Earlier attempts have been made to prepare nitrosyl complexes of cobalt and ruthenium porphyrins by passing the nitric oxide into solutions of cobalt(II) and carbonyl derivatives of ruthenium(II) porphyrins in organic solvents, which on isolation gave unstable and ill-defined products.[9-11] We wish to report the preparation, isolation, and characterization of (mesoporphyrin IX dimethyl esterato)dinitrosylruthenium(II) which to our knowledge is the first well-characterized nitrosylmetalloporphyrin.

The dinitrosyl derivative of ruthenium(II) mesoporphyrin IX dimethyl ester (A) was prepared by treating a well-stirred solution of carbonyl derivative of ruthenium(II) mesoporphyrin IX dimethyl ester[12] (35 mg) in benzene (60 ml) under argon with slightly more than 2 equiv of nitric oxide[13] to give the dinitrosyl derivative. The completion of reaction was determined by visible spectroscopy. The final solution was concentrated *in vacuo* and the complex precipitated with hexane. The precipitate was separated from the mother liquor by centrifugation, washed several times with hexane, and dried under vacuum. The dried solid was dissolved in chloroform (containing 0.75% ethyl alcohol) and crystallized from chloroform–ethyl alcohol in air. The crystals were washed with hexane and dried at 78° under vacuum for 1 hr. The complex A has mp ~245°. *Anal.* Calcd for Ru(NO)$_2$MPIXDME,[14] $C_{36}H_{40}N_6O_6Ru$: C, 57.29; H, 5.35; Ru, 13.40. Found: C, 56.36; H, 5.38; Ru, 13.17. Further support of this formulation has come from its mass spectrum which shows a parent peak at *m/e* 755 (M) and other important peaks at *m/e* 725 (M − NO), 695 (M − 2NO), and 30 (NO). However, no peak corresponding to *m/e* 28 (CO) was observed. The infrared spectrum (1600–2000 cm$^{-1}$) of complex A in the solid state (Nujol mull) showed two strong nitrosyl bands at 1786 and 1838 cm$^{-1}$ and carbonyl stretch of ester of the porphine at 1731 cm$^{-1}$. In methylene chloride solution, it showed one strong band at 1735 cm$^{-1}$ and another at 1853 cm$^{-1}$, assigned to nitrosyl groups and ester carbonyl stretch of MPIXDME, respectively.[15] The splitting of a nitrosyl band into two at 1786 and 1838 cm$^{-1}$ in the solid is probably due to a solid-state effect. The visible absorption spectrum of A in benzene has peaks at 396 (Soret band), 537 (I), and 572 (II) (relative intensity, II > I). The proton magnetic resonance (pmr) spectrum in CDCl$_3$ containing 1% tetramethylsilane showed a typical spectrum of mesoporphyrin IX dimethyl ester coordinated to a diamagnetic ion. Magnetic susceptibility measurements[16] on A confirmed its diamagnetism.

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[9] B. C. Chow and I. A. Cohen, *Bioinorg. Chem.*, 1, 57 (1971).

[10] L. M. Hoffman, Ph.D. Dissertation, New York University, 1970. The nitrosyl derivative of Ru$^{II}$MPIXDME was formulated as Ru(NO)$_2$MPIXDME on the basis of chemical analysis, but the per cent of Ru in the complex was found to be low.

[11] Co$^{II}$TPP (in CH$_2$Cl$_2$) and NO give a complex Co$^{II}$(NO)TPP (TPP is *meso*-tetraphenylporphine): W. R. Scheidt and J. L. Hoard, private communication.

[12] M. Tsutsui, D. Ostfeld, and L. M. Hoffman, *J. Amer. Chem. Soc.*, 93, 1820 (1971).

[13] Nitric oxide was used after passing through a trap which was cooled by Dry Ice–acetone slush.

[14] MPIXDME is the abbreviation of mesoporphyrin IX dimethyl ester.

