1612 *Inorg. Chem.* **1985**, *24*, 1612-1613

Reactions of Tetrachlorotetraborane, B_4Cl_4, with Trimethylstannane, Lithium Borohydride, and Diborane

Sir:

Due to the high symmetry of the compound and the unusual nature of the bonding within the cage, B_4Cl_4 is one of the more interesting small molecules known. In this cluster compound the four boron atoms are located at the corners of a tetrahedron with an exopolyhedral chlorine ligand attached to each boron atom[1] (see Figure 1). Much of the interest in B_4Cl_4 arises from the fact that when the usual framework-electron-counting procedures are employed there are only eight electrons delocalized within the cage. These eight electrons are thought to reside primarily in the four triangular faces of the tetrahedron.[2] In contrast, almost all other tetrahedral cage compounds—species like tetra-*tert*-butyltetrahedrane, white phosphorus, and $Ir_4(CO)_{12}$—have 12 framework electrons, which can be readily visualized as forming six localized 2-center-2-electron bonds, one bond between each pair of framework atoms.

While the bonding in B_4Cl_4 has been examined at a variety of levels, very little is known of the reactivity of this species. We wish to communicate the initial results of an ongoing study into the chemical consequences of electron deficiency in cluster compounds by reporting the products formed in the reaction of B_4Cl_4 with three typical hydrides: trimethylstannane, lithium borohydride, and diborane. During the interactions of B_4Cl_4 with these reagents the cage geometry is altered in three different fashions. Somewhat surprisingly, the isolated yields of the products formed in each of the reactions examined here are quite high, 63–95%.

Reaction with Trimethylstannane. In this reaction Me_3SnH was utilized as both solvent and reagent. When a solution of B_4Cl_4,[3] ca. 0.1 mmol, onto which a large excess of Me_3SnH had been condensed was allowed to warm from −196 °C, a violent reaction occurred immediately upon liquefaction and the solution assumed a dark red coloration. If the products of the reaction were separated within 3 min of warm-up, tetraborane(10) was recovered in 95% yield, based upon the amount of B_4Cl_4 originally taken. When longer residence times were employed, however, the isolated yield of B_4H_{10} decreased, becoming 26% after a 3-h period. Hexamethyldistannane and $ClSnMe_3$ were also produced during the course of the reaction.

Reaction with Lithium Borohydride. *n*-Butyl ether and B_4Cl_4 were condensed onto a 10-fold excess of $LiBH_4$, and the vessel was sealed and then allowed to warm from −196 °C. Boron-11 NMR spectra obtained within 5 min contained three sets of resonances, a singlet located at 85 ppm (B_4Cl_4) and two doublets found at −12.2 and 15.0 ppm (basal boron atoms of B_5H_9 and B_6H_{10}, respectively). After 5 min the relative molar ratios, as indicated by integration of the resonances, were 1.1:1.0:1.0. After 30 min at ambient temperature, B_4Cl_4 was no longer observed in the spectrum, whereupon the reactor was opened and noncondensable gas, presumably H_2, was removed. Boron NMR spectra of the volatile products indicated the presence of B_5H_9 and B_6H_{10} in a 3.4:1.0 molar ratio. Pentaborane(9), 0.0756 mmol, 63% yield, was separated by fractionation and identified by mass spectrometry. The yield of B_6H_{10} after the 30-min reaction was 19%.

Reaction with Diborane. Diborane, 0.820 mmol, B_4Cl_4, 0.0907 mmol, and *n*-pentane, 111.0 mg, were all sealed into a vessel that was then allowed to warm to ambient temperature. During the first 18 h, two liquid phases, a colorless, less dense phase and a bright yellow, more dense phase, began to separate. After 2–3 days the separation was complete.

If the reaction was terminated immediately after the yellow phase began to separate (6 h) and the bright yellow solids resulting were analyzed by mass spectrometry, the largest ions in the molecular ion region of the spectrum corresponded to the ion envelope expected for $B_6H_6Cl_4$ (calculated for $^{11}B_6{}^{35}Cl_4H_6$, 211.9768; measured, 211.9769). The next largest envelope of ions, 23% as intense, were centered about $m/e = 223$, which, as shown below, corresponds to $B_{10}Cl_3H_{11}$.

