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Reactions of the Octahydrotriborate (−1) Ion with Mercury Salts

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The octahydrotriborate ion ($B_3H_8^-$) reacts with $HgCl_2$, Hg_2Cl_2 (and complexes of Hg^I and Hg^{II}) in the presence of ligands, L, to give complexes LB_3H_7, and cleavage and chlorinated decomposition products.

Introduction

There has been considerable interest recently in the oxidation and substitution of the octahydrotriborate(−1) ion, $B_3H_8^-$, and its ligand derivatives, LB_3H_7. The $B_3H_8^-$ ion undergoes electrochemical oxidation in the presence of acetonitrile to give $MeCNB_3H_7$ [1], and reacts with hydrogen halides either by hydride abstraction and formation of LB_3H_7 [1, 2], or by substitution to give $B_3H_7X^-$ [3]. Other protonic acids lead to higher boranes through hydrogen abstraction and subsequent reaction of the $[B_3H_7]$ intermediate [4]. These reactions parallel those of the tetrahydroborate(−1) ion, BH_4^-. Although reactions of the tetrahydroborate(−1) ion with Lewis acids have often been used as methods of preparing diborane and its derivatives LBH_3 [5], few studies on the octahydrotriborate(−1) ion have been reported.

We now describe the products of reaction of the octahydrotriborate(−1) ion with $HgCl_2$ and Hg_2Cl_2 and their complexes in the presence of ligands. For comparison we have investigated the analogous reaction of the tetrahydroborate(−1) ion with $HgCl_2$ in the presence of triphenylphosphine.

Experimental

Solvents and Starting Materials

Tetrahydrofuran (THF) was stored over CaH_2 and distilled from either $LiAlH_4$ or Na–benzophenone under vacuum before use. $(Ph_3P)_2HgCl_2$, $(Ph_3P)_2Hg_2Cl_4$, and $(Me_3N)_2Hg_3Cl_6$ were prepared by direct reaction of the reagents in ethanol. Ph_3P, $Me_4NB_3H_8$, $NaBH_4$, $HgCl_2$ and Hg_2Cl_2 were dried under vacuum before use. $Me_3NB_3H_7$ was prepared from Me_3NHCl and $Me_4NB_3H_8$ by refluxing in THF, and was purified by vacuum sublimation.

N.m.r. Spectra

These were obtained on a JEOL-PS-100-PFT-100 nmr spectrometer operated at 25.15 MHz utilizing the ^{13}C probe, and operating unlocked at reduced field strength. Chemical shifts are reported relative to external BF_3OEt_2, or capillary BF_3OEt_2 inserted in the 8 mm sample tubes, and are quoted in ppm on the recently adopted convention (III^rd I.M.E. Boron Conference, Ettal, July, 1976) that positive shifts are to low field. Slight shift differences are observed between the external and capillary references. Coupling constants are in Hz.

Reaction of $NaBH_4$ with $HgCl_2$ in the Presence of Ph_3P

Sodium tetrahydroborate (0.38g, 10 mmol) was dissolved in 100 ml of THF and triphenylphosphine (2.62g, 10 mmol) and mercuric chloride (1.35g, 5 mmol) were added. The mixture was stirred at room temperature overnight, filtered under nitrogen, and the solvent removed under vacuum to give 2.6g of crude Ph_3PBH_3 (94%) which was recrystallised from methanol. It was identified by its IR spectrum (BH str.; 2378, 2340sh cm^{-1}), and its ^{11}B n.m.r. (1:3:3:1 quartet of 1:1 doublets, δ, 37.6; J_{BH}, 98; J_{BP}, 56 [6] and partial ^1H n.m.r. (broad 1:1:1:1 quartet, δ, 1.30; J_{BH}, 98).

