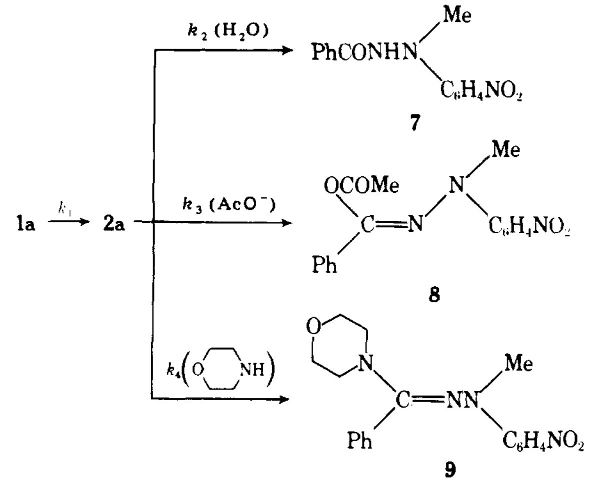
Scheme II



rate constants (measured in 4:1 dioxane–water at 25 °C): $k_1 = 8.6 \times 10^{-2}$/s^{-1}; $k_3/k_2 = 1100$; $k_3/k_4 = 6$; $k_4/k_2 = 160$

the unreactive N-acyl amide **6**). This is ensured by (a) the stereospecific formation of **3** and (b) by the presence of a group (NR^{2}R^3) attached to the imino nitrogen which slows the rate of inversion of this nitrogen.[5] Consequently, the acyl group and the lone pair on the adjacent nitrogen are mutually trans which inhibits intramolecular rearrangement and stabilizes intermediate **3**. Because of the relative stability of **3** it is possible to complete its formation with one carboxylic acid (or amino acid) before the amine (or a second amino acid) is added.

Since the intermediate **3** is an activated ester, the possibility of racemization α to the carboxylate function of an amino acid during peptide synthesis arises. This was tested using the Anderson method.[6] With reagent **1b** some racemization did occur, but this was pH dependent (21% racemate at pH 9.3, 2.5% at pH 7.8, and 1.0% at pH 7.2) consistent with racemization occurring via base-catalyzed isoxazoline formation.[7] It is thus an obvious advantage when chiral reagents are used to maintain the pH of the coupling medium ≤7. We have also found that racemization can be suppressed by varying the substituent (R^1) attached to carbon in the halide **1**. The most successful modification is the incorporation of a *t*-Bu group at this position. Using reagent **1c** we were unable to detect any racemization even at pH 9.5 (using the Anderson test).[8]

Although the highly selective nature of the reaction means that unprotected amino acids can be used, it is advisable to protect the nitrogen of the *first* amino acid (by, for example, a carbobenzoxy group). This has two advantages: (a) separation of the carbobenzoxylated peptide is facilitated; (b) intramolecular reaction of the growing peptide chain (which can be expected on going from two to three amino acid units) is suppressed.

Besides the advantages listed above, the imidoyl halide reagents **1**, unlike the related carbodiimides,[7b] make the nitrilium ion **2** available at all pH's without the necessity of acid or base catalysis. Moreover the hydrazide **5** formed during reaction can be recovered and reconverted to the active imidoyl halide reagents **1** and thus recycled.

Acknowledgment. This work was supported by a grant from the National Board for Science and Technology.

