Table VI. Angles (ϕ) between the Principal Tensor Axes R3[a] and the Normal to the $(\bar{2}01)$ Plane

Atom	ϕ, deg	Atom	ϕ, deg
Ge(1)	19 (1)	F(2)	144 (4)
Ge(2)	11 (1)	F(4)	37 (3)
Ge(3)	7 (1)	F(5)	51 (9)
F(1)	17 (1)	F(6)	55 (17)

[a] Corresponding to the largest mean square vibration.

Ge_5F_{12} as a Mixed-Valence Compound. The subject of mixed-valence chemistry has been reviewed by Robin and Day,[16] who list few mixed-valence binary halides. The structure of Cr_2F_5 ($CrF_2 \cdot CrF_3$) is known,[17] the environment around Cr^{II} being distorted octahedral and around Cr^{III} regular octahedral. No binary mixed-valence halides are given for the group IVb metals. Pb_3O_4[16] contains an octahedrally coordinated Pb^{IV} atom and a Pb^{II} atom at the apex of a trigonal pyramid; the bonding in Pb_3O_4 has been discussed in covalent terms by Dickens.[18]

Ge_5F_{12} is colorless, showing no additional absorption in the visible region; this is normal when the two types of metal atom are in sites of different symmetry and ligand field strength.[16]

It is interesting to speculate on the possibility of preparing other members of the $(GeF_2)_x \cdot GeF_4$ series. The compounds with $x = 3$ and $x = 4$ were prepared when the pressure of GeF_4 was less than 1 atm. It may be possible to prepare the compounds with $x = 1$ or $x = 2$ by using pressures of GeF_4 exceeding 1 atm, in a slightly modified reactor.[1] It may also be possible to prepare compounds the type $(GeF_2)_x \cdot MF_4$ where M is Si, Sn, or Pb. Obviously, M could not be C since lack of available d subshells precludes occupation of an octahedral crystal site. It may also prove possible to prepare compounds of the type $(M'F_2)_x \cdot M''F_4$ where M′ is not Ge; however, for reasons listed elsewhere,[1] this is unlikely.

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(16) M. B. Robin and P. Day, *Advan. Inorg. Chem. Radiochem.*, 10, 248 (1967).

(17) H. Steinfink and J. H. Burns, *Acta Crystallogr.*, 17, 823 (1964).

(18) B. Dickens, *J. Inorg. Nucl. Chem.*, 27, 1509 (1965).

Molybdenocene and Tungstenocene. New "Carbene" Intermediates in Reactions with Hydrogen, Nitrogen, Carbon Monoxide, Olefins, and Acetylenes

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Abstract: The generation and reactions of $(C_5H_5)_2Mo$, $[C_5(CH_3)_5]_2Mo$, and $(C_5H_5)_2W$ are described. Carbon monoxide and N_2 complexes of the above metallocenes as well as dimethyl derivatives of molybdenocene and tungstenocene have been characterized. The role of 14- and 16-electron species in nitrogen reduction reactions is discussed. $(C_5H_5)_2Mo(C_2H_4)$, $(C_5H_5)_2Mo(CH_3CCCH_3)$, $(C_5H_5)_2Mo(CH_2CHCHCH_2)$, $(C_5H_5)_2Mo(CF_3CCCF_3)$, and some similar complexes of tungstenocene have been prepared. Metallocyclopropane and metallocyclopropene structures are proposed for the olefin and acetylene complexes, respectively. Hydrolysis of some of these complexes resulted in reduction of the complexed hydrocarbon. Similarities to nitrogenase are noted. A systematic comparison of the reaction chemistry of $(C_5H_5)_2Mo$ and $(C_5H_5)_2W$ to carbenes was undertaken and revealed an unprecedented parallelism of reactivities and product stabilities.

Interest in the preparation of molybdenocene and tungstenocene resulted from a search for isolatable compounds that would coordinate and lead to reduction of molecular nitrogen. Previous studies with titanocene[1] and other titanium species[2] suggested that such a compound would be coordinatively unsaturated and electron deficient. Molybdenocene and tungstenocene satisfied these conditions. Interest in molybdenocene is especially high since molybdenum is one of the two metals known to be present in the nitrogenase enzyme.[3]

With the exception of group VIII, metallocenes of the second- and third-row transition metals are unknown.[4] Thus, while chromocene is stable and readily prepared,[5] neither molybdenocene nor tungstenocene has ever been synthesized. A very inert bis(pentaphenylcyclopentadienyl)molybdenum(II) has been reported,[6] and a few symmetrically bound olefin and acetylene complexes have been prepared by insertion of the hydrocarbon into $(C_5H_5)_2MoH_2$.[7] Tungstenocene has been postulated as an intermediate in the formation of aryl hydrides and some olefin complexes of that metallocene.[8,9] Recent investigations in these laboratories have led to the generation of molybdenocene as a highly reactive species and

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(1) J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Amer. Chem. Soc.*, 94, 1219 (1972).

(2) E. E. van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Akermark, *ibid.*, 91, 1551 (1969), and references therein.

(3) J. R. Postgate, "The Chemistry and Biochemistry of Nitrogen Fixation," Plenum Press, London, 1971, p 181.

(4) R. B. King, "Transition-Metal Organometallic Chemistry," Academic Press, New York, N. Y., 1969, p 18.

(5) G. Wilkinson, F. A. Cotton, and J. M. Birmingham, *J. Inorg. Nucl. Chem.*, 2, 95 (1956).

(6) W. Hubel and R. Merenyi, *J. Organometal. Chem.*, 2, 213 (1964).

(7) A. Nakamura and S. Otsuka, *J. Amer. Chem. Soc.*, 94, 1886 (1972).

(8) B. R. Francis, M. L. H. Green, and G. G. Roberts, *Chem. Commun.*, 1290 (1971).

(9) M. L. H. Green and P. R. Knowles, *J. Chem. Soc. A*, 1508 (1971).

to the observation that tungstenocene demonstrated similar reactivity.[10]

Results

I. Generation and Reactions of $(C_5H_5)_2Mo$ and $(C_5H_5)_2W$.

In an earlier report on the generation and reactions of molybdenocene,[10] a polymeric species, $[(C_5H_5)_2Mo]_x$, was briefly discussed. The suggested dimeric or polymeric structure containing regular $(h^5\text{-}C_5H_5)_2Mo$ units is supported by recent evidence. The mass spectrum of $[(C_5H_5)_2Mo]_x$ suggests an apparent molecular weight of 460, corresponding to $[(C_5H_5)_2Mo]_2$ (Table I). However, high source temperatures were required for obtaining this spectrum and may have caused decomposition of a higher polymer. The infrared spectrum of $[(C_5H_5)_2Mo]_x$ exhibits no absorptions in the region 2500–1500 cm^{-1} while strong absorptions have been observed in the region 1841–1905 cm^{-1} for a variety of molybdenocene hydride compounds.[7,11] The absence of such a Mo-H unit would preclude a bridging cyclopentadienyl structure similar to that of $(C_{20}H_{20})Nb_2$ or $(C_{20}H_{20})Ta_2$.[12] At room temperature, $[(C_5H_5)_2Mo]_x$ is inert to 200 atm of hydrogen, nitrogen, or carbon monoxide. At elevated temperatures, reaction with hydrogen and carbon monoxide yields products containing regular $(h^5\text{-}C_5H_5)_2Mo$ units.

Table I. Mass Spectrum of $[(C_5H_5)_2Mo]_x$ (Ionizing Voltage 30 eV)

m/e	Rel intensity	Ion
460	31	$(C_{20}H_{20})Mo_2^+$, $(C_{20}H_x)Mo_2^+$
430	5	$(C_{18}H_x)Mo_2^+$
394	7	$(C_{15}H_x)Mo_2^+$
294	16	$(C_8H_x)Mo_2^+$
230	100	$(C_5H_5)_2Mo^+$
204	44	$(C_8H_8)Mo^+$
180–170	11	$(C_6H_x)Mo^+$, $(C_7H_x)Mo^+$
165	3	$(C_5H_5)Mo^+$

$$[(C_5H_5)_2Mo]_x + H_2 \xrightarrow[110°]{200\text{ atm}} (C_5H_5)_2MoH_2 \quad (20\%) \tag{1}$$

$$[(C_5H_5)_2Mo]_x + CO \xrightarrow[110°]{200\text{ atm}} (C_5H_5)_4Mo_3(CO)_5 \quad (95\%) \tag{2}$$

$(C_5H_5)_4Mo_3(CO)_5$ is an orange-yellow solid exhibiting a sharp singlet in its nmr at τ 5.13 and carbonyl absorptions in the infrared region at 1990, 1963, 1900, and 1882 cm^{-1}. The four carbonyl absorptions reflect the low symmetry of this complex, and their position suggests that no bridging carbonyls are present.[13] The structure most consistent with these data is shown in Figure 1. The nmr singlet of $(C_5H_5)_4Mo_3(CO)_5$ may mean that the absorptions of the cyclopentadienyl protons fortuitously coincide.[14] All ions expected for the fragmentation of the molecule depicted in Figure 1 are contained in its mass spectrum (Table II). Treatment of $[(C_5H_5)_2Mo]_x$ with gaseous HCl yields $(C_5H_5)_2MoCl_2$ as the major product.

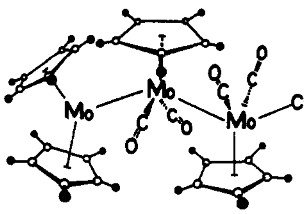

Figure 1. Proposed structure for $(C_5H_5)_4Mo_3(CO)_5$.

Table II. Mass Spectrum of $(C_5H_5)_4Mo_3(CO)_5$ (Ionizing Voltage 30 eV)

m/e	Rel intensity	Ion
700	12	$(C_5H_5)_4Mo_3(CO)_5^+$
451	9	$(C_5H_5)_3Mo_2(CO)_2^+$
442	3	$(C_5H_5)_2Mo_2(CO)_4^+$
414	6	$(C_5H_5)_2Mo_2(CO)_3^+$
386	9	$(C_5H_5)_2Mo_2(CO)_2^+$
358	6	$(C_5H_5)_2Mo_2(CO)^+$
330	36	$(C_5H_5)_2Mo_2^+$
293	57	$(C_5H_5)Mo_2(CO)^+$
249	26	$(C_5H_5)Mo(CO)_3$
230	9	$(C_5H_5)_2Mo^+$
202	100	$(C_8H_x)Mo^+$
165	27	$(C_5H_5)Mo^+$

$$[(C_5H_5)_2Mo]_x + 2HCl \longrightarrow (C_5H_5)_2MoCl_2 + H_2 \tag{3}$$

This reaction as well as reactions 1 and 2 demonstrate the possibility of producing $(h^5\text{-}C_5H_5)_2Mo$ species from $[(C_5H_5)_2Mo]_x$.

