O-Alkylation and Structural Rearrangement of CO Ligands in $[Fe_4(CO)_9(\mu\text{-}CO)_3(\mu_3\text{-}CO)]^{2-}$; *X*-Ray Crystal Structure of $[N(PPh_3)_2][Fe_4(CO)_{11}(\mu\text{-}CO)(\mu_3\text{-}COMe)]$

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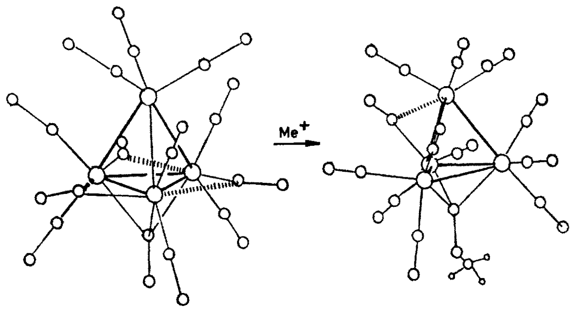
Summary The reaction of $[PPN]_2[Fe_4(CO)_9(\mu\text{-}CO)_3(\mu_3\text{-}CO)]$ [PPN^+ = bis(triphenylphosphine)iminium] with $MeSO_3F$ results in the methylidyne cluster $[PPN][Fe_4(CO)_{11}(\mu\text{-}CO)(\mu_3\text{-}COMe)]$ and *X*-ray crystallography demonstrates that *O*-methylation is accompanied by a rearrangement of CO ligands from the μ_2 bridges to the terminal positions.

The shift of terminal carbon monoxide to the bridging positions is well established for the co-ordination of a Lewis acid to the CO oxygen in $[Ru_2(cp)_2(\mu\text{-}CO)_2(CO)_2]$ and $[Ru_3(CO)_{12}]$.[1,2] The reverse shift, from bridging to terminal positions for the remaining CO's in the molecule, has been observed in the formation of an $AlBr_3$ adduct of $[Fe_2(\mu\text{-}CO)_3(CO)_6]$,[1] but the structural inference from the vibrational data is less conclusive. We report here *X*-ray crystallographic data which show that *O*-alkylation of a carbonyl-ligand in a metal cluster causes two semi-bridging carbonyl-groups to shift to terminal positions and a third semi-bridging carbonyl-group to assume a slightly bridging disposition toward the apical iron atom (equation 1).



(1)

When $[PPN]_2[Fe_4(CO)_9(\mu\text{-}CO)_3(\mu_3\text{-}CO)]$ is treated with $MeSO_3F$ at room temperature under nitrogen in CH_2Cl_2, $[PPN][Fe_4(CO)_{11}(\mu\text{-}CO)(\mu_3\text{-}COMe)]$ results in a *ca.* 54% yield [ν_{CO} (fluorolube) 2045 m, 1970 vs, 1933 w, 1920 w, 1912 w, and 1864 m cm^{-1}; ^1H n.m.r. $\delta(CD_2Cl_2)$ 7·58 multiplet (PPN^+) and 4·49 (CH_3); ^{13}C n.m.r. $\delta(CD_2Cl_2$, −90 °C) 361·2 s, 218·0 s, and 213·8 s (ratio 1 : 9 : 3)]. Analyses (CO, C, H, and N) agree with the indicated formula. Small single crystals were formed by slow cooling from a concentrated methanol solution.

Crystal data: $C_{50}H_{33}Fe_4NO_{13}P_2$, M = 1141·18, triclinic, space group $P\bar{1}$, a = 11·131(3), b = 14·064(1), c = 15·790(4) Å, α = 93·27(8), β = 95·07(3), γ = 91·66(4)°, U = 2456·7 Å^3, Z = 2, D_c = 1·54 g cm^{-1}, 4089 intensities

($2\theta_{max}$ 40°) were measured, on a Nonius CAD4 automated diffractometer using Mo-K_α radiation, of which 3191 were classed as observed [$I > 2{\cdot}5\sigma(I)$]. The structure was solved by heavy atom techniques. Refinement of scale factor, positional, and anisotropic thermal parameters for the 70 nonhydrogen atoms has progressed to $R = 0{\cdot}043$[$R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$].†

Comparison of the structure of $[Fe_4(CO)_{11}(\mu\text{-}CO)(\mu_3\text{-}COMe)]^-$ with that of the parent ion,[3] $[Fe_4(CO)_9(\mu\text{-}CO)_3(\mu_3\text{-}CO)]^{2-}$, illustrates the effect of the electron accepting carbocation on the arrangement of the carbonyl-ligands. The parent ion contains three unsymmetrically bridging carbonyl-groups, one at each edge of the triangle face to which the triply bridging CO is bound, whereas the methylated species contains only one slightly bridging CO which lies between the apical iron and an iron bonded to the methylidyne unit (Figure). The evidence for the semi-bridging nature of this ligand is the shift in Fe–C–O bond angle toward sp^2 hybridization (164·6° average, others 176·9°) and the shortness of the nonbonded Fe···C distance (2·42 Å, others $>$ 2·80 Å). The asymmetric bridge to the apical Fe can be explained by the greater relative electron density of that iron compared to the three basal irons which have become electron deficient owing to the electron withdrawing effect of the $[COMe]^+$ unit.

