the cyclopentadienyl protons, at δ 5.36 and 5.41, and for the carbons, at δ 90.4 and 94.0. The $^{13}$C NMR spectrum also shows separate signals for the three terminal carbonyl ligands, at δ 210.7, 209.0 and 205.4. These data suggested that the minor isomer **3b** has the structure shown in Scheme 1, in which the $\mu_3$-alkyne is π bound to ruthenium rather than iron.

*Synthesis and Characterisation of* [Ru$_3$(CO)$_3$($\mu$-CO)($\mu_3$-CO)($\mu_3$-C$_2$R$_2$)($\eta$-C$_5$H$_5$)$_2$] (R = Ph **4a** *or* CF$_3$ **5**).—The successful application of the unsaturated diruthenium complexes **1a** and **1b** in the synthesis of mixed-metal clusters was extended to allow the synthesis of the analogous triruthenium complexes by reaction with $[Ru(CO)_4(C_2H_4)]$, which was prepared by purging with ethene a heptane solution of $[Ru_3(CO)_{12}]$ in a water-jacketted reaction vessel while irradiating with a 500 W tungsten-halogen lamp, a modification of the literature method.[10] Complex **1a** reacts with $[Ru(CO)_4(C_2H_4)]$ at room temperature to form the purple crystalline solid $[Ru_3(CO)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(\mu_3\text{-}C_2Ph_2)(\eta\text{-}C_5H_5)_2]$ **4** in 80% yield. As with complex **3**, two isomers (ratio 7:2) of **4** are formed, with the major isomer **4a** again adopting the more symmetric structure. Spectroscopic data (see Experimental section) follow the patterns of the diruthenium–iron complexes. Complex **1b** reacts with $[Ru(CO)_4(C_2H_4)]$ in the same manner to produce red crystalline $[Ru_3(CO)_3(\mu\text{-}CO)(\mu_3\text{-}CO)\{\mu_3\text{-}C_2(CF_3)_2\}(\eta\text{-}C_5H_5)_2]$ **5** in 88% yield. Again two isomers are formed, **5a** and **5b** in ratio 1:70, but now the major isomer **5b** has the asymmetric structure, confirmed by an X-ray diffraction study.

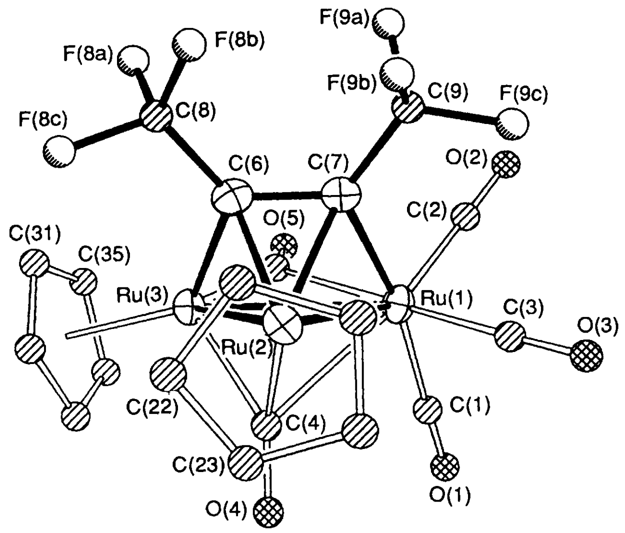


**Fig. 2** Molecular structure of complex **5b** showing labelling scheme; all hydrogen atoms have been omitted for clarity

Complex **5b** was recrystallised from dichloromethane–hexane as red plate-like crystals. The molecular structure, shown in Fig. 2, is similar in most respects to that of complex **2**, except that the alkyne is now π bound to one of the metal atoms carrying a cyclopentadienyl ligand, so that the plane of symmetry through the molecule is lost. The bridging carbonyl ligands are more asymmetric in **5b** than in **2**. The μ-CO is 'semi-bridging' [Ru(1)–C(5) 2.324(4) and Ru(3)–C(5) 1.921(4) Å] while the $\mu_3$-CO bond lengths are all different [Ru(1)–C(4) 2.560(4), Ru(2)–C(4) 1.981(4) and Ru(3)–C(4) 2.137(4) Å]. Therefore the rotation of the alkyne relative to the $\{M(C_5H_5)\}_2M(CO)_3$ triangle in **5b** compared with **2** is accompanied by a shift of the μ-CO ligand to bridge a $\{M(C_5H_5)\}M(CO)_3$ edge of the $M_3$ triangle. In both rotamers the M–M triangle edge opposite to the π-bound metal is bridged by the μ-CO. Other bond lengths and angles are listed in Table 2.

The isomers of complexes **3**–**5** can be regarded as 'rotamers' since their interconversion may be achieved by rotation of the alkyne relative to the $M_3$ cluster with concomitant migration of a carbonyl ligand. Such alkyne rotation is not uncommon and is often observed to occur at $M_3$ centres on the NMR time-scale as a fluxional process.[8b,11] A detailed study of ligand dynamics has been undertaken on the $[Os_3(CO)_9L(C_2R_2)]$ (L = CO or $PR'_3$) system.[12] Clearly, the NMR data for **2**–**5** show that no such rotation occurs for these species at room temperature. It was of interest to investigate whether interconversion of isomers could be effected at high temperature. Proton NMR studies were therefore carried out on the complexes **3**–**5**, which exist as isomers. For the hexafluorobut-2-yne clusters **3** and **5** no change in the cyclopentadienyl proton signals was seen even at 100 °C, *i.e.* separate signals were still observed for the two isomers. However, for complex **4** broadening of the three signals (one for the major symmetric isomer and two for the minor asymmetric isomer) begins to occur at 50 °C, followed by coalescence, until at 100 °C a single broad signal is observed, suggesting fast interconversion of the isomers on the NMR time-scale (Fig. 3). The electron withdrawing nature of the $CF_3$ groups probably accounts for the fact that the hexafluorobut-2-yne complexes **3** and **5** do not display any alkyne rotation. The $CF_3$ groups induce greater back-donation of electrons from the metal to the alkyne, strengthening the interaction and raising the energy barrier for rotation.