Reduction of $(C_5H_5)_2WCl_2$ gives products exactly analogous to those obtained in the reduction of $(C_5H_5)_2MoCl_2$.

$$(C_5H_5)_2WCl_2 + Na/Hg \longrightarrow (C_5H_5)_2W \begin{array}{l} \xrightarrow{9\%} (C_5H_5)_2WH_2 \\ \xrightarrow{35\%} [(C_5H_5)_2W]_x \end{array} \tag{4}$$

The physical and chemical properties and mass spectrum of $[(C_5H_5)_2W]_x$ are very similar to the molybdenum analog (see Table III). Similar reductions carried out in the presence of carbon monoxide yielded bis(cyclopentadienyl)molybdenum(II) monocarbonyl, described in an earlier publication,[10] and the tungsten analog.

Table III. Mass Spectrum of $[(C_5H_5)_2W]_x$

m/e	Rel intensity	Ion
630	100	$(C_{20}H_{20})W_2^+$, $(C_{20}H_x)W_2^+$
602	12	$(C_{18}H_x)W_2^+$
578	6	$(C_{16}H_x)W_2^+$
565	6	$(C_{15}H_x)W_2^+$
552	3	$(C_{14}H_x)W_2^+$
540	2	$(C_{13}H_x)W_2^+$
316	41	$(C_5H_5)_2W^+$
288	16	$(C_8H_x)W^+$
158	2	$(C_5H_5)_2W^{2+}$

$$\begin{array}{l} (C_5H_5)_2MCl_2 + CO + Na/Hg \\ M = Mo\text{ or }W \end{array} \begin{array}{l} \xrightarrow{35\%} (C_5H_5)_2M(CO) \\ \xrightarrow{20\%} [(C_5H_5)_2M]_x \end{array} \tag{5}$$

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(10) J. L. Thomas and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **94**, 1386 (1972).

(11) H. P. Fritz, Y. Hristidu, H. Hummel, and R. Schneider, *Z. Naturforsch. B*, **15**, 419 (1960).

(12) F. N. Tebbe and G. W. Parshall, *J. Amer. Chem. Soc.*, **93**, 3793 (1971).

(13) Cyclopentadienylmolybdenum species with bridging carbonyl groups are currently unknown.

(14) The nmr absorption of a freshly prepared sample of $[(C_5H_5)Mo(CO)_3]_2$ coincides exactly with that of $(C_5H_5)_4Mo_3(CO)_5$.

These monocarbonyls can be produced by using butyllithium as a reducing agent, but yields are diminished.

$$(C_5H_5)_2MCl_2 + CO + LiC_4H_9 \xrightarrow{14\%} (C_5H_5)_2M(CO) \qquad (6)$$
$$M = Mo \text{ or } W$$

Treatment of $(C_5H_5)_2MH_2$ or $[(C_5H_5)_2M]_x$ with carbon monoxide does not generate the above monocarbonyls. Bis(cyclopentadienyl)tungsten(II) monocarbonyl exhibits a single sharp absorption in the infrared spectrum at 1864 cm^{-1} and a sharp singlet in its nmr spectrum at τ 5.63. Mass spectra are given in Table IV.

Table IV. Mass Spectrum of $(C_5H_5)_2Mo(CO)$ and $(C_5H_5)_2W(CO)$

m/e	Rel intensity	Ion	*m/e*	Rel intensity	Ion
258	25	$(C_5H_5)_2Mo(CO)^+$	344	16	$(C_5H_5)_2W(CO)^+$
230	100	$(C_5H_5)_2Mo^+$	316	100	$(C_5H_5)_2W^+$
204	31	$(C_8H_8)Mo^+$	290	30	$(C_8H_8)W^+$
202	30	$(C_8H_6)Mo^+$	260	13	$(C_6H_x)W^+$
178	11	$(C_6H_6)Mo^+$	251	3	$(C_5H_5)W^+$
165	2	$(C_5H_5)Mo^+$	158	6	$(C_5H_5)_2W^{2+}$
115	10	$(C_5H_5)_2Mo^{2+}$			

One of the most interesting reactions of the proposed $(C_5H_5)_2Mo$ intermediate is its coordination to molecular nitrogen. If the sodium amalgam reduction of $(C_5H_5)_2MoCl_2$ is carried out under a high pressure of nitrogen, a nitrogen-containing complex is obtained that yields approximately 1 equiv of nitrogen per equivalent of molybdenum upon pumping under high vacuum at room temperature.

$$(C_5H_5)_2MoCl_2 + N_2 + Na/Hg \xrightarrow{350 \text{ atm}} [(C_5H_5)_2MoN_2]_x \qquad (7)$$

This complex is thermally very unstable, readily liberating nitrogen at room temperature and atmospheric pressure. While repeated experiments and comparison with blanks demonstrated conclusively that nitrogen was being coordinated in the molybdenocene system, the thermal instability frustrated all attempts to characterize this complex instrumentally. The structure of the compound is unknown at this time. It is important to note that acid hydrolysis of this nitrogen complex yielded no ammonia. Thus, while molybdenocene, a 16-electron species, does coordinate nitrogen, it apparently does not provide conditions sufficient for reduction of the nitrogen molecule. Similar nitrogen complexes of tungstenocene were generated, but no increased stability was noted, and chemical and physical behavior was essentially identical with that of the molybdenocene–nitrogen complex.

Synthesis of $(C_5H_5)_2Mo(CH_3)_2$ and $(C_5H_5)_2W(CH_3)_2$ was undertaken in the hope that these alkyl species would be thermally unstable and provide a method of isolating $(C_5H_5)_2Mo$ or $(C_5H_5)_2W$ as was possible for titanocene.[1] Treatment of $(C_5H_5)_2MoCl_2$ with stoichiometric amounts or large excesses of methyllithium at −78° in ether gave no products which could be identified as $(C_5H_5)_2Mo(CH_3)_2$. Upon warming to room temperature and removing the solvent, a yellow-brown, pyrophoric, involatile solid was obtained. When $(C_5H_5)_2MoCl_2$ or $(C_5H_5)_2WCl_2$ was treated with dimethylzinc, orange-red $(C_5H_5)_2Mo(CH_3)_2$ and yellow $(C_5H_5)_2W(CH_3)_2$ were obtained.

$$(C_5H_5)_2MCl_2 + Zn(CH_3)_2 \xrightarrow{0^\circ} (C_5H_5)_2M(CH_3)_2 \qquad (8)$$
$$M = Mo \text{ or } W$$

These compounds are very stable, sublimable solids which have only moderate sensitivity to the atmosphere. $(C_5H_5)_2Mo(CH_3)_2$ exhibits two sharp singlets in its nmr spectrum at τ 5.93 and 9.78 for the cyclopentadienyl and methyl peaks, respectively. The peaks integrate 10:5.6. $(C_5H_5)_2W(CH_3)_2$ has a similar spectrum with sharp singlets at τ 5.80 and 9.63 which integrate 10:5.8. The mass spectrum of $(C_5H_5)_2Mo(CH_3)_2$ is given in Table V.

Table V. Mass Spectrum of $(C_5H_5)_2Mo(CH_3)_2$

m/e	Rel intensity	Ion
260	44	$(C_5H_5)_2Mo(CH_3)_2^+$
245	58	$(C_5H_5)_2Mo(CH_3)^+$
243	13	$(C_5H_5)_2MoCH^+$
230	100	$(C_5H_5)_2Mo^+$
204	15	$(C_5H_5)_2Mo^+ - [C_2H_2]$
202	10	$(C_5H_5)_2Mo^+ - [C_2H_4]$
178	13	$(C_5H_5)MoCH^+$
165	10	$(C_5H_5)Mo^+$
121.5	10	$(C_5H_5)MoCH^{2+}$
115	10	$(C_5H_5)_2Mo^{2+}$
100	12	Mo^+

The observation of an abundant parent ion in $(C_5H_5)_2Mo(CH_3)_2$ is in sharp contrast to the total lack of such a peak in the mass spectrum of $(C_5H_5)_2Ti(CH_3)_2$.[15] This suggests a considerably decreased lability of the methyl groups as compared to the titanium analog.

$(C_5H_5)_2Mo(CH_3)_2$ and $(C_5H_5)_2W(CH_3)_2$ exhibit exceptional thermal stability for metal dialkyls. $(C_5H_5)_2Mo(CH_3)_2$ survives heating to 150° for 24 hr with no change in the nmr spectrum. This is in contrast to $(C_5H_5)_2Ti(CH_3)_2$ which readily decomposes at room temperature.[16] To date, no method of selective reduction or decomposition of these compounds to the free metallocene has been successful.

II. Preparation and Reactions of Transient Bis(pentamethylcyclopentadienyl)molybdenum(II) and Its Stable Dimer. In an attempt to stabilize and more adequately characterize the molybdenocene system, bis(pentamethylcyclopentadienyl)dihydridomolybdenum(IV) was prepared by the reduction of molybdenum pentachloride with sodium pentamethylcyclopentadienide and sodium borohydride.

$$MoCl_5 + 3NaC_5(CH_3)_5 + 2NaBH_4 \xrightarrow{37\%}$$
$$[C_5(CH_3)_5]_2MoH_2 + 5NaCl + C_5(CH_3)_5 + B_2H_6 \qquad (9)$$

The orange product exhibited a strong infrared absorption at 1857 cm^{-1} which is slightly higher than the hydride stretch of $(C_5H_5)_2MoH_2$ at 1847 cm^{-1}.[11] The nmr spectrum of $[C_5(CH_3)_5]_2MoH_2$ contained two singlets at τ 7.93 and 18.18 which integrated 15.1:1. The absorption at τ 18.18 is characteristic of hydride ligands coordinated to molybdenum[7] and is near the literature

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(15) J. E. Bercaw and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **92**, 6182 (1970).

