Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 46.[1] Synthesis of Heteronuclear Trimetal Compounds from the Dimetallic Compounds [ReM(≡CC₆H₄Me-4)(CO)₉] (M = Cr, Mo, or W) and [CoW(≡CC₆H₄Me-4)(CO)₈]; X-Ray Structure of [CrReFe(μ₃-CC₆H₄Me-4)(μ-CO)(CO)₁₁]*

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The compounds [ReCr(≡CC₆H₄Me-4)(CO)₉] and [Fe₂(CO)₉] in diethyl ether at room temperature afford the trimetal complex [CrReFe(μ₃-CC₆H₄Me-4)(μ-CO)(CO)₁₁]. An X-ray diffraction study established that there are two independent molecules in the asymmetric unit and that the molecular structure consists of a μ₃-CCrReFe core with the chromium and the rhenium atoms ligated by four carbonyl groups and the iron atom by three such groups. A carbonyl ligand bridges the Cr–Re vector, however, the chromium and rhenium sites are disordered (60:40) and since the molecules have pseudo-mirror planes relating the metal tetracarbonyl fragments the bridging CO group may not be symmetrically disposed. Reactions between the compounds [ReM(≡CC₆H₄Me-4)(CO)₉] (M = Mo or W) and [Fe₂(CO)₉] afford the related cluster compounds [MReFe(μ₃-CC₆H₄Me-4)(μ-CO)(CO)₁₁], but these species were shown to be formed *via* the intermediacy of the complexes [MReFe(μ-CC₆H₄Me-4)(CO)₁₃]. The compounds [CoW(≡CC₆H₄Me-4)(CO)₈] and [Fe₂(CO)₉] react to give the cluster complex [CoFe₂(μ₃-CC₆H₄Me-4)(μ-CO)(CO)₉], and reactions of the latter with PPh₃ and with Ph₂PCH₂PPh₂ are described. Spectroscopic data for the new complexes are reported and discussed. Analysis of the ¹³C-{¹H} n.m.r. data for [CoFe₂(μ₃-CC₆H₄Me-4)(μ-CO)(CO)₉] has shown that the aromatic ring of the tolylmethylidyne group is locked into a fixed position at −80 °C. However, in the closely related cluster [Co₃(μ₃-CC₆H₄Me-4)(CO)₉] the group is free to rotate about the μ₃-C–C¹ axis at this temperature. These results have been interpreted in the light of extended Hückel molecular orbital calculations on the bonding of these molecules.

We are currently investigating reactions of the compounds [ReM(≡CC₆H₄Me-4)(CO)₉] (1, M = Cr, Mo, or W) with low-valent metal species in the expectation that these dimetal complexes will be useful precursors to metal clusters. In the previous paper,[1] we showed that platinum(0) fragments will combine with the carbon–metal triple bonds present in the compounds (1) to give new tri- and penta-nuclear metal clusters. Earlier we reported[2] reactions with [Co₂(CO)₈] which afford the cluster complexes [MReCo₂(μ₃-CC₆H₄Me-4)(CO)₁₅]. Herein we describe reactions of [Fe₂(CO)₉] with the dimetal compounds (1) which yield 'mixed-metal' clusters containing iron. We also report some preliminary work using the compound [CoW(≡CC₆H₄Me-4)(CO)₈] (2)[3] as a reagent for metal cluster synthesis.

Results and Discussion

Treatment of the compounds (1b) and (1c) with one equivalent of [Fe₂(CO)₉], in diethyl ether at room temperature, afforded the orange crystalline complexes [MReFe(μ-CC₆H₄Me-4)-(CO)₁₃] (3b, M = Mo; 3c, M = W). However, the corresponding reaction with (1a) gave only a red-brown complex
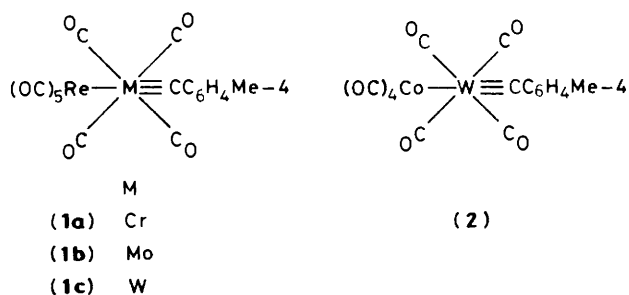
	M
(1a)	Cr
(1b)	Mo
(1c)	W

(2)

	M
(3a)	Cr
(3b)	Mo
(3c)	W

	M
(4a)	Cr
(4b)	Mo
(4c)	W
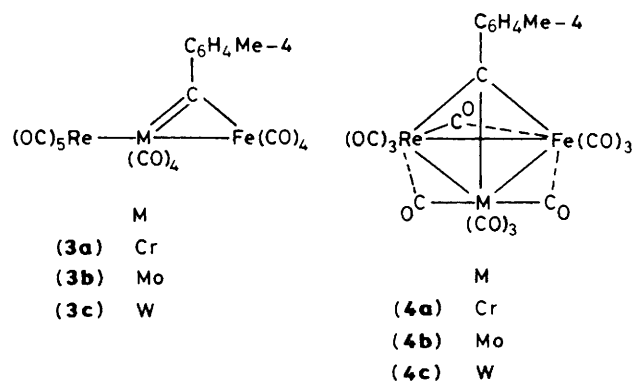
Table 1. Analytical[a] and physical data for the trimetal compounds

	Compound[b]	Colour	Yield (%)	$v_{max.}(CO)^c/cm^{-1}$	Analysis (%) C	H
(3b)	[MoReFe(μ-CR)(CO)$_{13}$]	Orange	30	d 2 110m, 2 072s, 2 020vs, 2 011s, 1 990m	31.2 (31.3)	1.0 (0.9)
(3c)	[WReFe(μ-CR)(CO)$_{13}$]	Orange	70	d 2 112m, 2 075s, 2 018vs, 2 011vs, 1 985m, 1 958w	28.7 (28.2)	0.8 (0.9)
(4a)	[CrReFe(μ$_3$-CR)(μ-CO)(CO)$_{11}$]	Red-brown	73	2 105w, 2 058s, 2 041s, 2 010m br, 1 973w (sh), 1 929w br, 1 854w br	32.3 (32.8)	1.1 (1.0)
(4b)	[MoReFe(μ$_3$-CR)(μ-CO)(CO)$_{11}$]	Red-brown	56	2 105w, 2 064s, 2 045s, 2 024s, 2 002s, 1 985m, 1 885m br	30.3 (30.9)	1.0 (0.9)
(4c)	[WReFe(μ$_3$-CR)(μ-CO)(CO)$_{11}$]	Brown	95	2 105w, 2 062s, 2 043s, 2 024m, 2 012m, 2 002m, 1 987m, 1 966w, 1 888w br	27.4 (27.8)	0.7 (0.8)
(5a)	[CoFe$_2$(μ$_3$-CR)(μ-CO)(CO)$_9$]	Brown	60	d 2 097w, 2 054vs, 2 047s, 2 036s, 2 007m, 1 844w br	39.5 (39.0)	1.2 (1.3)
(5b)	[CoFe$_2$(μ$_3$-CR)(μ-CO)(CO)$_8$(PPh$_3$)]	Red-brown	92	d 2 076m, 2 033vs, 2 023s, 1 984m, 1 800w br	53.3 (53.3)	2.9 (2.8)
(6)	[CoFe$_2$(μ$_3$-CR)(μ-CO)(μ-dppm)(CO)$_7$]	Red-brown	89	2 055s, 2 005s, 1 996s, 1 970m, 1 935w, 1 797s br	55.5 (55.8)	3.3 (3.3)
(7)	[CoFe$_2$(μ$_3$-CR)(μ-CO)(μ-dppm)$_2$(CO)$_5$]	Dark green	65	1 999s, 1 969vs, 1 937s, 1 762w br	63.0 (63.5)	4.4 (4.2)
(8)	[CoFe$_2$(μ-H)(μ$_3$-CR)(μ-CO)(μ-dppm)$_2$(CO)$_5$][BF$_4$]	Green	94	2 054m, 2 043m, 2 012vs, 1 991s, 1 856w br	59.0 (59.2)	3.8 (4.0)

[a] Calculated values are given in parentheses. [b] R = C$_6$H$_4$Me-4. [c] Measured in CH$_2$Cl$_2$ unless otherwise stated. [d] In hexane.