**Table 2** Selected bond lengths (Å) and angles (°) for complex **5b**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ru(1)–Ru(2) | 2.728(1) | Ru(3)–C(35) | 2.213(4) | Ru(2)–C(25) | 2.189(4) | Ru(2)–C(7) | 2.118(4) |
| Ru(1)–C(2) | 1.915(4) | C(3)–O(3) | 1.135(5) | Ru(3)–C(6) | 2.057(4) | Ru(2)–C(23) | 2.195(6) |
| Ru(1)–C(5) | 2.324(4) | C(6)–C(7) | 1.413(5) | Ru(3)–C(33) | 2.256(5) | Ru(3)–C(4) | 2.137(4) |
| Ru(2)–C(4) | 1.981(4) | Ru(1)–Ru(3) | 2.852(1) | C(1)–O(1) | 1.127(6) | Ru(3)–C(31) | 2.223(5) |
| Ru(2)–C(21) | 2.178(6) | Ru(1)–C(3) | 1.893(4) | C(4)–O(4) | 1.178(5) | Ru(3)–C(34) | 2.253(5) |
| Ru(2)–C(24) | 2.217(4) | Ru(1)–C(7) | 2.076(4) | Ru(1)–C(1) | 1.951(5) | C(2)–O(2) | 1.135(6) |
| Ru(3)–C(5) | 1.921(4) | Ru(2)–C(6) | 2.105(4) | Ru(1)–C(4) | 2.560(4) | C(5)–O(5) | 1.162(5) |
| Ru(3)–C(32) | 2.216(5) | Ru(2)–C(22) | 2.205(5) | Ru(2)–Ru(3) | 2.705(1) | | |
| Ru(2)–Ru(1)–Ru(3) | 57.9(1) | C(4)–Ru(2)–C(7) | 106.1(2) | Ru(2)–Ru(1)–C(1) | 121.5(1) | C(6)–Ru(2)–C(7) | 39.1(1) |
| Ru(3)–Ru(1)–C(1) | 101.6(1) | Ru(1)–Ru(3)–Ru(2) | 58.7(1) | Ru(2)–Ru(1)–C(2) | 141.6(1) | Ru(1)–Ru(3)–C(4) | 59.7(1) |
| Ru(3)–Ru(1)–C(2) | 121.3(1) | Ru(2)–Ru(3)–C(4) | 46.5(1) | C(1)–Ru(1)–C(2) | 96.8(2) | Ru(1)–Ru(3)–C(5) | 54.1(1) |
| Ru(2)–Ru(1)–C(3) | 81.1(1) | Ru(2)–Ru(3)–C(5) | 111.2(1) | Ru(3)–Ru(1)–C(3) | 137.9(1) | C(4)–Ru(3)–C(5) | 104.5(2) |
| C(1)–Ru(1)–C(3) | 91.1(2) | Ru(1)–Ru(3)–C(6) | 69.3(1) | C(2)–Ru(1)–C(3) | 96.2(2) | Ru(2)–Ru(3)–C(6) | 50.2(1) |
| Ru(2)–Ru(1)–C(4) | 43.9(1) | C(4)–Ru(3)–C(6) | 95.6(2) | Ru(3)–Ru(1)–C(4) | 46.1(1) | C(5)–Ru(3)–C(6) | 92.1(2) |
| C(1)–Ru(1)–C(4) | 81.1(2) | Ru(1)–C(1)–O(1) | 178.8(4) | C(2)–Ru(1)–C(4) | 165.5(1) | Ru(1)–C(2)–O(2) | 174.2(4) |
| C(3)–Ru(1)–C(4) | 98.2(2) | Ru(1)–C(3)–O(3) | 178.0(4) | Ru(2)–Ru(1)–C(5) | 98.7(1) | Ru(1)–C(4)–Ru(2) | 72.6(1) |
| Ru(3)–Ru(1)–C(5) | 42.0(1) | Ru(1)–C(4)–Ru(3) | 74.2(1) | C(1)–Ru(1)–C(5) | 89.5(2) | Ru(2)–C(4)–Ru(3) | 82.0(2) |
| C(2)–Ru(1)–C(5) | 83.6(2) | Ru(1)–C(4)–O(4) | 124.6(3) | C(3)–Ru(1)–C(5) | 179.3(2) | Ru(2)–C(4)–O(4) | 142.8(3) |
| C(4)–Ru(1)–C(5) | 82.1(1) | Ru(3)–C(4)–O(4) | 132.1(3) | Ru(2)–Ru(1)–C(7) | 50.1(1) | Ru(1)–C(5)–Ru(3) | 83.8(1) |
| Ru(3)–Ru(1)–C(7) | 69.9(1) | Ru(1)–C(5)–O(5) | 128.2(3) | C(1)–Ru(1)–C(7) | 170.2(2) | Ru(3)–C(5)–O(5) | 147.6(3) |
| C(2)–Ru(1)–C(7) | 92.1(2) | Ru(2)–C(6)–Ru(3) | 81.1(1) | C(3)–Ru(1)–C(7) | 92.1(2) | Ru(2)–C(6)–C(7) | 71.0(2) |
| C(4)–Ru(1)–C(7) | 89.3(1) | Ru(3)–C(6)–C(7) | 111.7(3) | C(5)–Ru(1)–C(7) | 87.3(1) | Ru(2)–C(6)–C(8) | 125.1(3) |
| Ru(1)–Ru(2)–Ru(3) | 63.3(1) | Ru(3)–C(6)–C(8) | 120.6(3) | Ru(1)–Ru(2)–C(4) | 63.5(1) | C(7)–C(6)–C(8) | 126.7(4) |
| Ru(3)–Ru(2)–C(4) | 51.5(1) | Ru(1)–C(7)–Ru(2) | 81.1(1) | Ru(1)–Ru(2)–C(6) | 71.4(1) | Ru(1)–C(7)–C(6) | 109.0(3) |
| Ru(3)–Ru(2)–C(6) | 48.7(1) | Ru(2)–C(7)–C(6) | 69.9(2) | C(4)–Ru(2)–C(6) | 98.9(2) | Ru(1)–C(7)–C(9) | 123.9(3) |
| Ru(1)–Ru(2)–C(7) | 58.8(1) | Ru(2)–C(7)–C(9) | 126.2(3) | Ru(3)–Ru(2)–C(7) | 72.6(1) | C(6)–C(7)–C(9) | 125.6(3) |

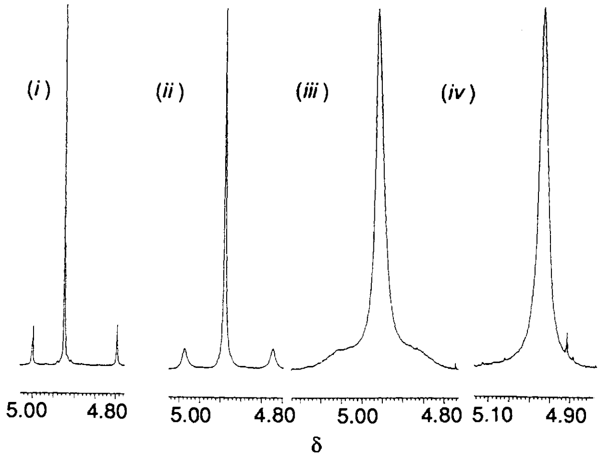
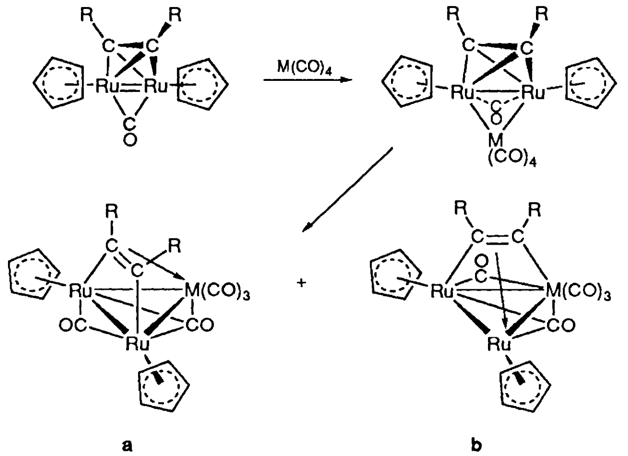


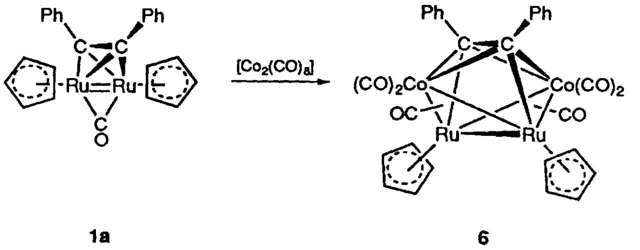
**Fig. 3** Proton NMR spectra of the cyclopentadienyl region for complex **4**; (*i*) +25, (*ii*) +50, (*iii*) +75 and (*iv*) +100 °C