Reactions of Hg_2Cl_2 and $HgCl_2$ with $Me_4NB_3H_8$

Typically, a reaction vessel, equipped with a magnetic stirrer, vacuum stopcock, and a side-arm with a glass sinter leading to an evacuated n.m.r. tube, was charged with the solid reagents $Me_4NB_3H_8$ (0.485g, 4.2 mmol) and Hg_2Cl_2 (1.0g, 2.1 mmol). The vessel was evacuated, and THF (20 ml) condensed in from the vacuum line. The vessel was warmed to room temperature and stirred overnight. After being frozen and the hydrogen pumped off the mixture was filtered into the n.m.r. tube which was then sealed under vacuum. The ^{11}B n.m.r. spectrum showed a weak 1:1 doublet (δ, 27; J, 161) due to $(BuO)_2BH$ [7, 8], a weak singlet (δ, 17.8) due to $(BuO)_3B$ [7, 8], a weak 1:2:1 triplet (δ, 4; J, 134) due to $THF{\cdot}BH_2Cl$ [9], and a strong asymmetric multiplet (δ, −8.7; J, 41) due to $THF{\cdot}B_3H_7$ [10]. A repeat reaction allowed to react for only 1 hour showed only the weak triplet (δ, 4.4; J, 134) and the asymmetric multiplet (δ, −8.3; J, 39). The reaction of a similar molar ratio of $HgCl_2$ and $Me_4NB_3H_8$ give the same products except that the n.m.r. signals due to the by-products, in particular the 1:2:1 triplet, were considerably more intense. Prolonged storage of the samples resulted in the intensity of the signals due to by-products, in particular the singlet, increased at the expense of the multiplets, and a precipitate formed.

Reactions of Hg_2Cl_2 or $HgCl_2$ with $Me_4NB_3H_8$ and the Amines Me_3N or Et_3N

As an example of a series of reactions carried out, Hg_2Cl_2 (1.18 g, 2.5 mmol) and $Me_4NB_3H_8$ (0.575g, 5 mmol) were placed in the apparatus described previously, and THF (10 ml) was condensed in under vacuum. The mixture was warmed to room temperature and stirred for 1/2 hr. The mixture was refrozen and Me_3N (0.345g, 5.8 mmol) was condensed in, the mixture stirred overnight, and then filtered into the n.m.r. tube. The ^{11}B n.m.r. spectrum showed a number of resonances of comparable intensity, comprising a multiplet (δ, −30.1; J, 33) due to $B_3H_8^-$ [7], an asymmetric multiplet (δ, −18.9; J, 35) due to $Me_3NB_3H_7$ [11], a 1:3:3:1 quartet (δ, −8.3; J, 98) due to Me_3NBH_3 [7, 12], and a 1:2:1 triplet (δ, −0.6; J, 121) due to Me_3NBH_2Cl. The identity of a number of the species ($Me_3NB_3H_7$, Me_3NBH_3, Me_3NBH_2Cl) was checked by comparison of the ^{11}B n.m.r. of authentic materials prepared by standard methods.

After storage for 3 months, the fraction of Me_3NBH_3 increased slightly at the expense of $Me_3NB_3H_7$, and a precipitate formed, whose ^{11}B n.m.r. in CH_2Cl_2 was broad and featureless.

A similar reaction was run between $Me_4NB_3H_8$ (0.485g, 4.2mmol) Hg_2Cl_2 (1.0g, 2.1 mmol) in THF (8 ml), stirred overnight, Et_3N (0.428g, 4.2 mmol) condensed in, and the mixture stirred for four days before being filtered into the n.m.r. tube. The ^{11}B n.m.r. spectrum showed a trace of a multiplet (δ, −30.5; J, 34) due to $B_3H_8^-$ [7], a strong broad resonance (δ, −21.8), a weak 1:3:3:1 quartet (δ, −13.6; J, 99) due to Et_3NBH_3, and a weak overlapping triplet (δ, −5.6; J, 127) due to Et_3NBH_2Cl [13, 14]. On storage at room temperature for 3 months, the ^{11}B spectrum changed by decreasing considerably the signal due to $Et_3NB_3H_7$, increasing that due to Et_3NBH_3, developing the signal due to $(BuO)_3B$ while that due to Et_3NBH_2Cl remained essentially unaltered. A precipitate also formed in the n.m.r. tube, whose ^{11}B spectrum in CH_2Cl_2 was broad and featureless.

