Preparation and Properties of Dinitrogen–Molybdenum Complexes

Masanobu Hidai,* Kenichi Tominari, and Yasuzo Uchida

Contribution from the Department of Industrial Chemistry, The University of Tokyo, Hongo, Tokyo, Japan. *Received June 4, 1971*

Abstract: Dinitrogen–molybdenum complexes of the types $Mo(N_2)(PPh_3)_2 \cdot C_6H_5CH_3$ (**1**) and *trans*-$Mo(N_2)_2(Ph_2P(CH_2)_nPPh_2)_2$ ($n = 1$, 2, and 3) were prepared from molybdenum(III) acetylacetonate, organoaluminum compounds, phosphine compounds, and molecular nitrogen. The bis(dinitrogen) complex *trans*-$Mo(N_2)_2(DPE)_2$ (**2**) (DPE, 1,2-bis(diphenylphosphino)ethane) reacts reversibly with hydrogen gas to give the molybdenum hydride complex *trans*-$MoH_2(DPE)_2$ (**3**) or [*trans*-$MoH_2(DPE)]_2$-μ-DPE (**4**) depending upon the solvent used. The former hydride complex was obtained in benzene or tetrahydrofuran, while the latter hydride complex was formed in toluene. The hydride complexes are interconvertible. The reaction of the bis(dinitrogen) complex **2** with trihydridotris(triphenylphosphine)cobalt(III) was carried out as an inorganic model of nitrogen reductase. The dinitrogen ligand transferred from the molybdenum atom to the cobalt atom and the hydride complex **3** or **4** was formed depending upon the solvent in addition to hydridodinitrogentris(triphenylphosphine)cobalt(I). Reactions of dinitrogen–molybdenum complexes with carbon monoxide were also studied.

Since the discovery of the first N_2 complex of a transition metal,[1] many N_2 complexes of group VIII transition metals have been prepared by several methods and their properties have been extensively studied in relationship to nitrogen fixation in biological systems.[2] Some nitrogen-fixing enzymes in biological systems contain molybdenum, nonheme iron, and labile sulfide. Reactions of molecular nitrogen with iron complexes[3] or sulfur-containing organic compounds[4] have been reported. In view of the key role of molybdenum in both chemical and biological nitrogen fixation, we have attempted to prepare dinitrogen–molybdenum complexes. Previously we reported briefly the preparation of dinitrogen–molybdenum complexes of two types, $Mo(N_2)(PPh_3)_2 \cdot C_6H_5CH_3$ (**1**) and *trans*-$Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2$ (**2**), which were obtained by the reduction of molybdenum(III) acetylacetonate with trialkylaluminum in the presence of triphenylphosphine or 1,2-bis(diphenylphosphino)ethane in an atmosphere of nitrogen.[5] Recently preparations of the latter dinitrogen–molybdenum complex by different routes have been briefly reported.[6] This paper is concerned with the syntheses and reactivities of the dinitrogen–molybdenum complexes.

Results and Discussion

Preparation and Properties of Dinitrogen–Molybdenum Complexes. When molybdenum(III) acetylacetonate was reduced with triethylaluminum in the presence of a tenfold excess of triphenylphosphine in toluene under nitrogen, an orange complex **1** was obtained, which was empirically formulated as $Mo(N_2)(PPh_3)_2 \cdot C_6H_5CH_3$. The N_2 complex is moderately air stable. The yield of the complex decreased to one-fifth when triisobutylaluminum was used in place of triethylaluminum. On the other hand, the complex was not obtained by using trimethylaluminum. Molar ratios of triphenylphosphine to molybdenum(III) acetylacetonate remarkably affect the yield of the complex. The yield decreased with the decrease in the molar ratio of $PPh_3/Mo(acac)_3$. At the ratio of $PPh_3/Mo(acac)_3 = 3$ the complex was scarcely obtained.

$$Mo(acac)_3 + PPh_3 + AlR_3 + N_2 \xrightarrow[\text{in toluene}]{} \underset{\textbf{1}}{Mo(N_2)(PPh_3)_2 \cdot C_6H_5CH_3}$$

$$R = Et \text{ or } i\text{-}Bu$$

The infrared spectrum of the complex shows a very strong absorption at 2005 cm^{-1} assignable to the coordinated N–N stretching frequency in addition to bands characteristic of triphenylphosphine. The complex decomposed *in vacuo* above *ca.* 90° evolving a gas containing 0.9 mol of nitrogen molecule, 0.2 mol of toluene, and 0.2 mol of benzene per mole of molybdenum in addition to a trace of hydrogen gas. The complex may be polynuclear since it has slight solubility in organic solvents such as benzene, ether, acetone, and tetrahydrofuran.

Using benzene or mesitylene as the solvent instead of toluene, an analogous orange complex with the N–N stretching frequency at 2005 cm^{-1} was obtained. The elemental analysis indicates that the complex does not contain the solvent and is formulated as $Mo(N_2)(PPh_3)_2$. The complex shows the same chemical properties as the above N_2 complex **1**.

No N_2 complex was obtained by using other monodentate phosphines such as tri-*n*-butylphosphine, tri-*p*-tolylphosphine, and ethyldiphenylphosphine. However, a new series of dinitrogen–molybdenum complexes of the type *trans*-$Mo(N_2)_2(Ph_2P(CH_2)_nPPh_2)_2$ ($n = 1$, 2, and 3) were prepared by using bidentate phosphines such as bis(diphenylphosphino)methane (DPM), 1,2-

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(1) A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1966).