**Scheme 2** Proposed pathway for formation of $\mu_3$-alkyne complexes

The formation of the new trinuclear complexes probably proceeds *via* initial addition of an $M(CO)_4$ fragment across the double bond of **1a** or **1b** to form a $\mu$-$M(CO)_4$ complex (Scheme 2). This is the case for the reaction of diazomethane with **1a**, in which a $\mu$-$CH_2$ complex is formed, and methylene can be considered isolobal with a $d^8$ $ML_4$ fragment. The $\mu$-alkyne can then switch to a $\mu_3$-mode, in concert with CO migration, to give the observed product. Whether isomer **a** or **b** is favoured will depend on the balance between alkyne substituent effects and the electronic requirements of the metal centres. For the triruthenium complexes it is likely that the favouring of the **b** form for **5**, compared with the **a** form for **4**, is a consequence of the strong electron-withdrawing ability of the $CF_3$ group. This will favour $\mu_3$-hexafluorobut-2-yne undergoing $\pi$-back bonding with the most electron rich ruthenium, *i.e.* one carrying a cyclopentadienyl ring, since that ligand is less effective at withdrawing electron density from the metal than three CO ligands.

*Synthesis of* $[Ru_2Co_2(CO)_4(\mu_3\text{-}CO)_2(\mu_4\text{-}C_2Ph_2)(\eta\text{-}C_5H_5)_2]$ **6**.—Reaction of **1a** with $[Co_2(CO)_8]$ at room temperature results in a mixture of five products. The first was a low-yield purple solid, with mass spectrometry and $^1H$ NMR spectroscopy suggesting it to be a mononuclear complex with no cyclopentadienyl ligands. Three yellow products were obtained in small yields and remain unidentified. A dark orange solid was also isolated, in 10% yield after chromatography, identified as the tetranuclear cluster $[Ru_2Co_2(CO)_4(\mu_3\text{-}CO)_2(\mu_4\text{-}C_2Ph_2)(\eta\text{-}C_5H_5)_2]$ **6**.



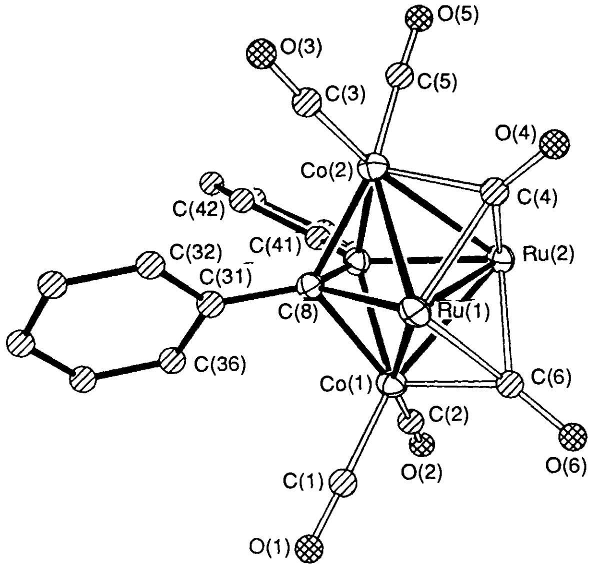


**Fig. 4** Molecular structure of complex **6** showing labelling scheme, cyclopentadienyl rings and all hydrogen atoms have been omitted for clarity

Dark orange crystals of **6**, grown from dichloromethane–hexane, were subjected to an X-ray diffraction study and the molecular structure is shown in Fig. 4, with selected bond lengths and angles given in Table 3. The complex has a butterfly type structure with the ruthenium atoms at the hinge and the cobalt atoms at the wing-tips, each $CoRu_2$ face being bridged by a $\mu_3$-CO ligand. The arrangement of metal atoms has a short Ru–Ru single bond at the hinge and four equal wing-tip–hinge Ru–Co distances of *ca.* 2.555 Å [Ru(1)–Ru(2) 2.735(1), Ru(1)–Co(2) 2.554(1), Ru(1)–Co(1) 2.553(1), Ru(2)–Co(1) 2.560(1) and Ru(2)–Co(2) 2.554(1) Å]. The diphenylethyne ligand is bound to all four metal atoms with the C–C bond almost parallel to the Ru–Ru hinge, thus giving the complex an octahedral $Ru_2Co_2C_2$ core. The alkyne bond length is similar to that of complex **2** with C(7)–C(8) 1.414(11) Å. The triply bridging carbonyl ligands are bound slightly closer to the cobalt atoms than the ruthenium atoms, average bond lengths being Ru–$\mu_3$-CO 2.15 Å and Co–$\mu_3$-CO 1.93 Å.

The complex can be viewed as a 60-electron, seven skeletal electron-pair $Ru_2Co_2C_2$ *closo*-octahedron, according to Wade–Mingos theory.[13] Complexes of this type are well known[9,14] and of interest as models for metal surface 'kink' sites.[15]

The IR spectrum of **6** shows a band at 1741 $cm^{-1}$ which may be assigned to the triply bridging carbonyl ligands and bands at 2014 and 1976 $cm^{-1}$ due to the four terminal CO ligands. The NMR spectra reflect the symmetry of the molecule, with single resonances for the cyclopentadienyl rings at δ 5.08 in the proton spectrum and δ 93.8 in the $^{13}C$ spectrum. The alkyne $\mu$-C signals occur at δ 152.8 while the terminal CO ligands are seen at δ 200.7 and the $\mu_3$-CO ligands downfield at δ 233.5. The FAB mass spectrum shows the parent ion at *m*/*z* 797 and peaks

