Stabilization of Lithium Borohydride with Nitrogen Donor, Chelating Ligands. Syntheses and Solid State Structures of $[HC(3,5\text{-}Me_2pz)_3]Li(\eta^3\text{-}BH_4)$, $\{[H_2C(3,5\text{-}Me_2pz)_2]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$, and $\{[4,4'\text{-}Me_2bipy]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$ (pz = pyrazolyl, bipy = bipyridyl)

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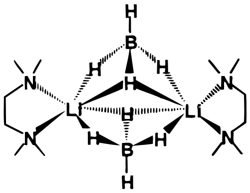
The reaction of $HC(3,5\text{-}Me_2pz)_3$ and $LiBH_4$ in THF yields $[HC(3,5\text{-}Me_2pz)_3]Li(\eta^3\text{-}BH_4)$ (pz = pyrazolyl). In the solid state, the borohydride ligand is tridentate with an octahedral arrangement about the lithium. A similar reaction using $HC(pz)_3$ yields the insoluble ionic compound $\{[HC(pz)_3]_2Li\}(BH_4)$. Reaction of equimolar amounts of $LiBH_4$ and $H_2C(3,5\text{-}Me_2pz)_2$ yields $\{[H_2C(3,5\text{-}Me_2pz)_2]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$. This complex is a centrosymmetric dimer in the solid state having two bridging $[\eta^3\text{-}BH_4]^-$ ligands. For each $[\eta^3\text{-}BH_4]^-$ ligand, there is one μ_3-H and two μ_2-H atoms. A similar reaction with $H_2C(pz)_2$ yields $\{[H_2C(pz)_2]Li(BH_4)\}_2$ and with 4,4′-dimethyl-2,2′-bipyridine (4,4′-Me_2bipy) yields $\{[4,4'\text{-}Me_2bipy]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$. The structure of $\{[4,4'\text{-}Me_2bipy]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$ in the solid state is similar to that of $\{[H_2C(3,5\text{-}Me_2pz)_2]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$, except the Li_2B_2 central core is not planar and both μ_3-H atoms are on the same side of this core.

Introduction

We are interested in the syntheses and characterization of novel chemical hydrides that may be useful for the controlled and safe delivery of hydrogen to polymer electrolyte membrane (PEM) fuel cells, cells that use the reaction of H_2 and O_2 to produce electricity. The use of chemical hydrides for hydrogen generation in man-portable fuel cells has been identified as having significant promise to replace batteries in specific applications.[1] We are studying the use of neutral chelate ligands for the development of new chemical hydrides with properties (e.g., such as stability and heat of reaction) that can be controlled. With ligands containing nitrogen donor atoms, only one fully characterized lithium tetrahydroborate complex of this type, $[(TMEDA)Li(\mu\text{-}\eta^3\text{-}BH_4)]_2$ (TMEDA = $Me_2NCH_2CH_2NMe_2$), has been reported.[2] This complex was shown to have an unusual dimeric structure in the solid state. The two lithium atoms are six coordinate and bridged by both BH_4 anions. Each $[BH_4]^-$ bonds through three hydrogen atoms forming two μ_2-H and one μ_3-H bonds (Chart 1). Of particular interest to us is the use of the tris(pyrazolyl)methane and bis(pyrazolyl)methane ligands, such as $HC(3,5\text{-}Me_2pz)_3$ and $H_2C(3,5\text{-}Me_2pz)_2$ (pz = pyrazolyl), to stabilize reactive group 1 compounds such as $LiBH_4$. These ligands are formally derived from the extensively studied poly(pyrazolyl)borate ligands[3] by replacing a boron anion with a carbon atom and are, thus, isoelectronic to them. These neutral ligands were needed for the preparation of molecular complexes of $LiBH_4$. The synthesis of the tris(pyrazolyl)methane and bis(pyrazolyl)methane ligands were first reported by Trofimenko[4] in 1970, and the preparations were later modified by Elguero.[5] We have recently used the tris(pyrazolyl)methane ligands for the syntheses of a variety of complexes of the transition and post-transition metals, many of which have been structurally characterized.[6] Reported here are

Chart 1



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the syntheses of several lithium borohydride complexes using (pyrazolyl)methane ligands and the solid state structures of $[HC(3,5\text{-}Me_2pz)_3]Li(\eta^3\text{-}BH_4)$ and $\{[H_2C(3,5\text{-}Me_2pz)_2]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$. The complex $\{[4,4'\text{-}Me_2bipy]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$ (bipy = bipyridyl) has also been prepared and structurally characterized.

