DOI: 10.1002/ejic.200901233

Studies in Solution and the Solid State of Coordination Compounds Derived from $LiBH_4$, $NaBH_4$, and Bidentate Aromatic Amines

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Keywords: Tetrahydroborates / Alkali metals / N ligands / Structure elucidation

The mixture of 2,2′-bipyridylamine, 2,2′-bipyridine, 1,10-phenanthroline, 1,2-phenylendiamine, and 1,4-phenylendiamine each with $LiBH_4$ and $NaBH_4$ in a 1:1 molar ratio in THF yields seven new complexes of the type MBH_4·L-THF and one complex of the type MBH_4·L. These compounds were characterized by IR and NMR spectroscopy and X-ray single-crystal structure determinations. In the solid state, the $[BH_4]^-$ group is bidentate, as deduced from the stretching patterns observed in IR spectra and confirmed by X-ray single-crystal structure analysis. NMR spectroscopy showed that all amines act as bidentate ligands and are symmetrically coordinated to the metal cation. Complexes $LiBH_4$-2,2′-bipyridine-THF (**1**), $NaBH_4$-2,2′-bipyridine-THF (**2**), $LiBH_4$-1,10-phenanthroline-THF (**3**), and $NaBH_4$-1,10-phenanthroline-THF (**4**) have a discrete molecular structure, whereas the complexes $LiBH_4$-1,2-phenylendiamine-THF (**5**), $NaBH_4$-1,2-phenylendiamine-THF (**6**), $LiBH_4$-2,2′-dipyridilamine (**7**), and $LiBH_4$-1,4-phenylendiamine-THF (**8**) have polymeric structures in the solid state. *N*-borane-dipyridylamine adduct **9** was isolated from an aged solution of **7**. IR spectroscopy of the new complexes showed that the structures of complexes **1**, **3**, **4**, and **6** are maintained in the solid state and in solution. A rotational barrier for the $[BH_4]^-$ group of less than 38 KJ mol^{-1} was estimated for some of the new complexes.

Introduction

Alkali metal tetrahydroborates constitute an important class of reducing reagents with wide applicability in both organic and inorganic chemistry. They are mainly applied in reductions of aldehydes and ketones.[1] In addition, alkali metal tetrahydroborates are used as starting materials for the synthesis of organometallic derivatives, precursors for the production of borides and hydrides, as well as other inorganic materials, and as catalysts for hydrogenation, isomerization, oligomerization, and polymerization.[2]

Modification of the alkali metal tetrahydroborates has been performed to augment their chemoselectivity.[3] One of these modifications includes the use of ligands containing nitrogen and oxygen atoms.[4] A fair number of these complexes have been studied by X-ray diffraction, which shows that the $[BH_4]^-$ moiety acts as a mono-, bi-, or tridentate ligand. The bidentate and tridentate coordination forms of $[BH_4]^-$ are the most commonly found in the solid state.[5] However, the structure in $LiBH_4$·*n*L compounds are influenced by stereoelectronic effects of both the ligand (L) and the $[BH_4]^-$ anion as shown by theoretical results.[6] Therefore, it is important to understand the circumstances that cause the $[BH_4]^-$ group to adopt one of the possible coordination forms, because this should have an influence on the chemical behavior of a particular complex.

We are interested in the synthesis and characterization of novel compounds from neutral amine chelate ligands and alkali metal tetrahydroborates with specific properties that can be used in reducing reactions. We have already described theoretically theses types of compounds.[6] The study showed us the importance of carrying out detailed analysis of the structure of the complexes in solution and in the solid state because the former is the medium in which the reduction reactions occur.

Only a few structures of alkali tetrahydroborate complexes with amines have been described.[5,7] Among alkali metal complexes, lithium compounds have been studied most comprehensively. Within this context, we studied the structure of some complexes of $LiBH_4$ and $NaBH_4$ with

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bidentate aromatic amines in solution and in the solid state to comprehend the influence of solvent and ligand in both structure and chemical behavior.

Results and Discussion

Infrared Spectra in the Solid State and in Solution

Eight new complexes, $LiBH_4$-2,2′-bipyridine-THF (**1**), $NaBH_4$-2,2′-bipyridine-THF (**2**), $LiBH_4$-1,10-phenanthroline-THF (**3**), $NaBH_4$-1,10-phenanthroline-THF (**4**), $LiBH_4$-1,2-phenylendiamine-THF (**5**), $NaBH_4$-1,2-phenylendiamine-THF (**6**), $LiBH_4$-2,2′-dipyridilamine (**7**), and $LiBH_4$-1,4-phenylendiamine-THF (**8**), were obtained from a $LiBH_4$ solution and a $NaBH_4$ suspension in THF by adding 2,2′-bipyridylamine, 2,2′-bipyridine, 1,10-phenanthroline, 1,2-phenylendiamine, and 1,4-phenylendiamine in a 1:1 molar ratio. These complexes were stable and easily handled under anhydrous conditions in the solid state.

To get some information about the structure of the new compounds, the IR spectra of the solid compounds were recorded by using KBr pellets. Data for the B–H, N–H, and aromatic ring stretching vibrations are summarized in Table 1. These compounds present between two and four B–H stretching bands, depending of the ligand type and metal present, which differ from the single and broad band observed in the IR spectra of solid $LiBH_4$ and $NaBH_4$.[8]

The pattern observed in the B–H stretching bands has been reported in $LiBH_4(NC_5H_5)_3$[5c] (four bands), $LiBH_4{\cdot}2[2,4,6\text{-}(CH_3)_3NC_5H_2]$[9] (three bands), and $LiBH_4(NC_5H_4\text{-}4\text{-}Me)_3$[10] (three bands), where the $[BH_4]^-$ group acts as a bidentate ligand. The IR data suggest that the $[BH_4]^-$ group is present in a dicoordinate interaction with the metal atom.

From Table 1, two kinds of B–H stretching band patterns are distinguished; one for compounds **1**, **3**, **4**, and **6** and the other for the remainder of the compounds (Figure 1). This means that there are two kinds of bidentate structures depending on the ligand and metal used. Therefore, it would be helpful to predict the type of structure associated with a specific ligand. To get some information about the stability of the structure of alkali-metal–amine complexes, we recorded the IR spectra in THF solution. The results are presented in Table 2.

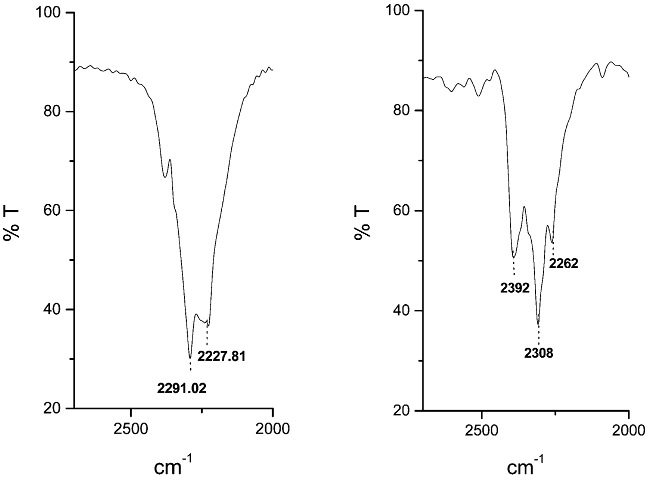

Figure 1. IR patterns for B–H stretching bands in compounds **3** (right) and **7** (left) in KBr.

