M represents the metal and the nonreacting ligands. NO*MNO could be either a transition state or an intermediate of increased coordination number. The occurrence of the reaction in the gas phase rather than on the wall of the container is substantiated by the invariance of the rate with increasing surface area. A mechanism with a rate-determining dissociation of a nitrosyl group followed by rapid incorporation of a molecule of NO is inconsistent with the dependence of the rate on the concentration of NO. Furthermore, the activation enthalpies are in the usual range of associative rather than dissociative reactions.[12] The rate dependence on NO concentration could be explained by a collision between NO and metal nitrosyl that leads to a vibrationally excited state of the latter. The mechanism can be eliminated, however, because the addition of large amounts of CO does not increase the reaction rate. This observation also eliminates rate-determining dissociation of a carbonyl group followed by a rapid exchange of nitrosyls, because CO and NO would be competing for the same active intermediate, and nitrosyl exchange would be retarded by added CO. Among the possible rationalizations of $(C_5H_5)NiNO$ inertness to nitrosyl exchange are, first, that negative charge on the cyclopentadienide strengthens the Ni–N bond *via* π bonding and, second, that the nickel compound cannot form a trigonal-bipyramidal transition state with the NO's in axial positions.

[12] S. Breitschaft and F. Basolo, *J. Am. Chem. Soc.*, **88**, 2702 (1966); S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 211–305.

CONTRIBUTION FROM THE SHIONOGI RESEARCH LABORATORY,
SHIONOGI & CO., LTD., FUKUSHIMA-KU, OSAKA, JAPAN

Amine-Catalyzed Hydrolysis of Bromomethylcarboranes

BY TAMOTSU YOSHIZAKI, MOTOO SHIRO, YUZO NAKAGAWA,
AND HARUYUKI WATANABE

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Zakharkin and Kalinin[1] described the facile degradation of 1,2-dicarba-*closo*-dodecaborane(12) (*o*-carborane) with piperidine to produce an adduct of piperidine with the piperidinium salt of dodecahydrodicarba-*nido*-undecaborate(1−). It was suggested that the piperidine molecule is loosely bound to the dodecahydrodicarba-*nido*-undecaborate(1−) anion[2] by a weak dative B–N bond. However, Hawthorne, *et al.*,[3] presumptively proved the piperidine molecule to be held in the crystal lattice by hydrogen bonds and not to be bound through a B–N dative bond. The reaction of 1,2-bis(bromomethyl)-*o*-carborane with aqueous ammonia solution leads to the formation of the inner salt of C,C′-bis(aminomethyl)dodecahydrodicarba-*nido*-undecaborate(1−), which involves no B–N dative bond.[4] The present paper describes a new type of amine-catalyzed solvolysis of C-halomethyl-*o*-carboranes and the formation of trimethylamine(N–B)-7-methylundecahydro-7,8-dicarba-*nido*-undecaboron (I) and its bromo derivative (II), through it. In these molecules, the trimethylamine is bonded to a cage boron atom through a B–N dative bond.

Experimental Section

Trimethylamine(N–B)-B-bromo-7,8-dimethylundecahydro-7,8-dicarba-*nido*-undecaboron (II).—In a typical run, 1.3 g of B-bromo-1-bromomethyl-2-methyl-*o*-carborane (mp 70–71.5°) prepared by the method of Smith, *et al.*,[5] was dissolved in a mixed solvent of 20 ml of methyl ethyl ketone and 4.7 ml of 30% aqueous trimethylamine. The solution was heated for 6 hr at 100° in a sealed tube, and the solvent was then removed by distillation under reduced pressure. The residue was washed with water and recrystallized from ethanol to give 0.75 g of colorless crystals, with a yield of 64% based on the composition $B_9H_{23}C_7NBr$ (II); mp 221° dec. *Anal.* Calcd for $B_9H_{23}C_7NBr$: mol wt, 298.5; C, 28.17; H, 7.77; N, 4.69; B, 32.60. Found: mol wt, 290; C, 28.16; H, 7.37; N, 4.93; B, 31.61. The molecular weight was measured in acetone with a Mechrolab Model 301A vapor pressure osmometer.

Compound II is soluble in acetone, alcohol, ether, benzene, and pyridine, but not in water.