Experimental Section

General Procedure. All operations were carried out under a nitrogen atmosphere using either standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. All solvents were dried, degassed, and distilled prior to use. Proton NMR chemical shifts are reported in parts per million (ppm) versus TMS. Lithium tetrahydroborate and 4,4′-dimethyl-2,2′-bipyridine were purchased from Aldrich and used as received. $HC(3,5\text{-}Me_2pz)_3$, $HC(pz)_3$, $H_2C(3,5\text{-}Me_2pz)_2$, and $H_2C(pz)_2$ were prepared according to literature procedures.[5] Elemental analyses were performed by National Chemical Consulting, Inc.

$[HC(3,5\text{-}Me_2pz)_3]Li(\eta^3\text{-}BH_4)$ (1). A THF (5 mL) suspension of $LiBH_4$ (0.050 g, 2.3 mmol) was treated with a THF solution (5 mL) of $HC(3,5\text{-}Me_2pz)_3$ (0.69 g, 2.3 mmol). Immediately, a white solid precipitated. This mixture was allowed to stir for 16 h before cannula filtering. The remaining white solid was washed with hexanes (5 mL) and collected after drying under vacuum (0.476 g, 1.49 mmol, 69%); mp = 266−267 °C. ^1H NMR ($CDCl_3$): δ 7.68 (1, s, $HC(Me_2pz)_3$), 5.83 (3, s, 4-*H* in pz), 2.45, 2.38 (9, 9, s, s, 3,5-$(CH_3)_2$), 0.20 (4, q, J_{BH} = 81 Hz, BH_4). IR (Nujol mull; cm^{-1}): 2374, 2314, 2223, 2163 (BH_4). MS (direct probe): *m/z* 305 ($[HC(3,5\text{-}Me_2pz)_3]Li$). Anal. Calcd for $C_{16}H_{26}BLiN_6$: C, 60.02; H, 8.19. Found: C, 59.55; H, 7.89. Crystals suitable for an X-ray structural determination were obtained by layering a saturated CH_2Cl_2 solution with hexanes.

$\{[HC(pz)_3]_2Li\}(BH_4)$ (2). A THF (5 mL) suspension of $LiBH_4$ (0.050 g, 2.3 mmol) was treated with a THF solution (5 mL) of $HC(pz)_3$ (0.98 g, 4.6 mmol). Immediately, a white solid precipitated. This mixture was allowed to stir 16 h before cannula filtering. The remaining white solid was washed with hexanes (5 mL) and collected after drying under vacuum (0.90 g, 2.0 mmol, 87%); mp = 228−233 °C. IR (Nujol mull; cm^{-1}): 2358, 2295, 2231, 2166 (BH_4). Anal. Calcd for $C_{20}H_{24}BLiN_{12}$: C, 53.35; H, 5.37. Found: C, 53.22; H, 5.93.

$\{[H_2C(3,5\text{-}Me_2pz)_2]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$ (3). A THF (5 mL) suspension of $LiBH_4$ (0.050 g, 2.3 mmol) was treated with a THF (5 mL) solution of $H_2C(3,5\text{-}Me_2pz)_2$ (0.47 g, 2.3 mmol). The solution was stirred for 16 h. After the mixture was filtered, the THF solution was reduced in volume to saturation (ca. 3 mL) and the total volume was adjusted to 5 mL by addition of CH_2Cl_2. This solution was layered with an equal volume of hexanes and set aside to allow for slow diffusion of the two layers. Colorless needles precipitated (0.26 g, 0.57 mmol, 50%); mp = 253−258 °C. ^1H NMR (THF-d_8): δ 6.00 (2, s, $H_2C(Me_2pz)_2$), 5.69 (2, s, 4-*H* in pz), 2.42, 2.06 (6, 6, s, s, 3,5-$(CH_3)_2$), −0.49 (4, q, J_{BH} = 81.1 Hz, BH_4). IR (Nujol mull; cm^{-1}): 2376 2332, 2292, 2259, 2241, 2221 2181, 2168, 2138 (BH_4). Anal. Calcd for $C_{11}H_{20}BLiN_4$: C, 58.45; H, 8.92. Found: C, 58.36; H, 8.84.

