

# Synthesis and X-ray Structural Characterization of the Metal Borylamide Complexes $\text{Li}(\text{Et}_2\text{O})_2\text{NPhBMe}_2$ , $(\text{THF})(\text{Et}_2\text{O})_2\text{LiClCo}\{\text{NPhBMe}_2\}_2$ , and $\text{Mn}\{\text{NMesBMe}_2\}_2\cdot 3\text{PhMe}$ (Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>): Modified Amide Ligands with Poor Bridging and $\pi$ -Donor Characteristics

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**Abstract:** The synthesis and characterization of the aminoboranes  $\text{HNRBMe}_2$  (R = Ph, **1**; R = Mes, **2**), the lithium salts  $\text{Li}(\text{Et}_2\text{O})_2\text{NRBMe}_2$  (R = Ph, **3**; R = Mes, **4**), and the transition-metal derivatives  $(\text{THF})(\text{Et}_2\text{O})_2\text{LiClCo}\{\text{NPhBMe}_2\}_2$  (**5**) and  $\text{Mn}\{\text{NMesBMe}_2\}_2\cdot 3\text{PhMe}$  (**6**) are reported. The X-ray crystal structures of **1**, **3**, **5**, and **6** are also described. The structures reveal that all the nitrogen and boron centers within the ligands are planar and that the twist angles between these planes are small. The multiple character of the B-N bond remains essentially unchanged in all compounds. As a result the boryl-substituted amide ligand is predicted to have poor  $\sigma$ -bridging characteristics. This is borne out by the structures of **3**, **5**, and **6** that are the first structurally characterized transition-metal complexes of a borylamide ligand. An interesting consequence of the low bridging tendency of the  $\text{-NRBMe}_2$  ligand is the isolation of the two-coordinate Mn(II) complex **6**, whereas more conventional amide ligands such as  $\text{-N}(\text{SiMe}_3)_2$  and  $\text{-NPh}_2$  have led to bridged products in the solid. Crystal data [Mo K $\alpha$  ( $\lambda = 0.71069 \text{ \AA}$ )] at 130 K are as follows: **1**, C<sub>24</sub>H<sub>28</sub>BN,  $a = 8.567$  (1)  $\text{\AA}$ ,  $b = 17.046$  (3)  $\text{\AA}$ ,  $c = 13.632$  (2)  $\text{\AA}$ ,  $\beta = 95.00$  (1) $^\circ$ ,  $Z = 4$ , monoclinic, space group  $P2_1/c$ ,  $R_w = 0.049$ ; **3**, C<sub>32</sub>H<sub>47</sub>O<sub>2</sub>NBLi,  $a = 10.818$  (3)  $\text{\AA}$ ,  $b = 16.155$  (4)  $\text{\AA}$ ,  $c = 17.842$  (5)  $\text{\AA}$ ,  $\beta = 103.75$  (2) $^\circ$ ,  $Z = 4$ , space group  $P2_1/n$ ,  $R_w = 0.057$ ; **5**, C<sub>60</sub>H<sub>82</sub>CoCl<sub>63</sub>N<sub>2</sub>B<sub>2</sub>Li,  $a = 47.375$  (21)  $\text{\AA}$ ,  $b = 11.616$  (3)  $\text{\AA}$ ,  $c = 22.983$  (10)  $\text{\AA}$ ,  $\beta = 114.65$  (3) $^\circ$ , space group  $C2/c$ ,  $Z = 8$ ,  $R_w = 0.063$ ; **6**, C<sub>75</sub>H<sub>90</sub>MnN<sub>2</sub>B<sub>2</sub>,  $a = 21.964$  (6)  $\text{\AA}$ ,  $b = 13.048$  (4)  $\text{\AA}$ ,  $c = 21.675$  (6)  $\text{\AA}$ ,  $\beta = 93.49$  (2) $^\circ$ , space group  $C2/c$ ,  $Z = 4$ ,  $R_w = 0.077$ .

Bulky amide ligands, for example,  $\text{-N}(\text{SiMe}_3)_2$ ,<sup>2-5</sup>  $\text{N}(i\text{-Pr})_2$ ,<sup>6</sup> or  $\text{-NPh}_2$ ,<sup>7,8</sup> have proved very effective in the synthesis of low-coordinate main-group, transition-metal, lanthanide, and actinide complexes. Their metal derivatives are, generally speaking, more stable than the corresponding alkyls or aryls due to the greater strength of the M-N bond.<sup>9</sup> Thus species such as  $[\text{M}(\text{NR}_2)_2]_2$  (M = Mn, Fe, Co<sup>10-13</sup> or Ni;<sup>8,14</sup> R = SiMe<sub>3</sub> or Ph) are isolable under ambient conditions whereas, to date, only a few corresponding alkyls or aryls have been well-characterized for manganese. On the other hand, alkoxides or aryloxides should be even more stable than the amides (bond strength of  $\text{M-O} > \text{M-N} > \text{M-C}$ ).<sup>9</sup> However, the  $\text{-OR}$  ligand bears only one organic group and as a result is not as sterically versatile as the amide having two organic substituents. In effect, the amide ligand combines high metal-ligand bond strength and high steric requirements

which has led to its widespread use in the synthesis of complexes with low-coordination numbers. The bis(trimethylsilyl)amide ligand  $\text{-N}(\text{SiMe}_3)_2$  has been most thoroughly explored throughout the periodic table.<sup>2-5</sup> The diphenylamide group  $\text{-NPh}_2$ , though not as large as  $\text{N}(\text{SiMe}_3)_2$ , has also attracted considerable interest.<sup>7,8</sup>

