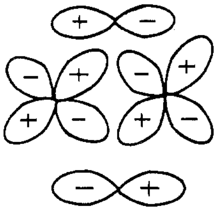
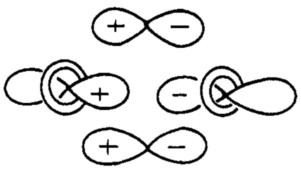


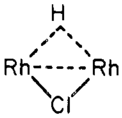
XIV



XV

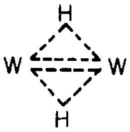
Thus, if we consider the sequence X = X′ = H; X = H, X′ = Cl; X = X′ = Cl, the maximum possible order of the metal-metal bond changes, sequentially, from 2 to 1 to 0.

We have previously published an account of the crystal structure of $[\pi\text{-}C_5(CH_3)_5RhCl]_2(\mu\text{-}H)(\mu\text{-}Cl)^{17}$ and have shown that the rhodium-rhodium distance in this molecule is 2.9064 (10) Å, which seems compatible with a *bonding* rhodium-rhodium interaction, particularly since the angle Rh-Cl-Rh′ is acute, with a value of 73.20 (6)°. [To our knowledge, there is no known Rh^{III}-Rh^{III} bond distance with which to compare the above value; however the Rh^{II}-Rh^{II} bond length in $[Ph_3P(dmg)_2Rh]_2$ is 2.936 Å.[33]] We regard the core of the $[\pi\text{-}C_5(CH_3)_5RhCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$ molecule as best written as in XVI.

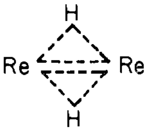


XVI

The present structural analysis of the $[H_2W_2(CO)_8{}^{2-}]$ ion and the study by Bennett, *et al.*, of $H_2Re_2(CO)_8{}^5$ each show metal-metal distances substantially below that accepted for single-bond lengths. The representation of the cores of these species by XVII and XVIII both illustrates the bridging nature of the hydride ligands and indicates pictorially that the metal-metal bond order may be greater than unity.



XVII



XVIII

Extension of this picture is both desirable and possible. Thus, both the species $[Re_2(CO)_6(\mu\text{-}H)_3{}^-]$ and $[Re_2(CO)_6(\mu\text{-}OEt)_3{}^-]$ are known.[34] A rather imprecise crystallographic study of $[Ph_4As^+][Re_2(CO)_6(OEt)_3{}^-]^{35}$ shows a (nonbonding) rhenium· · ·rhenium distance of ~3.17 Å. While no data are yet available, we would expect the rhenium-rhenium distance in the $[Re_2(CO)_6(\mu\text{-}H)_3{}^-]$ anion to be substantially shorter (perhaps as low as ~2.7-2.8 Å), since the maximum possible rhenium-rhenium bond order here is 3.

Acknowledgments. We are grateful to Professor A. Davison for providing the sample. This work was made possible by a generous allocation of computer time on an IBM 370/158 at the Computer Center, University of Illinois at Chicago Circle, and by financial support from the National Science Foundation (Grants GP-33018 and GP-42724X, to M. R. C.).

Registry No. $[Et_4N^+]_2[H_2W_2(CO)_8{}^{2-}]$, 52032-34-5.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-2413.

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[33] K. G. Caulton and F. A. Cotton, *J. Amer. Chem. Soc.*, **93**, 1914 (1971).

[34] A. P. Ginsberg and M. K. Hawkes, *J. Amer. Chem. Soc.*, **90**, 5930 (1968).

[35] M. R. Churchill, "Progress in Organometallic Chemistry," Proceedings of the Fourth International Conference on Organometallic Chemistry, Bristol, England, July 28–Aug 1, 1969, Paper A-13.

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A Metalloborane Zwitterion. Synthesis and X-Ray Crystal Structure of $8\text{-}[(C_2H_5)_3N(CH_2)_4O]\text{-}6\text{-}(CO)_3\text{-}6\text{-}MnB_9H_{12}$

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Reaction of $2\text{-THF-}6\text{-}(CO)_3\text{-}6\text{-}MnB_9H_{12}$ with Et_3N produces the title compound by a complex mechanism involving ether cleavage and an unusual internal rearrangement of the metalloborane cage. Its stereochemistry was determined from an X-ray analysis on crystals having the triclinic space group $P\bar{1}$ with cell parameters of $a = 10.018$ (2), $b = 12.843$ (3), $c = 9.305$ (2) Å; $\alpha = 99.661$ (15), $\beta = 94.545$ (14), $\gamma = 96.918$ (15)°; $Z = 2$; $\rho_{calcd} = 1.201$, $\rho_{exptl} = 1.207$ g cm^{-3}. Intensity data for 1803 independent reflections having $I > 2\sigma(I)$ were recorded at room temperature using monochromated Cu Kα radiation and a Syntex $P\bar{1}$ autodiffractometer. The structure was solved using conventional heavy-atom techniques and refined to $R_1 = 0.056$ and $R_2 = 0.061$. The structure is similar to that of $B_{10}H_{14}$, but with B(6) replaced by the Mn of the $Mn(CO)_3$ group. The coordination about the Mn is nearly octahedral, and the $\text{-}O(CH_2)_4N(Et)_3$ side chain is attached to the metalloborane cage at B(8) or B(10).