$Me_4NB_3H_8$ (0.57g, 5 mmol), and 80 ml of THF was treated with the preformed complex $(Me_3N)_2Hg_3Cl_6$ (0.85g, 0.97 mmol) with stirring for 6 hr. The solution, filtered under N_2, was concentrated to half its volume, and the ^{11}B n.m.r. spectrum obtained. This showed a weak multiplet (δ, −18.6; J, 34) due to $Me_3NB_3H_7$, a strong, poorly resolved multiplet (δ, −9.6; J, 34) due to $THF{\cdot}B_3H_7$, and traces of $(BuO)_3B$, $THF{\cdot}BH_2Cl$, and an unidentified product (δ, −27).

Reactions of $Me_4NB_3H_8$ with $HgCl_2$ in the Presence of Ph_3P

A slurry of $Me_4NB_3H_8$ (1.14g, 10 mmol) and Ph_3P (2.62g, 10 mmol) in 100 ml of THF was treated with $HgCl_2$ (1.35g, 5 mmol) with stirring overnight. The solution was filtered under N_2, and solvent removed under vacuum to give 2.7g of crude product whose IR and ^{11}B n.m.r. spectra indicated a mixture of Ph_3PBH_3 (δ, −39.7) [6], and $Ph_3PB_3H_7$ ($\delta_{2,3}$, −15.9; δ_1, −45.8).

A reaction of a slurry of $Me_4NB_3H_8$ (0.57g, 5 mmol) in 50 ml of THF with preformed $(Ph_3P)_2HgCl_2$ (1.98 g, 2.5 mmol) which was added in three successive portions in a total of 20 ml of THF. A series of n.m.r. samples were taken, and the ^{11}B spectrum recorded, at the reaction times after the addition; the results are presented in the Table.

Sample	Fraction of $(Ph_3P)_2HgCl_2$ added	Reaction time (min)	Spectrum observed
1	0	0	–
2	1/3	5	–
3	2/3	10	$Ph_3PB_3H_7$
4	all	15	$Ph_3PB_3H_7$
5	–	45	$Ph_3PB_3H_7$ + Trace Ph_3PBH_3
6	–	overnight	$Ph_3PB_3H_7$ + Ph_3PBH_3

$Me_4NB_3H_8$ (0.285g, 2.5 mmol and $(Ph_3P)_2HgCl_2$, (0.99g, 1.25 mmol), onto which 8 ml of THF was condensed under vacuum, were allowed to stir at room temperature for 15 min. The mixture was filtered into an n.m.r. tube and the ^{11}B spectrum showed only $Ph_3PB_3H_7$ ($\delta_{2,3}$, −16.3: δ_1, −46.1).

Reaction of $Me_4NB_3H_8$ (0.57g, 5 mmol) and preformed $(Ph_3P)_2Hg_2Cl_4$ (1.34g, 1.26 mmol) in 70 ml of THF resulted in an n.m.r. spectrum consistent with the mixed products from $HgCl_2$ and $(Ph_3P)_2HgCl_2$, namely $(BuO)_2BH$, $(BuO)_3B$, $THFBH_2Cl$, and superposition of $THFB_3H_7$ and $Ph_3PB_3H_7$ signals.

Results and Discussion

In an attempt to develop a convenient synthetic method for a range of LB_3H_7 adducts, we have examined reactions of the conveniently accessible octahydrotriborate anion, $B_3H_8^-$ with mercuric and mercurous chloride in the presence of a ligand, L. The methods previously described for the preparation of these derivatives either involve the inconvenient and hazardous hydride, B_4H_{10}, or have limited applicability, such as the reaction of salts of $B_3H_8^-$ with $Me_3NH^+Cl^-$ [15–19]. We wished to ascertain whether the reaction with a Lewis acid would offer the advantages that are apparent in the reactions of tetrahydroborate anion, BH_4^-, and whether further substitution of hydride by halide would occur as had been observed in borane derivatives [20, 21].