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(3) This is unexpected on the basis of the relative nucleophilicities of amines and carboxylate ions toward unsaturated carbon centers; however, we have preliminary data which indicates that the reactions of both species with the nitrilium ion may be diffusion controlled.
(4) We have typically used solvents in the range of 1:1 to 9:1 dioxane–water or acetone–water, the lower aqueous contents being used with the more reactive halides **1**.
(5) The rate of isomerization of *O*-acylisoimides of type **3** to **6** has been shown to be limited by the rate of *Z* to *E* isomerization about the C=N bond; see ref 1 and D. G. McCarthy and A. F. Hegarty, *J. Chem. Soc., Perkin Trans. 2*, 1080 (1977).
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(8) The reagents **1** were synthesized from the hydrazides **5** using either phosphorus pentachloride (in dry benzene) or triphenylphosphine–tetrahalomethane in acetonitrile.[9] A typical procedure is as follows. The bromide **1b** (0.6 g) in dry acetone (4 mL) was added over 2 min to acetone (20 mL) and water (6 mL) containing *N*-ethylmorpholine (0.35 g) and *N*-carbenzoxyglycine (0.21 g) at pH 7.0. After 5 min at room temperature Gly-OEt (0.30 g) was added, the pH of the solution adjusted to 7.8, and the solution was stirred until all of the yellow color had discharged (~2 h). The acetone was then removed in vacuo and the aqueous residue extracted with chloroform which was in turn extracted with 0.1 N HCl. Evaporation of the chloroform gave a 2:1 mixture of hydrazide **5b** and Z-Gly-GlyOEt (0.71 g, 95%). On base hydrolysis of the mixture the hydrazide was quantitatively extracted into ethyl acetate; acidification of the aqueous solution gave Z-GlyGly·OH, mp 175–177 °C (80% overall). Using Gly-OH in place of Gly-OEt, Z-Gly-GlyOH was obtained directly (78%); similarly prepared were Z-Gly-TrpOH (82%), Z-Trp-TrpOH (76%), and Z-Trp-Ser-OH (80%).
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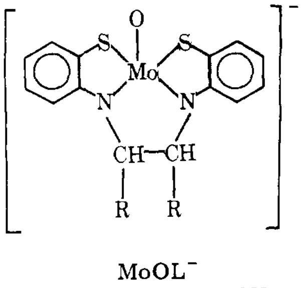
Monomeric Molybdenum Oxo Complexes with Tetradentate Aromatic Aminothiols. Model Redox Systems for Molybdenum Enzymes

Sir:

Molybdenum enzymes catalyze the transfer of electrons between a donor or acceptor and substrate. For oxidases and dehydrogenases, the evidence indicates substrate is oxidized in an irreversible two-electron step, with the molybdenum center undergoing initial reduction from the VI to the IV state.[1-3] Reoxidation by other cofactors (FAD, Fe$_2$S$_2$) occurs in two one-electron steps via an EPR active Mo(V) state with xanthine oxidase.[4] Electron transfer between the reduced Mo(IV) center and the Fe$_2$S$_2$ and FAD centers of this enzyme is rapid, with the distribution of electrons between the various oxidation states of each cofactor at a given level of enzyme reduction governed by their reduction potentials.[1,4,5]

The electrochemistry of a number of molybdenum(VI) dioxo and monomeric molybdenum(V) oxo complexes has been investigated.[6,7] The Mo(VI) complexes appear to be electrochemically reducible (usually irreversibly) to the IV state[6] but not, in general, to the V state.[7,8] Furthermore, monomeric molybdenum(V) oxo complexes that have been studied are not electrochemically oxidizable to the VI state.[7]

In the course of a study of monomeric molybdenum(V) oxo systems as enzymatic models, we have prepared two new complexes (MoOL$^-$) with tetradentate aromatic aminothiol



MoOL$^-$
L$_1$, R = H; L$_2$, R = CH$_3$

Table I. Spectroscopic Properties

complex	electronic[a] λ_{max}, nm	electronic[a] log ϵ, M^{-1} cm^{-1}	IR,[b] $\nu(Mo{=}O)$, cm^{-1}	EPR[c] g_x[d]	EPR[c] g_y[d]	EPR[c] g_z[d]	EPR[c] $A_z(^{95}Mo,^{97}Mo)$,[e] $cm^{-1} \times 10^4$ [f]
$[Et_4N][MoOL_1]$	760	3.00	898	1.974	1.977	2.005	56.9
	620	2.60					
	517	2.57					
$[Et_4N][MoOL_2]$	758	2.97	910	1.977	1.977	2.005	55.0
	592	2.64					
	500	2.81					

[a] DMF. [b] Solid mull. [c] 77 K, recorded at ~9.3 GHz. [d] ±0.001. [e] EPR parameters were calculated directly from the recorded spectrum by measuring the frequency and the magnetic field. [f] $\pm 1.0 \times 10^{-4}$ cm^{-1}.

Table II. Electrochemical Properties[a]

complex	E_{p_c},[b] V	E_{p_a},[c] V	ΔE_p, V	n, electrons/molecule	conductivity,[d] Λ^{-1} M^{-1} cm^2
$[Et_4N][MoOL_1]$	−1.00	−0.92	0.08	1.05[e]	51.8
	0.00	0.14	0.14	1.09[f]	
$[Et_4N][MoOL_2]$	−1.02	−0.95	0.07	1.10[e]	64.2
	0.09	0.17	0.08	1.05[f]	
$MoO_2L_1H_2$	−1.03	−0.94		2.01[e]	nonelectrolyte
	0.00	0.14	0.14		
$MoO_2L_2H_2$	−1.09	−0.99		2.04[f]	nonelectrolyte
	0.11	0.19	0.08		