We recently reported[1] the existence of a new class of metalloboranes in which the borane ligands $B_9H_{13}{}^{2-}$ or $B_9H_{12}L^-$ (L = ethers) are bound to manganese or rhenium by a σ-bonding interaction and two equivalent MHB bridge hydrogen bonds. This combination of bonding interactions from the tridentate borane ligands is probably responsible

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[1] J. W. Lott and D. F. Gaines, *Inorg. Chem.*, **13**, 2261 (1974).

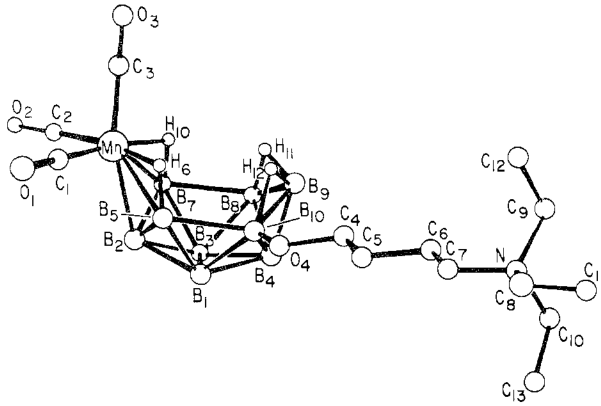

Figure 1. The solid-state structure of 10-[$(C_2H_5)_3N(CH_2)_4O$]-6-$(CO)_3$-6-MnB_9H_{12}. Terminal hydrogen atoms have been omitted on B_1–B_5, B_7–B_9, and C_4–C_{13}.

for the fact that these complexes exhibit unusual stability toward oxidation, hydrolysis, and thermal degradation when compared with most other metalloboranes.

A systematic study of the chemistry of these new metalloboranes has proved to be very interesting. In this report we will describe the results of an attempted ligand replacement reaction on 2-THF-6-$(CO)_3$-6-MnB_9H_{12}, using triethylamine as the replacement ligand.

Results and Discussion

Reaction of 2-THF-6-$(CO)_3$-6-MnB_9H_{12} with triethylamine (Et_3N) in refluxing tetrahydrofuran (THF) produces a good yield of a single product, I. The physical properties and spectral characteristics of I are very different from those expected if the THF on the starting material had been simply replaced by Et_3N. A single-crystal X-ray investigation of I was therefore undertaken in order to resolve its structure unequivocally.[2]

Structure Description. The unit cell of crystalline I contains centrosymmetrically related pairs of 8- and 10-[$(C_2H_5)_3N$-$(CH_2)_4O$]-6-$(CO)_3$-6-MnB_9H_{12} molecules. The molecular structure of I is shown in Figure 1, and interatomic distances and angles are listed in Tables I and II, respectively.

The structure may be described as that of a decaborane(14) cage derivative in which the manganese tricarbonyl moiety has replaced the B(6)-H group. The new substituent attached at the B(10) position results from attack of triethylamine on an α carbon atom of THF and subsequent opening of the ring. The new substituent is still bonded by a boron-oxygen bond to the borane cage. It should be noted that, since the crystal is composed of two centrosymmetrically related molecules per unit cell, the stereoisomers produced constitute a *d,l* pair, and B(8) in one stereoisomer is equivalent to B(10) in the other.

A pseudooctahedral environment about the manganese is maintained. Three nearly orthogonal carbonyl groups occupy three positions on one side of the central manganese and the boron cage occupies three positions on the other side. The borane is bound to the manganese by two Mn-H-B bridge bonds and a Mn-B(2) direct σ bond. The Mn-H and B-H distances in the Mn-H-B bridge bonds compare favorably with those found in other metalloboranes. The Mn-H distances in the Mn-H-B bridge bonds are 1.70 and 1.64 Å[3] compared to 1.83 and 1.67 Å for 5-THF-6-$(CO)_3$-6MnB_9H_{12}[1] and 1.71 and 1.73 Å found for the symmetric 2-THF-6-$(CO)_3$-6-MnB_9H_{12}.[4] In the complex $Mn_3(CO)_{10}(BH_3)_2H$,[5] the average Mn-H bridge hydrogen distance is 1.60 Å. The B-H distances in these Mn-H-B bridge bonds do not vary nearly as much and seem to be 1.15 ± 0.03 Å in all cases. The C(1)-Mn-C(2), C(2)-Mn-C(3), and C(1)-Mn-C(3) angles are 90.7, 93.3, and 93.0°, respectively, very close to values expected in an octahedral environment. The Mn-B distances to the three adjacent borons B(2), B(5), and B(7) are 2.216 (7), 2.209 (6), and 2.262 (7) Å, respectively, which are surprisingly similar except for a small distortion on the side

Table I. Interatomic Distances (Å)

Intramolecular Distances[a]

