

# Revisiting the 1,2,4-Triaza-3,5-diborolyl Ligand: $\sigma$ and $\pi$ Coordination Modes in the Alkali Metal and Rhodium Complexes of a Planar, 6- $\pi$ -Electron $B_2N_3^-$ Ring

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Lithium (**2a**), sodium (**2b**), and potassium (**2c**) salts of 1-methyl-3,5-diphenyl-4-methylamino-1,2,4-triaza-3,5-diborolyl were prepared by deprotonation of the ring nitrogen in neutral precursor **1**. The alkali metal derivatives were characterized by multinuclear NMR, mass spectrometry, and single-crystal X-ray diffraction. The structural determinations revealed extended 2D structures for **2a** and **2b** and an extended 1D structure for **2c**. All three solvent-free structures are dominated by  $\sigma$  interactions, and  $\pi$  interactions are also present for the potassium derivative. Addition of triphenylborane to **2a**, **2b**, and **2c** produced the adducts **3a**, **3b**, and **3c**, respectively, and these were characterized by multinuclear NMR and mass spectrometry. Structural determinations have been performed for the lithium and potassium salt, showing that  $Ph_3B$  coordinates at the 2 position of the ring, whereas the alkali metal is coordinated by the pendant methylamino group. The lithium ion is additionally coordinated by three acetonitrile molecules in the monomeric structure of **3a**, whereas the potassium ion is coordinated by three phenyl groups, forming the 1D polymeric structure of **3c**. Reaction of **2a** with  $[Rh(cod)Cl]_2$  yielded the dimeric **4**, containing two 1,2,4-triaza-3,5-diborolyl rings bridging two  $Rh(cod)$  fragments through the substituent-free ring nitrogen atoms.

## Introduction

The tremendous success of cyclopentadienyl as a ligand in organometallic chemistry and catalysis<sup>1</sup> has inspired for several decades now the search for heterocyclic analogues. Among the numerous derivatives incorporating main-group elements that were synthesized and characterized, the most-successful have been the boron- and the phosphorus-containing rings. The formal replacement of a HC–CH pair in cyclopentadienyl with the isolobal fragment RB–NR' produced the azaborolyl ligands **A**, and their coordination chemistry and catalytic applications have been extensively investigated.<sup>2</sup> Aiming to tune the electronic properties of cyclopentadienyl, we recently isolated sandwich complexes containing the anionic, heterocyclic ligands **B** obtained through the formal replacement of two HC–CH pairs in

cyclopentadienyl with RB–NR' fragments.<sup>3</sup> Structural investigations have shown that the ring carbon atoms play a key role in the binding of these ligands to metals. Chronologically, the heterocyclic anions **C** having a carbon-free framework were studied before their analogues **A** and **B**, mainly through the efforts of Nöth. The substituted  $B_2N_3$  ring framework was first reported in 1963,<sup>4a</sup> and the

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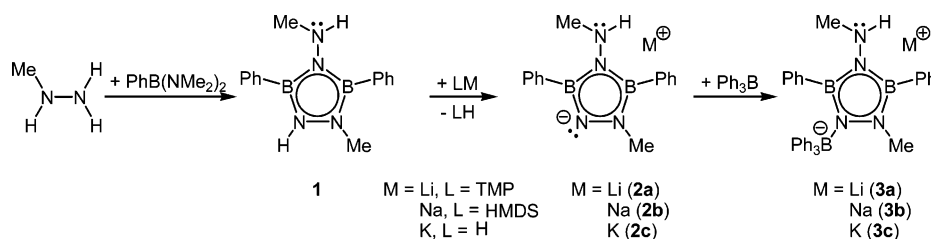
(1) (a) Togni, A.; Halterman, R. L. *Metalloenes*; Wiley VCH: Weinheim, Germany, 1998; Vol. I, II. (b) Long, N. J. *Metalloenes: An Introduction to Sandwich Complexes*; Blackwell Science Ltd.: London, 1998. (c) Patil, A. O.; Hlatky, G. G. *Beyond Metalloenes: Next-Generation Polymerization Catalysts*; American Chemical Society: Washington DC, 2003.

