Table I. Rate Constants for the Reaction of Co(III) Complexes with $CO_2\cdot^-$ Radicals[a]

Complex	X	$k(CO_2\cdot^- +$ complex), M^{-1} sec^{-1}
$Co(NH_3)_5X^{2+}$	NH_3	$1.1\ (\pm 0.3) \times 10^8$
	H_2O[b]	$1.7\ (\pm 0.3) \times 10^8$
	OH^-[c]	$<3\ (\pm 1.5) \times 10^7$
	Cl^-	$1.5\ (\pm 0.3) \times 10^8$
	NO_2^- (N bonded)	$<2\ (\pm 1) \times 10^7$
	NO_3^- (O bonded)	$2.1\ (\pm 0.3) \times 10^8$
	$CH_3CO_2^-$	$1.1\ (\pm 0.3) \times 10^8$
	$C_6H_5CO_2^-$	$4.5\ (\pm 2) \times 10^7$
	$C_6H_5CH_2CO_2^-$	$7.0\ (\pm 2) \times 10^7$
	$NC_5H_4CO_2^-$[d] (O bonded)	$5.1\ (\pm 2) \times 10^7$
	NC_5H_5[e] (N bonded)	$3.3\ (\pm 0.4) \times 10^8$
	p-$NCC_6H_4CO_2^-$	$4.6\ (\pm 2) \times 10^7$
	p-$O_2NC_6H_4CO_2^-$	$1.9\ (\pm 0.1) \times 10^9$
	p-$O_2NC_6H_4CH_2CO_2^-$	$1.2\ (\pm 0.1) \times 10^9$
$Co(bipy)_3{}^{3+}$		$7.6\ (\pm 0.1) \times 10^9$

[a] pH 6.9 unless otherwise indicated. [b] pH 5.2. [c] pH 7.8. [d] Pyridinecarboxylate. [e] Pyridine.

free ligands at a measurable rate ($k < 10^7\ M^{-1}\ sec^{-1}$). It should be noted, however, that although the $CO_2\cdot^-$ radical does not react at a measurable rate with 2,2′-bipyridyl in neutral solution, it reacts rapidly with the protonated forms of the free ligand. Thus, the reactivity of the radical must be governed more by the nature of the complex as a whole than by the properties of the particular free ligand. But it is also clear that the small differences in the reduction potentials of the complexes, and thus the free energy changes of the reactions, do not correlate with the differences in the values of k. $Co(NH_3)_6{}^{3+}$, with $E° = 0.1$ V,[14] exhibits a rate constant that is intermediate among the less reactive complexes and is about as reactive as $Co(NH_3)_5OH_2{}^{3+}$ with a reduction potential of 0.33 V.[15] No direct correlation can be seen among $Co(NH_3)_5NO_2{}^{2+}$ ($E° \approx 0.3$ V),[16] $Co(NH_3)_5$-Cl^{2+} ($E° \approx 0.4$),[16] or the carboxylato complexes ($E° \approx 0.3$ V).[16] A similar lack of correlation between the redox potential of the couple and the rate constant for reaction has been seen in the reaction of Co(III) complexes with $\cdot CH_2OH$ radicals.[8] Similarly, there is no direct correlation between $k(CO_2\cdot^- +$ complex) and the overall charge on the complex.

The compounds examined appear to fall into two distinct categories: those that are highly reactive in which the reaction with $CO_2\cdot^-$ involves the direct attack and electron transfer to an available orbital localized on the ligand and those that are only moderately reactive where the lower ligand orbitals are saturated and available antibonding orbitals are highly energetic. In the latter cases, the $e_g{}^*$ orbitals of the metal center are at lower energy than any available ligand orbitals; the energy of the $e_g{}^*$ orbital is affected by the nature of the X ligand, but again there does not appear to be any direct correlation with the position of the X ligand in the spectrochemical series.[17] However, the lower rate exhibited by these complexes could arise from radical attack at a face or edge of the octahedron which would be sterically restricted.

