# Stepwise Reduction of $[Fe_4(CO)_{13}]^{2-}$ by Successive Methylation and Hydrogenation; the *X*-Ray Crystal Structures of $[Fe_4(CO)_{12}COMe]^-$ and $[Fe_4H(CO)_{12}COMe]$†

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*Summary* The reaction of $[Fe_4(CO)_{13}]^{2-}$ with $[Me_3O][BF_4]$ leads to the reduction of a CO ligand to give $[Fe_4(CO)_{12}COMe]^-$, where the COMe ligand $\mu_3$-caps a face of the $Fe_4$ tetrahedron; subsequent protonation with $HSO_3F$ yields $[Fe_4H(CO)_{12}COMe]$, in which the COMe co-ordinates to the $Fe_4$ 'butterfly' *via* C and O atoms; the structures have been confirmed by *X*-ray analyses.

There has been considerable interest in the reduction of carbonyl groups in transition-metal carbonyl clusters because of the relevance to Fischer–Tropsch type catalysts.[1] The cluster offers the possibility of multiple reaction sites on the faces or edges of the species.[2] This may then permit or prevent further reaction depending upon the bonding mode of the reduced species. Rearrangements of the reduced species once co-ordinated to the cluster have also been observed.[3]

The best methods found so far for the reduction are protonation or methylation[4,5] and attack occurs at the carbonyl group exhibiting the highest co-ordination number. In this communication we report that the methylation of the anion $[Fe_4(CO)_{13}]^{2-}$ leads to the formation of $[Fe_4(CO)_{12}(\mu_3\text{-COMe})]$ and that subsequent protonation gives the neutral complex $[Fe_4H(CO)_{12}COMe]$. In this complex the $Fe_4$ tetrahedron has opened out and the COMe group co-ordinates *via* both carbon and oxygen in a manner previously observed in $[Fe_4H(CO)_{13}]^-$.[6]

The compound $[(Ph_3P)_2N]_2[Fe_4(CO)_{13}]$ was treated with $[Me_3O][BF_4]$ in $CH_2Cl_2$, under $N_2$ at room temperature, for 40 min. The solvent $CH_2Cl_2$ was removed *in vacuo* and the residue extracted with diethyl ether. The compound $[(Ph_3P)_2N][Fe_4(CO)_{12}COMe]$ (**1**) was then recrystallised by slow evaporation of the methanol solution to give rectangular, black–purple crystals. The compound was characterised by spectroscopic techniques (Table) and a single-crystal *X*-ray analysis.

*Crystal data:* (**1**) $C_{50}H_{33}Fe_4NO_{13}P_2$, $M = 1\,141{\cdot}11$, triclinic, space group $P\bar{1}$, $a = 11{\cdot}095(4)$, $b = 14{\cdot}036(5)$, $c = 15{\cdot}729(6)$ Å, $\alpha = 93{\cdot}19(2)$, $\beta = 95{\cdot}07(2)$, $\gamma = 91{\cdot}66(2)°$, $U = 2\,434{\cdot}7$ Å$^3$, $Z = 2$, $D_c = 1{\cdot}56$ g cm$^{-3}$; $\mu(\text{Mo-}K_\alpha) =$

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† The independent synthesis and structure determination of $[Fe_4(CO)_{12}COMe]^-$ and $[Fe_4H(CO)_{12}COMe]$ are reported in accompanying communications. (E. M. Holt, K. Whitmire, and D. F. Shriver, *J. Chem. Soc., Chem. Commun.*, 1980, 778; K. Whitmire, D. F. Shriver, and E. M. Holt, *J. Chem. Soc., Chem. Commun.*, 1980, 780.)

12·6 cm$^{-1}$. 8 635 intensities were recorded ($2\theta_{max} = 50·0°$) on a Stoe 4-circle diffractometer using graphite-monochromated Mo-$K_\alpha$ radiation. These were averaged to give 6 777 unique observed reflections [$F > 3\sigma(F)$]. The structure was solved by a combination of direct methods and Fourier difference techniques and refined by a blocked-cascade least-squares method to $R = 0·048$, $R_w = [\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_0|] = 0·052$.[‡]