Table 2. Selected IR stretching bands for complexes **1**, **3**, and **5**–**7** in THF solution.[a]

Stretching	1	3	5	6	7
B–H	2292 (i, br.) 2226 (i, br.)	2291 (i, br.) 2227 (i, br.)	2292 (m) 2225 (m)	2336 (m) 2360 (m)	2392 (m) 2308 (m) 2262 (m)
Aromatic ring	760 (i)	731 (i) 766 (i) 802 (i)	749 (i)	730 (i)	765 (i) 732 (i)
N–H			3387 (i) 3365 (i)		3328 (m)
Ligand	422 (br.) 3058 (m) 1417 (i) 1040 (i)	422 (i) 2963 (i) 1516 (i) 1423 (m) 1262 (i)	633 (i) 1592 (i) 1502 (i) 1459 (i) 1274 (i) 1249 (i)	695 (i) 1523 (m) 1459 (i) 1289 (i)	608 (m) 1531 (m) 1234 (m) 990 (i)

[a] (i) intense, (m) medium, (br.) broad, (sh.) shoulder.

Table 1. Important IR stretching bands for the alkali metal bidentate amine complexes in KBr.[a]

Stretching	1	2	3	4	5	6	7	8
B–H	2292 (i, br.) 2226 (i, br.) 2345 (sh.)	2292 (i, br.) 2224 (i, br.) 2368 (sh.)	2291 (i) 2227 (m, br.) 2378 (sh.)	2292 (i, br.) 2223 (i, br.) 2158 (sh.) 2381 (sh.)	2292 (i) 2225 (m) 2350 (m) 2387 (sh.)	2336 (m) 2360 (m)	2392 (m, br.) 2308 (i) 2262 (sh.)	2291 (i) 2225 (i)
Aromatic ring	760 (i)	757 (i)	731 (m) 766 (m) 802 (i)	736 (i) 769 (m) 856 (i)	750 (i)	730 (i)	765 (i) 732 (m)	834 (i)
N–H					3387 (i) 3365 (i)	3501 (br.)	3328 (m)	3389 (i) 3341 (i)
Ligand	3058 (m) 1417 (i) 1040 (i)	3054 (m) 1416 (i) 1040 (i)	2963 (i) 1516 (i) 1423 (m) 1262 (i)	2971 (m) 1508 (i) 1421 (i) 1267 (m)	1592 (i) 1502 (i) 1459 (m) 1274 (i)	1495 (i) 1459 (i) 1274 (i)	1531 (m) 1234 (m) 990 (i) 608 (m)	1256 (i) 1126 (i) 714 (i)

[a] (i) intense, (m) medium, (br.) broad, (sh.) shoulder.

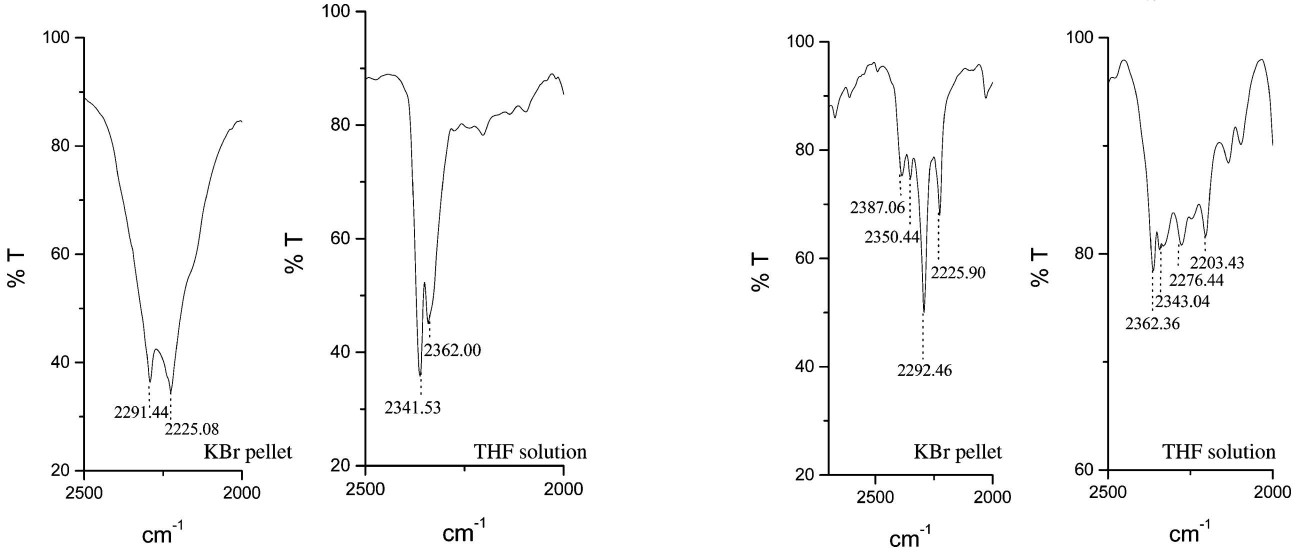

Figure 2. IR B–H stretching band pattern of compounds **1** (right) and **5** (left) in KBr and in THF solution.

Comparison of the B–H stretching patterns of the compounds in the solid state and in solution reveals a change in the number of stretching bands. Compounds **1**, **3**, and **6** conserved the pattern shown in the solid when in solution (they show an intense doublet; Figure 2), whereas a change (number and intensity of bands) occurred in the other compounds This is very important, because depending on the amine used, it is possible to get compounds whose structure is the same in the solid state and in solution.

All new complexes, in the solid state, can be stored in a vial, under normal conditions, for up to six months and no degradation was detected by IR or NMR spectroscopy. However, after a few months in solution, in some complexes, the formation of BH_3 adducts are detected (by the typical 1:3:3:1 quadruplet in the ^{11}B NMR spectra), for example, in compound **7**.

NMR Spectroscopy

The IR data provide some information about the denticity of the $[BH_4]^-$ group, but scarce information about the structure of the complex can be obtained. To determine the coordination mode of the ligand, the coordination sphere around the metal, and the presence of the $[BH_4]^-$ anion, we carried out multinuclear NMR experiments. The ^{11}B, ^7Li, and ^{23}Na NMR spectroscopic data are presented in Table 3.

The ^{11}B NMR chemical shift for all compounds is -40 ± 3 ppm, which gives a quintuplet with $^1J_{^{11}B,^1H}$ in the range 81–82 Hz. This shows that the geometry of the $[BH_4]^-$ group is similar in all compounds. In general, the ligand produces a somewhat better shielding in the ^{11}B chemical shift of the $[BH_4]^-$ group, except for compound **7**. The deshielding observed in **7** can be the result of a stronger interaction between the $[BH_4]^-$ group and the metal cation. In the ^1H NMR spectrum, the $[BH_4]^-$ group shows only one signal as a quartet (1:1:1:1, $^1J_{B,H} \approx 81$ Hz), around 0 ppm. This single signal means that the four hydrogen atoms are equivalent in solution. In compounds **1**, **3**, and **4** it is possible to see the ^{10}B,^1H coupling as a septet signal (1:1:1:1:1:1:1, $^1J_{B,H} \approx 30$ Hz).

Table 3. ^{11}B, ^7Li, and ^{23}Na NMR spectroscopic data (δ, ppm; J, Hz) for compounds **1**–**8**.