(2) For recent reviews, see (a) R. Murray and D. C. Smith, *Coord. Chem. Rev.*, 3, 429 (1968); (b) G. H. Olive and S. Olive, *Angew. Chem.*, **81**, 679 (1969); (c) Yu. G. Borod'ko and A. E. Shilov, *Usp. Khim.*, **38**, 761 (1969).

(3) (a) C. H. Campbell, A. R. Dias, M. L. H. Green, T. Saito, and M. G. Sandwick, *J. Organometal. Chem.*, **14**, 349 (1968); (b) A. Sacco and M. Aresta, *Chem. Commun.*, 1223 (1968); (c) G. M. Bancroft, M. J. Mays, and B. E. Prater, *ibid.*, 585 (1969); *J. Chem. Soc. A*, 2146 (1970).

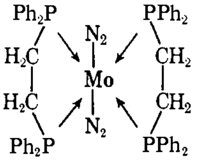
(4) D. C. Owsley and G. K. Helmkamp, *J. Amer. Chem. Soc.*, **89**, 4558 (1967); J. Ellermann, F. Poersch, R. Kunstmann, and R. Kramolowsky, *Angew. Chem.*, **81**, 183 (1969).

(5) M. Hidai, K. Tominari, Y. Uchida, and A. Misono, *Chem. Commun.*, 814 (1969); *ibid.*, 1392 (1969).

(6) J. Chatt and A. G. Wedd, *J. Organometal. Chem.*, **27**, C15 (1971); L. K. Atkinson, A. H. Mawby, and D. C. Smith, *Chem. Commun.*, 157 (1971).

bis(diphenylphosphino)ethane (DPE), and 1,3-bis(diphenylphosphino)propane (DPP). No N_2 complex was obtained, on the other hand, by using 1,4-bis(diphenylphosphino)butane and 1,2-bis(dimethylphosphino)ethane. *trans*-Bis(dinitrogen)bis[1,2-bis(diphenylphosphino)ethane]molybdenum(0) (**2**) is an orange crystalline solid and fairly air stable. It is soluble in toluene but insoluble in petroleum ether. The thermal decomposition of **2** occurred *in vacuo* above *ca.* 150° with evolution of 90% of the theoretical amount of nitrogen gas. In the case of DPM, the bis(dinitrogen) complex could not be isolated in a pure state since it was oily. However, tris[bis(diphenylphosphino)methane]molybdenum(0), $Mo(DPM)_3$, was obtained as reddish-brown crystals. The bis(dinitrogen) complex containing DPP, *trans*-$Mo(N_2)_2(DPP)_2$, is an orange solid and fairly air stable. It is less soluble in toluene than the complex **2**.

$$Mo(acac)_3 + Ph_2PCH_2CH_2PPh_2 + AlEt_3 + N_2 \longrightarrow$$



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Several examples of bis(dinitrogen) complexes have been reported and the nitrogen molecules are considered to be located cis to each other since their infrared spectra show two strong absorptions at *ca.* 2100 cm^{-1} assignable to the coordinated N–N stretching vibrations.[7] The infrared spectra of the bis(dinitrogen) complexes obtained here show, however, a very weak absorption near 2010 cm^{-1} and a very strong absorption in the range of 1925–1995 cm^{-1}, indicating a trans configuration about the molybdenum atom which belongs to D_{4h} point group. Thus, the weak band and the strong band are, respectively, assignable to an N–N symmetric stretching vibration (A_{1g}; Raman active) and an N–N antisymmetric stretching vibration (A_{2u}; ir active). Table I shows that $\nu_{N\equiv N}$ shifts to the lower frequency with increase in the length of the methylene chain of the ditertiary phosphines. This may indicate that the order of increase in the electron-donating power is $n = 1 < n = 2 < n = 3$ in the ditertiary phosphines of the type $Ph_2P(CH_2)_nPPh_2$ since dinitrogen and carbon monoxide exhibit similar properties as ligands.[2c,8]

Table I. Infrared Data of the Bis(dinitrogen) Complexes of Molybdenum

Compd	$\nu_{N\equiv N}$, cm^{-1} KBr disk
trans-$Mo(N_2)_2(Ph_2PCH_2PPh_2)_2$	1995 vs[a]
trans-$Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2$	2020 vw, 1970 vs
trans-$Mo(N_2)_2(Ph_2PCH_2CH_2CH_2PPh_2)_2$	2010 vw, 1925 vs

[a] In toluene solution.

The molecular structure of the complex **2** has been determined from three-dimensional X-ray analysis, which supports the above trans configuration about the molybdenum atom and will be reported separately.

Reactions of Dinitrogen–Molybdenum Complexes. The dinitrogen–molybdenum complexes of the types $Mo(N_2)(PPh_3)_2 \cdot C_6H_5CH_3$ (**1**) and *trans*-$Mo(N_2)_2(DPE)_2$ (**2**) were treated with sodium borohydride, hydrogen gas, sodium naphthalene, titanium trichloride, and concentrated sulfuric acid, but no reduction of the coordinated dinitrogen to ammonia was observed.