In the general sense, linear free energy correlations are certainly followed for $e_{aq}{}^-$, $CO_2\cdot^-$, other radicals, and the milder chemical reducing agents with the highest reactivities shown by the strongest reductants. The relative differences in the free energy change among the complexes when allowed to react with $CO_2\cdot^-$ are small and so the differences in the rate constants are likewise expected to be small. That there is no apparent correlation between the redox potential and the rate constant no doubt arises from other factors that contribute to the reactivity when the differences in the free energy changes are small.

Acknowledgment. The authors wish to thank Dr. E. Hayon of the U. S. Army Natick Laboratories for the use of the pulse radiolysis apparatus and his interest in the work.

Registry No. $CO_2\cdot^-$, 14485-07-5; $Co(NH_3)_6{}^{2+}$, 14695-95-5; $Co(NH_3)_5H_2O^{2+}$, 14403-82-8; $Co(NH_3)_5OH^+$, 16632-75-0; $Co(NH_3)_5$-Cl^+, 14970-14-0; $Co(NH_3)_5NO_2{}^+$, 16633-04-8; $Co(NH_3)_5NO_3{}^+$, 15077-47-1; $Co(NH_3)_5(CH_3CO_2)^+$, 16632-78-3; $Co(NH_3)_5(C_6H_5CO_2)^+$, 30931-77-2; $Co(NH_3)_5(C_6H_5CH_2CO_2)^+$, 40544-43-2; $Co(NH_3)_5$-$(NC_5H_4CO_2)^+$, 40544-44-3; $Co(NH_3)_5(NC_5H_5)^+$, 31011-67-3; Co-$(NH_3)_5(p$-$NCC_6H_4CO_2)^+$, 40544-46-5; $Co(NH_3)_5(p$-$O_2NC_6H_4CO_2)^+$, 36445-08-6; $Co(NH_3)_5(p$-$O_2NC_6H_4CH_2CO_2)^+$, 40544-48-7; Co-$(bipy)_3{}^{3+}$, 19052-39-2.

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(14) W. Latimer, "Oxidation Potentials," Prentice-Hall, Englewood Cliffs, N. J., 1952.

(15) R. G. Yalman, *Inorg. Chem.*, 1, 16 (1962).

(16) J. F. Endicott, private communication.

(17) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 170.

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Tris(dichloroboryl)methane, Bis(dichloroboryl)methane, and a Possible New Route to Carboranes[1]

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Received January 17, 1973

The availability of tetrakis(dimethoxyboryl)methane and related compounds[2] suggested to us the possibility of a new route to the smaller carboranes. However, our attempts at direct reduction failed,[2,3] and a good synthesis of carboranes from acetylene and pentaborane has been reported recently.[4] There remains some possible advantage in reducing the boron at a later stage of the synthesis and also the possibility of synthesizing new *nido*-carboranes, and we have explored the preparation and reduction of bis- and tris(dichloroboryl)methane with this objective in mind.

The rationale for using the chloro compounds was that their reduction should be easier than that of the alkoxy derivatives tried earlier, which undergo loss of boron and polymerization on treatment with basic reducing agents.[2] We began by trying to make tetrakis(dichloroboryl)methane, $C(BCl_2)_4$, from tetrakis(dimethoxyboryl)methane, $C[B(OCH_3)_2]_4$, and boron trichloride or other reactive chlorides but obtained only polymeric products,[3] even though $C(BCl_2)_4$ has been prepared in small quantities from carbon vapor and B_2Cl_4 and is stable when pure.[5] Tris(dichloroboryl)methane seemed more promising, inasmuch as Castle

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(1) (a) We thank the National Science Foundation for support, Grant GP 26348. (b) Abstracted from the Ph.D. Thesis of P. K. M.

(2) R. B. Castle and D. S. Matteson, *J. Amer. Chem. Soc.*, 90, 2194 (1968); *J. Organometal. Chem.*, 20, 19 (1969).

(3) Unpublished work with E. Kramer and J. B. Leach.

(4) J. F. Ditter, E. B. Klussman, J. D. Oakes, and R. E. Williams, *Inorg. Chem.*, 9, 889 (1970).

