

nature of the interlayer cation and the method used to desorb the porphyrin intermediate from the mineral surface. Layered mica-type silicates such as montmorillonite are ubiquitous products of hydrothermal reactions and the weathering of primary silicate minerals.²³ Also, at least 70 different aldehydes are known²⁴ to react with pyrrole in acidic media to form porphyrins in yields up to 20%. These facts, together with the 10^3 – 10^5 times greater yields of porphyrins achieved in this study, prompt us to suggest that the reactions of aldehydes and pyrroles on layered silicate minerals is a much more likely mechanism for the abiobiochemical formation of porphyrins than those proposed previously. This model, along with recent reports of polypeptide,²⁵ polynucleotide,²⁶ and monosaccharide²⁷ formation on related mineral surfaces, supports Bernal's²⁸ original suggestion that adsorptive and catalytic processes on layered silicates may have played an important role in the chemical evolution of biologically important molecules.

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Registry No. Montmorillonite, 1318-93-0; TPPH₂, 917-23-7; TPPH₂²⁺, 50849-35-9; Fe³⁺, 20074-52-6; VO²⁺, 20644-97-7; Cu²⁺, 15158-11-9; Zn²⁺, 23713-49-7; Co²⁺, 22541-53-3; Mg²⁺, 22537-22-0; Na⁺, 17341-25-2; benzaldehyde, 100-52-7; pyrrole, 109-97-7.

References and Notes

(1) For a review of the orientation and mobility of hydrated Cu²⁺ and Mn²⁺

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Molybdenocene Metalloporphyrins. Alkene and Alkyne Complexes Characterized by Spectroscopic and Chemical Means

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Synthesis of (C₅H₅)₂Mo(CH₃C≡CH) and an improved synthesis of (C₅H₅)₂Mo(C₂H₂) are reported. In addition to ¹H NMR spectra, decoupled and gated decoupled ¹³C NMR spectra are reported for these compounds as well as for (C₅H₅)₂Mo(C₂H₄). On the basis of comparisons of these NMR spectra to that of the corresponding carbocycles as well as other evidence, metallocyclic structures are proposed for the olefin and acetylene complexes of molybdenocene. Hydrolysis chemistry of (C₅H₅)₂MoC₂H₂, (C₅H₅)₂Mo(C₂H₄), and (C₅H₅)₂Mo(CH₃C≡CCH₃) is discussed and related to similar nitrogenase enzyme reductions.

Bonding in bis(cyclopentadienyl)metal complexes of olefins and alkynes continues to be a subject of great interest.¹ Descriptions of the nature of the metal-hydrocarbon bonding range from suggestions of π complexes capable of metal-olefin

bond rotation to metalloporphyrins as well as intermediate cases.²⁻⁵ Our investigations into molybdenocene chemistry have suggested that its olefin and acetylene complexes act chemically like metallocycloalkanes and metallocycloalkenes,⁶ respectively.

Table I. Mass Spectrum of $(C_5H_5)_2MoC_2H_2$

m/e	Relative intensity	Ion
256	31	$(C_5H_5)_2Mo(C_2H_2)$
230	100	$(C_5H_5)_2Mo^+$
202	46	$(C_8H_8)Mo^+$
179	11	$(C_6H_7)Mo^+$
115	38	$(C_5H_5)_2Mo^{2+}$
100	28	Mo^+

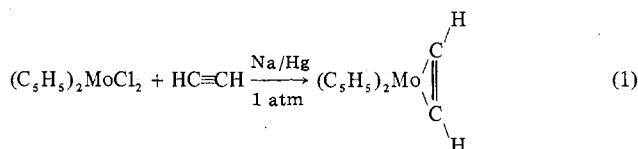
Table II. Mass Spectrum of $(C_5H_5)_2Mo(C_3H_4)$

m/e	Relative intensity	Ion
270	16	$(C_5H_5)_2Mo(C_3H_4)^+$
230	100	$(C_5H_5)_2Mo^+$
204	12	$(C_8H_8)Mo^+$
178	12	$(C_6H_6)Mo^+$
135	7	$(C_5H_5)_2Mo(C_3H_4)^{2+}$
115	16	$(C_5H_5)_2Mo^{2+}$
100	20	Mo^+

