Structural and Isotope Tracer Study of the Proton Induced Reduction of CO in $[Fe_4(CO)_{11}(\mu\text{-}CO)(\mu_3\text{-}COMe)]^-$; *X*-Ray Crystal Structure of $[Fe_4H(CO)_{12}COMe]$

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Summary Mild protonation of $[Fe_4(CO)_{11}(\mu\text{-}CO)(\mu_3\text{-}COMe)]^-$ yields $[Fe_4H(CO)_{12}(\eta^2\text{-}COMe)]$, this reacts further with strong acid to give CH_4, which originates from the $\eta^2\text{-}COMe^+$ ligand.

The recently discovered proton-induced reduction of co-ordinated CO provides a fundamentally new type of reaction for the conversion of CO into hydrocarbons.[1] In this reaction a proton acid serves as the source of hydrogen nuclei while a metal cluster provides the electrons necessary for the reduction of CO, equation (1).

$$[Fe_4(CO)_{13}]^{2-} + H^+ \rightarrow CH_4 + H_2O + Fe^{2+} + \text{metal cluster} + CO + H_2 + \quad (1)$$

In order better to define the course of this reaction and to pinpoint the CO ligand which is undergoing reduction, we have studied the analogous reaction for $[Fe_4(CO)_{11}(\eta\text{-}CO)(\mu_3\text{-}COMe)]^-$, the structure of which is reported in the preceding paper.[2] We first describe the addition of one proton to produce $[Fe_4H(CO)_{12}(\eta^2\text{-}COMe)]$.

The compound $[Fe_4H(CO)_{12}(\eta^2\text{-}COMe)]$ was prepared by treating an ether solution of $[PPN][Fe_4(CO)_{11}(\eta\text{-}CO)(\mu_3\text{-}COMe)]$ [PPN^+ = bis(triphenylphosphine)iminium] with a slight excess of HSO_3CF_3 [^1H n.m.r. δ 4·08 (CH_3, s, area = 3) and −26·24 (H, s, area = 1), C, H analyses were good, i.r. (cyclohexane) 2085 vw, 2046 vs, 2020 s, 1998 s, 1990 m, and 1890 w cm^{-1}]. Small single crystals were grown from a concentrated hexane solution by slow cooling. A crystal of $[Fe_4H(CO)_{13}Me]$ was mounted in a capillary on a Syntex $P\bar{1}$ automated diffractometer and the crystal structure determined during alignment procedures.

Crystal data $C_{14}H_4Fe_4O_{13}$, M = 603·57, triclinic, space group $P\bar{1}$, a = 9·137(2), b = 9·313(2), c = 14·759(4) Å, α = 97·13(2), β = 99·32(2), γ = 124·15(2)°. Data [3104 observations, $I > 3\sigma(I)$] were corrected for background, Lorentz, and polarization effects. Heavy-atom methods allowed location of all atoms including the four hydrogens. Refinement to R = 3·6% with isotropic thermal parameters for hydrogen and anisotropic thermal parameters for all other atoms shows the four irons forming a tetrahedron elongated on one side [5 Fe–Fe distances 2·604(1)—2·646(1), Fe(2)–Fe(3) 3·925(1), Figure].† Each iron has three terminal carbonyl-groups [average Fe–C distance 1·790(2) Å] and each is bonded to the C(1) atom of the *O*-methylated carbonyl-group, three of the Fe–C(1) distances range from 1·834(2) to 1·972(2) Å and the Fe(2)–C(1) distance is 2·318(2) Å. The atom Fe(2) also interacts with O(1), the oxygen of the methylated carbonyl-group, Fe(2)–O(1) 2·000(1) Å whereas the other three iron atoms are more than 2·91(2) Å from this oxygen atom. The atoms Fe(1) and Fe(4) are bridged by a hydrogen, average Fe–H distance being 1·69 Å. In brief $[Fe_4H(CO)_{12}(\eta^2\text{-}COMe)]$ is very similar in structure to $[Fe_4H(CO)_{12}(\eta^2\text{-}CO)]^-$.[3] The similarity of these two structures supports the proposed analogy between the reactions of each with neat HSO_3CF_3. The products and product ratios described below also support this hypothesis.