(2) (a) Schulze, J.; Schmid, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 54. (b) Schulze, J.; Boese, R.; Schmid, G. *Chem. Ber.* **1980**, *113*, 2348. (c) Schmid, G. *Comments Inorg. Chem.* **1985**, *4*, 17. (d) Ashe, A. J., III; Fang, X. *Org. Lett.* **2000**, *2*, 2089. (e) Liu, S.-Y.; Hills, I. D.; Fu, G. C. *Organometallics* **2002**, *21*, 4323. (f) Liu, S.-Y.; Lo, M. M.-C.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 174. (g) Ashe, A. J., III; Yang, H.; Fang, X.; Kampf, J. W. *Organometallics* **2002**, *21*, 4578. (h) Liu, S.-Y.; Hills, I. D.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 15352.

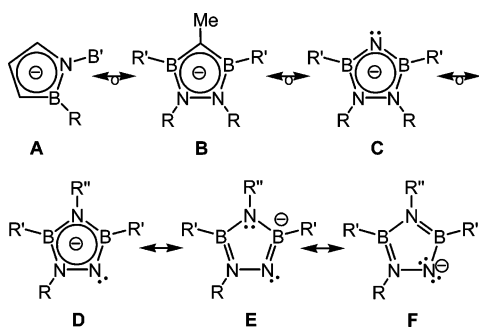
(3) (a) Ly, H. V.; Forster, T. D.; Maley, D.; Parvez, M.; Roesler, R. *Chem. Commun.* **2005**, 4468. (b) Ly, H. V.; Forster, T. D.; Corrente, A. M.; Eisler, D. J.; Konu, J.; Parvez, M.; Roesler, R. *Organometallics* **2007**, *26*, 1750. (c) Ly, H. V.; Forster, T. D.; Parvez, M.; McDonald, R.; Roesler, R. *Organometallics* **2007**, *26*, 3516.

(4) (a) Nöth, H.; Regnet, W. Z. *Naturforsch.* **1963**, *18 B*, 1138. (b) Niedenzu, K.; Fritz, P.; Jenne, H. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 506. (c) Nöth, H.; Regnet, W. Z. *Anorg. Allg. Chem.* **1967**, *352*, 1. (d) Nöth, H.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 126. (e) Nöth, D.; Nöth, H. Z. *Naturforsch.* **1972**, *27 B*, 1425. (f) Nöth, D.; Nöth, H.; Winterstein, W. Z. *Anorg. Allg. Chem.* **1974**, *406*, 235.

Scheme 1



protonated precursors to the anionic ligands were described 1 year later.<sup>4b</sup> The first metal complexes,<sup>4c</sup> and an improved synthesis of the ligand using boron thiolates followed shortly thereafter.<sup>4d,e</sup> A ferrocene analogue containing ligands of type **C** was prepared and extensively investigated; however a crystal structure confirming its identity and structure was not obtained. On the basis of <sup>1</sup>H NMR, <sup>11</sup>B NMR, and IR spectroscopy, molecular weight determination and elemental analysis, as well as taking into account the reduced reactivity, a symmetric structure containing  $\pi$ -coordinating ligands was postulated for the diamagnetic, crystalline compound.<sup>4c</sup> The synthesis and reactivity of the protonated precursors to the B<sub>2</sub>N<sub>3</sub><sup>-</sup> rings was further investigated,<sup>4f</sup> but no references to metal complexes incorporating these ligands were made in the literature after 1972. Much later, theoretical studies supported the sandwich structure proposed by Nöth,<sup>5a</sup> predicting that this compound would be a fully inorganic analogue of ferrocene.<sup>5b</sup> A fully inorganic analogue of ferrocene, a sandwich complex containing no carbon atoms in the ligand skeletons, remains elusive to date. No such complex could be characterized beyond doubt using single-crystal X-ray diffractometry, and the closest confirmed structures were those of phosphorus-containing derivatives such as [Cp\*Fe( $\eta^5$ -P<sub>5</sub>)]<sup>6a,b</sup> and the fully inorganic titanocene [Ti( $\eta^5$ -P<sub>5</sub>)<sub>2</sub>]<sup>2-</sup>.<sup>6c</sup>



Precursors to less-symmetric anionic rings **D**, having a ring proton in the 2 position instead of the 4 position as required for ligands of type **C**, have been reported as well.<sup>7a</sup> Most notably, the self-assembly of methylhydrazine with phenyl-

bis(dimethylamino)borane to give 1,2,4-triaza-3,5-diborole **1** was documented, and the resulting compound was structurally characterized.<sup>7b</sup> A similar reaction involving methylhydrazine and methyl(di(methylthio)borane had been observed before.<sup>7c</sup> Aside from **1**, structural data is available for only one other ring of this type, a dimeric 3,5-dichloro-1,2,4-trimethyl-1,2,4-triaza-3,5-diborol.<sup>8</sup> Being interested in the  $\pi$ -coordinating ability of ligands with main-group frameworks, we investigated and present herein the syntheses and structures of alkali metal salts derived from **1**. The assembly of a planar, tricyclic B<sub>4</sub>N<sub>8</sub> framework starting from **1** was recently communicated.<sup>7d</sup>