**Table 3** Selected bond lengths (Å) and angles (°) for complex **6**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ru(1)–Ru(2) | 2.735(1) | Ru(2)–C(25) | 2.231(11) | Ru(1)–Co(1) | 2.553(1) | Co(1)–C(1) | 1.786(10) |
| Ru(1)–Co(2) | 2.554(1) | Co(1)–C(2) | 1.760(9) | Ru(1)–C(4) | 2.091(8) | Co(1)–C(6) | 1.916(9) |
| Ru(1)–C(6) | 2.232(9) | Co(1)–C(7) | 2.049(8) | Ru(1)–C(8) | 2.163(7) | Co(1)–C(8) | 2.072(7) |
| Ru(1)-C(11) | 2.247(10) | Co(2)–C(3) | 1.750(9) | Ru(1)–C(12) | 2.243(11) | Co(2)–C(4) | 1.949(8) |
| Ru(1)–C(13) | 2.196(11) | Co(2)–C(5) | 1.759(10) | Ru(1)–C(14) | 2.201(11) | Co(2)–C(7) | 2.064(8) |
| Ru(1)–C(15) | 2.222(9) | Co(2)–C(8) | 2.053(8) | Ru(2)–Co(1) | 2.560(1) | O(1)–C(1) | 1.123(12) |
| Ru(2)–Co(2) | 2.554(1) | O(2)–C(2) | 1.154(11) | Ru(2)–C(4) | 2.165(8) | O(3)–C(3) | 1.157(12) |
| Ru(2)–C(6) | 2.116(9) | O(4)–C(4) | 1.185(10) | Ru(2)–C(7) | 2.203(8) | O(5)–C(5) | 1.139(13) |
| Ru(2)–C(21) | 2.240(11) | O(6)–C(6) | 1.190(10) | Ru(2)–C(22) | 2.205(10) | C(7)–C(8) | 1.414(11) |
| Ru(2)–C(23) | 2.214(10) | C(7)–C(41) | 1.491(11) | Ru(2)–C(24) | 2.243(10) | C(8)–C(31) | 1.503(11) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ru(2)–Ru(1)–Co(1) | 57.8(1) | Ru(1)–Co(2)–C(4) | 53.3(2) | Ru(2)–Ru(1)–Co(2) | 57.6(1) | Ru(2)–Co(2)–C(4) | 55.5(2) |
| Co(1)–Ru(1)–Co(2) | 86.6(1) | C(3)–Co(2)–C(4) | 102.6(4) | Ru(2)–Ru(1)–C(4) | 51.2(2) | Ru(1)–Co(2)–C(5) | 154.6(3) |
| Co(1)–Ru(1)–C(4) | 108.2(2) | Ru(2)–Co(2)–C(5) | 94.8(3) | Co(2)–Ru(1)–C(4) | 48.4(2) | C(3)–Co(2)–C(5) | 94.4(5) |
| Ru(2)–Ru(1)–C(6) | 49.2(2) | C(4)–Co(2)–C(5) | 103.2(4) | Co(1)–Ru(1)–C(6) | 46.6(2) | Ru(1)–Co(2)–C(7) | 77.9(2) |
| Co(2)–Ru(1)–C(6) | 105.8(2) | Ru(2)–Co(2)–C(7) | 55.8(2) | C(4)–Ru(1)–C(6) | 89.7(3) | C(3)–Co(2)–C(7) | 140.1(4) |
| Ru(2)–Ru(1)–C(8) | 73.0(2) | C(4)–Co(2)–C(7) | 107.1(3) | Co(1)–Ru(1)–C(8) | 51.3(2) | C(5)–Co(2)–C(7) | 103.9(4) |
| Co(2)–Ru(1)–C(8) | 50.8(2) | Ru(1)–Co(2)–C(8) | 54.7(2) | C(4)–Ru(1)–C(8) | 96.9(3) | Ru(2)–Co(2)–C(8) | 78.7(2) |
| C(6)–Ru(1)–C(8) | 95.0(3) | C(3)–Co(2)–C(8) | 106.4(4) | Ru(1)–Ru(2)–Co(1) | 57.5(1) | C(4)–Co(2)–C(8) | 105.3(3) |
| Ru(1)–Ru(2)–Co(2) | 57.6(1) | C(5)–Co(2)–C(8) | 139.6(4) | Co(1)–Ru(2)–Co(2) | 86.5(1) | C(7)–Co(2)–C(8) | 40.2(3) |
| Ru(1)–Ru(2)–C(4) | 48.8(2) | Co(1)–C(1)–O(1) | 179.1(9) | Co(1)–Ru(2)–C(4) | 105.6(2) | Co(1)–C(2)–O(2) | 179.5(8) |
| Co(2)–Ru(2)–C(4) | 47.9(2) | Co(2)–C(3)–O(3) | 178.4(9) | Ru(1)–Ru(2)–C(6) | 53.0(2) | Ru(1)–C(4)–Ru(2) | 79.9(3) |
| Co(1)–Ru(2)–C(6) | 47.2(2) | Ru(1)–C(4)–Co(2) | 78.3(3) | Co(2)–Ru(2)–C(6) | 109.5(2) | Ru(2)–C(4)–Co(2) | 76.5(3) |
| C(4)–Ru(2)–C(6) | 90.9(3) | Ru(1)–C(4)–O(4) | 134.4(6) | Ru(1)–Ru(2)–C(7) | 71.8(2) | Ru(2)–C(4)–O(4) | 130.9(6) |
| Co(1)–Ru(2)–C(7) | 50.3(2) | Co(2)–C(4)–O(4) | 134.2(7) | Co(2)–Ru(2)–C(7) | 50.8(2) | Co(2)–C(5)–O(5) | 176.6(10) |
| C(4)–Ru(2)–C(7) | 95.3(3) | Ru(1)–C(6)–Ru(2) | 77.9(3) | C(6)–Ru(2)–C(7) | 95.5(3) | Ru(1)–C(6)–Co(1) | 75.5(3) |
| Ru(1)–Co(1)–Ru(2) | 64.7(1) | Ru(2)–C(6)–Co(1) | 78.6(3) | Ru(1)–Co(1)–C(1) | 93.1(3) | Ru(1)–C(6)–O(6) | 128.8(7) |
| Ru(2)–Co(1)–C(1) | 152.6(3) | Ru(2)–C(6)–O(6) | 134.1(7) | Ru(1)–Co(1)–C(2) | 163.0(3) | Co(1)–C(6)–O(6) | 138.0(8) |
| Ru(2)–Co(1)–C(2) | 102.0(3) | Ru(2)–C(7)–Co(1) | 73.9(2) | C(1)–Co(1)–C(2) | 96.2(4) | Ru(2)–C(7)–Co(2) | 73.4(2) |
| Ru(1)–Co(1)–C(6) | 57.9(3) | Co(1)–C(7)–Co(2) | 116.8(4) | Ru(2)–Co(1)–C(6) | 54.2(3) | Ru(2)–C(7)–C(8) | 107.1(5) |
| C(1)–Co(1)–C(6) | 101.1(4) | Co(1)–C(7)–C(8) | 70.8(4) | C(2)–Co(1)–C(6) | 106.3(4) | Co(2)–C(7)–C(8) | 69.5(4) |
| Ru(1)–Co(1)–C(7) | 78.2(2) | Ru(2)–C(7)–C(41) | 126.5(6) | Ru(2)–Co(1)–C(7) | 55.8(2) | Co(1)–C(7)–C(41) | 124.4(5) |
| C(1)–Co(1)–C(7) | 138.6(4) | Co(2)–C(7)–C(41) | 118.6(5) | C(2)–Co(1)–C(7) | 103.5(4) | C(8)–C(7)–C(41) | 126.2(7) |
| C(6)–Co(1)–C(7) | 107.5(3) | Ru(1)–C(8)–Co(1) | 74.1(2) | Ru(1)–Co(1)–C(8) | 54.6(2) | Ru(1)–C(8)–Co(2) | 74.5(2) |
| Ru(2)–Co(1)–C(8) | 78.3(2) | Co(1)–C(8)–Co(2) | 116.3(4) | C(1)–Co(1)–C(8) | 102.6(4) | Ru(1)–C(8)–C(7) | 108.1(5) |
| C(2)–Co(1)–C(8) | 135.9(4) | Co(1)–C(8)–C(7) | 69.1(4) | C(6)–Co(1)–C(8) | 108.7(3) | Co(2)–C(8)–C(7) | 70.3(5) |
| C(7)–Co(1)–C(8) | 40.1(3) | Ru(1)–C(8)–C(31) | 122.5(5) | Ru(1)–Co(2)–Ru(2) | 64.7(1) | Co(1)–C(8)–C(31) | 117.8(5) |
| Ru(1)–Co(2)–C(3) | 100.1(3) | Co(2)–C(8)–C(31) | 125.9(5) | Ru(2)–Co(2)–C(3) | 157.8(3) | C(7)–C(8)–C(31) | 129.1(7) |

due to subsequent loss of the six carbonyl ligands. An attempt to prepare the hexafluorobut-2-yne analogue of **6** was unsuccessful, the reaction between **1b** and $[Co_2(CO)_8]$ resulting only in the addition of two CO molecules to **1b** and its conversion to its precursor $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}\sigma{:}\sigma'\text{-}C_2(CF_3)_2\}(\eta\text{-}C_5H_5)_2]$.[5]

## Conclusion

This work shows that the unsaturated 32-electron complexes **1a** and **1b** are versatile and reactive precursors of new alkyne cluster complexes. The reactions occur readily at room temperature, the yields are mostly excellent and the resulting complexes are air stable. There is potential for extending this work by adding different metal fragments to these starting materials in a systematic approach to cluster aggregation. The reactivity of the new complexes is now being investigated with particular attention to carbon–carbon bond-forming and -breaking reactions involving unsaturated hydrocarbons and diazoalkanes.

