$(Et_3Si)_3Sb$,[16b] and bismuth derivatives, $(Ph_3Si)_3Bi$,[16a] have also been shown to react with 1,2-dibromoethane to give ethylene, along with the corresponding metal and $R_3MBr$ (M = Si or Ge). A concerted mechanism has also been suggested recently for the reaction of mercurials.[12]

We propose, however, a free-radical chain mechanism for the reaction of organodisilanes with 1,2-dibromoethane that involves the attack of a bromine atom on the Si–Si bond.[17] Bromine atoms are generated from β-bromoethyl radicals, which are in turn derived from 1,2-dibromoethane by bromine abstraction with the silyl radicals.

$$\mathrm{Br\cdot + R_3SiSiR_3 \longrightarrow BrSiR_3 + R_3Si\cdot} \tag{5}$$

$$\mathrm{R_3Si\cdot + BrCH_2CH_2Br \longrightarrow R_3SiBr + \cdot CH_2CH_2Br} \tag{6}$$

$$\mathrm{\cdot CH_2CH_2Br \longrightarrow CH_2{=}CH_2 + Br\cdot} \tag{7}$$

The following facts support the mechanism. Although hexamethyldisilane, one of the most reactive organodisilanes, did not undergo reaction with 1,2-dibromoethane, even after prolonged heating without initiators in the dark at 90°, a small amount of BPO catalyzed the reaction markedly, an apparent kinetic chain length being estimated as 80–100. Irradiation with a 450-W high-pressure mercury arc lamp also initiated the reaction slowly. Since even in the presence of BPO, galvinoxyl[18] inhibits the reaction completely, this is strongly indicative of the free-radical nature of the reaction. The reaction can be carried out in benzene and in cyclohexane, but in carbon tetrachloride no such bond cleavage occurs. This is rationalized by considering a competing chlorine abstraction from carbon tetrachloride by silyl radicals,[19] the resulting trichloromethyl radical being capable only of dimerizing under the present reaction conditions.

$$\mathrm{R_3Si\cdot + CCl_4 \longrightarrow R_3SiCl + CCl_3\cdot} \tag{8}$$

$$\mathrm{2CCl_3\cdot \longrightarrow Cl_3CCCl_3} \tag{9}$$

An alternative mechanism may be considered that involves a low concentration of bromine produced by the decomposition of 1,2-dibromoethane. Subsequently, bromine may react with disilanes to cleave the silicon–silicon bond. The slow production of

$$\mathrm{Br\cdot + BrCH_2CH_2Br \longrightarrow Br_2 + \cdot CH_2CH_2Br} \tag{10}$$

$$\mathrm{Br_2 + Me_3SiSiMe_3 \longrightarrow 2Me_3SiBr} \tag{11}$$

bromine in a similar system has been suggested in the bromine-sensitized photochemical decomposition of 1,2-dibromotetrachloroethane.[20] However, a bromine

$$\mathrm{Br\cdot + BrCCl_2CCl_2Br \longrightarrow Br_2 + \cdot CCl_2CCl_2Br} \tag{12}$$

atom could not abstract bromine from 1,2-dibromoethane because it would be endothermic by 35 kcal[21] and thus reaction 10 cannot be an effective propagation step in the long chain. Furthermore, bromine ought to cleave not only the silicon–silicon bond but also the phenyl–silicon bond(s) when phenyl-substituted disilanes (**1d–h**) are subjected to the reaction; however, no such cleavage of phenyl groups was observed with these compounds. In fact, treatment of **1h** with bromine resulted in phenyl–silicon rather than silicon–silicon cleavage,[22] while the present reaction yielded diphenylmethylbromosilane almost quantitatively.

Hexamethyldigermane behaves quite similarly to **1a** and hence we believe that free trimethylgermyl radicals[23] are also key intermediates.

$$\mathrm{Br\cdot + Me_3GeGeMe_3 \longrightarrow Me_3GeBr + Me_3Ge\cdot} \tag{13}$$

$$\mathrm{Me_3Ge\cdot + BrCH_2CH_2Br \longrightarrow Me_3GeBr + \cdot CH_2CH_2Br} \tag{14}$$

Finally we note that these reactions are also useful in synthetic organosilicon chemistry. Thus, bromosilanes such as dimethylbromosilane and methyldiphenylbromosilane, which are difficult or at least tedious to prepare by other methods, can be obtained easily in high yield.[24]

The structure of disilanes and their reactivity will be discussed in a forthcoming paper.

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[23] (a) L. Kaplan, *Chem. Commun.*, 106 (1969); (b) H. Sakurai and K. Mochida, *ibid.*, 1581 (1971) (c) H. Sakurai, K. Mochida, A. Hosomi, and F. Mita, *J. Organometal. Chem.*, in press.

[24] However, when chlorine-substituted disilanes were subjected to the reaction, the redistribution of halogens (Cl–Br exchange) on silicon occurred rapidly under the condition. Accordingly, pure bromochlorosilanes are still difficult to prepare by this method.

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## Unusual Metalloporphyrins IX. Preparation of a New (Mesoporphyrin IX dimethyl esterato)dinitrosylruthenium(II)

*Sir:*

There has been considerable biological interest in the interaction of nitric oxide with ferro- or ferriheme,[1,2] ferro- or ferrihemochromes,[1,3] as well as iron–porphyrin bound to proteins.[1,3,4] Magnetic measurements on a nitric oxide derivative of hemoglobin[5] have shown that this complex has only one unpaired electron, whereas NO–ferricytochrome c was shown to be diamagnetic.[6] Recently esr solution spectroscopy has shown that nitric oxide derivatives of ferrihemochrome,[3] hemoglobin,[3,7] myoglobin,[3] and ferrocytochrome c[3,8] have one unpaired electron.

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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 $\sim$245°. *Anal.* Calcd for $Ru(NO)_2MPIXDME$,[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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[10] L. M. Hoffman, Ph.D. Dissertation, New York University, 1970. The nitrosyl derivative of $Ru^{II}MPIXDME$ was formulated as $Ru(NO)_2MPIXDME$ 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 $CH_2Cl_2$) 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).

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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 $\tau$ 5.50 in its nmr spectrum; its ir spectrum shows only those absorptions typical of $\pi$-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-

$$(C_5H_5)_2MoCl_2 \xrightarrow[\text{Na-Hg, THF}]{}$$

$$[(C_5H_5)_2Mo]\ \left|\begin{array}{ll}
\xrightarrow{\text{Ar}} \underset{30\%}{[(C_5H_5)_2Mo]_x} + \underset{1\%}{(C_5H_5)_2MoH_2} & (1)\\
\xrightarrow{\text{H}_2\text{, 200 atm}} \underset{32\%}{(C_5H_5)_2MoH_2} + \underset{25\%}{[(C_5H_5)_2Mo]_x} & (2)\\
\xrightarrow{\text{CO, 1 atm}} \underset{35\%}{(C_5H_5)_2Mo(CO)} + \underset{20\%}{[(C_5H_5)_2Mo]_x} & (3)\\
\xrightarrow{\text{N}_2\text{, 250 atm}} \underset{80\%}{(C_5H_5)_2MoN_2} & (4)
\end{array}\right.$$

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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.