systematically altered and it was found that a reactant weight ratio of *ca.* 2.5:1:4 heated for 2–2.5 hr at 150° maximized the yield, although this was still only moderate. So, from *p*-xylene (30.0 ml), aluminum (10.0 g), boron trichloride (40.0 g), and 0.1 g of methyl iodide and 0.1 g of iodine as activators after multiple fractionation at 0.4–0.5 mm and 65–70°, 8 g of product was obtained. The presence of a small amount of unreacted aluminum at the end of the reaction indicated the absence of appreciable concentrations of HCl during the reaction.

The nmr spectrum of the product indicated that the product was a 9:1 ratio of the *meta* (3,5-dimethyl) to *ortho* (3,4-dimethyl) isomers. It was not found possible to separate them, but the mixture analyzed correctly. *Anal.* Calcd for $C_8H_9BCl_2$: C, 51.4; H, 4.9. Found: C, 49.8; H, 4.9. Further, the dipole moment of the mixture, 2.517 and 2.519 D., the two measurements being on samples from different preparations, agrees well with that calculated, 2.506 D. (The dipole moment of the pure *o*-xylyl compound is 2.681 D. and that of the pure *meta* isomer 2.487 D., all measurements being made in carbon tetrachloride solution at 25°.[13]) Pure *ortho* and *meta* isomers were made by Muetterties' method[5,6] (xylene:boron trichloride: aluminum weight ratio of *ca.* 2:2:1, heating at 150° for 1 hr); no rearrangements occurred in these preparations.

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Chemistry of Boranes. XXXII.[1] Borane Carbonyls as Acylating Agents; Bis-Boranyl Ketones

BY W. H. KNOTH, N. E. MILLER, AND W. R. HERTLER

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The reaction of 1,10-$B_{10}Cl_8(CO)_2$ with N,N-dimethylaniline has given 1,10-$B_{10}Cl_8[COC_6H_4N(CH_3)_2]_2^{2-}$. The reactions of various carbonyl derivatives of $B_{10}H_{10}^{2-}$ with $B_{10}H_{10}^{2-}$ and several of its derivatives have given a series of bis-boranyl ketones, exemplified by $(CH_3)_2SB_{10}H_8COB_{10}H_9^{3-}$. The carbonyl groups in these ketones are exceedingly basic, and the anions are customarily isolated as salts of protonated species, *e.g.*, $(CH_3)_2SB_{10}H_8COHB_{10}H_9^{2-}$.

A diverse chemistry has previously been reported for carbonyl derivatives of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$.[1-5] Carbonyls such as 1,10-$B_{10}H_8(CO)_2$, 1,10-$B_{10}Cl_8(CO)_2$, $B_{12}H_{10}(CO)_2$, and 1,6-$(CH_3)_2SB_{10}H_8CO$ have been used as intermediates to carboxyl,[2-5] isocyanate,[2-4] hydroxymethyl,[1] nitrile,[2,3] and other derivatives of the B_{10} and B_{12} cage anions. They have also been treated with organomercurials to obtain acyl derivatives.[3] Acyl derivatives had previously been obtained[5,6] by the reaction of aromatic acid halides with $B_{10}H_{10}^{2-}$ and had been shown[6] to have ketonic properties

$$1,10\text{-}B_{10}Cl_8(CO)_2 \xrightarrow{(C_2H_5)_2Hg} 1,10\text{-}B_{10}Cl_8(COC_2H_5)_2^{2-} \quad {}^{3}$$

$$B_{10}H_{10}^{2-} + C_6H_5COCl \longrightarrow 2\text{-}B_{10}H_9COC_6H_5^{2-} \quad {}^{6}$$

We wish to report that a third route to such organo-inorganic ketones consists of using borane carbonyls as acylating agents for active organic aromatic compounds. Furthermore, these carbonyls acylate the B_{10} cage to give a series of bis-boranyl ketones. The first type of acylation is exemplified by the reactions of 1,7-$B_{12}H_{10}(CO)_2$ and 1,10-$B_{10}Cl_8(CO)_2$ with N,N-dimethylaniline

$$1,10\text{-}B_{10}Cl_8(CO)_2 \xrightarrow{C_6H_5N(CH_3)_2} 1,10\text{-}B_{10}Cl_8[COC_6H_4N(CH_3)_2]_2^{2-}$$

$$1,7\text{-}B_{12}H_{10}(CO)_2 \xrightarrow{C_6H_5N(CH_3)_2} 1,7\text{-}B_{12}H_{10}[COC_6H_4N(CH_3)_2]_2^{2-}$$

