a solvent molecule coordinated in the trans position to the oxo group. Previous work[20] indicates that NO_3^- must coordinate in a position cis to the oxo group for reduction by molybdenum(V) oxo complexes. Models also indicate that the deprotonated ligand could coordinate with solvent or an open position cis to oxo only with considerable distortion.

(20) R. D. Taylor, P. G. Todd, N. D. Chasteen, and J. T. Spence, *Inorg. Chem.*, **18**, 44 (1979).

(21) J. T. Spence, M. Minelli, and C. A. Rice in "Molybdenum Chemistry of Biological Significance", W. E. Newton and S. Otsuka, Eds., Plenum Press, New York, 1980, p 263.

(22) Reduction of MoO_2LH_2 by ligand (possibly catalyzed by SO_3^{2-}) as occurs with MoO_2 (ethylcysteine)$_2$,[25] is ruled out since quantitative formation of $MoOL^-$ is observed. Because of the difficulty in detecting small amounts of SO_4^{2-} in the presence of a large excess of SO_3^{2-}, SO_4^{2-} has not yet been identified as a product.

(23) If reaction 1 is an equilibrium with $K \geq 100$, the $MoO_2LH_2/MoOL^-$ reversible potential ≥ -0.84 V vs. SCE.

(24) Reported values for xanthine oxidase are −0.355 and −0.355 V[5] and +0.220 and +0.180 V for nitrate reductase: S. P. Vincent, *Biochem. J.*, **177**, 757 (1979).

(25) C. D. Garner, R. Durrant, and F. E. Mabbs, *Inorg. Chim. Acta*, **24**, L29 (1977).

(26) NOTE ADDED IN PROOF. A five-line shift of 2.14×10^{-4} cm^{-1} due to two equivalent ^{14}N nuclei is observed for $[Et_4N][MoOL]$ in DMF at −30 °C. This is similar to ^{14}N splitting reported in the nitrogen deprotonated $Mo(abt)_3^-$ complex,[14] and is further evidence in support of the proposed structures.

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Metal Clusters. 25.[1] A Uniquely Bonded C–H Group and Reactivity of a Low-Coordinate Carbidic Carbon Atom

Sir:

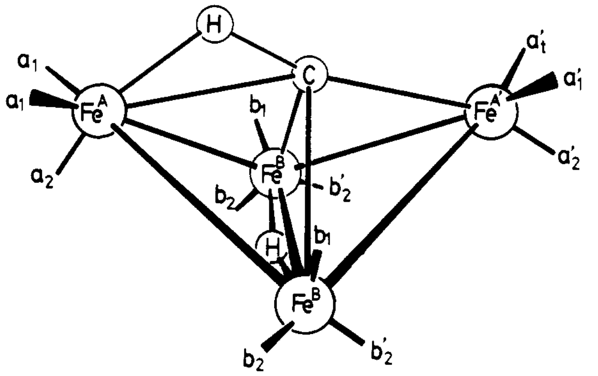
In seeking[1-4] metal clusters containing carbidic carbon atoms of low coordination number and high reactivity,[5] we have prepared a unique cluster containing a methylidyne group bonded to the iron cluster atoms, namely $HFe_4(\eta^2\text{-}CH)(CO)_{12}$. Deprotonation of the cluster with base successively yielded $[HFe_4(\mu_4\text{-}C)(CO)_{12}^-]$ and $[Fe_4(\mu_4\text{-}C)(CO)_{12}^{2-}]$ clusters, the first clusters to contain four-coordinate carbidic carbon atoms.[2] Oxidation of $Fe_4C(CO)_{12}^{2-}$ in the presence of hydrogen to form $HFe_4(\eta^2\text{-}CH)(CO)_{12}$ has established a unique cluster carbidic carbon atom reactivity that is formally analogous to that of carbide carbon atoms at a metal surface.[5]