(16) K. Clauss and H. Bestian, *Justus Liebigs Ann. Chem.*, **654**, 8 (1962).

value of τ 18.76 for $(C_5H_5)_2MoH_2$.[17] The air-sensitive dihydride was converted to air-stable bis(pentamethylcyclopentadienyl)dichloromolybdenum(IV) by treatment with chloroform.

$$[C_5(CH_3)_5]_2MoH_2 + 2CHCl_3 \longrightarrow [C_5(CH_3)_5]_2MoCl_2 + 2CH_2Cl_2 \quad (10)$$

A sodium amalgam reduction of the above dichloride was carried out under argon and a bright yellow compound, $[[C_5(CH_3)_5]_2Mo]_2$, resulted.

$$2[C_5(CH_3)_5]_2MoCl_2 + 4Na/Hg \xrightarrow{90\%} [[C_5(CH_3)_5]_2Mo]_2 + 4NaCl \quad (11)$$

This compound is quite stable thermally, its nmr spectrum being unchanged after heating at 100° for 7 hr. $[[C_5(CH_3)_5]_2Mo]_2$ is much more soluble than $[(C_5H_5)_2Mo]_x$ in aliphatic and aromatic solvents. This property particularly facilitated the determination of the structure and chemistry of the pentamethyl-substituted dimer. The sodium amalgam reduction of $[C_5(CH_3)_5]_2MoCl_2$ yields one product, nearly quantitatively, in contrast to $(C_5H_5)_2MoCl_2$. Freezing point depressions of a 0.41 *m* solution of $[[C_5(CH_3)_5]_2Mo]_2$ in benzene gave an apparent molecular weight of 740 ± 40; 732 is the calculated molecular weight of the dimer.

Formulation of $[[C_5(CH_3)_5]_2Mo]_2$ as a sterically crowded molybdenum–molybdenum bonded dimer is consistent with its nmr spectrum (Figure 2). Bis(pentamethylcyclopentadienyl)molybdenum(II) dimer is not in equilibrium with any monomeric species observable from −200 to +200 ppm, and absorptions attributable to hydridic protons were not found. The infrared spectrum contained no molybdenum–hydride stretch, discounting the possibility of any hydride ligands being present.

There is a similarity between the mass spectrum of $[[C_5(CH_3)_5]_2Mo]_2$ and that of $[(C_5H_5)_2Mo]_x$ (Table VI) except for the total absence of dimer peaks in pentamethyl-substituted compounds. More striking is the similarity of the mass spectrum of $[C_5(CH_3)_5]_2Ti$ dimer[1] to that of $[[C_5(CH_3)_5]_2Mo]_2$. The titanium derivative shows no dimer peaks, even though it too was shown to be dimeric in solution. The absence of dimer peaks in $[[C_5(CH_3)_5]_2Mo]_2$ and the titanium analog suggests that the metal–metal bonds are weak and very readily cleaved in the source of the mass spectrometer.

Table VI. Mass Spectra of $[[C_5(CH_3)_5]_2Mo]_2$

m/e	Rel intensity	Ion
370	100	$[C_5(CH_3)_5]_2Mo^+$
369	100	$[C_5(CH_3)_5]_2Mo^+ - [H]$
368	40	$[C_5(CH_3)_5]_2Mo^+ - [H_2]$
355–351	12	$(C_{19}H_x)Mo^+$
185	12	$[C_5(CH_3)_5]_2Mo^{2+}$
136	9	$C_{10}H_{16}^+$
135	6	$C_{10}H_{15}^+$
134	6	$C_{10}H_{14}^+$

Support for the proposed dimer structure of $[[C_5(CH_3)_5]_2Mo]_2$ was obtained by chemically cleaving the molybdenum–molybdenum bond to yield various derivatives of $[C_5(CH_3)_5]_2Mo^{II}$. When $[[C_5(CH_3)_5]_2Mo]_2$ was treated with hydrogen at atmospheric pressure, a 3% yield of $[C_5(CH_3)_5]_2MoH_2$ was obtained. When the pressure of hydrogen was increased to 200 atm, an 85% yield of the dihydride was obtained.

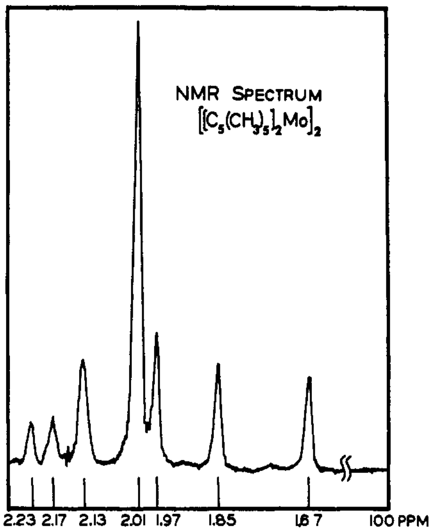

Figure 2. Nmr spectrum of $[[C_5(CH_3)_5]_2Mo]_2$ at 30°.

$$[[C_5(CH_3)_5]_2Mo]_2 + 2H_2 \begin{array}{c} \xrightarrow[3\%]{1\ atm} \\ \xrightarrow[85\%]{200\ atm} \end{array} 2[C_5(CH_3)_5]_2MoH_2 \quad (12)$$

This is in contrast to the results of an analogous treatment of $[(C_5H_5)_2Mo]_x$ with hydrogen which yielded no $(C_5H_5)_2MoH_2$. Further evidence for the facile molybdenum–molybdenum bond cleavage of $[[C_5(CH_3)_5]_2Mo]_2$ was obtained when this compound was treated with carbon monoxide at a pressure of 1 atm. In contrast to $[(C_5H_5)_2Mo]_x$, $[[C_5(CH_3)_5]_2Mo]_2$ gave the monocarbonyl in high yield.

$$[[C_5(CH_3)_5]_2Mo]_2 + 2CO \xrightarrow{68\%} 2[C_5(CH_3)_5]_2Mo(CO) \quad (13)$$

Bis(pentamethylcyclopentadienyl)molybdenum(II) monocarbonyl was isolated as a volatile, bright green sublimate of extreme solubility in common organic solvents. This compound exhibits a strong, sharp infrared absorption at 1868 cm^{-1}. The lower frequency of this carbonyl absorption as compared to the carbonyl absorption in $(C_5H_5)_2Mo(CO)$ reflects the increased electron-donating capability of molybdenum in the former case. $[C_5(CH_3)_5]_2Mo(CO)$ is characterized by a sharp singlet in its nmr spectrum at τ 8.06. The mass spectrum of $[C_5(CH_3)_5]_2Mo(CO)$ is very similar to that of $(C_5H_5)_2Mo(CO)$, and the methyl-substituted derivative shows the same tendency to fragment with loss of carbon monoxide in preference to loss of one of the pentamethylcyclopentadienyl rings (Table VII).

In an attempt to obtain a more stable nitrogen complex than was possible in the unsubstituted system, $[C_5(CH_3)_5]_2MoCl_2$ was reduced in the presence of nitrogen.

$$[C_5(CH_3)_5]_2MoCl_2 + Na/Hg + N_2 \xrightarrow{350\ atm} [[C_5(CH_3)_5]_2MoN_2] \quad (14)$$

This complex showed no increased stability over that obtained with the unsubstituted system. In an attempt to produce the same product by treatment of [[C5-

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[17] M. L. H. Green, J. McCleaverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4854 (1961).

Table VII. Mass Spectrum of $[C_5(CH_3)_5]_2Mo(CO)$

m/e	Rel intensity	Ion
398	29	$[C_5(CH_3)_5]_2Mo(CO)^+$
370	100	$[C_5(CH_3)_5]_2Mo^+$
355-349	11	$(C_{19}H_x)Mo^+$
185	9	$[C_5(CH_3)_5]_2Mo^{2+}$
137	43	$C_{10}H_{17}^+$
136	43	$C_{10}H_{16}^+$
135	34	$C_{10}H_{15}^+$

$(CH_3)_5]_2Mo]_2$ with nitrogen, the dimer was placed in an autoclave and stirred under 250 atm of nitrogen.

$$[[C_5(CH_3)_5]_2Mo]_2 + N_2 \xrightarrow[\text{toluene}]{250\text{ atm}} [[C_5(CH_3)_5]_2MoN_2] \quad (15)$$

Similar results were obtained when the dry powdered dimer was treated with nitrogen.

$$[[C_5(CH_3)_5]_2Mo]_2 + N_2 \underset{\text{vacuum}}{\overset{250\text{ atm}}{\rightleftharpoons}} [[C_5(CH_3)_5]_2MoN_2] \quad (16)$$

This equilibrium is reversible and may be performed repeatedly. Although the solid nitrogen product obtained is somewhat more stable than its solutions, the complex is still very fragile thermally. Its stability remains comparable to that of the nitrogen complex in the unsubstituted system, and adequate instrumental characterization, particularly determination of the infrared spectrum, was unsuccessful.

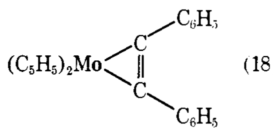
Treatment of $[[C_5(CH_3)_5]_2MoN_2]$ with excess carbon monoxide resulted in the expected evolution of nitrogen and consumption of carbon monoxide (eq 17); 0.75 equiv of nitrogen was released per equivalent of carbon monoxide taken up. The slightly low result is probably due to incomplete conversion of $[[C_5(CH_3)_5]_2Mo]_2$ to $[[C_5(CH_3)_5]_2MoN_2]$. $[[C_5(CH_3)_5]_2MoN_2]$ yields no ammonia when hydrolyzed.

$$[[C_5(CH_3)_5]_2MoN_2] + CO \longrightarrow [C_5(CH_3)_5]_2Mo(CO) + N_2 \quad (17)$$

III. Preparation of Alkene and Alkyne Complexes of Molybdenocene and Tungstenocene and Reduction of the Complexed Hydrocarbon. While molybdenocene and tungstenocene form only marginally stable nitrogen complexes and do not provide conditions sufficient for the reduction of nitrogen, it was hoped that olefin or acetylene complexes might be more stable and amenable to isolation and study. The preparation of a diphenylacetylene complex of molybdenocene had been reported[18] and acetylene complexes of molybdenum and tungsten containing no cyclopentadienyl groups were known.[19-21]

The diphenylacetylene complex was now prepared by reduction of molybdenocene dichloride in the presence of the olefin (eq 18). The red complex was characterized by a strong infrared absorption at 1771 cm^{-1}, attributed to the C≡C stretch. This absorption occurs 451 cm^{-1} below that of the parent acetylene. Data reported in other literature[7] agreed well with the above values.

$$(C_5H_5)_2MoCl_2 + Na/Hg + C_6H_5CCC_6H_5 \longrightarrow$$

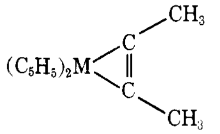


(18)

Two new complexes were synthesized by a similar reaction (eq 19). Generation of copious amounts of the dihydride was evident in both cases. Nmr spectroscopy showed the sublimable products were a 50:50 mixture of the dihydride and 2-butyne complex of molybdenocene and a 70:30 mixture of the dihydride and 2-butyne complex of tungstenocene. The mechanism for this production of dihydride will be discussed below. Increased production of tungstenocene dihydride over that of molybdenocene dihydride suggests that with respect to hydride abstraction, tungstenocene is a more reactive species. This observation agrees with earlier results in which simple reductions of the respective dichlorides in tetrahydrofuran yielded much more tungstenocene dihydride than molybdenocene dihydride.

$$(C_5H_5)_2MCl_2 + Na/Hg + CH_3CCCH_3 \longrightarrow$$

M = Mo or W



(19)

The 2-butyne complexes of molybdenocene and tungstenocene are orange and tan solids, respectively, and are readily sublimable. $(C_5H_5)_2Mo(CH_3CCCH_3)$ exhibits absorptions at τ 5.55 and 7.42 in its nmr spectrum which integrate 10:5.9, respectively. $(C_5H_5)_2W(CH_3CCCH_3)$ has a very similar spectrum with absorptions at τ 5.67 and 7.53 which integrate 10:6.4. The mass spectra of these compounds are given in Table VIII. $(C_5H_5)_2Mo(CH_3CCCH_3)$ exhibits a medium intensity absorption at 1830 cm^{-1} and $(C_5H_5)_2W(CH_3CCCH_3)$ exhibits a weak infrared absorption at about 1750 cm^{-1}, which are attributed to the C≡C stretch. These are reductions of approximately 483 and 563 cm^{-1} from the parent acetylene. This very substantial reduction of stretching frequency is comparable to those reported for various platinum(0), palladium(0), and nickel(0) compounds.[22,23] It suggests a considerable thermodynamic stability of the complexes and a large decrease in the bond order of the acetylene.