These anions can be isolated as inner salts, *e.g.*, 1,10-$B_{10}Cl_8[COC_6H_4NH(CH_3)_2]_2$, or as normal salts. The infrared carbonyl stretching frequencies for $[(CH_3)_4N]_2$-1,10-$B_{10}Cl_8[COC_6H_4N(CH_3)_2]_2$ and Cs_2-1,7-$B_{12}H_{10}[COC_6H_4N(CH_3)_2]_2$ are at 1620 and 1600 cm^{-1}, respectively. A value of 1615 cm^{-1} was previously reported[6] for $[(CH_3)_4N]_2B_{10}Cl_9COC_6H_5$.

The reaction of 1,10-$B_{10}H_8(CO)_2$ with $(NH_4)_2B_{10}H_{10}$ proceeds smoothly in acetonitrile to give, after work-up in aqueous solution, $B_{10}H_9COB_{10}H_8COOH^{4-}$. However, the ketocarbonyl group in this inorganic ketone is extremely basic; the isolated salts of this anion are invariably protonated so that a more realistic representation of this species is $B_{10}H_9COHB_{10}H_8COOH^{3-}$

$$B_{10}H_8(CO)_2 + B_{10}H_{10}^{-2} \xrightarrow{-H^+} [B_{10}H_9COB_{10}H_8CO^{3-}] \xrightarrow[-H^+]{H_2O}$$

$$B_{10}H_9COB_{10}H_8COOH^{4-} \overset{H^+}{\rightleftharpoons} B_{10}H_9COHB_{10}H_8COOH^{3-}$$

Titration in water of the conjugated acid of this anion shows the presence of three strongly acidic protons, one weakly acidic, and one very weakly acidic, in agreement with this representation. Similar protonated species and their preparations include

$$B_{10}H_8(CO)_2 + B_{10}H_9S(CH_3)_2^{-} \longrightarrow (CH_3)_2SB_{10}H_8COHB_{10}H_8COOH^{2-}$$

$$B_{10}Cl_8(CO)_2 + B_{10}H_8[S(CH_3)_2]_2 \longrightarrow [(CH_3)_2S]_2B_{10}H_7COHB_{10}Cl_8COOH^{-}$$

$$(CH_3)_2SB_{10}H_8CO + B_{10}H_{10}^{2-} \longrightarrow (CH_3)_2SB_{10}H_8COHB_{10}H_9^{2-}$$

$$(CH_3)_3NB_{10}H_8CO + B_{10}H_{10}^{2-} \longrightarrow (CH_3)_3NB_{10}H_8COHB_{10}H_9^{2-}$$

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The protonated anions are all yellow; solutions in strong base are colorless.

The extreme basicity of the ketone groups is quite reasonable. The $B_{10}H_9^{2-}$ moiety is a strongly electron-donating group,[4,6] sufficiently so that $2\text{-}B_{10}H_9COC_6H_5^{2-}$ readily forms the protonated species $2\text{-}B_{10}H_9COHC_6H_5^{-}$.[6] The polar nature of the ketone group in $2\text{-}B_{10}H_9COC_6H_5^{2-}$ is also shown by its low infrared stretching frequency, 1570 cm^{-1}.[6] The ketocarbonyl group should be even more basic when flanked by two B_{10} cage species, thus accounting for the extreme basicity of the bisboranyl ketones. No infrared absorption bands attributable to ketone groups are evident in the spectra of $(CH_3)_3NB_{10}H_8COHB_{10}H_9^{2-}$ or $(CH_3)_2SB_{10}H_8COHB_{10}H_9^{2-}$. The BC(OH)B moiety therefore can be described alternatively as containing a stabilized carbonium ion.