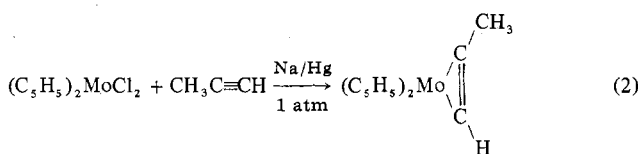
Further, our earlier demonstration of the carbene-like nature of molybdenocene^{6,7} and Hoffmann's subsequent theoretical support¹ for this view also suggested that these molecules might be demonstrable metallocycles. Molybdenocene is one of the few species that complexes both ethylene and acetylene to yield complexes of sufficient stability for normal spectroscopic investigations. We therefore proceeded to synthesize a series of these uniquely stable alkene and alkyne complexes of molybdenocene and investigated their structure by instrumental and chemical means.

Results and Discussion

We have previously reported the synthesis of $(C_5H_5)_2Mo(C_2H_4)$ ⁶ and $(C_5H_5)_2Mo(C_2H_2)$.⁸ However, a more simple, direct method of synthesizing the acetylene complex has been found.



The acetylene complex was identified by its ¹H NMR and infrared spectrum as well as its mass spectrum shown in Table I. Similarly, a new complex, $(C_5H_5)_2Mo(C_3H_4)$, was synthesized.



This compound is characterized by a ¹H NMR singlet at 4.47 ppm, a doublet ($J_{H-H} = 2$ Hz) at 2.75 ppm, and a multiplet at 7.05 ppm integrating 10:3.1:0.95, assigned to cyclopentadienyl, methyl, and acetylenic protons, respectively. The compound exhibits a significant reduction in the alkyne bond order as evidenced by the C=C stretch at 1736 cm⁻¹ in its infrared spectrum. This is a reduction of approximately 404 cm⁻¹ compared to the parent acetylene. The mass spectrum of the compound was determined and is listed in Table II.

Treatment of $(C_5H_5)_2Mo(C_2H_2)$ with gaseous HCl yields ethylene, nearly quantitatively. This is depicted in Figure 1 as well as in our previously reported⁶ hydrolyses of other similar molybdenocene complexes. The consistent reduction of alkynes and alkenes to alkenes and alkanes by acid hydrolysis of their molybdenocene complexes suggests a Mo-C

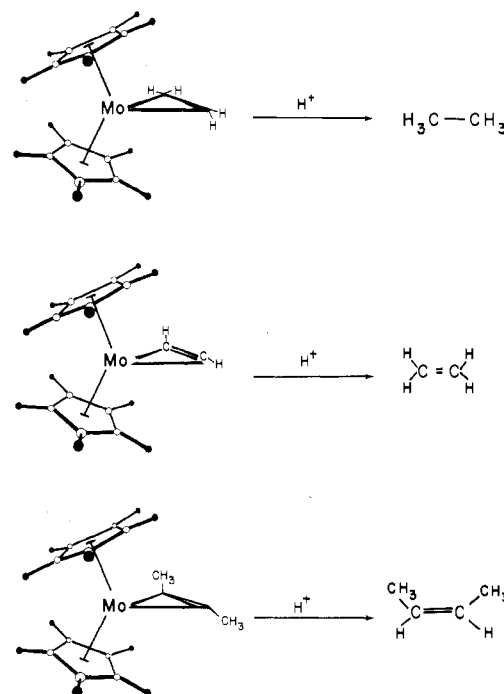


Figure 1. Molybdenocene-induced reduction of alkenes and alkynes.

σ bond. This reactivity parallels that observed for metal-alkyl groups which readily protonate^{9a} in a fashion analogous to the molybdenum complexes and contrasts with the regeneration of the unchanged olefin when other olefin complexes are treated with acid.^{9a} A recent photoelectron study¹⁰ of several molybdenocene complexes also suggests a metallocycle structure for some of these complexes. For instance, a comparison of the photoelectron spectrum of $(C_5H_5)_2MoC_2H_4$ and $(C_5H_5)_2Mo(CH_3)_2$ strongly suggests Mo-C σ bonds in both cases and thus a metallocyclopropane structure for $(C_5H_5)_2MoC_2H_4$. The presence of metal-carbon σ bonds in olefin complexes had also been previously indicated by a ¹⁹F NMR study¹¹ of $(PPh_3)_2Pt(CF_3CF=CF_2)$. Here, the geminal F-F coupling constant falls in the range expected for a saturated fluorocarbon. Finally, the actual reduction of acetylene to ethylene is of considerable biological interest since this is precisely the reduction catalyzed by the nitrogenase enzyme¹² and thus suggests a mechanism for the reduction. This demonstrated pathway is even more notable when one takes into account that a single molybdenum atom in the nitrogenase enzyme is believed to be an active reduction site.^{13,14}