[CrReFe(μ$_3$-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_{11}$] (4a). Compound (3b) was unstable, and in solution after several hours yields [MoReFe(μ$_3$-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_{11}$] (4b), an analogue of (4a). The complex (3c) is more stable, and stirring in light petroleum for ca. 2 d is required for complete conversion into [WReFe(μ$_3$-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_{11}$] (4c). However, the transformation of (3c) into (4c) is complete within ca. 2 th in the presence of one equivalent of [Fe$_2$(CO)$_9$]. Accelerated formation of (4c) in this manner may be related to the ability of di-iron nonacarbonyl to release Fe(CO)$_4$ fragments.[4] The latter could abstract CO forming [Fe(CO)$_5$], and thus promote condensation of (3c) to the trimetallatetrahedrane (4c). A chromium-containing compound (3a) was not isolated, but from the decomposition behaviour of (3b) and (3c) it seems likely that (3a) is an intermediate in the synthesis of (4a).

The compounds (3b) and (3c) were characterised by microanalysis and by n.m.r. spectroscopy (Tables 1 and 2). The ^{13}C-{^{1}H} n.m.r. spectra of both species showed characteristic resonances for μ-CC$_6$H$_4$Me-4 groups bridging two metal centres.[5] The spectrum of (3c), measured at −40 °C, was especially informative in the CO region, showing six signals (Table 2). The radial W(CO)$_4$ and Re(CO)$_4$ groups each give rise to one peak, as does the axial ReCO group, and the four carbonyls bound to the iron display three resonances (relative intensity 1:1:2). Assuming that co-ordination around the iron is pseudo-octahedral, with the ligating μ-C and W atoms in the equatorial plane, the two axial CO groups would be equivalent and the two CO ligands trans to μ-C or trans to W, respectively, would be in different chemical environments, thus explaining the pattern of FeCO resonances observed. The spectrum of (3b), measured at −30 °C, indicates that at this temperature some degree of site exchange of CO groups on iron is occurring.

As mentioned above, compound (4a) is obtained directly from (1a) and [Fe$_2$(CO)$_9$]. Similarly, compounds (4b) and (4c) may be prepared directly from (1b) and (1c), respectively, by stirring diethyl ether solutions of the complexes with two equivalents of [Fe$_2$(CO)$_9$] for ca. 8 h. The compounds were characterised in the usual manner (Tables 1 and 2). The ^{13}C-

{^{1}H} n.m.r. spectra showed characteristic peaks for triply bridging[5,6] alkylidyne nuclei at δ 285.9 (4a), 283.3 (4b), and 272.0 p.p.m. (4c). As expected, the chemical shifts are considerably less deshielded than those for the μ-C nuclei in (3b) (366.0 p.p.m.) and (3c) (338.9 p.p.m.), in which the alkylidyne groups are bridging only two metal centres.

Although from their ^{13}C-{^{1}H} n.m.r. spectra there was clear evidence for CC$_6$H$_4$Me-4 ligands capping three metal centres in the complexes (4), the spectroscopic data did not define fully the molecular structures. Consequently, a single-crystal X-ray diffraction study was carried out on (4a), suitable crystals being available. The results are summarised in Table 3, and the molecule is shown in Figure 1.

Crystals of (4a) have two very similar crystallographically independent molecules of the complex per asymmetric unit. Only molecule 1 is shown in Figure 1 and discussed in the text; salient data for both molecules are listed in Table 3. As anticipated, the structural core is a CrReFe triangle of metal atoms capped by a tolylmethylidyne ligand. However, the Cr and Re atoms are disordered. In ca. 40% of the molecules they are interchanged, adopting the new sites labelled Cr(1a) and Re(1a). The Fe atom carries three approximately orthogonal terminal carbonyl ligands (mean Fe–C–O 177°), whilst the Cr or Re metal centres are each ligated by four carbonyl groups, three of which adopt terminal positions whilst the fourth is weakly semi-bridged to the Fe atom [Cr(1)–C(5a)–O(5a) 166.2(8), Re(1)–C(10a)–O(10a) 168.1(9)°]. Overall the molecule has a pseudo-mirror plane relating the two M(CO)$_4$ (M = Cr or Re) fragments and this accounts for the apparent absence of serious disorder amongst the carbonyl ligands in this complex. It should be noted that (4a) may in reality be appreciably less symmetric than the superimposition of the two disordered components might suggest. Thus although the Cr–Re bond is apparently quite symmetrically bridged by a carbonyl ligand [Cr(1)–C(2a) 2.17(2), Re(1)–C(2a) 2.30(1) Å], a band in the i.r. spectrum at 1 854 cm^{-1} suggests that in CH$_2$Cl$_2$ solution at least, this ligand adopts a semi-bridging rather than a purely bridging geometry.