Chlorination of $2\text{-}B_{10}H_9COC_6H_5^{2-}$ to $2\text{-}B_{10}Cl_9COC_6H_5^{2-}$ reduces the basicity of the ketone group so that protonated salts are no longer isolated from acidic solution.[6] Similarly, chlorination of $B_{10}H_9COHB_{10}H_8COOH^{3-}$ reduces the basicity of the ketone group because of inductive electron withdrawal by the chlorine substituents, so that tetrabasic salts of $B_{10}Cl_9COB_{10}Cl_8COOH^{4-}$ can be isolated without much difficulty. The tetrakis(tetramethylammonium) salt of this anion has infrared absorption bands at 1680 and 1545 cm^{-1} which are assigned to the carboxyl and the still highly polarized ketocarbonyl groups, respectively.

Experimental Section

$1,10\text{-}B_{10}Cl_8[COC_6H_4N(CH_3)_2]_2^{2-}$.—A mixture of $1,10\text{-}B_{10}Cl_8(CO)_2$[3] (3.1 g, 6.4 mmoles), N,N-dimethylaniline (25 ml), and acetonitrile (25 ml) was refluxed for 1 hr, cooled, and filtered to obtain 6.8 g of a red-brown solid, presumably $[C_6H_5N(CH_3)_2H]_2\text{-}1,10\text{-}B_{10}Cl_8[COC_6H_4N(CH_3)_2]_2$ (96%). This was dissolved in 300 ml of 0.5% aqueous sodium hydroxide; the solution was extracted three times with ether. It was then filtered and acidified with hydrochloric acid to obtain 4.0 g (83%) of $1,10\text{-}B_{10}Cl_8[COC_6H_4N(CH_3)_2H]_2$, a yellow solid (dec pt 233°). *Anal.* Calcd for $B_{10}Cl_8[COC_6H_4N(CH_3)_2H]_2$: C, 31.3; H, 3.2; B, 15.7; N, 4.1. Found: C, 31.1; H, 3.8; B, 15.0; N, 4.1. Ultraviolet $\lambda_{\max}^{\mathrm{CH_3CN}}$: 460 ($\epsilon$ 60,000), 438 (ϵ 47,800), 322 (ϵ 5800), 270 (ϵ 49,700), 237 (ϵ 13,800).

Proton nmr analysis revealed that the acylation occurred predominantly at the *para* position of the dimethylaniline.

Boiling a mixture of $1,10\text{-}B_{10}Cl_8[COC_6H_4N(CH_3)_2H]_2$ and 10% aqueous sodium hydroxide briefly gave $Na_2\text{-}1,10\text{-}B_{10}Cl_8[COC_6H_4N(CH_3)_2]\cdot 3H_2O$, a yellow solid which was recrystallized from water. This salt is essentially insoluble in 10% sodium hydroxide solution. It slowly darkens above 250°. *Anal.* Calcd for $Na_2B_{10}Cl_8[COC_6H_4N(CH_3)_2]_2\cdot 3H_2O$: C, 27.4; H, 3.3; B, 13.7; N, 3.6; Na, 5.8. Found: C, 27.5; H, 3.7; B, 13.8; N, 3.6; Na, 5.6.

The addition of aqueous tetramethylammonium chloride to aqueous $Na_2\text{-}1,10\text{-}B_{10}Cl_8[COC_6H_4N(CH_3)_2]_2$ precipitated the corresponding tetramethylammonium salt (dec pt 355°). This was recrystallized from 50% aqueous alcohol. *Anal.* Calcd for $[(CH_3)_4N]_2B_{10}Cl_8[COC_6H_4N(CH_3)_2]_2$: C, 37.3; H, 5.3; B, 12.9; N, 6.7. Found: C, 37.2; H, 6.0; B, 13.0; N, 6.7. Ultraviolet $\lambda_{\max}^{\mathrm{CH_3CN}}$: 463 ($\epsilon$ 210), 437 (ϵ 1730), 337 (ϵ 60,000), 270 (ϵ 9400), 238 (ϵ 17,900).

