

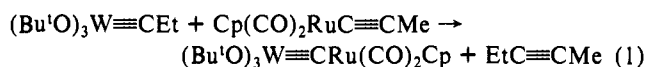
**An Agostic μ -Methyne Molybdenum-Iron Complex
from Protonation of a μ -Carbide Precursor,
 $\text{Tp}'(\text{CO})_2\text{Mo}\equiv\text{CFe}(\text{CO})_2\text{Cp}$**

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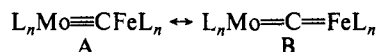
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Molecular metal carbide complexes have attracted attention as models for surface carbide species¹ which are formed by dissociation of carbon monoxide on metal surfaces.² The accuracy of this analogy remains to be established. Shriver has noted that while four-atom carbide clusters exhibit intriguing reactivity patterns, the carbide site in large clusters tends to be unreactive.³ Dinuclear iron porphyrin carbide derivatives are known,⁴ but the bridging carbide most germane to the chemistry reported here is $(\text{RO})_3\text{W}\equiv\text{CRu}(\text{CO})_2\text{Cp}$,⁵ which was prepared by Latesky and Selegue (eq 1). We now report the synthesis and several reactions



of $\text{Tp}'(\text{CO})_2\text{Mo}\equiv\text{CFe}(\text{CO})_2\text{Cp}$ [$\text{Tp}' = \text{tris}(3,5\text{-dimethylpyrazolyl})\text{borate}$; $\text{Cp} = \pi\text{-C}_5\text{H}_5$] as depicted in Scheme I.

Reactions of Lalor's chlorocarbonyl $\text{Tp}'(\text{CO})_2\text{Mo}\equiv\text{CCl}$ [$\nu_{\text{CO}} = 2003, 1916 \text{ cm}^{-1}$] with Fp anion [Fp = $\text{CpFe}(\text{CO})_2$] in THF rapidly forms $\text{Tp}'(\text{CO})_2\text{Mo}\equiv\text{CFp}$ (1), which was isolated in 75% yield. The solution infrared spectrum of 1 reveals four carbonyl absorptions, and neglecting coupling of the $\text{M}(\text{CO})_2$ units through the carbide link, we assign the two higher frequencies to the Fp fragment (2040 and 1991 cm^{-1}) while the lower frequencies (1947 and 1865 cm^{-1}) reflect an increase in electron density at molybdenum when Fp^- replaces Cl^- as the carbene substituent. Lalor has prepared other carbene products by nucleophilic displacement of chloride from the chlorocarbonyl reagent.⁷ A vinylidene⁸ resonance form with both metals in the same oxidation state may contribute to the bonding in 1 as in form B. The bridging carbide



resonates at 381 ppm in the ^{13}C NMR spectrum, near the range expected for vinylidene C_α chemical shifts [$\text{Tp}'(\text{CO})_2\text{Mo}=\text{C}=\text{CH}_2$, 350 ppm;⁹ $\text{Tp}'(\text{CO})_2\text{Mo}=\text{C}=\text{C}(\text{CN})\text{CO}_2\text{Et}$, 300 ppm¹⁰] and below carbene chemical shifts¹¹ in related complexes [Tp' -

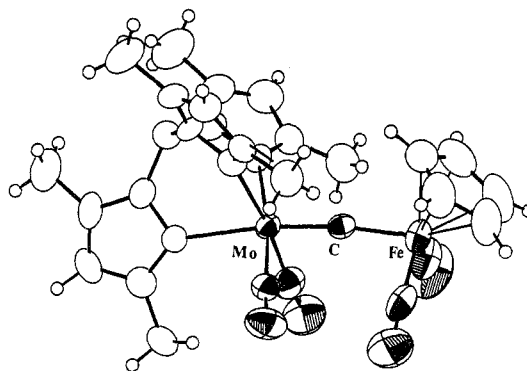
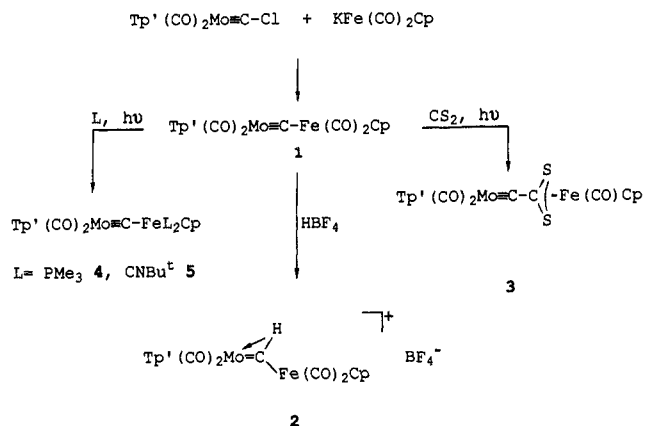


