Conversion of a Bridged Vinylalkylidene Complex into Cluster Complexes of Cobalt, Iron, and Manganese: X-Ray Crystal Structures of [Fe₃(CO)₆-(μ-CO)₂(μ₃-CMe)(η-C₅H₅)] and [FeCo₃(CO)₇(μ-CO)₂(μ₄-C=CH₂)(η-C₅H₅)]
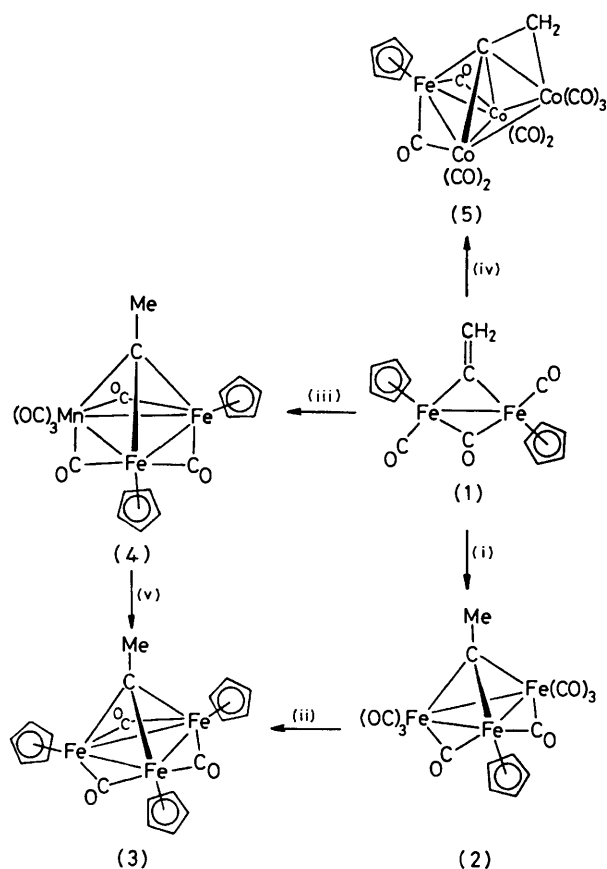
By Pascual Brun, Gordon M. Dawkins, Michael Green, Rona M. Mills, Jean-Yves Salaün, F. Gordon A. Stone, and Peter Woodward

(Department of Inorganic Chemistry, The University, Bristol BS8 1TS)

Summary The compound [Fe₂(CO)₂(μ-CO)(μ-C=CH₂)-(η-C₅H₅)₂] reacts with [Fe₂(CO)₉], [H₃Mn₃(CO)₁₂], [Co₂(CO)₈], or [Co₄(CO)₁₂] to afford, respectively, [Fe₃(CO)₆(μ-CO)₂(μ₃-CMe)(η-C₅H₅)], [Fe₂Mn(CO)₃(μ-CO)₃- (μ₃-CMe)(η-C₅H₅)₂], and [Co₃Fe(CO)₇(μ-CO)₂(μ₄-C=CH₂)- (η-C₅H₅)], the structures of the Fe₃ and Co₃Fe clusters being established by X-ray diffraction studies.

Although dimetal complexes with bridging C=CR$_2$ ligands are well established, addition of metal–ligand systems to these species as a route to metal cluster compounds has not been investigated. Our knowledge of multi-site metal-co-ordinated vinylalkylidene ligands is limited to the compounds [Os$_3$(CO)$_9$(μ-H)$_2$(μ_3-C=CH$_2$)] (ref. 1), [NiRu$_3$-(CO)$_9${μ_4-C=C(H)Bu^t}(η-C$_5$H$_5$)] (ref. 2), and [Ru$_4$(CO)$_{10}$-(μ_3-OR)(μ_2-PPh$_2$){μ_4-C=C(H)Pr^i}] (ref. 3). The observation[1,4] that the triosmium compound can be readily transformed into [Os$_3$(CO)$_9$(μ-H)$_3$(μ_3-CMe)] suggests that bridged vinylalkylidene compounds might serve as precursors to a variety of triply bridged methylalkylidyne complexes. Development of a simple synthesis[5] of [Fe$_2$(CO)$_2$(μ-CO)-(μ-C=CH$_2$)(η-C$_5$H$_5$)$_2$] (1) provides an opportunity to explore these ideas.