Although the cluster as a whole is co-ordinatively saturated,

Table 2. Hydrogen-1 and carbon-13 n.m.r. data[a] for the trimetal compounds

Compound	^{1}H (δ)[b]	^{13}C (δ)[c]
(3b)	[d] 2.31 (s, 3 H, Me-4), 7.06, 7.33 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) 8]	[e] 366.0 (μ-C), 220.3 (MoCO), 214.6, 206.4 (FeCO), 194.3 (4 CO, ReCO), 183.1 (1 CO, ReCO), 157.8 [C^1(C$_6$H$_4$)], 140.9, 129.3, 126.4 (C$_6$H$_4$), 21.8 (Me-4)
(3c)	2.34 (s, 3 H, Me-4), 7.16, 7.44 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) 8]	[f] 338.9 [μ-C, J(WC) 125], 214.3 (1 CO, FeCO), 210.8 [4 CO, WCO, J(WC) 122], 209.6 (1 CO, FeCO), 205.4 (2 CO, FeCO), 192.9 (4 CO, ReCO), 182.6 (1 CO, ReCO), 160.3 [C^1(C$_6$H$_4$)], 139.8, 129.3, 125.0 (C$_6$H$_4$), 21.9 (Me-4)
(4a)	2.43 (s, 3 H, Me-4), 7.20, 7.42 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) 8]	285.9 (μ_3-C), 208.0, 185.7 (CO), 157.4 [C^1(C$_6$H$_4$)], 137.2, 128.4, 128.0 (C$_6$H$_4$), 20.0 (Me-4)
(4b)	2.42 (s, 3 H, Me-4), 7.13, 7.42 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) 8]	283.3 (μ_3-C), 210.1, 205.1, 189.5 (CO), 158.7 [C^1(C$_6$H$_4$)], 137.7, 129.5, 128.7 (C$_6$H$_4$), 20.8 (Me-4)
(4c)	2.42 (s, 3 H, Me-4), 7.12, 7.48 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) 8]	272.0 (μ_3-C), 210.1, 194.6, 189.7 (CO), 159.5 [C^1(C$_6$H$_4$)], 138.1, 131.0, 129.3 (C$_6$H$_4$), 21.2 (Me-4)
(5a)	2.44 (s, 3 H, Me-4), 7.25, 7.44 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) 7]	[g] 296.1 (μ_3-C), 250.3 (μ-CO), 212.2, 208.7, 202.3 (FeCO), 201.1 (br, CoCO), 156.6 [C^1(C$_6$H$_4$)], 139.7, 131.9, 129.8, 128.7, 126.9 (C$_6$H$_4$), 21.9 (Me-4)
(5b)	2.41 (s, 3 H, Me-4), 7.20—7.60 (m, 19 H, C$_6$H$_4$ and Ph)	295.9 (μ_3-C), 211.0 (FeCO), 202.8 (br, CoCO), 157.5 [C^1(C$_6$H$_4$)], 138.2—128.8 (C$_6$H$_4$ and Ph), 21.4 (Me-4)
(6)	2.66 (s, 3 H, Me-4), 3.75—4.06 (m, 2 H, CH$_2$), 6.60—7.60 (m, 24 H, C$_6$H$_4$ and Ph)	[g] 299.8 (μ_3-C), 258.9 (μ-CO), 216.6 [d, FeCO, J(PC) 12], 209.4, 208.0, 207.6, 206.4 (FeCO), 205.0 (vbr, CoCO), 157.1 [C^1(C$_6$H$_4$)], 139.2—125.3 (C$_6$H$_4$ and Ph), 25.5 [d of d, CH$_2$, J(PP) 28, 28], 21.4 (Me-4)
(7)	2.15 (s, 3 H, Me-4), 3.78—4.04 (m, 4 H, CH$_2$), 6.50—7.50 (m, 44 H, C$_6$H$_4$ and Ph)	309.6 (μ_3-C), 274.0 (μ-CO), 215.2 (CO), 159.9 [C^1(C$_6$H$_4$)], 139.9—125.6 (C$_6$H$_4$ and Ph), 38.6 (m, br, CH$_2$), 21.1 (Me-4)
(8)	- 20.55 (br, 1 H, μ-H), 2.35 (s, 3 H, Me-4), 3.31—3.47 (m, 2 H, CH$_2$), 4.12—4.43 (m, 2 H, CH$_2$), 6.50—7.60 (m, 44 H, C$_6$H$_4$ and Ph)	211.4 (br, FeCO), 158.6 [C^1(C$_6$H$_4$)], 139.0—126.1 (C$_6$H$_4$ and Ph), 44.3 (m, br, CH$_2$), 21.2 (Me-4)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at room temperature unless otherwise stated. [b] Measured in CD$_2$Cl$_2$ unless otherwise stated. [c] Hydrogen-1 decoupled, to high frequency of SiMe$_4$ and measured in CD$_2$Cl$_2$–CH$_2$Cl$_2$. [d] In CDCl$_3$. [e] Measured at -30 °C. [f] Measured at -40 °C. [g] Measured at -80 °C.
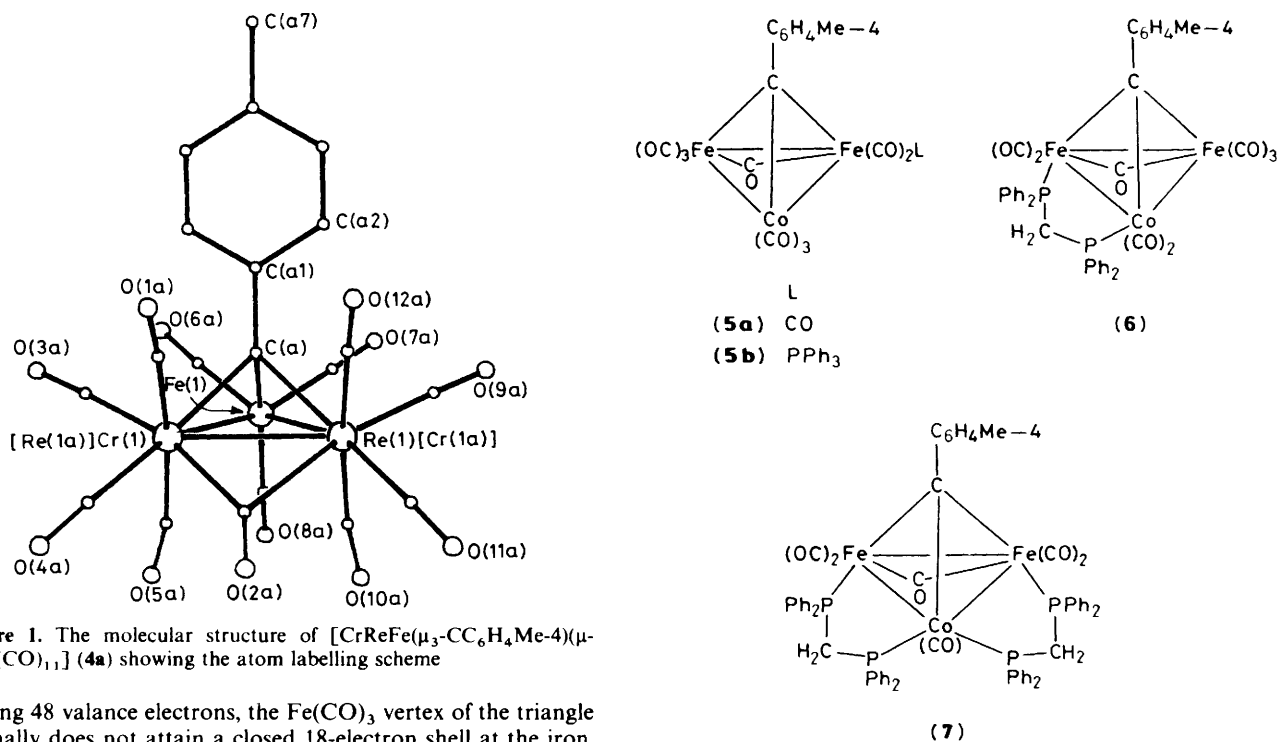
Figure 1. The molecular structure of [CrReFe(μ_3-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_{11}$] (4a) showing the atom labelling scheme


L
(5a) CO
(5b) PPh$_3$

(6)

(7)

having 48 valance electrons, the Fe(CO)$_3$ vertex of the triangle formally does not attain a closed 18-electron shell at the iron. However, the μ-C–Fe separation [1.872(8) Å] is appreciably shorter than that found[6] in the closely related complex [Fe$_2$W(μ_3-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_8$(η-C$_5$H$_5$)] [1.969(5) and 2.036(5) Å] in which both iron atoms have filled valence shells. It is therefore possible that the relatively short μ-C–Fe separation in (4a) reflects some degree of multiple bond character which, together with the semi-bridging carbonyl ligands C(5a)–O(5a) and C(10a)–O(10a), would help to delocalise electron density within the cluster. We have previously observed and discussed similar features for the Fe(CO)$_3$ moieties in the

clusters [FePtW(μ_3-CC$_6$H$_4$Me-4)(CO)$_5$(PMePh$_2$)$_2$(η-C$_5$H$_5$)] and [FePtW(μ_3-CC$_6$H$_4$Me-4)(CO)$_6$(PEt$_3$)(η-C$_5$H$_5$)].[7]

Complex (2) also seemed a likely precursor to trimetal cluster compounds, and here we report its reaction with [Fe$_2$(CO)$_9$]. In diethyl ether at room temperature the two reactants give a separable mixture of [W(CO)$_6$], [Fe(CO)$_5$], [Fe$_3$(CO)$_{12}$], and [CoFe$_2$(μ_3-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_9$] (5a). The i.r. spectrum of the latter (Table 1) showed a band at 1 844 cm^{-1} attributable to a bridging carbonyl group. In agreement there was a