(5) J. E. Dobson, P. M. Tucker, R. Schaeffer, and F. G. A. Stone, *Chem. Commun.*, 452 (1968).

has previously obtained an unstable but distillable partially chlorinated product on reaction of the corresponding methoxy compound with boron trichloride.[2]

Results and Discussion

Synthesis of Dichloroboryl Compounds. The reaction of tris(dimethoxyboryl)methane (**1**) with boron trichloride at 0 to −10° is slow, apparently requiring several days to reach equilibrium, and the equilibrium is not very favorable. Some formation of polymeric by-products occurs, and there is considerable loss each time the product is distilled. Higher temperatures increase the amount of by-product formation. By equilibrating a sample of **1** with about 20 mol of boron trichloride, distilling the product mixture, and repeating this procedure a total of 12 times, a 7% yield of fairly pure tris(dichloroboryl)methane (**2**) was obtained.

$$\underset{\mathbf{1}}{HC[B(OCH_3)_2]_3} + BCl_3\ (\text{excess}) \rightarrow\rightarrow \underset{\mathbf{2}}{HC(BCl_2)_3} + CH_3OBCl_2$$

After about the fourth or fifth equilibration, the amount of methoxy groups remaining in the product is down to about one per molecule, and removal of the remainder is very slow. The addition of a small amount of aluminum chloride, as small as 0.65% of the weight of the crude product **2** at this point, results in a polymerization which removes essentially all of the remaining methoxy groups and leaves about half the product recoverable as pure tris(dichloroboryl)methane (**2**) by distillation. The loss is no greater than that in the repeated equilibrations with boron trichloride, and, of course, the process is much faster.

The greatest improvement in yields was achieved by the addition of a small amount of lithium borohydride, as little as 20 mg in 2 kg of boron trichloride being sufficient. The active catalyst is presumably dichloroborane, $BHCl_2$.

Further points affecting the yields include the purity of the tris(dimethoxyboryl)methane (**1**) and the care taken in the first equilibration step. The product **2** is most vulnerable to decomposition during the first equilibration and distillation. It is important that enough boron trichloride (ten times the weight of **1**) be used in the first step and that the crude product be distilled rapidly and, since it is particularly unstable to storage, promptly treated with a second batch of boron trichloride. The subsequent steps are not nearly so critical.

One of the modes of decomposition is probably the reaction of methoxy groups with boron trichloride to form methyl chloride and a boron-oxygen-boron linkage, which by exchange with other similar groups can lead to polymeric material.

The successful preparation of tris(dichloroboryl)methane (**2**) prompted a few more attempts to make tetrakis(dichloroboryl)methane, $C(BCl_2)_4$, but we were unable to isolate any of this compound even when the optimum conditions for the preparation of **2** were applied to tetrakis(dimethoxyboryl)methane.

Bis(dichloroboryl)methane, $CH_2(BCl_2)_2$ (**3**), was easily prepared by treating bis(dimethoxyboryl)methane, $CH_2[B(OCH_3)_2]_2$,[2] with excess boron trichloride and a catalytic amount of lithium borohydride. Two equilibrations were used, and final purification was accomplished by treatment with aluminum chloride. This compound is both more stable and more volatile than tris(dichloroboryl)methane (**2**), and with the use of a more efficient fractionating column our rather low (10–22% overall) yields could probably be substantially improved.

Characterization. The proton nmr spectrum of tris(dichloroboryl)methane (**2**) consists of a single broad band at δ 3.85, about 13 Hz wide at half-height. This is considerably downfield from the B_3CH peak of tris(dimethoxyboryl)methane (**1**) which is at δ 0.30. Our best material still showed small amounts of impurities between δ 0.4 and 1.3, though, of course, the low proportion of hydrogen in **2** and the breadth of the peak make it necessary to take the spectrum under conditions of high gain which make hydrocarbon-like impurities particularly prominent.

For structure proof, we treated tris(dichloroboryl)methane (**2**) with methanol and obtained tris(dimethoxyboryl)methane (**1**). The identity was confirmed by its infrared spectrum.