The above acetylene compounds could have resulted from insertion of the acetylene into the dihydride coproduced in the reduction of $(C_5H_5)_2MoCl_2$. To clearly demonstrate that the acetylene compounds were produced by direct reaction of the acetylene with the free metallocene, the synthesis of $(C_5H_5)_2Mo(CF_3CCCF_3)$ was undertaken. Nakamura and Otsuka[7] attempted preparation of this compound by reaction of molybdenocene dihydride with the free acetylene. However, they were only able to isolate a very stable hydrido-σ-alkenyl complex, $(C_5H_5)_2Mo(H)[C(CF_3){=}CHCF_3]$. In contrast, the sodium amalgam reduction of $(C_5H_5)_2MoCl_2$ in the presence of CF_3CCCF_3 yielded $(C_5H_5)_2Mo(CF_3CCCF_3)$ (eq 20). This orange complex exhibited a single sharp ^1H nmr absorption at τ 5.50 with no other peaks observable from −100 to +100 ppm. The ^{19}F

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[18] S. Otsuka, A. Nakamura, and H. Minamida, *Chem. Commun.*, 1148 (1969).

[19] R. B. King, *J. Organometal. Chem.*, **8**, 139 (1967).

[20] R. B. King, *Inorg. Chem.*, 7, 1044 (1968).

[21] D. P. Tate, J. Augl, W. Ritchey, B. Ross, and J. Grasselli, *J. Amer. Chem. Soc.*, **86**, 3261 (1964).

[22] J. H. Nelson, H. B. Jonassen, and D. M. Roundhill, *Inorg. Chem.*, **8**, 2591 (1969).

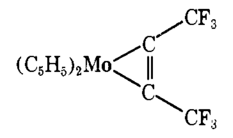
[23] E. O. Graves, C. J. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968).

Table VIII. Mass Spectra of $(C_5H_5)_2Mo(CH_3CCCH_3)$ and $(C_5H_5)_2W(CH_3CCCH_3)$[a]

m/e	Rel intensity	Ion	*m/e*	Rel intensity	Ion
284	10	$(C_5H_5)_2Mo(CH_3CCCH_3)^+$	370	26	$(C_5H_5)_2W(CH_3CCCH_3)^+$
230	100	$(C_5H_5)_2Mo^+$	315	100	$(C_5H_5)_2W^+$
202	10	$(C_5H_5)_2Mo^+ - [C_2H_4]$	290	13	$(C_5H_5)_2W^+ - [C_2H_4]$
115	1	$(C_5H_5)_2Mo^{2+}$	262	4	$(C_6H_4)W^+$
			158	2	$(C_5H_5)_2W^{2+}$

[a] Traces of $(C_5H_5)_2MoH_2$ and $(C_5H_5)_2WH_2$ were observed in these spectra and the associated peaks deleted from the reported spectrum.

$(C_5H_5)_2MoCl_2$ + Na/Hg + CF_3CCCF_3 ⟶



(20)

nmr showed a sharp single absorption 19.1 ppm downfield from trifluoroacetic acid. $(C_5H_5)_2Mo(CF_3CCCF_3)$ exhibited a strong infrared absorption at 1782 cm^{-1}, a reduction of 518 cm^{-1} in the C≡C stretch. This is among the largest reductions of the acetylene C≡C stretch known.[23] The mass spectrum, shown in Table IX, confirms the molecular weight of this complex.

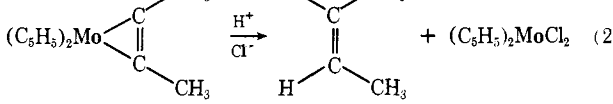
Table IX. Mass Spectrum of $(C_5H_5)_2Mo(CF_3CCCF_3)$

m/e	Rel intensity	Ion
392	48	$(C_5H_5)_2Mo(CF_3CCCF_3)^+$
230	100	$(C_5H_5)_2Mo^+$
202	13	$(C_8H_6)Mo^+$
184	9	$(C_5H_5)MoF^+$
178	11	$(C_6H_6)Mo^+$

The total lack of $(C_5H_5)_2MoH_2$ production in the preparation of $(C_5H_5)_2Mo(CF_3CCCF_3)$ contrasts with its excessive generation in the preparation of $(C_5H_5)_2Mo(CH_3CCCH_3)$. This result implies that dihydride production in the preparation of $(C_5H_5)_2Mo(CH_3CCCH_3)$ is due to the presence of relatively acidic protons in 2-butyne. Absence of such protons in hexafluoro-2-butyne precluded the possibility of $(C_5H_5)_2MoH_2$ production.[24]

The ability of any system to reduce acetylenes to alkenes is of great interest as either a possible model for the enzyme nitrogenase or for further elucidation of metal induced reductions of unsaturated hydrocarbons. In terms of a nitrogenase model, interest is even more acute when a molybdenum metal site is involved since molybdenum is one of the two metals known to be present in the protein *Azotobacter vinelandii* nitrogenase.[25] Accordingly, the hydrolysis of $(C_5H_5)_2Mo(CH_3CCCH_3)$ was investigated.

$(C_5H_5)_2Mo(CH_3CCCH_3)$ was inert to pure water, but addition of HCl caused vigorous reaction and gas evolution. After destroying any excess HCl, the remaining gases were passed through a −78° trap and into a gas infrared cell. The product was identified by infrared spectroscopy as pure *cis*-2-butene (eq 21). This result is similar to that obtained by Mann, *et al.*, for the protonation of $Pt(acetylene)(PPh_3)_2$[26] complexes which also gave pure cis olefins, in contradiction to some earlier work by Tripathy and Roundhill.[27] Some fluoroacetylene complexes of platinum also yield cis olefins upon protonation.[28] Perhaps the closest inorganic analog to nitrogenase is the recently reported molybdenum-thiol system.[29] Here, the olefinic reduction products of 2-butyne were essentially pure *cis*-2-butene. All of these products parallel those obtained in the biological reduction of acetylene to pure ethylene of cis form as reported by Schollhorn and Burris[30] and by Dilworth.[31]



(21)

Although none of the above systems reduce alkenes to alkanes, it seemed reasonable to both investigate the possibility of formation of olefin complexes with molybdenocene and tungstenocene and to determine whether reduction of the complexed olefin would occur upon hydrolysis. A small number of olefin complexes of $(C_5H_5)_2Mo$ had been previously prepared by insertion of the olefin into $(C_5H_5)_2MoH_2$.[7] However, formation of such complexes was possible *only* if the olefin contained strongly electron-attracting groups. Ethylene complexes of molybdenocene and tungstenocene were now prepared by sodium amalgam reduction of the respective dichlorides under a high pressure of ethylene.

$$(C_5H_5)_2MCl_2 + Na/Hg + C_2H_4 \xrightarrow{150\ atm} (C_5H_5)_2M(C_2H_4) \qquad (22)$$

M = Mo or W

$(C_5H_5)_2Mo(C_2H_4)$ and $(C_5H_5)_2W(C_2H_4)$ may also be prepared by carrying out reaction 22 in the presence of 1 atm of ethylene, but the yields are low. The ethylene complex fails to react with carbon monoxide, but is readily attacked by chloroform to yield green molybdenocene dichloride and black tars.

$$(C_5H_5)_2Mo(C_2H_4) + 2CHCl_3 \longrightarrow (C_5H_5)_2MoCl_2 + \text{tar} \qquad (23)$$

$(C_5H_5)_2MoCl_2$ production was nearly quantitative and was identified by its X-ray powder pattern. The ethylene complexes are very stable thermally and possess sufficient vapor pressure to easily determine their mass spectra (Table X). $(C_2H_5)_2Mo(C_2H_4)$ exhibits absorptions at τ 5.90 and 8.52 which integrate 10:3.9.

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(24) Sodium amalgam reduction of $(C_5H_5)_2MoCl_2$ in tetrahydrofuran generates small amounts of $(C_5H_5)_2MoH_2$. Presumably, the slightly acidic α proton is readily abstracted.

(25) R. C. Burns, R. D. Holsten, and R. W. F. Hardy, *Biochem. Biophys. Res. Commun.*, **39**, 90 (1970).

(26) B. E. Mann, B. L. Shaw, and N. I. Tucker, *Chem. Commun.*, 1333 (1970).

(27) P. B. Tripathy and D. M. Roundhill, *J. Amer. Chem. Soc.*, **92**, 3825 (1970).

(28) D. M. Burley, R. D. W. Kimmitt, and G. W. Littlecott, *Chem. Commun.*, 613 (1969).

(29) G. N. Schrauzer and P. A. Doemeny, *J. Amer. Chem. Soc.*, **93**, 1608 (1971).

(30) R. Schollhorn and R. G. Burris, *Fed. Proc., Fed. Amer. Soc. Exp.*, **25**, 710 (1966).

(31) M. J. Dilworth, *Biochim. Biophys. Acta*, **127**, 285 (1966).

