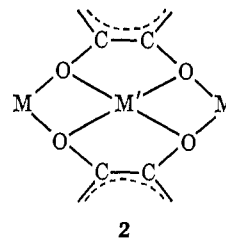


Figure 1. View of $\text{Mo}_2(\text{O}_2\text{C}_6\text{Cl}_4)_6$ down the twofold axis of the molecule. Ring chlorine atoms have been omitted.

complexes. Spectral properties of the complex suggest a highly symmetric coordination geometry of D_3 or higher symmetry. Structurally, $\text{Cr}(\text{O}_2\text{C}_6\text{Cl}_4)_3$ is iso-electronic with 1,2-dithiolene complexes known to possess trigonal prismatic (D_{3h}) coordination geometries.⁹ If effects which stabilize this geometry with related S and Se donor ligands are significant in the present case, a D_{3h} molecular structure is expected. The electrochemical properties of $\text{Cr}(\text{O}_2\text{C}_6\text{Cl}_4)_3$, however, are quite different from similar 1,2-dithiolene complexes. Neutral complexes of related sulfur donor ligands readily undergo reversible reduction reactions with the S analog of the present complex $\text{Cr}(\text{S}_2\text{C}_6\text{Cl}_4)_3$ undergoing reduction to complexes with charges of -1 , -2 , and -3 .¹⁰ The oxidation reactions observed for $\text{Cr}(\text{O}_2\text{C}_6\text{Cl}_4)_3$ are more similar to the oxidation of $\text{M}(\text{PPh}_3)_2(\text{O}_2\text{C}_6\text{Cl}_4)$, $\text{M} = \text{Pd}, \text{Pt}$.¹¹ Balch has recently reported the chemical and electrochemical formation of $[\text{M}(\text{PPh}_3)_2(\text{O}_2\text{C}_6\text{Cl}_4)]^+$ with evidence to show that the unpaired electron is localized mainly on the partially reduced *o*-benzoquinone ligand. Thus, oxidation of $\text{Cr}(\text{O}_2\text{C}_6\text{Cl}_4)_3$ probably involves oxidation of the reduced benzoquinone ligands. It is surprising that reduction of the Cr(VI) metal ion is not observed.

The properties of $\text{Mo}(\text{O}_2\text{C}_6\text{Cl}_4)_3$ and $\text{W}(\text{O}_2\text{C}_6\text{Cl}_4)_3$ are mutually similar and indicate much lower symmetry than the Cr analog. The preliminary results of a crystallographic study on the Mo complex show this to be the case.¹² The molecule is dimeric with crystallographic C_2 symmetry. Each Mo atom is chelated by two terminal $\text{C}_6\text{Cl}_4\text{O}_2^{2-}$ ligands and bonded to one oxygen of two bridging ligands (Figure 1) with a distorted octahedral coordination geometry about the metal. The bridging ligands bond to the metals through outer electron pairs of the oxygen donors creating a puckered 10-membered $\text{Mo}_2\text{O}_4\text{C}_4$ ring. The inner donor orbitals normally used for chelated coordination are available for coordination to an additional metal at the center of the ring, 2. However, attempts to prepare such a compound have, so far, been unsuccessful. The effects resulting in the preferred dimeric configuration of the



2

complex over a monomeric molecule of either D_3 or D_{3h} symmetry are not clear but appear related to the restrictive chelate bite of the *o*-benzoquinone ligand.

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New Transition Metal Derivatives of the Triborohydride Ion and the First Example of Reversible Bidentate-Tribidentate Borane Ligand Functionality

Sir:

In recent years there has been a great deal of interest in the preparation of metal derivatives of the triborohydride ion, B_3H_8^- .¹⁻⁴ We wish to report here the preparation of several new neutral transition metal triborohydride derivatives and to illustrate the previously unknown fact that the B_3H_8^- group can function as both a bidentate and a tridentate ligand.