## Experimental

All reactions were carried out using dried and degassed solvents under a nitrogen atmosphere using standard Schlenk techniques. Column chromatography was carried out on alumina columns (*ca.* 3 × 30 cm). IR spectra were recorded on a Perkin Elmer 1710 Fourier transform spectrometer, using calcium fluoride cells of 1 mm path length. Proton, $^{13}C$ and $^{19}F$ NMR spectra were obtained using JEOL FX-90 and GX-270 spectrometers. Elemental analyses were performed by the Microanalytical Laboratory of the School of Chemistry. Fast atom bombardment mass spectra were recorded by the SERC Mass Spectrometery Service Centre at the University of Swansea. The complex $[Ru(CO)_4(C_2H_4)]$ was prepared by an adaptation of a literature method.[10] The complexes $[Ru_2(\mu\text{-}CO)(\mu\text{-}C_2R_2)(\eta\text{-}C_5H_5)_2]$ (R = Ph **1a** or $CF_3$ **1b**) were prepared by known methods.[4,5]

*Synthesis.*—$[Ru_2Fe(CO)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(\mu_3\text{-}C_2Ph_2)(\eta\text{-}C_5H_5)_2]$ **2**. To a thf solution (200 $cm^3$) of $[Fe_2(CO)_9]$ (0.10 g, 0.27 mmol) was added 0.10 g (0.18 mmol) of complex **1a** in 50 $cm^3$ of thf. After stirring for 3 h, IR spectroscopy showed the presence of some starting material, so several portions of *ca.* 0.05 g (0.14 mmol) of solid $[Fe_2(CO)_9]$ were added over the next 2 h. After this time the solution had changed from dark green to dark purple. The solvent was removed under reduced pressure and the product chromatographed. Elution with dichloromethane–hexane (1 : 4) afforded a purple band from which 0.11 g (85%) of the dark purple crystalline solid $[Ru_2Fe(CO)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(\mu_3\text{-}C_2Ph_2)(\eta\text{-}C_5H_5)_2]$ **2** was obtained (Found: C, 49.60; H, 2.95%; *M* 707. $C_{29}H_{20}FeO_5Ru_2$ requires C, 49.30; H, 2.85%; *M* 707); ν(CO) (hexane) at 2028s, 1974m, 1963w, 1812w and 1759w $cm^{-1}$. NMR ($CDCl_3$): $^1H$, δ 7.24–6.99 (m, 10 H, 2 Ph) and 4.91 (s, 10 H, 2 $C_5H_5$); $^{13}C$, δ 243.6 (s, $\mu_3$-CO), 228.0 (s, μ-CO), 215.2 (s, 3 CO), 181.0 (s, 2 *C*Ph), 149.9, 127.5, 127.1, 126.5 (2 Ph) and 96.4 (s, 2 $C_5H_5$). Recrystallisation at −20 °C from dichloromethane–hexane afforded dark purple diamond shaped plate-like crystals.

$[Ru_2Fe(CO)_3(\mu\text{-}CO)(\mu_3\text{-}CO)\{\mu_3\text{-}C_2(CF_3)_2\}(\eta\text{-}C_5H_5)_2]$ **3**. A

**Table 4** Structure analyses

| | $[Ru_2Fe(CO)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(\mu_3\text{-}C_2Ph_2)(\eta\text{-}C_5H_5)_2]$ **2** | $[Ru_3(CO)_3(\mu\text{-}CO)(\mu_3\text{-}CO)\{\mu_3\text{-}C_2(CF_3)_2\}(\eta\text{-}C_5H_5)_2]$ **5b** | $[Ru_2Co_2(CO)_4(\mu_3\text{-}CO)_2(\mu_4\text{-}C_2Ph_2)(\eta\text{-}C_5H_5)_2]$ **6** |
|---|---|---|---|
| Crystal data | | | |
| Formula | $C_{29}H_{20}FeO_5Ru_2$ | $C_{19}H_{10}F_6O_5Ru_3$ | $C_{30}H_{20}Co_2O_6Ru_2$ |
| $M$ | 706.4 | 735.5 | 796.5 |
| Crystal system | Monoclinic | Orthorhombic | Orthorhombic |
| Space group (no.) | $P2_1/c$ (14) | $Pbca$ (61) | $P2_12_12_1$ (19) |
| $a$/Å | 10.283(2) | 15.678(4) | 9.950(3) |
| $b$/Å | 17.574(4) | 12.846(4) | 16.274(5) |
| $c$/Å | 14.078(3) | 20.342(5) | 16.600(4) |
| $\beta$/° | 91.23(3) | 90 | 90 |
| $U$/Å$^3$ | 2543.6(9) | 4097(2) | 2687.9(13) |
| $Z$ | 4 | 8 | 4 |
| $D_c$/g cm$^{-3}$ | 1.845 | 2.39 | 1.97 |
| $\mu$(Mo-K$\alpha$)/mm$^{-1}$ | 1.774 | 2.27 | 2.36 |
| $F(000)$ | 1392 | 2800 | 1560 |
| Data collection and reduction | | | |
| Crystal size/mm | 0.1 × 0.6 × 0.7 | 0.35 × 0.4 × 0.75 | 0.25 × 0.5 × 0.5 |
| $2\theta$ range /° | 4–55 | 3–50 | 3–56 |
| Scan width $\omega$ | 0.9 | 1.20 | 1.0 |
| Scan method | Wyckoff $\omega$ | $\theta$–$2\theta$ | $\theta$–$2\theta$ |
| Total data | 9216 | 4050 | 3678 |
| Unique data | 5847 | 3600 | 3652 |
| $R_{int}$ | 0.039 | 0.021 | — |
| Observed data ($N_o$) | 4072 | 2742 | 3012 |
| Observation criterion [$F^2 > n\sigma(F^2)$] | 2.0 | 2.0 | 2.0 |
| No. azimuthal scan data | 374 | 315 | 518 |
| Minimum, maximum transmission coefficients | 0.312, 0.405 | 0.190, 0.227 | 0.434, 0.634 |
| Extinction correction $\chi^a$ | — | 0.000 55(2) | 0.000 20(4) |
| Refinement | | | |
| No. of least-squares variables ($N_v$) | 334 | 296 | 252 |
| $R^b$ | 0.044 | 0.020 | 0.039 |
| $R'^b$ | 0.044 | 0.023 | 0.046 |
| $S^b$ | 1.16 | 0.90 | 1.01 |
| $g$ | 0.0004 | 0.000 25 | 0.0010 |
| Largest final difference map features/e Å$^{-3}$ | +0.80, −0.80 | +0.30, −0.29 | +0.92, −75 |