	$LiBH_4$	**1**	**3**	**5**	**7**	**8**
$\delta(^{11}B)$	–40	–42	–41	–40	–38	–42
$^1J_{B,H}$	81	81	81	81	82	82
^7Li	0.02	2.78	4.22	0.77	3.45	0.10
	$NaBH_4$	**2**	**4**	**6**		
$\delta(^{11}B)$	–40	–43	–42	–43		
$^1J_{B,H}$	81	81	81	81		
^{23}Na	2.85	3.34	2.25	4.0		

To determine the value of $\Delta G^{\neq}$ for the rotation of the $[BH_4]^-$ group in the new complexes, we lowered the temperature to –90 °C for **1** in $[D_8]$THF and to –60 °C for **3** and **4** in $CDCl_3$, but we did not reach the coalescence temperature. Nevertheless, those temperatures allowed us to estimate the value of $\Delta G^{\neq}$ (by using the Eyring equation)[11] as 31.5 KJ mol^{-1} for compound **1** and 36.9 KJ mol^{-1} for **3** and **4**. These values are lower than those obtained for transition metals[2a,2b](V, Nb, and Ta, ionic radii 0.65, 0.70, and 0.95 Å, respectively) and indicate that in the compounds prepared here the $[BH_4]^-$ group rotates faster than in the corresponding transition-metal complexes.

On the other hand, the ^7Li and ^{23}Na chemical shifts are deshielded by 2–4 ppm with respect to the corresponding alkali metal tetrahydroborate, depending on the amine. This is a result of the coordination of the ligand with the alkali metal cation. The ^7Li chemical shift agrees with a tetracoordinate atom.[5c,7a]

With the use of ^1H and ^{13}C NMR spectroscopy, we determined that each amine uses two nitrogen atoms to coordinate in a symmetric form with the alkali metal cation. The carbon and hydrogen atoms next to the nitrogen atom are deshielded by 2–6 and 0.2–0.3 ppm, respectively, depending on the amine. In compounds **5**, **6**, and **8**, the NH_2 group is also deshielded by 3–4 ppm, indicating that this group is coordinated to the metal cation. However, in compound **7**, the ^1H chemical shift for the NH proton does not change, meaning that it is not coordinated. All these facts evidence the formation of complexes **1**–**8** and agree with the IR data. In all compounds, except compound **7** (probably due to steric effects), a molecule of THF is coordinated to the metal cation. The amine/THF/MBH_4 ratio was 1:1:1 for all complexes, except for compound **7** where the amine/MBH_4 ratio was 1:1.

All these data allow us to propose a discrete molecular structure, where the metal cation is surrounded by one amine molecule, one THF molecule, and the $[BH_4]^-$ group in a tetrahedral geometry (Figure 3). This agrees with our previous theoretical study suggesting that the discrete structures were formed by one amine molecule, one THF molecule, and the $[BH_4]^-$ group are global minimum.[6] However, in compounds **5**–**8**, polymeric structures are also possible because of the position of the nitrogen atom and the flexibility of the ligand (Figure 4).

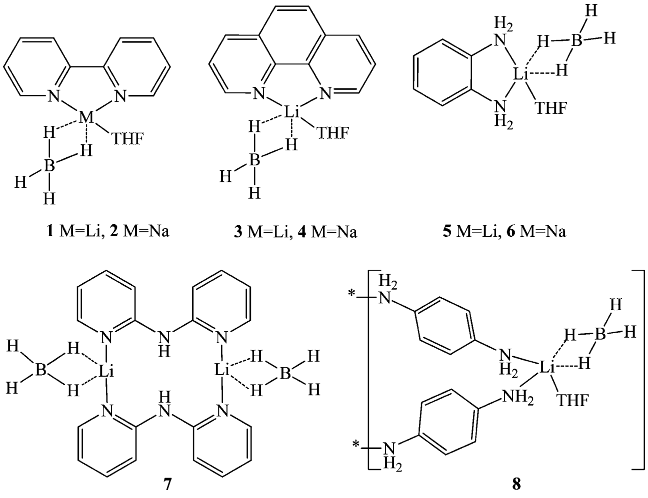

Figure 3. Proposed structures for compounds **1**–**8**.

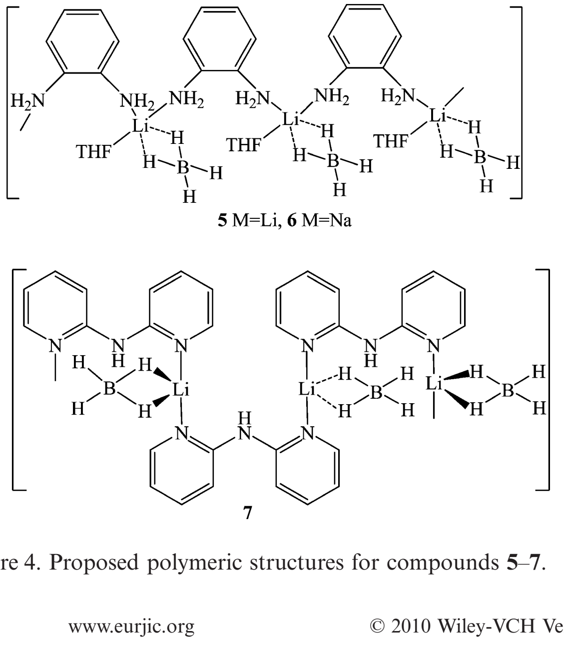

Figure 4. Proposed polymeric structures for compounds **5**–**7**.

Crystal Structures

It was possible to grow single crystals from compounds **1**–**8**; unfortunately, not all of them were suitable for X-ray analysis. The solid-state structures of compounds **1**, **5**, and **8** and that of adduct **9** were determined crystallographically. Selected bond lengths and angles are presented in Table 4.

Compound **1** is a 1:1:1 complex formed by 2,2-bipyridine, $LiBH_4$, and one THF molecule. It crystallizes in the orthorhombic space group *Pnma* with $Z = 4$. Figure 5 depicts the asymmetric unit, which shows a discrete molecule with a lithium atom in a distorted tetrahedral geometry [N–Li–N 81.1(4)°, N–Li–O 103.1(4)°, N–Li–B 126.1(4)°, O–Li–B 111.8(5)°] surrounded by 2,2-bipyridine, THF, and the $[BH_4]^-$ group. The 2,2′-bipyridine is planar and coordinates symmetrically to the lithium atom in a bidentate form with a N–Li bond length of 2.048(9) Å. The lithium atom lies almost in the molecular plane of the amine (just bent off 13°). The THF molecule has an envelope conformation with the oxygen atom out of plane and pointing towards the lithium atom; two cooperative C–H···π interactions[2c,12] stabilize the THF approach. The O–Li bond length is 2.01(1) Å. Regarding the $[BH_4]^-$ group, it has a slightly distorted tetrahedral array with bond angles ranging from 105.0 to 113.0° due to the multiple hydride proton interactions B–H···H–C[13] with the C–H protons of six bipyridine molecules (Figure 6). This group interacts with the Li atom [distance B···Li is 2.34(1) Å] by two hydrogen atoms. The H–Li bond length is 2.010 Å. The terminal B–H bond is shorter (1.060 Å) than the B–H bridging bond (1.130 Å).

The molecules are packed in the crystal in an alternate form, with the $[BH_4]^-$ group laying in the center (Supporting Information, Figure S1).