Studies in this laboratory have focussed on the structural characterization of both amide and alkoxide/aryloxide derivatives<sup>15-17</sup> of transition metals. One of the objectives has been the synthesis and characterization of linear, two-coordinate, open-shell transition-metal compounds.<sup>18,19</sup> To date neither  $\text{-N}(\text{SiMe}_3)_2$  nor  $\text{-NPh}_2$  have proved effective in achieving two coordination in the solid, although there is molecular weight and electron diffraction data on  $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2]$  (M = Fe or Co) that suggests major degrees of dissociation in solution and a monomeric existence in the vapor phase. The alkoxides  $[\text{Co}(\text{OR})_2]_2$  (R =  $\text{-CPh}_3$ ,  $\text{-C}(\text{C}_6\text{H}_{11})_3$ , or  $\text{-C}(\text{4-MeC}_6\text{H}_4)_3$ ) are also apt to dissociate. For these, coalescence of the bridging and terminal ligand <sup>1</sup>H NMR signals in C<sub>6</sub>D<sub>6</sub> solution indicate an energy barrier of ca. 15 kcal mol<sup>-1</sup> to dissociation.<sup>17</sup>

It is, in principle, possible to increase the size of the organic substituent in amides or alkoxides until two-coordination is achieved. However, an alternative approach is to reduce the Lewis basicity of the nitrogen or oxygen atoms so that the likelihood of bridging is decreased. For the amides one method is to use boron substituents ( $\text{-BR}_2$ ) in place of one or both of the organic groups on nitrogen. In this paper we describe the syntheses of the aminoboranes  $\text{HNRBMe}_2$  (R = Ph, **1**; R = Mes, **2**), the

- (1) Fellow of the A. P. Sloan Foundation 1985-1987.
- (2) Harris, D. H.; Lappert, M. F. *J. Organomet. Chem. Libr.* **1976**, 2, 13. Bradley, D. C. *Chem. Brit.* **1975**, 11, 393.
- (3) (a) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis-Horwood: Chichester, 1980. (b) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, 9, 273.
- (4) Andersen, R. A. *Inorg. Chem.* **1979**, 18, 1507. Tilley, T. D.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1984**, 23, 2271.
- (5) Ghotra, J. S.; Hursthouse, M. B.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1973**, 669.
- (6) Bradley, D. C.; Hursthouse, M. B.; Newing, C. W. *J. Chem. Soc., Chem. Commun.* **1971**, 411.
- (7) Dermer, O. C.; Fernelius, W. C. *Z. Anorg. Allg. Chem.* **1935**, 221, 83. Frölich, H. O.; Märkisch, V. *Z. Chem.* **1975**, 15, 276. Brito, V.; Frölich, H. O.; Müller, B. *Z. Chem.* **1979**, 19, 28. Frölich, H. O.; Römhild, W. *Z. Chem.* **1980**, 20, 154.
- (8) Hope, H.; Olmstead, M. M.; Murray, B. D.; Power, P. P. *J. Am. Chem. Soc.* **1985**, 107, 712.
- (9) Lappert, M. F.; Patil, D. S.; Pedley, J. B. *J. Chem. Soc., Chem. Commun.* **1975**, 830.
- (10) Bradley, D. C.; Hursthouse, M. B.; Malik, K. M. A.; Moseler, R. *Transition Met. Chem. (Weinheim, Ger.)* **1978**, 3, 253.
- (11) Murray, B. D.; Power, P. P. *Inorg. Chem.* **1984**, 23, 4584.
- (12) Andersen, R. A., personal communication.
- (13) Bürger, H.; Wannagat, U. *Monatsh. Chem.* **1963**, 94, 1007.
- (14) Bürger, H.; Wannagat, U. *Monatsh.* **1964**, 95, 1099.

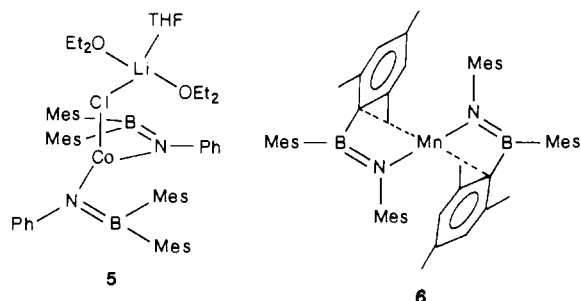
- (15) Hvoslief, J.; Hope, H.; Murray, B. D.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1983**, 1438.

- (16) Olmstead, M. M.; Power, P. P.; Sigel, G. A. *Inorg. Chem.* **1986**, 25, 1027.

- (17) Sigel, G. A.; Bartlett, R. A.; Decker, D.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.*, in press.
- (18) Buttrus, N. H.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1985**, 1380.