Table 3. Selected bond lengths (Å) and angles (°) for [CrReFe(μ₃-CC₆H₄Me-4)(μ-CO)(CO)₁₁] (4a)

Molecule 1		Molecule 2		Molecule 1		Molecule 2	
Re(1)–Cr(1)	2.944(2)	Re(2a)–Cr(2a)	2.941(2)	Re(1)–Fe(1)	2.748(2)	Re(2a)–Fe(2)	2.773(2)
Re(1)–C(a)	2.212(9)	Re(2a)–C(b)	2.227(8)	Re(1)–C(2a)	2.30(1)	Re(2a)–C(2b)	2.28(1)
Re(1)–C(9a)	1.908(9)	Re(2a)–C(9b)	1.97(1)	Re(1)–C(10a)	1.951(9)	Re(2a)–C(10b)	1.95(1)
Re(1)–C(11a)	1.94(1)	Re(2a)–C(11b)	1.918(8)	Re(1)–C(12a)	1.977(9)	Re(2a)–C(12b)	1.97(1)
Cr(1)–Fe(1)	2.755(2)	Cr(2a)–Fe(2)	2.739(2)	Cr(1)–C(a)	2.184(7)	Cr(2a)–C(b)	2.175(8)
Cr(1)–C(1a)	1.968(9)	Cr(2a)–C(1b)	1.923(9)	Cr(1)–C(2a)	2.17(2)	Cr(2a)–C(2b)	2.20(1)
Cr(1)–C(3a)	1.87(1)	Cr(2a)–C(3b)	1.85(1)	Cr(1)–C(4a)	1.930(8)	Cr(2a)–C(4b)	1.96(1)
Cr(1)–C(5a)	1.939(9)	Cr(2a)–C(5b)	1.95(1)	Fe(1)–C(a)	1.872(8)	Fe(2)–C(b)	1.873(9)
Fe(1)–C(6a)	1.78(1)	Fe(2)–C(6b)	1.78(1)	Fe(1)–C(7a)	1.776(8)	Fe(2)–C(7b)	1.86(1)
Fe(1)–C(8a)	1.836(8)	Fe(2)–C(8b)	1.770(9)				
Cr(1)–Re(1)–Fe(1)	57.8(1)	Cr(2a)–Re(2a)–Fe(2)	57.2(1)	Cr(1)–Re(1)–C(a)	47.5(2)	Cr(2a)–Re(2a)–C(b)	47.3(2)
Fe(1)–Re(1)–C(a)	42.7(2)	Fe(2)–Re(2a)–C(b)	42.3(2)	Re(1)–Cr(1)–Fe(1)	57.5(1)	Re(2a)–Cr(2a)–Fe(2)	58.3(1)
Re(1)–Cr(1)–C(a)	48.4(2)	Re(2a)–Cr(2a)–C(b)	48.8(2)	Fe(1)–Cr(1)–C(a)	42.6(2)	Fe(2)–Cr(2a)–C(b)	42.9(2)
Re(1)–Fe(1)–Cr(1)	64.7(1)	Re(2a)–Fe(2)–Cr(2a)	64.5(1)	Re(1)–Fe(1)–C(a)	53.2(3)	Re(2a)–Fe(2)–C(b)	53.1(2)
Cr(1)–Fe(1)–C(a)	52.2(2)	Cr(2a)–Fe(2)–C(b)	52.3(2)	Re(1)–C(a)–Cr(1)	84.1(2)	Re(2a)–C(b)–Cr(2a)	83.8(3)
Re(1)–C(a)–Fe(1)	84.1(3)	Re(2a)–C(b)–Fe(2)	84.6(3)	Cr(1)–C(a)–Fe(1)	85.2(3)	Cr(2a)–C(b)–Fe(2)	84.8(4)
Re(1)–C(a)–C(a1)	130.0(6)	Re(2a)–C(b)–C(b1)	127.6(6)	Cr(1)–C(a)–C(a1)	129.5(6)	Cr(2a)–C(b)–C(b1)	130.8(5)
Fe(1)–C(a)–C(a1)	127.7(5)	Fe(2)–C(b)–C(b1)	128.9(6)	Re(1)–C(2a)–Cr(1)	82.5(3)	Re(2a)–C(2b)–Cr(2a)	82.0(3)
Re(1)–C(2a)–O(2a)	133.9(9)	Re(2a)–C(2b)–O(2a)	136.2(9)	Cr(1)–C(2a)–O(2a)	143.5(9)	Cr(2a)–C(2b)–O(2b)	142(1)
Cr(1)–C(5a)–O(5a)	166.2(8)	Cr(2a)–C(5b)–O(5b)	165.7(7)	Re(1)–C(10a)–O(10a)	168.1(9)	Re(2a)–C(9b)–O(9b)	169.3(8)
Mean terminal		Mean terminal		Mean terminal		Mean terminal	
Cr(1)–C–O	177	Cr(2a)–C–O	177	Re(1)–C–O	178	Re(2a)–C–O	178
Mean Fe–C–O	177	Mean Fe–C–O	177				
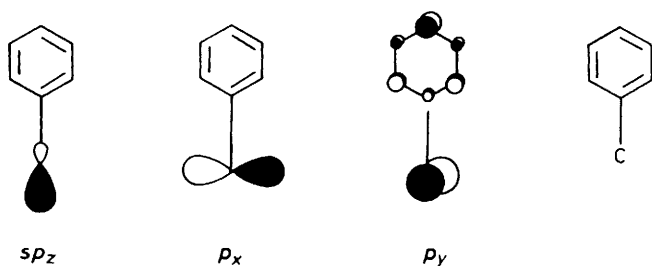
Figure 2. Frontier orbitals of the C–C₆H₅ fragment. The localised carbyne p_x orbital is more effective in cluster bonding than p_y, by virtue of the conjugation of the latter with the aromatic π system

(I)   (II)
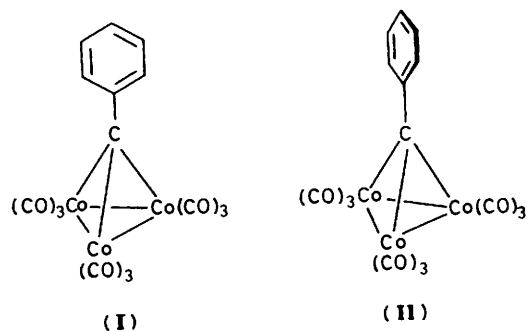
resonance in the ¹³C-{¹H} n.m.r. spectrum at δ 250.3 p.p.m. (Table 2) which is characteristic for a μ-CO ligand.[8] The ¹³C-{¹H} n.m.r. spectrum also revealed the expected signal for the μ₃-C nucleus at δ 296.1 p.p.m. In the spectrum recorded at ambient temperatures a pattern of four distinct peaks for the C₆H₄ group of the tolylmethylidyne moiety is observed [δ(C₆H₄) 157.3 (C¹), 139.9 (C⁴), 129.7 (C² and C⁶), and 129.3 p.p.m. (C³ and C⁵)]. On cooling the sample to −80 °C, however, an interesting change in the spectrum is apparent. At the lower temperature there are six separate resonances for the C₆H₄ group [δ(C₆H₄) 156.6 (C¹), 139.7 (C⁴), 131.9, 129.8, 128.7, and 126.9 p.p.m.], indicating that rotation about the

μ₃-C–C₆H₄Me-4 bond has ceased, and furthermore that the plane of the tolyl ring lies in the plane of symmetry of the molecule defined by the Co, μ₃-C, and μ-CO atoms. In general, in compounds such as (5a), with a trimetallatetrahedrane core, a pattern of four peaks is observed in the ¹³C-{¹H} n.m.r. spectrum for the C₆H₄ group, even at low temperatures. Thus, for example, in the spectrum of [Co₃(μ₃-CC₆H₄Me-4)(CO)₉] at −80 °C we have observed these four resonances at δ 155.9 (C¹), 138.7 (C⁴), 129.3 (C² and C⁶), and 128.7 p.p.m. (C³ and C⁵).