Mn–C(1)	1.791 (8)	B(8)–B(9)	1.801 (10)
Mn–C(2)	1.773 (7)	B(7)–H(7)	1.18
Mn–C(3)	1.793 (7)	B(8)–H(8)	1.06
Mn–B(2)	2.216 (7)	B(8)–H(11)	1.32
Mn–B(5)	2.209 (6)	B(9)–H(11)	1.21
Mn–B(7)	2.262 (7)	B(9)–H(9)	1.23
Mn–H(6)	1.64	B(9)–H(12)	1.17
Mn–H(10)	1.70	B(10)–H(12)	1.43
C(1)–O(1)	1.147 (7)	B(1)–H(1)	1.02
C(2)–O(2)	1.161 (7)	B(2)–H(2)	1.32
C(3)–O(3)	1.150 (6)	B(3)–H(3)	1.10
B(2)–B(1)	1.779 (9)	B(4)–H(4)	0.96
B(1)–B(3)	1.769 (9)	B(5)–H(5)	1.07
B(3)–B(2)	1.774 (9)	B(5)–H(6)	1.17
B(4)–B(1)	1.796 (9)	B(7)–H(10)	1.15
B(4)–B(3)	1.783 (9)	O(4)–B(10)	1.391 (7)
B(5)–B(1)	1.743 (9)	C(4)–O(4)	1.427 (6)
B(5)–B(2)	1.783 (9)	C(5)–C(4)	1.499 (7)
B(7)–B(2)	1.816 (10)	C(6)–C(5)	1.519 (8)
B(7)–B(3)	1.740 (9)	C(7)–C(6)	1.506 (7)
B(10)–B(1)	1.734 (10)	C(8)–C(11)	1.511 (7)
B(10)–B(4)	1.793 (9)	C(9)–C(12)	1.472 (8)
B(10)–B(5)	2.027 (9)	C(10)–C(13)	1.481 (8)
B(9)–B(4)	1.706 (10)	C(7)–N	1.533 (7)
B(9)–B(10)	1.811 (10)	N–C(8)	1.529 (6)
B(8)–B(3)	1.731 (10)	N–C(9)	1.519 (7)
B(8)–B(4)	1.768 (10)	N–C(10)	1.533 (7)
B(8)–B(7)	1.978 (9)		
C(4)–H(13)	0.99	C(9)–H(24)	1.04
C(4)–H(14)	1.00	C(10)–H(25)	1.11
C(5)–H(15)	1.04	C(10)–H(26)	0.89
C(5)–H(16)	1.00	C(11)–H(27)	1.07
C(6)–H(17)	0.98	C(11)–H(28)	0.90
C(6)–H(18)	0.96	C(11)–H(29)	0.97
C(7)–H(19)	1.04	C(12)–H(30)	0.87
C(7)–H(20)	1.00	C(12)–H(31)	0.99
C(8)–H(21)	0.91	C(13)–H(33)	1.00
C(8)–H(22)	1.08	C(13)–H(34)	1.09
C(9)–H(23)	0.94	C(13)–H(35)	0.96

Intermolecular Distances Less Than 3.9 Å[b]

O(1)–O(3)$^{\mathrm{I}}$	3.246 (7)	O(3)–C(4)$^{\mathrm{III}}$	3.520 (8)
O(1)–O(2)$^{\mathrm{I}}$	3.283 (6)	O(2)–C(9)$^{\mathrm{II}}$	3.531 (7)
O(3)–C(11)$^{\mathrm{IV}}$	3.309 (7)	O(3)–C(8)$^{\mathrm{IV}}$	3.538 (7)
O(2)–C(9)$^{\mathrm{III}}$	3.382 (8)	O(1)–C(10)$^{\mathrm{V}}$	3.561 (8)
O(1)–C(3)$^{\mathrm{I}}$	3.450 (8)	O(2)–C(12)$^{\mathrm{II}}$	3.593 (8)
O(2)–C(12)$^{\mathrm{III}}$	3.466 (8)	O(2)–C(11)$^{\mathrm{II}}$	3.583 (8)
O(1)–C(2)$^{\mathrm{I}}$	3.477 (7)		

[a] The estimated standard deviation in the last digit is given in parentheses. [b] The distances are given from the indicated atoms in one molecule to those in another molecule related by the following symmetry transformations: (I) $1 - x, -y, -z$; (II) $x, -1 + y, 1 + z$; (III) $1 - x, 1 - y, -z$; (IV) $1 - x, 1 - y, -1 - z$; (V) $x, -1 + y, z$.

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(2) For a preliminary report see D. F. Gaines, J. W. Lott, and J. C. Calabrese, *J. Chem. Soc., Chem. Commun.*, 295 (1973).

(3) Although hydrogen atomic coordinates were not varied in the least-squares analysis, estimated standard deviations of hydrogen-bond lengths are probably not less than 0.1 Å.

(4) J. W. Lott, D. F. Gaines, H. Shenhav, and R. Schaeffer, *J. Amer. Chem. Soc.*, **95**, 3042 (1973).

(5) H. D. Kaesz, W. Fellman, G. R. Wilkes, and L. F. Dahl, *J. Amer. Chem. Soc.*, **87**, 2753 (1965).