Decoupled Fourier-transform natural-abundance ¹³C NMR of $(C_5H_5)_2MoC_2H_4$ shows singlet resonances at 77.9 and 11.8 ppm. The gated decoupled spectrum of the same complex shows the largest peak at 77.9 ppm split into two doublets ($J_{13C-1H} = 177$ Hz) of quintets ($J = 6.5$ Hz) while the smaller peak gives a triplet with ($J_{13C-1H} = 153$ Hz). These splittings confirm that the smaller peak is due to the two equivalent carbons in ethylene while the peak at 77.9 ppm is due to the cyclopentadienyl carbons. Table III shows the ¹³C NMR data for some olefin complexes. It is interesting to note that ¹³C NMR parameters of $(C_5H_5)_2Mo(C_2H_4)$ most closely resemble $(C_5H_5)_2Nb(H)(C_2H_4)$ and $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)$. The crystal structure of $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)$ is consistent with a metallocyclopropane and neither niobium compound exhibits olefin rotation on the NMR time scale.¹⁶ On the other hand, olefin rotation has been observed for $K^+PtCl_3(C_2H_4)^{-18}$ and $(C_5H_5)Rh(C_2H_4)_2$,¹⁹ the olefin complexes whose ¹³C NMR parameters least resemble $(C_5H_5)_2Mo(C_2H_4)$. Whether ¹³C chemical shift and coupling constant data may be useful in predicting olefin rotation awaits a somewhat larger sample of compounds. However, it is gratifying that the available data

Table III. Chemical Shifts and Coupling Constants for Ethylene Complexes

	$\delta(\text{C}), \text{ppm}$ C_2H_4	$J(\text{C-H}),$ Hz	Ref
$(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{H}_4)$	39.6		15
$\text{K}^+\text{PtCl}_3(\text{C}_2\text{H}_4)^-$	67.1		15
$(\text{C}_5\text{H}_5)_2\text{Nb}(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_4)$	27.63 ^a	154.5	16
	29.35	153	
$(\text{C}_5\text{H}_5)_2\text{Nb}(\text{H})(\text{C}_2\text{H}_4)$	13.44 ^a	153	16
	7.96	156	
$(\text{C}_5\text{H}_5)_2\text{Mo}(\text{C}_2\text{H}_4)$	11.8	153	This work
$(\text{acac})\text{Rh}(\text{C}_2\text{H}_4)_2$	36.3 ^b	158	17
$(\text{C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)_2$	60.0 ^b	160	17

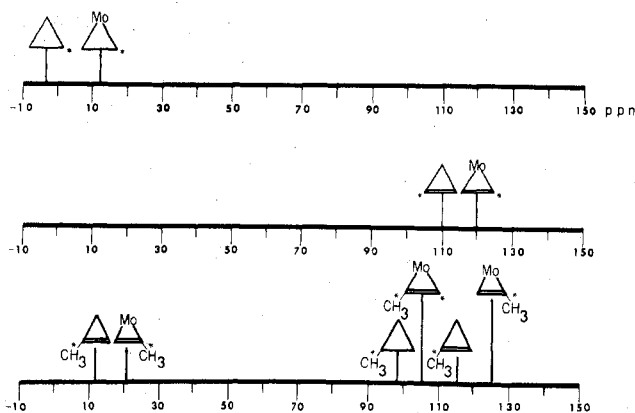
^a The olefinic carbons are inequivalent. ^b Chemical shifts were referenced to CS_2 in the original work and were converted to a Me_4Si standard assuming CS_2 absorbs 192.8 downfield from Me_4Si .

groups $(\text{C}_5\text{H}_5)_2\text{MoC}_2\text{H}_4$ with compounds that do not exhibit olefin rotation and that have been shown to have structures consistent with a metallocyclopropane.