We have found that BH_4^- reacts smoothly and cleanly with a stoichiometric quantity of $HgCl_2$ in the presence of triphenylphosphine to give triphenylphosphine-borane uncontaminated with chlorinated by-products.

In contrast, the reactions of $B_3H_8^-$ do not proceed so cleanly. In the absence of ligands other than the solvent tetrahydrofuran, reactions with either $HgCl_2$ or Hg_2Cl_2 lead predominantly to the adduct $THFB_3H_7$, although $HgCl_2$ gives a higher proportion of by-products. In both cases, particularly on standing for several hours at room temperature, cleavage of the THF by B–H bonds, and rupture of the triborane moiety occur with the formation of $(BuO)_3B$ and $(BuO)_2BH$. We were unable to observe either $THFBH_3$ [22] or $BuOBH_2$ in THF despite repeated attempts to observe them. The absence of the former is curious in that cleavage of $THFB_3H_7$ by excess THF ligand might have been expected to lead to $THFBH_3$ and $(THF)_2B_2H_4$ according to the reported cleavage of LB_3H_7 by excess ligands [6, 18, 23]. Even on prolonged storage neither decomposition product is observed, in contrast with the decomposition of B_3H_7CO which degrades to $B_2H_4(CO)_2$. The absence of $BuOBH_2$ in THF is perhaps less surprising in that it has been suggested that this compound is thermodynamically unstable with respect to disproportionation to $(BuO)_2BH$ and $THFBH_3$ [8]. In order to account for the observation of $THFBH_2Cl$, chlorination of a boron moiety must occur. This may be accomplished in either of two ways; direct chlorination of a B–H bond by the mercury halide undoubtedly occurs with $HgCl_2$ at least, analogous to reactions previously reported [20, 21]. In addition, some competition for the vacant coordination site of the intermediate $[B_3H_7]$ by THF and Cl^- may lead to a proportion of $B_3H_7Cl^-$ which subsequently reacts further and cleaves to $THFBH_2Cl$.

Reactions of $Me_4NB_3H_8$ with mercury chlorides in THF in the presence of added ligand, L, resulted in formation of the LB_3H_7 adduct. However, when the ligand was present in excess, some cleavage occurred and a significant amount of LBH_3 was observed. It is probable that some $L_2B_2H_4$ was also formed. In attempts to reduce the proportions of by-products to the desired LB_3H_7 species, a stoichiometric quality of ligand, L, was added to the reaction mixture after initial formation of $THFB_3H_7$ had occurred. Even under these conditions some cleavage was still apparent. All reactions with amine ligands yielded chlorinated by-products, LBH_2Cl, although the amount of this was greater in reactions involving $HgCl_2$ than those of Hg_2Cl_2.

Attempts to obtain purer products were made by examining reactions of preformed ligand–mercuric halide complexes. The adduct of stoichiometry $(Me_3N)_2Hg_3Cl_6$ reacted as might be expected for a mixture of Me_3N and $HgCl_2$; $Me_3NB_3H_7$ and $THFB_3H_7$ were the major products. Similarly, the adduct $(Ph_3P)_2Hg_2Cl_4$ produced $Ph_3PB_3H_7$, $THFB_3H_7$ and their decomposition products. A study of the reaction of $(Ph_3P)_2HgCl_2$ with $Me_4NB_3H_8$ showed that $Ph_3PB_3H_7$ was formed rapidly, but that prolonged storage resulted in cleavage to Ph_3PBH_3 and presumably $(Ph_3P)_2B_2H_4$.

In summary, reactions of $Me_4NB_3H_8$ with Hg_2Cl_2 can yield the adduct $THFB_3H_7$ in reasonable purity provided that the reaction time is kept to a minimum. Similarly $Ph_3PB_3H_7$ may be prepared from $(Ph_3P)_2HgCl_2$ if the time of reaction is limited. Displacement reactions with amine ligands on $THFB_3H_7$ yields LB_3H_7 products of moderate purity.

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