A. **Reactions with Hydrogen.** It has been reported that the dinitrogen–cobalt complex $CoH(N_2)(PPh_3)_3$ reacts reversibly with hydrogen gas to give the hydride complex $CoH_3(PPh_3)_3$.[9] This reversibility is interesting because hydrogen gas is a competitive inhibitor of natural nitrogen fixation.

When hydrogen gas was bubbled through a suspension of the N_2 complex **1**, the complex decomposed and no definite complex was isolated. On the other hand, when hydrogen gas was bubbled through a solution of the N_2 complex **2** for several days at ambient temperature, two kinds of molybdenum hydride complexes were obtained depending upon the solvent used. One is *trans*-dihydridobis[1,2-bis(diphenylphosphino)ethane]molybdenum(II), *trans*-$MoH_2(DPE)_2$ (**3**), which is obtained by using benzene or tetrahydrofuran as the solvent. The complex is a yellow crystalline solid and fairly air stable. It is slightly soluble in benzene and tetrahydrofuran but scarcely soluble in petroleum ether. It decomposed *in vacuo* above *ca.* 90° evolving in addition to benzene 90% of the theoretical amount of hydrogen gas based on the above formula. The infrared spectrum shows a medium band at 1745 cm^{-1} assignable to ν_{Mo-H}. This indicates a trans configuration about the molybdenum atom since trans dihydrides always give rise to very low metal–hydrogen stretching frequencies in the range of 1615–1750 cm^{-1}. The other is obtained by using toluene as the solvent. The complex is a pale yellow crystalline solid and is tentatively formulated as a binuclear complex in which two trigonal-bipyramidal trans dihydrides are bridged by a DPE ligand, *i.e.*, μ-1,2-bis(diphenylphosphino)ethane-bis[*trans*-dihydrido-1,2-bis(diphenylphosphino)ethanemolybdenum(II)], [*trans*-$MoH_2(DPE)]_2$-μ-(DPE) (**4**), based on the following results. (1) The elemental analysis is in accord with the formula $Mo_2H_4(DPE)_3$. (2) The complex decomposed *in vacuo* above *ca.* 130° evolving 85% of the theoretical amount of hydrogen gas based on the above formula in addition to benzene. Toluene was not observed in the decomposed product. This indicates that the complex does not contain toluene and is therefore a different type of hydride complex. (3) The infrared spectrum shows a medium band at 1715 cm^{-1} which disappears in the corresponding complex obtained by using deuterium and can therefore be assigned to the Mo–H stretching frequency. This indicates the presence of a trans dihydride as in the above case. (4) Unfortunately the slight solubility of the complex in usual organic solvents precluded the direct determination of the molecular weight by cryoscopic method and of the molecular structure by nmr spectros-

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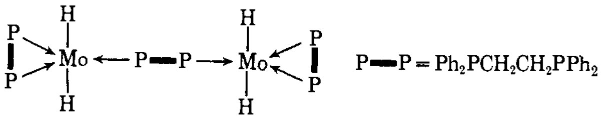
(7) L. A. P. Kane-Maguire, P. S. Sheridan, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **90**, 5295 (1968); H. A. Scheidegger, J. N. Armor, and H. Taube, *ibid.*, **90**, 3263 (1968); J. E. Fergusson and J. L. Love, *Chem. Commun.*, 399 (1969).

(8) A. Misono, Y. Uchida, T. Saito, M. Hidai, and M. Araki, *Inorg. Chem.*, **8**, 168 (1969).

(9) (a) A. Yamamoto, L. S. Pu, S. Kitazume, and S. Ikeda, *J. Amer. Chem. Soc.*, **89**, 3071 (1967); *ibid.*, **93**, 371 (1971); (b) A. Sacco and M. Rossi, *Chem. Commun.*, 316 (1967); *Inorg. Chim. Acta*, **2**, 127 (1968).

copy as in the case of the complex **3**. However, the complex may be diamagnetic since peaks due to toluene are sharp in the nmr spectrum of a toluene solution of the complex. (5) Bridging DPE molecules have been observed previously in molybdenum and tungsten carbonyl systems by several groups of workers;[10] this lends further support to our formulation of the complex.[10a]



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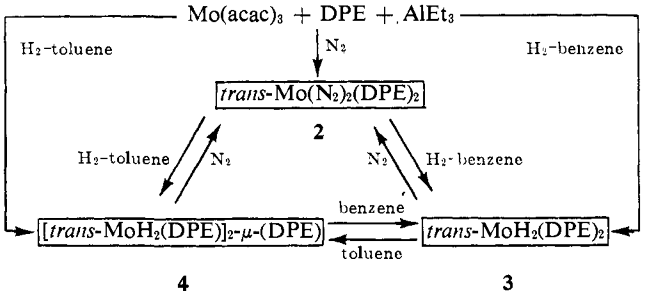
The complex **4** is fairly air stable and slightly soluble in toluene but insoluble in petroleum ether. In general, hydridic hydrogen reacts with carbon tetrachloride to give chloroform. However, the reaction of this hydride complex **4** with carbon tetrachloride at ambient temperature gave the hydride complex **3** and a molybdenum chloride, while only a trace of chloroform was formed.