$(\text{C}_5\text{H}_5)_2\text{MoC}_2\text{H}_2$ shows resonances in its ^{13}C -decoupled FT NMR spectrum at 84.8 and 117.7 ppm. The gated decoupled spectrum of this complex shows the larger peak at 84.8 ppm split into a doublet ($J_{^{13}\text{C}-^1\text{H}} = 181 \text{ Hz}$) of quintets ($J = 6.6 \text{ Hz}$) and the smaller peak split into a doublet ($J_{^{13}\text{C}-^1\text{H}} = 200 \text{ Hz}$) which is consistent with assignment to cyclopentadienyl and acetylenic carbons, respectively. The related methylacetylene complex $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{C}_3\text{H}_4)$ shows peaks at 21.6, 84.1, 106.0, and 126.1 ppm in its decoupled FT ^{13}C NMR. Assignment of the peaks is accomplished by observing the gated decoupled ^{13}C NMR spectrum which shows the peak at 21.6 ppm split into a quartet ($J_{^{13}\text{C}-^1\text{H}} = 126 \text{ Hz}$), the peak at 84.1 ppm split into a doublet ($J_{^{13}\text{C}-^1\text{H}} = 177 \text{ Hz}$) of quintets ($J = 6.6 \text{ Hz}$), the peak at 106 ppm split into a doublet ($J_{^{13}\text{C}-^1\text{H}} = 198 \text{ Hz}$) of quartets ($J = 4.2 \text{ Hz}$) while the peak at 126.1 ppm is unchanged. This requires assignment of the peaks as methyl, cyclopentadienyl, $=\text{C}-\text{H}$, and the unique methyl-bearing carbon, respectively. The origin of the 4.2 Hz quartets of the acetylenic carbon may be long range coupling with the methyl protons. Support for this view is found in the observed coupling between the methyl and acetylenic protons in the ^1H NMR of the same compound. Origin of the quintets ($J = 6.6 \text{ Hz}$) for the cyclopentadienyl carbons in the gated decoupled ^{13}C spectrum is less clear although it may be similarly due to long range coupling to the other four protons in the cyclopentadienyl ring. In all cases observed, rapid rotation of the cyclopentadienyl groups about the bond axis is indicated by the equivalence of the cyclopentadienyl carbons on the NMR time scale.

Since chemical reactivity of these olefin and acetylene complexes suggests metal-carbon σ bonds and in view of the already demonstrated chemical⁶ and theoretical¹ similarity of methylene and molybdenocene, a comparison of the spectroscopic properties of the molybdenum compounds and the related carbocycles was undertaken. Magnetic environment of the carbon and hydrogen nuclei of cyclopropane, cyclopropene, and 1-methylcyclopropene and their molybdenocene analogues were compared using the data in the Experimental Section.

^{13}C NMR chemical shifts are generally believed to be dominated by local paramagnetic effects²⁵⁻²⁷ which usually reflect electron density²⁷ and, crudely, hybridization at the carbon nucleus, although other parameters must be considered.²⁸ If the above ^{13}C chemical shifts are dominated by the usual effects and the olefin and acetylene complexes of molybdenocene are metallocycles, then their ^{13}C chemical shifts should resemble those of the carbocyclic analogues. A graphic summary of the ^{13}C chemical shift data for the cyclopropenes, cyclopropane, and their molybdenocene analogues

Figure 2. Pertinent ^{13}C NMR absorptions of cyclopropane, cyclopropene, methylcyclopropane, and their molybdenocene analogues.Table IV. ^{13}C Coupling Constants for Selected Hydrocarbons and Their Substituted Analogues

Ref	Compd ^a	$J_{\text{C-H}}^b$ Hz	$J_{\text{C-H}}^b$ Hz	Compd ^a	Ref
22	\triangle^*	162	153	Mo \triangle^*	This work
20	\triangle^*	228	200	Mo \triangle^*	This work
20	\triangle^* CH ₃	225	198	Mo \triangle^* CH ₃	This work





^a Asterisk denotes atom to which the coupling constant is assigned. ^b $^{13}\text{C}-^1\text{H}$ coupling.