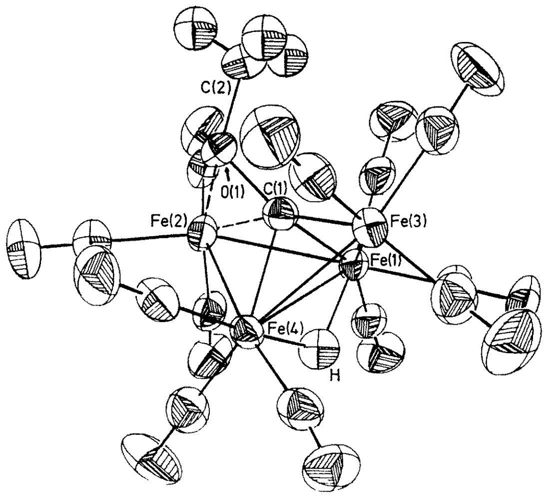

Figure The structure of $Fe_4(\mu\text{-}H)(CO)_{12}(\eta^2\text{-}COMe)$. Relevant bond distances Fe–Fe (average bonded only) 2·621(1) Fe–C (average terminal CO) 1·790 (2) C–O (average, terminal) 1·138 Fe(1)–C(1) 1·973(2) Fe(2)–C(1) 2·138(2) Fe(3)–C(1) 1·834(2) Fe(4)–C(1) 1·947(2) Fe(2)–O(1) 2·000(2) and C(1)–O(1) 1·394(2) Å. Relevant bond angles C(1)–O(1)–C(2) 119·5(2) and Fe(2)–Fe(1)–Fe(4)/Fe(3)–Fe(1)–Fe(4) (dihedral angle) 119°.

When $[PPN][Fe_4(CO)_{11}(\mu\text{-}CO)(\mu_3\text{-}COMe)]$ (0·16 mmol) was treated with neat HSO_3CF_3 (2 ml) and allowed to react for three days the following yields of gases were obtained (mol gas/mol cluster) CH_4 0·14, H_2 0·20, and CO 3·1. The reaction of $[PPN][Fe_4(CO)_{11}(\mu_3\text{-}COMe)]$ with DSO_3CF_3 yielded predominantly CD_4. A sample of $[PPN]_2[Fe_4(CO)_9(\mu\text{-}CO)_3(\mu_3\text{-}CO)]$ was enriched (56%) in ^{13}CO and then allowed to react with $MeSO_3F$ to form the methyl derivative. This product was then treated with

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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.

HSO_3CF_3 to yield CH_4 which was found to be enriched to 50% ^{13}CO, equation (2). These experiments clearly

$$[Fe_4(CO)_{11}(\mu\text{-}CO)(\mu_3\text{-}CO)]^{2-} \xrightarrow{*CO} [Fe_4(*CO)_{11}(\mu\text{-}*CO)(\mu_3\text{-}*CO)]^{2-} \xrightarrow{CH_3^+} [Fe_4(*CO)_{12}(*COMe)]^- \xrightarrow{H^+} *CH_4 + *CO + \ldots \quad (2)$$

demonstrate that the CH_4 originates from CO in the metal cluster, but they do not reveal the particular CO involved. The ^{13}C n.m.r. peak for the methylated CO (δ 362·9 p.p.m.) in $[Fe_4(CO)_{11}(\mu\text{-}CO)(\mu_3\text{-}COMe)]^-$ remains distinct from the twelve other carbonyl-groups (δ 218·5 p.p.m.) at 40 °C in CD_2Cl_2. This observation suggested that the CO in $(\mu_3\text{-}COMe)^+$ might be immobilized for a longer time and prompted a ^{13}C tracer study to determine whether or not the CO in the μ_3-COMe is being reduced.

A sample of $[PPN][Fe_4(CO)_{11}(\mu\text{-}CO)(\mu_3\text{-}COMe)]$ was enriched with ^{13}CO (21%) and then allowed to react with HSO_3CF_3 to yield normal, isotopic CH_4 and CO containing 19% ^{13}CO. This sequence of events, which is summarized in equation (3), demonstrates that ^{13}CO does not exchange with μ_3-COMe and that the CH_4 is derived from the CO in the $(\mu_3\text{-}COMe)^+$ ligand.

$$[Fe_4(CO)_{11}(\mu\text{-}CO)(\mu_3\text{-}COMe]^- \xrightarrow{*CO} [Fe(*CO)_{11}(\mu\text{-}*CO)(\mu_3\text{-}COMe)]^- \xrightarrow{H^+} CH_4 + *CO + \ldots \quad (3)$$

One attractive route for the reduction of the $(\eta^2\text{-}COMe)^+$ ligand is *via* protonation of O, cleavage of the CO bond by the elimination of HOMe or H_2OMe^+, and finally either direct protonation of the co-ordinated carbide or successive transfer of hydrogen from the metal cluster to the carbon.[4]

We thank the National Science Foundation for support of this research and Drs. J. A. Bertrand and D. G. van Derveer for the use of the diffractometer at the Georgia Institute of Technology and for their kind assistance.

(*Received*, 31*st March* 1980; *Com.* 338.)

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[3] M. Manassero, M. Sansoni and G. Longoni, *J. Chem. Soc., Chem. Commun.*, 1976, 919.

[4] The independent synthesis and structure determination of $[Fe_4H(CO)_{12}(\eta^2\text{-}COMe)]$ are reported in the following communication (P. A. Dawson, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1980, 781).