as indicating either (a) ImH remains bound but the Fe–N bond is forced out of the ImH plane or (b) the number of bound histidines is reduced from two in the native enzyme to one in the inhibitor–enzyme complex. We favor (b) since previous binding studies[8,10] of 3-ClHB and its fluoro analogue, 3-FHB, demonstrated that prior ionization of the relatively acidic *p*-hydroxyl in these inhibitors was not responsible for high potency. Instead, it was suggested that a base, likely a histidine, was present at the active site to provide for removal of even relatively nonacidic *p*-hydroxyl protons (such as those found in all known PCD substrates), as the hydroxyl nears the coordination sphere of iron. When considered together with the fact that 3-ClHB forms an Fe–O bond with PCD iron,[9] these conclusions rationalize the displacement of one histidine ligand in the enzyme–inhibitor complex. In the enzyme–substrate complex, approach of the *o*-dihydroxyphenyl group accompanied by displacement of the two cis histidines and consequent conversion of the hydroxy functionalities to the oxyanion form provides an attractive picture for the eventual storage of substrate as a chelating ligand.[9] The replacement of a backbone amino acid ligand by an inhibitor (and likely substrate) is noteworthy, since metalloenzymes usually possess a vacancy or labile water in the first coordination shell so as to accommodate the binding molecule.

Analysis of EXAFS data in terms of first-shell composition is currently under investigation.

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A Reactive Three-Metal Carbide Cluster Mimic, $[Fe_3(CO)_9(CCO)]^{2-}$

J. W. Kolis,[†] E. M. Holt,*[‡] M. Drezdzon,[†] K. H. Whitmire,[†] and D. F. Shriver*[†]

Departments of Chemistry, Northwestern University
Evanston, Illinois 60201
and Oklahoma State University
Stillwater, Oklahoma 74078

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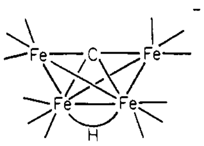
In view of the importance of surface carbides in the heterogeneous catalytic reduction of CO, there is considerable interest in the reactivity of the carbide ligand in molecular metal cluster compounds.[1-4] Recently, molecular cluster compounds containing four metal atoms (e.g., **1**) have been shown to be reactive at the carbide atom,[5-7] which contrasts with the inertness at the carbide in previously studied five-metal and higher carbide molecules. This trend in reactivity has been correlated with the degree of exposure of the C in the Fe_4 butterfly carbides[4-6] and with the relative proximity to the HOMO–LUMO gap of molecular orbitals having high C-orbital coefficients.[8] These same considerations lead one to expect high reactivity at a carbide coordinated to an array of three metal atoms, **2a,b**.[8] In this communication we report the first evidence for an isolable three-metal system having carbide-like reactivity.



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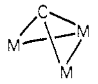
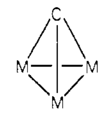
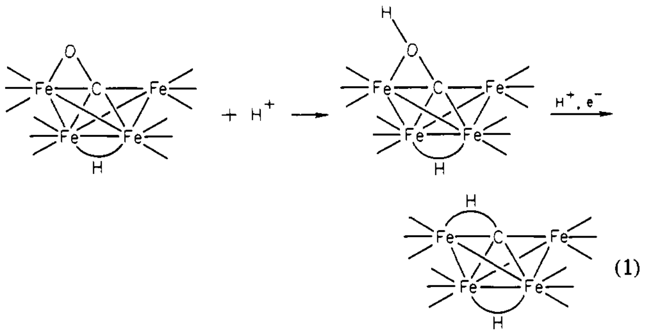


2a



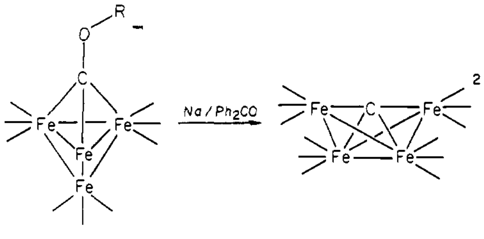
2b

The synthetic approach to an Fe_3 carbide is based on our recent observation that CO can be converted to a carbide or methyne in a strong acid medium.[9,10] The proposed key reactions, eq 1, are the formation of a good O-containing leaving group via protonation and the reduction of this species by a second metal cluster.[9,10]



(1)