The crystals of **5** are monoclinic, space group *C*2/*c* and $Z = 8$. We should mention that there is a residual electron density due to a disordered toluene molecule (used to crystallize). The crystal structure of compound **5** shares some characteristics with compound **1**. For example, it has a lithium atom in a distorted tetrahedral geometry [N–Li–N 107.9(5)°, N–Li–O 100.8(5)°, and 98.7(5)°, N–Li–B 115.4(5), 114.6(5)°, O–Li–B 117.5(5)°] surrounded by two molecules of 1,2-phenylendiamine, THF, and the $[BH_4]^-$ group (Figure 7). Each amine acts as bidentate ligand and binds two different lithium atoms, with N1–Li bond lengths of 2.136(11) and 2.140(10) Å, respectively, which produces a polymeric array. The THF has an envelope conformation with the oxygen atom lying in plane; O–Li bond length 1.946(11) Å. The chain is stabilized by two N–H···H–B interactions that have $H^{\delta+}\cdots H^{\delta-}$ bond lengths of 2.362(4) and 2.423(7) Å, respectively (Figure 8).

The chains are joined by $H^{\delta+}\cdots H^{\delta-}$ interactions with N–H···H–B distances of 2.483(4) and 2.209(4) Å. Also, one C–H···H–B interaction with a distance of 2.474(5) Å can be

Table 4. Selected bond lengths [Å] and angles [°] for compounds **1**, **5**, **8**, and **9**.

Compound **1**			
O–Li	2.01(1)	B–H1	1.1300
N2–Li	2.048(9)	B–H2	1.0600
N1–Li	2.048(9)	B–H4	1.0600
B–Li	2.34(1)	B–H3	1.1300
Li–H1	2.0100		
C8–O–Li	121.8(3)	H1–B–H2	113.00
C8–O–C8′	103.4(4)	N2–Li–B1	126.1(4)
C1–N2–C3	117.9(4)	N2–Li–N3	81.1(4)
N2–C1–C6	121.2(4)	O–Li–N2	103.1(4)
H1–B–H3	106.00	O–Li–B	111.8(5)
H2–B–H3	106.00	H1–Li–H1′	55.00

Compound **5**			
N8–Li	2.136(11)	O10–C14	1.418(12)
N9–Li	2.142(10)	C1–C6	1.3893
N8–C1	1.421(7)	B–Li	2.364(14)
N9–C2	1.434(6)	B–H1	1.23(7)
N8–H1	0.9000	B–H2	1.02(8)
N8–H2	0.9000	B–H3	0.99(9)
N9–H1	0.9000	B–H4	1.07(12)
N9–H2	0.9000	Li–H1	2.04(6)
O10–Li	1.946(11)	Li–H3	2.08(9)
O10–C11	1.409(11)		
C11–O10–C14	108.6(7)	H2–B–H3	95(7)
C11–O10–Li1	120.8(6)	H2–B–H4	112(7)
H1–N8–H2	107.00	H3–B–H4	103(8)
H1–N9–H2	107.00	H1–B–H2	103(5)
C2–C3–C4	120.02	O10–Li–N8	100.8(5)
C3–C4–C5	120.00	O10–Li1–N9	98.7(5)
Li–B5–H3	61(5)	O10–Li–B5	117.5(5)
Li–B5–H1	60(3)	N8–Li–N9	107.9(5)
Li–B5–H52	69(4)	N8–Li–B5	114.6(5)
H1–B5–H3	105(5)	N9–Li–B5	115.4(5)
H1–B–H4	132(6)	H1–Li–H3	51(3)

Compound **8**			
N1–Li1	2.127(5)	N3–H1	0.93(3)
N2–Li1	2.146(5)	N3–H2	0.87(3)
N3–Li1	2.095(4)	O10–C11	1.416(3)
N1–C1	1.428(4)	O10–C14	1.412(4)
N2–C4	1.418(3)	O10–Li1	1.924(4)
N3–C7	1.424(3)	B1–H1	1.15(3)
N1–H2	0.92(3)	B1–H2	1.01(5)
N1–H1	0.86(3)	B1–H3	1.10(3)
N2–H1	0.89(3)	B1–H4	1. 04(5)
N2–H2	0.86(3)		
N1–Li1–N2	105.5(2)	H1–N3–H2	107(3)
N1–Li1–N3	105.5(2)	C11–O–C14	109.4(2)
N2–Li1–N3	108.9(2)	C11–O–Li1	123.6(2)
O–Li1–N1	115.0(2)	C14–O–Li1	118.5(2)
O–Li1–N2	108.1(2)	H1–B–H3	115(2)
O–Li1–N3	113.4(2)	H1–B–H4	107(3)
C1–N1–Li1	119.9(2)	H1–B–H2	104(3)
C4–N2–Li1	106.5(2)	H2–B–H4	111(4)
C7–N3–Li1	120.9(2)	H3–B–H4	106(3)
H1–N1–H2	111(3)	H2–B–H3	114(3)
H1–N2–H2	104(3)		

Compound **9**			
N2–C1	1.361(3)	N9–C1	1.347(3)
N2–C3	1.359(3)	N7–H7	0.8600
N2–B	1.604(3)	B–H1	1.1400
N7–C7	1.367(3)	B–H2	1.1100
N7–C8	1.404(3)	B–H3	1.0700
N9–C8	1.321(3)		
C1–N2–C3	118.3(2)	N7–C8–N9	119.1(2)
C1–N2–B1	122.3(2)	N2–B–H1	106.00
C3–N2–B1	119.4(2)	N2–B–H2	109.00
C8–N9–C1	116.2(2)	N2–B–H3	106.00
C8–N7–H7	115.00	H1–B–H2	111.00
C1–N7–H7	114.00	H1–B–H3	114.00
N2–C3–C4	123.2(2)	H2–B–H3	111.00

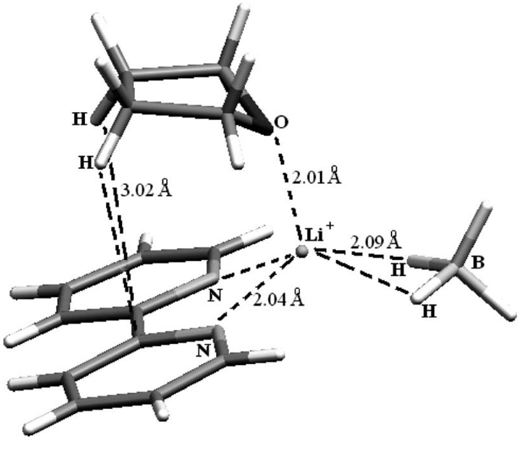

Figure 5. Molecular structure of compound **1**.

seen (Figure 9). The four N–H···H–B interactions and the one C–H···H–B interaction (Supporting Information, Figure S2) produce a distorted tetrahedral array with bond angles ranging from 95 to 132°. This group interacts with the Li atom [B···Li 2.364(14) Å] through two hydrogen atoms. The H–Li bond lengths are 2.04(6) and 2.08(9) Å. The B–H bond length varies from 1.00(9) to 1.23(7) Å.