Table II. Bond Angles (deg) for Nonhydrogen Atoms

C(1)-Mn-C(2)	90.7 (3)	Mn-B(7)-B(2)	64.8 (3)
C(1)-Mn-C(3)	93.0 (3)	Mn-B(7)-B(3)	118.2 (4)
C(1)-Mn-B(2)	98.5 (3)	Mn-B(7)-B(8)	121.8 (4)
C(1)-Mn-B(5)	81.7 (3)	B(2)-B(7)-B(3)	59.8 (4)
C(1)-Mn-B(7)	144.8 (3)	B(3)-B(7)-B(8)	55.1 (4)
C(2)-Mn-C(3)	93.3 (3)	B(3)-B(8)-B(4)	61.3 (4)
C(2)-Mn-B(2)	97.7 (3)	B(3)-B(8)-B(7)	55.5 (4)
C(2)-Mn-B(7)	83.5 (3)	B(4)-B(8)-B(7)	108.4 (5)
C(3)-Mn-B(2)	164.0 (3)	B(4)-B(8)-B(9)	57.1 (4)
C(3)-Mn-B(5)	124.3 (3)	B(7)-B(8)-B(9)	118.7 (5)
C(3)-Mn-B(7)	122.6 (3)	B(4)-B(9)-B(10)	61.2 (4)
B(2)-Mn-B(5)	47.5 (2)	B(4)-B(9)-B(8)	60.5 (4)
B(2)-Mn-B(7)	47.8 (2)	B(10)-B(9)-B(8)	105.1 (5)
B(5)-Mn-B(7)	81.4 (2)	B(1)-B(10)-B(4)	61.2 (4)
B(2)-B(1)-B(3)	60.0 (4)	B(1)-B(10)-B(5)	54.5 (3)
B(2)-B(1)-B(4)	114.4 (5)	B(1)-B(10)-B(9)	108.1 (5)
B(2)-B(1)-B(5)	60.8 (4)	B(4)-B(10)-B(9)	56.5 (4)
B(4)-B(1)-B(10)	61.1 (3)	B(1)-B(10)-O(4)	124.0 (5)
Mn-B(2)-B(1)	118.6 (4)	B(4)-B(10)-B(5)	105.9 (4)
Mn-B(2)-B(5)	66.0 (3)	B(4)-B(10)-O(4)	132.1 (5)
Mn-B(2)-B(7)	67.4 (3)	B(5)-B(10)-B(9)	114.9 (4)
B(1)-B(2)-B(3)	59.7 (4)	B(5)-B(10)-O(4)	113.0 (5)
B(1)-B(2)-B(5)	58.6 (4)	B(9)-B(10)-O(4)	123.2 (5)
B(3)-B(2)-B(7)	58.0 (4)	C(7)-N-C(8)	106.8 (4)
B(5)-B(2)-B(7)	108.2 (5)	C(7)-N-C(9)	110.9 (4)
B(1)-B(3)-B(2)	60.3 (4)	C(7)-N-C(10)	110.4 (4)
B(1)-B(3)-B(4)	60.7 (4)	C(8)-N-C(9)	110.8 (4)
B(2)-B(3)-B(4)	115.2 (4)	C(8)-N-C(10)	110.9 (4)
B(2)-B(3)-B(7)	62.2 (4)	C(9)-N-C(10)	107.1 (4)
B(4)-B(3)-B(8)	60.4 (4)	Mn-C(1)-O(1)	178.4 (6)
B(7)-B(3)-B(8)	69.5 (4)	Mn-C(2)-O(2)	178.4 (5)
B(1)-B(4)-B(10)	57.8 (4)	Mn-C(3)-O(3)	178.7 (7)
B(3)-B(4)-B(8)	58.4 (4)	O(4)-C(4)-C(5)	110.4 (5)
B(10)-B(4)-B(9)	62.3 (4)	C(4)-C(5)-C(6)	110.9 (5)
B(9)-B(4)-B(8)	62.4 (4)	C(5)-C(6)-C(7)	109.9 (5)
B(1)-B(4)-B(3)	59.3 (4)	N-C(7)-C(6)	116.4 (4)
B(10)-B(4)-B(8)	107.3 (5)	N-C(8)-C(11)	114.4 (4)
Mn-B(5)-B(1)	120.7 (4)	N-C(9)-C(12)	114.6 (5)
Mn-B(5)-B(2)	66.5 (3)	N-C(10)-C(13)	115.8 (5)
Mn-B(5)-B(10)	124.6 (4)	B(10)-O(4)-C(4)	118.6 (4)
B(1)-B(5)-B(2)	60.6 (4)		
B(1)-B(5)-B(10)	54.1 (3)		

opposite to the substituent. The borane cage distances and angles closely resemble those in $B_{10}H_{14}$.[6]

In the previously determined X-ray structures of 2-THF-6-$(CO)_3$-6-MnB_9H_{12}[4] and 5-THF-6-$(CO)_3$-6-MnB_9H_{12},[1] the oxygen atoms of the complexed THF molecules were found in the plane defined by the α carbon atoms and the adjacent boron atom. The sum of the three angles about the oxygen atom was nearly 360°, suggesting an sp^2 environment. In the present case, attack of triethylamine allows displacement of positive charge from the oxygen of the THF to the nitrogen in the cleavage product, I. This results in shortening of the B-O distance from 1.520 (5) Å in the two isomers of the THF complex to 1.391 (7) Å in I. This latter distance is similar to the B-O distance of 1.37 (2) Å found in $Co_3(CO)_{10}$-$BH_2N(C_2H_5)_3$.[7] The sp^2 hybridization environment may still be present in I as the B-O-C angle is nearly 120°.