Trimethylamine(N–B)-7-methylundecahydro-7,8-dicarba-*nido*-undecaboron (I) and Its Isomer (III).—On treating 1-bromomethyl-*o*-carborane in the same manner as described above, a homologous compound $B_9H_{22}C_6N$ (I), mp 152° dec, was obtained as a minor product (15% yield) along with an isomeric compound (III) (75% yield), mp 267° dec. The latter is less soluble in ethanol and is isolated from I by recrystallization from ethanol. *Anal.* I and III calcd for $B_9H_{22}C_6N$: mol wt, 205.6; C, 35.05; H, 10.78; N, 6.81; B, 47.4. Found for I: mol wt, 227; C, 35.27; H, 10.81; N, 6.76. Found for III: mol wt, 210; C, 35.22; H, 10.86; N, 6.79; B, 47.4.

Spectra.—Proton magnetic resonance spectra were recorded at room temperature with a Varian A-60 high-resolution nmr spectrometer at 60 Mc. Results are given in Table I. The nmr signals of protons attached to boron atoms extend over 3 ppm and are flattened to prevent their analysis.

Mass spectra were recorded on a Hitachi mass spectrometer, Model RMU-6. All spectra consist of several groups of prominent

TABLE I

PMR SPECTRA

Compd (solvent)	τ value	Rel intens	Assignment
I	7.020	9.5	$N(CH_3)_3$
(pyridine-d_5)	7.330	1.0 (broad)	C–H
	8.350	3.0	$C–CH_3$
II	6.758	9.0	$N(CH_3)_3$
(acetone-d_6)	8.425	6.0 (broad)	CH_3, CH_3
III	5.860	9.0	$N(CH_3)_3$
(pyridine-d_5)	6.092, 6.300 6.535, 6.682	2.0 (AB type)	CH_2
	7.6	0.8 (broad)	CH

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[1] L. I. Zakharkin and V. N. Kalinin, *Tetrahedron Letters*, 407 (1965).

[2] R. A. Wiesboeck and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 1642 (1964).

[3] M. F. Hawthorne, P. A. Wegner, and R. C. Stafford, *Inorg. Chem.*, **4**, 1675 (1965).

[4] L. I. Zakharkin and A. V. Grebennikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2019 (1966).

[5] H. D. Smith, T. A. Knowles, and H. Schroeder, *Inorg. Chem.*, **4**, 107 (1965).

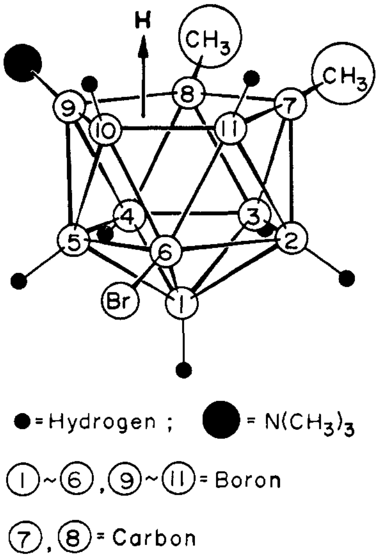


Figure 1.—A possible structure of $[CH_3(B_9C_2H_8Br)CH_3]N(CH_3)_3$.

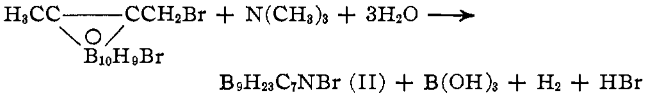
peaks which have characteristic patterns spread over a range of 9–10 mass numbers due to their boron isotopic compositions. The spectra of I and III were almost identical and contained a group of peaks with the highest at *m/e* 205 and with a clear cutoff at *m/e* 207 corresponding to the parent ion $^{11}B_9H_{22}C_6N$. Compound II displayed a similar pattern, with the highest peak at *m/e* 298 and with a clear cutoff at *m/e* 301 corresponding to $^{11}B_9H_{23}C_7N^{81}Br$. All of these products gave peaks due to ions of the parent minus trimethylamine and of trimethylamine.