- (19) Andersen, R. A.; Haaland, A.; Rypdal, K.; Volden, H. V. *J. Chem. Soc., Chem. Commun.* **1985**, 1807.

lithium salts  $\text{Li}(\text{Et}_2\text{O})_2\text{NPhBMe}_2$  (**3**) and  $\text{Li}(\text{Et}_2\text{O})_2\text{NMesBMe}_2$  (**4**), and the transition-metal derivatives  $(\text{THF})(\text{Et}_2\text{O})_2\text{LiClCo}\{-\text{NPhBMe}_2\}_2$  (**5**) and  $\text{Mn}(\text{NMesBMe}_2)_2\cdot 3\text{PhMe}$  (**6**). The X-ray



crystal structures of **1**, **3**, **5**, and **6** are also reported. Those of **3**, **5**, and **6** confirm that neither the  $-\text{NPhBMe}_2$  nor  $-\text{NMesBMe}_2$  entities behave as bridging ligands in these three cases and suggest that this behavior will also be seen in other complexes. Compound **6** is a rare example<sup>17</sup> of a two-coordinate, non-d<sup>10</sup>, transition-metal complex. Its structure, however, is not linear as in  $\text{Mn}[\text{CH}_2-t\text{-Bu}]_2$ <sup>19</sup> and  $\text{Mn}[\text{C}(\text{SiMe}_3)_3]_2$ <sup>18</sup> but is distorted by interaction with a carbon atom in one of the boron mesityls giving an  $\text{NMnN}$  angle of  $160.6^\circ$ .

### Experimental Section

**General Procedures.** All work was performed by using Schlenk techniques under  $\text{N}_2$  or a Vacuum Atmospheres HE43-2 drybox under Ar. Solvents were freshly distilled under  $\text{N}_2$  from Na/K alloy–benzophenone ketyl and degassed twice immediately before use.

**Physical Measurements.**  $^{11}\text{B}$  NMR spectra were obtained by using a Nicolet NT-200 spectrometer operating at 64.17 MHz. All  $^{11}\text{B}$  NMR spectra were referenced to external  $\text{BF}_3\cdot\text{Et}_2\text{O}$ . Absorption spectra were recorded on a Hewlett-Packard 8450A UV/vis spectrometer.

**Starting Materials.** The compounds  $\text{PhNH}_2$  (aniline), 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2\text{NH}_2$  (mesidine), 1.6 M *n*-BuLi in hexane, and *t*-BuLi in pentane were purchased from Aldrich, and the amines were distilled off  $\text{CaH}_2$  under reduced pressure at  $<100^\circ\text{C}$ .  $\text{Mes}_2\text{BF}$  was synthesized by the method of Pelter,<sup>20</sup> and  $\text{MnBr}_2(\text{THF})_2$  was obtained via a procedure identical with that for  $\text{MnCl}_2(\text{THF})_2$ .<sup>21</sup> All compounds gave satisfactory C, H, and N analyses.

**Synthesis of Compounds 1–6.**  $\text{HNPhBMe}_2$  (**1**). Solid dimesitylboron fluoride (0.67 g, 2.5 mmol) was added to an  $\text{Et}_2\text{O}$  (30 mL) solution of  $\text{LiNHPh}$ , generated in situ, from aniline (0.23 mL, 2.5 mmol) and *n*-BuLi (1.6 mL of a 1.6 M hexane solution). The mixture became orange and was refluxed for 1 h. The volume was halved under reduced pressure and the solution filtered. Cooling in a  $-20^\circ\text{C}$  freezer over 24 h gave pale yellow (almost colorless) crystals of  $\text{HNPhBMe}_2$  (**1**): yield 0.45 g, 60%; mp  $154\text{--}158^\circ\text{C}$ ;  $^{11}\text{B}$  NMR  $\delta$  39.1 (br).

$\text{HNMesBMe}_2$  (**2**). The procedure for **2** was very similar to that for **1**. At ca.  $0^\circ\text{C}$ , mesidine (3.4 g, 25 mmol) in  $\text{Et}_2\text{O}$  (20 mL) was treated with *n*-BuLi (15.6 mL of a 1.6 M solution) giving a white suspension of  $\text{LiNHMe}_2$ . After the solution was stirred 1 h,  $\text{Mes}_2\text{BF}$  (6.8 g, 25 mmol) in  $\text{Et}_2\text{O}$  (20 mL) was added dropwise. The solution became clear yellow with slight warming. After the solution was stirred for 12 h, the volatiles were removed under reduced pressure. The residue was redissolved in toluene (30 mL) and filtered. The volume was reduced to 20 mL under reduced pressure. Cooling in a  $-20^\circ\text{C}$  freezer for 12 h gave **2** as colorless needles: yield 5.7 g, 65%;  $^{11}\text{B}$  NMR  $\delta$  38.0 (br); mp  $169\text{--}170^\circ\text{C}$ .