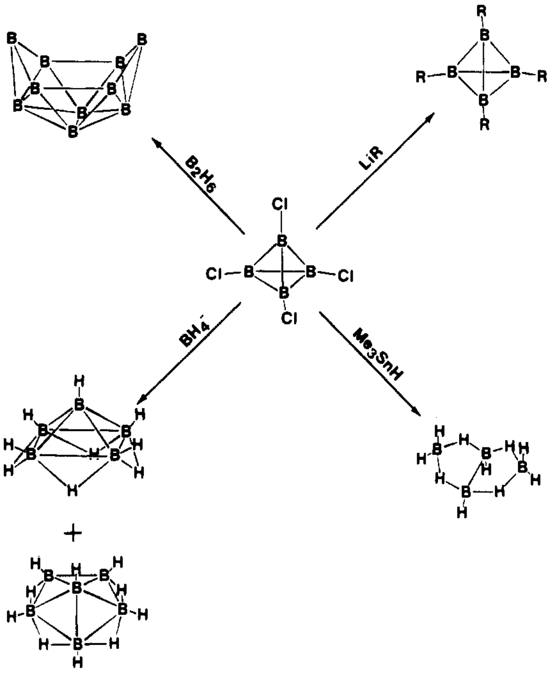

Figure 1. Illustration of the four different modes of reactivity encountered in B_4Cl_4: (1) ligand-exchange reactions with lithium alkyls, which leave the B_4 core symmetry essentially unchanged;[7] (2) the six-electron reduction of the B_4Cl_4 cage with Me_3SnH, which generates the butterfly-shaped B_4H_{10}; (3) insertion of two-electron-donating BH units from BH_4^- accompanied by the addition of four bridging hydrogens, yielding *nido*-B_5H_9 and B_6H_{10}; (4) framework fusion in the reaction with B_2H_6, ultimately leading to chlorinated decaborane derivatives (ligands omitted for clarity).

If the reaction was allowed to proceed for 2 days, mass spectrometry of the yellow material then obtained indicated that the products were predominantly chlorinated decaborane derivatives, $B_{10}H_nCl_{14-n}$, $n = 8$–12. Mass spectrometry indicated the following composition: $B_{10}Cl_6H_8$, 2.2%; $B_{10}Cl_5H_9$, 10.9%; $B_{10}Cl_4H_{10}$, 21.7%; $B_{10}Cl_3H_{11}$, 43.5%; $B_{10}Cl_2H_{12}$, 100%. To confirm the elemental composition of the trichloride, exact mass data were obtained: calculated for $^{11}B_{10}{}^{35}Cl_3H_{11}$, 226.0847; measured, 226.0840. The only other molecular ion of significant intensity was centered at m/e 211 ($B_6H_6Cl_4$, 41%).

While the boron NMR data from the bright yellow material obtained after 2 days reaction time were consistent with the formulation of the products as polychlorinted decaborane derivatives,[4] more conclusive confirmation was obtained from the reaction of B_4Cl_4 with B_2D_6. The most intense ion in each of the ion envelopes described above was then increased by one m/e unit per hydrogen atom replaced. For example, the ion envelope originally assigned to $B_{10}Cl_5H_9$ ($m/e = 293$) was observed at $m/e = 302$ when B_2D_6 had been utilized.

Ligand exchange between the more highly halogenated decarborane derivatives and B_2H_6 was demonstrated by sealing a fresh aliquot of B_2H_6 and solvent onto the bright yellow products obtained as above. Boron NMR indicated the formation of BCl_3, $BHCl_2$, and B_2H_5Cl while low-resolution mass spectra indicated an increase in the relative intensity of the less substituted chlorodecaboranes, e.g., $B_{10}Cl_2H_{12}$, at the expense of the more fully substituted species like $B_{10}Cl_5H_9$. On the basis of B_4Cl_4, the combined yield of the halodecaboranes was 80%; the residual was present as $B_6H_6Cl_4$, $B_6H_7Cl_3$, and $B_6H_8Cl_2$.

Discussion. When they are taken together, these reactions well illustrate the exceptional reactivity of the smallest tetrahedral

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[2] Hall, J. H. Jr.; Lipscomb, W. N. *Inorg. Chem.* **1974**, *13*, 710. Guest, M. F.; Hillier, I. H. *J. Chem. Soc., Faraday Trans 2* **1974**, *70*, 398.

[3] Davan, T.; Morrison, J. A. *Inorg. Chem.* **1979**, *18*, 3194.

[4] The boron NMR spectra of these products will be discussed separately. Typically, however, resonances were observed near −26 (2 B), +1.9 ($J_{B-H} = 178$ Hz, 4 B), and 26.5 ppm (4 B).

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cluster, B_4Cl_4. Both the speed and the selectivity of the first reaction (that with Me_3SnH) are remarkable. The halogen ligands are exchanged, two hydrogen atoms are positioned along one of the B–B vectors, and the four newly exposed edges of the former tetrahedron are hydrogenated, all within seconds and in 95% yield overall. The only product isolated, B_4H_{10}, clearly arises from a 6 electron reduction of the 4 vertex–8 electron B_4Cl_4 core, generating a 14 electron cluster with the appropriate butterfly geometry.

The second reaction (that with $LiBH_4$) indicates the ease with which electron-rich fragments can be incorporated into the B_4Cl_4 framework. Here, the insertion of one or two two-electron-donating BH vertices is accompanied by the formation of four BHB bridges to again form reduced (nido) species, B_5H_9 and B_6H_{10}, in 82% combined yield.