Compound **8** crystallizes in the same system and space group as compound **5**, that is, monoclinic, space group *C*2/*c*, and $Z = 8$, but the structure is quite different. Compound **8** shows an ionic, 3D polymeric array with lithium atoms having a slightly distorted tetrahedral geometry and bond angles ranging from 105 to 115°. The lithium atom is surrounded by three molecules of 1,4-phenylendiamine and one THF molecule (Figure 10). Each amine acts as a bidentate ligand and binds two different lithium atoms, in a 3D array, with the same bond lengths but different from other amines, N1–Li 2.127(5) Å, N2–Li 2.146(5) Å, N3–Li 2.095(4) Å. These amines are arranged almost perpendicular to each other (Figure 11). The THF shows an envelope conformation with the oxygen atom lying in the plane; the O–Li bond length is 1.924(4) Å. Something that distinguishes this structure from the previous ones is that the $[BH_4]^-$ group is not coordinated to the lithium atom. The $[BH_4]^-$ group has a lightly distorted tetrahedral geometry (H–B–H bond angles between 104 and 115°) and the B–H

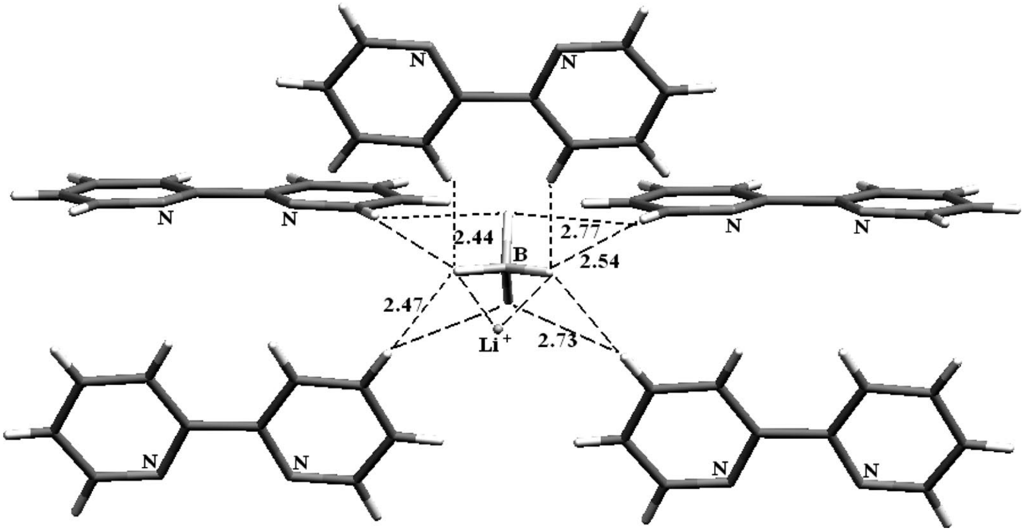

Figure 6. B–H···H–C interactions in the crystal of compound **1**.

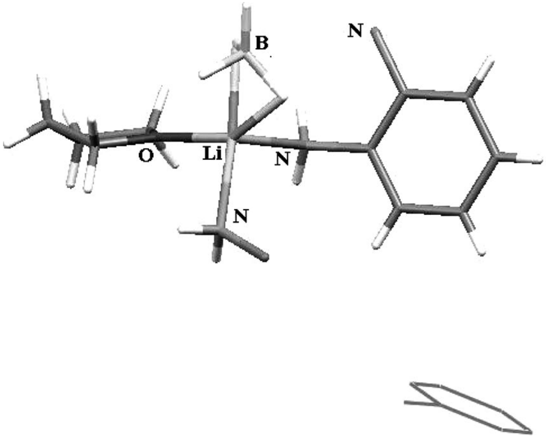

Figure 7. Asymmetric unit in compound **5**, showing a disordered toluene molecule.

bond lengths span in a range from 1.01 to 1.15 Å. The longest B–H bond is involved in a hydride–proton interaction [$H^{\delta+}\cdots H^{\delta-}$ 2.214(7) Å, angle N–H···$H^{\delta-}$ 171.3°] with a NH_2 group. The second longest B–H bond participates in a triple hydride–proton interaction with three neighboring NH_2 groups [$H^{\delta+}\cdots H^{\delta-}$ 2.114(7) Å, angle N–H···$H^{\delta-}$ 166.2°, $H^{\delta+}\cdots H^{\delta-}$ 2.187(7) Å, angle N–H···$H^{\delta-}$ 146.3°, $H^{\delta+}\cdots H^{\delta-}$ 2.241(7) Å, angle N–H···$H^{\delta-}$ = 145.7°, see Supporting Information].

On the other hand, from an aged THF solution of compound **7** (6 months) we collected nice needles of **9** having the solid-state structure shown in Figure 12. In this figure we can see that 2,2-dipyridilamine coordinates with one nitrogen atom of the pyridine ring and to one BH_3, group, giving an asymmetric adduct. Formation of compound **9** implies the loss of LiH.[5a]

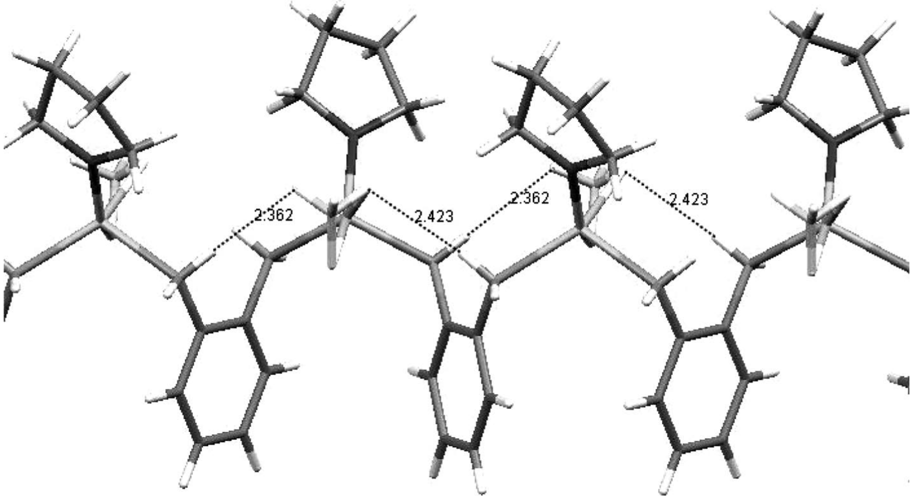

Figure 8. Chain formed in compound **5**.

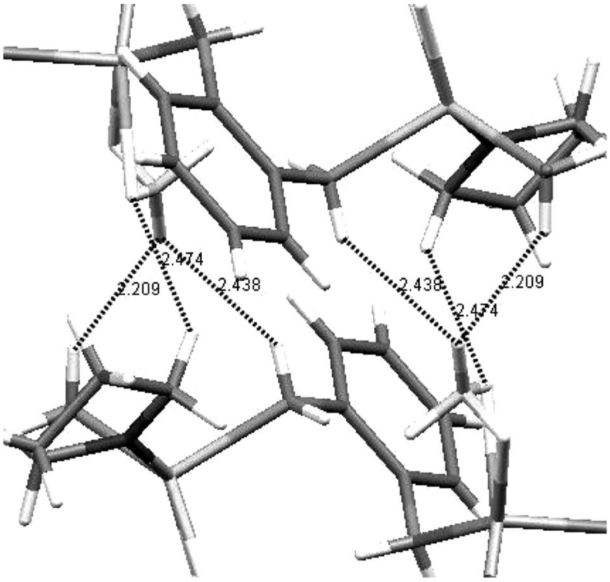

Figure 9. Interactions between chains in compound **5**.

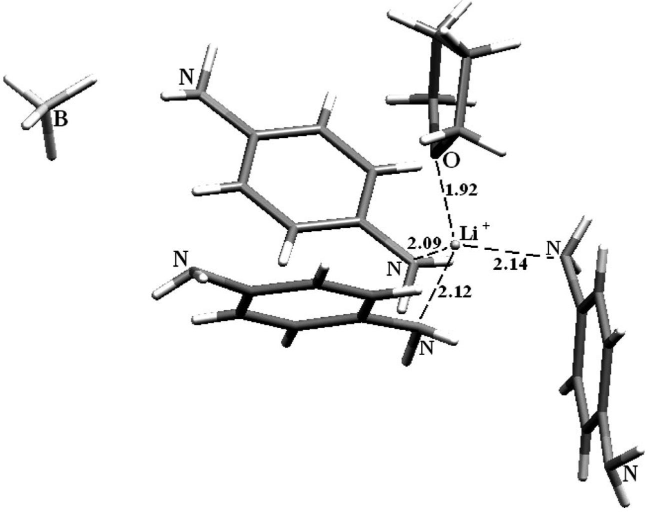

Figure 10. Molecular structure of compound **8**.