Reaction of (1) with excess of [Fe$_2$(CO)$_9$] in diethyl ether (25 °C; 3 days) affords [Fe$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] and the black tri-iron complex (2) (11% yield) (see Scheme).† A single-

crystal X-ray diffraction study established the molecular structure (Figure 1).‡

Crystal data: C$_{15}$H$_8$Fe$_3$O$_8$, M = 483·4, monoclinic, space group $P2_1/c$ (No. 14), a = 8·943(4), b = 12·156(4), c = 15·904(8) Å, β = 103·57(4)°, U = 1 681(2) Å^3, Z = 4, D_c = 1·91 g cm^{-3}, $F(000)$ = 960, μ(Mo-K_α) = 26·0 cm^{-1}. Current R 0·0265 (R' 0·0258) for 2 771 reflections [220 K, 2·9 $\leqslant$ 2θ $\leqslant$ 55°, I $\geqslant$ 3·0$\sigma(I)$, Nicolet $P2_1$ diffractometer, Mo-K_α X-radiation, graphite monochromator, $\bar{\lambda}$ = 0·710 69 Å].

The cluster (2) is characterised by an Fe$_3$C core, which has near, but not exact, mirror symmetry. The Fe$_3$ triangle is near-isosceles, and the μ_3-CMe ligand has C(9) at approximately equal distances from Fe(1) and Fe(2), but significantly closer to Fe(3). The C(9)–C(10) vector is perpendicular to the plane of the metal atom triangle. Of the eight carbonyl groups, two bridge the 'equal' sides of the metal triangle; the other six form mutually orthogonal groups of three on Fe(1) and Fe(2). The formally analogous structure [Fe$_3$(CO)$_8$(μ_3-CEt)(η-C$_5$H$_2$Me$_2$Et)] shows[6] similar asymmetry in the location of the μ_3-C atom where the comparable Fe–C distances are 1·938(4), 1·974(5), and 1·910(4) Å.
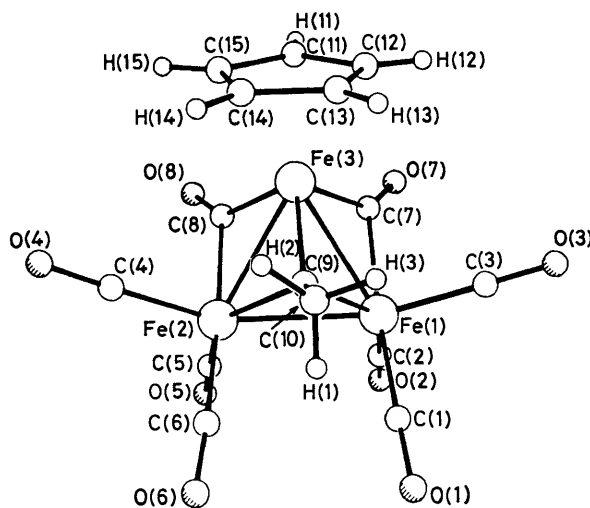
SCHEME. (i) [Fe$_2$(CO)$_9$]; (ii) C$_{10}$H$_{12}$; (iii) [Mn$_3$(μ-H)$_3$(CO)$_{12}$]; (iv) [Co$_2$(CO)$_8$] or [Co$_4$(CO)$_{12}$]; (v) toluene, reflux.

FIGURE 1. Molecular structure of [Fe$_3$(CO)$_8$(μ-CO)$_2$(μ_3-CMe)-(η-C$_5$H$_5$)] (2). Important bond lengths include: Fe(1)–Fe(2) 2·602(1), Fe(1)–Fe(3) 2·519(1), Fe(2)–Fe(3) 2·509(1), Fe(1)–C(9) 1·934(2), Fe(2)–C(9) 1·959(3), Fe(3)–C(9) 1·902(3) Å.

Formation of (2) from (1) evidently involves a complex reaction sequence with break-up of (1) and hydrogen abstraction. Reaction of (2) with dicyclopentadiene (refluxing toluene; 12 h) affords (3).† Treatment (benzene, reflux; 3 h) of (1) with [Mn$_3$(μ-H)$_3$(CO)$_{12}$] provides a rational synthesis of the black crystalline mixed-metal cluster (4)

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† Selected spectroscopic data (i.r. measured in cyclohexane and n.m.r. in [^{2}H$_6$]-acetone, unless otherwise indicated): (2), v$_{CO}$ 2 068s, 2 021vs, 2 013s, 1 981m, 1 971m, 1 859m, and 1 825w cm^{-1}; n.m.r.: ^{1}H, δ(C$_6$D$_6$), 4·6 (s, 3 H, Me) and 4·0 (s, 5 H, C$_5$H$_5$); ^{13}C{^{1}H}, δ (p.p.m.), 333 (μ_3-C), 221 (CO), 95 (C$_5$H$_5$), and 52 (Me). (3), v$_{CO}$ (tetrahydrofuran) 1 813s and 1 761m cm^{-1}; n.m.r.: ^{1}H, δ 6·2 (s, 3 H, Me) and 4·6 (s, 15 H, C$_5$H$_5$); ^{13}C{^{1}H}, δ (p.p.m.), 364·5 (μ_3-C), 268 (μ-CO), 92 (C$_5$H$_5$), and 57 (Me). (4), v$_{CO}$ 2 025s, 1 974s, 1 944s, 1 846s, 1 820s, and 1 790m cm^{-1}; n.m.r.: ^{1}H, δ 5·9 (s, 3 H, Me) and 4·9 (s, 10 H, C$_5$H$_5$); ^{13}C{^{1}H}, δ (p.p.m.), 350 (μ_3-C), 263 (μ-CO), 254 (μ-CO), 224 (CO), 219 (CO), 94 (C$_5$H$_5$), and 54 (Me). (5), v$_{CO}$ (pentane), 2 081s, 2 040vs, 2 003m, 1 994w, 1 851s, and 1 809w cm^{-1}.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