These two types of hydride complexes are interconvertible; *i.e.*, when the former hydride complex **3** is dissolved in toluene, the latter hydride complex **4** is formed and *vice versa*. Both of them react with nitrogen gas to yield the bis(dinitrogen) complex **2**. They are also directly prepared by bubbling hydrogen gas through the benzene or toluene solution containing molybdenum(III) acetylacetonate, DPE, and triethylaluminum as shown in Scheme I.

Scheme I. Preparation and Reactivities of Dinitrogen and Hydride Complexes of Molybdenum



In order to prepare a more soluble hydride complex and examine the molecular structure by nmr spectroscopy, 1,2-bis(dimethylphosphino)ethane was used instead of DPE, but no hydride complex was formed.

B. Reactions of Dinitrogen–Molybdenum Complexes with Hydride Complexes of Iron and Cobalt. Hardy, *et al.*,[11] proposed that nitrogen-fixing enzymes have an electron-activating site and a substrate-binding site in which molybdenum or iron plays an important role. Parshall[12] studied the reaction of the platinum hydride $PtHCl(PEt_3)_2$ with a diazonium salt as an inorganic analog of nitrogen reductase. We used the above dinitrogen–molybdenum complexes and iron or cobalt hydride complexes as the corresponding model compounds.

When the N_2 complex **1** was mixed with $FeH_2(PPh_2Et)_3$ or $CoH_3(PPh_3)_3$, both the dinitrogen and hydride complexes decomposed with evolution of hydrogen and nitrogen gas, and the formation of ammonia was not observed.

When the N_2 complex **2** was allowed to react with $CoH_3(PPh_3)_3$ in benzene or toluene, the hydride complex of molybdenum **3** or **4** was, respectively, obtained depending on the solvent. In both cases, the infrared

$$\textit{trans}\text{-}Mo(N_2)_2(DPE)_2 + CoH_3(PPh_3)_3$$

$$\xrightarrow{\text{benzene}} \textit{trans}\text{-}MoH_2(DPE)_2 + CoH(N_2)(PPh_3)_3$$

$$\xrightarrow{\text{toluene}} [\textit{trans}\text{-}MoH_2(DPE)]_2\text{-}\mu\text{-}(DPE) + CoH(N_2)(PPh_3)_3$$

spectra of the reaction solutions show a strong absorption at 2088 cm^{-1} due to $\nu_{\mathrm{N\equiv N}}$ of $CoH(N_2)(PPh_3)_3$,[9] in addition to a strong band at 1980 cm^{-1} due to $\nu_{\mathrm{N\equiv N}}$ of the unreacted N_2 complex **2**. This indicates that the nitrogen molecule moves from the molybdenum atom to the cobalt atom. However, $CoH(N_2)(PPh_3)_3$ could not be isolated from the reaction mixture.

C. Reactions with Carbon Monoxide. Dinitrogen and carbon monoxide are isoelectronic molecules and have strikingly similar properties as ligands to transition metals. Furthermore, carbon monoxide is known as an inhibitor of nitrogen fixation in biological systems. In view of these facts, the reactions of the dinitrogen–molybdenum complexes with carbon monoxide were studied.

When carbon monoxide was bubbled through a suspension of the N_2 complex **1** in toluene, a reddish orange complex, empirically formulated as $Mo(CO)(PPh_3)_2$, was obtained. The complex may be polynu-

$$Mo(N_2)(PPh_3)_2C_6H_5CH_3 + CO \longrightarrow Mo(CO)(PPh_3)_2$$

clear as the N_2 complex **1**. The infrared spectrum shows two strong bands at 1800 and 1820 cm^{-1} assignable to $\nu_{\mathrm{C\equiv O}}$. This splitting of $\nu_{\mathrm{C\equiv O}}$ bands may be due to a crystal effect, since the splitting is not observed sometimes. However, the conditions under which the splitting appears are yet uncertain.

On the other hand, when carbon monoxide was bubbled through the solution containing molybdenum(III) acetylacetonate, triisobutylaluminum, and triphenylphosphine, two kinds of molybdenum carbonyl complexes were isolated. One is a brownish yellow crystalline complex and formulated as $Mo(CO)_2(PPh_3)_4$. The complex shows two strong ir bands at 1840 and 1940 cm^{-1} assignable to $\nu_{\mathrm{C\equiv O}}$, indicating a cis configuration about the molybdenum atom. The other is the known tetracarbonyl complex *trans*-$Mo(CO)_4(PPh_3)_2$, which is easily prepared by the reaction of $Mo(CO)_6$ with triphenylphosphine.[13]

$$Mo(acac)_3 + PPh_3 + Al(\textit{i}\text{-}Bu)_3 + CO \longrightarrow$$
$$\textit{cis}\text{-}Mo(CO)_2(PPh_3)_4 + \textit{trans}\text{-}Mo(CO)_4(PPh_3)_2$$

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(10) P. M. Treichel, K. W. Barnett, and R. L. Shubkin, *J. Organometal Chem.*, **7**, 449 (1967); K. W. Barnett and P. M. Treichel, *Inorg. Chem.*, **6**, 294 (1967); R. J. Haines, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc. A*, 94 (1967); M. W. Anker, R. Colton, C. J. Rix, and I. B. Tomkins, *Aust. J. Chem.*, **22**, 1341 (1969).