$\text{Li}(\text{Et}_2\text{O})_2\text{NPhBMe}_2$  (**3**). *t*-BuLi (0.5 mL of a 1.68 M pentane solution) was added slowly, via syringe, to **1** (0.39 g, 0.86 mmol) in  $\text{Et}_2\text{O}$  (10 mL) at ca.  $-78^\circ\text{C}$ . After 1 h the resultant pale green-yellow solution was warmed to ambient temperature and stirred for a further 1 h. Filtration and reduction of the volume to ca. 5 mL under reduced pressure and cooling in a  $-20^\circ\text{C}$  freezer for 12 h gave  $\text{Li}(\text{Et}_2\text{O})_2\text{NPhBMe}_2$  (**3**) as colorless crystals: yield 0.25 g, 61%; mp dec at ca.  $120^\circ\text{C}$ ;  $^{11}\text{B}$  NMR  $\delta$  33.3 (br).

$\text{Li}(\text{Et}_2\text{O})_2\text{NMesBMe}_2$  (**4**). This complex was generated in solution.  $\text{HNMesBMe}_2$  (**2**) (2.94 g, 7.7 mmol) in 1:1  $\text{Et}_2\text{O}/\text{THF}$  (25 mL) was treated dropwise with 4.8 mL of *t*-BuLi (1.6 M in hexane) at  $\sim 0^\circ\text{C}$  and stirred 1 h. Deprotonation at the nitrogen is supported by  $^{11}\text{B}$  NMR ( $\delta$

30.8) and its subsequent use in the preparation of **6**.

$(\text{THF})(\text{Et}_2\text{O})_2\text{LiClCo}\{-\text{NPhBMe}_2\}_2$  (**5**). A solution of  $\text{LiNPhBMe}_2$  (**3**) (generated in situ from  $\text{HNPhBMe}_2$ , **1**, in  $\text{THF}$  (20 mL), and *t*-BuLi (3.7 mL of 1.68 M pentane solution) at ca.  $-78^\circ\text{C}$  was added dropwise to a  $\text{THF}$  (10 mL) suspension of  $\text{CoCl}_2$  (0.4 g, 3.1 mmol) at  $\sim 0^\circ\text{C}$ . The solution became dark green when the addition was complete. Upon stirring for a further 3 h, the volatiles were removed under reduced pressure. The dark green residue was redissolved in  $\text{Et}_2\text{O}$  (30 mL) and the solution filtered. Cooling overnight in a  $-20^\circ\text{C}$  freezer gave the product **5** as green crystals: yield 1.25 g, 40%; mp  $130\text{--}132^\circ\text{C}$  (crystals begin to change appearance at  $\sim 80^\circ\text{C}$ );  $^{11}\text{B}$  NMR  $\delta$  46.9; UV-vis ( $\epsilon$  values in parentheses) 610 (649), 660 (410), 680 nm (395).

$\text{Mn}\{-\text{NMesBMe}_2\}_2\cdot 3\text{PhMe}$  (**6**). The solution formed by the generation of **4** was added dropwise to a suspension of  $\text{MnBr}_2(\text{THF})_2$  (1.38 g, 3.8 mmol) in  $\text{THF}$  (10 mL) at  $0^\circ\text{C}$ . The solution became orange and was stirred at room temperature for a further 16 h. The volatiles were removed under reduced pressure, and the residue was dissolved in toluene (20 mL). Filtration and reduction of the volume to 10 mL followed by cooling in a  $-20^\circ\text{C}$  freezer gave **6** as colorless crystals: yield 3.58 g, 42%; mp dec slowly  $>100^\circ\text{C}$ .

**X-ray Data Collection, Solutions, and Refinement of the Structures.** All X-ray data were collected with use of a Syntex P2<sub>1</sub> diffractometer equipped with a graphite monochromator and a modified LT-1 device for low-temperature work. Crystallographic programs used were those of SHELXTL, version 4 installed on a Data General Eclipse computer. Scattering factors were from Vol. IV of ref 22. An absorption correction was applied by using the method described in ref 23. All compounds were coated with a layer of hydrocarbon oil upon removal from the Schlenk tube. A suitable crystal was selected, attached to a glass fiber by using silicone grease, and immediately placed in the low-temperature nitrogen stream. Table S1 (supplementary material) summarizes the crystal data and refinement for each compound. Notes on the solution of each structure and a description of the disorder in the ether groups of **5** and the toluene of solvation of **6** are also provided therein.

### Results and Discussion

The reaction between either  $\text{LiNHPh}$  or  $\text{LiNHMe}_2$ , generated in situ, and  $\text{Mes}_2\text{BF}$  affords the ligand precursors **1** and **2** in good yield. This straightforward synthetic route needs no further comment except to note that the substituent  $\text{Mes}_2\text{B}-$  was chosen because it is the largest, readily available, diorganoboryl substituent. Also, two mesityl groups on boron afford the boron center adequate steric protection from further attack.<sup>25–27</sup> The addition of *t*-BuLi to either **1** or **2** at  $-78^\circ\text{C}$  gives solutions of **3** or **4** in virtually quantitative yield. Compound **3** could be isolated in 61% yield (not optimized). The reactions may be monitored by using  $^{11}\text{B}$  NMR. Treatment with *t*-BuLi results in an upfield shift ( $\sim 6\text{--}7$  ppm) of the broad singlet. Treatment of  $\text{CoCl}_2$  in  $\text{THF}$  with a solution of **3** (2 equiv) gave a green solution from which crystals of **4** were isolated in good yield. Related work in this area has involved the in situ generation of species such as  $\text{LiN-MeBMe}_2$  by Nöth and co-workers.<sup>37</sup> These have been reacted further to give other main group metal derivatives involving mercury<sup>38</sup> or tin.<sup>39</sup> However, no structures of lithium derivatives have appeared. Attempts to remove  $\text{LiCl}$  by heating a toluene solution of the complex have not thus far yielded crystals suitable for X-ray diffraction. The three-coordinate found for cobalt in **5** suggested the use of a somewhat bulkier ligand,  $\text{NMesBMe}_2$ , to obtain a two-coordinate metal. Although several metal salts have been used in reactions, thus far suitable crystals for X-ray diffraction have only been obtained for manganese in the case of complex **6**. It is interesting to note that the halide-free manganese complex was obtained with only gentle heating upon extraction