Spectral Discussion. The 100-MHz ^1H nmr (^{11}B-decoupled) spectrum of I is shown in Figure 2(A). An expanded ^1H spectrum of the CH region, shown in Figure 2(B), clearly exhibits the methyl and methylene triplet and quartet, respectively, for the triethylammonium moiety at τ 6.9 and 8.8. A ^1H spectrum with ^{14}N decoupled confirmed that the small coupling on the triplet was due to coupling to ^{14}N. The hydrogens on the butyl chain have been tentatively assigned as indicated in Figure 2(B) at τ 6.3 (2), 8.4 (4) and 6.9 (2) under the quartet (relative intensities in parentheses). In addition, there are two types of B-H-B bridge hydrogen resonances at τ 11.0 and 13.1 and two types of M-H-B bridge hydrogens at τ 20.8 and 21.8. Resonances at τ 9.3 and 10.6 arise from B-H terminal hydrogens.

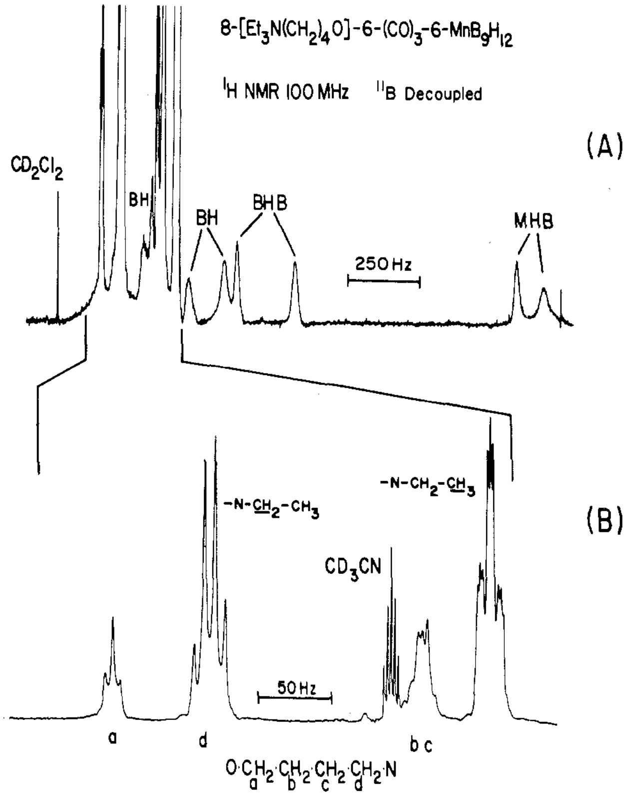

Figure 2. The ^1H nmr spectrum (100 MHz) of 8-$[(C_2H_5)_3N(CH_2)_4$-O]-6-$(CO)_3$-6-MnB_9H_{12}: (A) with ^{11}B decoupled; (B) with the C-H region expanded.

The additional ^1H nmr resonances for the opened tetrahydrofuran along with resonances for the ethyl groups on triethylamine were the first indications that I was an addition-cleavage rather than a substitution product. Further indications of an unusual structure were evident from the two different B-H-B and M-H-B bridge hydrogen resonances. These perturbations suggested substitution in the upper tier (B(5)-B(10)) of the B_9 cage. After-the-fact rationalization indicates that when different environments are observed for *both* sets of bridging hydrogens, substitution is likely to be at the 8(10) position. (It was previously found that substitution of the THF at the 5 and 7 positions perturbed only the M-H-B bridge hydrogens.)

The ^{11}B nmr (32.1 MHz, $BF_3{\cdot}OEt_2$ reference) spectrum of I is much more complex than that of the starting material. Decoupling ^1H allowed identification of a singlet and seven B-H doublets. With the successful refinement of this structure and several others in the series it is possible to assign the boron resonances in an internally consistent manner. Using decaborane as a model and assuming that the effect of the metal is to shift resonances of adjacent borons downfield and that the strongly charged side chains also shift boron resonances downfield, the resonances are tentatively assigned as follows: the singlet at −21.8 ppm arises from B(8) (or B(10) depending on the stereoisomer). The doublet

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(6) J. S. Kasper, C. M. Lucht, and D. Harker, *Acta Crystallogr.*, 3, 436 (1950).

(7) F. Klanberg, W. B. Askew, and L. J. Guggenberger, *Inorg. Chem.*, 7, 2265 (1968).

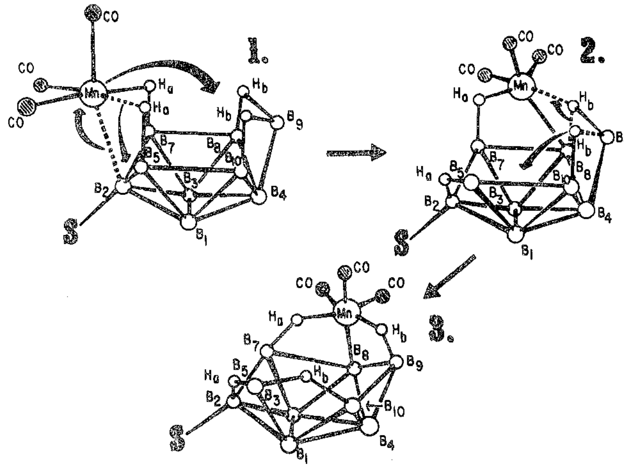

Figure 3. A possible rearrangement mechanism in the synthesis of 10-[$(C_2H_5)_3N(CH_2)_4O$]-6-$(CO)_3$-6-MnB_9H_{12}. The S designates the substituent. To illustrate the rearrangement the boron atom numbers are not changed from 1 to 3.

of intensity 2 at −14.8 ppm is ascribed to B(1) and B(3). The remaining doublets of unit intensity are assigned based on the B(8)-substituted isomer: B(5), 4.98; B(7), −1.1; B(10), 11.4; B(9), 13.4; B(2), 30.2; B(4), 36.0 ppm.