Treatment of $[(C_2H_5)_4N^+]_2[Fe_5C(CO)_{14}^{2-}]$ with HCl quantitatively yielded $[(C_2H_5)_4N^+][HFe_5C(CO)_{14}^-]$. Prolonged reaction of the hydride derivative with HCl gave $HFe_4(CH)(CO)_{12}$ in 95–100% yield:[6,7]

$$HFe_5C(CO)_{14}^- + 3HCl \rightarrow HFe_4(CH)(CO)_{12} + 2CO + FeCl_2 + Cl^- + H_2 \quad (1)$$

Cluster stability to electron impact was high; mass spectral analysis showed stepwise loss of CO to $HFe_4(CH)(CO)^+$ and then Fe_4C^+ formation. Only terminal M–CO bonding was evident in the cluster IR spectrum. Two types of hydrogen atom environments, one a CH and the other a hydridic hydrogen atom, were established by NMR spectroscopy: there were two resonances of equal intensity and of doublet form due to HH coupling (0.9 Hz); the CH doublet at the unusual position of −1.31 ppm showed ^{13}C satellites ($J_{H^{13}C} = 103.4$), and the Fe_x–H doublet was at −27.95 ppm.[8] Consistently, the ^{13}C CH resonance was a doublet of doublets ($J_{H^{13}C} = 103.4$ and $J_{H(Fe)^{13}C} = 6.4$ Hz) at 335 ppm at 35 to −50 °C. Both proton resonances were sharp up to 65 °C, but hydrogen exchange, which is probably intramolecular, does occur between the two sites as shown by spin saturation experiments.[9] Hydrogen exchange between CH and FeH sites in our cluster is a dynamic phenomenon expected for most hydrocarbon fragments bound to a metal surface. In addition, H–D exchange between both hydrogen sites and D_2O was established by the dimunition of ^1H NMR intensities on addition of D_2O to a cluster solution and intensity restoration on H_2O addition. For the case of intermediate H–D exchange, the C–H ^1H NMR intensity was more sharply reduced than that for Fe_x–H resonance. This is an equilibrium isotope effect, with a ratio of $HFe_4(CD)(CO)_{12}$ to $DFe_4(CH)(CO)_{12}$ of 1.73:1 at 35 °C;[10] a similar ratio of 1.74:1 has been reported[11] for a methyl(hydrido)osmium cluster which showed H exchange between C–H and Os_x–H sites.

These spectroscopic data define a cluster with a metal hydride and a methylidyne, CH, hydrogen atom. A three-center C–H–Fe bond is clearly indicated by the NMR chemical shift for the CH hydrogen atom.[11,12] Thus, $HFe_4(\eta^2\text{-}CH)(CO)_{12}$ is a 62-electron four-atom cluster and should have a butterfly array of iron atoms. Our proposed structure[13] based on the spectroscopic data is shown in **1**. Originally, we thought that the hydride might be displaced toward the $Fe^B{}_2Fe^{A'}$ face, but crystallographic studies[14] have now established the structure as shown in **1** with the hydride bridging between the two basal iron atoms. Structure **1** has seven different CO environments, but $HFe_4(\eta^2\text{-}CH)(CO)_{12}$ is highly fluxional and only four ^{13}C CO resonances, of 4:2:4:2 intensity ratios, were present in the −90 °C ^{13}C NMR spectrum and these reduced to one sharp and two broad resonances of relative 4:6:2 intensities at 20 °C. The chemical exchange data and the ^{13}C and ^1H DNMR studies establish several dynamic processes to be operative in the cluster: H site (CH) exchange, CO site exchange, and hydrogen exchange between CH and Fe_2H sites. CH-hydrogen site exchange comprises an apparent shift of the bridging CH hydrogen atom from one apical iron atom (Fe^A) to the other ($Fe^{A'}$), an exchange that is fast on the NMR time scale even at −90 °C.