(22) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(23) Program XABS Hope, H.; Moezzi, B. The program obtains an absorption tensor from  $F_o - F_c$  differences.

(24) Doty, J. C.; Babb, B.; Grisdale, P. G.; Glogowski, M.; Williams, J. L. R. *J. Organomet. Chem.* **1972**, *38*, 228. Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 7020. Brown, H. C.; Dodson, V. H. *J. Am. Chem. Soc.* **1957**, *79*, 2302.

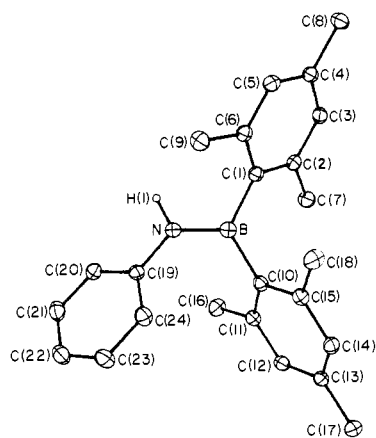
(25) Wilson, J. W. *J. Organomet. Chem.* **1980**, *186*, 297. Brown, N. M. D.; Davidson, F.; Wilson, J. W. *J. Organomet. Chem.* **1980**, *185*, 277.

(26) Pelter, A.; Singaram, B.; Williams, L.; Wilson, J. W. *Tetrahedron Lett.* **1983**, *24*, 621. Pelter, A.; Briaden, G.; Roesser, R. *Tetrahedron Lett.* **1985**, *26*, 5097.

(27) Bartlett, R. A.; Feng, X.; Power, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 6817.

(20) We are grateful to Professor Pelter for providing us with a good synthesis for  $\text{Mes}_2\text{BF}$  when the published procedure did not work in our hands.

(21) Horvath, B.; Mössler, R.; Horvath, E. G. *Z. Anorg. Allg. Chem.* **1979**, *450*, 165.



**Figure 1.** Computer-generated thermal ellipsoid plot of **1**. H atoms (except N-H) are omitted for clarity. Important bond distances (Å) and angles (deg) are as follows: B-N = 1.407 (2), N-C(19) = 1.424 (2), B-C(1) = 1.591 (2), B-C(10) = 1.590 (2), C(1)BC(10) = 122.6 (1), NBC(1) = 116.9 (1), NBC(10) = 120.6 (1), BNC(19) = 130.6 (1), BNH(1) = 117 (1), H(1)NC(19) = 112 (1).

**Table I.** Ligand Bond Distances (Å) and Angles (deg) in **1**, **3**, **5**, and **6**

	<b>1</b> <sup>a</sup>	<b>3</b> <sup>a</sup>	<b>5</b> <sup>a</sup>	<b>6</b> <sup>a</sup>
BN	1.407 (2)	1.385 (3)	1.404 (7)	1.402 (7)
BC	1.590 (2)	1.614 (3)	1.610 (6)	1.618 (8)
	1.591 (2)	1.615 (3)	1.602 (8)	1.603 (8)
			1.609 (7)	
NC	1.424 (2)	1.402 (3)	1.612 (8)	1.428 (7)
			1.418 (7)	
CBC	122.6 (1)	122.0 (2)	120.6 (4)	122.0 (5)
			120.4 (5)	
CBN	120.6 (1)	121.6 (2)	121.2 (5)	127.5 (5)
	116.9 (1)	116.3 (2)	118.2 (4)	110.5 (5)
			123.3 (5)	
			116.2 (4)	
BNM	117 (1)	120.4 (2)	112.5 (3)	104.6 (3)
			111.6 (4)	
BNC	130.6 (1)	124.4 (2)	123.7 (4)	127.1 (4)
MNC	112 (1)	115.2 (2)	122.0 (3)	128.2 (3)
twist angle between B and N planes	9.8	8.8	5.3	7.5

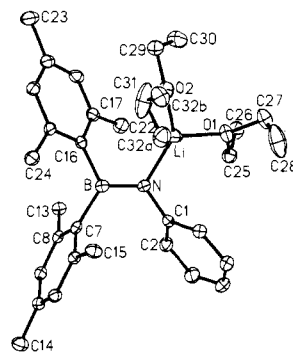
<sup>a</sup> HNPhMes<sub>2</sub> (**1**); Li(Et<sub>2</sub>O)<sub>2</sub>NPhBMes<sub>2</sub> (**3**); (THF)(Et<sub>2</sub>O)<sub>2</sub>LiClCo-[NPhBMes<sub>2</sub>]<sub>2</sub> (**5**); Mn[NMesBMes<sub>2</sub>]<sub>2</sub> (**6**).

with toluene. Whether this is due to increased bulk of the ligand or some other factors, such as ligand field or crystallographic effects, awaits the synthesis of a wider range of compounds.