Rearrangement Mechanism. We propose that the formation of I is most likely an intramolecular rearrangement process that can be visualized as a shift of the $Mn(CO)_3$ moiety from its position in the starting material to an adjacent position, as shown in Figure 3. The sequence of events may reasonably be expected to be as follows. The strongly nucleophilic triethylamine attacks an α carbon of the tetrahydrofuran and initiates cleavage of the five-membered ring. During, or after, this process, the metalloborane rearranges. The rearrangement is then accomplished by a shift of the $Mn(CO)_3$ moiety along the upper tier of boron atoms as shown in part 2 of Figure 3. The Mn-B(2) bond and the Mn-H-B(5) bridge bond must first break; then the $Mn(CO)_3$ group shifts into the B(7)-B(8)-B(9) "corner" and the manganese reestablishes a Mn-B σ bond with B(8). The bridge hydrogens are shifted as illustrated so that the least amount of movement occurs. The shift illustrated in Figure 3 with the cleavage of the Mn-H-B(5) bridge gives the B(10)-substituted isomer. Cleavage of the Mn-H-B(7) bridge and rotation of the $Mn(CO)_3$ group onto the foreground borons would produce the B(8)-substituted isomer. The borons which initially were the B(7), B(8), and B(9) in the starting material become B(5), B(2), and B(7), respectively, in the product.

Experimental Section

Tetrahydrofuran, THF, was distilled from $LiAlH_4$ just prior to use. Triethylamine was distilled prior to use. The 2-THF-6-$(CO)_3$-6-MnB_9H_{12} was prepared as previously described.[1] Other solvents were reagent grade and were used as received.

The nmr spectra were obtained using a Varian XL-100 spectrometer at 100 and 32.1 MHz for ^1H and ^{11}B, respectively.

Synthesis of 8-[$(C_2H_5)_3N(CH_2)_4O$]-6-$(CO)_3$-6-MnB_9H_{12}, I. In a typical reaction, 0.266 g (0.82 mmol) of 2-THF-6-$(CO)_3$-6MnB_9H_{12} and excess $(C_2H_5)_3N$ (5 ml) were refluxed in THF for 3 hr in a nitrogen atmosphere. Purification of I was effected by elution from a Florisil liquid chromatography column with acetone. No material was eluted by solvents of lower polarity. The acetone was removed by evaporation leaving an oil, which was recrystallized from a dichloromethane–heptane mixture. The yield of purified product was 0.2146 g (0.51 mmol) or 62%; mp 156-169° dec.

Table III. Final Atomic Parameters for Compound I

	x	y	z
Mn	0.38938 (8)	0.18797 (7)	0.07082 (9)
C(1)	0.3278 (6)	0.0747 (6)	−0.0687 (7)
O(1)	0.2857 (5)	0.0033 (4)	−0.1589 (6)
O(2)	0.4272 (4)	0.0472 (4)	0.2843 (5)
O(3)	0.6689 (5)	0.1946 (4)	−0.0071 (5)
C(2)	0.4140 (6)	0.1037 (5)	0.2004 (7)
C(3)	0.5594 (8)	0.1907 (5)	0.0227 (7)
B(1)	0.1256 (7)	0.3357 (5)	0.0555 (7)
B(2)	0.1924 (7)	0.2331 (5)	0.1332 (7)
B(3)	0.1887 (7)	0.3597 (5)	0.2428 (7)
B(4)	0.1934 (7)	0.4685 (5)	0.1461 (7)
B(5)	0.2297 (6)	0.2575 (5)	−0.0434 (6)
B(7)	0.3330 (7)	0.2987 (5)	0.2655 (7)
B(8)	0.3324 (7)	0.4527 (6)	0.2661 (7)
B(9)	0.3515 (7)	0.5016 (5)	0.0974 (7)
B(10)	0.2271 (7)	0.4159 (5)	−0.0364 (8)
O(4)	0.1873 (4)	0.4408 (3)	−0.1719 (4)
N	0.1525 (4)	0.7945 (3)	−0.5572 (4)
C(4)	0.2197 (6)	0.5478 (5)	−0.1940 (6)
C(5)	0.1658 (6)	0.5588 (4)	−0.3449 (6)
C(6)	0.1943 (6)	0.6735 (5)	−0.3675 (6)
C(7)	0.1407 (6)	0.6821 (4)	−0.5203 (6)
C(8)	0.1075 (5)	0.7818 (4)	−0.7208 (5)
C(9)	0.2966 (5)	0.8506 (4)	−0.5216 (5)
C(10)	0.0630 (7)	0.8625 (5)	−0.4656 (6)
C(11)	0.1035 (6)	0.8857 (4)	−0.7757 (6)
C(12)	0.3981 (6)	0.7943 (5)	−0.5967 (6)
C(13)	−0.0847 (6)	0.8309 (4)	−0.5005 (7)
H(1)[a]	0.0254	0.3229	0.0178
H(2)	0.1053	0.1514	0.1503
H(3)	0.1345	0.3730	0.3412
H(4)	0.1375	0.5227	0.1725
H(5)	0.1758	0.2143	−0.1443
H(6)	0.3429	0.2500	−0.0610
H(7)	0.3524	0.2863	0.3875
H(8)	0.3625	0.5055	0.3672
H(9)	0.3878	0.5951	0.0905
H(10)	0.4263	0.2993	0.2018
H(11)	0.4267	0.4635	0.1762
H(12)	0.3701	0.4488	−0.0125
H(13)	0.3188	0.5659	−0.1806
H(14)	0.2178	0.6096	−0.1125
H(15)	0.0625	0.5336	−0.3516
H(16)	0.2112	0.5050	−0.4072
H(17)	0.2910	0.6988	−0.3426
H(18)	0.1459	0.7114	−0.2950
H(19)	0.1953	0.6392	−0.5940
H(20)	0.0437	0.6551	−0.5550
H(21)	0.1684	0.7407	−0.7603
H(22)	0.0056	0.7403	−0.7455
H(23)	0.3206	0.8539	−0.4208
H(24)	0.2971	0.9292	−0.5375
H(25)	0.0992	0.9430	−0.4875
H(26)	0.0868	0.8559	−0.3735
H(27)	0.1846	0.9504	−0.7593
H(28)	0.0817	0.8680	−0.8737
H(29)	0.0697	0.9515	−0.7375
H(30)	0.4447	0.7500	−0.5598
H(31)	0.4032	0.7791	−0.7043
H(32)	0.4778	0.8289	−0.6195
H(33)	−0.1420	0.8611	−0.4236
H(34)	−0.0957	0.7504	−0.4778
H(35)	−0.1478	0.8087	−0.5863