Discussion

The structure shown in Figure 1 is postulated for II on the basis of its mass and pmr spectra. The pmr signal at τ 6.758 can be assigned to the three methyl groups attached to the nitrogen atom which is inferred from the chemical shift to bear a positive charge. The broad signal at τ 8.425 is doublet-like and has been ascribed to two methyl groups attached to the two nonequivalent skeleton carbons. The presence of two methyl groups implies that the bromine atom attached to the carbon atom in the starting material is replaced by a hydrogen atom, and the trimethylamine molecule must be bonded to a skeletal boron atom or must be present as an ammonium cation. Thus, an alternative conceivable structure is the ammonium salt $NH(CH_3)_3{}^+B_9H_9C_2(CH_3)_2Br^-$. This is, however, incompatible with the above-mentioned solubilities in various organic solvents and lack of an ^+N–H stretching band in the ir spectrum. The mass number of the parent peak is also smaller than that of the ionic structure by 2.

The remaining $B_9H_8BrC_2(CH_3)_2$ must be negatively charged. Although the structure has not been unequivocally established, it is quite reasonable to assume an icosahedral geometry with one vertex missing, *i.e.*, a skeleton similar to dodecahydrodicarba-*nido*-undecaborate(1−) ion.[2] The position of trimethylamine is not clear. The bromine atom is probably attached to the 9 or 12 position in the starting material and consequently to the same position in II. A single-crystal X-ray analysis now in progress would afford conclusive evidence for the structure. Preliminary X-ray data yield the cell constants a = 14.45 Å, b = 16.32 Å, and c = 25.89 Å; Z = 16, d(calcd) = 1.298 g/cm³, d(found) = 1.299 g/cm³, and space group Pbca-$D_{2h}{}^{15}$.

The stoichiometry of the reaction can thus be written



$$\underset{B_{10}H_9Br}{H_3CC\overset{\diagdown O \diagup}{\text{———}}CCH_2Br} + N(CH_3)_3 + 3H_2O \longrightarrow B_9H_{23}C_7NBr\ (II) + B(OH)_3 + H_2 + HBr$$

This scheme also receives further support from the observation of hydrogen evolution and recovery of trimethylammonium bromide.

Only one of the protons in II exchanged in an CH_3CN–D_2O mixed solvent at room temperature within 10 min, as evidenced by the increment in mass number of the parent peak in the mass spectrum. This fact suggests the presence of one bridge hydrogen atom according to Hyatt, *et al.*,[6] consistent with the structure shown in Figure 1, and excludes coordination of the amine molecule to the open face.

Compound I is concluded to have the same skeleton as II on the basis of its mass, ir, and pmr spectra. The ir spectrum is quite different from that of $NH(CH_3)_3{}^+$-$B_9H_{11}C_2(CH_3)^-$ prepared by the method of Hawthorne, *et al.*,[2] from 1-methyl-*o*-carborane. The pmr spectrum of III gives an AB-type quartet as shown in Table I to indicate the presence of a methylene group. This is in contrast to the methyl signal of I and leads to the inner-salt structure $(HCB_9H_{10}C^-)CH_2N(CH_3)_3{}^+$ for III.

Thus, it is concluded that the two isomeric undecaborane derivatives I and III are produced by amine-catalyzed hydrolysis of C-halomethyl-*o*-carborane and that one of the products involves a B–N dative bond binding an amine molecule.

[6] D. E. Hyatt, D. A. Owen, and L. J. Todd, *Inorg. Chem.*, **5**, 1749 (1966).

CONTRIBUTION FROM THE CATEDRA DE QUIMICA INORGANICA,
FACULTAD DE QUIMICA, MONTEVIDEO, URUGUAY,
AND THE DEPARTMENT OF CHEMISTRY,
STATE UNIVERSITY OF NEW YORK AT STONY BROOK,
STONY BROOK, NEW YORK 11790

The Synthesis of the Cyano-Bridged Binuclear Complex μ-Cyano-pentacyanopentaamminedicobaltate(III, III)[1a]

BY RENATA A. DE CASTELLÓ, CARLOS PÍRIZ MAC-COLL,[1b]
NED B. EGEN, AND ALBERT HAIM

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Reference to compounds of formula $[M(NH_3)_5OH_2][M'(CN)_6]$, where M = Co or Cr and M′ = Co,

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