All previously known[15] methyne cluster complexes achieved coordination saturation with simple M–C bonding as in $(\mu_3\text{-}HC)Co_3(CO)_9$ and $(\mu_3\text{-}HC)Os_3H_3(CO)_9$. Our new η^2-CH cluster derivative represents another possible mode of C–H bonding at a surface, one more probable than a η^1-CH interaction for the typically coordinately unsaturated, electropositive metal surface atoms.[16]

The hydrogen atoms in $HFe_4(\eta^2\text{-}CH)(CO)_{12}$ were removed by triethylamine to give first $[HFe_4(\mu_4\text{-}C)(CO)_{12}^-]$ and then $[Fe_4(\mu_4\text{-}C)(CO)_{12}^{2-}]$ which were isolated as PPN^+ salts.[17] From +35 to −90 °C, the dianion exhibited two carbonyl ^{13}C resonances of equal intensity at 220.8 and 222.8 ppm consistent with our proposed structure **2** assuming that intramolecular CO exchange localized on single iron sites is fast at these temperatures.[18] The monoanion had a 20 °C single broad high-field hydride resonance at −26.8 ppm ($\omega_{1/2} = 30$ Hz) which sharpened on temperature decrease (δ −26.9 ppm and $\omega_{1/2} = 3$ Hz at −70 °C); this carbide cluster has structural

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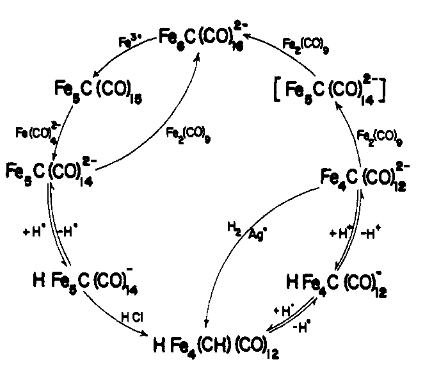
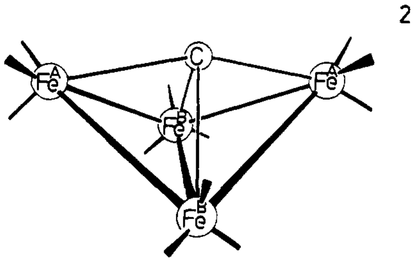


Figure 1. This cyclic scheme summarizes the demonstrated relationships among the Fe_4C and Fe_5C carbonyl systems.

form **2** with a hydride bridging between the two basal, Fe^B, iron atoms. There were similarities between the carbonyl ^{13}C DNMR spectra of the monoanion with those of $HFe_4(\eta^2\text{-}CH)(CO)_{12}$; carbonyl site exchange barriers increase in the series $[Fe_4C(CO)_{12}^{2-}] < [HFe_4C(CO)_{12}^-] < HFe_4(\eta^2\text{-}CH)(CO)_{12}$. Intermolecular exchange of H between $HFe_4(CH)(CO)_{12}$ and $HFe_4C(CO)_{12}^-$ was not observable on the NMR time scale. Single crystals of salts of the two cluster carbide anions are under crystallographic study.



Protonation of the exposed, four-coordinate carbide carbon atom in $[HFe_4(\mu_4\text{-}C)(CO)_{12}^-]$ is fast and represents the first protonation of an exposed carbide carbon atom in a metal cluster. The five-coordinate carbon atom in $Fe_5(\mu_5\text{-}C)(CO)_{15}$ is not protonated by strong acids, although the generation of $HFe_4(\eta^2\text{-}CH)(CO)_{12}$ by reaction of $[Fe_5C(CO)_{14}^{2-}]$ with HCl must involve at some step transfer of hydrogen to the carbide carbon atom. In addition, $[Fe_4C(CO)_{12}^{2-}]$ undergoes framework expansion when allowed to react with mononuclear transition metal complexes. The previously[1] reported $[RhFe_4C(CO)_{14}^-]$ was obtained from the reaction of the dianion with $[Rh(CO)_2Cl]_2$, and a new octahedral carbide, $[Mo_2Fe_4C(CO)_{18}^{2-}]$, was formed with $Mo(CO)_3(THF)_3$. Cyclic interconversions in the Fe_4C and Fe_5C systems are summarized in Figure 1.