[15] *Cf.* the carbonyl derivative of Ru$^{II}$MPIXDME showed one carbonyl stretch band at 1940 cm$^{-1}$ and another due to ester carbonyl stretch at 1740 cm$^{-1}$ in solution. However, in the solid state, the infrared spectrum (KBr) showed two bands of ester carbonyl stretch at 1690 and 1740 cm$^{-1}$ and another carbonyl stretch at 1916 cm$^{-1}$. In the solid, the sixth coordination site, trans to carbonyl group, is probably occupied by an ester carbonyl of porphine and the band at 1690 cm$^{-1}$ is assigned to the coordinated ester: M. Tsutsui, D. Ostfeld, and L. Hoffman, *J. Amer. Chem. Soc.*, 93, 1820 (1971).

[16] D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

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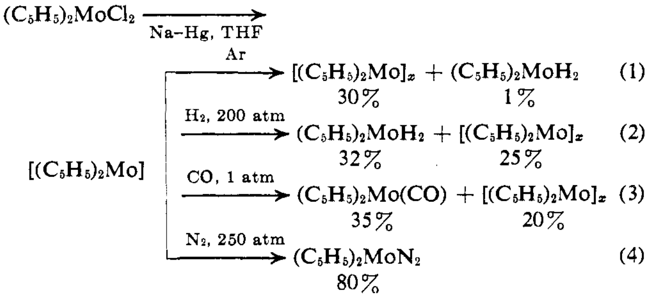
## Molybdenocene as an Intermediate in Reactions with Hydrogen, Nitrogen, and Carbon Monoxide

*Sir:*

In our attempts to study new coordinatively unsaturated species, we have tried to prepare the hitherto unknown sandwich compound molybdenocene by reduction of bis(cyclopentadienyl)molybdenum(IV) dichloride. While the monomeric species $(C_5H_5)_2Mo^{II}$ was not isolated, we have obtained evidence for its occurrence as a transient, highly reactive intermediate.

The reduction of $(C_5H_5)_2MoCl_2$ by sodium amalgam in tetrahydrofuran (THF) under argon yields two isolatable products, the known dihydride $(C_5H_5)MoH_2$ and a novel compound $[(C_5H_5)_2Mo]_x$, which crystallizes from the reaction mixture as a sparingly soluble, red-brown solid. $[(C_5H_5)_2Mo]_x$ is characterized by a singlet at τ 5.50 in its nmr spectrum; its ir spectrum shows only those absorptions typical of π-bound metallocenes.[1] These data, a low vapor pressure, and low solubility in solvents like THF or toluene indicate the presence of a polymeric or dimeric structure containing regular $(h^5\text{-}C_5H_5)_2Mo$ units. In accord with this, the mass spectrum of the compound shows a strong parent peak at *m/e* 460 for $[(C_5H_5)_2Mo]_2^+$ and a very intense *m/e* 230 peak for $[(C_5H_5)_2Mo]^+$,[2] indicating that $[(C_5H_5)_2Mo]_2$ and possibly also $(C_5H_5)_2Mo$ are present in the vapor phase at about 200°. At ambient temperatures solid $[(C_5H_5)_2Mo]_x$ shows little reactivity except for a noticeable air sensitivity.

Whereas any primarily generated $[(C_5H_5)_2Mo]$ appears either to rapidly polymerize to inert $[(C_5H_5)_2Mo]_x$ or to form $(C_5H_5)_2MoH_2$ by hydrogen abstraction from the solvent, a variety of products is obtained if $[(C_5H_5)_2Mo]$ is generated in the presence of reactive gases (eq 1–4). Oxidative addition of hydrogen to the inter-



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[1] H. P. Fritz, *Advan. Organometal. Chem.*, 1, 239 (1964).