Figure 1. An ORTEP view of $\text{Tp}'(\text{CO})_2\text{Mo}\equiv\text{CFe}(\text{CO})_2\text{Cp}$ (1).

Scheme I



$(\text{CO})_2\text{Mo}\equiv\text{CR}$,⁹ R = Ph, 288 ppm; R = Me, 304 ppm; $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{CX}$,¹² X = SME, 264 ppm; X = NEt_2 , 255 ppm].

The X-ray crystal structure of 1 is shown in Figure 1.¹³ The single carbon (C5) bridge between iron and molybdenum is almost linear ($\text{Fe-C5-Mo} = 172.2(5)^\circ$). The molybdenum-carbon bond is definitely a triple bond ($\text{Mo-C5}, 1.819(6) \text{ \AA}$) (cf.: $\text{Tp}'(\text{CO})_2\text{Mo}\equiv\text{CS}(4\text{-C}_6\text{H}_4\text{NO}_2)$,⁷ 1.80(4) \AA ; $[\text{B}(\text{C}_2\text{H}_3\text{N}_2)_4](\text{C-O})_2\text{Mo}\equiv\text{CCl}$,⁶ 1.894(9) \AA). The iron-carbon bond length [1.911(8) \AA] is appropriate for a σ -bond between an sp -type carbon and an iron center ($\text{FpC}\equiv\text{CPh}$,¹⁴ 1.92 \AA). The relative conformation of the two metals is staggered with the carbonyl groups 23.1° away from the eclipsed conformation. A 2:1 pattern is observed for the three pyrazole rings of the Tp' ligand in the ^1H NMR spectrum down to -80°C in CD_2Cl_2 , so the eclipsed form is easily accessible in solution.

Protonation of 1 with fluoroboric acid at low temperature affords a yellow precipitate, which can be recrystallized to form yellow needles of a cationic μ_2 -methyne complex. The four carbonyl absorptions of the neutral carbide reagent blue-shift about 50 cm^{-1} each due to addition of the proton at the carbide carbon. Prominent NMR data include a ^1H singlet at 1.94 ppm which integrates for one proton and a ^{13}C signal at 344 ppm which splits into a doublet with $^1J_{\text{CH}} = 72 \text{ Hz}$ in the coupled spectrum. One-bond CH coupling constants in this range are the most reliable spectral diagnostic for agostic bonds.¹⁵ A symmetry plane is present on the ^1H NMR time scale even at low temperature, so clearly the barrier to oscillation of the two metal fragments is quite small.

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(13) Crystal data: $P2_1/n$, $a = 11.640(5) \text{ \AA}$, $b = 18.646(7) \text{ \AA}$, $c = 14.1781(5) \text{ \AA}$, $\beta = 98.37(3)^\circ$, $V = 3160(2) \text{ \AA}^3$, Mo $K\alpha$ $\gamma = 0.70930 \text{ \AA}$, $Z = 4$, $\rho_{\text{calcd}} = 1.58 \text{ g cm}^{-3}$, $\mu_{\text{calcd}} = 10.5 \text{ cm}^{-1}$; the final residuals for 371 variables refined against 2659 data with $I > 2.5\sigma(I)$ were $R = 5.3\%$ and $R_w = 6.1\%$. Details of the structure are available as supplementary available.

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[‡] X-ray crystallography.