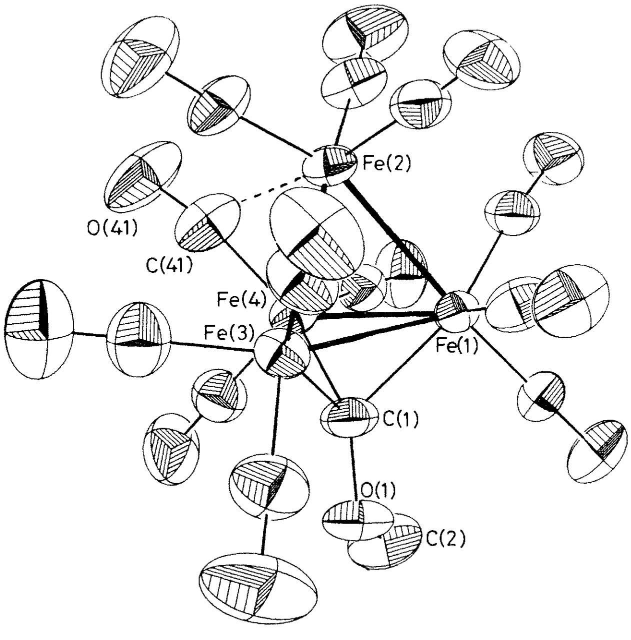


FIGURE. Structure of $[Fe_4(CO)_{11}(\mu\text{-}CO)(\mu_3\text{-}COMe)]^-$. Relevant bond distances: Fe(1)–C(1) 1·97(3), Fe(3)–C(1) 1·92(4), Fe(4)–C(1) 1·90(3), Fe(4)–C(41) 1·78(4), Fe(2)–C(41) 2·45(4), C(1)–O(1) 1·36(4), Fe–C (terminal, average) 1·76(4), Fe (bridged)–Fe (bridged, average) 2·557(7), and Fe (bridged)–Fe (unique, average) 2·609(7) Å. Relevant bond angles: Fe(4)–C(41)–O(41) 164(3) and C(1)–O(1)–C(2) 118(3)°.

Basicity of the triply bridging carbonyl-group is well documented[4] and methylation of the doubly bridging CO's has been observed for $[(\mu\text{-}H)Fe_3(CO)_{10}(\mu\text{-}CO)]^-$,[5] $[(\mu\text{-}H)Ru_3(CO)_{10}(\mu\text{-}CO)]^-$,[6] and $[(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}CO)]^-$,[7] however, the present work provides the first example of the generation of a μ_3-methylidyne compound by direct alkylation of a (μ_3-CO) ligand.[8] It is likely that this reaction will provide a general route to methoxymethylidyne complexes and thus a new general entry into an important class of compounds. Face bridging methoxymethylidyne complexes have been obtained by alternative methods, such as the reaction of Cl_3COMe with $Co_2(CO)_8$ to yield $Co_3(CO)_9(\mu_3\text{-}COMe)$[9] and the hydrogenation of $[(\mu\text{-}H)Ru_3(CO)_{10}(\mu\text{-}COMe)]$ to yield $[(\mu\text{-}H)_3Ru_3(CO)_9(\mu_3\text{-}COMe)]$.[10]

In the present system the triply bridging C–O bond length is increased from 1·20 to 1·36 Å and the corresponding average Fe–C distance is decreased by 0·07 Å, indicating a significant decrease in the C–O bond order and an increase in the Fe–C bond order. This pattern is also seen for the methylation of $[(\mu\text{-}H)Fe_3(CO)_{10}(\mu\text{-}CO)]^-$ where the C–O bond length is increased by 0·1 Å and the Fe–C(bridge) distances are decreased.[5]

There is evidence from relative C–O bond distances, C–O stretching frequencies, and O-basicity that the bridging CO ligands are stronger electron acceptors toward a metal cluster than are the terminal CO ligands.[11,4] This observation supplies a ready explanation for the tendency toward more CO bridges in negative or donor-substituted carbonyl-groups relative to their neutral or unsubstituted analogues and, in the present case, for the shift of bridging CO ligands into terminal positions when the μ_3-CO ligand is converted into the more electron seeking $(\mu_3\text{-}COMe)^+$.[12]

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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 CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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