Salts of B_3H_8^- react with equimolar quantities of $\text{Mn}(\text{CO})_5\text{Br}$ or $\text{Re}(\text{CO})_5\text{Br}$ in CH_2Cl_2 solvent at room temperature to produce the volatile yellow liquids $(\text{CO})_4\text{-MnB}_3\text{H}_8$ and $(\text{CO})_4\text{-ReB}_3\text{H}_8$, respectively, in good yield. For example, $(\text{CH}_3)_4\text{NB}_3\text{H}_8$ and $\text{Mn}(\text{CO})_5\text{Br}$ react to form a 76% yield of $(\text{CO})_4\text{-MnB}_3\text{H}_8$ in 69 hr. Reaction of $(\text{CH}_3)_4\text{NB}_3\text{H}_8$ with $\text{Re}(\text{CO})_5\text{Br}$ requires ultraviolet radiation to produce a 43% yield in 27 hr. The yellow $(\text{CO})_4\text{-MnB}_3\text{H}_8$ is purified by high-vacuum distillation through a trap at -10° and condensation in a trap at -36° . The rhenium complex is a colorless liquid which is purified by distillation through a 0° trap and condensation in a -30° trap. The composition of each of these products was confirmed by mass spectrometry. The following parent fragment ions were identified: $(\text{CO})_4\text{-MnB}_3\text{H}_8$, ($^{12}\text{C}^{16}\text{O}$)₄⁵⁵ $\text{Mn}^{11}\text{B}_3^1\text{H}_8$, found 208.0086 (calcd 208.0083); $(\text{CO})_4\text{-ReB}_3\text{H}_8$, ($^{12}\text{C}^{16}\text{O}$)₄¹⁸⁷ $\text{Re}^{11}\text{B}_3^1\text{H}_8$, found 340.0256 (calcd 340.0262); ($^{12}\text{C}^{16}\text{O}$)₄¹⁸⁷ $\text{Re}^{11}\text{B}_3^1\text{H}_6$, found 338.0109 (calcd 338.0105); ($^{12}\text{C}^{16}\text{O}$)₄¹⁸⁵ $\text{Re}^{11}\text{B}_3^1\text{H}_6$, found 336.0078 (calcd 336.0075). The loss of each of the four carbonyls is observed for both of these complexes. The infrared spectra of these two species are almost identical. For example the prominent gas phase absorptions from $(\text{CO})_4\text{-MnB}_3\text{H}_8$

(1) (a) F. Klanberg and L. J. Guggenberger, *Chem. Commun.*, 1293 (1967); (b) F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *Inorg. Chem.*, **7**, 2272 (1968); (c) L. J. Guggenberger, *ibid.*, **9**, 367 (1970).

(2) (a) S. J. Lippard and D. A. Ucko, *Inorg. Chem.*, **7**, 1051 (1968); (b) S. J. Lippard and K. M. Melmed, *ibid.*, **8**, 2755 (1969); (c) E. L. Muetterties, W. G. Peet, P. A. Wegner, and C. W. Alegranti, *ibid.*, **9**, 2447 (1970); (d) H. Beall, C. H. Bushweller, W. J. Dewkett, and M. Grace, *J. Amer. Chem. Soc.*, **92**, 3484 (1970); (e) C. H. Bushweller, H. Beall, M. Grace, W. Dewkett, and H. Bilofsky, *J. Amer. Chem. Soc.*, **93**, 2145 (1971).

(3) J. Borlin and D. F. Gaines, *J. Amer. Chem. Soc.*, **95**, 1367 (1972).

(4) (a) A. R. Kane and E. L. Muetterties, *J. Amer. Chem. Soc.*, **93**, 1041 (1971); (b) L. J. Guggenberger, A. R. Kane, and E. L. Muetterties, *ibid.*, **94**, 5665 (1972).

(9) R. Eisenberg, *Prog. Inorg. Chem.*, **12**, 925 (1970).

(10) E. J. Wharton and J. A. McCleverty, *J. Chem. Soc. A*, 2258 (1969).

(11) A. L. Balch, *J. Amer. Chem. Soc.*, **95**, 2723 (1973).