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Protonation of Fischer carbynes has been invoked as the initial step in numerous reactions where a trapping reagent then adds to maintain the metal electron count.^{11,16} The product of simple protonation here resembles the high oxidation state agostic alkylidene complexes of groups V¹⁷ and VI¹⁸ where the hydrogen on the α -carbon is also bound simultaneously to the metal. Bridging μ_2 -methyne units prepared by other methods have been well characterized in dinuclear iron,¹⁹ ruthenium,²⁰ and rhenium²¹ complexes. An agostic methyne entity was also produced by protonation of the four-iron butterfly cluster, $[\text{Fe}_4\text{C}(\text{CO})_{14}]^{2-}$.²²

Reaction of the dinuclear μ_2 -carbide with carbon disulfide is promoted by light. The net result is insertion of CS_2 into the carbide-iron bond to form a dithio acid derivative which is chelated to iron in the $\text{Tp}'(\text{CO})_2\text{Mo}\equiv\text{CCS}_2\text{Fe}(\text{CO})\text{Cp}$ product. The lone iron carbonyl is assigned to the 1960-cm^{-1} absorption; the molybdenum dicarbonyl unit then accounts for infrared bands at 2003 and 1924 cm^{-1} in accord with insertion of the electrophilic CS_2 moiety into the C-Fe bond.

No thermal reaction was observed between **1** and either PMe_3 or $\text{Bu}'\text{NC}$, but upon photolysis substitution of both iron carbonyl ligands occurred. Formation of $\text{Tp}'(\text{CO})_2\text{Mo}\equiv\text{CFeL}_2\text{Cp}$ was evident from IR and NMR spectra for $\text{L} = \text{PMe}_3$ (**4**) and $\text{L} = \text{Bu}'\text{NC}$ (**5**). Particularly noteworthy are the low-frequency carbonyl absorptions (1910 and 1820 cm^{-1} for **4**; 1920 and 1830 cm^{-1} for **5**) and the very low field carbide ^{13}C chemical shifts (500 ppm for **4**; 452 ppm for **5**).

Access to the μ_2 -carbide here is made possible by the unique ligating properties of Tp' , both electronic and steric.²³ In spite of the reactions reported here for this neutral carbide, we have been struck by the reluctance of this dinuclear carbide to undergo facile chemical transformations at the central carbon site. This reticence may reflect the dominant role of the Tp' ligand in imparting kinetic, and perhaps thermodynamic, stability to $\text{Tp}'(\text{CO})_2\text{Mo}\equiv\text{CFe}(\text{CO})_2\text{Cp}$.

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Supplementary Material Available: Details of syntheses and full analytical and spectral data for **1-5** and tables of crystal data.

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positional and thermal parameters, bond lengths, bond angles, and torsion angles for **1** (12 pages); listing of calculated and observed structure factors for **1** (15 pages). Ordering information is given on any current masthead page.

Inclusion Complexation by Bis(cyclodextrins) in the Presence of Phospholipid Vesicles

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Molecular recognition of organic ligands by synthetic receptors has been widely studied in both organic¹ and aqueous² solvents. In each circumstance the challenge is to design a recognition site that overcomes the tendency of the guest to partition into the bulk solvent. However, receptors in the biological setting must compete with both hydrophobic and aqueous microenvironments into which the ligand might partition. Synthetic receptors for organic ligands that model this complication have received less attention.^{3,4} We have succeeded in constructing water-soluble receptors with sufficient specificity to overcome the tendency of organic ligands to partition into the hydrophobic interior of a phospholipid bilayer.

β -Cyclodextrin (β -CD), a macrocyclic oligomer of seven glucoses, has been widely studied as a water-soluble receptor that binds organic ligands by inclusion complexation.⁵ The cooperative action of two covalently linked cyclodextrins (bis-CDs) has been shown by several groups⁶⁻⁹ to provide powerful binding of ligands designed to exploit the extended recognition site, with equilibrium constants for binding (K_a) ranging from 10^5 to 10^9 M^{-1} . In contrast, β -CD binds organic guests with K_a values⁵ of 10^2 – 10^4 M^{-1} (e.g., $K_a = 1800\text{ M}^{-1}$ for 6-toluidino-2-naphthalenesulfonate (TNS)).^{7,8,10} We have prepared bis-CDs **1**,^{8a} **2**, and **3**¹¹ and

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