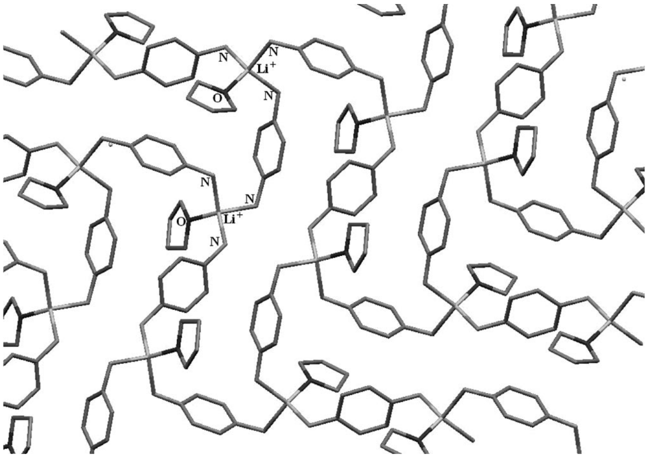

Figure 11. Crystal packing of compound **8**.

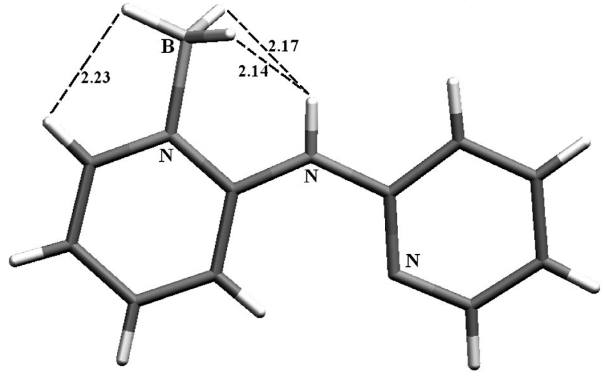

Figure 12. Crystalline structure of adduct **9**.

The solid-state structure of adduct **9** presents some very interesting structural features. First, an intermolecular dihydrogen bond is observed with a C–H···H–B distance of 2.58 Å with a symmetry-related molecule, resulting in the formation of a dimer. The C–H···H and B–H···H angles are 142.9 and 80.0°, respectively (Supporting Information, Figure S3). Second, there is a C–H···π interaction between two adduct molecules that are located perpendicular to each other. The C–H···aromatic ring distance and the C–H–aromatic ring angle are 2.88 Å and 155°, respectively. Both the C–H···aromatic ring distance, in the range of the accepted value (2.6–3.0 Å) for this kind of interaction,[12] and the angle close to linearity, are consistent with the C–H···π interaction (Supporting Information, Figure S4).

All of these unconventional hydrogen bonds are the supramolecular array scaffolds observed in the adduct derived from compound **9**. This array is shown in Figure 13 and consists of a chain of dimers kept together by C–H···H–B and C–H···π hydrogen bonds in a zigzag array.

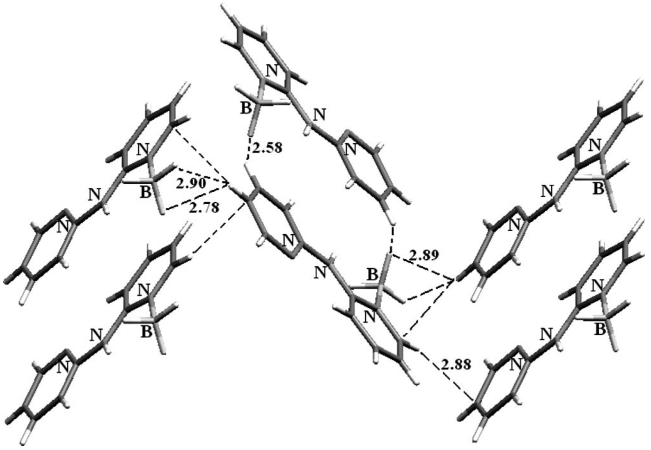

Figure 13. Intermolecular array in the lattice of the adduct derived from compound 7.

It is important to mention that all dihydrogen bonds where the $[BH_4]^-$ group is involved can be shorter by 0.10 Å. This shortening comes from the correction that should be made to the B–H bond lengths obtained by X-ray diffraction (increment of 0.10 Å)[14a] due to the combination of both the displacement of the electron cloud on the H atoms (major contributor) and the liberation effect of the $[BH_4]^-$ group.[14] Besides, the slightly distorted tetrahedral geometry of the $[BH_4]^-$ group is consistent with the observed dihydrogen bonds.[12e,14b]

Conclusions

Eight new complexes were prepared from a mixture of 2,2′-bipyridylamine, 2,2′-bipyridine, 1,10-phenanthroline, 1,2-phenylendiamine, and 1,4-phenylendiamine with $LiBH_4$ and $NaBH_4$, respectively, in a 1:1 molar ratio in THF. In all complexes but **8**, the $[BH_4]^-$ group is bidentate in the solid state, with an estimated rotational energy of less than 38 KJ mol^{-1}. All amines act as bidentate ligands and coordinate to metal cations in a symmetric form. Depending on the amine, we can get discrete molecular or polymeric complexes. In all studied complexes, the metal cation and the $[BH_4]^-$ group show a tetrahedral distorted geometry. The use of bidentate amines augments the stability in the solid state and in solution (except in **7**) under normal conditions of $LiBH_4$ and $NaBH_4$ and also determines the complex–structure type and its prevalence in the solid state and in solution.

Experimental Section

General: All manipulations were carried out under a nitrogen atmosphere by using Schlenk techniques. All solvents were dried and distilled prior to use. Sodium and lithium tetrahydroborate, 2,2′-dipyridylamine, 2,2′-bipyridine, 1,10-phenanthroline, and 1,2-phenylendiamine were purchased from Aldrich and used as received. Infrared, in KBr and THF solution, are reported in cm^{-1}. ^{1}H, ^{13}C ^{11}B, ^{7}Li, and ^{23}Na NMR spectra were recorded with a Bruker Avance 400 spectrometer at 400.1, 100.6, 128.4, 155.4, and 71.5 MHz, respectively; chemical shifts are reported in parts per million; δ = ^{1}H and ^{13}C were referenced to TMS, ^{11}B to $BF_3{\cdot}OEt_2$, and ^{7}Li to $LiCl{\cdot}H_2O$ (9.7 M). Elemental analyses were performed with a Flash 1112 Thermo Finnigan analyzer. Melting points were measured with a Büchi B-540 apparatus. X-ray crystallography data (Table 5) were measured by using standard procedures with a Nonius Kappa CCD instrument with CCD area detector by using graphite-monochromated Mo-K_α radiation at 293 K. Intensities were measured by using $\phi + \omega$ scans. The structure was solved and refined by using SHELX-97.[15] All non-hydrogen atoms were refined anisotropically. Almost all hydrogen atoms were found in the difference map (except hydrogen atoms in the $[BH_4]^-$ group in compounds **1** and **9** and the NH_2 group in compound **5**) and allowed to ride on their respective atoms, except for those whose coordinates were refined.