Oxidation of $Fe_4C(CO)_{12}^{2-}$ with $AgBF_4$ in the presence of H_2 and of D_2, respectively, yielded $HFe_4(CH)(CO)_{12}$ and $DFe_4(CD)(CO)_{12}$ implicating oxidative addition of hydrogen to a coordinately unsaturated $Fe_4C(CO)_{12}$ intermediate. This is the first facile H_2 reduction of a carbide carbon atom in metal cluster chemistry and is a formal analogue of a step proposed[3,5] in Fischer-Tropsch reactions.

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References and Notes

(1) Preceeding paper in this series: M. Tachikawa and E. L. Muetterties, *J. Am. Chem. Soc.*, **102**, 1725 (1980).

(2) M. Tachikawa and E. L. Muetterties, *Prog. Inorg. Chem.*, in press (a comprehensive review of metal carbide clusters).

(3) E. L. Muetterties and J. Stein, *Chem. Rev.*, **79**, 479 (1979).

(4) E. L. Muetterties, *J. Organomet. Chem.*, in press.

(5) Carbide-like carbon atoms are postulated to be intermediates in Fischer-Tropsch reactions effected by metal surfaces like Fe, Ru, and Co.[3] The surface carbides, which are likely to have relatively low metal atom coordination numbers, react with hydrogen at 25 °C to form hydrocarbons. See discussion and references to original literature in ref 3.

(6) A Schlenk flask (500 mL) which contained a suspension of $[(C_2H_5)_4N]_2[Fe_5C(CO)_{14}]$ (500 mg) in 30 mL of toluene was filled with hydrogen chloride to give a rapid formation of an oily layer of $[(C_2H_5)_4N][HFe_5C(CO)_{14}]$. Vigorous stirring was maintained for 24 h. A white solid separated. The solution phase was evaporated to give black, crystalline $HFe_4(\eta^2\text{-}CH)(CO)_{12}$ (236 mg, 98% yield).

(7) This cluster after recrystallization from hexane analyzed for $[HFe_4(\eta^2\text{-}CH)(CO)_{12}]$. Anal. Calcd for $C_{13}H_2Fe_4O_{12}$: C, 27.22; H, 0.18; Fe, 38.95. Found: C, 27.38; H, 0.36; Fe, 39.2. Mass spectrum (crystals from hexane): 574 (parent), 546 (P − CO), 518 (P − 2CO), 490 (P − 3CO), 462 (P − 4CO), 434 (P − 5CO), 406 (P − 6CO), 378 (P − 7CO), 350 (P − 8CO), 322 (P − 9CO), 294 (P − 10CO), 266 (P − 11CO), 236 (P − 12CO − 2H). IR (hexane solution): ν_{CO} 2099 (vw), 2053 (vs), 2036 (s), 2031 (m), 2015 (sh), 1987 (m).

(8) ^{13}C satellites were observed for a saturated dichloromethane solution of the cluster. When the cluster was prepared from ^{13}CO-enriched $Fe_5C(CO)_{14}^{2-}$, there was no enhancement of the CH ^{13}C satellite intensity establishing that the CH carbon atom is not derived from a carbonyl carbon in the synthesis step.

(9) Irradiation of the δ −27.95 resonance at 35 and 65 °C resulted in an intensity from the −1.31 resonance that was 65 and 6%, respectively, relative to the intensity in the absence of the irradiation.

(10) Integration of the C–H and Fe_x–H resonances for a mixture of $HFe_4(CH)(CO)_{12}$, $HDFe_3C(CO)_{12}$, and $DFe_4(CD)(CO)_{12}$ (ratios determined by mass spectrometry) yielded a ratio of $HFe_4(CD)(CO)_{12}$ to $DFe_4(CH)(CO)_{12}$ of 1.73 at 35 °C.