It is clear, therefore, that the energy barriers to rotation of the aryl ring in the closely related clusters [Co₃(μ₃-CC₆H₄Me-4)(CO)₉] and [CoFe₂(μ₃-CC₆H₄Me-4)(μ-CO)(CO)₉] are quite different. The origin of this difference may be rationalised from a molecular orbital viewpoint in the following way. The analysis is based on elementary symmetry and perturbation theory arguments, supported by extended Hückel[9,10] molecular orbital calculations, with the parameters given in the Appendix. In each case the molecular orbitals (m.o.s) of the cluster are most readily derived from the frontier orbitals of an M₃(CO)ₙ (n = 9 or 10) triangle and a capping C–C₆H₅ group. The replacement of C₆H₄Me-4 by C₆H₅, for reasons of computational expediency, makes no difference to the conclusions derived from the calculations. The frontier orbitals of the latter fragment (Figure 2) consist of a low-lying sp hybrid, and two higher-lying orbitals derived predominantly from carbon 2p. In the case of an axially symmetric carbyne fragment such as C–H or C–CH₃, these orbitals are degenerate but in the case of the C–C₆H₅ fragment one orbital is lower lying and less localised on the carbyne carbon by virtue of its being conjugated with the π system of the aromatic ring.

The frontier orbitals of the symmetrical C_{3v} Co₃(CO)₉ triangle have been discussed by Schilling and Hoffmann[11] and are illustrated on the left of Figure 3. The carbyne sp hybrid interacts with, and is stabilised by, a cluster m.o. of a_1 symmetry, whilst each of the carbyne p orbitals interacts with the appropriate component of the 2e set of metal orbitals. By virtue of the degeneracy of the latter, the orientation of the C–C₆H₅ ring with respect to the triangle is almost immaterial and indeed the calculated energy difference between conformers (I) and (II) is negligible.
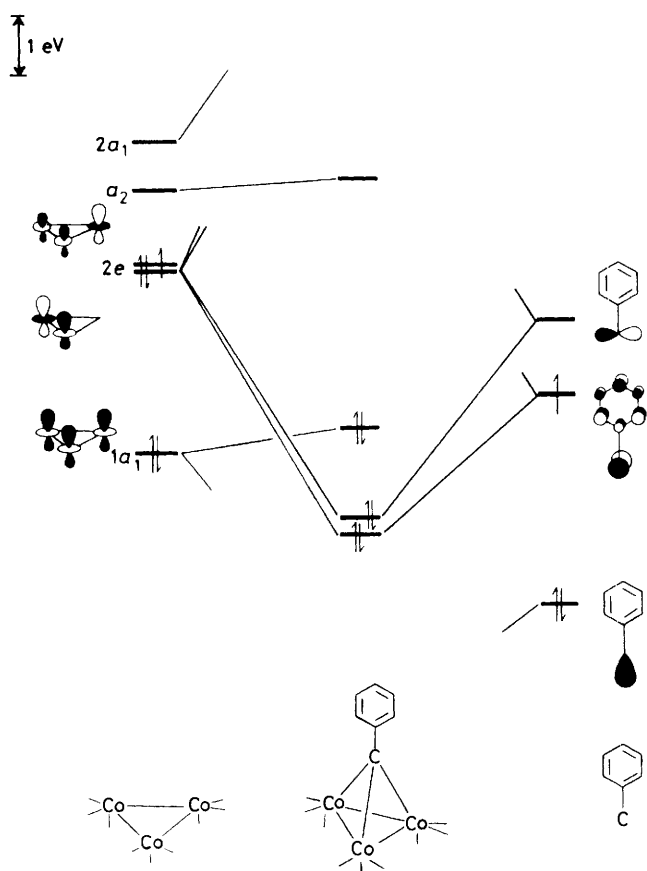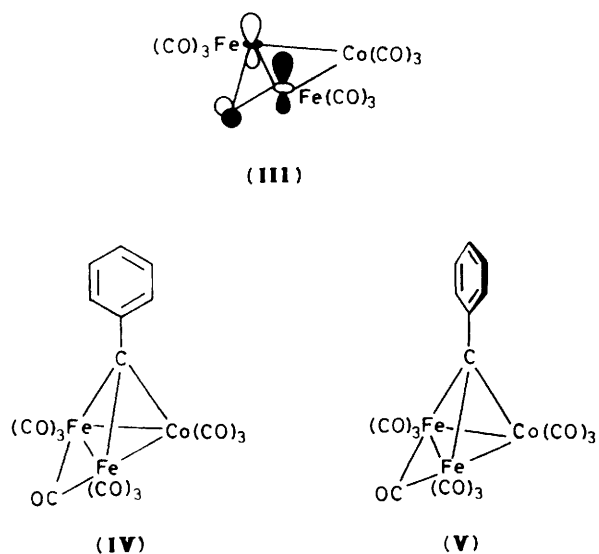
Figure 3. Molecular orbital interaction diagram for $[Co_3(\mu_3\text{-}CC_6H_5)(CO)_9]$. The two carbyne p orbitals interact with the appropriate component of the $2e$ set of cluster orbitals, so that the interaction is essentially independent of the orientation of the two fragments

(III)

(IV)

(V)

The frontier m.o.s of the less symmetrical $CoFe_2(\mu\text{-}CO)(CO)_9$ triangle are quite similar to those of $Co_3(CO)_9$. The major difference is that the degeneracy of the $2e$ set in the latter has been raised; one component being extensively delocalised onto the bridging carbonyl ligand *via* its π^* orbital as shown in (III). In this case the capping $C\text{-}C_6H_5$ group exhibits a marked

conformational preference, with (IV) being favoured over (V). In (IV) the large overlap between the most effective tangential orbitals, *i.e.* those most highly localised on the carbyne carbon and the M_3 triangle, results in tangential bonding in the cluster being maximised. In the alternative conformer (V), the two most effective fragment tangential orbitals are orthogonal and the overall tangential bonding is correspondingly weaker. This conformer is calculated to be some 58 kJ mol^{-1} less stable than (IV). Conformer (IV) places the aryl ring in the molecular symmetry plane, exactly in agreement with the low-temperature n.m.r. results.

It is interesting to compare the products from the reactions of compounds (1) and (2) with $[Fe_2(CO)_9]$. The ability of the latter to release $Fe(CO)_4$ fragments has already been mentioned[4] and the stepwise addition of such species to alkylidynetungsten compounds is well known.[6] Thus treatment of the complexes (1) with one equivalent of $[Fe_2(CO)_9]$ yields (3). Further addition of $[Fe_2(CO)_9]$ might be expected to give a cluster containing an ReMFe$_2$ core. However, in practice the $[Fe_2(CO)_9]$ promotes loss of CO from the initially formed complex to give (4). Treatment of (2) with $[Fe_2(CO)_9]$ could be envisaged to give initially a trimetal complex $[CoWFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_{12}]$ analogous to (3). Further treatment with $[Fe_2(CO)_9]$ might then yield $[CoWFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_{14}]$, a tetranuclear metal cluster containing a pendant $Co(CO)_4$ moiety. A similar species $[MReCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{15}]$ with a pendant $Re(CO)_5$ group has been characterised and shown to release readily an $M(CO)_x$ fragment to afford $[Co_2Re(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{10}]$.[2] Loss of a tungsten carbonyl fragment from the hypothetical species $[CoWFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_{14}]$ would yield the observed product (5a). Interestingly, compound (2) reacts with $[Co_2(CO)_8]$ to afford the homonuclear metal cluster $[Co_3(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_9]$, mentioned above, and identified by i.r. and n.m.r. spectroscopy. No product containing tungsten could be isolated. This provides another example of the facile loss of a $W(CO)_x$ fragment from a tetranuclear metal cluster.