$\{[H_2C(pz)_2]Li(BH_4)\}_2$ (4). A THF suspension of $LiBH_4$ (0.050 g, 2.3 mmol) was treated with a THF (5 mL) solution of $H_2C(pz)_2$ (0.34 g, 2.3 mmol). The resulting reaction solution was stirred for 16 h. After the mixture was filtered, the THF solution was reduced in volume to saturation (ca. 3 mL) and the total volume was adjusted to 5 mL by addition of CH_2Cl_2. This solution was layered with an equal volume of hexanes and set aside to allow for slow diffusion of the two layers. Colorless needles precipitated (0.27 g, 0.80 mmol, 69%); mp = 241−248 °C. ^1H NMR (THF-d_8): δ 7.75, 7.40 (2, 2, d, d, J_{HH} = 2.1, 1.5 Hz, 3-*H*, 5-*H*), 6.35 (2, s, $H_2C(pz)_2$), 6.19 (2, dd, J_{HH} = 2.1, 1.5 Hz, 4-*H*); −0.45 (4, q, J_{BH} = 81 Hz, BH_4). IR (Nujol mull; cm^{-1}): 2359, 2321, 2291, 2262, 2227 (BH_4). Anal. Calcd for $C_7H_{12}BLiN_4$: C, 49.47; H, 7.12. Found: C, 49.07; H, 7.09.

Table 1. Crystallographic Data for the Structural Analyses of $[HC(3,5\text{-}Me_2pz)_3]Li(\eta^3\text{-}BH_4)$ (**1**), $\{[H_2C(3,5\text{-}Me_2pz)_2]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$ (**3**), and $\{[4,4'\text{-}Me_2bipy]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$ (**5**)

	1	**3**	**5**
formula	$C_{16}H_{26}BLiN_6$	$C_{22}H_{40}B_2Li_2N_8$	$C_{24}H_{32}B_2Li_2N_4$
fw	320.18	452.12	412.04
space group	*Pnma*	$P2_1/n$	$P2_1/c$
a, Å	17.875(8)	7.6924(4)	13.183(3)
b, Å	13.467(13)	10.7572(7)	12.348(3)
c, Å	8.004(2)	16.7977(10)	16.709(6)
β, deg	107.779(3)	104.23(3)	
V, Å^3	1926.8(5)	1361.4(2)	2636.6(12)
Z	4	2	4
cryst color	colorless dipyramid	colorless block	colorless block
D(calcd), g cm^{-3}	1.104	1.103	1.038
μ(Mo Kα), cm^{-1}	0.68	0.66	0.59
temp, K	295	218	243
radiation	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
$R(F)^a$, $R(wF^2)^a$	5.30, 13.84	6.67, 14.85	5.87, 12.73

[a] Quantity minimized = $R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |F_o - F_c|$.

$\{[4,4'\text{-}Me_2bipy]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$ (5). A THF (5 mL) suspension of $LiBH_4$ (0.050 g, 2.3 mmol) was treated with a THF (5 mL) solution of 4,4′-Me_2bipy (0.42 g, 2.3 mmol). The yellow reaction solution was allowed to stir for 16 h. The solution was cannula-filtered before removing the THF under reduced pressure. A pale yellow solid remained (0.42 g, 1.0 mmol, 89%); mp = 252−253 °C. Crystals suitable for the X-ray structural determination were obtained by layering a saturated CH_2Cl_2 solution with hexanes. ^1H NMR (THF-d_8): δ 8.45, 8.32, 7.13 (2, 2, 2, d, t, dd, J_{HH} = 4.9, 0.8 Hz, C*H*), 2.40 (6, s, CH_3), −0.53 (4, q, J_{BH} = 81 Hz, BH_4). IR (Nujol mull; cm^{-1}): 2390, 2293, 2227 (BH_4).