(10a) NOTE ADDED IN PROOF. The reactions of the hydride complexes **3** and **4** with excess of iodine in benzene afforded respectively 92 and 73% of the theoretical amount of hydrogen gas. On reaction of the complex **4** with excess of concentrated sulfuric acid, 93% of the theoretical amount of hydrogen gas was released. These results lend further support to our formulation of the complexes **3** and **4**.

(11) R. W. F. Hardy, E. Knight, and A. J. D'Eustachio, *Biochem. Biophys. Res. Commun.*, **20**, 539 (1965); R. W. F. Hardy and E. Knight, *Biochim. Biophys. Acta*, **122**, 520 (1966).

(12) G. W. Parshall, *J. Amer. Chem. Soc.*, **89**, 1822 (1967).

(13) R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. Fr.*, 1301 (1962).

The reaction of the bis(dinitrogen) complex **2** with carbon monoxide gave the known dicarbonyl complex *cis*-$\text{Mo(CO)}_2\text{(DPE)}_2$.[14] It is interesting to note that the

$$trans\text{-Mo(N}_2)_2\text{(DPE)}_2 + \text{CO} \longrightarrow cis\text{-Mo(CO)}_2\text{(DPE)}_2$$

dicarbonyl complex obtained has only the cis configuration, while the corresponding bis(dinitrogen) complex is isolated only as the trans form.

Experimental Section

General. All preparations and recrystallizations were carried out in nitrogen, argon, or hydrogen atmospheres. Solvents were purified by usual methods and used after distillation under argon or nitrogen over metallic sodium. Thermal decompositions of the complexes were carried out in a closed vacuum system and the evolved gases were analyzed by gas chromatography and mass spectroscopy.

Materials. Molybdenum(III) acetylacetonate,[15] dihydridotris(ethyldiphenylphosphine)iron(II),[3b] and trihydridotris(triphenylphosphine)cobalt(III)[16] were prepared as described in the literature. Trialkylaluminum compounds were used as purchased from Ethyl Corp. Ltd. Triphenylphosphine and tri-*n*-butylphosphine were used as purchased. Ethyldiphenylphosphine was prepared by the reaction of ethylphosphorus dichloride[17] with phenylmagnesium bromide. Tri-*p*-tolylphosphine,[18] bis(diphenylphosphino)methane,[19] 1,2-bis(diphenylphosphino)ethane,[19] 1,3-bis(diphenylphosphino)propane,[19] 1,4-bis(diphenylphosphino)butane,[19] and 1,2-bis(dimethylphosphino)ethane[20] were prepared by published methods.

Preparation of the Dinitrogen–Molybdenum Complex Containing Triphenylphosphine. (1) Reaction in Toluene. To a stirred solution of 5.70 g (14.5 mmol) of molybdenum(III) acetylacetonate and 38.0 g (145 mmol) of triphenylphosphine in 250 ml of toluene was added 10 ml (73 mmol) of triethylaluminum at −40° under nitrogen. An immediate reaction took place and the solution turned dark brown. Nitrogen gas was bubbled through the reaction mixture and the temperature was gradually raised to ambient temperature. After 1 day, some of the orange complex $\text{Mo(N}_2)\text{(PPh}_3)_2\cdot\text{C}_6\text{H}_5\text{CH}_3$ (**1**) precipitated. The reaction was continued for another 5 days and addition of 50 ml of *n*-hexane to the mixture deposited an additional quantity of the orange complex. The precipitate was filtered, washed several times with toluene and *n*-hexane, and dried *in vacuo*, yield 1.42 g (13%). *Anal.* Calcd for $\text{C}_{43}\text{H}_{38}\text{N}_2\text{P}_2\text{Mo}$: C, 69.73; H, 5.17; N, 4.10; Mo, 12.95. Found: C, 69.28; H, 5.24; N, 4.10; Mo, 14.0.

(2) Reaction in Benzene. The N_2 complex $\text{Mo(N}_2)\text{(PPh}_3)_2$ was prepared as above, except that benzene was used instead of toluene, yield 6%. *Anal.* Calcd for $\text{C}_{36}\text{H}_{30}\text{N}_2\text{P}_2\text{Mo}$: C, 66.67; H, 4.66; N, 4.32. Found: C, 65.60; H, 5.03; N, 3.82.

(3) Reaction in Mesitylene. The N_2 complex $\text{Mo(N}_2)\text{(PPh}_3)_2$ was prepared as above, except that mesitylene was used in place of toluene, yield 10%. *Anal.* Calcd for $\text{C}_{36}\text{H}_{30}\text{N}_2\text{P}_2\text{Mo}$: C, 66.67; H, 4.66; N, 4.32. Found: C, 64.90; H, 4.66; N, 3.95.