An attempt to prepare a trimethylamine adduct of **2** apparently yielded a mixture of products. Equilibration of **2** with boron tribromide failed to lead to pure tris(dibromoboryl)methane, $HC(BBr_2)_3$, but bromine-chlorine exchange did occur and the B_3CH peak of $HC(BBr_2)_3$ appeared in the nmr at δ 5.0.

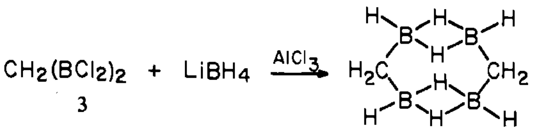
The nmr spectrum of bis(dichloroboryl)methane (**3**) consisted of a single broad line (20 Hz wide at half-weight) at δ 2.40, with some minor additional peaks due to impurities. Reaction of **3** with methanol gave an 83% yield of bis(dimethoxyboryl)methane, which had the same infrared spectrum as an authentic sample.

Reduction. Our results show that volatile carboranes are produced by the reaction of tris(dichloroboryl)methane (**2**) with lithium borohydride and aluminum chloride in paraffin oil. The instability of the products precluded complete separation and characterization in our simple vacuum line equipment.

Formally, the reduction of **2** should lead to triborylmethane, $HC(BH_2)_3$, which would be unstable as written but might rearrange slightly to a pyramidal B–H–B bridged carborane, CB_3H_7, which is isoelectronic with the recently reported anion $B_4H_7^-$.[6] We obtained very small amounts of an unstable volatile product, *m/e* 52, which is probably CB_3H_7. Considerably larger amounts were obtained of a less volatile compound believed to be CB_4H_{10} ($CB_3H_7 + BH_3$), *m/e* 65 (M − 2), which had an infrared spectrum somewhat resembling that of pentaborane(11).[7] The bulk of the material was still less volatile and presumably contained dimer or polymers of CB_3H_7.

Pyrolysis of the unfractionated reduction product mixture at 350° under high vacuum with a short contact time yielded material with a mass cutoff at *m/e* 98 ($C_2{}^{11}B_6H_8{}^+$). Pyrolysis of the fractionated *m/e* 65 reduction product at 500° under vacuum yielded material having a mass cutoff at *m/e* 86 ($C_2{}^{11}B_5H_7{}^+$). These pyrolysis products probably consist largely of *closo*-carboranes.

Reduction of bis(dichloroboryl)methane (**3**) with lithium borohydride and aluminum chloride gave a low yield of one stable, volatile liquid product which appears to be diborylmethane dimer **4** on the basis of the following data. The proton nmr spectrum showed a broad peak at δ 0.37, characteristic of CH_2B_2 compounds.[2] The infrared spectrum showed a weak CH_2 band at 2895 cm^{-1}, a strong ter-



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4

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[6] C. Kodama, U. Engelhardt, C. Lafrenz, and R. W. Parry, *J. Amer. Chem. Soc.*, 94, 407 (1972).

[7] L. V. McCarty, G. C. Smith, and R. S. McDonald, *Anal. Chem.*, 26, 1027 (1954).

minal BH band at 2530 cm^{-1}, and a strong BHB bridge band at 1619 cm^{-1}. The mass spectrum showed a fairly sharp cutoff at *m/e* 78 (M − 2), with a weak peak at *m/e* 79. There is good precedent for high stability of BH_2B bridge linkages in six-membered rings.[8]

Our original reason for preparing diborylmethane dimer **4** was to determine whether boron–carbon bond cleavage might be a substantial side reaction in the reduction of tris(dichloroboryl)methane (**2**). It clearly is not. We tried pyrolyzing a sample of diborylmethane dimer **4** *in vacuo* at 500° and obtained products showing characteristics of *closo*-carboranes in the infrared but lost the sample when air leaked into the infrared cell. It appears that diborylmethane dimer **4** is a promising candidate for future attempts at carborane synthesis.

Experimental Section

Reactions involving boron trichloride were carried out under argon. Reductions were carried out in a vacuum line, and some transfers involving lithium borohydride and other air-sensitive solids were done under argon in a glove bag. Proton nmr spectra were recorded on a Varian A-60 or T-60 instrument and chemical shifts are relative to external tetramethylsilane. Infrared spectra were recorded on a Beckman IR-18A. Mass spectra were obtained with a Varian M-66.