[a] Where $F^* = F[1 + 0.002\ \chi F^2/\sin(2\theta)]^{-\frac{1}{4}}$. [b] $R = \Sigma|\Delta|/\Sigma|F_o|$, $R' = [\Sigma w\Delta^2/\Sigma wF_o^2]^{\frac{1}{2}}$, $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$, $\Delta = F_o - F_c$, $w = [\sigma_c^2(F_o) + gF_o^2]^{-1}$, $\sigma_c^2(F_o)$ = variance in $F_o$ due to counting statistics.

solution of complex **1b** (0.10 g, 0.19 mmol) in thf (50 cm$^3$) was added to a stirred thf solution (150 cm$^3$) of $[Fe_2(CO)_9]$ (0.14 g, 0.28 mmol). Every 0.5 h for 4 h *ca.* 0.05 g (0.14 mmol) of solid $[Fe_2(CO)_9]$ was added to the reaction mixture, which changed from dark green to dark purple. Removal of solvent followed by chromatography yielded a dark red band, eluted with dichloromethane–hexane (1 : 10), which afforded 0.07 g (52%) of the purple crystalline solid $[Ru_2Fe(CO)_3(\mu\text{-}CO)(\mu_3\text{-}CO)\{\mu_3\text{-}C_2(CF_3)_2\}(\eta\text{-}C_5H_5)_2]$ **3** (Found: C, 33.05; H, 1.50%; *M* 692. $C_{19}H_{10}F_6FeO_5Ru_2$ requires C, 33.05; H, 1.45%; *M* 692); ν(CO) (hexane) at 2053s, 2018m, 1986w, 1844w and 1771w cm$^{-1}$. NMR ($CDCl_3$): $^1H$, major isomer **3a** δ 5.33 (s, 10 H, 2 $C_5H_5$), minor isomer **3b** δ 5.41 (s, 5 H, $C_5H_5$) and 5.36 (s, 5 H, $C_5H_5$); $^{13}C$, major isomer **3a** δ 239.6 (s, $\mu_3$-CO), 219.7 (s, μ-CO), 210.7 (s, 3 CO), 157.7 [q, *J* 44, 2 *C*($CF_3$)], 127.6 (q, *J* 276, 2 $CF_3$) and 95.6 (s, 2 $C_5H_5$), minor isomer **3b** δ 243.9 (s, $\mu_3$-CO), 221.5 (s, μ-CO), 210.7 (s, CO), 209.0 (s, CO), 205.4 (s, CO), 94.0 (s, $C_5H_5$) and 90.4 (s, $C_5H_5$); $^{19}F\text{-}\{^1H\}$, major isomer **3a** δ −51.5 (s, 2 $CF_3$), minor isomer **3b** δ −50.0 (q, *J* 12.2, $CF_3$) and −52.2 (q, *J* 12.2 Hz, $CF_3$).

$[Ru_3(CO)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(\mu_3\text{-}C_2Ph_2)(\eta\text{-}C_5H_5)_2]$ **4**. The complex $[Ru(CO)_4(C_2H_4)]$ was prepared from irradiation of an ethene-purged heptane solution (200 cm$^3$) of $[Ru_3(CO)_{12}]$ (0.15 g, 0.23 mmol) with a 500 W tungsten-halogen lamp. The reaction goes to completion in *ca.* 1.5 h (the solution goes from orange to colourless). This solution was then added dropwise over *ca.* 0.25 h to a dichloromethane solution (100 cm$^3$) of **1a** (0.30 g, 0.56 mmol). The solution changed from dark green to dark red after stirring for *ca.* 1.5 h. Removal of solvent under reduced pressure then chromatography produced a purple band, eluted with dichloromethane–hexane (3 : 7), which yielded 0.34 g (80%) of the purple microcrystalline solid $[Ru_3(CO)_3(\mu\text{-}CO)(\mu_3\text{-}CO)(\mu_3\text{-}C_2Ph_2)(\eta\text{-}C_5H_5)_2]$ **4** (Found: C, 46.35; H, 2.65%; *M* 754. $C_{29}H_{20}O_5Ru_3$ requires C, 46.15; H, 2.65%; *M* 754); ν(CO) (hexane) at 2053s, 1991m, 1987m, 1809m and 1742 cm$^{-1}$. NMR ($CDCl_3$): $^1H$, major isomer **4a** δ 7.18–6.75 (m, 10 H, 2 Ph) and 4.98 (s, 10 H, 2 $C_5H_5$), minor isomer **4b** δ 7.18–6.75 (m, 10 H, 2 Ph), 5.15 (s, 5 H, $C_5H_5$) and 4.98 (s, 5 H, $C_5H_5$); $^{13}C$, major isomer **4a** δ 245.8 (s, $\mu_3$-CO), 229.8 (s, μ-CO), 198.0 (s, 3 CO), 176.3 (s, 2 *C*Ph), 149.8, 128.0, 127.3, 125.5 (2 Ph) and 94.6 (s, 2 $C_5H_5$), minor isomer **4b** δ 248.0 (s, $\mu_3$-CO), 217.1 (s, μ-CO), 196.9 (s, CO), 195.6 (s, CO), 193.8 (s, CO), 180.7 (s, *C*Ph), 151.0, 149.3, 128.6, 127.7, 127.1, 124.9 (2 Ph), 94.8 (s, $C_5H_5$) and 89.2 (s, $C_5H_5$).

$[Ru_3(CO)_3(\mu\text{-}CO)(\mu_3\text{-}CO)\{\mu_3\text{-}C_2(CF_3)_2\}(\eta\text{-}C_5H_5)_2]$ **5**. The complex $[Ru(CO)_4(C_2H_4)]$ was prepared from $[Ru_3(CO)_{12}]$ (0.18 g, 0.28 mmol) in 200 cm$^3$ of heptane and then added dropwise over *ca.* 0.25 h to a dichloromethane solution (100 cm$^3$) of complex **1b** (0.35 g, 0.67 mmol). Over a period of *ca.* 3.5 h, the solution changed from dark green to red. The solvent was removed under reduced pressure and the residue chromatographed. Elution with dichloromethane–hexane (1 : 5) gave a red band from which 0.43 g (88%) of the red crystalline complex $[Ru_3(CO)_3(\mu\text{-}CO)(\mu_3\text{-}CO)\{\mu_3\text{-}C_2(CF_3)_2\}(\eta\text{-}C_5H_5)_2]$ **5** was ob-