Table X. Mass Spectra of $(C_5H_5)_2Mo(C_2H_4)$ and $(C_5H_5)_2W(C_2H_4)$

m/e	Rel intensity	Ion	*m/e*	Rel intensity	Ion
258	18	$(C_5H_5)_2Mo(C_2H_4)^+$	344	5	$(C_5H_5)_2W(C_2H_4)^+$
230	100	$(C_5H_5)_2Mo^+$	332	2	$(C_5H_5)_2WCH_4^+$
204	14	$(C_5H_5)_2Mo^+ - [C_2H_2]$	316	100	$(C_5H_5)_2W^+$
202	18	$(C_5H_5)_2Mo^+ - [C_2H_4]$	290	14	$(C_8H_8)W^+$
178	7	$(C_6H_6)Mo^+$	262	5	$(C_6H_x)W^+$
165	4	$(C_5H_5)Mo^+$	158	3	$(C_5H_5)_2W^{2+}$
115	7	$(C_5H_5)_2Mo^{2+}$			
100	7	Mo^+			

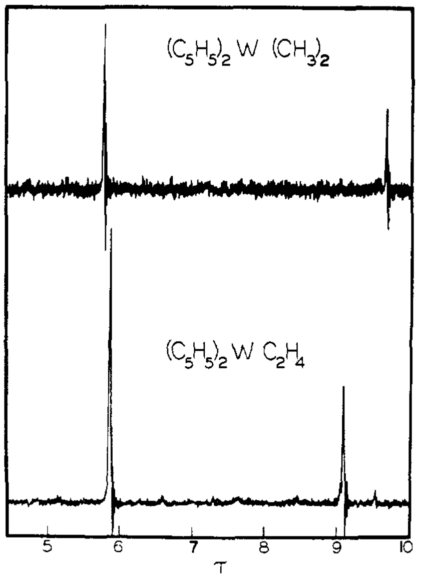

Figure 3. Nmr of $(C_5H_5)_2W(C_2H_4)$ and $(C_5H_5)_2W(CH_3)$.

$(C_5H_5)_2W(C_2H_4)$ show similar absorptions at τ 5.87 and 9.07 which integrate 10:4.2. The higher field absorption of the ethylene ligand in $(C_5H_5)_2W(C_2H_4)$ is consistent with W(II) being more reducing than Mo(II). Perhaps the most striking feature of the nmr data is the close proximity of the CH_2 protons in the ethylene complexes to those of the methyl protons in the corresponding dimethyl metallocene. This is particularly notable for the tungstenocene complexes, shown in Figure 3, where the methyl protons of $(C_5H_5)_2W(CH_3)_2$ absorb at τ 9.63, only 0.56 ppm upfield from the CH_2 protons in $(C_5H_5)_2W(C_2H_4)$. The implication is that the methyl and ethylene protons exist in a similar environment and that the metal–carbon bond in the ethylene complex could be accurately described as one of σ character. This suggests that the complex should be described as a metallocyclopropane. Production of such metallocycles is analogous to the generation of cyclopropane from ethylene and methylene.[32] This observation is consistent with our previous assertions that molybdenocene and tungstenocene resemble carbenes in their reaction chemistry.[10]

A particularly noteworthy reaction of $(C_5H_5)_2Mo(C_2H_4)$ was the reduction of coordinated ethylene to ethane observed upon hydrolysis.

$$(C_5H_5)_2Mo(C_2H_4) \xrightarrow{H^+} C_2H_6 + (C_5H_5)_2MoCl_2 \qquad (24)$$

Considerable importance is attached to this reaction

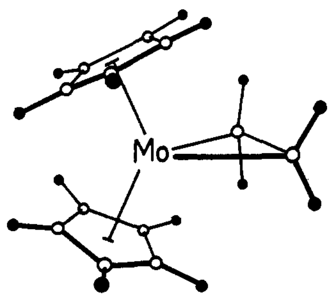

Figure 4. Proposed structure of $(C_5H_5)_2Mo(C_2H_4)$.

since only a very few reported complexes[12,33,34] permit the reduction of ethylene to ethane under ambient conditions. The acid hydrolysis of $(C_5H_5)_2Mo(C_2H_4)$ to yield ethane further supports the characterization of this compound as a metallocyclopropane since such behavior is very characteristic of σ-bound alkyl groups.[35] The lack of an identifiable C=C stretch in the infrared spectrum of $(C_5H_5)_2Mo(C_2H_4)$ (Figure 4) is consistent with the ethylene molecule being essentially σ bound to the metal forming a metallocyclopropane ring. A similar structure has been suggested for $(PPh_3)Pt(CF_3CFCFCF_3)$[36] on this basis. Support for analogous metallocyclopropane structures has been obtained from ^{19}F nmr studies of $(PPh_3)Pt(CF_2CFCF_3)$[37] and $(PPh_3)Pt(C_2F_4)$.[38] Further evidence for the proposed metallocyclopropane structures resulted from the preparation and examination of a 1,3-butadiene complex of molybdenocene.

$$(C_5H_5)_2MoCl_2 + Na/Hg + CH_2CHCHCH_2 \longrightarrow (C_5H_5)_2Mo(CH_2CHCHCH_2) \qquad (25)$$

The resulting dark orange sublimate yielded the mass spectrum shown in Table XI. Figure 5 shows the nmr spectrum of $(C_5H_5)_2Mo(CH_2CHCHCH_2)$ with a sharp doublet at τ 5.92 and 5.95 and other complex and overlapping multiplets at τ 3.9, 5.1, 6.4, 7.1, and 8.3. Integration showed the ratio of the doublet to all other absorptions combined was 10:6.5. Such a spectrum could be expected only for a 1,2-addition of molybdenocene to 1,3-butadiene. If the butadiene ligand is rigidly bound to the molybdenum center, cyclopenta-

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(32) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, pp 16–34.

(33) L. Vaska and R. E. Rhodes, *J. Amer. Chem. Soc.*, 87, 4970 (1965).

(34) F. Unguary, B. Babos, and L. Marko, *J. Organometal. Chem.*, 8, 329 (1967), and references therein.

(35) G. E. Coats, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. 2, Methuen, London, 1968, p 225.

(36) D. M. Roundhill and G. Wilkinson, *J. Chem. Soc. A*, 506 (1968).

(37) M. Green, R. Osborn, A. Rest, and F. G. A. Stone, *Chem. Commun.*, 502 (1966).

(38) M. Green, R. Osborn, A. Rest, and F. G. A. Stone, *J. Chem. Soc. A*, 2525 (1968).

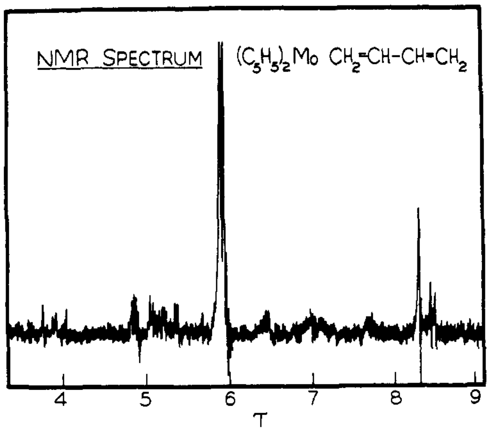

Figure 5.

Table XI. Mass Spectrum of $(C_5H_5)_2Mo(CH_2CHCHCH_2)$

m/e	Rel intensity	Ion
284	22	$(C_5H_5)_2Mo(C_4H_6)^+$
283	20	$(C_5H_5)_2Mo(C_4H_6)^+$
230	100	$(C_5H_5)_2Mo^+$
204	13	$(C_5H_5)_2Mo^+ - [C_2H_2]$
202	13	$(C_5H_5)_2Mo^+ - [C_2H_4]$

dienyl groups become magnetically inequivalent, yielding a doublet, and all the hydrogens on butadiene become magnetically inequivalent, yielding complex patterns spanning the normal nmr region. At temperatures up to 110°, the ^1H nmr spectrum of $(C_5H_5)_2Mo(CH_2CHCHCH_2)$ remains unchanged, suggesting the olefin is rigidly bound.

The significance of the confirmed 1,2-addition of 1,3-butadiene should be noted. It is well known that carbenes react nearly exclusively with this olefin by a 1,2-addition.[32] Methylene, for instance, adds to give vinylcyclopropane. Molybdenocene is the only inorganic species that reacts similarly. Thus, a 1,2-addition by molybdenocene to yield a metallovinylcyclopropane provides a strong argument for characterizing molybdenocene, and by analogy tungstenocene, as "carbenes." Based on the above evidence and by analogy to the ethylene complexes, the structure shown in Figure 6 is proposed for the butadiene complex.

Discussion

The inability of molybdenocene or tungstenocene to provide conditions suitable for the reduction of nitrogen was not totally unexpected. To date, the only isolatable metallocene nitrogen complexes that can be subsequently reduced to ammonia are titanocene derivatives.[1] While molybdenocene and tungstenocene resemble titanocene in many aspects, having metallocene structures as well as being coordinatively unsaturated and electron deficient, there are important and apparently crucial differences. Titanocene has *two* vacant coordination sites and thus requires four electrons to complete its valence shell. Molybdenocene and tungstenocene, being 16-electron species, have only one vacant coordination site each. Moreover, of all the nitrogen complexes of 16-electron species known, none promote reduction of nitrogen. Considering all the similarities of the group VI metallocenes and titanocene, an essential requirement for reduction of nitrogen in metallocenes seems to be two vacant coordination sites which would allow the edge-on coordination of nitrogen suggested by Bercaw, *et al.*[1]

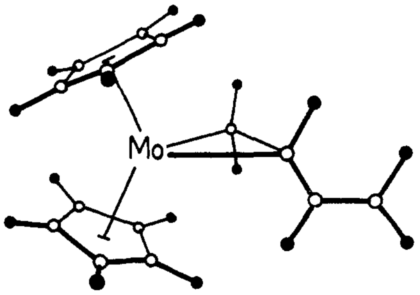

Figure 6. Proposed structure for $(C_5H_5)_2Mo(CH_2CHCHCH_2)$.

The parallelism of the structures of the acetylene and olefin complexes of molybdenocene and tungstenocene with those of cyclopropenes and cyclopropanes is a very important facet of the chemistry of these reactive compounds. Preparation of pure cis olefins by the hydrolysis of these metallocyclopropenes is potentially a useful reaction. The formation of metallocyclopropenes seems to be a general reaction and affords a simple route to a large variety of cis olefins.

