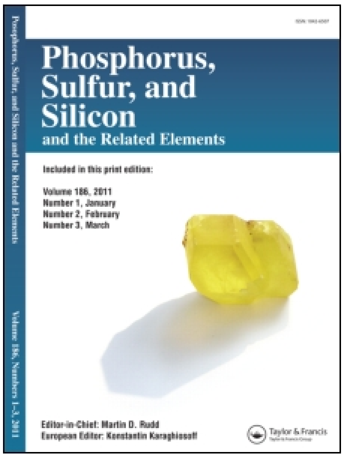

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Hydride Abstraction from the Octahydrotriborate Ion and Formation of Bridged Triborane(7)-Phosphane Complexes

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Hydride Abstraction from the Octahydrotriborate Ion and Formation of Bridged Triborane(7)-Phosphane Complexes

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Reaction of two equivalents of $(Bu_4N)[B_3H_8]$ *with a variety of metal halides* ($TiBr_4$, $TiCl_4$, WCl_6, *or* $GeCl_4$) *results in nearly instantaneous hydride abstraction and the formation of* $THF{\cdot}B_3H_7$. *Subsequent reactions with bidentate phosphanes lead to the first triborane(7)-phosphane complexes with a bridging phosphane ligand:* (B_3H_7)-$P(Ph_2)$-$(CH_2)_m$-$P(Ph_2)$-(B_3H_7) (***1****,* $m = 1$*;* ***2****,* $m = 2$*;* ***3****,* $m = 4$*;* ***4****,* $m = 6$*). (Compounds* ***1–4*** *also can be made in "one-pot" syntheses.) Compounds* ***1–4*** *and the previously reported* $Ph_3P{\cdot}B_3H_7$ *are characterized by* ^{11}B *and* ^{31}P *NMR spectroscopy.*

Keywords Borane; phosphane; bridging; ^{11}B NMR; ^{31}P NMR

INTRODUCTION

Homoleptic complexes of the octahydrotriborate ligand can be used as chemical vapor deposition (CVD) precursors.[1,2] However, the rarity of such complexes makes this application quite limited. Therefore, in this article, we endeavored to expand this class of compounds.

To achieve this goal, we allowed two equivalents of $(Bu_4N)[B_3H_8]$ to react with a variety of metal halides ($TiBr_4$, $TiCl_4$, WCl_6, or $GeCl_4$). However, rather than forming new metal-octahydrotriborate complexes, the metal halides caused nearly instantaneous hydride abstraction and the formation of $THF{\cdot}B_3H_7$. Subsequent reactions with bidentate phosphanes led to the first triborane(7)-phosphane complexes with a bridging phosphane ligand.

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RESULTS AND DISCUSSION

The only reported homoleptic complexes of the octahydrotriborate ligand are $Cr(B_3H_8)_2$ and $Be(B_3H_8)_2$.[1,3–5] Both complexes are synthesized by reacting a $[B_3H_8]^-$ salt with the respective metal chloride ($CrCl_3$ or $BeCl_2$). We anticipated that allowing $(Bu_4N)[B_3H_8]$ to react with the metal halides $TiBr_4$, $TiCl_4$, WCl_6, and $GeCl_4$ might lead to new homoleptic complexes. However, the metal halides cause nearly instantaneous hydride abstraction, and the formation of $THF{\cdot}B_3H_7$, along with small amounts of $(BuO)_3B$, $(BuO)_2BH$, and, for the chlorides, $THF{\cdot}BH_2Cl$. Hydride abstraction (and the same collection of by-products) also occurs when either Hg_2Cl_2 or $HgCl_2$ are allowed to react with $(Me_4N)[B_3H_8]$.[6]

No obvious periodic trend exists for the seven metal chlorides employed in the above syntheses. A main-group metal (Be) and a transition metal (Cr) give homoleptic complexes, while two main-group metals (Hg, Ge) and two transition metals (Ti, W) promote hydride abstraction. (Interestingly, Cr and W are in the same triad.) However, an examination of the solid state character of the chlorides reveals significant differences. The five compounds that promote hydride abstraction are all covalent compounds (WCl_6 is best described as a coordination compound) that exist as discrete molecules in the solid state.[7] By comparison, $CrCl_3$ is an ionic compound and $BeCl_2$, while a molecular compound with covalent bonds, forms chains in which the Be atoms are linked by Cl bridges.[7] This empirical observation might provide a clue to the different reactivity of these two sets of chlorides.

When triphenylphosphane is included in the reaction mixture with $(Me_4N)[B_3H_8]$ and either mercury chloride, $Ph_3P{\cdot}B_3H_7$ is produced.[6] Likewise, adding PPh_3 to a mixture of $TiCl_4$, WCl_6, or $GeCl_4$ and $(Bu_4N)[B_3H_8]$ gave $Ph_3P{\cdot}B_3H_7$. Alternately, adding PPh_3 after the $THF{\cdot}B_3H_7$ has formed also yields $Ph_3P{\cdot}B_3H_7$. The ^{11}B NMR spectrum ($\delta = -15.8$ (2B), $\delta = -44.9$ (1B)) is similar to that reported earlier.[6] In the $^{11}B\ \{^1H\}$ NMR spectrum the upfield signal appears as a doublet ($J_{B-P} = 88$ Hz). This coupling constant is comparable to those of the adducts $(CH_3)_mPH_{3-m}{\cdot}B_3H_7$ ($m = 1, 2, 3$).[8]

The ^{31}P NMR chemical shift fits the trend observed for a series of phosphane-borane adducts (Table I). For the borane(3) adducts $(CH_3)_mPH_{3-m}{\cdot}BH_3$, the ^{31}P NMR chemical shift moves *upfield* as ‘m’ increases; furthermore, as phenyl groups replace the methyl groups, the ^{31}P NMR chemical shift moves even further upfield. Conversely, for the triborane(7) adducts $(CH_3)_mPH_{3-m}{\cdot}B_3H_7$ the ^{31}P NMR chemical shift moves *downfield* as ‘m’ increases. Thus, one would expect the ^{31}P NMR chemical shift to move even further downfield as $P(CH_3)_3$ is replaced by $P(C_6H_5)_3$, as is observed.