**Table 5** Atomic coordinates ( × $10^4$) for complex **2**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Ru(1) | 1967(1) | 1338(1) | 3162(1) |
| Ru(2) | 4920(1) | 1767(1) | 2530(1) |
| Fe | 2835(1) | 784(1) | 1523(1) |
| C(1) | 1152(7) | 824(5) | 1169(5) |
| C(2) | 3119(7) | −110(4) | 998(4) |
| C(3) | 3447(7) | 1319(4) | 551(4) |
| C(4) | 2457(5) | 2100(3) | 2137(4) |
| C(5) | 3701(5) | 1489(3) | 3860(4) |
| C(6) | 697(6) | 966(4) | 4348(5) |
| C(7) | 1005(6) | 1736(4) | 4507(5) |
| C(8) | 471(7) | 2159(4) | 3738(5) |
| C(9) | −135(6) | 1656(5) | 3108(5) |
| C(10) | 12(6) | 907(4) | 3475(5) |
| C(11) | 6002(6) | 2106(4) | 1710(5) |
| C(12) | 6434(6) | 1954(4) | 2660(5) |
| C(13) | 5829(6) | 2488(4) | 3239(5) |
| C(14) | 5072(6) | 2972(4) | 2662(5) |
| C(15) | 5176(6) | 2735(4) | 1725(5) |
| C(16) | 3016(5) | 367(3) | 2878(4) |
| C(17) | 4237(5) | 591(3) | 2534(4) |
| C(18) | 2585(5) | −373(3) | 3291(4) |
| C(19) | 1706(6) | −859(4) | 2846(5) |
| C(20) | 1279(7) | −1511(4) | 3300(6) |
| C(21) | 1706(7) | −1692(4) | 4193(6) |
| C(22) | 2564(7) | −1212(4) | 4647(5) |
| C(23) | 3015(6) | −559(4) | 4219(4) |
| C(24) | 5465(5) | 137(3) | 2482(4) |
| C(25) | 5999(6) | −210(3) | 3279(4) |
| C(26) | 7172(6) | −585(4) | 3245(5) |
| C(27) | 7852(6) | −629(4) | 2423(6) |
| C(28) | 7343(6) | −278(4) | 1631(5) |
| C(29) | 6170(6) | 104(4) | 1652(5) |
| O(1) | 90(5) | 845(5) | 906(5) |
| O(2) | 3315(6) | −696(3) | 670(4) |
| O(3) | 3804(7) | 1657(3) | −88(3) |
| O(4) | 1944(4) | 2591(2) | 1706(3) |
| O(5) | 4135(4) | 1440(3) | 4635(3) |

tained (Found: C, 31.00; H, 1.35%; *M* 737. $C_{19}H_{10}F_6O_5Ru_3$ requires C, 31.05; H, 1.35%; M 737); ν(CO) (hexane) at 2085s, 2036s, 2018m, 1862w and 1750w cm$^{-1}$; NMR ($CDCl_3$) $^1H$, major isomer **5b** δ5.39 (s, 5 H, $C_5H_5$) and 5.32 (s, 5 H, $C_5H_5$), minor isomer **5a** δ 5.17 (s, 2 $C_5H_5$); $^{13}C$, major isomer **5b** δ 242.5 (s, $\mu_3$-CO), 212.8 (s, μ-CO), 193.3 (s, CO), 192.6 (s, CO), 191.4 (s, CO), 156.6 [coincident q, *J* 44, 2 *C*($CF_3$)], 128.2 (q, *J* 274, $CF_3$), 126.7 (q, *J* 274 Hz, $CF_3$), 93.4 (s, $C_5H_5$) and 88.4 (s, $C_5H_5$), minor isomer **5a** δ 93.8 (s, 2 $C_5H_5$); $^{19}F$-{$^1H$}, major isomer **5b** δ −47.8 (q, *J* 12.2, $CF_3$) and −51.9 (q, *J* 12.2 Hz, $CF_3$). Recrystallisation from dichloromethane–hexane at −20 °C produced red plate-like crystals.

[$Ru_2Co_2(CO)_4(\mu_3$-$CO)_2(\mu_4$-$C_2Ph_2)(\eta$-$C_5H_5)_2$] **6**. Solid [$Co_2(CO)_8$] (0.11 g, 0.32 mmol) was added to a dichloromethane solution (150 cm$^3$) of complex **2a** (0.15 g, 0.28 mmol) and the mixture stirred for 1 h. Removal of solvent afforded a dark brown solid which was purified by chromatography. Elution with dichloromethane–hexane (2:3) produced a dark orange band which afforded 0.02 g (10%) of the dark orange solid [$Ru_2Co_2(CO)_4(\mu_3$-$CO)_2(\mu_4$-$C_2Ph_2)(\eta$-$C_5H_5)_2$] **6** (Found: C, 45.55; H, 2.55%; *M* 797. $C_{30}H_{20}Co_2O_6Ru_2$ requires C, 45.25; H, 2.55%; *M* 797); ν(CO) (hexane) at 2014s, 1976m and 1741w cm$^{-1}$; NMR ($CDCl_3$): $^1H$, δ 7.26–7.02 (m, 10 H, 2 Ph) and 5.08 (s, 10 H, 2 $C_5H_5$); $^{13}C$ δ 233.5 (s, 2 $\mu_3$-CO), 200.7 (br, 4 CO), 152.8 (s, 2 *C*Ph), 149.8, 130.4, 126.9, 126.1 (Ph) and 93.8 (s, 2 $C_5H_5$). A purple band and three yellow bands were eluted from the column in small yields and were unidentified. Recrystallisation of **6** at −20 °C from dichloromethane–hexane solution yielded dark orange plate-like crystals.

**Table 6** Atomic coordinates ( × $10^4$) for complex **5b**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Ru(1) | −442(1) | 2356(1) | 6431(1) |
| Ru(2) | 1286(1) | 2321(1) | 6590(1) |
| Ru(3) | 701(1) | 2737(1) | 5367(1) |
| C(1) | −1083(3) | 3657(4) | 6462(2) |
| O(1) | −1463(3) | 4401(3) | 6488(2) |
| C(2) | −1404(3) | 1450(4) | 6333(2) |
| O(2) | −1942(2) | 860(3) | 6313(2) |
| C(3) | −398(3) | 2297(3) | 7360(2) |
| O(3) | −396(2) | 2254(3) | 7917(1) |
| C(4) | 789(3) | 3633(3) | 6249(2) |
| O(4) | 752(2) | 4536(2) | 6348(2) |
| C(5) | −490(2) | 2409(3) | 5289(2) |
| O(5) | −1083(2) | 2333(3) | 4949(2) |
| C(6) | 964(2) | 1330(3) | 5804(2) |
| C(7) | 411(2) | 1129(3) | 6339(2) |
| C(8) | 1555(3) | 575(4) | 5486(2) |
| F(8A) | 1206(2) | 152(3) | 4951(1) |
| F(8B) | 1789(2) | −226(2) | 5868(1) |
| F(8C) | 2296(2) | 1001(3) | 5292(2) |
| C(9) | 312(3) | 105(3) | 6681(2) |
| F(9A) | 46(3) | −639(2) | 6270(2) |
| F(9B) | 1006(2) | −280(2) | 6976(1) |
| F(9C) | −272(2) | 129(2) | 7161(2) |
| C(21) | 2453(4) | 1633(5) | 6975(3) |
| C(22) | 2664(3) | 2597(5) | 6717(3) |
| C(23) | 2231(4) | 3316(5) | 7079(3) |
| C(24) | 1764(3) | 2842(4) | 7561(2) |
| C(25) | 1885(3) | 1786(4) | 7501(2) |
| C(31) | 1471(4) | 2550(4) | 4457(2) |
| C(32) | 1847(3) | 3314(5) | 4843(2) |
| C(33) | 1288(3) | 4149(4) | 4886(2) |
| C(34) | 554(3) | 3905(4) | 4548(2) |
| C(35) | 651(3) | 2905(4) | 4284(2) |

*Structure Determinations for* [$Ru_2Fe(CO)_3(\mu$-$CO)(\mu_3$-$CO)(\mu_3$-$C_2Ph_2)(\eta$-$C_5H_5)_2$] **2**, [$Ru_3(CO)_3(\mu$-$CO)(\mu_3$-$CO)\{\mu_3$-$C_2(CF_3)_2\}(\eta$-$C_5H_5)_2$] **5** *and* [$Ru_2Co_2(CO)_4(\mu_3$-$CO)_2(\mu_4$-$C_2Ph_2)(\eta$-$C_5H_5)_2$] **6**.—Many of the details of the structure analyses carried out on **2**, **5b** and **6** are listed in Table 4. X-ray diffraction measurements were made at room temperature using Siemens four-circle P3m diffractometers on single crystals mounted in thin-walled glass capillaries with graphite-monochromated Mo-Kα X-radiation ($\bar{\lambda}$ = 0.710 73 Å). Cell dimensions for each analysis were determined from the setting angle values of 20, 27 and 40 centred reflections respectively.