(60% yield).† Probably the initial step in the formation of (4) involves 'insertion' of the μ-C=CH₂ fragment into an MnH bond. Interestingly, in refluxing toluene (48 h), compound (4) affords (3).

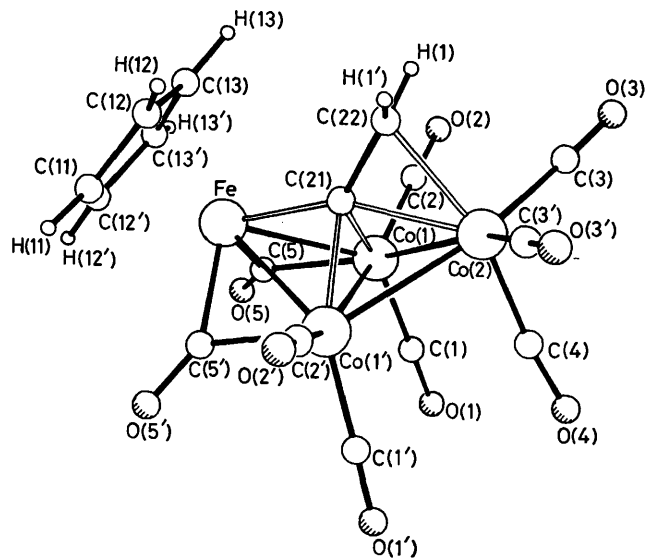FIGURE 2. Molecular structure of [FeCo₃(CO)₇(μ-CO)₂(μ₄-C= CH₂)(η-C₅H₅)] (5); mirror relationships are denoted by primes. Important bond lengths include: Co(1)–Fe 2·499(2), Co(1)–Co(1') 2·456(3), Co(1)–Co(2) 2·581(3), C(21)–Fe 1·933(8), C(21)–Co(1) = C(21)–Co(1') 1·917(6), C(21)–Co(2) 2·087(8), C(22)–Co(2) 2·085(10), C(21)–C(22) 1·431(12) Å.

A third type of cluster-forming reaction occurs on treatment (diethyl ether; 25 °C; 40 h) of (1) with [Co₂(CO)₈] {or with [Co₄(CO)₁₂] in toluene at reflux}. The product (5) (55% yield)† was structurally identified by an X-ray diffraction study.‡

Crystal data: $C_{16}H_7Co_3FeO_9$, $M = 575\cdot6$, orthorhombic, space group *Pcam* (non-standard setting of *Pbcm*, No. 57), $a = 18\cdot135(16)$, $b = 8\cdot194(9)$, $c = 12\cdot711(10)$ Å, $U = 1\,889(3)$ Å³, $Z = 4$, $D_c = 2\cdot03$ g cm⁻³, $F(000) = 1\,128$, $\mu(\text{Mo-}K_\alpha) = 33\cdot9$ cm⁻¹. Current R 0·0541 (R' 0·0537) for 1 772 reflections [220 K, $2\cdot9 \leqslant 2\theta \leqslant 60°$, $I \geqslant 2\cdot0\sigma(I)$].

The molecule (Figure 2) has a 'butterfly' arrangement of the metal atom core, with overall mirror symmetry (crystallographically required). Atoms Co(1), and its mirror image Co(1'), define the body of the butterfly, atoms Fe and Co(2) the wingtips, and the mirror plane passes through O(4), C(4), Co(2), C(21), C(22), Fe, C(11), H(11), and the midpoint of C(13)–C(13'). The torsion angle Co(2)–Co(1)–Co(1')–Fe is 124·1(1)°. Two of the nine carbonyl ligands bridge the Fe–Co edges, approximately symmetrically; the others are approximately mutually orthogonal. The bridging C=CH₂ moiety lies astride the mirror; C(21) is nearly equivalently bonded to all four metal atoms with η²-interaction of Co(2) with C(21)–C(22). This mode of co-ordination is closely analogous to that found in the NiRu₃ and Ru₄ clusters mentioned above,[2,3] and similar[7] to the co-ordination of one of the CO ligands in [HFe₄-(CO)₁₃]⁻ and of CH in [HFe₄(CO)₁₂(CH)].[8]

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