Preparation of *trans*-Bis(dinitrogen)bis[bis(diphenylphosphino)methane]molybdenum(0) and Tris[bis(diphenylphosphino)methane]molybdenum(0). To a stirred solution of 1.01 g (2.58 mmol) of molybdenum(III) acetylacetonate and 1.98 g (5.16 mmol) of bis(diphenylphosphino)methane in 40 ml of toluene was added 2.1 ml (15 mmol) of triethylaluminum at −40° under nitrogen. The temperature was gradually raised to ambient temperature with bubbling nitrogen gas through the mixture. The reaction was continued for about 5 days. When 20 ml of *n*-hexane was added to the mixture, a dark brown oil was deposited. The infrared spectrum of the oily product showed a strong absorption at 1995 cm^{-1} assignable to $\nu_{\text{N}\equiv\text{N}}$. After separation of the oily product, Mo(DPM)_3 precipitated from the solution as reddish brown crystals. The complex was collected by filtration, washed with *n*-hexane, and dried *in vacuo*, yield 0.164 g (5.1%). *Anal.* Calcd for $\text{C}_{75}\text{H}_{66}\text{P}_6\text{Mo}$: C, 72.12; H, 5.33. Found: C, 72.13; H, 5.28.

Preparation of *trans*-Bis(dinitrogen)bis[1,2-bis(diphenylphosphino)ethane]molybdenum(0) (2). To a stirred solution of 4.0 g (10.2 mmol) of molybdenum(III) acetylacetonate and 8.1 g (20.4 mmol) of 1,2-bis(diphenylphosphino)ethane in 60 ml of toluene was added 8.3 ml (60.4 mmol) of triethylaluminum at −40° under nitrogen. The color of the solution immediately changed from reddish brown to dark brown. The temperature was gradually raised to ambient temperature and the solution was stirred for about 5 days with bubbling nitrogen gas into the mixture. Then some of the orange N_2 complex precipitated. When 25 ml of *n*-hexane was added to the solution, an additional quantity of the orange complex was deposited. The precipitate was filtered, washed several times with *n*-hexane or ether, and dried *in vacuo*. The complex was recrystallized from toluene–*n*-hexane, yield 1.3 g (13%). *Anal.* Calcd for $\text{C}_{52}\text{H}_{48}\text{N}_4\text{P}_4\text{Mo}$: C, 65.83; H, 5.10; N, 5.91. Found: C, 65.35; H, 5.38; N, 6.31.

Preparation of *trans*-Bis(dinitrogen)bis[1,3-bis(diphenylphosphino)propane]molybdenum(0). The complex was prepared as above, except that 1,3-bis(diphenylphosphino)propane was used instead of 1,2-bis(diphenylphosphino)ethane, yield 4%. *Anal.* Calcd for $\text{C}_{54}\text{H}_{52}\text{N}_4\text{P}_4\text{Mo}$: C, 66.40; H, 5.37; N, 5.74. Found: C, 65.19; H, 5.15; N, 5.77.

Preparation of *trans*-Dihydridobis[1,2-bis(diphenylphosphino)ethane]molybdenum(II) (3). All operations were carried out under hydrogen or argon. To a stirred solution of 1.687 g (4.29 mmol) of molybdenum(III) acetylacetonate and 3.43 g (8.58 mmol) of 1,2-bis(diphenylphosphino)ethane in 30 ml of benzene was added 2.9 ml (23 mmol) of triethylaluminum at −40° under hydrogen. The temperature was gradually raised to ambient temperature and hydrogen gas was bubbled through the mixture at that temperature over a period of 5 days. Then some of the yellow hydride complex precipitated. The addition of 20 ml of *n*-hexane to the mixture deposited an additional quantity of the complex. The precipitate was filtered, washed several times with *n*-hexane, and dried *in vacuo*. The complex was recrystallized from benzene–*n*-hexane, yield 0.51 g (13%). *Anal.* Calcd for $\text{C}_{52}\text{H}_{50}\text{P}_4\text{Mo}$: C, 69.80; H, 5.63. Found: C, 68.68; H, 5.72.

Preparation of μ-1,2-Bis(diphenylphosphino)ethane-bis[*trans*-dihydrido-1,2-bis(diphenylphosphino)ethanemolybdenum(II)] (4). The hydride complex was prepared as above, except that toluene was used as the solvent in place of benzene. Recrystallization of the complex from toluene–*n*-hexane gave pale yellow needles, yield 22%. *Anal.* Calcd for $\text{C}_{78}\text{H}_{76}\text{P}_6\text{Mo}$: C, 67.34; H, 5.51. Found: C, 68.06; H, 5.88.

Reaction of the Bis(dinitrogen) Complex 2 with Hydrogen. (1) Reaction in Benzene. Hydrogen gas was bubbled through a stirred solution of 0.135 g (0.142 mmol) of *trans*-$\text{Mo(N}_2)_2\text{(DPE)}_2$ (**2**) in 15 ml of benzene over a period of 3 days. The solution turned yellow and a yellow solid precipitated. Recrystallization of the precipitate from benzene–*n*-hexane gave *trans*-$\text{MoH}_2\text{(DPE)}_2$ (**3**) as yellow crystals, yield 0.064 g (50%)

(2) Reaction in Tetrahydrofuran. The reaction was carried out as above, except that tetrahydrofuran was used as the solvent instead of benzene. The hydride complex *trans*-$\text{MoH}_2\text{(DPE)}_2$ (**3**) was obtained from the solution, yield 42%.

(3) Reaction in Toluene. The reaction was carried out as above, except that toluene was used as the solvent in place of benzene. The binuclear hydride complex [*trans*-$\text{MoH}_2\text{(DPE)}]_2$-$\mu$-(DPE) (**4**) was obtained as pale yellow needles, yield 55%. *Anal.* Calcd for $\text{C}_{78}\text{H}_{76}\text{P}_6\text{Mo}_2$: C, 67.34; H, 5.51; N, 0. Found: C, 67.71; H, 5.61; N, 0.0.