[a] DMF, 0.10 M Et_4NCl; potentials vs. SCE, ±0.015 V; cyclic voltammograms, scan rate 0.100 V/s; Pt electrode. [b] Reduction peak. [c] Oxidation peak. [d] 1.00×10^{-3} M solution in DMF. [e] Controlled potential reduction. [f] Controlled potential oxidation.

ligands having redox behavior similar to that of enzymatic molybdenum centers.[9,10]

In these complexes, isolated as the tetraethylammonium salts, the amino groups are deprotonated. This formulation is based on analysis, conductivity measurements (which show the complexes to be 1:1 electrolytes), and the lack of absorption in the N-H stretching region of the infrared spectrum (Tables I and II).[11] While deprotonated amino groups are present in complexes of *o*-aminobenzenethiol (abt) with other metals,[12,13] and the nonoxo Mo(VI) complex, $Mo(abt)_3$,[14] this is the first reported case of amino deprotonation in a molybdenum oxo complex.[15] The unusual redox properties are likely due to this deprotonation, which gives the complexes dithiolene characteristics.[14]

The complexes undergo both one-electron oxidation and reduction at a platinum electrode in DMF (Figure 1, Table II).[2] This result led us to examine the electrochemistry of the corresponding molybdenum(VI) dioxo complexes, MoO_2LH_2, first reported by Gardner et al.[14] (MoO_2LH_2 has fully protonated amino groups.) The MoO_2LH_2 complexes are reduced in a two-electron step to the same Mo(IV) species[16] obtained by the one-electron reduction of $[Et_4N][MoOL]$, and are subsequently reoxidized in two consecutive one electron steps to $MoOL^-$ and MoO_2LH_2, respectively[17] (Figures 2 and 3). A second less negative reduction peak, not present in the original cathodic cyclic voltammetric scans, appears upon consecutive cathodic, anodic, cathodic scanning for both $MoOL^-$ and MoO_2LH_2 (Figures 2 and 3). This reduction peak, which is coupled to the oxidation peak for $MoOL^-$, appears to be due to an unstable Mo(VI) complex, which is rapidly converted into MoO_2LH_2 (after controlled potential oxidation of $MoOL^-$, or controlled potential reduction of MoO_2LH_2 to the IV state followed by controlled potential reoxidation to the VI state, this peak is not seen in initial cathodic scans; it appears only on the time scale of cyclic voltammetry as described). It is uncertain whether this unstable Mo(VI) species is an intermediate in the oxidation of $MoOL^-$, since scanning at rates up to 100 V/s does not increase the relative height of the peak appreciably.

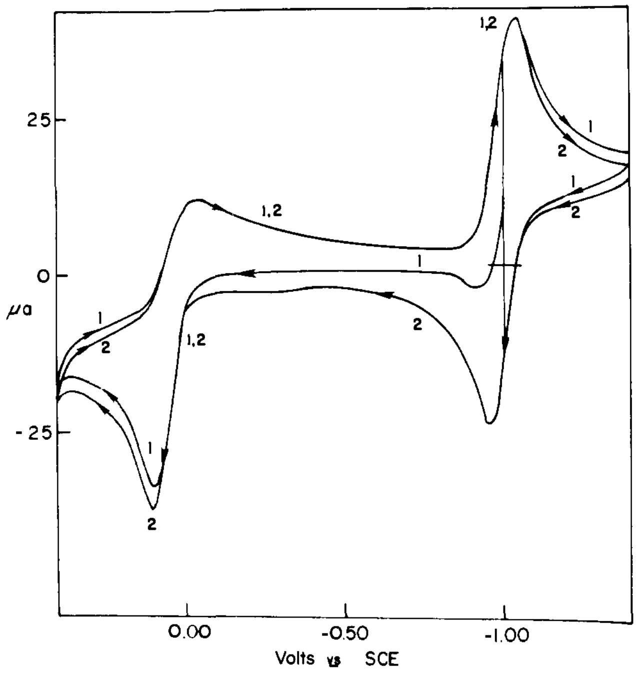


Figure 1. Cyclic voltammogram for $[Et_4N][MoOL_1]$, 5.00×10^{-4} M, DMF, 0.10 M $[Et_4N]Cl$, scan rate 0.100 V/s: (1) anodic scan; (2) cathodic scan. Scans begin at −1.05 V vs. SCE.