(12) Crystallographic data are: $C_{2h}^2-C_2/c$; $\rho_{\text{calcd}} = 1.833$, $\rho_{\text{exptl}} = 1.83$ (1) g/cm^3 ; $Z = 4$ for $\text{Mo}_2(\text{O}_2\text{C}_6\text{Cl}_4)_6 \cdot 3\text{C}_6\text{H}_6$; $a = 22.450$ (3), $b = 11.592$ (3), $c = 27.303$ (3) Å; $\beta = 104.27$ (5)°. The conventional R factor obtained from the full-matrix least-squares refinement of 2891 reflections measured on a Picker diffractometer is currently 0.065.

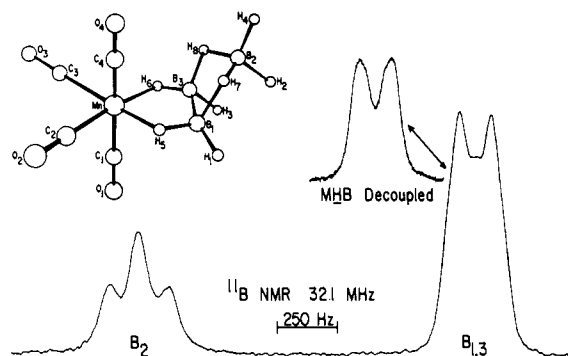


Figure 1. The ^{11}B nmr spectrum of $(\text{CO})_4\text{MnB}_3\text{H}_8$ in $(\text{C}_2\text{H}_5)_2\text{O}$. Chemical shifts in ppm relative to $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ are -0.4 (B_2) and $+42.2$ ($\text{B}_{1,3}$).

are the following: 2570 (m) and 2505 (w) [$\text{B}-\text{H}_{\text{terminal}}$]; 2215(w), 2155(m), 2060(s), and 2015(s) [carbonyl]; 1830(w) cm^{-1} [BHB].

An iron derivative has also been prepared in 86% yield by ultraviolet irradiation of equimolar mixtures of $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ and $(\text{CH}_3)_4\text{NB}_3\text{H}_8$ in CH_2Cl_2 at room temperature for 3 hr. This iron complex, $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{B}_3\text{H}_8$ (mp $53\text{--}54^\circ$), is easily purified by sublimation at room temperature and 10^{-4} Torr. Loss of only one carbonyl was observed in the mass spectrum and identification of the parent ion, $(\pi\text{-}^{12}\text{C}_5\text{H}_5)^{56}\text{Fe}(^{12}\text{C}\text{-}^{16}\text{O})^{11}\text{B}_3\text{H}_8$, gave the following result, found 190.0599 (calcd 190.0595). The infrared spectrum of this complex (KBr pellet) exhibits the following characteristic absorbances: 2520(m), 2475(m), and 2440(w, sh) [$\text{B}-\text{H}_{\text{terminal}}$]; 2175 (w) [BHB ?]; 1990 (s) cm^{-1} [carbonyl].

The structures of these new metalloborane complexes were elucidated by infrared and ^1H and ^{11}B nmr spectroscopy. The ^1H and ^{11}B nmr spectra provide conclusive evidence for the structure and bonding in these complexes. The ^{11}B nmr spectra of these metalloboranes are almost identical (see Figure 1), consisting of a low field triplet of area 1 and a more complex high field group of area 2. This indicates the presence of one BH_2 group and two BH groups per molecule. That the triborohydride unit is bonded to the metal through hydrogen was confirmed in part by selectively decoupling the $\text{M}-\text{H}-\text{B}$ hydrogens and observing that the shape of the upfield group changes to a broad doublet. The ^1H nmr spectra are likewise very similar for these complexes and indicate the presence of five distinct hydrogen environments, most important of which is the resonance far upfield from tetramethylsilane of intensity 2 which is assigned to the hydrogens bridging between the metal and the adjacent boron atoms⁵ (Figure 2).⁶ For $(\text{CO})_4\text{MnB}_3\text{H}_8$, $(\text{CO})_4\text{ReB}_3\text{H}_8$, and $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{B}_3\text{H}_8$ the presence of two well-separated absorptions in the $\text{B}-\text{H}_{\text{terminal}}$ region of the low resolution infrared spectrum also implies (but does not demand) the presence of a BH_2 group on each of these complexes.