Comparison of the olefin and acetylene complexes of molybdenocene and tungstenocene to similar complexes of other metals reveals several unique features of the group VI complexes. Molybdenocene and tungstenocene are the only metallocenes reported to form stable complexes with both olefins and acetylenes. Except for the recently reported $(C_5H_5)_2Nb(H)(C_2H_4)$,[12] these compounds are the only monoolefin and monoacetylene adducts sufficiently stable and volatile to allow purification by vacuum sublimation. On the basis of the decrease of $\nu(C{\equiv}C)$ in the infrared region, Mo(II) is about as reducing as Pt(0), Pd(0), or Ni(0).[22,23] Molybdenocene complexes of nonfluorinated acetylenes yield $\Delta\nu(C{\equiv}C)$ of 451–483 cm^{-1}, and the hexafluoro-2-butyne complex of molybdenocene yields a $\Delta\nu(C{\equiv}C)$ of 518 cm^{-1}. These values lie at the high end of a $\Delta\nu(C{\equiv}C)$ range of 397–478 cm^{-1} for nonfluorinated acetylene complexes of Pt(0), Pd(0), and Ni(0) and a range of 475–542 cm^{-1} for hexafluoro-2-butyne complexes of the same metals.[22,23] Only platinum has yielded complexes of both olefins and acetylenes suitable for X-ray crystallographic studies.[39,40] Similar, very stable complexes of molybdenocene crystallize easily from solution and may provide more accurate data since the metal center in the molybdenum complexes is much lighter than that in the platinum analogs and thus may allow a more accurate determination of the metal–carbon and nearby carbon–carbon distances.

The demonstration of the striking similarity of molybdenocene and tungstenocene to a carbene is a major result of this study. In particular, the congruence of the reaction chemistry of methylene[32] and molybdenocene is impressive (see Scheme I).

The analogy can be carried even further by pointing out that both methylene[32] and molybden-

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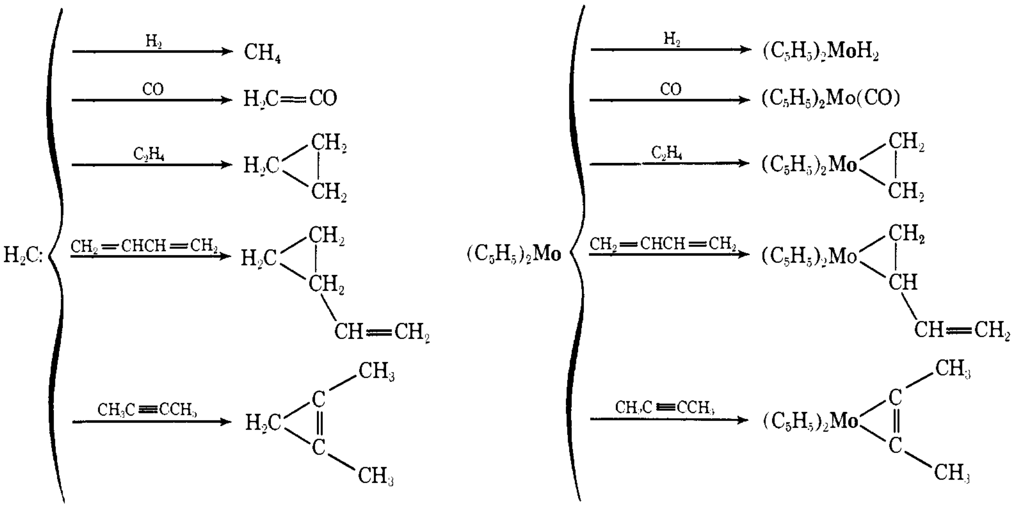
(39) P. M. Maitlis, "The Organic Chemistry of Palladium," Academic Press, New York, N. Y., 1971, pp 112–123.

(40) P. T. Cheng and S. C. Nyburg, *Can. J. Chem.*, 50, 912 (1972).

Scheme I



ocene can be generated by sodium reduction of dichloride precursors and that their nitrogen adducts are thermally unstable. The carbene behavior demonstrated by molybdenocene is also evidenced by tungstenocene. Titanocene,[1] another organometallic "carbene," reacts with H_2 and CO in a manner similar to molybdenocene and methylene. Comparatively, molybdenocene and tungstenocene exhibit much greater similarity to organic carbenes than to other inorganic "carbenes."[41] R_2Si: and I_2Ge: form only very unstable metallocyclopropanes and metallocyclopropenes that rapidly decompose by isomerization and polymerization. Treatment of X_2Ge: and HN: with 1,3-butadiene yields only 1,4 addition products rather than the 1,2 product expected for a carbene. Overall, no other previously reported systems so faithfully mimic the reaction chemistry of a carbene as do molybdenocene and tungstenocene.

Experimental Section

Mass spectra were obtained in an AEI SP902 mass spectrometer with direct inlet system. In a typical determination, the accelerating voltage was 8000 V and the source pressure 4 × 10^{-7} Torr. The ionizing voltage was 40 eV; all spectra were monoisotopic for ^{100}Mo, ^{186}W, ^{12}C, and ^{1}H, and expected isotopic distributions were observed unless otherwise stated. The source temperature was 35° for $(C_5H_5)_2Mo(CO)$ and $[C_5(CH_3)_5]_2Mo(CO)$ while it was increased to 70° for $(C_5H_5)_2MoC_2H_4$, $(C_5H_5)_2Mo(CF_3CCCF_3)$, $(C_5H_5)_2MoC_4H_6$, $(C_5H_5)_2Mo(CH_3)_2$, $[[C_5(CH_3)_5]_2Mo]_2$, $(C_5H_5)_2Mo(CH_3CCCH_3)$, $(C_5H_5)_2W(CO)$, $(C_5H_5)_2WC_2H_4$, and $(C_5H_5)_2W(CH_3CCCH_3)$, to 150° for $(C_5H_5)_4Mo_3(CO)_5$, and to 185° for $[(C_5H_5)_2Mo]_x$ and $[(C_5H_5)_2W]_x$. Infrared spectra were determined using a Perkin-Elmer 457 infrared spectrometer. A 500-ml Parr autoclave was used for all high-pressure experiments. Elemental analyses were performed by Spang Microanalytical Laboratories, Inc., Ann Arbor, Mich.

$(C_5H_5)_2MoH_2$, $(C_5H_5)_2MoCl_2$, $(C_5H_5)_2WH_2$, and $(C_5H_5)_2WCl_2$ were prepared using methods of Green, *et al.*,[42] and Cooper, *et al.*[43] Molybdenum pentachloride was prepared by chlorination of the metal.[44] Tetrahydrofuran and ethyl ether were dried over methyllithium while hexane and toluene were dried over butyllithium. All solvents were freshly distilled just prior to use. The preparation of 1,2,3,4,5-pentamethylcyclopentadiene and its sodium salt has been described elsewhere.[1] All materials were handled under an atmosphere of prepurified argon. All nmr data are relative to tetramethylsilane and were obtained from solutions in toluene-d_8 unless otherwise stated.

A. Preparation of Derivatives of Bis(cyclopentadienyl)molybdenum(II), $(C_5H_5)_2Mo$, and Their Reactions. 1. Formation of Bis(cyclopentadienyl)dihydridomolybdenum(IV), $(C_5H_5)_2MoH_2$, in the Reduction of Bis(cyclopentadienyl)dichloromolybdenum(IV), $(C_5H_5)_2MoCl_2$. $(C_5H_5)_2MoCl_2$ (103 mg, 0.348 mmol) was suspended in 20 ml of dry tetrahydrofuran. Na/Hg alloy (1 ml, 0.78 mg-atom of Na/ml) was added to this suspension and the mixture allowed to warm to 0°. The mixture was placed in an autoclave which was then pressurized with hydrogen to 200 atm. The reaction mixture was stirred for 18 hr at room temperature. At the end of this period, the autoclave was depressurized and the reaction mixture removed. The flask was attached to a vacuum line and the solvent removed *in vacuo*. A water-cooled sublimation probe was introduced and bright yellow molybdenocene dihydride (24 mg, 0.11 mmol) sublimed at 55° at 10^{-3} Torr (yield *ca.* 32%): infrared ν_{Mo-H} at 1850 cm^{-1}; lit.,[11] 1847 cm^{-1}. $[(C_5H_5)_2Mo]_x$ was isolated from the mixture (yield *ca.* 25%). A similar experiment performed in the absence of hydrogen generated molybdenocene dihydride in 1% yield.

2. Preparation of $[(C_5H_5)_2Mo]_x$. $(C_5H_5)_2MoCl_2$ (200 mg, 0.674 mmol) was suspended in 30 ml of tetrahydrofuran. Na/Hg alloy (5 ml, 0.78 mg-atom of Na/ml) was added and the mixture stirred at room temperature. The solution slowly acquired a dark red color. Three hours later, the solution was filtered yielding a dark red-brown filtrate from which the solvent was removed *in vacuo*. Upon warming to 55° at 10^{-3} Torr, a small amount (*ca.* 2 mg) of yellow $(C_5H_5)_2MoH_2$ collected on a water cooled sublimation probe. At 130°, $[(C_5H_5)_2Mo]_x$ began to sublime with decomposition. In subsequent experiments, the dihydride was removed by washing with *ca.* 10 ml of hexane and $[(C_5H_5)_2Mo]_x$ was used without further purification. $[(C_5H_5)_2Mo]_x$ is a red-brown diamagnetic solid that is moderately soluble in tetrahydrofuran, slightly soluble in toluene, and very slightly soluble in hexane (yield *ca.* 30%).

3. Reaction of $[(C_5H_5)_2Mo]_x$ with CO to Yield $(C_5H_5)_4Mo_3(CO)_5$. $[(C_5H_5)_2Mo]_x$ (60 mg) was suspended in 50 ml of hexane. The slurry was placed in an autoclave and pressurized with carbon monoxide to 200 atm. The reaction mixture was then stirred for 24 hr at 110°. At the end of this period, the slurry had become a homogeneous yellow solution and was taken from the autoclave. Removal of the solvent *in vacuo* yielded a yellow solid that could be slowly sublimed at 130° at 10^{-4} Torr (yield 95%).

4. Reaction of $[(C_5H_5)_2Mo]_x$ with Hydrogen. $[(C_5H_5)_2Mo]_x$ (60 mg) was treated exactly as in section A3 except that hydrogen was substituted for carbon monoxide. After removal of solvent, $(C_5H_5)_2MoH_2$ was sublimed from the residue at 60° and 10^{-3} Torr (yield *ca.* 20%). The remainder of the residue was unreacted $[(C_5H_5)_2Mo]_x$.

5. Reaction of $[(C_5H_5)_2Mo]_x$ with HCl. $[(C_5H_5)_2Mo]_x$ (36 mg) was allowed to react with 1 atm of HCl on a vacuum line. HCl was liquified several times on the sample over a period of 8 hr. The gases were then passed through a series of liquid nitrogen traps and collected *via* a Toepler pump. Hydrogen (0.067 mmol) was collected as shown by its quantitative oxidation to H_2O when heated to 400° over CuO. Thus 0.43 mmol of H_2 was liberated

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(41) O. M. Nefedov and M. N. Manakov, *Angew. Chem., Int. Ed. Engl.*, 5, 1021 (1966).

(42) M. H. L. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4854 (1961).

(43) R. L. Cooper and M. H. L. Green, *J. Chem. Soc. A*, 1155 (1967).