$1,7\text{-}B_{12}H_{10}[COC_6H_4N(CH_3)_2]_2^{2-}$.[7]—A solution of $1,7\text{-}B_{12}H_{10}(CO)_2$[3] (0.5 g, 2.7 mmoles) and N,N-dimethylaniline (2 ml) in acetonitrile (10 ml) was refluxed for 30 min. The acetonitrile was removed from the resulting orange solution to leave an oil which was dissolved in aqueous ethanol. The solution was basified with sodium hydroxide. The addition of aqueous cesium fluoride precipitated $Cs_2\text{-}1,7\text{-}B_{12}H_{10}[COC_6H_4N(CH_3)_2]_2$ as tan needles which were recrystallized from water (dec pt 228°). *Anal.* Calcd for $Cs_2B_{12}H_{10}[COC_6H_4N(CH_3)_2]_2$: C, 30.8; H, 4.3; B, 18.5; N, 4.0. Found: C, 30.8; H, 4.8; B, 18.2; N, 4.1.

$B_{10}H_9COHB_{10}H_8N(CH_3)_3^{2-}$.—A mixture of $(CH_3)_3NB_{10}H_8CO$[4] (0.1 g, 0.5 mmole), $(NH_4)_2B_{10}H_{10}$ (0.11 g, 0.7 mmole), and acetonitrile (50 ml) was refluxed until a clear solution formed. The acetonitrile was evaporated, and the residue was treated with aqueous tetramethylammonium chloride to obtain $[(CH_3)_4N]_2B_{10}H_9COHB_{10}H_8N(CH_3)_3$ (0.1 g, 42%), a yellow solid which was recrystallized from water. *Anal.* Calcd for $[(CH_3)_4N]_2B_{10}H_9COHB_{10}H_8N(CH_3)_3$: C, 30.7; H, 11.0; N, 8.9. Found: C, 30.2; H, 11.1; N, 8.7.

$B_{10}H_9COHB_{10}H_8S(CH_3)_2^{2-}$.—A mixture of $1,6\text{-}(CH_3)_2SB_{10}H_8CO$[4] (0.21 g, 1 mmole), $[(CH_3)_4N]_2B_{10}H_{10}$ (0.27 g, 1 mmole), and acetonitrile was refluxed for 30 min. The acetonitrile was evaporated. The residue was dissolved in aqueous tetramethylammonium hydroxide to obtain a colorless solution. Acidification with dilute hydrochloric acid precipitated $[(CH_3)_4N]_2B_{10}H_9COHB_{10}H_8S(CH_3)_2$ (0.35 g, 74%, mp >300°), which was recrystallized from water. *Anal.* Calcd for $[(CH_3)_4N]_2B_{10}H_9COHB_{10}H_8S(CH_3)_2$: B, 45.8; H, 10.2; N, 5.9; S, 6.8. Found: B, 45.7; H, 10.4; N, 4.9; S, 7.1.

$B_{10}H_9COHB_{10}H_8COOH^{3-}$.—A mixture of $(NH_4)_2B_{10}H_{10}$ (1.0 g, 6.5 mmoles), $1,10\text{-}B_{10}H_8(CO)_2$[3] (1.1 g, 6.4 mmoles), and acetonitrile (25 ml) was stirred at ambient temperature for 1.5 hr, forming a clear orange solution. This was concentrated to obtain a viscous orange mass which was dissolved in water (30 ml). The addition of tetramethylammonium chloride (5 g, 46 mmoles) in water (10 ml) precipitated a bright yellow solid. Recrystallization from water (50 ml) followed by drying at 80° under vacuum gave 2 g (57%) of the hydrated salt, $[(CH_3)_4N]_3B_{10}H_9COHB_{10}H_8COOH\cdot H_2O$ (reddens at 250°, no melting point to 360°). *Anal.* Calcd for $[(CH_3)_4N]_3B_{10}H_9COHB_{10}H_8COOH\cdot H_2O$: C, 30.7; H, 10.4; B, 39.5; N, 7.9. Found: C, 30.5; H, 10.5; B, 40.3; N, 7.9. Ultraviolet $\lambda_{\max}^{\mathrm{CH_3CN}}$: 382 ($\epsilon$ 3200), 313 (ϵ 5760), 237 (ϵ 14,500).

Passage of an aqueous solution of this salt through an acidic ion-exchange column followed by alkaline titration of the effluent gave a titration curve displaying three end points. The first led to an observed neutral equivalent of 190 (calcd for tribasic acid, 183), the second end point indicated a neutral equivalent of 143 (calcd for tetrabasic acid, 137), and the third end point was quite indistinct but was in the correct region for neutralization of a fifth proton.