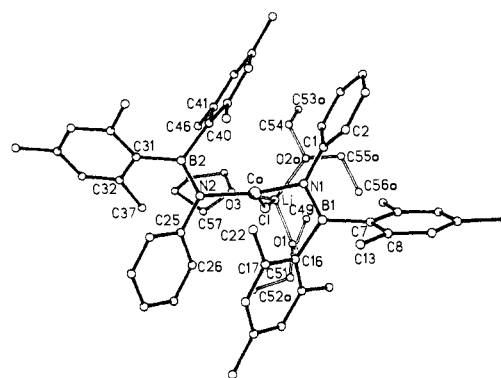
**Structures.** The structures of **1**, **3**, **5**, and **6** are illustrated in Figures 1-4. Important bond distances and angles surrounding the boron, nitrogen and metal centers are given in the figure captions. For comparison purposes selected ligand parameters for the four structures are given in the Table I. The major structural features are as follows: (i) in all compounds the boron and nitrogen centers are planar; (ii) the twist angles between the B and N planes are small, <10°; (iii) the B-N bond lengths are, with some variations, near to 1.4 Å; (iv) in the metal complexes **3**, **5**, and **6** the nitrogen centers are terminal and not bridging; (v) although there are only four structures to hand, there is an approximate inverse relationship between trends in B-N and B-C bond lengths. For example, when the B-N bond decreases in length, the B-C bond tends to increase. However, the more ionic nature of **2** makes the BN distance unusually short.

The common structural parameters outlined in the preceding paragraph confirm the fact that the multiple boron-nitrogen bond remains almost unchanged throughout the four compounds. The B-N bond lengths of ~1.4 Å are very similar to those found<sup>28</sup>

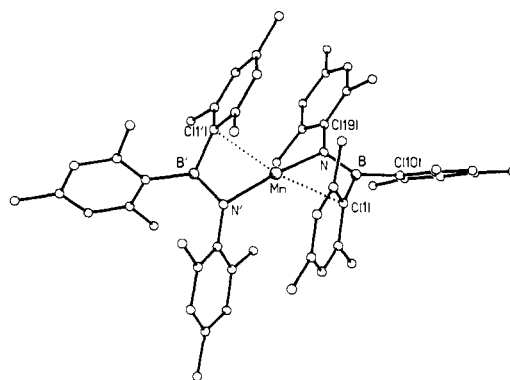
(28) For aminoboranes B-N bond lengths range from 1.379 (6) in Cl<sub>2</sub>BNMe<sub>2</sub> to 1.485 (22) Å in F<sub>2</sub>BN(SiH<sub>3</sub>)<sub>2</sub>. Reference 3 a, p 90.



**Figure 2.** Computer-generated thermal ellipsoid plot of **3**. H atoms are omitted for clarity. Important bond distances (Å) and angles (deg) are as follows: B-N = 1.385 (3), B-C(7) = 1.614 (3), B-C(16) = 1.615 (3), C(1)-N = 1.402 (3), Li-N = 1.943 (3), Li-O(1) = 1.932 (5), Li-O(2) = 1.934 (4), C(7)BC(16) = 122.0(2), NBC(7) = 121.6 (2), NBC(16) = 116.3 (2), BNC(1) = 124.4 (2), BNLi = 120.4 (2), LiNC(1) = 115.2 (2), O(1)LiO(2) = 112.8 (2), O(1)LiN = 114.8 (2), O(2)LiN = 130.8 (2).



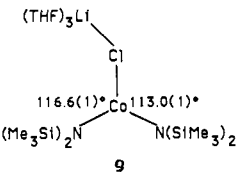
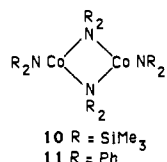
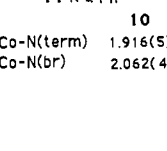
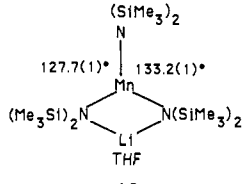
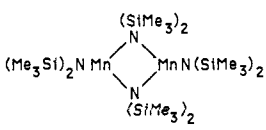
**Figure 3.** Computer-generated plot of **5**. H atoms are omitted for clarity. Important bond distances (Å) and angles (deg) are as follows: Co-Co = 2.300 (2), Co-N(1) = 1.928 (3), Co-N(2) = 1.927 (4), B(1)-N(1) = 1.405 (7), N(2)-B(2) = 1.404 (7), N(1)-C(1) = 1.408 (6), N(2)-C(25) = 1.418 (7), B(1)-C(7) = 1.610 (6), B(1)-C(16) = 1.602 (8), B(2)-C(31) = 1.609 (7), B(2)-C(40) = 1.612 (8), Li-O(Et<sub>2</sub>O) = 1.950 (10), 1.979 (11), Li-O(THF) = 1.960 (8), Li-Cl = 2.353 (11), N(1)-CoN(2) = 136.7 (2), ClCoN(1) = 112.4 (1), ClCoN(2) = 110.9 (1), CoN(1)C(1) = 122.0 (3), CoN(1)B(1) = 112.5 (3), C(1)N(1)B(1) = 123.7 (4), C(7)B(1)C(16) = 120.6 (4), C(7)B(1)N(1) = 121.2 (5), C(16)B(1)N(1) = 118.2 (4), CoN(2)B(2) = 111.6 (4), CoN(2)C(25) = 121.7 (3), N(2)B(2)C(31) = 123.3 (5), N(2)B(2)C(40) = 116.2 (4), C(31)B(2)C(40) = 120.4 (5).