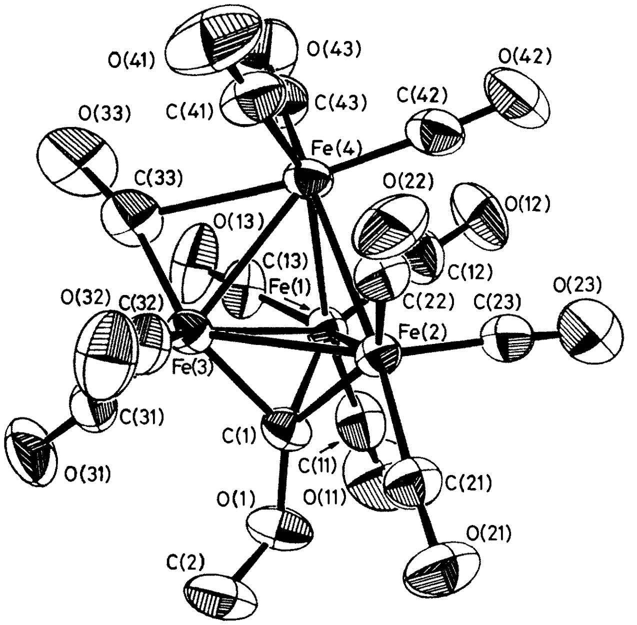

FIGURE 1. The molecular geometry of the $[Fe_4(CO)_{12}COMe]^-$ anion, including the atom numbering scheme. Bond lengths: Fe(1)–Fe(2) 2·541(2), Fe(1)–Fe(3) 2·548(2), Fe(1)–Fe(4) 2·632(2), Fe(2)–Fe(3) 2·555(2), Fe(2)–Fe(4) 2·605(2), Fe(3)–Fe(4) 2·561(2), Fe(1)–C(1) 1·907(4), Fe(2)–C(1) 1·957(4), Fe(3)–C(1) 1·896(4), and C(1)–O(1) 1·361(5) Å. Bond angles: Fe(1)–C(1)–Fe(2) 82·2(1), Fe(1)–C(1)–Fe(3) 84·1(2), and Fe(2)–C(1)–Fe(3) 83·1(1)°.

The structure of the anion $[Fe_4(CO)_{12}COMe]^-$ is shown in Figure 1, which includes some important bond parameters. The molecular geometry closely resembles that of $[Fe_4(CO)_{13}]^{2-}$,[7] where the face-capping carbonyl group has been methylated. The dianion has three semi-bridging carbonyl groups bridging the iron triangle that is capped by the thirteenth carbonyl-group, while in (**1**) there is only one carbonyl group that bridges an edge [Fe(3)–Fe(4) 2·561(1), Fe(3)–C(9) 1·796(5), and Fe(4)–C(9) 2·449(5) Å]. The C(13)–O(13) bond length shows a significant increase over the corresponding distance of 1·20(3) Å in the dianion. This is in keeping with a reduction in the bond order towards unity since C(13) may be considered as formally sp$^3$ hybridised. Thus methylation occurs at the most basic carbonyl group without effecting the geometry of the metal cluster skeleton.

Reaction of (**1**) with $HSO_3F$ in $CH_2Cl_2$, under $N_2$ for 10 min, followed by extraction with diethyl ether and hexane (t.l.c.) gave $[Fe_4H(CO)_{12}COMe]$ (**2**) in *ca.* 80% yield. Compound (**2**) may also be prepared by methylation of $[(Ph_3P)_2N][Fe_4H(CO)_{13}]$ with $[Me_3O][BF_4]$. The complex was characterised by spectroscopic (Table) and crystallographic techniques. Green–black rectangular blocks were deposited by recrystallisation from hexane and mounted in Lindemann tubes under $N_2$, since (**2**) is unstable to air in the solid and in solution.

*Crystal data:* (**2**) $C_{14}H_4Fe_4O_{13}$, $M = 603·57$, triclinic, space group $P\bar{1}$, $a = 9·140(4)$, $b = 9·312(5)$, $c = 14·681(7)$ Å, $\alpha = 99·23(2)$, $\beta = 96·00(2)$, $\gamma = 124·07(2)°$, $U = 992·4$ Å$^3$, $Z = 2$, $D_c = 2·02$ g cm$^{-3}$; $\mu$(Mo-$K_\alpha$) = 29·0 cm$^{-1}$. 3 625 reflections were measured ($2\theta_{max} = 55·0°$) on a Stoe 4-circle diffractometer using graphite-monochromated Mo-$K_\alpha$ radiation. Data were merged to give 3 036 unique observed intensities [$F > 5\sigma(F)$]. The structure was solved by a combination of direct methods and Fourier difference techniques and refined by a blocked-cascade least-squares method to $R = 0·096$ and $R_w = [\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_0|] = 0·093$.[‡]