## Results and Discussion

Ligand precursor **1** was prepared using the aforementioned reported procedure.<sup>7b</sup> The <sup>1</sup>H and <sup>13</sup>C NMR spectra of this compound featured different signals for the chemically inequivalent methyl and phenyl substituents. The singlet resonance corresponding to the ring proton appears at 7.49 ppm, significantly downfield shifted with respect to the quartet resonance, corresponding to the proton of the pendant methylamino group (4.14 ppm). A much smaller difference following the same trend is observed for the methyl groups (3.21 at the ring nitrogen vs 2.45 ppm at the pendant nitrogen). In the <sup>11</sup>B NMR spectrum, however, the signals corresponding to the two distinct boron atoms overlapped into a broad singlet at 27.5 ppm. Deprotonation of **1** occurred easily in THF in the presence of various metalating agents (Scheme 1), yielding the alkali metal salts **2**, with little influence on the appearance of the NMR spectra. The disappearance of the signal corresponding to the ring proton was accompanied by a 0.3 ppm upfield shift of the resonance corresponding to the proton on the pendant methylamino group, and the lithium and sodium salts **2a** and **2b** featured distinct <sup>11</sup>B NMR resonances for the inequivalent boron nuclei. The mass spectrum of **2a** displayed signals corresponding to protonated ligand **1** and the [L-Me]<sup>+</sup> fragment. The attempted double deprotonation at the ring and the pendant methylamino group in presence of the same metalating agents led to decomposition of the ring with the formation of unidentified products.

Single-crystal X-ray analyses have been performed for **2a**, **2b**, and **2c** (Table 1), and the results showed that the metric parameters of the ligand vary very little between the three structures (Table 2). The ring is basically planar, with the sum of the pentagonal angles situated between 539.7 and

(5) (a) Su, M.-D.; Chu, S.-Y. *J. Phys. Chem.* **1989**, *93*, 6043. (b) Bridgeman, A. J.; Rothery, J. *Inorg. Chim. Acta* **1999**, *288*, 17.  
 (6) (a) Scherer, O. J.; Brück, T. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 59. (b) Scherer, O. J.; Brück, T.; Wolmershäuser, G. *Chem. Ber.* **1988**, *121*, 935. (c) Urnežius, E.; Brennessel, W. W.; Cramer, C. J.; Ellis, J. E.; Schleyer, P. v. R. *Science* **2002**, *295*, 832.  
 (7) (a) Geschwentner, M.; Elter, G.; Meller, A. *Z. Naturforsch.* **1994**, *49 B*, 459. (b) Engelhardt, U.; Park, S. S. *Acta. Cryst.* **1996**, *C 52*, 3248. (c) Nölle, D.; Nöth, H. *Chem. Ber.* **1978**, *111*, 469. (d) Ly, H. V.; Tuononen, H. M.; Parvez M.; Roesler R. *Chem. Commun.*, submitted for publication.

(8) Fuszstetter, H.; Nöth, H.; Peters, K.; von Schnering, H. G.; Huffman, J. C. *Chem. Ber.* **1980**, *113*, 3881.

**Table 1.** Selected Data and Structure Refinement Details for **2a**, **2b**, **2c**, **3a(CH<sub>3</sub>CN)<sub>3</sub>**, **3c**, and **4·THF**