Crystallographic Structural Determination. Crystal, data collection, and refinement parameters are given in Table 1. Suitable crystals for single-crystal X-ray diffraction of each compound were selected and mounted with epoxy cement on thin glass fibers on a Siemens P4/CCD diffractometer. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections (20° ≤ 2θ ≤ 25°). The systematic absences in the diffraction data are consistent with the orthorhombic space groups $Pna2_1$ and *Pnma* for **1** and uniquely consistent for the space groups of **3** and **5** reported in Table 1. The *E*-statistics, the value of *Z*, and the presence of a molecular mirror plane in **1** suggested the centrosymmetric option, which was subsequently verified by chemically reasonable and computationally stable results of refinement. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Absorption corrections were not required because there was less than 10% variation in the integrated Ψ-scan intensities. The cation−anion pair of **1** lies on a mirror plane, and the dication−dianion pair of **3** lies on an inversion center. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The unique hydrogen atoms on the BH_4 anions were located from the difference map. In **1** and **5,** the geometry of the BH_4 anions was fixed as rigid tetrahedra, and the thermal parameters in **5** were constrained. All other hydrogen atoms were treated as calculated contributions.

All software and sources of the scattering factors are contained in the SHELXTL (version 5.3, 1996) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Results and Discussion

Syntheses of Complexes. Addition of an equimolar amount of $HC(3,5\text{-}Me_2pz)_3$ to $LiBH_4$ in THF results in the precipitation

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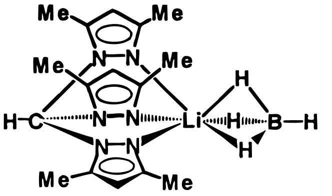
of the complex $[HC(3,5\text{-}Me_2pz)_3]Li(\eta^3\text{-}BH_4)$ (**1**, eq 1). This

$HC(3,5\text{-}Me_2pz)_3 + LiBH_4 \longrightarrow$

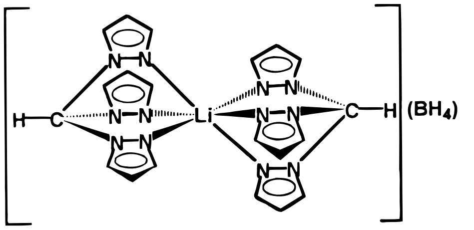


(1)

complex reacts slowly over time with moisture in the air (detailed thermal and hydrolytic decomposition studies on the borohydride complexes have been published elsewhere[7]). It is moderately soluble in chlorinated solvents.

A similar reaction using $HC(pz)_3$ with $LiBH_4$, whether carried out with 1:1 or 2:1 stoichiometry, yields $\{[HC(pz)_3]_2Li\}(BH_4)$ (eq 2). This complex is not soluble in CH_2Cl_2 or THF and, thus, could not be characterized by NMR. Its formula was determined by elemental analysis. We have prepared and structurally characterized the Na^+ analog, $\{[HC(pz)_3]_2Na\}^+$, with I^- as the counterion.[6f] Presumably, it is the insolubility of this ionic compound that leads to its formation rather than a complex analogous to **1**.

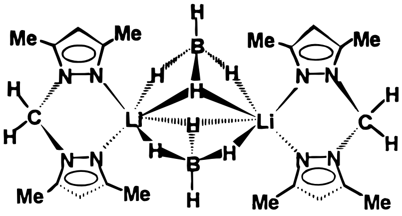
$LiBH_4 + 2\,HC(pz)_3 \longrightarrow$



(2)

Complexes with a bis(pyrazolyl)methane ligand to metal ratio of 1:1 are produced in the reactions of equimolar amounts of $LiBH_4$ and either $H_2C(3,5\text{-}Me_2pz)_2$ (eq 3) or $H_2C(pz)_2$. An