Tris(dichloroboryl)methane) (2). A 216-g (0.929 mol) sample of tris(dimethoxyboryl)methane (**1**)[2] was distilled under vacuum into a 2-l. flask equipped with a magnetic stirring bar. The flask was then cooled with Dry Ice and methylene chloride (recommended to minimize hazard in case of flask breakage) and 2340 g (20 mol) of boron trichloride was condensed into it under argon. About 20 mg of lithium borohydride was added quickly through a powder funnel. (Contact of lithium borohydride with boron trichloride in the presence of air may result in ignition of the chloroboranes produced.) The flask was closed with a ground glass stopper which had been generously coated with Dow Corning high vacuum silicone grease, and the stopper was secured with Parafilm paraffin film and copper wire. The flask was stored in a refrigerator at −7° (±5°) for 4 days. Its condition was checked and the contents were briefly stirred once daily. The flask was then equipped for vacuum distillation and the boron trichloride was distilled into a Dry Ice cooled receiver. The residue of crude tris(dichloroboryl)methane (**2**) was stirred under vacuum at 20–25° for 15 min after the boron trichloride was apparently removed. The receiver was then changed to a fresh 2-l. flask and the crude product was distilled rapidly, bp ~40° (0.1–0.3 mm), yield 174 g. Onto this material was immediately condensed 1700 g (14.5 mol) of boron trichloride, a 20-mg portion of lithium borohydride was added, and the mixture was again stored at −7° for 4 days. Similar work-up yielded 156 g of crude **2**, which was treated with 1550 g (13.2 mol) of boron trichloride, yielding 143 g of crude **2**, which with 1440 g of boron trichloride yielded 133 g of crude **2**. This material was distilled onto 2.04 g of anhydrous aluminum chloride (Mallinckrodt) in an ice-cooled receiver. After an induction period of several minutes, a fairly vigorous reaction took place in the receiver, diminishing near the end of the distillation. The mixture was stored at −7° for 4 days, with occasional swirling. The final result consisted of a brown viscous oil floating on an orange liquid with some unreacted aluminum chloride at the bottom. The liquids were decanted from the solid into a separatory funnel and the denser orange liquid was separated and distilled, bp ~40° (0.3 mm). The yield of tris(dichloroboryl)methane (**2**) was 75 g (31%): mp ~−17°; infrared spectrum[9] (CCl_4) 2835 (w, CH), 1380 (m), 1337 (m), 1297 (m), 1210 (strong shoulder), 1155 (s, BCl), 1030–1040 (vs, BCl), 930–940 (vs, BCl), and 644 cm^{-1} (m); nmr[9] (neat) δ 3.85 (s, CH). *Anal.* Calcd for CHB_3Cl_6: C, 4.65; H, 0.39; B, 12.56; Cl, 82.39. Found: C, 5.83; H, 0.40; B, 11.61; Cl, 82.30.

Reaction of Tris(dichloroboryl)methane (2) with Methanol. In the vacuum line, ~2 ml of methanol distilled from barium oxide was condensed in small portions onto 1.50 g of tris(dichloroboryl)methane (**2**) dissolved in 20 ml of pentane. The mixture was stirred after each portion was added. Distillation of the solvent left a residue of 1.1 g (83%) of tris(dimethoxyboryl)methane (**1**), mp 50–51° (lit.[2] ~45°), identified by its infrared and nmr spectra.