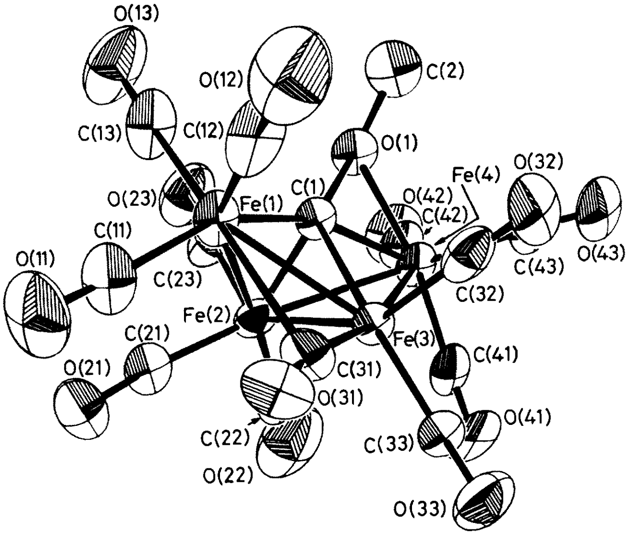

FIGURE 2. The molecular geometry of $[Fe_4H(CO)_{12}COMe]$, including the atom numbering scheme. Bond lengths: Fe(1)–Fe(2) 2·644(4), Fe(1)–Fe(3) 2·606(3), Fe(2)–Fe(3) 2·606(4), Fe(2)–Fe(4) 2·629(3), Fe(3)–Fe(4) 2·625(3), Fe(1)–C(1) 1·846(7), Fe(2)–C(1) 1·975(13), Fe(3)–C(1) 1·983(10), Fe(4)–C(1) 2·142(8), Fe(4)–O(1) 2·010(8), and C(1)–O(1) 1·376(10) Å. Bond angles: Fe(1)–C(1)–Fe(2) 87·5(4), Fe(1)–C(1)–Fe(3) 85·7(3), Fe(2)–C(1)–Fe(3) 82·4(4), Fe(1)–C(1)–Fe(4) 160·9(6), Fe(2)–C(1)–Fe(4) 79·3(4), Fe(3)–C(1)–Fe(4) 79·0(3), and C(1)–O(1)–C(2) 119·5(9)°.

Figure 2 illustrates the molecular geometry of (**2**) and includes some important bond parameters. Protonation of (**1**) has had the effect of breaking a bond in the $Fe_4$ tetrahedron to give the open 'butterfly' arrangement of metal atoms. The carbonyl group, which was methylated in the first reaction, now lies over the open face and co-ordinates to Fe(1), Fe(2), and Fe(3) *via* C(1) and to Fe(4) *via* O(1). This mode of bonding of a carbonyl group to a cluster has only previously been observed in $[Fe_4H(CO)_{13}]^-$.[6] As in this complex, the distribution of the carbonyl groups in (**2**)

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[‡] 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 CB1 1EW. Any request should be accompanied by the full literature citation for this communication.

TABLE.

| Complex | $^1$H N.m.r./$\delta$[a] | $\nu_{CO}$/cm$^{-1}$ |
|---|---|---|
| $[(Ph_3P)_2N]_2[Fe_4(CO)_{12}COMe]$ | 2·43 s | 2050w, 1980vs, 1952sh, 1931sh[b] |
|  | 5·46 s | 2051w, 1986s, 1971s, 1948sh, 1935w, 1920w, 1912w, 1864w, 1187w |
| $[Fe_4H(CO)_{12}COMe]$ | 36·31 s | 2089w, 2049vs, 2038vs, 2025s, 2010m, 2002m |
|  | 5·92 s | 1997sh, 1987vw, 1974w, 1968w, 1949sh,[d] 1173w, 1055m, 941w[c] |

[a] $CD_2Cl_2$ solution. [b] $CH_2Cl_2$ solution. [c] Nujol mull. [d] Hexane solution.

indicates that the hydride bridges the Fe(2)–Fe(3) 'hinge' edge, with an average *cis*-Fe–Fe–C(O) angle of 111·1(8)° for this bond compared to that of 95·3(10)° for the other edges. A feature not observed in $[Fe_4H(CO)_{13}]^-$ is the very asymmetric carbonyl bridge along the Fe(1)–Fe(3) edge, with Fe(3)–C(31) 1·786(9) and Fe(1)–C(31) 2·538(12) Å.

Treatment of (**2**) with the $[BH_4]^-$ anion reverses the protonation reaction and (**1**) is recovered in good yield.

This study indicates that the novel mode of bonding of the carbonyl ligand to the cluster, acting as a four-electron donor *via* carbon and oxygen, is not restricted to $[Fe_4H(CO)_{13}]^-$, but that a similar ligand arrangement is observed with the previously methylated species. Thus, both (**1**) and (**2**) are feasible models for steps in the reduction of carbonyl groups on metal surfaces which lead to the production of hydrocarbons.[2,4]

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