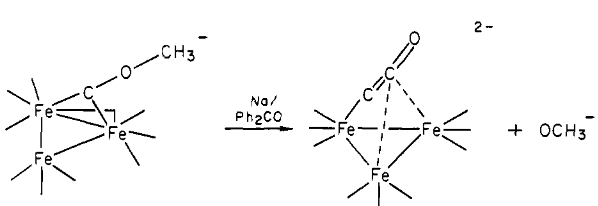
In analogy with these reactions, we explored the reduction of metal cluster carbonyl compounds in which a variety of oxophilic groups are attached to the carbonyl oxygen, eq 2. Success in the preparation of the known cluster $[Fe_4(CO)_{12}C]^{2-}$ has led us to extend this technique to the Fe_3 system.[11]



(2)

R = acetyl, CH_3

In a typical preparation, 0.3 g of $[PPN]_2[Fe_3(CO)_{11}]$ was O-methylated or O-acetylated as previously described,[12] and this was reduced over a period of 4 h by benzophenoneketyl (1,2-dimethoxyethane or THF, containing 0.3 g of Na and 0.1 g of benzophenone), eq 3. The solution was filtered to remove excess



(3)

2c

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[‡] Oklahoma State University.

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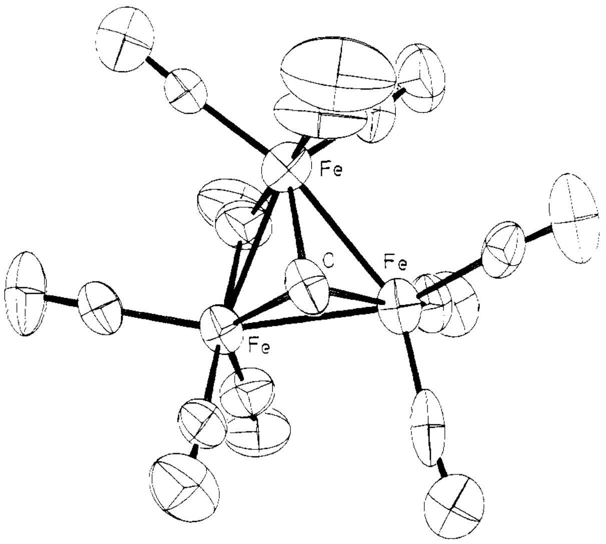


Figure 1. ORTEP drawing of the $[Fe_3(CO)_{10}(CH)]^-$ structure. The methyne hydrogen, which was not located in the X-ray structure determination, is omitted from this figure.

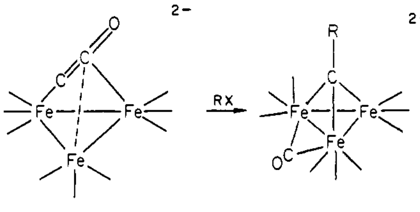
sodium, solvent was removed under vacuum, and the resulting red-orange oil was redissolved in 10 mL of CH_2Cl_2. Excess [PPN]Cl was added, and deep red-orange crystals of $[PPN]_2[Fe_3(CO)_{10}C]$, **2c**, were collected by the addition of methylcyclohexane; IR (Nujol mull) 1920 (s), 1892 (sh), 1868 (m) cm^{-1}; ^{13}C NMR (CD_3CN, -40 °C) δ 222.6, 182.2, and 90.1. Anal. Calcd for $C_{83}H_{60}N_2O_{10}P_4Fe_3$: C, 64.87; H, 3.94; N, 1.82. Found: C, 64.12; H, 4.04; N, 1.81. Upon protonation the 182- and 90-ppm signals disappear, the terminal carbonyl resonance shifts slightly to 220 ppm, and a doublet is produced in the methyne region, indicating that the compound may be a reactive carbide.

The coupling of the carbide carbon to H in the protonated product, as indicated by the ^{13}C NMR, indicates the formulation of this material as $[Fe_3(CO)_{10}(CH)]^-$. The ^1H resonance, δ 12.34 (in acetone-d_6), of this anion is in reasonable agreement with known methynes (cf. $H_3Ru_3(CO)_9(CH)$, δ 9.75,[13] and $Co_3(CO)_9(CH)$, δ 12.08.[14]) and the low-field ^{13}C, δ 262 (doublet, J = 165 Hz), resonance is typical of μ_3-alkylidyne complexes.[15] The formulation was demonstrated conclusively by a single-crystal X-ray structure determination.[16,17] One of the two independent iron carbonyl anions in this crystal has refined satisfactorily to show three irons in an approximately equatorial triangle (Fe–Fe distances are 2.565 (7), 2.536 (6), and 2.570 (5) Å), Figure 1. The shortest Fe–Fe distance separates two iron atoms which are bridged by a CO ligand (Fe–C 1.90 (2) and 1.94 (2) Å; C–O 1.22 (3) Å. The face of the Fe_3 triangle is bridged by the μ_3-CH group (hydrogen not located). The two irons bridged by CO have distances to the μ_3-CH of 1.96 (2) and 1.98 (2) Å, and the distance to the unique iron is 1.91 (2) Å. Both PPN cations show normal structures with a bent P–N–P skeleton [average 138.5 (10)°].