The fact that these three complexes are rigid on the

(5) For previous examples see J. W. Lott, D. F. Gaines, H. Shenhav, and R. Schaeffer, *J. Amer. Chem. Soc.*, **95**, 3042 (1973); D. F. Gaines, J. W. Lott, and J. C. Calabrese, *J. Chem. Soc., Chem. Commun.*, 295 (1973).

(6) The doublet-like appearance of this resonance is a result of the rather broad line widths compared to the coupling constant to ^{11}B ($I = 3/2$) and to the contribution from coupling to ^{10}B [20%, $I = 3$, $J(\text{H}-^{10}\text{B}) \sim 0.33 J(\text{H}-^{11}\text{B})$].

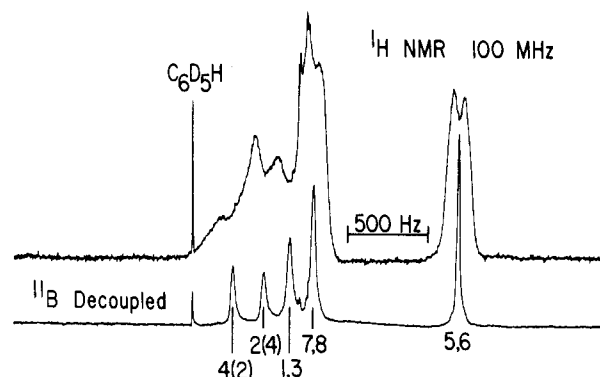
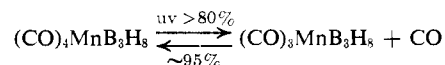


Figure 2. The ^1H nmr spectrum of $(\text{CO})_4\text{ReB}_3\text{H}_8$ in C_6D_6 . Chemical shifts in τ units relative to tetramethylsilane are 5.32 (H_4 or H_2), 7.26 (H_2 or H_4), 7.79 ($\text{H}_{1,3}$), 10.26 ($\text{H}_{7,8}$), and 19.26 ($\text{H}_{5,6}$). The numbering system is as shown in Figure 1.

nmr time scale (at ambient probe temperature) is intriguing. Of the previously studied metal B_3H_8^- derivatives only the $(\text{CO})_4\text{MB}_3\text{H}_8^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) species appear to be rigid (but fine structure in the ^{11}B nmr spectra of these anions was not observed as it is in the ^{11}B nmr of these new neutral metalloboranes).¹ Complexes of the type $(\text{R}_3\text{P})_2\text{PtB}_3\text{H}_7$ also appear to be rigid, but the bonding is quite different from that in the complexes reported here.⁴

These new metalloborane complexes undergo several interesting reactions, the most important of which involves the loss of one carbonyl from $(\text{CO})_4\text{MnB}_3\text{H}_8$ to produce $(\text{CO})_3\text{MnB}_3\text{H}_8$. This transformation is carried out by exposing the $(\text{CO})_4\text{MnB}_3\text{H}_8$ to ultraviolet light either in the gas phase or in CH_2Cl_2 solution at room temperature. The $(\text{CO})_3\text{MnB}_3\text{H}_8$ reacts with excess carbon monoxide in CH_2Cl_2 solvent to regenerate the $(\text{CO})_4\text{MnB}_3\text{H}_8$. Thus the equilibrium below has been established