Bis(dichloroboryl)methane (3). The procedure described for the preparation of tris(dichloroboryl)methane (**2**) was used with the following variations. A 49.4-g (0.291 mol) sample of redistilled bis(dimethoxyboryl)methane[2] was treated with 453 g (3.86 mol) of boron trichloride and ~20 mg of lithium borohydride and allowed to stand 3 days at −7°. The boron trichloride and methoxydichloroborane were distilled at atmospheric pressure through a 15-cm column packed with glass helices until a head temperature of 49° was reached and the temperature began to fall. [Crude bis(dichloroboryl)methane (**3**) appears to be much more stable thermally than crude tris(dichloroboryl)methane (**2**).] The column was removed and the product (44.6 g) was distilled under vacuum. A second treatment with 269 g of boron trichloride and ~20 mg of lithium borohydride was carried out, yielding 30 g of crude product. This product was treated with 0.46 g of anhydrous aluminum chloride under argon in a glove bag. After about 1 min exothermic reaction set in, which was controlled by cooling with a Dry Ice–acetone bath. The stoppered flask was then stored 3 days at −7°. The liquid was decanted and distilled to yield 11.2 g (22%) of bis(dichloroboryl)methane (**3**): bp ~25° (0.3 mm); infrared[9] (CCl_4) 2975 (w, CH), 2940 (w), 2885 (w), 1385 (w), 1315 (w), 1200 (s, BCl), 1100 (s, BCl), 1060 (s, BCl), 1020 (vs, BCl), 970 (vs, BCl), 918 (vs, BCl), and near 600 cm^{-1} (w); nmr[9] (neat) δ 2.40 (broad singlet, CH_2). *Anal.* Calcd for $CH_2B_2Cl_4$: C, 6.77; H, 1.14; B, 12.18; Cl, 79.91. Found: C, 8.62; H, 1.39; B, 11.56; Cl, 78.30.

Reaction of Bis(dichloroboryl)methane (3) with Methanol. The procedure used for reaction of **2** with methanol was followed with minor variations. The yield of liquid bis(dimethoxyboryl)methane, $CH_2[B(OCH_3)_2]_2$, was 82%, identity confirmed by infrared.

Reduction of Tris(dichloroboryl)methane (2). In a glove bag under argon, 0.562 g (4.21 mmol) of anhydrous aluminum chloride, 0.846 g (38.9 mmol) of lithium borohydride, and 10 ml of paraffin oil were placed in a 100-ml round-bottom flask equipped with a Teflon-coated magnetic stirring bar and a 20 cm long neck with a suitable joint for attaching to the vacuum line. The flask was transferred quickly to the vacuum line and the argon was pumped out, taking care to avoid loss of liquid due to extensive foaming. Degassing with stirring was continued for 1 hr. The slurry was cooled with liquid nitrogen and 1.66 g (6.41 mmol) of tris(dichloroboryl)methane (**2**) was condensed into the flask. By allowing the neck of the flask to warm, the condensate **2** was melted down onto the frozen paraffin oil slurry. The cooling bath was then removed, argon was admitted to a pressure of 1 atm, and the reaction vessel was connected through a stopcock to a trap at −196°. After the reaction vessel warmed to room temperature, a vigorous reaction with gas evolution and foaming set in. The reaction mixture was stirred overnight, and diborane was collected in the −196° trap. The reaction vessel was cooled, to −196°, the system was pumped out, and fresh traps at −23 (sometimes omitted), −78, and −196° were connected, allowing the reaction vessel and adjacent trap to warm to room temperature and stirring the slurry for 4 hr. The diborane collected in the −196° trap was disposed of by allowing it to bubble through acetone in a stream of nitrogen. (*Caution*: the ~0.5 ml of diborane formed is a serious fire and explosion hazard in case of contact with air.) The condensate from the −78° trap was refractionated (in some but not all experiments) by passing it through traps at −42 and −78°. In one experiment the fractionation was allowed to proceed only a short time and the small amount of material collected in the −78° trap showed a maximum *m/e* at 52 in the mass spectrum.[9] This compound was tentatively assigned the formula HCB_3H_6. Longer fractionation led to collection of a larger amount of material in the −78° trap: *m/e* 65;[9] infrared[9] (CCl_4) 2980 (w, CH), 2880 (w), 2609 (s sh, BH), 2570 (vs, BH_2), 2518 (s, BH_2), 2040 (w, broad, BH), 1620 (m, probably due to impurity which is major substance of −42° trap), 1470–1500 (m, BHB), 1340 (m), 1275 (m), 1090 (s), 1040 (s), 1005 (s), 955 (m), 923 (s), 842 (m), and 819 cm^{-1} (ms). This compound was tentatively assigned the formula CB_4H_{10}. The material in the −42° trap was found to be no longer volatile, evidently having polymerized to some extent on condensation: infrared[9] (CCl_4) 2920 (w, CH), 2600 (m, BH), 2535 (s, BH), 1590–1610 (vs, BHB), 1180 (s), 1145 (s), 1090–1100 (s), and 890 cm^{-1} (s). From its initial volatility and the resemblance of the infrared spectrum to that of diborylmethane dimer **4**, this compound appears to have started out as triborylmethane dimer, $HC[BH(H)_2BH]_3CH$, which then polymerized, perhaps to $[\text{-}CH(HBH_2BH)_2CH\text{-}HBH_2BH\text{-}]_n$. Treatment of the polymer with methanol yielded tris(dimethoxyboryl)methane (**2**), identity checked by infrared, and hydrogen, free from hydrogen chloride according to the infrared spectrum.