After controlled potential addition of one electron/molecule to MoO_2LH_2, the solution has the same visible absorption spectrum as a solution of $[Et_4N][MoOL]$, and EPR analysis shows a high level (90 ± 10% of total Mo) of $MoOL^-$ present. When MoO_2LH_2 is reduced coulometrically to the IV state, and an equivalent amount of MoO_2LH_2 is added, $MoOL^-$ is rapidly formed in high yield, probably according to the reaction

$$MoO_2LH_2 + Mo(IV) \rightarrow 2MoOL^- \qquad (1)$$

Reactions between Mo(VI) and Mo(IV) oxo complexes have been previously reported, but the product is the oxo-bridged Mo(V) dimer.[18] The apparent thermodynamic stability of $MoOL^-$ with respect to MoO_2LH_2 and Mo(IV) is unique, and may be a result of the geometrical restraints of the ligand,

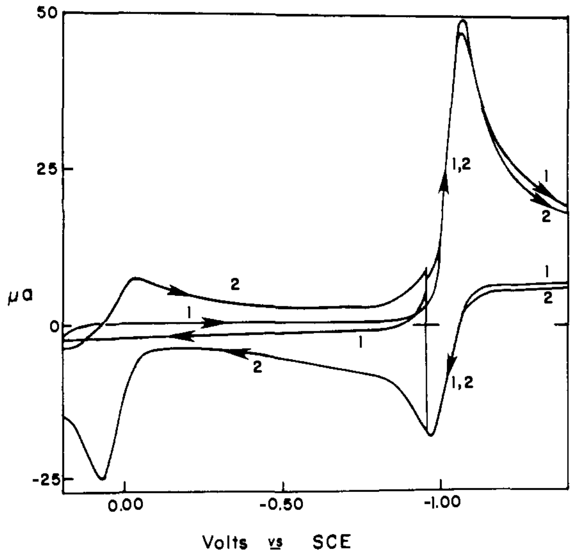


Figure 2. Cyclic voltammogram for $MoO_2L_1H_2$, 5.00×10^{-4} M, DMF, 0.10 M $[Et_4N]Cl$ scan rate 0.100 V/s: (1) anodic scan; (2) cathodic scan. Scans begin at −0.95 V vs. SCE.

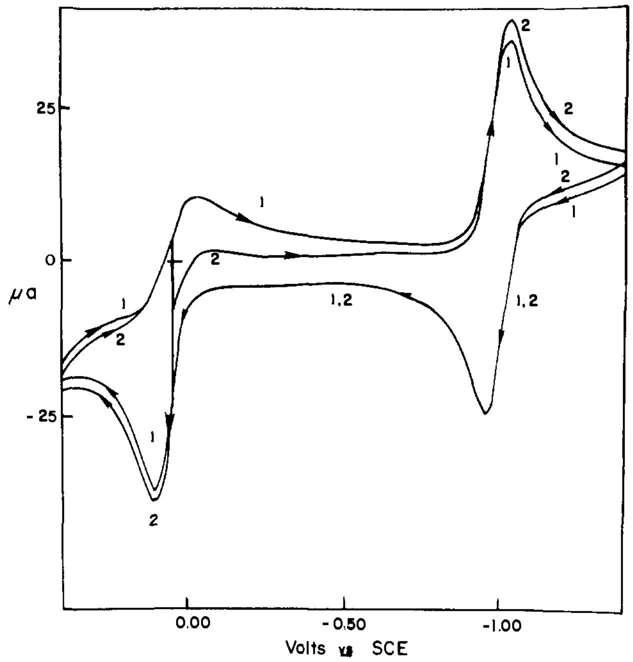


Figure 3. Cyclic voltammogram for $[Et_4N][MoOL_1]$, 5.00×10^{-4} M, DMF, 0.10 M $[Et_4N]Cl$, scan rate 0.100 V/s: (1) anodic scan; (2) cathodic scan. Scans begin at 0.05 V vs. SCE.

which precludes oxo bridging through a position cis to the oxo group.[19]

Preliminary experiments using these complexes in model substrate redox reactions are most promising. MoO_2LH_2 is reduced in the presence of excess SO_3^{2-}, while solutions of MoO_2LH_2 reduced electrochemically to the IV state are oxidized by NO_3^-. In both cases, $MoOL^-$ is produced, as determined by visible absorption and EPR spectrometry. Since the reaction with NO_3^- is likely to be a two-electron process, it appears $MoOL^-$ is formed from MoO_2LH_2 and Mo(IV) by reaction 1.[19] While the reduction of NO_3^- by both Mo(V) and Mo(IV) oxo complexes has been reported previously,[20,21] this appears to be the first reported reduction of an Mo(VI) complex in the presence of SO_3^{2-}.[22] Detailed studies of these reactions are underway and will be reported later.