$2LiBH_4 + 2H_2C(3,5\text{-}Me_2pz)_2 \longrightarrow$

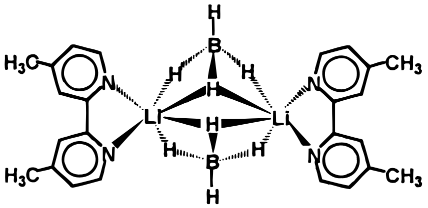


(3)

X-ray crystal structure for the complex involving the ligand $H_2C(3,5\text{-}Me_2pz)_2$ demonstrated that in the solid state it exists as a dimer with the formulation $\{[H_2C(3,5\text{-}Me_2pz)_2]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$ (**3**). Presumably, $\{[H_2C(pz)_2]Li(BH_4)\}_2$ has a similar structure.

The reaction of $LiBH_4$ with 4,4′-dimethyl-2,2′-bipyridine also produces a similar 1:1 complex, eq 4. An X-ray crystal structure

$2LiBH_4 + 2[4,4'\text{-}Me_2\text{-}bipy] \longrightarrow$



(4)

for the complex demonstrated that in the solid state it also exists

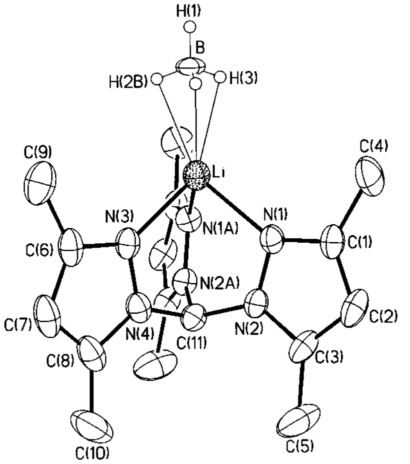


Figure 1. ORTEP diagram of $[HC(3,5\text{-}Me_2pz)_3]Li(\eta^3\text{-}BH_4)$ (**1**) showing atom-labeling scheme. Unlabeled pyrazole ring atoms are numbered using the same numbering scheme as the labeled pyrazole ring. Thermal ellipsoids are shown at 30% probability, and hydrogen atoms, except for those on $[BH_4]^-$, are omitted for clarity.

as a dimer, $\{[4,4'\text{-}Me_2bipy]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$ (**5**). All three of these complexes with bidentate ligands are insoluble in CH_2Cl_2 but soluble in THF.

The solid state structures (vide infra) of the complexes show that there are nonequivalent hydrogen atoms in the $[BH_4]^-$ ligands, but the ^1H NMR spectra all show a characteristic 1/1/1/1 quartet centered around 0 ppm (^{11}B is 80% abundant with $s = 3/2$), indicating the hydrogen atoms are dynamic on the NMR time scale. Also observed is a septet set of resonances expected for the ^{10}B isotope (20% abundant, $s = 3$). Lowering the temperature to −80 °C for $\{[H_2C(3,5\text{-}Me_2pz)_2]Li(BH_4)\}_2$ in THF-d_8 did not change this pattern.

Solid-State Structures. The solid-state structures of $[HC(3,5\text{-}Me_2pz)_3]Li(\eta^3\text{-}BH_4)$, $\{[H_2C(3,5\text{-}Me_2pz)_2]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$, and $\{[4,4'\text{-}Me_2bipy]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$ have been determined crystallographically. Crystallographic data are provided in Table 1.

$[HC(3,5\text{-}Me_2pz)_3]Li(\eta^3\text{-}BH_4)$ (1). Figure 1 shows the ORTEP diagram of $\{[HC(3,5\text{-}Me_2pz)_3]Li(\eta^3\text{-}BH_4)\}$. Selected bond distances and angles are presented in Table 2. In this structure, the lithium ion is six coordinate with an octahedral arrangement of donor atoms. The borohydride ligand is tridentate.

This structure appears to be the first example of a tridentate $[BH_4]^-$ ligand in a monomeric group 1 complex. A few group 2 complexes,[8] such as $(diglyme)_2Sr(\eta^3\text{-}BH_4)_2$, show this coordination mode, but this type of bonding in mononuclear main-group metal complexes is still rare.

