$(HNBH)_3$ and $(CH_3NBH)_3$, as well as $(CH_3)_2NB_2H_5$, showed spectra agreeing well with the literature.[7] The unstable aminodiborane $H_2NB_2H_5$ showed the characteristic aminodiborane pattern,[7] with δ 43.9 ppm (upfield of methyl borate); $J_1 = 130$ cps; $J_2 = 29$ cps. A similar pattern for $CH_3NHB_2H_5$ appeared at δ 40.6 ppm; $J_1 = 129$ cps; $J_2 = 29$ cps. The ammonia reaction yielded a trace of a substance X, for which δ is 6.6 ppm ($J = 165$ cps, triplet); according to the literature, this could not have been $(H_2NBH_2)_3$, for which δ is $11.3 + 18.2 = 29.5$ ($J = 100$ cps).[8] However, the CH_3NH_2 reaction yielded a trace of slightly volatile crystals which could have been $(CH_3NHBH_2)_3$.

The results were not very different when the reactants CH_3NH_2 and B_5H_9 were first combined below 25° and then flash heated at 175°. Possibly much of the adduct was dissociated before step 1 made much progress, or step 1 could have gone through adduct formation in any case. Conjectures about the specific processes constituting step 1 do not seem useful.

It is interesting that the flash reaction of $CH_3NH_2 \cdot BH_3$ with B_5H_9 consumed a smaller proportion of B_5H_9 than the more direct CH_3NH_2–B_5H_9 reaction, but gave the same yield of B_2H_6 per B_5H_9 consumed. The chief difference was a far higher yield of $CH_3NHB_2H_5$ at the expense of $(CH_3NBH)_3$. In this case it is possible that the base which actually attacked the B_5H_9 was at least mostly CH_3NHBH_2.

The weakest base here employed was CH_3PH_2, which was far from all consumed by the excess B_5H_9. Then since the complex $CH_3PH_2 \cdot BH_3$ is stable against loss of BH_3, no diborane was obtained. The low yield of the BH_3 complex could have been due to loss of H_2 to form the CH_3PHBH_2 high polymers.[5]

It is interesting that one trimethylamine experiment yielded a trace of what seemed to be $(CH_3)_3N \cdot B_3H_7$, detected as an ^{11}B nmr signal at δ 33 ppm (lit.[9] δ $15 + 18 = 33$ ppm, unresolved). It could not be attributed to a B_5H_{11} impurity in the B_5H_9, which had been stored in glass for more than 12 years and was strictly pure.

The nonvolatile products of these experiments conform well to earlier observations of resins made of similar components.[10] They were destructively dissolved by acetone or partially extractable by benzene, in which they showed broad and unresolved ^{11}B nmr signals. Especially those involving phosphorus showed thermoplastic character on heating *in vacuo*: small evolution of volatiles caused large, viscous bubbles. There seemed to be plasticizing components of fairly low molecular weight range, sublimation of which at 250–300° left light brown, fragile, glassy residues richer in boron and poorer in hydrogen than average formulas such as (base)B_4H_5. Such glasses retained their light colors even above 400°, where the evolved noncondensable gases began to include methane. Such resins, showing more intrinsic thermal stability than the usual $(BH)_x$ polymers, seem worthy of further study if and when appropriate techniques become available.

Registry No. B_5H_9, 19624-22-7; NH_3, 7664-41-7; CH_3NH_2, 74-89-5; $CH_3NH_2 \cdot BH_3$, 1722-33-4; $(CH_3)_2NH$, 124-40-3; $(CH_3)_3N$, 75-50-3; CH_3PH_2, 593-54-4; $(CH_3)_2PH$, 676-59-5; $(CH_3)_3P$, 594-09-2; $(CH_3)_3P \cdot BH_3$, 1898-77-7; H_2, 1333-74-0; B_2H_6, 19287-45-7; $(NHBH)_3$, 6569-51-3; $H_2NB_2H_5$, 39046-41-8; $(CH_3NBH)_3$, 1004-35-9; $CH_3NHB_2H_5$, 27073-27-4; $(CH_3)_2NB_2H_5$, 23273-02-1; $(CH_3)_2NBH_2$, 1838-13-7; $[(CH_3)_2N]_2BH$, 2386-98-3; $(CH_3)_3N \cdot BH_3$, 75-22-9; $(CH_3)_3N \cdot B_3H_7$, 12076-72-1; $H_3CPH_2 \cdot BH_3$, 14975-23-6; $(CH_3)_2PH \cdot BH_3$, 4268-35-3.