$LiBH_4$-2,2′-bipyridine-THF (1): A THF (15 mL) solution of $LiBH_4$ (139 mg, 6.6 mmol) was treated with a THF solution (5 mL) of 2,2′-bipyridine (400 mg, 2.6 mmol). This mixture was stirred for 30 min before filtering. The remnant white solid was dried by a nitrogen stream (577 mg, 90%). M.p. 158–162 °C. Crystals suitable for X-ray structural determination were obtained by slow evaporation. ^{1}H NMR ($CDCl_3$): δ = 8.26 (d, 3-H, 2,2′-bipyridine), 7.31 (t, 4-H, 2,2′-bipyridine), 7.82 (t, 5-H, 2,2′-bipyridine), 8.67 (d, 6-H, 2,2′-bipyridine), 0.08 (q, $[BH_4]^-$), 1.83 (t, 2-H,THF), 3.72 (t, 1-H, THF) ppm. ^{13}C NMR ($CDCl_3$): δ = 155 (C-2), 120 (C-3), 137 (C-4), 123 (C-5), 149 (C-6), 68.5 (C-2, THF), 25.5 (C-3, THF) ppm.

Table 5. Crystallographic data for the structural analyses of compounds **1**, **5**, **8**, and **9**.

	1	**5**	**8**	**9**
Formula	$C_{14}H_{20}BLiN_2O$	$C_{14}H_{20}BLiN_2O$	$C_3H_4BLiN_3O$	$C_{10}H_{12}BN_3$
Formula weight	250.08	244.1	2048.82	185.04
Crystal size [mm]	0.25 × 0.2 × 0.1	0.60 × 0.25 × 0.13	0.10 × 0.14 × 0.13	0.35 × 0.2 × 0.15
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	*Pnma*	*C*2/*c*	*C*2/*c*	$P2_1/c$
a [Å]	9.7864(7)	24.416(1)	23.468(3)	5.1123(2)
b [Å]	11.6589(8)	12.8108(7)	9.308(2)	15.3366(7)
c [Å]	12.8680(9)	10.1523(7)	17.583(6)	12.7199(6)
α [°]	90	90	90	90
β [°]	90	97.354(2)	123.65(2)	92.265(2)
γ [°]	90	90	90	90
V [Å^3]	1468.2(2)	3149.5(3)	996.53(8)	996.53(8)
Z	4	8	8	4
$\rho_{calcd.}$ [Mg m^{-3}]	1.131	1.029	1.064	1.233
μ [mm^{-1}]	0.07	0.06	0.07	0.08
F(000)	536	1048	1112	392
Index range	$12\leq h \leq 12$	$-30 \leq h \leq 30$	$-26 \leq h \leq 0$	$-6 \leq h \leq 6$
	$-14 \leq k \leq 14$	$0 \leq k \leq 16$	$-10 \leq k \leq 0$	$-19 \leq k \leq 19$
	$-16 \leq l \leq 16$	$-12 \leq l \leq 12$	$-16 \leq l \leq 20$	$-16 \leq l \leq 16$
2θ [°]	55.60	54.9	47.95	55.2
T [K]	293	293	293	293
Refl. collected	3134	6452	2752	4339
Refl. unique	1730	3230	2503	2270
Refl. obs. 2σ	791	1119	1685	1191
R (int.)	0.165	0.00	0.0094	0.069
No. variables	92	156	236	127
GOOF	1.43	1.07	1.06	1.10
Final $R(2\sigma)$	0.086	0.149	0.0445	0.056
Final wR_2	0.089	0.416	0.1339	0.061
Larg. res. peak [e Å^{-3}]	0.35	0.24	0.17	0.17

^{11}B NMR ($CDCl_3$): δ = –40.7 (q, $[BH_4]^-$) ppm. ^{7}Li NMR ($CDCl_3$): δ = 3.98 (s, $LiBH_4$) ppm. IR (KBr or THF): $\tilde{\nu}$ = 1591, 2226, 2292 ($[BH_4]^-$), 760, 3422, 3058, 1417, 1040 (2,2′-bipyridine) cm^{-1}. $C_{14}H_{20}BLiN_2O$ (250): calcd. C 67.25, H 8.00, N 11.20; found C 67.45, H 8.14, N 11.55.

$NaBH_4$-2,2′-bipyridine-THF (2): Following the procedure outlined for **1**, a suspension of $NaBH_4$ (680 mg, 1.7 mmol) in THF (15 mL) was treated with a THF solution (5 mL) of 2,2′-bipyridine (278 mg, 1.7 mmol). This mixture was stirred for 30 min before filtering. The remnant white solid was dried by a nitrogen stream (670 mg, 98%). M.p. 100–104 °C. ^{1}H NMR ($CDCl_3$): δ = 8.42 (d, 3-H, 2,2′-bipyridine), 7.25 (t, 4-H, 2,2′-bipyridine), 7.83 (t, 5-H, 2,2′-bipyridine), 8.73 (d, 6-H, 2,2′-bipyridine), 0.06 (q, $[BH_4]^-$), 1.85 (t, 2-H, THF), 3.75 (t, 1-H, THF) ppm. ^{13}C NMR ($CDCl_3$): δ = 156 (C-2), 123 (C-3), 137 (C-4), 121 (C-5), 149 (C-6), 67.8 (C-2, THF), 25.6 (C-3, THF) ppm. ^{11}B NMR ($CDCl_3$): δ = –43.3 (q, $[BH_4]^-$) ppm. IR (KBr or THF): $\tilde{\nu}$ = 1578, 2224, 2292 (BH_4), 757, 3439, 3054, 1416, 1040 (2,2′-bipyridine) cm^{-1}. $C_{14}H_{20}BN_2NaO\cdot 1/2bipy$ (345.2): calcd. C 66.10, H 7.30, N 12.17; found C 65.60, H 6.10, N 12.90.

$LiBH_4$-1,10-phenanthroline-THF (3): Following the procedure outlined for **1**, a THF (15 mL) solution of $LiBH_4$ (25 mg, 1.1 mmol) was treated with a THF solution (5 mL) of 1,10-phenanthroline (207 mg, 1.1 mmol). This mixture was stirred for 30 min before filtering. The remnant yellow solid was dried by a nitrogen stream (0.20 g, 97%). M.p. 150–154 °C. ^{1}H NMR ($CDCl_3$): δ = 8.99 (d, 2-H, amine), 7.63 (q, 3-H amine), 8.26 (d, 4-H, amine), 7.82 (s, 5-H amine), 0.23 (q, $[BH_4]^-$), 1.82 (t, 2-H THF), 3.72 (t, 1-H THF) ppm. ^{13}C NMR ($CDCl_3$): δ = 150 (C-2), 126 (C-3), 136 (C-4), 123 (C-5), 146 (C-11), 128 (–), 68.2 (C-2, THF), 25.8 (C-3, THF) ppm. ^{11}B NMR ($CDCl_3$): δ = –41.5 (q, $[BH_4]^-$) ppm. IR (KBr or THF): $\tilde{\nu}$ = 2291, 2227 (BH_4), 731, 766, 802, 422, 2963, 1516, 1423, 1262 (amine) cm^{-1}. $C_{16}H_{20}BLiN_2O$ (274.1): calcd. C 70.11, H 7.35, N 10.20; found C 69.45, H 8.10, N 11.25.