The tridentate bonding of the $[BH_4]^-$ ligand in $[HC(3,5\text{-}Me_2pz)_3]Li(\eta^3\text{-}BH_4)$ differs from the bidentate bonding previously observed in $[HB(3,5\text{-}Me_2pz)_3]Cd(\eta^2\text{-}BH_4)$.[9] These complexes are similar in that the extra positive charge of Cd^{2+} versus Li^+ is balanced by the minus charge of the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand versus the neutral $[HC(3,5\text{-}Me_2pz)_3]$ ligand. The bonding properties of tris(pyrazolyl)borate ligands have been shown to be similar to those of tris(pyrazolyl)methane ligands.[6] It is surprising that the $[BH_4]^-$ ligand bonds very differently to two closed-shell ions with essentially the same ionic radii (Cd^{2+} is 0.05 Å larger[10]).

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Table 2. Selected Bond Distances (Å) and Angles (deg) for Lithium Borohydride Complexes

distances		angles	
$[HC(3,5\text{-}Me_2pz)_3]Li(\eta^3\text{-}BH_4)$			
Li−N(1)	2.038(5)	N(1)−Li−N(1A)	86.4(3)
Li−N(3)	2.092(7)	N(1)−Li−N(3)	89.8(2)
Li···B	2.223(7)	N(2)−C(11)−N(2A)	113.0(3)
C(11)−N(2)	1.449(3)	N(2)−C(11)−N(4)	110.7(2)
C(11)−N(4)	1.455(4)		
$\{[H_2C(3,5\text{-}Me_2pz)_2]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$			
Li−N(1)	2.098(7)	N(1)−Li−N(3)	90.7(2)
Li−N(3)	2.067(6)	B−Li−B(A)	89.8(2)
Li···B	2.584(8)	Li−B−LiA	80.9(3)
Li···Li	3.277(11)	N(2)−C(11)−N(4)	112.3(3)
C(11)−N(2)	1.449(4)		
C(11)−N(4)	1.450(4)		
$\{[4,4'\text{-}Me_2bipy]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$			
Li(1)−N(1)	2.003(8)	N(1)−Li−N(2)	80.5(3)
Li(1)−N(2)	2.068(8)	N(3)−Li−N(4)	80.8(3)
Li(2)−N(3)	2.019(9)	B(1)−Li(1)−B(2)	99.7(3)
Li(2)−N(4)	2.060(8)	B(1)−Li(2)−B(2)	98.9(3)
Li(1)···B(1)	2.479(9)	Li(1)−B(1)−Li(2)	79.3(3)
Li(1)···B(2)	2.407(9)	Li(1)−B(2)−Li(2)	79.1(3)
Li(2)···B(1)	2.417(9)		
Li(2)···B(2)	2.498(10)		
Li···Li	3.124(10)		

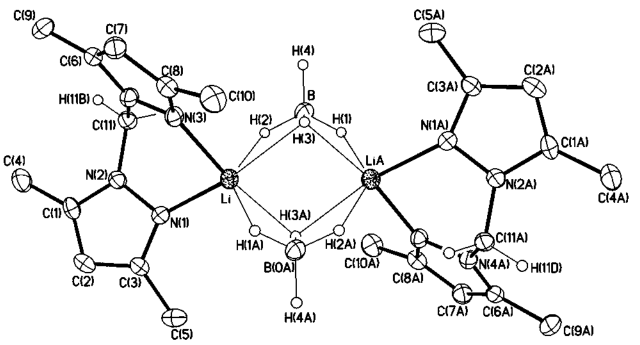

Figure 2. ORTEP diagram of $\{[H_2C(3,5\text{-}Me_2pz)_2]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$ (**3**) showing atom-labeling scheme. Thermal ellipsoids are shown at 30% probability, and hydrogen atoms, except for those on $[BH_4]^-$, are omitted for clarity.