Treatment of (5a) with PPh$_3$ in light petroleum affords the dark red-brown compound $[CoFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(PPh_3)]$ (5b), data for which are given in Tables 1 and 2. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed a sharp singlet resonance at 59.5 p.p.m. characteristic of a $Fe(PPh_3)$ group rather than a $Co(PPh_3)$ moiety, since signals for the latter tend to be broad due to the ^{59}Co quadrupole effect.

Compound (5a) reacts with one or with two equivalents of $Ph_2PCH_2PPh_2$ (dppm) to give the complexes $[CoFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(\mu\text{-}dppm)(CO)_7]$ (6) and $[CoFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(\mu\text{-}dppm)_2(CO)_5]$ (7), respectively, characterised by the data given in Tables 1 and 2. A derivative of (5a) containing three dppm ligands could not be obtained. The i.r. spectra of (6) and (7) show characteristic bands for the μ-CO ligands at $1\,797$ and $1\,762$ cm^{-1}, respectively. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (6) measured at $-80\,^\circ C$ was informative. Resonances at 299.8 and 258.9 p.p.m. may be assigned to the μ_3-C and μ-CO groups. There are five peaks for terminal FeCO groups, one of which is a doublet signal due to $^{31}P\text{-}^{13}C$ coupling (Table 2). The two CO ligands on the cobalt exhibit a broad resonance. Peaks due to the C_6H_4 group occur with the many signals due to the phenyl rings and hence it was not possible to discern whether the C_6H_4 ring was displaying six resonances as observed in the spectrum of (5a) at $-80\,^\circ C$.

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (6) was in accord with the dppm ligand bridging a Co–Fe bond since two doublet resonances were observed at 60.9 and 50.2 p.p.m. [$J(PP)$ 82 Hz], with the latter signal being very broad due to the ^{59}Co quadrupole effect. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (7) was very similar in appearance to that of (6), as expected for the symmetrical structure proposed. There were two resonances [$J(PP)$ 100 Hz]

at δ 57.0 and 34.5 p.p.m., with the latter very broad and therefore assigned to the CoP$_2$ group.

There are previously reported examples of μ$_3$-alkylidyne–trimetal complexes with a bridging dppm ligand, e.g. [Co$_3$(μ$_3$-CMe)(μ-dppm)(CO)$_7$],[12] [Co$_2$W(μ$_3$-CC$_6$H$_4$Me-4)(μ-CO)$_3$(μ-dppm)(CO)$_3$(η-C$_5$H$_5$)],[13] and [Fe$_2$W(μ$_3$-CC$_6$H$_4$Me-4)(μ-CO)-(μ-dppm)(CO)$_6$(η-C$_5$H$_5$)].[6] However, there appears to be no known species with two μ-dppm groups akin to (7). The latter cluster would be expected to be electron rich, due to the strong electron-donor properties of the dppm ligands. In accord with this property, compound (7) was readily protonated with HBF$_4$·Et$_2$O affording the salt [Co$_2$Fe(μ-H)(μ$_3$-CC$_6$H$_4$Me-4)-(μ-CO)(μ-dppm)$_2$(CO)$_5$][BF$_4$] (8). The ^{1}H n.m.r. spectrum shows a resonance at δ − 20.55 which was broad in character suggesting that the hydride ligand bridges a Co–Fe bond. Since the cation of (8) no longer retains the plane of symmetry of the precursor (7), the ^{31}P-{^{1}H} n.m.r. spectrum shows two pairs of peaks at δ 53.5 and 42.6 p.p.m. [J(PP) 77 Hz], and at δ 46.8 and 23.8 p.p.m. [J(PP) 77 Hz]. In both pairs the more shielded resonance (δ 42.6 and 23.8) is very broad indicating that these peaks are due to phosphorus atoms attached to cobalt. Unfortunately, due to poor solubility, a good quality ^{13}C-{^{1}H} n.m.r. spectrum could not be obtained.

Formation of (8) provides a further example of protonation of a trimetal cluster containing a μ$_3$-CC$_6$H$_4$Me-4 ligand. It has recently been shown that the salt [Rh$_2$W(μ-H)(μ$_3$-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_2$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)$_2$][BF$_4$] can be obtained by treating [Rh$_2$W(μ$_3$-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_2$(η-C$_5$H$_5$)-(η-C$_5$Me$_5$)$_2$] with HBF$_4$·Et$_2$O.[14] With the dirhodiumtungsten species, however, there was some evidence that initial H$^+$ attack occurs at the μ$_3$-CC$_6$H$_4$Me-4 group, with subsequent transfer of the proton to a Rh–W edge of the Rh$_2$W triangle. No evidence for an intermediate containing a μ-C(C$_6$H$_4$Me-4)H fragment was obtained in the synthesis of (8).

Experimental

All experiments were carried out under an atmosphere of oxygen-free nitrogen, using Schlenk-tube techniques. All solvents were dried and deoxygenated before use. Light petroleum refers to that fraction of b.p. 40—60 °C. The reagent HBF$_4$·Et$_2$O (Aldrich Chemical Co.) consists of a 54% solution of HBF$_4$ in diethyl ether. Chromatography columns were either Florisil (Fluka, 100—200 mesh) or Kieselgel (Merck, 70—230 mesh). The instrumentation used for spectroscopic studies has been described in earlier parts of this series. Phosphorus-31 n.m.r. spectra were measured in CD$_2$Cl$_2$–CH$_2$Cl$_2$ (1:4), and chemical shifts (p.p.m.) are positive to high frequency of 85% H$_3$PO$_4$ (external). The compounds [ReM(≡CC$_6$H$_4$Me-4)-(CO)$_9$] and [CoW(≡CC$_6$H$_4$Me-4)(CO)$_8$] were prepared by the methods used to obtain their phenylmethylidyne analogues.[3,15]

Analytical and other data for the new compounds are given in Tables 1 and 2.

Preparation of the Compounds [MReFe(μ-CC$_6$H$_4$Me-4)-(CO)$_{13}$] (M = Mo or W).—The complex (1c) (0.51 g, 0.70 mmol) and [Fe$_2$(CO)$_9$] (0.25 g, 0.70 mmol) were stirred in Et$_2$O (15 cm^3) for 4 h, after which all the di-iron nonacarbonyl had dissolved. Volatile material was removed in vacuo and the residue dissolved in CH$_2$Cl$_2$ (5 cm^3). Florisil (ca. 2—3 g) was added to adsorb the product. After pumping, all solid material was transferred to the top of a Florisil-packed chromatography column (20 × 3 cm), and the product eluted with light petroleum. After removal of solvent in vacuo, orange micro-crystals of [WReFe(μ-CC$_6$H$_4$Me-4)(CO)$_{13}$] (3c) (0.34 g) were obtained.

The compound [MoReFe(μ-CC$_6$H$_4$Me-4)(CO)$_{13}$] (3b) (0.07

g) was similarly prepared from (1b) (0.19 g, 0.30 mmol) and [Fe$_2$(CO)$_9$] (0.11 g, 0.30 mmol).