	<b>2a</b>	<b>2b</b>	<b>2c</b>	<b>3a(CH<sub>3</sub>CN)<sub>3</sub></b>	<b>3c</b>	<b>4·THF</b>
empirical formula	C <sub>14</sub> H <sub>17</sub> B <sub>2</sub> LiN <sub>4</sub>	C <sub>14</sub> H <sub>17</sub> B <sub>2</sub> Na <sub>4</sub>	C <sub>14</sub> H <sub>17</sub> B <sub>2</sub> KN <sub>4</sub>	C <sub>38</sub> H <sub>41</sub> B <sub>3</sub> LiN <sub>7</sub>	C <sub>32</sub> H <sub>32</sub> B <sub>3</sub> KN <sub>4</sub>	C <sub>26</sub> H <sub>37</sub> B <sub>2</sub> N <sub>4</sub> ORh
fw	269.88	285.93	302.04	635.15	544.15	546.13
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic	triclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 1
<i>a</i> (Å)	13.464(2)	13.419(7)	7.746(4)	32.087(12)	9.111(4)	9.818(2)
<i>b</i> (Å)	10.0183(15)	10.143(5)	11.973(4)	11.022(5)	17.582(4)	10.130(3)
<i>c</i> (Å)	11.2470(17)	11.526(8)	16.742(9)	23.883(7)	18.059(6)	13.284(3)
α (deg)	90	90	90	90	90	77.906(13)
β (deg)	100.283(3)	99.82(3)	90	118.10(2)	91.344(14)	77.701(13)
γ (deg)	90	90	90	90	90	87.761(15)
<i>V</i> (Å <sup>3</sup> )	1492.7(4)	1545.8(15)	1552.7(13)	7451(5)	2892.1(17)	1262.2(5)
<i>Z</i>	4	4	4	8	4	2
<i>d</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.201	1.229	1.292	1.132	1.250	1.437
2θ <sub>max</sub> (deg)	52.94	55.00	50.06	50.00	55.00	55.20
μ(Mo Kα) (mm <sup>-1</sup> )	0.071	0.098	0.338	0.067	0.212	0.703
independent reflns	3072	3520	2711	6573	6566	5750
	(Rint = 0.0922)	[R(int) = 0.076]	[R(int) = 0.0256]	[R(int) = 0.046]	[R(int) = 0.034]	[R(int) = 0.037]
data/restraints/params	3072/1/239	3520/0/193	2711/0/193	6573/0/447	6566/0/366	5750/0/307
GOF on <i>F</i> <sup>2</sup>	1.038	1.01	1.056	1.020	1.00	1.03
R1( <i>F</i> ) [ <i>I</i> > 2σ( <i>I</i> )]	0.0621	0.0600	0.0379	0.0620	0.0460	0.038
wR2( <i>F</i> <sup>2</sup> ) (all data)	0.1995	0.1820	0.1014	0.1770	0.1260	0.098

**Table 2.** Selected Bond Lengths (Angstroms) and Angles (Degrees) for **1**, **2a**, **2b**, **2c**, **3a(CH<sub>3</sub>CN)<sub>3</sub>**, **3c**, and **4·THF**

	<b>1<sup>b</sup></b>	<b>2a (M = Li)</b>	<b>2b (M = Na)</b>	<b>2c (M = K)</b>	<b>3a(CH<sub>3</sub>CN)<sub>3</sub> (M = Li)</b>	<b>3c (M = K)</b>	<b>4·THF (M = Rh)</b>
N(1)–N(2)	1.414(5)	1.435(3)	1.433(3)	1.430(3)	1.448(3)	1.447(2)	1.447(3)
N(3)–N(4)	1.441(4)	1.439(3)	1.437(3)	1.440(3)	1.440(3)	1.439(2)	1.435(3)
B(1)–N(1)	1.404(6)	1.400(4)	1.411(4)	1.410(4)	1.412(4)	1.405(2)	1.406(4)
B(2)–N(2)	1.399(6)	1.407(4)	1.400(4)	1.401(4)	1.420(4)	1.414(2)	1.460(4)
B(1)–N(3)	1.432(6)	1.443(4)	1.446(4)	1.454(3)	1.422(4)	1.437(3)	1.446(4)
B(2)–N(3)	1.446(6)	1.446(4)	1.448(4)	1.470(4)	1.452(4)	1.452(2)	1.419(4)
B(1)–C(3)	1.547(6)	1.572(4)	1.561(4)	1.574(4)	1.573(4)	1.575(3)	1.566(4)
B(2)–C(9)	1.538(6)	1.571(4)	1.587(4)	1.579(4)	1.581(4)	1.580(3)	1.584(4)
N(1)–C(1)	1.440(7)	1.448(3)	1.444(3)	1.455(4)	1.450(3)	1.451(2)	1.444(4)
N(4)–C(2)	1.463(7)	1.465(4)	1.458(4)	1.468(4)	1.465(3)	1.466(3)	1.453(4)
N(3)–B(1)–N(1)	104.9(4)	105.2(2)	104.7(2)	104.6(2)	105.9(2)	105.87(16)	105.7(2)
N(3)–B(1)–C(3)	130.0(4)	125.9(2)	127.1(3)	129.7(2)	129.5(2)	128.53(16)	129.2(3)
C(3)–B(1)–N(1)	125.1(4)	128.7(3)	128.2(3)	125.6(2)	124.5(3)	125.49(17)	125.0(3)
N(3)–B(2)–N(2)	104.2(4)	109.3(2)	109.9(2)	109.7(2)	107.6(2)	108.06(16)	108.7(2)
N(3)–B(2)–C(9)	131.8(4)	125.3(2)	126.0(2)	126.3(2)	120.4(2)	121.82(16)	123.3(3)
C(9)–B(2)–N(2)	124.0(4)	125.4(2)	124.1(2)	124.0(2)	131.9(2)	129.88(16)	128.0(3)
B(1)–N(1)–N(2)	109.6(3)	112.5(2)	112.7(2)	113.4(2)	110.9(2)	111.09(14)	111.9(2)
B(1)–N(1)–C(1)	133.8(4)	130.4(2)	131.1(2)	131.1(2)	126.3(2)	127.53(15)	131.5(2)
C(1)–N(1)–N(2)	116.4(4)	116.6(2)	115.9(2)	114.6(2)	120.5(2)	114.68(13)	116.1(2)
N(1)–N(2)–B(2)	110.3(3)	105.06(19)	104.9(2)	104.9(2)	106.10(19)	106.21(13)	104.3(2)
B(1)–N(3)–B(2)	110.9(3)	108.0(2)	107.8(2)	107.1(2)	109.4(2)	108.72(14)	109.3(2)
B(1)–N(3)–N(4)	124.7(3)	126.5(2)	127.4(2)	125.4(2)	125.5(2)	126.61(15)	124.3(2)
B(2)–N(3)–N(4)	124.3(3)	124.8(2)	124.1(2)	127.3(2)	124.8(2)	124.59(15)	126.4(2)
N(3)–N(4)–C(2)	110.4(3)	108.42(19)	110.8(2)	110.5(2)	111.2(2)	110.80(15)	111.0(3)
Σpentagon angles	539.9	540.0	540.0	539.7	539.9	539.9	539.9