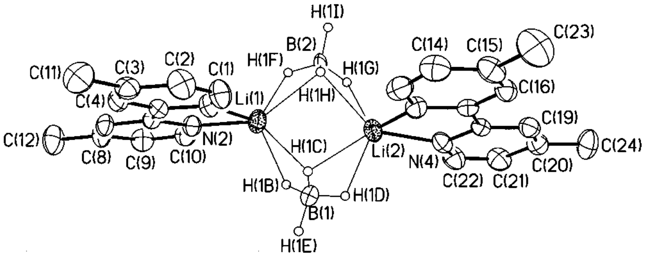

Figure 3. ORTEP diagram of $\{[4,4'\text{-}Me_2bipy]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$ (**5**) showing atom-labeling scheme. Thermal ellipsoids are shown at 30% probability, and hydrogen atoms, except for those on $[BH_4]^-$, are omitted for clarity.

$\{[H_2C(3,5\text{-}Me_2pz)_2]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$ (3) and $\{[4,4'\text{-}Me_2bipy]Li(\mu\text{-}\eta^3\text{-}BH_4)\}_2$ (5). Both of these complexes have similar dimeric solid-state structures having two bridging $[\eta^3\text{-}BH_4]^-$ ligands. For each $[\eta^3\text{-}BH_4]^-$, there is one μ_3-H and two μ_2-H atoms, but there is an important difference between the structures. The structure of **3** is centrosymmetric with a planar Li_2B_2 central core. One of the μ_3-H atoms is above this plane and one is below. For **5**, the Li_2B_2 central core has a butterfly shape with the Li(1)—B(1)—Li(2) plane making a 16.8° angle with the Li(1)—B(2)—Li(2) plane. In this structure, both μ_3-H atoms are on the same side of the Li_2B_2 central core. One other difference is that in **5** the N(1)—Li(1)—N(2) plane makes a 93.4° angle with the B(1)—Li(1)—B(2) plane, whereas the analogous angle in **3** is 71.8°.

These structures, especially for **3**, are very similar to the centrosymmetric structure of $[(TMEDA)Li(\mu\text{-}\eta^3\text{-}BH_4)]_2$ (Chart 1).[2] Similar $[\mu\text{-}\eta^3\text{-}BH_4]^-$ bridging is observed in the polymeric structure of $(diglyme)Na(BH_4)$,[11] and a related bonding pattern is found in $[(thf)_2M(BH_4)_2]_n$ (M = Sr, Ba).[8] Our work, taken in conjunction with these studies, shows that this unusual μ-η^3-bonding arrangement is favorable for borohydride complexes of the group 1 and 2 metals. This bonding type was first observed in the structure of $[(Ph_2P(CH_2)_5PPh_2)Co(\mu\text{-}\eta^3\text{-}BH_4)]_2$.[12] Note that in the structure of the related complex of $[AlH_4]^-$, $\{[HN(t\text{-}Bu)CH(t\text{-}Bu)CH_2N(H)(t\text{-}Bu)]Li(\mu\text{-}H)_2AlH_2\}_2$, the $[AlH_4]^-$ groups act as simple μ_2-bridging ligands.[13]

Conclusion

Tris(pyrazolyl)methane and bis(pyrazolyl)methane ligands and 4,4′-dimethyl-2,2′-bipyridine react with $LiBH_4$ to yield coordination compounds that are much more stable in air than $LiBH_4$. Whereas $HC(3,5\text{-}Me_2pz)_3$ yields the monomeric, octahedral molecule $[HC(3,5\text{-}Me_2pz)_3]Li(\eta^3\text{-}BH_4)$, the unsubstituted $HC(pz)_3$ yields the ionic compound $\{[HC(pz)_3]_2Li\}(BH_4)$, presumably because this compound is insoluble and precipitates. The bidentate ligands $H_2C(3,5\text{-}Me_2pz)_2$, 4,4′-$Me_2$bipy, and TMEDA[2] all yield dimers of the formula $[(ligand)Li(\mu\text{-}\eta^3\text{-}BH_4)]_2$ in which the bridging $[\eta^3\text{-}BH_4]^-$ group has one μ_3-H and two μ_2-H atoms.

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Supporting Information Available: Tables of complete data collection information, bond distances and angles, positional parameters, and anisotropic thermal parameters (16 pages). Ordering information is given on any current masthead page.

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