Preparation of the Compounds [MReFe(μ$_3$-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_{11}$] (M = Cr, Mo, or W).—Compound (1c) (0.15 g, 0.70 mmol) and [Fe$_2$(CO)$_9$] (0.63 g, 1.75 mmol) in Et$_2$O (15 cm^3) were stirred together for 8 h, after which time all the di-iron nonacarbonyl had dissolved. Solvent was removed in vacuo, and the residue dissolved in CH$_2$Cl$_2$ (20 cm^3) and filtered through a Florisil pad (4 × 3 cm). Removal of solvent in vacuo, washing the product with light petroleum (5 × 10 cm^3), and drying, gave brown microcrystals of [WReFe(μ$_3$-CC$_6$H$_4$Me-4)(μ-CO)-(CO)$_{11}$] (4c) (0.58 g).

The compound [CrReFe(μ$_3$-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_{11}$] (4a) (0.15 g), was similarly obtained from (1a) (0.14 g, 0.24 mmol) and [Fe$_2$(CO)$_9$] (0.22 g, 0.59 mmol), as was [MoReFe(μ$_3$-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_{11}$] (4b) (0.13 g) from (1b) (0.20 g, 0.31 mmol) and [Fe$_2$(CO)$_9$] (0.28 g, 0.77 mmol).

Preparation of the Compound [CoFe$_2$(μ$_3$-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_9$].—Compound (2) (1.71 g, 3.00 mmol) was dissolved in Et$_2$O (200 cm^3) and treated with [Fe$_2$(CO)$_9$] (3.28 g, 9.00 mmol). The mixture was stirred (3 h) until all the di-iron nonacarbonyl had dissolved, producing a dark brown solution. Volatile material was removed in vacuo and the residue dissolved in light petroleum (25 cm^3) and chromatographed on a Kieselgel column (ca. 40 × 4 cm). Elution with the same solvent afforded some [Fe$_3$(CO)$_{12}$] (green), followed by a dark brown eluate. The latter was collected, solvent removed in vacuo, and the residue crystallised at − 78 °C from light petroleum (ca. 30 cm^3) giving dark brown microcrystals of [CoFe$_2$(μ$_3$-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_9$] (5a) (1.00 g).

Reactions of the Compound [CoFe$_2$(μ$_3$-CC$_6$H$_4$Me-4)(μ-CO)-(CO)$_9$] (5a) with Tertiary Phosphines.—(a) With PPh$_3$. A mixture of (5a) (0.14 g, 0.25 mmol) and PPh$_3$ (0.067 g, 0.25 mmol) in light petroleum (25 cm^3) was stirred at room temperature for 4 h. Solvent was removed in vacuo, and the residue was dissolved in light petroleum–CH$_2$Cl$_2$ (5 cm^3, 4:1) and chromatographed on a Kieselgel column (20 × 3 cm). Elution with the same solvent mixture afforded, after removal of solvent in vacuo, dark red-brown microcrystals of [CoFe$_2$(μ$_3$-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_8$(PPh$_3$)] (5b) (0.18 g); ^{31}P-{^{1}H} n.m.r., δ 59.5 p.p.m. (s, FeP).

(b) With Ph$_2$PCH$_2$PPh$_2$. A mixture of (5a) (0.11 g, 0.20 mmol) and dppm (0.08 g, 0.20 mmol) in light petroleum (30 cm^3) was stirred at room temperature for 3 h. After cooling to ca. − 40 °C, the supernatant liquid was removed with a syringe. Crystallisation of the residue from Et$_2$O (20 cm^3) at − 78 °C afforded red-brown microcrystals of [CoFe$_2$(μ$_3$-CC$_6$H$_4$Me-4)(μ-CO)(μ-dppm)(CO)$_7$] (6) (0.16 g); ^{31}P-{^{1}H} n.m.r., δ 60.9 [d, PFe, J(PP) 82] and 50.2 p.p.m. [d, br, PCo, J(PP) 82 Hz].

A mixture of (5a) (0.22 g, 0.40 mmol) and dppm (0.31 g, 0.80 mmol) in CH$_2$Cl$_2$ (30 cm^3) was stirred at room temperature for 5 d, the colour changing from brown to dark green. Solvent was removed in vacuo and the residue dissolved in CH$_2$Cl$_2$–light petroleum (10 cm^3, 1:1) and chromatographed on Kieselgel (20 × 3 cm column). Elution with the same solvent mixture developed a dark brown band followed by a dark green band. The former was identified (i.r.) as compound (6). The green eluate was evaporated in vacuo, giving dark green microcrystals of [CoFe$_2$(μ$_3$-CC$_6$H$_4$Me-4)(μ-CO)(μ-dppm)$_2$(CO)$_5$] (7) (0.26 g); ^{31}P-{^{1}H} n.m.r., δ 57.0 [d, PFe, J(PP) 100 Hz] and 34.5 p.p.m. (m, br, PCo).

Compound (7) (0.30 g, 0.25 mmol) in CH$_2$Cl$_2$ (30 cm^3) was protonated with HBF$_4$·Et$_2$O (0.1 cm^3, ca. 0.25 mmol). After stirring for 30 min, solvent was removed in vacuo and the residue washed with Et$_2$O (3 × 20 cm^3). Crystallisation from CH$_2$Cl$_2$–

Table 4. Atomic positional parameters (fractional co-ordinates, × 10^4), with estimated standard deviations in parentheses, for (**4a**)