The $MoOL^-$/Mo(IV) couple is nearly electrochemically reversible (Table II); the $MoO_2LH_2/MoOL^-$ couple, however, is clearly irreversible [the observed reduction peaks near 0.00 V are due to the unstable Mo(VI) species referred to above], since the observed potential for the two-electron reduction of MoO_2LH_2 to Mo(IV) is more negative than the potential for the reduction of $MoOL^-$ to Mo(IV). Reaction 1 between MoO_2LH_2 and Mo(IV) to produce $MoOL^-$ in essentially quantitative yield indicates that the potential for the $MoO_2LH_2/MoOL^-$ couple is more positive than the potential of the $MoOL^-$/Mo(IV) couple.[23]

The results indicate that the $MoO_2LH_2/MoOL^-$/Mo(IV) system exhibits redox behavior similar to that reported for xanthine oxidase [two-electron irreversible reduction of the Mo(VI) center to Mo(IV), followed by two one-electron reoxidations[1,4,24]]. Such redox behavior has not been reported for other molybdenum oxo complexes. Furthermore, the stability of $MoOL^-$ appears to be a consequence of deprotonation of the amino groups of the ligand, indicating that coupled proton/electron transfer occurs in the redox reactions of these complexes, a mechanism proposed for xanthine oxidase.[1,2,26]

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(15) $[Et_4N][MoOL_1]$ was prepared from $[Et_4N][MoO(SPh)_4]$ [I. W. Boyd, I. G. Dance, K. S. Murray, and A. G. Wedd, *Aust. J. Chem.*, **31**, 279 (1978)] by addition of the Zn salt of the ligand to a solution of this complex and $[Et_4N]Cl$ in CH_2Cl_2. After warming at 35 °C, the green complex precipitated. It was dried and stored under vacuum. $[Et_4N][MoOL_2]$ was prepared by dissolving the free ligand, $[Et_4N][MoO(SPh)_4]$, and $[Et_4N]Cl$ in CH_3CN and heating at 60 °C until a green solution was obtained. Upon addition of CH_3OH, the complex precipitated. It was dried and stored under vacuum. Anal. Calcd for $MoC_{22}H_{32}N_3OS_2$ ($[Et_4N][MoOL_1]$): C, 51.35; H, 6.27, N, 8.17; S, 12.46. Found: C, 51.02; H, 6.10; N, 7.89; S, 12.13. Anal. Calcd for $MoC_{24}H_{36}N_3OS_2$ ($[Et_4N][MoOL_2]$): C, 53.12; H, 6.69; N, 7.74; S, 11.82. Found: C, 53.21; H, 6.45; N, 7.48; S, 11.64. Both compounds are unstable in air and must be stored under vacuum.

(16) It is likely the Mo(IV) species is an oxo complex, although it has not been isolated. A number of Mo(IV)O complexes have been prepared and they appear to be identical in DMF solution with the one-electron reduction products of the corresponding Mo(V)O complexes.[21] Until the Mo(IV) complexes are prepared and characterized, however, the reduction product is designated Mo(IV).

(17) The products of the electrochemical reactions were identified by their electronic and EPR spectra and their cyclic voltammograms.

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(19) $[Et_4N][MoOL]$ does not react with NO_3^-. This suggests that $MoOL^-$ in solution is either pentacoordinate with square pyramidal geometry or has

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.

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(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).

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(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:

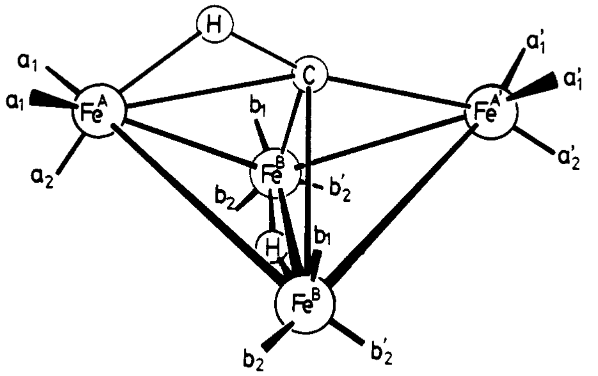
In seeking[1-4] metal clusters containing carbidic carbon atoms of low coordination number and high reactivity,[5] we have prepared a unique cluster containing a methylidyne group bonded to the iron cluster atoms, namely $HFe_4(\eta^2\text{-}CH)(CO)_{12}$. Deprotonation of the cluster with base successively 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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