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Iodination of Dicarbahexaboranes

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The chlorination or bromination of *nido*-4,5-dicarbahexaborane(8) ($C_2B_4H_8$) leads only to the enantiomorphs 3-$XC_2B_4H_7$ and 6-$XC_2B_4H_7$; the 1- or 2-halogenated derivatives seem to be excluded.[1] For the somewhat analogous B_5H_9, it appears that 1-halogenation occurs but that conversion to the 2 isomer is fairly easy. In contrast, 1-IB_5H_8 is decidedly more stable than 2-IB_5H_8.[2] Thus, it seemed that iodination of $C_2B_4H_8$ might produce 1-$IC_2B_4H_7$, since the ^{11}B nmr spectra indicate the 1-B atoms of B_5H_9 and $C_2B_4H_8$ to be very similar. In fact, however, we now have found the 25°, Al_2I_6-catalyzed iodination of $C_2B_4H_8$ to be like the chlorination or bromination: only the enantiomorphic mixture of 3-$IC_2B_4H_7$ and 6-$IC_2B_4H_7$ is obtained. The similar iodination of the *closo*-carborane $C_2B_4H_6$ yields only 2-$IC_2B_4H_5$; here only one species is possible, and no diiodo derivative could be observed.

Iodination of the *nido*-Carborane. The carborane $C_2B_4H_8$ was treated with iodine in a sealed tube wherein a trace of Al_2I_6 had been made from aluminum powder and iodine (24 hr at 180°). The iodination proceeded during 24 hr at 20° (with occasional shaking); the end of the process was indicated by a color change from violet to light brown. One H_2 was formed per I_2 consumed, and the yield of the colorless liquid $IC_2B_4H_7$ represented 25% of the consumed $C_2B_4H_8$. No HI was found, apparently because it would have been removed rapidly by reaction with $IC_2B_4H_7$ (but not $C_2B_4H_8$ at all) to form H_2. The main nonvolatile product had an ^{11}B nmr spectrum too broad and complex for interpretation. Boron triiodide was a minor by-product (^{11}B nmr spectrum, a singlet at 26.3 ppm upfield of methyl borate); it was easily removed when the iodocarborane was purified by high-vacuum fractional condensation.

The product $IC_2B_4H_7$ showed an equilibrium vapor pressure of 3.5 mm at 28°. Its vapor-phase molecular weight was 201.2 (calcd, 201.1). Its mass spectrum showed a parent ion with the right isotopic pattern for a 4-boron

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nido-carborane, with the expected cutoff at *m/e* 202. Its ^{11}B nmr spectrum (with methyl borate as the standard) showed the 1-B as a doublet at δ 67.3 ppm (J = 188 cps), the iodinated boron as a doublet at δ 30.9 ppm (J = 56 cps, due to one bridge H), and the other two basal boron atoms as an unresolved mound surmounted by sharp peaks, centered at δ 19 ppm, with two-boron intensity. The only possible interpretation was for single iodination at a basal boron adjacent to carbon (3 or 6 position), with the remaining basal boron atoms giving a doublet of doublets superposed upon a doublet of triplets. This is consistent with the better resolved pattern for $ClC_2B_4H_7$.[1]

Iodination of the *closo*-Carborane. The reaction of $C_2B_4H_6$ (in excess) with iodine and a trace of Al_2I_6 was just like the iodination of $C_2B_4H_8$ except that the process was very slow at 25°; it was completed during 24 hr at 75°. Again the major by-products were H_2 and nonvolatile brown material; the yield of the colorless liquid $IC_2B_4H_5$ (vapor pressure 7.9 mm at 0°) represented 20% of the consumed carborane. Its mass spectrum was consistent with a four-boron *closo*-carborane, with the expected cutoff at *m/e* 200. Its ^{11}B nmr spectrum proved to be simply interpretable: a singlet for 2-BI at δ 50.8 ppm, a doublet for 4-BH at δ 38.2 ppm (J = 196 cps), and a doublet twice as intense for 3-BH and 5-BH at δ 34.0 ppm (J = 189 cps).

Iodine-Replacement Attempts. Both iodocarboranes proved to be remarkably resistant toward attempts to replace the iodine atom by other atoms or groups. The less stable $IC_2B_4H_7$ (which still required 17 hr at 200° for complete decomposition to H_2 and hydrocarbon-insoluble light-yellow transparent resin and was unaffected by 2537 Å during 24 hr at 20°) reacted with $HgCl_2$ only when heated but was wholly destroyed during 24 hr at 140° to give 1.0 HCl, 0.40 BCl_3, and 0.10 H_2 per $IC_2B_4H_7$. The more stable $IC_2B_4H_5$ failed to react with $HgCl_2$ under similar conditions. Also $Hg(SCF_3)_2$ failed to react with $IC_2B_4H_7$ at 20°. An attempt to methylate $IC_2B_4H_7$ by dimethylzinc at 20° showed a fast reaction, leading only to hydrogen and nonvolatiles.