Mutual Conversion of Molybdenum Hydride Complexes. (1) Conversion of the Hydride Complex 3 to the Hydride Complex 4. *trans*-$\text{MoH}_2\text{(DPE)}_2$ (**3**) (0.0415 g, 0.046 mmol) was dissolved in 8 ml of toluene under argon. Addition of 8 ml of *n*-hexane gave the hydride complex [*trans*-$\text{MoH}_2\text{(DPE)}]_2$-$\mu$-(DPE) (**4**), yield 0.016 g (48%).

(2) Conversion of the Hydride Complex 4 to the Hydride Complex 3. [*trans*-$\text{MoH}_2\text{(DPE)}]_2$-$\mu$-(DPE) (**4**) (0.0488 g, 0.035 mmol) was dissolved in 8 ml of benzene under argon. The solution turned reddish brown. Addition of 8 ml of *n*-hexane to the solution gave the hydride complex *trans*-$\text{MoH}_2\text{(DPE)}_2$ (**3**), yield 0.030 g (62%).

Reaction of the Hydride Complex 4 with Carbon Tetrachloride. A suspension of 0.0816 g (0.059 mmol) of [*trans*-$\text{MoH}_2\text{(DPE)}]_2$-$\mu$-(DPE) (**4**) and 0.25 ml of CCl_4 in 0.5 ml of toluene was stirred for 24 hr under argon. The solution was analyzed by gas chromatography which showed the presence of a trace of chloroform. The mixture was evaporated to dryness and the residue showed an ir band at 1745 cm^{-1} due to *trans*-$\text{MoH}_2\text{(DPE)}_2$ (**3**). Recrystallization of the solid from benzene–*n*-hexane afforded 0.030 g (0.033 mmol)

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of *trans*-$MoH_2(DPE)_2$ (**3**) and 0.010 g of a brownish yellow complex. The structure of the latter complex is yet uncertain. *Anal.* Found: C, 64.86; H, 5.44; Cl, 9.51.

Reactions of Molybdenum Hydride Complexes with Nitrogen. (1) Reaction of the Hydride Complex 3 with Nitrogen. Nitrogen gas was bubbled into a stirred solution of 0.075 g (0.083 mmol) of *trans*-$MoH_2(DPE)_2$ (**3**) in 15 ml of benzene at ambient temperature for 3 days. After addition of 10 ml of *n*-hexane, yellow crystals of the unreacted hydride complex **3** were precipitated. The crystals were filtered off and the filtrate was concentrated to a volume of *ca* 5 ml under a reduced pressure. Addition of 5 ml of *n*-hexane to the solution gave *trans*-$Mo(N_2)_2(DPE)_2$ (**2**) as orange crystals, yield 0.010 g (13%).

(2) Reaction of the Hydride Complex 4 with Nitrogen. The reaction was carried out as above, except that toluene was used as the solvent instead of benzene. Most of the hydride complex remained unreacted, but a small amount of *trans*-$Mo(N_2)_2(DPE)_2$ (**2**) was obtained, yield 11%.

Reaction of the Bis(dinitrogen) Complex 2 with Trihydridotris(triphenylphosphine)cobalt(III). (1) Reaction in Benzene. To a stirred solution of 0.119 g (0.125 mmol) of *trans*-$Mo(N_2)_2(DPE)_2$ (**2**) in 6 ml of benzene was added a solution of 0.120 g (0.142 mmol) of $CoH_3(PPh_3)_3$ in 6 ml of benzene at ambient temperature under argon. The reaction mixture turned gradually dark. A small amount of dark brown solid precipitated with evolution of nitrogen and hydrogen gas. The mixture was stirred for 3 days. The infrared spectrum of the solution showed two bands at 2088 and 1980 cm^{-1} assignable to the N–N stretching frequencies of $CoH(N_2)(PPh_3)_3$ and *trans*-$Mo(N_2)_2(DPE)_2$ (**2**), respectively. After removal of the dark brown precipitate by filtration, 10 ml of *n*-hexane was added to the filtrate. Then yellow crystals were deposited in addition to a small amount of orange crystals of the unreacted N_2 complex **2**. The yellow complex was recrystallized from benzene–*n*-hexane, giving the pure hydride complex *trans*-$MoH_2(DPE)_2$ (**3**) as yellow crystals, yield 0.020 g (18%). *Anal.* Calcd for $C_{52}H_{50}P_4Mo$: C, 69.80; H, 5.63; N, 0. Found: C, 69.53; H, 6.15; N, 0.0. However, the dinitrogen–cobalt complex $CoH(N_2)(PPh_3)_3$ could not be isolated from the solution.

(2) Reaction in Toluene. The reaction was carried out as above, except that toluene was used instead of benzene as the solvent. The infrared spectrum of the mixture showed the formation of the dinitrogen–cobalt complex $CoH(N_2)(PPh_3)_3$, but the complex was not isolated. However, the hydride complex [*trans*-$MoH_2(DPE)]_2$-μ-(DPE) (**4**) was isolated from the solution, yield 25%.