**Figure 4.** Computer-generated plot of **6**. Hydrogen atoms omitted for clarity. Bond distances (Å) and angles (deg) are as follows: Mn-N = 2.046 (4), N-B = 1.402 (7), B-C(1) = 1.618 (8), B-C(10) = 1.603 (8), N-C(19) = 1.428 (7), Mn...C(1) = 2.536 (5), NMnN' = 160.4 (2), C(1)Mn(C1)' = 151.9 (3), MnNB = 104.6 (3), MnNC(19) = 128.2 (3), NBC(1) = 110.5 (5), NBC(10) = 127.5 (5), C(1)BC(10) = 122.0 (5).

in many aminoboranes of the general formula R<sub>2</sub>BNR'<sub>2</sub> (R and R' = a variety of alkyl, aryl amide, or halogen groups). These compounds are often considered to be the boron-nitrogen ana-

**Table II.** Some Structural Features of Complexes Related to **5** and **6**

 <p style="text-align: center;"><b>9</b></p> <p>Co-N 1.924(2) ave Co-Cl 2.305(1) N-Co-N 130.2(1)°</p>	 <p style="text-align: center;"><b>10</b> R = SiMe<sub>3</sub></p>	 <p style="text-align: center;"><b>11</b> R = Ph</p>
	Co-N(term) 1.916(5)	1.889(8)
	Co-N(br) 2.062(4)	2.004(7)
 <p style="text-align: center;"><b>12</b></p> <p>Mn-N(term) 2.023(3) Mn-N(br) 2.143(2) N-Mn-N 99.0(1)°</p>	 <p style="text-align: center;"><b>13</b></p> <p>Mn-N(term) 1.998(3) Mn-N(br) 2.174(3)</p>	

logues of substituted alkenes and have many properties consistent with a double B-N bond formulation. Of the four structurally characterized compounds, Li(Et<sub>2</sub>O)<sub>2</sub>NPhBMe<sub>2</sub> (**3**) has the shortest B-N length of 1.385 (3) Å. This is significantly shorter than the corresponding length, 1.407 (2) Å, in the parent aminoborane HNPhBMe<sub>2</sub> (**1**). This shortening is probably due to the more electropositive lithium allowing more electron density on nitrogen in **3** which in turn gives a stronger B-N bond. A similar phenomenon has been noted in the related phosphorus compounds [Li(Et<sub>2</sub>O)<sub>2</sub>PMesBMe<sub>2</sub>]<sub>2</sub><sup>27</sup> (**7**) and Mes<sub>2</sub>BPPH<sub>2</sub><sup>29</sup> (**8**), where not only a contraction in the P-B bond but also a change in the geometry at phosphorus was observed when lithium was substituted for one of the phenyl groups.

Compound **3** is also notable because its structure involves a terminal lithium amide whereas most lithium amides are associated in the solid state. Even with bulky substituents at nitrogen, terminal lithium amides have only been observed when multidentate or macrocyclic solvate ligands are used as in Li(12-crown-4)NR<sub>2</sub> (R = SiMe<sub>3</sub>,<sup>30</sup> Ph<sup>31</sup>) or Li(TMEDA)N(SiMe<sub>3</sub>)<sub>2</sub>.<sup>32</sup> Presumably **3** is nonbridging because one of the lone pairs on nitrogen is used in multiple bonding to boron and is thereby unavailable for participation in bridge bonding.

Treatment of a THF suspension of CoCl<sub>2</sub> or MnBr<sub>2</sub>(THF)<sub>2</sub> with 2 equiv of **3** or **4** results in the novel complexes **5** and **6** which are the first well-characterized transition-metal complexes of borylamide ligands. As already mentioned the B-N bond retains its double bond character so it can be assumed that it is little affected by the transition-metal-nitrogen bond. It has often been held that, in transition-metal amides, there is p-d π-interaction between the nitrogen lone-pair orbital and the metal d orbitals which results in a planar nitrogen configuration. However, in the case of **5** or **6** the π-B-N interaction clearly dominates because of the unchanged B-N length. The metal-nitrogen bond lengths are also of significant interest. The Co-N distances are 1.927 (3) and 1.928 (3) Å, and the Mn-N bond length is 2.046 (4) Å. The N(1)CoN(2) angle, 136.7 (2)°, is quite wide, attesting to the large steric requirements of the -N(Ph)BMe<sub>2</sub> ligand. Data