Dissolution of $[(CH_3)_4N]_3B_{10}H_9COHB_{10}H_8COOH\cdot H_2O$ in aqueous sodium hydroxide gave a colorless solution. Excess tetramethylammonium chloride was added followed by the dropwise addition of hydrochloric acid until a solid precipitated. This proved to be the recovered tris(tetramethylammonium) salt and not a tetrakis(tetramethylammonium) salt.

$B_{10}Cl_9COB_{10}Cl_8COOH^{4-}$.—Chlorine was passed through a mixture of $[(CH_3)_4N]_3B_{10}H_9COHB_{10}H_8COOH\cdot H_2O$ (2.0 g, 3.6 mmoles) and acetonitrile (40 ml) with cooling in a water–ice bath. The temperature rose to 28°. When it fell back to 15°, the cooling bath was removed; the chlorine flow was continued while the clear orange solution warmed to room temperature and for 1 hr after that. Evaporation of the solution left a residue which was recrystallized from water (160 ml) which contained tetramethylammonium chloride (1 g). The yield of $[(CH_3)_4N]_4B_{10}Cl_9COB_{10}Cl_8COOH$ (dec pt 352°) was 0.9 g (20%). *Anal.* Calcd for $[(CH_3)_4N]_4B_{10}Cl_9COB_{10}Cl_8COOH$: C, 18.2; H, 4.2; B, 18.4; Cl, 50.7; N, 4.7. Found: C, 18.8; H, 4.4; B, 18.4; Cl, 49.7; N, 4.4.

If excess tetramethylammonium chloride is not present in the recrystallization medium, an impure product is obtained, ap-

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(7) Acknowledgment is made to Dr. H. C. Miller for contributing this experiment.

parently due to the partial formation of $[(CH_3)_4N]_3B_{10}Cl_9COH$-$B_{10}Cl_8COOH$.

$(CH_3)_2SB_{10}H_8COHB_{10}H_8COOH^{2-}$.—A solution of $(CH_3)_4N$-1-$B_{10}H_9S(CH_3)_2$[8] (6.0 g, 23.7 mmoles) and 1,10-$B_{10}H_8(CO)_2$[3] (4.0 g, 23.3 mmoles) was refluxed for 6 hr. Filtration gave 0.2 g (0.8 mmole) of recovered $(CH_3)_4N$-1-$B_{10}H_9S(CH_3)_2$ and a light yellow filtrate which was concentrated until it became a viscous oil. This was stirred in water (80 ml), liberating 3.0 g of a yellow solid which was recrystallized from water and then from aqueous tetramethylammonium chloride to obtain $[(CH_3)_4N]_2(CH_3)_2SB_{10}H_8COHB_{10}H_8COOH \cdot H_2O$ (mp 162–164°). *Anal.* Calcd for $[(CH_3)_4N]_2(CH_3)_2SB_{10}H_8COHB_{10}H_8COOH \cdot H_2O$: C, 26.9; H, 9.4; N, 5.2; S, 6.0. Found: C, 27.2; H, 9.5; N, 5.2; S, 6.2. Ultraviolet $\lambda_{max}^{CH_3CN}$: 365 (ϵ 27,600), 305 (ϵ 6800), 237 (ϵ 17,600).

$[(CH_3)_2S]_2B_{10}H_7COHB_{10}Cl_8COOH^-$.—A solution of 1,10-$B_{10}Cl_8(CO)_2$[3] (10.8 g, 23.1 mmoles) and 1,10-$B_{10}H_8[S(CH_3)_2]_2$[8] (10.8 g, 31.8 mmoles) in acetonitrile (125 ml) was refluxed in a nitrogen atmosphere for 3 hr. The acetonitrile was removed by evaporation. The residue was extracted with 1.6% aqueous sodium hydroxide (240 ml). The extracts were filtered and acidified with hydrochloric acid; the extract was initially colorless but became yellow during the acidification. A gummy solid separated after a considerable excess of hydrochloric acid had been added. This solid was recrystallized twice from dilute cesium chloride solution to obtain $Cs[(CH_3)_2S]_2B_{10}H_7COHB_{10}Cl_8COOH \cdot H_2O$ as a yellow solid (2.4 g, 11%). *Anal.* Calcd for $Cs[(CH_3)_2S]_2B_{10}H_7COHB_{10}Cl_8COOH \cdot H_2O$: C, 8.4; H, 2.7; B, 25.3; S, 7.5. Found: C, 8.3; H, 2.8; B, 24.3; S, 7.4.