Atom	x	y	z	Atom	x	y	z
Re(1)	5 514(1)	3 539(1)	1 676(1)	O(9a)	7 991(8)	2 913(5)	3 048(4)
Cr(1a)	5 514(1)	3 539(1)	1 676(1)	C(11a)	5 916(11)	4 713(6)	1 512(5)
Cr(1)	3 191(1)	3 033(1)	737(1)	O(11a)	6 083(9)	5 411(4)	1 420(4)
Re(1a)	3 191(1)	3 033(1)	737(1)	C(12a)	7 262(11)	3 230(5)	889(5)
Cr(2)	487(1)	3 160(1)	6 968(1)	O(12a)	8 296(7)	3 061(4)	449(4)
Re(2a)	487(1)	3 160(1)	6 968(1)	C(b)	2 017(10)	2 459(5)	6 053(4)
Re(2)	3 852(1)	2 024(1)	7 005(1)	C(b2)	2 738(10)	1 317(6)	5 160(5)
Cr(2a)	3 852(1)	2 024(1)	7 005(1)	Hb(2)	3 856	1 194	5 314
Fe(1)	3 860(1)	2 322(1)	2 342(1)	C(b3)	2 310(11)	851(6)	4 601(5)
Fe(2)	2 757(1)	3 489(1)	5 821(1)	Hb(3)	3 140	415	4 377
C(a)	5 296(9)	2 225(5)	1 475(5)	C(b4)	686(10)	1 017(5)	4 367(4)
C(a2)	8 163(10)	1 208(5)	1 608(5)	C(b5)	−486(11)	1 642(6)	4 693(5)
Ha(2)	8 458	1 619	1 893	Hb(5)	−1 604	1 755	4 544
C(a3)	9 303(10)	443(5)	1 499(5)	C(b6)	−71(10)	2 113(5)	5 237(5)
Ha(3)	10 372	316	1 724	Hb(6)	−916	2 558	5 444
C(a4)	8 944(10)	−163(5)	1 063(5)	C(b1)	1 537(10)	1 966(5)	5 499(5)
C(a5)	7 375(10)	25(6)	783(5)	C(b7)	190(11)	510(6)	3 766(5)
Ha(5)	7 074	−386	500	Hb(7a)	1 139	98	3 596
C(a6)	6 227(10)	806(6)	908(5)	Hb(7b)	−333	930	3 306
Ha(6)	5 146	927	700	Hb(7c)	−545	185	4 021
C(a1)	6 586(9)	1 410(5)	1 319(4)	C(1b)	5 099(11)	1 374(6)	7 955(6)
C(a7)	10 249(10)	−986(5)	904(5)	O(1b)	5 840(9)	1 009(5)	8 508(4)
Ha(7a)	11 255	−1 000	1 145	C(2b)	2 291(17)	2 482(7)	8 000(6)
Ha(7b)	10 384	−962	333	O(2b)	2 303(9)	2 455(4)	8 669(4)
Ha(7c)	9 933	−1 516	1 134	C(3b)	5 562(12)	1 573(6)	6 352(6)
C(1a)	4 819(10)	2 760(6)	−106(5)	O(3b)	6 629(8)	1 295(5)	5 961(4)
O(1a)	5 685(8)	2 597(5)	−613(4)	C(4b)	3 121(10)	945(6)	7 046(5)
C(2a)	3 666(13)	4 326(7)	674(6)	O(4b)	2 818(8)	289(4)	7 054(4)
O(2a)	3 251(8)	5 064(4)	373(4)	C(5b)	4 784(11)	3 002(6)	7 095(5)
C(3a)	2 357(10)	2 085(6)	615(5)	O(5b)	5 573(8)	3 437(5)	7 243(4)
O(3a)	1 793(8)	1 526(4)	543(4)	C(6b)	4 276(11)	3 176(6)	5 096(6)
C(4a)	1 754(11)	3 782(5)	−120(5)	O(6b)	5 185(8)	2 976(5)	4 605(5)
O(4a)	853(8)	4 224(5)	−583(4)	C(7b)	3 379(11)	4 512(6)	5 912(6)
C(5a)	1 376(12)	3 479(5)	1 415(5)	O(7b)	3 784(9)	5 120(4)	5 924(5)
O(5a)	128(7)	3 778(4)	1 675(4)	C(8b)	1 313(11)	3 976(6)	5 031(5)
C(6a)	3 400(10)	1 287(6)	2 334(5)	O(8b)	373(8)	4 267(4)	4 510(4)
O(6a)	3 172(8)	613(4)	2 340(4)	C(9b)	1 099(10)	4 249(6)	7 091(5)
C(7a)	5 245(10)	1 777(5)	3 152(5)	O(9b)	1 294(9)	4 877(4)	7 262(4)
O(7a)	6 109(8)	1 405(4)	3 682(4)	C(10b)	−899(11)	3 430(6)	7 888(6)
C(8a)	2 233(11)	2 773(5)	3 021(5)	O(10b)	−1 689(8)	3 574(5)	8 424(4)
O(8a)	1 251(8)	3 015(5)	3 452(4)	C(11b)	−1 287(11)	3 869(6)	6 270(5)
C(10a)	3 855(11)	4 035(5)	2 423(5)	O(11b)	−2 341(8)	4 273(4)	5 880(4)
O(10a)	3 011(9)	4 443(4)	2 850(4)	C(12b)	−352(11)	2 106(6)	7 039(5)
C(9a)	7 094(11)	3 140(6)	2 526(5)	O(12b)	−905(8)	1 515(4)	7 119(4)

light petroleum (1:1) afforded dark green *microcrystals* of [CoFe$_2$(μ-H)(μ$_3$-CC$_6$H$_4$Me-4)(μ-CO)(μ-dppm)$_2$(CO)$_5$][BF$_4$] (**8**) (0.31 g); ^{31}P-{^{1}H} n.m.r., δ 53.5 [d, PFe, J(PP) 77], 46.8 [d, PFe, J(PP) 77], 42.6 (m, br, PCo), and 23.8 p.p.m. [d, br, PCo, J(PP) 77 Hz].

Crystal Structure Determination of Compound (**4a**).—Crystals of (**4a**) were grown from CH$_2$Cl$_2$–light petroleum. Diffracted intensities were collected at 200 K on a Nicolet *P3m* four-circle diffractometer (θ–2θ scans) using a crystal of dimensions *ca.* 0.10 × 0.15 × 0.25 mm. Of the 7 594 reflections, measured to 2θ ⩽ 50°, 6 888 had $I ⩾ 3σ(I)$, and only these were used in the refinement of the structure after the data had been corrected for Lorentz, polarisation and X-ray absorption effects (the latter by an empirical method using azimuthal scan data [16]).

Crystal data. C$_{20}$H$_7$CrFeO$_{12}$Re, M = 733.4, triclinic, a = 8.569(5), b = 15.744(6), c = 16.84(1) Å, α = 79.80(5), β = 87.74(5), γ = 73.98(4)°, U = 2 149(2) Å^3, space group $P\bar{1}$ (no. 2), Z = 4, D_c = 2.26 g cm^{-3}, $F(000)$ = 1 392, Mo-K_α X-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 69.1 cm^{-1}.

The structure was solved by heavy-atom methods, and was refined by blocked-cascade least squares with anisotropic thermal parameters for all non-hydrogen atoms. The Cr and Re atoms were found to be disordered such that *ca.* 60% of the time they adopted sites labelled Cr(1) and Re(1) whilst 40% of the time they were interchanged occupying sites Cr(1a) and Re(1a). An identical feature was observed for a second independent molecule of the complex in the asymmetric unit. Hydrogen atoms were included in calculated positions. Refinement converged at R = 0.056 (R' = 0.065) with a weighting scheme of the form $w = [\sigma^2(F_o) + 0.000\ 8|F_o|^2]^{-1}$. A final electron-density difference synthesis showed peaks of *ca.* 4 e Å^{-3} in the vicinity of the metal atoms with much lower values elsewhere. All computations were carried out on an Eclipse S 230 (Data General) computer with the SHELXTL systems of programs.[16] Atomic scattering factors were taken from ref. 17. Atomic co-ordinates are given in Table 4.

Appendix

All calculations were performed using the extended Hückel method[9,10] with the weighted H_{ij} formalism.[18] The following bond lengths were used: Co–Co 2.47, Co–Fe 2.56, Fe–Fe 2.51,

Table 5. Parameters used in the extended Hückel calculations

Orbital		H_{ii}/eV^a	ζ_1	ζ_2	C_1^b	C_2^b
Fe	4s	−9.17	1.90			
	4p	−5.37	1.90			
	3d	−12.70	5.35	1.80	0.5366	0.6678
Co	4s	−9.21	2.00			
	4p	−5.29	2.00			
	3d	−13.18	5.55	2.10	0.5679	0.6059
C	2s	−21.40	1.625			
	2p	−11.40	1.625			
O	2s	−32.30	2.275			
	2p	−14.80	2.275			
H	1s	−13.60	1.30			

^{a} eV $\approx$ 1.60 $\times$ 10^{-19} J. ^{b} Contraction coefficients used in the double zeta expansion.

Co–C(O) 1.80, Fe–C(O) (terminal) 1.86, Fe–C(O) (bridging) 1.95, C–O 1.13, $C_{carbyne}$–C_{ring} 1.47, C–C (ring) 1.39, and C–H 1.0 Å. The capping carbyne was placed 1.5 Å above the metal triangle. The $Co(CO)_3$ fragments comprised one axial and two equatorial carbonyls; the latter separated by 115°, whilst the local geometry of the $Fe_2(\mu\text{-CO})(CO)_6$ unit in $[CoFe_2(\mu_3\text{-}CC_6H_5)(\mu\text{-CO})(CO)_9]$ was based on that observed in the crystal structure of $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-CO})(CO)_8(\eta\text{-}C_5H_5)]$.[6] The parameters used in the extended Hückel calculations are given in Table 5.[11] The calculations were performed on the ICL 2988 computer of the South West Universities Regional Computer Centre, using the programs ICON 8 and FMO.[19]

Acknowledgements

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