[a] The isotropic thermal parameter for each hydrogen atom was set at 6.0 Å^2.

The infrared spectrum of I was obtained as a KBr mull using a Perkin-Elmer 700 spectrophotometer. The following absorptions were observed (cm^{-1} ± 10 cm^{-1}): 3880 (m, b), 3420 (m, b), 2980 (m, sh), 2950 (m), 2860 (m, sh), 2530 (vs), 2490 (vs, sh), 2450 (vs, sh), 2005 (vvs), 1915 (vvs), 1485 (s), 1455 (s), 1395 (m), 1370 (w), 1210 (vs), 1165 (m, sh), 1095 (w), 1065 (w), 1010 (s), 935 (w), 860 (vs), 830 (w), 805 (m, sh), 795 (m, sh), 775 (s), 720 (w), 665 (m).

The electronic spectrum of I in CH_2Cl_2 contains maxima at 465 nm (ε 540) and 313 nm (ε 2770).

X-Ray Crystal Structure. The crystal chosen for the study was a platelike parallelepiped centrosymmetrically bounded by the (010), (10$\bar{1}$), and (1$\bar{1}$1) planes with dimensions 0.04 mm × 0.3 mm × 0.3

Table IV. Thermal Parameters for Nonhydrogen Atoms[a]

	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Mn	84 (1)	35 (1)	95 (2)	17 (1)	45 (1)	10 (1)
C(1)	127 (9)	60 (6)	102 (10)	28 (6)	−35 (8)	1 (7)
O(1)	213 (8)	65 (4)	186 (9)	38 (5)	−71 (7)	−47 (5)
O(2)	151 (7)	57 (4)	182 (8)	−3 (4)	−20 (6)	56 (5)
O(3)	117 (7)	85 (4)	208 (9)	23 (4)	65 (6)	27 (5)
C(2)	76 (8)	33 (5)	158 (11)	2 (5)	−13 (7)	17 (7)
C(3)	124 (10)	42 (5)	134 (11)	16 (6)	46 (9)	14 (6)
B(1)	86 (9)	41 (6)	76 (10)	8 (6)	4 (8)	2 (6)
B(2)	103 (10)	47 (6)	75 (10)	15 (6)	16 (8)	15 (6)
B(3)	106 (10)	46 (6)	63 (10)	16 (6)	24 (8)	8 (6)
B(4)	102 (9)	27 (5)	94 (11)	24 (6)	−1 (8)	4 (6)
B(5)	76 (8)	32 (5)	107 (10)	12 (5)	0 (7)	14 (6)
B(7)	92 (9)	42 (6)	92 (10)	18 (6)	16 (8)	15 (6)
B(8)	89 (9)	48 (6)	101 (11)	24 (6)	4 (8)	6 (7)
B(9)	100 (10)	44 (6)	104 (11)	23 (6)	7 (8)	16 (7)
B(10)	91 (9)	22 (5)	112 (12)	18 (6)	10 (8)	6 (7)
O(4)	131 (6)	46 (4)	87 (6)	26 (3)	3 (5)	27 (4)
N	94 (7)	26 (4)	69 (7)	9 (4)	−3 (5)	0 (4)
C(4)	143 (9)	38 (5)	114 (10)	11 (6)	−2 (8)	43 (6)
C(5)	114 (8)	43 (5)	101 (10)	18 (5)	14 (7)	28 (6)
C(6)	129 (9)	44 (5)	81 (9)	−1 (5)	−11 (7)	26 (5)
C(7)	125 (9)	23 (5)	86 (9)	12 (5)	−6 (7)	9 (5)
C(8)	95 (8)	43 (5)	60 (8)	17 (5)	−10 (6)	−6 (5)
C(9)	95 (8)	45 (4)	105 (8)	−7 (5)	−15 (7)	10 (5)
C(10)	151 (10)	39 (5)	82 (9)	19 (6)	−6 (8)	16 (5)
C(11)	148 (9)	25 (5)	98 (9)	−20 (5)	−5 (7)	23 (5)
C(12)	105 (9)	115 (7)	152 (10)	121 (6)	−3 (8)	41 (7)
C(13)	120 (10)	58 (6)	143 (11)	16 (6)	47 (8)	24 (6)