Perhaps the most interesting reaction is that between B_4Cl_4 and diborane, the latter at least potentially a 2 vertex–8 framework electron donor. The first product observed, after 6 h, is the 6 framework atom–16 electron cluster $B_6H_6Cl_4$. The final products, the chlorinated decaboranes, arise from the fusion of a second molecule of B_4Cl_4 with $B_4H_6Cl_4$, generating a 10 vertex–24 framework electron cluster in the process. The cluster fusion reaction is followed by ligand-exchange reactions with the excess B_2H_6 present. Under the conditions examined, the overall stoichiometry of the reaction corresponds very closely to $2B_4Cl_4 + 2B_2H_6 \rightarrow B_{10}Cl_xH_{14-x} + 2BCl_3$, $x \approx 2$.[5]

Collectively, as shown in Figure 1, the reactions of B_4Cl_4 demonstrate in a most concise fashion four different modes of cluster reactivity: ligand exchange, core reduction, framework atom incorporation, and cluster fusion. While these types of reactions have been previously observed in other chemical systems, it is very rare to find all four modes of reactivity demonstrated in the same substrate. These results suggest that B_4Cl_4 may prove to be a very suitable model compound for both experimental and theoretical studies of cluster reactivity. They also suggest that cluster fusion reactions of B_4Cl_4 with larger boranes or their halogenated derivatives might result in the formation of very large cluster compounds, boranes whose structures are based upon transicosahedral geometries.[6]

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Registry No. B_4Cl_4, 17156-85-3; Me_3SnH, 1631-73-8; B_4H_{10}, 18283-93-7; $LiBH_4$, 16949-15-8; B_5H_9, 19624-22-7; B_6H_{10}, 23777-80-2; B_2H_6, 19287-45-7; $B_6H_6Cl_4$, 95979-59-2; $B_{10}Cl_3H_{11}$, 95979-60-5; $B_{10}Cl_6H_8$, 95979-61-6; $B_{10}Cl_5H_9$, 95979-62-7; $B_{10}Cl_4H_{10}$, 95979-63-8; $B_{10}Cl_2H_{12}$, 93385-83-2; BCl_3, 10294-34-5; $BHCl_2$, 10325-39-0; B_2H_5Cl, 17927-57-0; $B_6H_7Cl_3$, 95979-64-9; $B_6H_8Cl_2$, 95979-65-0.

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Articles

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Synthesis of Unusual Phosphine Ligands. Use of the 1-Naphthylmethyl Moiety as a P–H Protecting Group in the Synthesis of a Phosphino Macrocycle That Contains a Secondary-Phosphino Ligating Site[1]

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A protecting group for a P–H group in a secondary phosphine has been developed, which is a (1-naphthylmethyl)phosphine sulfide. This has been used to convert (1-naphthylmethyl)phosphine into bis(3-chloropropyl)(1-naphthylmethyl)phosphine sulfide, which upon reaction with bis(lithiophenylphosphino)benzene, was transformed into the 11-P_3 macrocycle *cis*-2,10-diphenyl-6-(1-naphthylmethyl)-2,6,10-triphosphabicyclo[9.4.0]pentadeca-1(11),12,14-triene 6-sulfide. The 1-naphthylmethyl moiety was removed quantitatively with potassium naphthalenide to give the 11-P_3 molecule with a secondary phosphine sulfide at the 6-position. This was reduced with a reagent derived from lithium aluminum hydride and trimethylsilyl chloride to give the 11-P_3 macrocycle containing a secondary phosphine, *cis*-2,10-diphenyl-2,6,10-triphosphabicyclo[9.4.0]pentadeca-1(11),12,14-triene (**2a**), which exists as two isomers (H cis and trans to the phenyl groups). Ligand **2a** forms complexes with Rh(I) and Mo(0) in which all three ligating sites are involved in the metal coordination.

Introduction

As part of our longstanding interest in phosphino macrocycles, we have wished to synthesize such species that contain secondary-phosphino sites. Such ligands could be converted into bicyclic species and linked to other cycles to give clam-like ligands. In metal complexes, the PH could be deprotonated, thereby easily changing (fine-tuning) the properties of the coordinated metal. In addition, the secondary phosphine could serve as a precursor to a bridging phosphide in bi- and polynuclear complexes.[2] We have described three macrocycles that contain PH sites, but these were of the arylalkylphosphine types (**1**),[3] and we sought to have a more general approach that would allow us to incorporate dialkylphosphines into macrocyclic ligands, as exemplified by **2**.

Results and Discussion

In order to synthesize **2**, it would be necessary to prepare **6** (eq 1) or a functional-group equivalent. We had established that commercially available **3** could be transformed into **4** and then

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