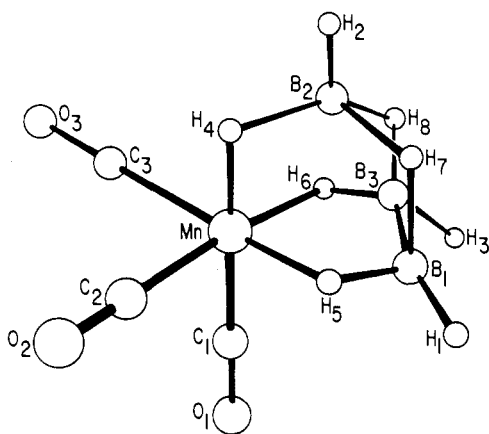


The yellow liquid, $(\text{CO})_3\text{MnB}_3\text{H}_8$, is slightly more volatile than $(\text{CO})_4\text{MnB}_3\text{H}_8$ but isolation of $(\text{CO})_3\text{MnB}_3\text{H}_8$ free of $(\text{CO})_4\text{MnB}_3\text{H}_8$ impurity is very difficult to achieve. One can obtain $(\text{CO})_3\text{MnB}_3\text{H}_8$ in greater than 90% purity by many short term distillations through a -36° trap or by using a specially designed low temperature distillation column.⁷ Mass spectral characterization of $(\text{CO})_3\text{MnB}_3\text{H}_8$ included identification of the parent ion $(^{12}\text{C}^{16}\text{O})_3^{55}\text{Mn}^{11}\text{B}_3\text{H}_8$, found 180.0131 (calcd 180.0134). Prominent gas phase infrared absorptions for $(\text{CO})_3\text{MnB}_3\text{H}_8$ are the following: 2575(m) [$\text{B}-\text{H}_{\text{terminal}}$]; 2090 (s), 1990 (s), and 1970 (w) [carbonyl]; 1880 (m) cm^{-1} [BHB]. The presence of only one absorption in the $\text{B}-\text{H}(\text{terminal})$ stretching region of the infrared spectrum suggests that no BH_2 groups are present.⁸ The ^{11}B nmr spectrum of $(\text{CO})_3\text{MnB}_3\text{H}_8$ consists of a single resonance at $+47.1$ ppm relative to $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$. The spectrum is temperature dependent with unresolved fine structure noted at about 0° . This fine structure decreases as the temperature is raised or

(7) D. F. Gaines, design to be submitted for publication.

(8) As a general rule the low resolution gas phase infrared spectrum of a compound possessing a BH_2 group contains two (or more) moderately strong, well-separated, absorptions in the $\text{B}-\text{H}(\text{terminal})$ region (2400–2600 cm^{-1}), while most compounds containing only $\text{B}-\text{H}(\text{terminal})$ groups exhibit a single absorption in this region. See W. J. Lehman, *et al.*, *Advan. Chem. Ser.*, No. 32, 139 (1961).

lowered. Upon decoupling ^1H , a single very narrow resonance is observed, indicating magnetic equivalence of all three boron atoms. The ^1H nmr spectrum of this complex consists of a broad signal of intensity 5 at τ 10.1 and a somewhat narrower signal of intensity 3 at τ 21.6. Decoupling ^{11}B results in narrowing of these two broad resonances to sharp singlets. The presence of three protons far upfield from tetramethylsilane suggests that the B_3H_8^- ion is bound to the metal through three Mn-H-B bridge hydrogen bonds. The presence of a single type of hydrogen at lower field suggests that the hydrogens that are not involved in Mn-H-B bridge bonding are magnetically equivalent, most likely as a result of rapid intramolecular exchange (on the nmr timescale) around the periphery of the B_3 triangle. Such exchange would also render the three boron atoms magnetically equivalent, as observed. Thus this new type of complex can be considered to be partially, or selectively, nonrigid. More important, however, this complex appears to be the first example in which the B_3H_8^- ion acts as a tridentate ligand. The proposed static structure for $(\text{CO})_3\text{MnB}_3\text{H}_8$ is shown below.



Further studies of these and related new metal metalloboranes and their reactions are in progress and will be reported more fully later.

Acknowledgments. This work was supported in part by a grant from the National Science Foundation. S. J. H. thanks the E. I. du Pont de Nemours & Co. for a 1973 Summer Research Assistantship. The nmr and mass spectral facilities were provided in part by institutional grants from the National Science Foundation.