[2] All molybdenum-containing ions showed the expected isotopic distribution; for simplicity only ions monoisotopic for $^{100}Mo$ and $^{12}C$ are reported.

mediate $[(C_5H_5)_2Mo]$ gives $(C_5H_5)_2MoH_2$ in high yields.[3] This type of addition is similar to that occurring with $[(C_5H_5)_2Ti]$,[4–6] another electron-deficient molecule, except that in the molybdenocene system there is no indication of a reversible formation of the metallocene by loss of $H_2$ from the dihydride. The reactive molybdenocene monomer may be trapped also with carbon monoxide to yield a novel, bright green molybdenocene monocarbonyl, $(C_5H_5)_2Mo(CO)$. This compound is also obtained, although in lower yields, by a butyllithium reduction of $(C_5H_5)_2MoCl_2$ in THF solution in the presence of CO. $(C_5H_5)_2Mo(CO)$ is characterized by a single sharp nmr absorption at $\tau$ 5.65, a single sharp carbonyl stretching absorption at 1905 $cm^{-1}$, and a mass spectrum with peaks at $m/e$ 258 and 230, corresponding to $[(C_5H_5)_2Mo(CO)]^+$ and $[(C_5H_5)_2Mo]^+$.[2]

The molybdenocene intermediate also coordinates 1 equiv of $N_2$ (eq 4). When the reduction of $(C_5H_5)_2MoCl_2$ is performed under a pressure of 250 atm of $N_2$, the autoclave containing the reaction vessel cooled to $-78°$, and the reaction mixture warmed to room temperature on a vacuum line, close to 1 mol of $N_2$/mol of molybdenocene is recovered. The thermal instability of this complex has thus far thwarted a structural characterization.

In an attempt to more fully characterize the molybdenocene system, bis(pentamethylcyclopentadienyl)molybdenum dichloride was prepared in a manner similar to that described for $(C_5H_5)_2MoCl_2$.[7] Upon sodium amalgam reduction of $(C_5(CH_3)_5)_2MoCl_2$ under argon, a bright yellow crystalline decamethylmolybdenocene species was obtained. The mass spectrum of the compound shows its highest mass peak at $m/e$ 370 corresponding to $[(C_5(CH_3)_5)_2Mo]^+$. Freezing point depressions measured in benzene yield a molecular weight of 740, in accord with the presence of $[(C_5(CH_3)_5)_2Mo]_2$ in these solutions.[8] The absence of a dimer peak in the mass spectrum is probably due to a weak and readily cleaved molybdenum–molybdenum bond in the decamethyl-substituted dimer.[9]

The reactivity of $[(C_5(CH_3)_5)_2Mo]_2$ with $H_2$ and CO far exceeds that of the relatively inert unsubstituted $[(C_5H_5)_2Mo]_x$ (eq 5, 6). Both products have been fully

$$[(C_5(CH_3)_5)_2Mo]_2 \left[ \begin{array}{ll} \xrightarrow[\text{toluene, } 20^\circ]{H_2,\ 200\text{ atm}} (C_5(CH_3)_5)_2MoH_2 & (5) \\ \qquad\qquad 85\% & \\ \xrightarrow[\text{toluene, } 20^\circ]{CO,\ 1\text{ atm}} (C_5(CH_3)_5)_2Mo(CO) & (6) \\ \qquad\qquad 67\% & \end{array} \right.$$

characterized by nmr, ir, and mass spectral data and will be described in detail in a later communication. The fact that the *in situ* reactions of the $[(C_5H_5)_2Mo]$ intermediate are reproduced by the compound $[(C_5(CH_3)_5)_2Mo]_2$ indicates again that the monomer $(C_5(CH_3)_5)_2Mo$ is relatively easily available from the dimer. The higher reactivity of $[(C_5(CH_3)_5)_2Mo]_2$ as compared to that of $[(C_5H_5)_2Mo]_x$ is also demonstrated in that the methyl-substituted dimer reacts reversibly with molecular nitrogen in toluene (eq 7). Even the dry crys-

$$[(C_5(CH_3)_5)_2Mo]_2 \underset{\text{vacuum}}{\overset{N_2,\ 250\text{ atm}}{\rightleftharpoons}} (C_5(CH_3)_5)_2MoN_2 \tag{7}$$

talline powder of $[(C_5(CH_3)_5)_2Mo]_2$ reacts with nitrogen at 250 atm to yield a product that evolves 1 equiv of $N_2$/equiv of molybdenum upon warming to room temperature under vacuum; as a solid, the nitrogen complex $(C_5(CH_3)_5)_2MoN_2$ is somewhat more stable than in solution. Its structural characterization is presently being undertaken, together with similar studies on $(C_5H_5)_2W$ derivatives.[10,11]