[a] Anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}lk)]$ were used for these atoms.

mm between the respective faces. The crystal was mounted approximately parallel to the (010) face on a glass fiber and carefully centered on a Syntex $P\bar{1}$ autodiffractometer equipped with graphite monochromated Cu Kα radiation. After accurate determination of 2θ, ω, and χ settings for 15 different maxima, the preliminary Syntex routines indicated that the material possessed triclinic symmetry C_i-$\bar{1}$ with cell parameters of $a = 10.018$ (2), $b = 12.843$ (3), $c = 9.305$ (2) Å; $\alpha = 99.661$ (15), $\beta = 94.545$ (14), $\gamma = 96.918$ (15)°; and $U = 1165.54$ (35) Å^3. Intensity data were collected in the usual θ–2θ scan mode with the takeoff angle of the tube set to 4°. A total of 3307 reflections in the four unique reciprocal octants (positive l) were measured in the range $5° < 2\theta < 90°$. During the collection of the data the two standard reflections, monitored after every 50 reflections, indicated no significant deviation of intensity. The data were reduced in the usual fashion[8] with a value of $0.003(I^2)$ introduced into the $\sigma(F)$ values to avoid overweighting the strong reflections in the least-squares analysis. The data were then merged to yield 1803 independent observations with $I > 2\sigma(I)$. Later, the data were also corrected to account for the rather large effects of crystal absorption. An absorption coefficient of $\mu = 49.76$ cm^{-1} combined with the shape of the crystal caused the transmission factors to vary from 0.29 to 0.82.

Solution and Refinement of Structure. The solution of the structure was accomplished by the standard heavy-atom method. The Patterson function[9] was easily interpreted in terms of one heavy atom assuming the centric space group $P\bar{1}$. Phasing with the one manganese ($R_1 = 37.9\%$) yielded the structure directly. The coordinates of the unexpected side chain were verified by a second Fourier map phased on the coordinates of the metal, carbonyl, and boron cage atoms only. A measurement of the density yielded a value of 1.207 g cm^{-3} compared to a calculated density of 1.201 g cm^{-3} for two molecules per unit cell, further verifying the correctness of the structure.

Several preliminary cycles of full-matrix least-squares refinement[10] of nonhydrogen atom coordinates with isotropic temperature factors reduced R_1 and R_2 to 0.126 and 0.156, respectively.[11] At this stage the data were corrected for absorption effects and ideal coordinates were calculated for all hydrogen atoms based on previously known geometries.[1] The ideal hydrogens were included as fixed isotropic (6.0 Å^2) atom contributions in further least-squares cycles with anisotropic thermal vibration for all 28 nonhydrogen atoms and including a correction for the anomalous scattering of manganese.[12] A final difference function, phased on nonhydrogen atoms only, revealed actual coordinates for all the hydrogens. These were included again as fixed-atom contributions in the final least-squares cycles reducing R_1 and R_2 to 0.056 and 0.061, respectively. Bond lengths and angles involving hydrogen atoms (Tables I, II) were calculated using the hydrogen coordinates obtained from the final difference Fourier.

Positional parameters appear in Table III; anisotropic thermal parameters for nonhydrogen atoms are listed in Table IV.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-2419.

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(8) V. A. Uchtman and L. F. Dahl, *J. Amer. Chem. Soc.*, 91, 3756 (1969).

(9) Programs used in the structure analysis included FOBS and SORTMERGE for data reduction; MAP, for all Fourier calculations; MIRAGE, for ideal coordinates, written by J. C. C.; DEAR, the J. F. Blount absorption correction program; ORFLS and ORFFE, the W. P. Busing, K. O. Martin, and H. A. Levy least-squares and error analysis programs; and ORTEP, the C. K. Johnson thermal ellipsoid plotting program. All initial calculations leading to the solution of the structure were performed on a Raytheon 706 computer (16k), while the remaining calculations (least squares, absorption corrections) were performed on a UNIVAC 1108 computer.

(10) All least-squares refinements were based on the minimization of $\Sigma w_i||F_o| - |F_c||^2$ with individual weights $w_1 = 1/\sigma(F_o)^2$. Atomic scattering factors used for all nonhydrogen atoms are from H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964); those for the hydrogen atoms are from R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(11) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w_i||F_o| - |F_c||^2/\Sigma w_i \cdot F_o|^2]^{1/2}$.

(12) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 215.