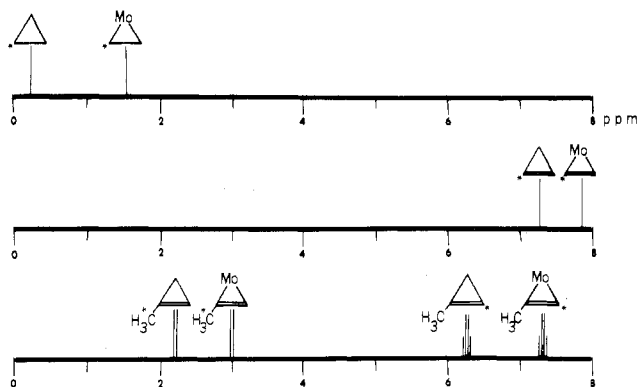
is shown in Figure 2. All of the molybdenum compound absorptions occur slightly downfield of the corresponding absorption in the carbocycle. The effect seems to pervade all nuclei in these small ring compounds since even the methyl group in 1-methylcyclopropene is upfield of the molybdenocycle by about the same amount as the ring carbons. These data strongly suggest that the nuclear environment and probably the hybridization at the carbons in the molybdocycles and carbocycles differ only by a slight, rather constant amount, possibly due to the inductive effect of the molybdenum atom.

Conclusions drawn from chemical shift data are supported by comparing $J_{\text{C-H}}$ of the molybdocycles, calculated from the gated decoupling experiments, with those of the carbocycles (Table IV). Again, the origin of C-H couplings is complex but believed to generally reflect the hybridization at the carbon atom²⁹ particularly in a series of related compounds. Here, the molybdocycles mirror the ^{13}C chemical shift data by suggesting an approximately uniform change of carbon hybridization in the molybdenum compounds compared to those of the carbocycles. In every case, the coupling constant for the molybdocycle is slightly smaller than the corresponding coupling constant in the cyclic hydrocarbon. This, again, may be attributed to a slight inductive effect of the metal. Finally, the close relationship between the two series of cyclic compounds is supported by the observation that even the small reduction in coupling constant of the vinylic carbon of cyclopropene that occurs upon methylation of one of the vinylic carbons is faithfully reproduced by the molybdenum analogues.

If, as suggested by both ^{13}C chemical shift and coupling constant data, the carbon hybridization in the metallocycles assumed a slightly decreased s character compared to the carbocycles, then the bond order of the C-C multiple bond should be lower in the molybdocycle than in the analogous carbocycle. This is usually reflected in a reduction of the C-C multiple bond stretch in the infrared region.³¹⁻³³ Table V shows just such a reduction of very similar magnitudes for both

Table V. Multiple Bond Infrared Absorptions of Cyclopropene and Their Molybdenum Analogues

Ref	Compd	Multiple bond IR abs, cm ⁻¹	Multiple bond IR abs, cm ⁻¹	Compd	Ref
30		1656	1613	Mo 	8
30	 CH ₃	1788	1736	Mo  CH ₃	This work

**Figure 3.** Pertinent ¹H NMR absorptions of cyclopropene, cyclopropene, methylcyclopropene, and their molybdenocene analogues.

molybdocycles when compared to their carbocyclic analogues. Thus the infrared spectra are consistent with the conclusions suggested by the NMR data.

The original suggestion of a metallocyclic structure for olefin complexes of molybdenocene resulted, among other things, from a temperature-dependent ¹H NMR study⁶ of (C₅H₅)₂Mo(CH₂=CHCN) which showed the olefin did not rotate on the NMR time scale. A more extensive ¹H NMR examination of olefin and acetylene complexes of molybdenocene has now been undertaken and the resulting spectra are compared to their hydrocarbon analogues as shown in Figure 3. All absorptions of the molybdenum-substituted compounds are shifted slightly downfield from the corresponding absorptions of the analogous carbocycle. These data suggest that the magnetic environment of the hydrogen nuclei of the molybdocycles and carbocycles are very similar with the hydrogen nuclei in the molybdocycle being only slightly more deshielded. As in the case of the ¹³C chemical shifts, the ¹H deshielding in the molybdocycles is presumably due to a slight inductive effort of the molybdenum atom. In all other respects, the spectra of the carbocycles and molybdocycles are nearly identical. Nowhere is this similarity more evident than in the spectra of 1-methylcyclopropene and its molybdenum analogue. These spectra are nearly superimposable, except for the chemical shift difference.³⁴ The above data again suggest, as did the ¹³C-¹H coupling constants, that changes in magnetic shielding or hybridization induced by the presence of the metal seem to extend throughout these small ring compounds, including even the methyl substituents, and that these molybdenum compounds are metallocycles with spectroscopic properties very similar to their carbon analogues.