The postulated intermediate $[(C_5H_5)_2Mo]$ exhibits a striking analogy of its reaction patterns to those of a carbene. Similar observations were reported earlier for the titanium analog $[(C_5H_5)_2Ti]$.[6] The reducibility of $N_2$ in $(C_5H_5)_2Ti–N_2–Ti(C_5H_5)_2$ as opposed to the lack of such a reactivity in $(C_5H_5)_2Mo–N_2$, and the implication of these findings for the respective roles of 14- and 16-electron species in $N_2$ reduction reactions, will be the subject of further reports.

**Acknowledgment.** These investigations were supported by a grant (GP 19421) from the National Science Foundation.

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[3] Under the reaction conditions of eq 2 (20°, 200 atm), $H_2$ does not react with the polymerization product $[(C_5H_5)_2Mo]_x$.

[4] J. E. Bercaw and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **93**, 2045 (1971).

[5] R. H. Marvich and H. H. Brintzinger, *ibid.*, **93**, 2046 (1971).

[6] J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *ibid.*, **94**, 1219 (1972).

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

[8] A solution in toluene-$d_8$ exhibits an nmr spectrum with ten equivalent and ten inequivalent methyl groups which can be interpreted as being due to a sterically hindered dimer.

[9] An increased tendency of the permethyl derivative to form a monomeric species is also observed in the titanocene system. See ref 6.

[10] The occurrence of $(C_5H_5)_2W$ as a reaction intermediate in alkane eliminations from $(C_5H_5)_2WHR$ has also been postulated recently by B. R. Francis, M. L. H. Green, and G. G. Roberts, *Chem. Commun.*, 1290 (1971).

[11] $(C_5H_5)_2WH_2$ and the novel compounds $(C_5H_5)_2W(CO)$ and $[(C_5H_5)_2W]_x$ are obtained under conditions analogous to those described above: J. L. Thomas, unpublished results.

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## Solvent Dependence in the Photochemical Dimerization and $[_\pi2_a + {}_\sigma2_a]$ Rearrangement of a Bridged 3,5-Cycloheptadienone[1]

*Sir:*

We wish to report the unique solvent-dependent competition between intramolecular $[_\pi2_a + {}_\sigma2_a]$ rearrangement and intermolecular dimerization which occurs in the photochemistry of the tropone–cyclopentadiene [6 + 4] adduct **1**,[2] which incorporates both $\beta,\gamma$-unsaturated ketone and diene moieties.

Direct photolysis of $\beta,\gamma$-unsaturated ketones generally results in [1s,3s] sigmatropic shifts, while sensitized photolysis of these ketones results in $[_\pi2_a + {}_\sigma2_a]$ rearrangements.[3] Conjugated dienes, in which

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[1] Photochemistry of Tricyclo[4.4.1.1$^{2,5}$]dodeca-3,7,9-trienes. II. Part I: K. N. Houk and D. J. Northington, *J. Amer. Chem. Soc.*, **93**, 6693 (1971).

[2] (a) R. C. Cookson, B. V. Drake, J. Hudec, and A. Morrison, *Chem. Commun.*, 15 (1966); (b) S. Ito, Y. Fujise, T. Okuda, and Y. Inoue, *Bull. Chem. Soc. Jap.*, **39**, 135 (1966).

[3] For recent discussions, see: (a) R. S. Givens, W. F. Oettle, R. L. Coffin, and R. G. Carlson, *J. Amer. Chem. Soc.*, **93**, 3957, 3963 (1971); (b) D. I. Schuster, G. R. Underwood, and T. P. Knudsen, *ibid.*, **93**, 4304 (1971).