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Photochemical Rearrangement of 4,4-Disubstituted-4-sila-2,5-cyclohexadienones

Sir:

Reports of photochemical skeletal rearrangements of silicon heterocycles are rare,¹ especially when compared

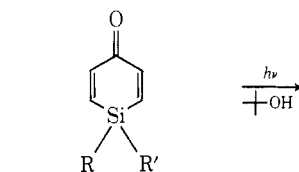
(1) The only photorearrangements of silicon heterocycles are the Norrish type I cleavages of silacyclohexan-2-ones and the ring contraction of 1,2,3-trisilacycloheptanes. M. Ishikawa and M. Kumada, *Chem. Commun.* 612 (1970); A. G. Brook, H. W. Kucers, and R. Pearce, *Can. J. Chem.*, **49**, 1618 (1971); A. G. Brook, R. Pearce, and J. B. Pierce, *ibid.*, **49**, 1622 (1971); H. Sakurai, Y. Kobayashi, and Y. Nakadaira, *J. Amer. Chem. Soc.*, **93**, 5272 (1971).

with the numerous photorearrangements of carbocycles and oxygen and nitrogen heterocycles. We wish to report a novel photochemical ring contraction of a silicon heterocycle to a carbocycle, the photorearrangement of 4,4-disubstituted-4-sila-2,5-cyclohexadienones to cyclopentenone derivatives.

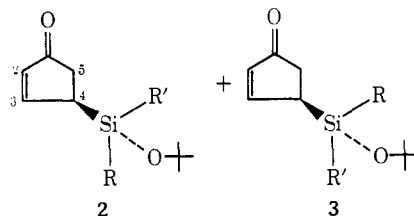
4,4-Dimethyl-4-sila-2,5-cyclohexadienone (**1a**) and 4,4-diphenyl-4-sila-2,5-cyclohexadienone (**1b**) were prepared by oxidation of the corresponding saturated ketones with DDQ as described by Felix and Weber.² 4-Methyl-4-phenyl-4-sila-2,5-cyclohexadienone (**1c**) was prepared by an analogous procedure.^{2,3} Grignard reaction of allylmagnesium bromide with dichloromethylphenylsilane gave 4-methyl-4-phenyl-4-sila-1,6-heptadiene. Hydroboration-oxidation of the diene followed by Jones oxidation, esterification, Diekmann cyclization, decarboxylation, and DDQ oxidation gave the desired dienone **1c**⁴ in 4% overall yield.

The three 4-sila-2,5-cyclohexadienone derivatives all have $n-\pi^*$ bands in the region of 350–400 nm. Consequently, the photoreactions were conducted in a Rayonet reactor equipped with 350-nm lamps. Additionally, the irradiation solutions were filtered with three concentric Pyrex filters to minimize light absorption by the photoproducts. With these irradiation conditions, 150-mg samples of the dienones in 100 ml of dry *tert*-butyl alcohol were irradiated under a nitrogen atmosphere for 2–3 hr, resulting in 65–70% destruction of dienones as indicated by glpc. Yields of isolated products based on starting materials destroyed were in the range of 20–40%. Photoproducts and unreacted starting materials were isolated by preparative glpc and medium pressure, silica gel, solid-liquid chromatography.

The photoproducts of **1a**, **1b**, and **1c** were characterized as 4-(*tert*-butoxydimethylsilyl)cyclopent-2-enone (**2a**), 4-(*tert*-butoxydiphenylsilyl)cyclopent-2-enone (**2b**), and two diastereoisomeric 4-(*tert*-butoxymethylphenylsilyl)cyclopent-2-enones (**2c** + **3c**), respectively, from



- 1a, R = R' = CH₃
b, R = R' = Ph
c, R = CH₃; R' = Ph



their spectroscopic data. The nmr spectra were recorded in the presence and absence of Euroshift F, tris-2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octane-

(2) R. A. Felix and W. P. Weber, *J. Org. Chem.*, **37**, 2323 (1972).

(3) W. P. Weber, R. A. Felix, and A. K. Willard, *J. Org. Chem.*, **36**, 4060 (1971).

(4) The structural assignment for **1c** is consistent with the following spectroscopic evidence: nmr (DCCl₂) δ 0.57 (3 H, s), 6.8–7.1 (4 H, m), and 7.15–7.65 ppm (5 H, m); ir 6.08, 6.31, 6.38, and 6.72 μ ; mass spectrum, m/e 200 (P, 29% of base).