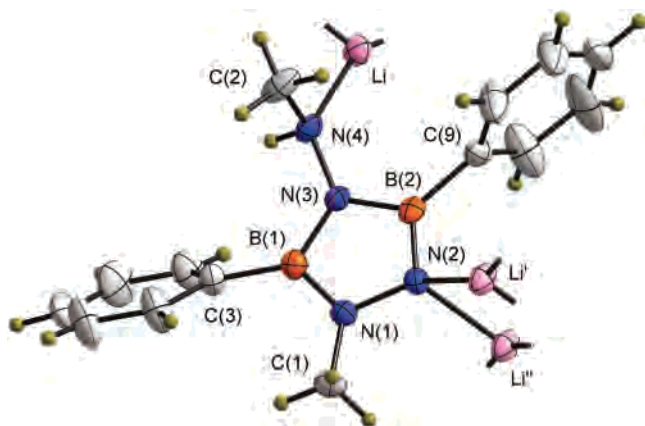
540.0°, and the ring substituents show little deviation from the ring plane. The intra- and extraannular N–N bonds are equal (1.44 Å) and comparable in length to the N–N single bond in hydrazine (1.45 Å),<sup>9</sup> clearly indicating no significant multiple bond character. The two B–N bonds involving the hydrazine unit that contributes with both nitrogen atoms to the ring skeleton are equal and relatively short (1.40 Å) in comparison with the other two B–N bonds (1.45 Å). The length of the B–N bonds in borazines is usually situated between these two values (1.42–1.44 Å),<sup>10</sup> whereas the B–N bonds observed in 1,2-azaborolynyl (**A**) complexes (1.46–1.50 Å)<sup>2</sup> and alkali metal 1,2-diaza-3,5-diborolyl (**B**) salts (ca. 1.46 Å)<sup>3b</sup> are generally slightly longer. The alternating bond lengths in the ring framework suggest that the cyclopentadiene-like resonance structure **E** has a major contribu-

tion to the structure of salts **2**. With 1.56–1.59 and 1.44–1.47 Å, respectively, the B–C and N–C bonds lengths are situated in the expected single-bond ranges.