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The Reactions of Lewis Bases with Tetrahydroborate Derivatives of the Group IVa Elements. The Preparation of New Zirconium Hydride Species

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Bis(π-cyclopentadienyl)zirconium bistetrahydroborate,[1] $(C_5H_5)_2Zr(BH_4)_2$, reacts with 1 and 2 moles of trialkylamines to produce the new hydride species bis(π-cyclopentadienyl)zirconium hydride tetrahydroborate, $(C_5H_5)_2Zr(H)BH_4$, and bis(π-cyclopentadienyl)zirconium dihydride, $[(C_5H_5)_2ZrH_2]_n$, respectively. The formation of these hydrides has been rationalized by postulating successive bridge cleavage reactions, and the physical and spectral properties of these compounds are discussed. The results of similar reactions attempted with bis(π-cyclopentadienyl)titanium(III) tetrahydroborate, $(C_5H_5)_2TiBH_4$, and bis(triphenylphosphine)copper(II) tetrahydroborate, $((C_6H_5)_3P)_2CuBH_4$, are also reported.

Introduction

While several transition metal hydride compounds are now known, no distinct hydride species has been isolated for the group IVa elements, although recently it has been suggested, as a result of an esr spectrum, that dimeric bis(cyclopentadienyl)titanium hydride, $[(C_5H_5)_2TiH]_2$, occurs as a reaction intermediate.[2]

In general, the two extremes of behavior of metal tetrahydroborates with ligand molecules (*e.g.*, trialkylamines) are (i) to form addition compounds with the ionic tetrahydroborates, probably by coordination with the metal cation,[3] *e.g.*

$$LiBH_4 + N(CH_3)_3 \longrightarrow LiBH_4(N(CH_3)_3)_n \qquad n = 1 \text{ or } 2$$

and (ii) to cleave the hydrogen bridge bonds in the covalent tetrahydroborates,[4] although this reaction may be preceded by coordination at the central metal atom if suitable vacant orbitals are available, *e.g.*

$$Al(BH_4)_3 + (CH_3)_3N \longrightarrow (CH_3)_3N \cdot Al(BH_4)_3$$

$$(CH_3)_3N \cdot Al(BH_4)_3 + (CH_3)_3N \longrightarrow (CH_3)_3N \cdot Al(H)(BH_4)_2 + (CH_3)_3N \cdot BH_3, \text{ etc.}$$

The latter reaction thus offers an alternative route to hydride derivatives of various metals. It was therefore of interest to compare the reactions of titanium, zirconium, hafnium, and copper tetrahydroborate compounds in the light of this reaction.

Experimental Section

Solvents and ligands used were dried over lithium aluminum hydride or calcium hydride and distilled (in a vacuum line where appropriate) before use. Trimethylphosphine was prepared from a Grignard reagent, isolated as the silver iodide complex, and liberated from the latter by heating under vacuum.[5]

Preparation of $(C_5H_5)_2Zr(BH_4)_2$ and $(C_5H_5)_2Hf(BH_4)_2$.—The method previously described for the zirconium compound[6] was used for both compounds, and the products were purified by sublimation under vacuum at 120°. The very pale yellow solids were subsequently handled in a nitrogen-filled glove box; yield, ~70% in each case.

Preparation of $(C_5H_5)_2TiBH_4$.—The method of Nöth, *et al.*,[7] was used, and the violet product was sublimed under vacuum at 110° prior to use. Rigorous precautions had to be taken to exclude any contact with oxygen, solutions proving especially sensitive to oxidation.

Reaction of $(C_5H_5)_2Zr(BH_4)_2$ with Trialkylamines. (i) **Isola-**

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[1] We accept the suggestion of a referee that bistetrahydroborate is more suitable than the name of diborohydride since the latter has sometimes been used to designate the $B_2H_7^-$ ion. Unfortunately no unambiguous name yet exists for differentiating between the presence of a discrete BH_4^- ion and a BH_4 group bonded to a metal by hydrogen bridges as in this case.

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