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(8) H. C. Brown, E. Negishi, and P. L. Burcke, *J. Amer. Chem. Soc.*, **93**, 3400 (1971).

(9) The spectral plot is recorded in Peter Mattschei's thesis, W.S.U., 1972, available from University Microfilms, Ann Arbor, Mich.

Reduction of Bis(dichloroboryl)methane (3). Using the same procedure described for the reduction of tris(dichloroboryl)methane (2), 0.80 g (6.0 mmol) of aluminum trichloride and 1.40 g (64.4 mmol) of lithium borohydride in 10 ml of paraffin oil were allowed to react with 0.834 g (4.71 mmol) of bis(dichloroboryl)methane (3). The material collected in the −196° trap was refractionated separately under high vacuum through traps at −97 and −196°. The material from the reaction flask was fractionated through traps at −78 and −196°, and the material from the −196° trap were refractionated through traps at −95 and −196°. The diborane in the −196° traps was destroyed by passing through acetone in a stream of nitrogen. The product in the warmer traps was combined. From the nmr spectrum, the yield of diborylmethane dimer 4 was estimated to be about 1%: infrared[9] (gas phase) 2975 (w), 2895 (m, CH), 2590 (m), 2520 (vs, BH), 1570–1630 (vs, BHB), 1375 (m), 1215 (ms), 1160 (s), 1120 (ms), 862 (m), 770 (w), 717 (w), and below 600 cm^{-1} (m or s); nmr (CCl_4) δ 0.37 (s, broad, CH_2); mass spectrum[9] *m/e* 78 ($C_2{}^{11}B_4H_{10}{}^+$), weaker peak (15–20%) at *m/e* 79 ($C_2{}^{11}B_4H_{11}{}^+$).

Pyrolysis of Reduction Products from Tris(dichloroboryl)methane (2). Tris(dichloroboryl)methane (2) was reduced with lithium borohydride and aluminum chloride under the conditions already described, and the volatile products were collected under high vacuum in traps at −78 and −196°. The material in the −78° trap was held at −42° for 2 hr and allowed to vaporize under high vacuum through a 3 cm diameter 15 cm long Vycor tube packed with stainless steel sponge and heated to about 350°, with collection of the pyrolysate in a −196° trap. The source trap was then held at −23° for 1 hr and room temperature for 0.5 hr while pyrolysis was continued. The pyrolysate was fractionated under high vacuum through traps at 0, −78, and −196°. Nothing condensed in the 0° trap. The material in the −78° trap was a mixture and showed carborane-like mass patterns at *m/e* 90, 98, 111, and 120. The infrared spectrum which lacked any BHB band near 1600 cm^{-1} showed prominent bands at 2995 (m), 2615 (s), 1275 (vs), 1105 (s), 1080 (vs), 845 (vs), 820 (vs), and 685 cm^{-1} (w). The peaks at 1275, 1080, 845, and 820 cm^{-1} are believed to be due to chloroalkane or ether contaminants, being found also in the spectrum of the unpyrolyzed reduction product. The material in the −196° trap was refractionated through traps at −112 and −196°. The material collected at −112° showed a sharp cutoff in the mass spectrum[9] at *m/e* 98 ($C_2{}^{11}B_6H_8{}^+$). The infrared spectrum (gas phase) showed no BHB peak near 1600 cm^{-1} and showed prominent bands at 2980 (w), 2615 (vs), 1285 (s), 1215 (s), 1175 (vs), 1100 (s), and 900 cm^{-1} (m).