Although transition-metal complexes of ethylene and acetylene have only rarely been referred to as metallocyclopropanes and metallocyclopropenes, main group metallocycloalkanes of silicon,³⁵ germanium,³⁶ and tin³⁷ are well-known and studied. Simple ethylene and alkyne complexes of silicon are referred to and characterized as silacyclopropanes³⁸ and silacyclopropenes.³⁹ Even five-membered metallocycles of some metallocenes such as titanocene have been reported.⁴⁰⁻⁴² Based on the chemical re-

activity and physical evidence cited here, the ethylene and acetylene complexes of molybdenocene seem to be true metallocycles. Furthermore, their spectroscopic properties seem remarkably similar to cyclopropane and cyclopropene, respectively, further supporting the characterization of molybdenocene as a carbene-like molecule. Finally, the unique ability of molybdenocene to form stable, monomeric complexes with acetylene as well as several stable metallaazirines⁴⁶ may be related to the function of this metal center in the nitrogenase enzyme and to provide clues to the reduction mechanisms in that system.

Experimental Section

All proton NMR spectra were determined using a Varian EM360, while ¹³C spectra were obtained on either a Varian CFT-20 or Bruker DP-80. Deuteriobenzene was used as the solvent in all cases and peaks were referenced to Me₄Si. Infrared spectra were obtained from a Varian MAT-111. All mass spectra are presented as monoisotopic for ¹⁰⁰Mo, ¹²C, and ¹H and expected isotopic distributions were observed. In a typical determination, the accelerating voltage was 820 V, the source pressure 5 × 10⁻⁶ Torr, and the ionizing voltage was 80 eV.

The following NMR data were obtained from the references indicated and all data were relative to Me₄Si.

Cyclopropane absorbs at 0.22 ppm in its ¹H spectrum²¹ and -3.5 ppm in its ¹³C spectrum.²² Vinyl protons in cyclopropene absorb at 7.01 ppm²³ while the vinylic carbons absorb at 108.9 ppm.²⁰ The vinylic proton in 1-methylcyclopropene absorbs at 6.40 ppm²⁴ while the attached carbon absorbs at 98.8 ppm. Proton NMR spectra of (C₅H₅)₂Mo(C₂H₄) and (C₅H₅)₂Mo(C₂H₂) show absorption for the C₂H₄ and C₂H₂ groups at 1.48 and 7.68 ppm, respectively.⁶

(C₅H₅)₂MoCl₂ was prepared from (C₅H₅)₂MoH₂ using the methods of Green et al.⁴³ and Cooper et al.⁴⁴ Molybdenum pentachloride was prepared by direct chlorination of the metal.⁴⁵ The synthesis of (C₅H₅)₂MoC₂H₄ has been previously described.⁶ All solvents were dried over LiAlH₄ and distilled just prior to use. All materials were handled under purified nitrogen, argon, or under vacuum unless otherwise stated.

1. Synthesis of (C₅H₅)₂Mo(C₂H₂). (C₅H₅)₂MoCl₂ (200 mg, 0.67 mmol) was suspended in 50 mL of toluene and 1 mL of Na/Hg alloy (2 mmol of Na) was added. The mixture was then stirred for 18 h under 1 atm. of pressure of acetylene. The mixture was then filtered and the solvent removed in vacuo. A water-cooled probe was introduced and the orange solid sublimed at 40 °C at 10⁻³ Torr (yield ca. 25%). The product was identified by comparison of its infrared and ¹H NMR spectra, with those previously reported.⁸

2. Synthesis of (C₅H₅)₂Mo(CH₃C≡CH). (C₅H₅)₂MoCl₂ (200 mg, 0.67 mmol) was suspended in 50 mL of toluene and treated as in (1) above except that the acetylene atmosphere was replaced with methylacetylene. The resulting solution was filtered and the solvent removed in vacuo to yield a dark solid. Sublimation at 50 °C and 10⁻³ Torr yielded red (C₅H₅)₂Mo(CH₃C≡CH) (yield ca. 30%).