TABLE I ^{31}P NMR Chemical Shift Data for Phosphane-Borane Complexes

Complex	δ(ppm)[a]	Complex	δ(ppm)[a]
$PH_3{\cdot}BH_3$	+113[b]	$PH_3{\cdot}B_3H_7$	−96.3[c]
$(CH_3)PH_2{\cdot}BH_3$	+68.5[b]	$(CH_3)PH_2{\cdot}B_3H_7$	−56.3[c]
$(C_6H_5)PH_2{\cdot}BH_3$	+49.3[b]	$(CH_3)_2PH{\cdot}B_3H_7$	−24.5[c]
$(CH_3)_3P{\cdot}BH_3$	+1.8[b]	$(CH_3)_3P{\cdot}B_3H_7$	−1.3[c]
$(C_6H_5)(CH_3)_2P{\cdot}BH_3$	−49.0[b]	$(C_6H_5)_3P{\cdot}B_3H_7$	+27.6[d]

[a]Relative to external 85% H_3PO_4; [b]Cowley and Damasco;[11] [c]Bishop and Kodama;[8] and [d]this work.

Substituting the bidentate phosphanes (*bis*) diphenylphosphinomethane (dppm), (*bis*) diphenylphosphinoethane (dppe), (*bis*)diphenylphosphinobutane (dppb), and (*bis*) diphenylphosphinohexane (dpph), respectively, for the triphenylphosphane leads to the first triborane(7)-phosphane complexes with a bridging phosphane ligand: (B_3H_7)-$P(Ph_2)$-$(CH_2)_m$-$P(Ph_2)$-(B_3H_7) (**1**, m = 1; **2**, m = 2; **3**, m = 4; **4**, m = 6). The only other reported complex with two bridged triborane(7) units is the anion $[H_7B_3\text{-}NC\text{-}B_3H_7]^-$.[9] Compounds **1–4** are obtained either by adding the phosphane to the previously generated $THF{\cdot}B_3H_7$, or by mixing together the metal chloride, $(Bu_4N)[B_3H_8]$, and phosphane in a "one-pot" synthesis. Compounds **1–4** are unstable and decompose within a day at room temperature to borane(3)-phosphane adducts, which is also the fate of several other triborane(7)-phosphane complexes.[6,8]

The $^{11}B\{^1H\}$ NMR spectra of **1–4** (Table II) resemble that of $Ph_3P{\cdot}B_3H_7$, with the upfield signal likewise appearing as a doublet. The bridging nature of these phosphane ligands was established by allowing two equivalents of $THF{\cdot}B_3H_7$ to react with each phosphane. As

TABLE II NMR Data for Triborane(7) Complexes with Bridging Phosphanes

Compound	$^{11}B\{^1H\}$ (ppm)[a]	J_{B-P} (Hz)	^{31}P (ppm)[b]
1	−16.3 (s, 2B), −44.5 (d, 1B)	78	+19.5
2	−15.2 (s, 2B), −47.3 (d, 1B)	76	+22.1
3	−15.4 (s, 2B), −46.8 (d, 1B)	107	+18.3
4	−15.5 (s, 2B), −47.1 (d, 1B)	98	+19.2

[a]Relative to external $BF_3{\cdot}OEt_2$; [b]Relative to external 85% H_3PO_4.

observed in the ^{11}B NMR spectrum, all the THF·B_3H_7 was consumed, and only the respective compound **1–4** was present.

EXPERIMENTAL

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. THF was distilled under nitrogen from sodium benzophenone ketal. $TiBr_4$ and WCl_6 (Strem), $GeCl_4$ (Gelest), and $TiCl_4$ (1.0 M in toluene), PPh_3, dppm, dppe, dppb, and dpph (Aldrich) were used as received. $(Bu_4N)B_3H_8$ was prepared by the method described by Ryschkewitsch and Nainan.[10] NMR spectra were measured at room temperature on a Varian-300 FT-NMR spectrometer operating at 96.3 MHz for ^{11}B spectra and 121.5 MHz for ^{31}P spectra. $BF_3{\cdot}OEt_2$ ($\delta = 0$ ppm) and 85% H_3PO_4 ($\delta = 0$ ppm) were used as external references for ^{11}B and ^{31}P spectra, respectively.

The following describes a typical experiment: A 100-mL two-necked flask was charged with $TiBr_4$ (0.074 g, 0.20 mmol), dppe (0.080 g, 0.20 mmol), $(Bu_4N)B_3H_8$ (0.113 g, 0.400 mmol), and a stir bar. A stopcock-adapter was inserted in one neck, and the second neck was plugged with a septum. The system was evacuated on a Schlenk line and filled with nitrogen; a nitrogen atmosphere was maintained throughout the experiment. THF (10 mL) was added via syringe, and the solution was stirred vigorously for several seconds. A sample was removed via syringe for NMR spectroscopy.

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