The structure of $[Fe_3(CO)_{10}(CH)]^-$, Figure 1, is similar to that of $Fe_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCH_3)$.[18] The longer Fe–Fe distances [average 2.557 (6) Å] in the latter are consistent with the lengthening that often is observed for protonated M–M bonds. The Fe–C distance to the μ_3-CCH_3 ligand [average 1.947 Å][18] is similar to iron–methyne carbon distance [average 1.95 (2) Å] observed in the present work.

Despite the positive identification of the methylidyne protonation product, the unprotonated precursor **2c** does not have the spectroscopic signatures of a carbide. Thus carbide stretching modes are missing in the expected 950–650 cm^{-1} region, and the characteristic low-field carbide resonance is absent in the ^{13}C NMR. These observations prompted the preparation of a highly ^{13}C-enriched (60%) sample of compound **2c** from enriched $Fe_3(CO)_{11}^{2-}$. The ^{13}C NMR spectrum reveals the presence of two doublets (J = 73.2 Hz) which are nearly centered on the previously mentioned singlets at 182.2 and 90.1 ppm. These doublets do not collapse on broad-band proton decoupling, and the coupling constant is reasonable for a direct C–C bond, suggesting the formulation of the product of reaction 3 as a ketenylidene.

Exchange of a normal isotopic sample of compound **2c** with ^{13}CO leads to a material that displays ^{13}C resonances in the terminal CO region, plus a singlet at 182.2 ppm, which is assigned to the CO in the ketenylidene ligand. The lability of this CO attached to a cluster framework carbon is in keeping with CO rearrangement, which must occur upon protonation to produce a methylidyne, and alkylation to produce an ethylidyne, eq 4.



(4)

2c

$R = H$ for $X = CH_3COO^-$; $R = CH_3$ for $X = SO_3F_3$

The carbide-like ketenylidene described here is unique. By contrast, the cationic ($[Co_3(CO)_9(CCO)]^+$,[19] $[H_3Ru_3(CO)_9(CCO)]^+$ [13]) and neutral ($H_2Os_3(CO)_9(CCO)$,[20] $Fe_4(CO)_{12}(CCO)$[5]) analogues are good electrophiles. Mass spectral evidence has been presented for the existence of the neutral iron ketenylidene $Fe_3(CO)_{10}(CCO)$, but the chemistry of this species is unexplored.[21] The tendency of a variety of exposed carbides to add CO raises the possibility that this type of interaction may occur between CO and reactive surface carbides in heterogeneous catalytic systems. We are currently directing our attention to the preparation and reactions of other anionic ketenylidenes and carbides.

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Registry No. $[PPN]_2[Fe_3(CO)_{11}]$, 66039-65-4; $[PPN][Fe_3(CO)_{10}(CH)]$, 83220-20-6.

Supplementary Material Available: Tables of positional and thermal parameters (6 pages). Ordering information is given on any current masthead page.

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[16] The crystal used for the X-ray structural work was isolated as a minor product of the proton-induced reduction of $Fe_4(CO)_{13}^{2-}$. ^1H NMR and infrared spectra for the $[Fe_3(CO)_{10}(CH)]^-$ ion from this source are identical with those obtained on samples prepared from $[Fe_3(CO)_{10}C]^{2-}$.

[17] Crystal data: unit cell dimensions, a = 16.878 (4) Å, b = 18.605 (9) Å, c = 29.196 (10) Å, β = 90.89 (2)°; V = 9168 (6) $Å^3$; space group $P2_1/a$ (Z = 8, density (calcd) = 1.448 g cm^{-1}); Mo radiation, λ 0.71069 Å; 5395 observed data points collected by using ω scan mode. Two iron cluster anions and two PPN cations comprise the asymmetric unit. Block-matrix least-squares refinement (parameters for each cluster and each PPN cation being varied in a separate block) has reached 10.6% with satisfactory refinement of both cations and one of the iron cluster anions. Disorder is evident in the remaining iron cluster, and partial occupancy treatments have not yet satisfactorily resolved this complication. The well-behaved cluster is discussed in the text.

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