(44) G. Brauer, "Handbook of Preparative Chemistry," Academic Press, New York, N. Y., 1965, p 1405.

per millimole of molybdenum. The solid residue was identified by X-ray powder patterns to be primarily $(C_5H_5)_2MoCl_2$.

6. **Preparation of $(C_5H_5)_2Mo(CO)$ by Reduction with Sodium Amalgam.** $(C_5H_5)_2MoCl_2$ (100 mg, 0.336 mmol) was suspended in 30 ml of tetrahydrofuran. Na/Hg alloy (1 ml, 0.78 mg-atom of Na) was added and the mixture stirred at room temperature under 1 atm of carbon monoxide. After stirring for 3 hr, the solution became green. The mixture was filtered and the solvent removed *in vacuo*. A water-cooled probe was introduced and bright green $(C_5H_5)_2Mo(CO)$ sublimed upon warming to 35° at 10^{-3} Torr (yield *ca.* 35%). $[(C_5H_5)_2Mo]_x$ was isolated from the residue by extraction with tetrahydrofuran (yield *ca.* 20%).

7. **Preparation of $(C_5H_5)_2Mo(CO)$ by Reduction with Butyllithium.** $(C_5H_5)_2MoCl_2$ (200 mg, 0.672 mmol) was suspended in 50 ml of tetrahydrofuran and cooled to −78°. Butyllithium (2 mmol) in hexane was syringed onto the stirring solution in the presence of 1 atm of carbon monoxide. The mixture was allowed to warm to room temperature and react overnight. Upon removal of the solvent *in vacuo*, a black tar was obtained from which 24 mg (0.095 mmol) of $(C_5H_5)_2Mo(CO)$ was isolated by sublimation (yield *ca.* 14%).

8. **Preparation of a $(C_5H_5)_2Mo$–N_2 Complex.** $(C_5H_5)_2MoCl_2$ (206 mg, 0.694 mmol) was suspended in 30 ml of toluene and 2.5 ml of Na/Hg alloy (0.78 mg-atom of Na/ml) was added. This mixture was placed in an autoclave and pressurized to 350 atm with nitrogen. The reaction mixture was stirred for 18 hr at room temperature. Upon removal from the autoclave, the solution had a slight greenish tinge. The mixture was cooled to −78° while under 1 atm of nitrogen. The flask containing the mixture was then evacuated and pumped under high vacuum for 10 min. At the end of this period, the mixture was slowly warmed to 50°, and the evolved gases (0.686 mmol) were collected *via* a Toepler pump. The gases were then heated to 400° in the presence of CuO and cycled through a liquid nitrogen trap. This treatment caused no change in the total volume of gases. Mass spectral analysis showed the collected gas to be essentially pure N_2. A blank run under the same conditions but without $(C_5H_5)_2MoCl_2$ yielded less than 0.1 mmol of nitrogen, which was probably occluded by the amalgam. Correcting for the blank, the total yield of nitrogen is 0.545 mmol which is 0.8 N_2/Mo. A repeat experiment carried out under 210 atm of nitrogen yielded 0.7 N_2/Mo after correcting for the blank.

9. **Preparation of $(C_5H_5)_2Mo(C_2H_4)$.** $(C_5H_5)_2MoCl_2$ (200 mg, 0.67 mmol) was placed in a flask containing 2 ml of Ng/Hg alloy (1.0 mg-atom of Na/ml) and 75 ml of hexane. In an autoclave, the system was pressurized with 150 atm of ethylene and stirred for 2 days. Upon removal of the slurry from the autoclave and subsequent filtration, a red hexane solution was obtained. Removal of the solvent yielded bright red needles of $(C_5H_5)_2Mo(C_2H_4)$ which could be sublimed (10^{-4} Torr) at 50° (yield *ca.* 35%). $(C_5H_5)_2Mo(C_2H_4)$ is air sensitive and dissolves readily in aliphatic and aromatic hydrocarbons.

10. **Preparation of $(C_5H_5)_2Mo(CH_3CCCH_3)$.** A toluene slurry of $(C_5H_5)_2MoCl_2$ (200 mg, 0.674 mmol) was stirred with 1 ml of 2-butyne and 2 ml of Na/Hg alloy (1.0 mg-atom of Na/ml). After the mixture was allowed to react overnight, a brown solution was obtained. Upon filtration and removal of the solvent *in vacuo*, two products cosublimed (40°, 10^{-4} Torr) from the brown powder. The first product, yellow $(C_5H_5)_2MoH_2$, sublimes somewhat more readily than $(C_5H_5)_2Mo(CH_3CCCH_3)$. The acetylene complex can be purified by repeated fractional sublimations (yield *ca.* 30%). $(C_5H_5)_2Mo(CH_3CCCH_3)$ is an orange air-sensitive solid which dissolves in toluene, hexane, or ethyl ether.

11. **Preparation of $(C_5H_5)_2Mo(C_6H_5CCC_6H_5)$.** $(C_5H_5)_2MoCl_2$ (200 mg, 0.674 mmol) was suspended in 40 ml of toluene. To this slurry, 2 ml of Na/Hg alloy (2.0 mg-atoms of Na) and a slight excess of diphenylacetylene were added. After stirring overnight, the solution became red. Upon filtration and removal of the solvent, a red solid was obtained. Excess diphenylacetylene was removed by sublimation at 50° and 10^{-4} Torr. The nmr and infrared spectrum of the residue was identical with that previously reported[7] for $(C_5H_5)_2Mo(C_6H_5CCC_6H_5)$ (yield *ca.* 20%).

12. **Preparation of $(C_5H_5)_2Mo(CH_2CHCHCH_2)$.** $(C_5H_5)_2MoCl_2$ (100 mg, 0.337 mmol) and 1 ml of Na/Hg alloy (1.0 mg-atom of Na) were slurried in 50 ml of hexane. A slight excess of 1,3-butadiene was distilled into the mixture at −78°. Upon warming to room temperature and stirring overnight, a red-brown solution resulted. Filtration and removal of the solvent *in vacuo*, followed by sublimation (10^{-4} Torr) at 60°, yielded a dark orange sublimate. $(C_5H_5)_2Mo(CH_2CHCHCH_2)$ is a very air-sensitive solid which dissolves readily in aliphatic and aromatic solvents (yield *ca.* 25%).

13. **Preparation of $(C_5H_5)_2Mo(CH_3)_2$.** $(C_5H_5)_2MoCl_2$ (100 mg, 0.337 mmol) was added to 40 ml of toluene. $Zn(CH_3)_2$ (0.1 ml) was distilled onto the slurry and the mixture stirred overnight at 0°. Upon filtration, removal of solvent *in vacuo*, and sublimation at 10^{-4} Torr and 48°, an orange-red sublimate was obtained (yield *ca.* 30%). $(C_5H_5)_2Mo(CH_3)_2$ is only moderately air sensitive, surviving several hours of exposure to air. It is soluble in common organic solvents.

14. **Preparation of $(C_5H_5)_2Mo(CF_3CCCF_3)$.** $(C_5H_5)_2MoCl_2$ (150 mg, 0.506 mmol) and 2 ml of Na/Hg alloy (1.0 mg-atom of Na/ml) were stirred in 30 ml of toluene under 1 atm of hexafluoro-2-butyne for 12 hr. The resulting viscous, gray-black slurry was then filtered to yield a golden solution. Removal of solvent *in vacuo* and subsequent sublimation at 10^{-4} Torr at 70° yielded an orange sublimate (yield *ca.* 30%). No traces of $(C_5H_5)_2MoH_2$ or any other sublimable material were found. $(C_5H_5)_2Mo(CF_3CCCF_3)$ is soluble in aromatic and aliphatic solvents and exhibits only a slight air sensitivity as a solid.

Anal. Calcd for $(C_5H_5)_2Mo(CF_3CCCF_3)$: C, 43.4; H, 2.6; Mo, 24.7; F, 29.4. Found: C, 43.8; H, 3.1; Mo, 24.8; F, 30.5.

15. **Reaction of $(C_5H_5)_2Mo(C_2H_4)$ with $CHCl_3$.** Dry deoxygenated $CHCl_3$ (10 ml) was distilled into a flask containing $(C_5H_5)_2Mo(C_2H_4)$ (40 mg, 0.16 mmol). The solid immediately dissolved. After heating for several hours at 50°, the solution lost its red color and dark green crystals deposited on the bottom of the flask. Upon evaporation of the solvent and washing the residue with several 10-ml portions of $CHCl_3$, approximately 29 mg (0.10 mmol) of pure $(C_5H_5)_2MoCl_2$ was recovered.

16. **Hydrolysis of $(C_5H_5)_2Mo(CH_3CCCH_3)$.** Approximately 25 mg of $(C_5H_5)_2Mo(CH_3CCCH_3)$ was sublimed onto a water-cooled probe. The probe was transfered to another flask into which 5 ml of water was distilled at liquid nitrogen temperatures. Upon warming and refluxing the water onto the probe, no apparent reaction took place. $(C_5H_5)_2Mo(CH_3CCCH_3)$ seemed to be slightly soluble in water as evidenced by the light tan coloration of the drops on the probe and the deposition of small amounts of $(C_5H_5)_2Mo(CH_3CCCH_3)$ on the bottom of the flask. The flask was again cooled to liquid nitrogen temperatures and HCl gas condensed into the flask. Upon warming, a vigorous evolution of gases from the solid on the probe took place, leaving a black residue. Excess HCl was destroyed by exposing the gases to wet NaOH pellets for 8 hr. The gases were then passed through a Dry Ice trap and condensed into a gas-phase infrared cell. The resultant gas was identified by its infrared spectrum as pure *cis*-2-butene.

17. **Hydrolysis of $(C_5H_5)_2Mo(C_2H_4)$.** Approximately 2 ml o water was distilled into a flask containing approximately 20 mg of $(C_5H_5)_2Mo(C_2H_4)$ on a sublimation probe. The water was refluxed for several hours onto the probe with no apparent reaction. A slight solubility of $(C_5H_5)_2Mo(C_2H_4)$ was noted as evidenced by the red coloration of the refluxing drops and the slow accumulation of $(C_5H_5)_2Mo(C_2H_4)$ on the bottom of the flask. The lower half of the flask was subsequently cooled to −196° and HCl condensed into the flask. Upon warming, a vigorous reaction ensued. Gas evolution was evident and a greenish residue was left on the sublimation probe. Excess HCl was destroyed by exposing the gases to wet NaOH pellets. The remaining gas was condensed into a gas-phase infrared cell. The gas was shown to be pure C_2H_6 by comparison with authentic samples. No C_2H_4 was present.