Neither iodocarborane would cleave dimethyl ether at 25°, in contrast to the very interesting cleavage of dimethyl ether by $1\text{-}IB_5H_8$ at lower temperatures.[3]

A Quaternary Ammonium Salt. Trimethylamine reacted with $2\text{-}IC_2B_4H_5$ in solution in hexane, precipitating a white solid adduct accurately described by the formula $IC_2B_4H_5 \cdot (CH_3)_3N$. It is suggested that this is a quaternary ammonium salt in which one substituent is the $2\text{-}C_2B_4H_5$ group. The instantaneous formation of this salt at 25° would suggest that replacement of iodine from its B–I bond in such carboranes can be done well enough if a base is present, sufficiently strong to displace iodide from the fairly strong B–I bond. However, this would be less likely to succeed in the case of $IC_2B_4H_7$, because this nido structure is relatively sensitive to base action for conversion to resins, whereas $C_2B_4H_6$ is inert toward $(CH_3)_3N$.

Registry No. $3\text{-}IC_2B_4H_7$, 34228-48-3; $2\text{-}IC_2B_4H_5$, 38744-24-0; $C_2B_4H_8$, 18972-20-8; $C_2B_4H_6$, 20693-67-8; $IC_2B_4H_5 \cdot (CH_3)_3N$, 38744-25-1; iodine, 7553-56-2; trimethylamine, 75-50-3.

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Isomer Characterization of the Ammonia Photoaquation Product of Thiocyanatopentaamminechromium(III)

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The major product of thiocyanatopentaamminechromium(III) photoaquation was earlier reported to be *trans*-$Cr(NH_3)_4(H_2O)(NCS)^{2+}$.[1] This configuration was inferred from spectral characteristics, which differed from those of a synthetic sample of *cis*-thiocyanatoaquotetraamminechromium(III). The trans isomer was not known at that time. Subsequently, this result became an exception to the pattern emerging for chromium(III) photosubstitutions, since the main photoproducts of other $Cr(NH_3)_5X^{2+}$ ions, where R = Cl,[2,3] Br,[4] RCOO,[5] were found, in all cases, to be *cis*-$Cr(NH_3)_4(H_2O)X^{2+}$. The exception gave rise to some discussion[3,6] about possible stereochemical consequences of Adamson's empirical rules for chromium(III) photolysis.[7,8] The case of $Cr(NH_3)_5(NCS)^{2+}$ has thus assumed a special importance and the recent availability of a reliable synthetic route for the preparation of *trans*-$Cr(NH_3)_4(H_2O)(NCS)^{2+}$ [9] prompted us to seek a positive characterization of the isomer form of the photoproduced thiocyanatoaquotetraamminechromium(III) complex. Through accurate spectral and kinetic measurements we have obtained definitive evidence that, contrary to the previous assignment, the photoproduct consists of at least 95% *cis*-$Cr(NH_3)_4(H_2O)(NCS)^{2+}$.

$[Cr(NH_3)_5(NCS)](ClO_4)_2$ and *cis*-$Cr(NH_3)_4(H_2O)(NCS)^{2+}$ were prepared as described,[1] the latter complex being obtainable only in solution. *trans*-$Cr(NH_3)_4(H_2O)(NCS)^{2+}$ was precipitated as the perchlorate salt after controlled acid hydrolysis, in the dark, of *trans*-$Cr(NH_3)_4(NCS)Cl^+$, which, in turn, was synthesized[9] by thiocyanate anation of *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$.[10] *Anal.* Calcd for $[Cr(NH_3)_4(H_2O)(NCS)](ClO_4)_2$: Cr, 13.16; NCS, 14.70; N, 17.72. Found: Cr, 12.9; NCS, 14.4; N, 17.4. The maxima of the ligand field absorption bands, L_1 and L_2,[8] for the two aquothiocyanato isomers are reported in Table I along with the crossing points with the spectrum of thiocyanatopentaamminechromium(III). The extinction coefficients of the cis isomer are found to be slightly higher than previously reported.[1] The absorption spectra of both isomers in acid solution remain unchanged over a period of at least 12 hr.

Aqueous solutions of *ca.* 10^{-2} *M* thiocyanatopentaamminechromium(III) in 5×10^{-3} *M* $HClO_4$ were irradiated at room temperature in 1-cm cells with 480-nm light (selected by means of a Baird-Atomic interference filter 11-94-5). The photoproduct has a much lower absorption than the starting

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