$NaBH_4$-1,10-phenanthroline-THF (4): Following the procedure outlined for **1**, a THF (15 mL) suspension of $NaBH_4$ (36 mg, 0.95 mmol) was treated with a THF solution (5 mL) of 1,10-phenanthroline (178 mg, 0.98 mmol). This mixture was stirred for 30 min before filtering. The yellow solid was dried by a nitrogen stream (182 mg, 99%). M.p. 188–190 °C. ^{1}H NMR ($CDCl_3$): δ = 9.18 (d, 2-H, amine), 7.62 (q, 3-H, amine), 8.25 (d, 4-H, amine), 7.79 (s, 5-H, amine), 0.29 (q, $[BH_4]^-$), 1.84 (t, 2-H, THF), 3.73 (t, 1-H, THF) ppm. ^{13}C NMR ($CDCl_3$): δ = 150 (C-2), 126 (C-3), 136 (C-4), 123 (C-5), 146 (C-11), 128 (C-12), 68.1 (C-2, THF), 26.0 (C-3, THF) ppm. ^{11}B NMR ($CDCl_3$): δ = –42.9 (q, $[BH_4]^-$) ppm. IR (KBr or THF): $\tilde{\nu}$ = 1619, 2293, 2222 (BH_4), 736, 769, 804, 2971, 1507, 1421, 1267 (amine) cm^{-1}. $C_{12}H_{16}B_2N_2Na_2$ (256.1): calcd. C 56.33, H 6.30, N 10.95; found C 56.67, H 5.00, N 10.61.

$LiBH_4$-1,2-phenylenediamine-THF (5): Following the procedure outlined for **1**, a THF (15 mL) solution of $LiBH_4$ (68 mg, 1.7 mmol) was treated with a THF solution (5 mL) of 1,2-phenylenediamine (278 mg, 1.7 mmol). This mixture was stirred for 30 min before filtering. The orange solid was dried by a nitrogen stream (131 mg, 35%). M.p. 178 °C. Crystals suitable for X-ray structural determination were obtained by slow evaporation of a THF/toluene solution. ^{1}H NMR ($CDCl_3$): δ = 7.4 (d, 3-H, amine), 7.0 (d, 4-H, amine), –0.03 (q, $[BH_4]^-$), 1.75 (t, 2-H, THF), 3.85 (t, 1-H, THF) ppm. ^{13}C NMR ($CDCl_3$): δ = 138 (C-2), 120 (C-3), 110 (C-4), 68.0 (C-2, THF), 26.1 (C-3, THF) ppm. ^{11}B NMR ($CDCl_3$): δ = –41 (q, $[BH_4]^-$) ppm. IR (KBr or THF): $\tilde{\nu}$ = 1616, 2224, 2291 (BH_4), 633, 1592, 1502, 1459, 1274, 1249 (amine) cm^{-1}. $C_{10}H_{20}BLiN_2O$ (202.18): calcd. C 59.45, H 9.98, N 13.87; found C 58.39, H 8.14, N 12.55.

$NaBH_4$-1,2-phenylenediamine-THF (6): Following the procedure outlined for **1**, a THF (15 mL) suspension of $NaBH_4$ (38 mg, 1.0 mmol) was treated with a THF solution (5 mL) of 1,2-phenylenediamine (110 mg, 1.0 mmol). This mixture was stirred for 30 min before filtering. The orange solid was dried by a nitrogen stream (68 mg, 62%). M.p. 101–105 °C. ^{1}H NMR ($CDCl_3$): δ = 7.5 (d, 3-H, amine), 7.0 (d, 4-H amine), –0.03 (q, $[BH_4]^-$), 1.73 (t, 2-H, THF), 3.75 (t, 1-H, THF) ppm. ^{13}C NMR ($CDCl_3$): δ = 138 (C-2), 120 (C-3), 110 (C-4), 68.2 (C-2, THF), 25.6 (C-3, THF) ppm. ^{11}B NMR ($CDCl_3$): δ = –43.3 (q, $[BH_4]^-$) ppm. IR (KBr or THF): $\tilde{\nu}$ = 1604, 2336.8, 2360.4 (BH_4), 730, 3501, 1495, 1459 (amine) cm^{-1}. $C_6H_{16}B_2N_2Na_2$ (184.13): calcd. C 39.21, H 8.77, N 15.24; found C 39.16, H 5.64, N 14.75.

$LiBH_4$-2,2-dipyridylamine (7) and *N*-BH_3-2,2-Dipyridylamine (9): Following the procedure outlined for **1**, a THF (15 mL) solution of $LiBH_4$ (80 mg, 2.15 mmol) was treated with a THF solution (5 mL) of 2,2′-dipyridylamine (362 mg, 2.11 mmol). This mixture was stirred for 30 min before filtering. The yellow solid was dried by a nitrogen stream (307 mg, 83%). M.p. 172–176 °C. ^{1}H NMR ($CDCl_3$): δ = 8.51 (d, 3-H, amine), 7.44 (t,4-H, amine), 7.95 (d, 5-H, amine), 8.81 (s, 6-H, amine), 0.31 (q, $[BH_4]^-$) ppm. ^{13}C NMR ($CDCl_3$): δ = 146 (C-2), 113 (C-3), 138 (C-4), 116 (C-5), 153 (C-6) ppm. ^{11}B NMR ($CDCl_3$): δ = –40.8 (q, $[BH_4]^-$) ppm. IR (KBr or THF): $\tilde{\nu}$ = 22392, 2308.9, 2262 (BH_4), 765, 732, 3328, 608, 153, 1234, 990 (amine) cm^{-1}. $C_{20}H_{26}B_2Li_2N_6$ (385.68): calcd. C 62.27, H 6.74, N 21.77; found C 63.04, H 7.10, N 21.45. From a THF solution of **7**, left aside for six months, crystals of compound **9** were obtained and analyzed by X-ray diffraction. $C_{10}H_{12}BN_3\cdot THF$ (257.0): calcd. C 65.36, H 7.78, N 16.3; found C 64.06, H 7.29, N 17.14.

$LiBH_4$-1.5(1,4-phenylenediamine)-THF (8): Following the procedure outlined for **1**, to a solution of *p*-phenylendiamine (310 mg) in THF (15 mL) was added a solution of $LiBH_4$ (622 mg) in THF (10 mL). After 30 min, the mixture was filtered and the volume was reduced to 20 mL. The brown solution was kept at 5 °C and brown prisms had formed after 1 d (370 mg, 75%). M.p. 185 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ = 7.20 (m, 2-H), 7.00 (m, 3-H), 3.80 (2-H, THF), 1.80 (3-H, THF), –0.3 (q, $[BH_4]^-$) ppm. ^{13}C NMR ($CDCl_3$): δ = 135.7 (C-1), 119.0 (C-2), 111.0 (C-3), 68.0 (C-2, THF), 26.0 (C-3, THF) ppm. ^{11}B NMR ($CDCl_3$): δ = –41.8 (q, $[BH_4]^-$) ppm. ^{7}Li NMR ($CDCl_3$): δ = 0.10 ppm. IR (KBr): $\tilde{\nu}$ = 2292, 2225 (BH_4), 3421, 3208, 1256, 1126, 834, 714 (amine) cm^{-1}. $C_{13}H_{24}BLiN_3O$ (255.83): calcd. C 60.99, H 9.38, N 16.42; found C 59.40, H 9.30, N 16.46.

CCDC-743489 (for **1**), -743490 (for **5**), -743491 (for **8**), and -743492 (for **9**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

The authors thank Consejo Nacional de Ciencia y Tecnologia [CONACYT-Mexico] for financial support and scholarships for M.A.M., G.F.B., and C.P.M.

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Received: December 21, 2009