B. Preparation of Derivatives of Bis(pentamethylcyclopentadienyl)molybdenum(II), $[C_5(CH_3)_5]_2Mo$. 1. Preparation of Bis(pentamethylcyclopentadienyl)dihydridomolybdenum(IV), $[C_5(CH_3)_5]_2MoH_2$. $NaC_5(CH_3)_5$ (7.0 g, 44 mmol) was placed in a 300-ml three-neck flask. Molybdenum pentachloride, freshly prepared (3 g, 11 mmol), and sodium borohydride (2.5 g, 74 mmol) were added to the flask, and the mixture was stirred dry for 1 hr to yield a homogeneous finely divided powder. The reaction mixture was then cooled to −78° and 60 ml of toluene condensed on the powder. Upon stirring the mixture, a black solution was obtained, to which an additional 150 ml of tetrahydrofuran was slowly added at −78°. The reaction mixture was warmed to room temperature and then refluxed overnight. Upon subsequent removal of solvent, evacuation to 10^{-3} Torr, and heating to 110°, approximately 1 ml of orange-yellow oil and 1.5 g (4.1 mmol) of red-orange, air-sensitive $[C_5(CH_3)_5]_2MoH_2$ was sublimed to a cold finger probe equipped with a small cup to collect the oil. The solid product could be further purified by resublimation at 60° to yield a bright yellow product, but this was generally unnecessary (yield *ca.* 37%).

$[C_5(CH_3)_5]_2MoH_2$ is very soluble in aliphatic and aromatic hydrocarbons, tetrahydrofuran, and ethyl ether, giving yellow solutions.

2. **Preparation of Bis(pentamethylcyclopentadienyl)dichloromolybdenum(IV), $[C_5(CH_3)_5]_2MoCl_2$.** $[C_5(CH_3)_5]_2MoH_2$ (1.5 g, 4.1 mmol) was dissolved in 30 ml of $CHCl_3$ previously dried over P_2O_5. The yellow solution quickly darkened as it was heated to 55°. After 8 hr at this temperature, the solution was evaporated to dryness *in vacuo* and a dark blue-green product was obtained. The product was washed three times with 30-ml portions of hexane and then with 20 ml of benzene. This procedure yielded bright blue $[C_5(CH_3)_5]_2MoCl_2$ (1.35 g, 3.1 mmol). $[C_5(CH_3)_5]_2MoCl_2$ is an air-stable solid somewhat sensitive to moisture. It is very soluble in $CHCl_3$, slightly soluble in CCl_4 and dimethoxyethane, and insoluble in hexane or toluene.

Anal. Calcd for $[C_5(CH_3)_5]_2MoCl_2$: C, 54.9; Cl, 16.3; H, 6.85. Found: C, 52.5; Cl, 17.8; H, 6.86.

The slightly high chlorine analysis is probably due to the presence of small amounts of $[C_5(CH_3)_5]_2MoCl_3$.

3. **Preparation of $[[C_5(CH_3)_5]_2Mo]_2$.** $[C_5(CH_3)_5]_2MoCl_2$ (100 mg, 0.228 mmol) was placed in a 50-ml flask and 25 ml of either hexane or toluene distilled onto the solid. Na/Hg alloy (1 ml, 0.78 mg-atom of Na) was added to the mixture and the solution was stirred for 12 hr. As the reaction proceeds, the solution becomes orange-yellow. After filtration and removal of the solvent *in vacuo*, yellow crystals are obtained (yield *ca.* 90%). $[[C_5(CH_3)_5]_2Mo]_2$ is an air sensitive, diamagnetic solid that is very soluble in aliphatic and aromatic hydrocarbons, tetrahydrofuran, and ethyl ether. Contamination of this solid with small amounts of oxygen yields a deeper orange color while larger amounts of oxygen cause decomposition to black tars. $[[C_5(CH_3)_5]_2Mo]_2$ sublimes slowly at 65° at 10^{-4} Torr.

4. **Reaction of $[[C_5(CH_3)_5]_2Mo]_2$ with Hydrogen.** $[[C_5(CH_3)_5]_2Mo]_2$ (100 mg, 0.135 mmol) was dissolved in 20 ml of toluene and placed in an autocalve. The system was then pressurized to 200 atm with hydrogen and stirred 18 hr. Upon removal from the autoclave, the solvent was evaporated *in vacuo*. The remaining yellow crystals were dissolved in 1 ml of toluene-d_8. Nmr spectroscopy showed that the solution contained principally $[C_5(CH_3)_5]_2MoH_2$ (yield 85%).

5. **Reaction of $[[C_5(CH_3)_5]_2Mo]_2$ with Carbon Monoxide.** $[C_5(CH_3)_5]_2MoCl_2$ (104 mg, 0.238 mmol) was reduced with Na/Hg alloy as previously described. The filtered solution was then allowed to react with 0.537 mmol of carbon monoxide. After stirring for 5 hr at room temperature, the solution became bright green. The carbon monoxide consumed amounted to 0.137 mmol or 0.58 mmol of CO consumed per mmol of Mo. The solvent was removed from the reaction mixture and green $[C_5(CH_3)_5]_2Mo(CO)$ was sublimed from the residue at 35° and 10^{-3} Torr. In a repeat experiment, 0.68 mmol of CO was consumed per mmol of Mo.

6. **Reduction of $[C_5(CH_3)_5]_2MoCl_2$ in the Presence of Nitrogen.** $[C_5(CH_3)_5]_2MoCl_2$ (112 mg, 0.257 mmol) was treated as in section A7 above and yielded 0.80 mmol of N_2/mmol of Mo after correction for the blank.

7. **Reaction of $[[C_5(CH_3)_5]_2Mo]_2$ with Nitrogen.** $[[C_5(CH_3)_5]_2Mo]_2$, prepared from $[C_5(CH_3)_5]_2MoCl_2$ (102 mg, 0.234 mmol) as described above, was dissolved in toluene and placed in an autoclave. The system was pressurized to 250 atm with nitrogen. After the reaction mixture was stirred for 18 hr, the autoclave and its contents were cooled to −78°. The autoclave was then depressurized and the contents removed and cooled with a −78° slush. The solution was placed on a vacuum line and pumped under high vacuum for 15 min at −78°. The solution was slowly warmed, and the evolved gases (0.164 mmol) were collected and identified by mass spectrometry to be essentially pure nitrogen. The overall yield of nitrogen was 0.70 mmol/mmol of Mo. Repeat experiments gave 0.80 and 0.56 mmol of N_2/mmol of Mo.

8. **Reaction of Nitrogen with Dry $[[C_5(CH_3)_5]_2Mo]_2$ Powder.** Dry $[[C_5(CH_3)_5]_2Mo]_2$ (88 mg, 0.101 mmol) was placed in a flask. The flask was placed in an autoclave and the system pressurized with 250 atm of nitrogen. After stirring the dry powder for 24 hr under these conditions, the flask was removed from the autoclave, cooled to −78°, and pumped on a vacuum line. The flask was then warmed to room temperature. The solid released 0.254 mmol of nitrogen (1.25 mmol of N_2/mmol of Mo) over a 50-min period. The gas was identified as pure nitrogen by mass spectrometry. Repeat experiments yielded 1.24 and 0.8 mmol of N_2/mmol of Mo.

9. **Reaction of the Decamethylmolybdenocene–N_2 Complex with Carbon Monoxide.** $[C_5(CH_3)_5]_2MoCl_2$ (100 mg, 0.228 mmol) was placed in the autoclave and treated as described in section B7. After removal from the autoclave and pumping under high vacuum for 20 min, the sample was treated with carbon monoxide (0.440 mmol) and allowed to react for 5 hr with stirring. The gases present (0.412 mmol) were passed through a series of liquid nitrogen traps and collected *via* a Toepler pump. The gases were subsequently passed over CuO at 400° for 12 hr. The gas not condensable amounted to 0.081 mmol and was shown by mass spectrometry to be pure nitrogen. The trap was warmed to −78°, and the total gases collected amounted to 0.412 mmol. No further increase in volume of gases was observed upon warming the trap to room temperature. Thus, the total amount of carbon monoxide consumed was 0.109 mmol. This corresponds to 0.75 mmol of nitrogen released per mmol of carbon monoxide consumed.

C. **Preparation of Derivatives of Bis(cyclopentadienyl)tungsten(II).** 1. **Preparation of $[(C_5H_5)_2W]_x$.** Under the exact conditions described in section A2, $(C_5H_5)_2WCl_2$ (200 mg, 0.52 mmol) was reduced with sodium amalgam. Substantial quantities (*ca.* 15 mg) of yellow $(C_5H_5)_2WH_2$ were produced and separated from red $[(C_5H_5)_2W]_x$ by sublimation. $[(C_5H_5)_2W]_x$ was isolated as in section A2 in 35% yield.

2. **Preparation of $(C_5H_5)_2W(CO)$.** $(C_5H_5)_2W(CO)$ was prepared in exactly the same manner as described for $(C_5H_5)_2Mo(CO)$. The green product was sublimed at 60° (yield 35%). $[(C_5H_5)_2W]_x$ was isolated from the residue in *ca.* 20% yield.

3. **Preparation of $(C_5H_5)_2W(C_2H_4)$.** $(C_5H_5)_2W(C_2H_4)$ was prepared in the same manner as $(C_5H_5)_2Mo(C_2H_4)$. After taking the yellow solution from the autoclave and removing the solvent *in vacuo*, the orange-red product sublimed readily at 50° at 10^{-4} Torr together with a small amount (*ca.* 10% of the total sublimables) of $(C_5H_5)_2WH_2$ (yield *ca.* 25%). $(C_5H_5)_2W(C_2H_4)$ is air sensitive and quite soluble in solvents such as tetrahydrofuran, toluene, or hexane.

4. **Preparation of $(C_5H_5)_2W(CH_3CCCH_3)$.** $(C_5H_5)_2W(CH_3CCCH_3)$ was prepared in the same manner as $(C_5H_5)_2Mo(CH_3CCCH_3)$. Filtration of the reaction mixture yields a reddish orange solution. Removal of the solvent *in vacuo* and sublimation at 60° at 10^{-4} Torr gave $(C_5H_5)_2WH_2$ as the principal product (*ca.* 70%) cosublimed with smaller amounts (*ca.* 30%) of tan $(C_5H_5)_2W(CH_3CCCH_3)$. The acetylene complex is air sensitive and soluble in toluene or hexane.

5. **Preparation of $(C_5H_5)_2W(CH_3)_2$.** Using the same procedure as that for the synthesis of $(C_5H_5)_2Mo(CH_3)_2$, $(C_5H_5)_2W(CH_3)_2$ was prepared in approximately 30% yield. The bright yellow compound was sublimed from the reaction mixture at 70° at 10^{-4} Torr. Its solubility and air sensitivity closely resembles that of $(C_5H_5)_2Mo(CH_3)_2$.

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