For each structure analysis intensity data were collected for unique portions of reciprocal space and corrected for Lorentz, polarisation, and long-term intensity fluctuations, the latter on the basis of the intensities of three check reflections repeatedly measured during data collection. Corrections for X-ray absorption effects were applied on the basis of azimuthal scan data. The structures were solved by heavy-atom (Patterson or direct and Fourier difference) methods, and refined by full-matrix least squares against *F*. All non-hydrogen atoms were assigned anisotropic thermal parameters except for cyclopentadienyl and phenyl group carbon atoms of **6**, which were assigned isotropic thermal parameters. All hydrogen atoms were constrained to ideal geometries with C–H 0.96 Å and assigned fixed isotropic thermal parameters. The absolute structure of **6** was assigned on the basis of refinement of the Rogers η parameter [η = 1.00(8)].[16] Extinction corrections were applied for **5b** and **6**.

Final difference syntheses showed no chemically significant features, the largest being close to the metal atoms. Refinements converged smoothly to residuals given in Table 4. Tables 5–7 report the positional parameters for these structure determinations.

All calculations were made with programs of the SHELXTL PLUS[17] system as implemented on a Siemens R3m/V structure

**Table 7** Atomic coordinates ($\times 10^4$) for complex **6**

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Ru(1) | 5 810(1) | 157(1) | 1 132(1) |
| Ru(2) | 8 336(1) | 812(1) | 1 225(1) |
| Co(1) | 6 215(1) | 1702(1) | 1 249(1) |
| Co(2) | 7 280(1) | 8(1) | 2 385(1) |
| O(1) | 3 500(8) | 2 102(5) | 731(5) |
| O(2) | 7 311(9) | 3 351(4) | 1 057(6) |
| O(3) | 5 928(9) | −1 348(5) | 3 185(5) |
| O(4) | 8 118(6) | −1 067(3) | 1 082(4) |
| O(5) | 9 802(8) | −280(7) | 3 209(5) |
| O(6) | 6 853(7) | 1 123(4) | −365(3) |
| C(1) | 4 552(10) | 1 951(6) | 926(6) |
| C(2) | 6 882(9) | 2 696(5) | 1 133(6) |
| C(3) | 6 450(10) | −802(6) | 2 868(5) |
| C(4) | 7 641(8) | −444(5) | 1 319(5) |
| C(5) | 8 804(10) | −147(7) | 2 899(5) |
| C(6) | 6 850(9) | 1 074(6) | 350(5) |
| C(7) | 7 162(8) | 1 267(5) | 2 259(5) |
| C(8) | 5 870(8) | 910(5) | 2 205(4) |
| C(11) | 5 144(11) | −584(6) | 62(6) |
| C(12) | 5 031(12) | −1 070(7) | 733(6) |
| C(13) | 4 130(11) | −707(7) | 1 264(7) |
| C(14) | 3 640(11) | 24(7) | 911(6) |
| C(15) | 4 303(10) | 108(6) | 146(6) |
| C(21) | 9 997(11) | 329(6) | 448(6) |
| C(22) | 10 387(10) | 301(6) | 1 277(6) |
| C(23) | 10 430(11) | 1 104(7) | 1 577(6) |
| C(24) | 10 075(11) | 1 642(6) | 946(6) |
| C(25) | 9 779(11) | 1 154(7) | 253(7) |
| C(31) | 4 650(8) | 1 062(5) | 2 718(5) |
| C(32) | 3 934(11) | 442(6) | 3 086(6) |
| C(33) | 2 794(11) | 592(6) | 3 546(6) |
| C(34) | 2 376(12) | 1 397(6) | 3 665(7) |
| C(35) | 3 067(11) | 2 020(7) | 3 310(6) |
| C(36) | 4 197(10) | 1 876(6) | 2 854(5) |
| C(41) | 7 668(9) | 1 796(5) | 2 927(7) |
| C(42) | 7 204(9) | 1 694(5) | 3 717(5) |
| C(43) | 7 659(12) | 2 201(7) | 4 337(6) |
| C(44) | 8 619(13) | 2 801(8) | 4 194(7) |
| C(45) | 9 121(13) | 2 893(7) | 3 427(7) |
| C(46) | 8 622(11) | 2 414(6) | 2 797(6) |

determination system. Complex neutral-atom scattering factors were taken from ref. 18.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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## References

1 S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 173.
2 L. A. Brady, A. F. Dyke, S. E. Garner, V. Guerchais, S. A. R. Knox, J. P. Maher, S. M. Nicholls and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1992, 4.
3 L. A. Brady, A. F. Dyke, S. E. Garner, S. A. R. Knox, A. Irving, S. M. Nicholls and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1993, 487.
4 R. E. Colborn, A. F. Dyke, B. P. Gracey, S. A. R. Knox, K. A. Macpherson, K. A. Mead and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1990, 761.
5 S. M. Nicholls, Ph.D. Thesis, University of Bristol, 1991.
6 G. Natile and G. Bor, *J. Organomet. Chem.*, 1972, **35**, 185; F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, 1974, **96**, 3438.
7 B. E. R. Schilling and R. Hoffmann, *J. Am. Chem. Soc.*, 1979, **101**, 3456.
8 (*a*) E. Sappa, A. Tiripicchio and P. Braunstein, *Chem. Rev.*, 1983, **3**, 203; (*b*) S. Aime, R. Gobetto, L. Milone, D. Osella, L. Violano, A. J. Arce and Y. DeSanctis, *Organometallics*, 1991, **10**, 2854; (*c*) H. Bantel, A. K. Powell and H. Vahrenkamp, *Chem. Ber.*, 1990, **123**, 1607.
9 J. F. Halet, J. Y. Saillard, R. Lissillour, M. J. McGlinchey and G. Jaouen, *Inorg. Chem.*, 1985, **24**, 218.
10 B. F. G. Johnson, J. Lewis and M. V. Twigg, *J. Organomet. Chem.*, 1974, **67**, C75.
11 See for example, L. Busetto, M. Green, B. Hessner, J. A. K. Howard, J. C. Jeffery and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1983, 519; F. W. B. Einstein, K. G. Tyers, A. S. Tracey and D. Sutton, *Inorg. Chem.*, 1986, **25**, 1631; R. S. Dickson, O. M. Paravagna and H. Pateras, *Organometallics*, 1990, **9**, 2780.
12 E. Rosenberg, J. Bracker-Novak, R. W. Gellert, S. Aime, R. Gobetto and D. Osella, *J. Organomet. Chem.*, 1989, **365**, 163.
13 K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1; D. M. P. Mingos, *Acc. Chem. Res.*, 1984, **17**, 311.
14 See, for example, R. Rumin, F. Robin, F. Y. Pétillon, K. W. Muir and I. Stevenson, *Organometallics*, 1991, **10**, 2274.
15 E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker and W. R. Pretzer, *Chem. Rev.*, 1979, **2**, 91.
16 D. Rogers, *Acta Crystallogr., Sect. A*, 1981, **37**, 734.
17 G. M. Sheldrick, SHELXTL PLUS, Revision 4.2, Göttingen, 1990.
18 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

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