(11) (a) R. B. Calvert and J. R. Shapley, *J. Am. Chem. Soc.*, **100**, 7726 (1978); (b) R. B. Calvert, J. R. Shapley, A. J. Schultz, J. M. Williams, S. L. Suib, and G. D. Stucky, *Ibid.*, **100**, 6240 (1978).

(12) J. M. Williams, R. K. Brown, A. J. Schultz, G. D. Stucky, and S. D. Ittel, *J. Am. Chem. Soc.*, **100**, 7407 (1978).

(13) An isoelectronic and isostructural cluster is $HFe_4(\eta^2\text{-}CO)(CO)_{12}^-$; cf. M. Manassero, M. Sansoni, and G. Longoni, *J. Chem. Soc., Chem. Commun.*, 919 (1976).

(14) M. A. Beno, J. M. Williams, M. Tachikawa, and E. L. Muetterties, *J. Am. Chem. Soc.*, following paper in this issue.

(15) (a) D. Seyferth, *Adv. Organomet. Chem.*, **14**, 97 (1976); (b) R. B. Calvert and J. R. Shapley, *J. Am. Chem. Soc.*, **99**, 5225 (1977).

(16) EHMO calculations for CH on a Ni(111) surface suggest that the system energy is reduced in going from a μ_3-CH binding with the CH vector normal to the surface to a η^2-CH binding with both the carbon and the hydrogen atoms bound to surface nickel atoms (R. M. Gavin and E. L. Muetterties, unpublished calculations). In addition, J. E. Demuth and H. Ibach, *Surf. Sci.*, **78**, L238 (1978), propose on the basis of spectroscopic data that chemisorbed CH on Ni(111) does not have the CH vector normal to the surface.

(17) (a) Anal. Calcd for $(PPN^+)_2[Fe_4C(CO)_{12}^{2-}]$: C, 61.92; H, 3.67; N, 1.70. Found: C, 61.12; H, 3.74; N, 1.70. IR (dichloromethane): ν_{CO} 2003 (w), 1968 (s), 1942 (vs), 1912 (m). ^{13}C NMR (CH_2Cl_2, 20 °C, 45.3 MHz): 220.8 (6) and 222.8 (6) ppm for carbonyl carbon atoms. (b) Anal. Calcd for $[PPN^+][HFe_4C(CO)_{12}^-]$: C, 52.97; H, 2.81; N, 1.26. Found: C, 52.91; H, 2.89; N, 1.27. IR (CH_2Cl_2): ν_{CO} 2010 (s, sh), 2005 (vs), 1987 (s), 1978 (m, sh), 1927 (w). ^1H NMR (CD_2Cl_2, 20 °C, 180 MHz): hydride at −26.8 ppm ($\omega_{1/2}$ = 30.3 Hz).

(18) Low barriers to CO site exchange localized on single metal sites is common in metal clusters: E. Band and E. L. Muetterties, *Chem. Rev.*, **78**, 639 (1978).

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Fischer-Tropsch Chemistry: Structure of a Seminal η^2-CH Cluster Derivative, $HFe_4(\eta^2\text{-}CH)(CO)_{12}$

Sir:

We have completed a high-precision low-temperature [−100 (3) °C] X-ray crystal structure study of a Fe_4 "butterfly" cluster containing an unusual η^2-CH ligand. This cluster,[1] $HFe_4(\eta^2\text{-}CH)(CO)_{12}$, **1**, occupies a central role in transformations that document the proposed[2] high reactivity of low-coordinate carbon (carbide) ligands in clusters and that *formally* may relate to intermediates[3] in some metal surface catalyzed Fischer-Tropsch reactions.[4-6]

After collection of an extensive low temperature data set[7] for crystals of **1** recrystallized from hexane, the structure was solved using MULTAN.[8] There is a butterfly array of four iron atoms, each with three terminal carbonyl ligands, with the carbidic carbon atom nestled near the center of the top of the "wings" of the Fe_4 array where it forms a strong C–H–Fe interaction as depicted in Figure 1.[9] The most striking feature

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