Reactions of Dinitrogen–Molybdenum Complexes with Carbon Monoxide. (1) Reaction of the Dinitrogen–Molybdenum Complex 1 with Carbon Monoxide. Through a stirred suspension of 0.314 g of $Mo(N_2)(PPh_3)_2 \cdot C_6H_5CH_3$ (**1**) in 80 ml of toluene was bubbled carbon monoxide at ambient temperature for 17 days. The mixture turned gradually red and became almost homogeneous. The unreacted N_2 complex **1** was filtered off and the red filtrate was concentrated to a volume of *ca.* 25 ml under a reduced pressure. Addition of 25 ml of *n*-hexane to the solution deposited orange crystals, which were filtered, washed several times with *n*-hexane, and dried *in vacuo*, yield 0.150 g (55%). *Anal.* Calcd for $C_{37}H_{30}OP_2Mo$: C, 68.52; H, 4.66; N, 0. Found: C, 67.17; H, 4.77; N, 0.0.

(2) Reaction of the Bis(dinitrogen) Complex 2 with Carbon Monoxide. Through a stirred solution of 0.120 g (0.126 mmol) of *trans*-$Mo(N_2)(DPE)_2$ (**2**) in 15 ml of toluene was bubbled carbon monoxide at ambient temperature for 4 days. Addition of 15 ml of methanol to the solution gave pale yellow crystals as well as the unreacted bis(dinitrogen) complex **2**. The pale yellow complex was washed several times with methanol and dried *in vacuo*, yield 0.025 g (21%). *Anal.* Calcd for $C_{54}H_{48}O_2P_4Mo$: C, 68.36; H, 5.10; N, 0. Found: C, 68.63; H, 5.27; N, 0.0.

The infrared spectrum of the pale yellow complex showed two strong bands at 1855 and 1785 cm^{-1} assignable to $\nu_{C\equiv O}$ (lit.[21] 1852 and 1786 cm^{-1}).

Preparation of *trans*-Tetracarbonylbis(triphenylphosphine)molybdenum(0) and *cis*-Dicarbonyltetrakis(triphenylphosphine)molybdenum(0). To a stirred solution of 0.723 g (1.84 mmol) of molybdenum(III) acetylacetonate and 4.840 g (18.4 mmol) of triphenylphosphine in 35 ml of toluene was added 2.2 g (11.1 mmol) of triisobutylaluminum at $-40°$ under argon. The temperature was gradually raised to ambient temperature and carbon monoxide was bubbled into the reaction mixture for 30 min at that temperature. Addition of 30 ml of *n*-hexane to the solution gave *cis*-$Mo(CO)_2(PPh_3)_4$ as brownish yellow crystals. The complex was filtered, washed with *n*-hexane, and dried *in vacuo*, yield 0.02 g (0.9%). *Anal.* Calcd for $C_{74}H_{60}O_2P_4Mo$: C, 74.00; H, 5.04. Found: C, 73.40; H, 5.48.

The filtrate was concentrated under reduced pressure to a volume of 30 ml. Addition of 20 ml of *n*-hexane to the solution gave *trans*-$Mo(CO)_4(PPh_3)_2$ as a pale yellow solid. The complex was washed with *n*-hexane and dried *in vacuo*, yield 0.120 g (8.9%). *Anal.* Calcd for $C_{40}H_{30}O_4P_2Mo$: C, 65.56; H, 4.13. Found: C, 65.31; H, 4.51.

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The Structure of the 7,7′-*commo*-Bis[dodecahydro-7-nickela-*nido*-undecaborate] Dianion

L. J. Guggenberger

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Abstract: The crystal structure of tetramethylammonium 7,7′-*commo*-bis[dodecahydro-7-nickela-*nido*-undecaborate](2−), $[(CH_3)_4N]_2Ni(B_{10}H_{12})_2$, was determined by single crystal X-ray techniques. Crystals are monoclinic, space group $P2_1/c$, with $a = 7.34$ (1), $b = 11.97$ (2), $c = 15.73$ (2) Å, and $\beta = 93.8$ (1)°. There are two formula units per cell with observed and calculated densities of 1.09 g/cm^3. The structure was refined by least-squares to an R of 0.096. The anion has $C_i(\bar{1})$ space group imposed molecular symmetry. The nickel atom bonds to eight boron atoms and fuses two 11-atom polyhedral fragments giving two chemically different Ni–B distances of 2.23 and 2.15 Å. All the hydrogen atoms were located and refined. The two nonterminal hydrogen atoms bridge edge positions of the open pentagonal faces of the borane polyhedron. Extended Hückel molecular orbital calculations on the $Ni(B_{10}H_{12})_2$ dianion show that the primary metal bonding comes from the 4s atomic orbital of nickel.

A variety of transition metal derivatives of $B_{10}H_{12}{}^{2-}$ have been prepared recently.[1] Complexes reported are of the type $M(B_{10}H_{12})_2{}^{2-}$ (M = Co, Ni, Pd, Pt), $M(B_{10}H_{12})(PR_3)_2$ (M = Pd, Pt), and $M(B_{10}H_{12})L_3{}^-$ (M = Co, Rh, Ir). Greenwood and Travers have also reported $M(B_{10}H_{12})_2{}^{2-}$ complexes of zinc, cadmium,

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