for related complexes are presented in Table II. Comparison of the Co-N lengths in **5** with those in the closely related complex **9**<sup>33</sup> and complexes **10**<sup>11</sup> and **11**<sup>8</sup> show only slight differences in the case of the silylamides **9** and **10**. However, the terminal Co-N bond length in {Co(NPh<sub>2</sub>)<sub>2</sub> (**11**) is significantly shorter at 1.889 (8) Å. One explanation is that both the silylamide ligand -N(SiMe<sub>3</sub>)<sub>2</sub> and -NPhBMe<sub>2</sub> have the nitrogen lone pair involved in multiple bonding to their silicon d orbitals or boron p orbitals. The lone pair is therefore less available for donation to the metal d orbitals.<sup>34</sup> This results in a longer M-N bond that would normally be seen with nonmultiply bonding groups on nitrogen. The data therefore indicate that -NPhBMe<sub>2</sub> is electronically similar to -N(SiMe<sub>3</sub>)<sub>2</sub> although its bridging tendency is much less as indicated by the ready formation of the bridged complexes {Li(Et<sub>2</sub>O)N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub><sup>35</sup> or [M{N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (M = Mn or Co),<sup>10,11</sup>

The manganese species **6** has several interesting features. The most notable is the two-coordination of the metal. A crystallographic twofold axis passes through manganese and bisects the line connecting N and N'. However, the geometry is not linear, as might be expected, but is distorted to an angle of 160.4 (2)°. This is presumably due to an interaction at 2.536 (5) Å between manganese and the C(1) atom of one of the boron mesityls. For comparison purposes the shortest distance of this type in the cobalt species is 2.884 Å. Further evidence for this interaction comes from the large asymmetry (17°) in the N-B-C(1) [110.5 (5)°] and N-B-C(10) [127.5 (5)°] angles and the fact that the MnC(1) vector deviates only 12.5° from the normal to the C(1) ring plane. This interaction is similar to that seen in the dimeric neophyl complex [Mn{CH<sub>2</sub>CMe<sub>2</sub>Ph]<sub>2</sub>,<sup>36</sup> however, the aromatic ring-metal contact in this compound is significantly longer, ~2.7 Å. The distortions in **6** are presumably due to the extreme electron deficiency of the manganese center caused by the low coordination number and the poor π-donor ability of this particular amide ligand. The manganese-nitrogen bond length is 2.046 (4) Å which is very close to those seen for the terminal ligands in the three-coordinate complexes **12**<sup>11</sup> and **13**<sup>11</sup> in Table II. The Mn-N distance in **6** must therefore be regarded as slightly long since it is, strictly speaking, two-coordinate. Perhaps the longer Mn-N bonds are further evidence for the strong interaction with the mesityl ring and **6** could be regarded, in some ways, as a pseudo-four-coordinate complex which would result in a longer Mn-N bond. An alternative explanation is that the lack of π-donation by the amide ligand results in a weaker Mn-N interaction resulting in a longer Mn-N bond.

In summary, the structures of **3**, **5**, and **6** suggest that amide ligands of the type -NRBR'<sub>2</sub> (which are the boron-nitrogen analogues of substituted alkenyls) may have wide applicability achieving low- (two- or three-) coordinate molecular compounds due to their low bridging tendency and steric versatility.

**Acknowledgment.** We thank the National Science Foundation for financial support.

**Supplementary Material Available:** Summary of data collection and refinement and tables of atom coordinates, thermal parameters, bond distances and angles, and hydrogen coordinates (29 pages). Ordering information is given on any current masthead page.

(33) Olmstead, M. M.; Power, P. P.; Sigel, unpublished work.

(34) Andersen, R. A.; Beach, D. B.; Jolly, W. L. *Inorg. Chem.* **1985**, *24*, 4741. This paper discusses the π-bonding character of the -NMe<sub>2</sub> amide ligand.

(35) Lappert, M. F.; Slade, M. J.; Singh, A.; Atwood, J. L.; Rogers, R. D.; Shakir, R. *J. Am. Chem. Soc.* **1983**, *105*, 302. Engelhardt, L. M.; May, A. S.; Raston, C. L.; White, A. L. *J. Chem. Soc., Dalton Trans.* **1983**, 1671.

(36) Andersen, R. A.; Carmona-Guzman, E.; Gibson, J. F.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 2204.

(37) Fusstetter, H.; Kopietz, G.; Nöth, H. *Chem. Ber.* **1980**, *113*, 728. Nöth, H.; Prigge, H.; Rotsch, A. *Chem. Ber.* **1986**, *119*, 1361.

(38) Fusstetter, H.; Nöth, H. *Chem. Ber.* **1980**, *113*, 791.

(39) Fusstetter, H.; Nöth, H. *Chem. Ber.* **1979**, *112*, 3672.

(29) Feng, X.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1986**, *25*, 4616.

(30) Power, P. P.; Xu, X. *J. Chem. Soc., Chem. Commun.* **1984**, 358.

(31) Bartlett, R. A.; Dias, H. V. R.; Hope, H.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 6821.

(32) The structure of Li(TMEDA)N(SiMe<sub>3</sub>)<sub>2</sub> has also been solved by M. F. Lappert and co-workers, and it has a terminal -N(SiMe<sub>3</sub>)<sub>2</sub> group.