3. Hydrolysis of (C₅H₅)₂Mo(C₂H₂). (C₅H₅)₂MoC₂H₂ (50 mg, 0.20 mmol) was placed in a flask and attached to a vacuum line. Ten milliliters of toluene was distilled into the flask in vacuo and frozen with liquid nitrogen. Exactly 1 mmol of gaseous HCl was then similarly distilled into the flask and frozen. The system was isolated from the vacuum line and allowed to warm to room temperature with stirring. Upon warming, a precipitate of (C₅H₅)₂MoCl₂ was rapidly formed. The mixture stirred for 2 h at room temperature to assure complete reaction. Then 5 mL of Na/Hg alloy (10 mmol of Na) was added to convert the excess HCl to hydrogen and NaCl. After stirring an additional 12 h, the mixture was frozen with liquid nitrogen and the residual hydrogen pumped away. The remaining mixture was allowed to warm and was passed through a trap cooled at -100 °C with an isopentane bath. The hydrocarbons passing through this trap were collected in a tube by cooling with liquid nitrogen. The hydrocarbons were identified by gas chromatography over a silver nitrate column as over 90% ethylene and a few percent ethane.

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Preparation and Characterization of Five-Coordinate Iron(II) Chelates and Their Reaction with Dioxygen¹

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New iron(II) complexes with pentadentate Schiff base ligands have been isolated and characterized by elemental analyses, magnetic susceptibility measurements, and vibrational and electronic spectral techniques. The compounds are stable in the solid state and are compared to other metal complexes with the same type of ligands. They do not form stable adducts with nitrogenous bases but do react with molecular oxygen in solution. This reactivity toward oxygen is different for different ligand derivatives. Two μ -oxo compounds have been isolated and characterized. Their formation is discussed in terms of a dioxygen-complex intermediate.

Introduction

The preparation of iron(II) complexes with multidentate ligands has received considerable attention in the past few years. One reason for this is the interest in finding compounds that will reversibly coordinate dioxygen.^{2a} Such compounds could then be used as models for more complex molecules such as hemoglobin, myoglobin, or hemerythrin.^{2b} Toward this end we have synthesized several new iron(II) complexes with pentadentate Schiff base ligands (Figure 1). Although these compounds do not react reversibly with oxygen, they do represent a class of iron chelates about which little is known. For example, in 1969 Sacconi and Bertini³ reported a series of complexes employing the same type of ligands. Of the metals studied (Zn(II), Cu(II), Ni(II), Co(II), and Mn(II)), iron was not included. The only mention of the ferrous compounds in the literature is in a 1946 paper by Calvin and Barkeley⁴ which deals with the magnetic properties of a number of Schiff base complexes.

In contrast to the relatively few data available for the iron compounds, the corresponding cobalt and nickel complexes have received extended study. *N,N'*-(3,3'-Dipropylamine)-bis(salicylideneiminato)cobalt(II), Co(SALDPT), and its derivatives have been used as model compounds due to their reactivity with dioxygen to form stable adducts.^{5,6} Some of these compounds have been found to be reversible oxygen carriers.^{7,8} Recent work⁹ involving the reaction of dioxygen with the manganese complexes has also appeared in the literature. Such reports provided a precedent for studying the iron compounds in a similar manner. Herein we convey our results regarding the characteristics of these complexes.

Experimental Section

Materials. Ferrous sulfate (FeSO₄·7H₂O) and ferrous chloride (FeCl₂·4H₂O) were purchased from Fischer Scientific Co. Salicylaldehyde (SAL), 3-methoxysalicylaldehyde (3-CH₃OSAL), and bis(3-aminopropyl)amine (DPT) were purchased from Aldrich Chemical Co. and distilled prior to use. 5-Nitrosalicylaldehyde