Registry No. $HC(BCl_2)_3$, 40710-69-8; $HC[B(OCH_3)_2]_3$, 18067-51-1; $H_2C(BCl_2)_2$, 40710-68-7; $H_2C[B(OCH_3)_2]_2$, 17936-82-2; 4, 40802-62-8; BCl_3, 10294-34-5.

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Study of the Ligand Exchange Reaction of a Five-Coordinate Nickel(II) Complex

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Received March 8, 1973

In recent years a great deal of interest has been directed toward the preparation and characterization of five-coordinate complexes of the first row transition metal ions. However, relatively little work has been done to characterize the solution behavior of five-coordinate complexes. Thus, we have undertaken a program to explore the properties of some five-coordinate complexes of Ni(II) and Co(II) in nonaqueous solvents. In the present paper we report our results concerning the ligand exchange reaction of $Ni(LUNO)_5{}^{2+}$ with excess LUNO, where LUNO represents 2,6-lutidine 1-oxide, in the solvent acetone-d_6.

The complex $[Ni(LUNO)_4](ClO_4)_2$ was prepared and characterized according to previously reported methods.[1-3] This compound when dissolved in nonaqueous solvents containing large amounts of excess LUNO gives a yellow solution having an electronic spectrum characteristic of a five-coordinate trigonal-bipyramidal Ni(II) complex[2,4-6] presumably due to formation of the $Ni(LUNO)_5{}^{2+}$ species. To establish the conditions under which the complex $Ni(LUNO)_5{}^{2+}$ is the only important species in solution, the electronic spectrum was observed as a function of the ratio of the concentrations of excess LUNO and $[Ni(LUNO)_4](ClO_4)_2$ in the solvents acetone and propylene carbonate. In propylene carbonate Beer's law behavior was observed at ligand to complex ratios above 250:1 (where the complex concentration was in the range 0.01–0.05 *M*) and under these conditions $Ni(LUNO)_5{}^{2+}$ appears to be the only complex present in detectable amounts. At lower ligand to complex ratios significant deviations from Beer's law are observed. The band found at ~1250 mμ at high ligand to complex ratios shifts toward higher energy and the intensities of the other four bands increase as the ligand to complex ratio decreases. These results seem to suggest that another five-coordinate species becomes significant in solutions with low ligand to complex ratios. The spectral results obtained in acetone as solvent are similar except that the $Ni(LUNO)_5{}^{2+}$ species appears to be more stable in acetone. Beer's law behavior and the absence of any changes in the spectrum are observed in solutions containing a ligand to complex ratio of approximately 100:1 or greater (where the complex concentration was in the range of 0.02–0.05 *M*).

To study the exchange reaction between the $Ni(LUNO)_5{}^{2+}$ complex and LUNO acetone solutions were prepared containing large excesses of ligand, and the chemical shift and line width of the nmr signal due to the 2,6-methyl protons were studied as a function of temperature. Typical results of the line width measurements are shown in Figure 1. Note that these data are characteristic of a system undergoing chemical exchange at rates in the range which affect the line width of the exchanging ligand. The system appears to be in the near-fast-exchange region at high temperatures and the signal exhibits characteristic behavior as the temperature is lowered and the exchange rate slows down.[7] In Figure 2 the observed chemical shift of the methyl signal from that of the free ligand is shown as a function of temperature. The behavior of the chemical shift is consistent with the line width data discussed above. However, note that at temperatures which should correspond to the slow-exchange-limiting region ($10^3/T > 4.1$), the observed chemical shift is more than 10 Hz from the free ligand position and increases as the temperature is lowered. This strongly indicates that another exchanging species is present in solution. This conclusion is supported by the fact that at low temperatures ($10^3/T > 4.4$) the slope of the line width plot is about twice that expected for a relaxation process controlled by the electron spin relaxation rate.[8] It is possible that the behavior of the chemical shift at low temperatures is due to pseudocontact shifts of ligand mole-

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