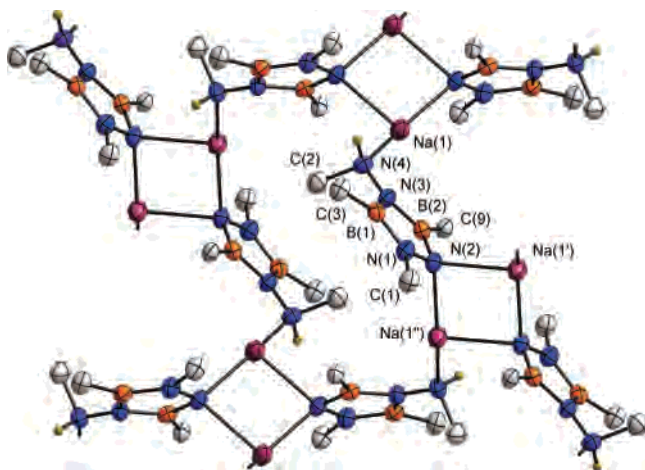
The structures of **2a** and **2b** are isomorphous and will be discussed together. In the crystal, each ligand coordinates in a σ fashion to three alkali metals, and each alkali metal is coordinated by three nitrogen atoms (Figure 1). Two ligands bridge two alkali metals in a dimeric arrangement through the substituent-free ring nitrogen atoms N(2), which achieve in this way a distorted tetrahedral coordination environment. The resulting M<sub>2</sub>N<sub>2</sub> rhombs feature relatively short M–N distances (2.013(5) and 2.068(5) for M = Li and 2.350(3) and 2.416(3) Å for M = Na) and the M<sub>2</sub>N<sub>2</sub> planes are perpendicular to the planes of the B<sub>2</sub>N<sub>3</sub> rings (82.8 for M =

(10) (a) Boese, R.; Maulitz, A. H.; Stellberg, P. *Chem. Ber.* **1994**, *127*, 1887. (b) Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. J. *Am. Chem. Soc.* **2003**, *125*, 9424. (c) Jäschke, T.; Jansen, M. *Z. Anorg. Allg. Chem.* **2004**, *630*, 239.

(9) Kohata, K.; Fukuyama, T.; Kuchitsu, K. *J. Phys. Chem.* **1982**, *86*, 602.



**Figure 1.** Fragment from the 2D polymeric structure of **2a** with 50% probability level thermal ellipsoids, illustrating the environment of the ligand.



**Figure 2.** Fragment from the 2D polymeric structure of **2b** with 50% probability level thermal ellipsoids. For clarity, only the ipso carbon atom of the phenyl groups is represented, and all of the hydrogen atoms on the organic substituents have been omitted.

Li and  $88.9^\circ$  for  $M = \text{Na}$ ). The pyramidal coordination environment of each metal (sum of the angles at the metal of  $353.8$  for  $M = \text{Li}$  and  $336.6^\circ$  for  $M = \text{Na}$ ) is completed by an exocyclic nitrogen atom N(4) from a different ligand. These  $M\text{--}N(4)$  bonds, involving the pendant methylamino group, are only slightly longer than the  $M\text{--}N(2)$  bonds ( $2.100(5)$  for  $M = \text{Li}$  and  $2.449(3)$  Å for  $M = \text{Na}$ ) and connect the dimers, forming a 2D structure (Figure 2). A good comparison for **2a** and **2b** is provided by the structures of the alkali metal salts of the isoelectronic pyrrolyl, which were crystallized with the aid of crown ethers.<sup>11</sup> The solid-state structures of pyrrolyl lithium, sodium, and potassium are very similar to each other, featuring the pyrrolyl ligand  $\sigma$ -coordinated to the alkali metal that is additionally coordinated by the crown ether. The  $M\text{--}N$  distances measure  $1.950(4)$  and  $2.319$  Å for lithium and sodium, respectively, being slightly shorter than the shortest  $M\text{--}N$  distances in **2a** and **2b**. In the solid state, the lithium carbazoyl forms  $\sigma$ -bonded dimers very similar to those of **2a**, with  $N\text{--}Li$  distances measuring  $2.012(2)\text{--}2.165(2)$  Å, and two THF molecules, completing the tetrahedral environ-

ment of each lithium ion.<sup>12</sup> The lithium salt of the sterically more-demanding 2,3-ditertbutylpyrrole features a monomeric  $\sigma$ -bonded structure with a  $Li\text{--}N$  distance of  $1.932(7)$  Å and two THF molecules coordinated to the trigonal-planar lithium ion.<sup>13</sup> For sodium, the crown-ether-containing indolyl salt is similar to the sodium pyrrolyl, and the  $Na\text{--}N$  distance measures  $2.331(2)$  Å.<sup>14</sup> In the presence of tertiary amines completing the tetrahedral coordination environment of the metal, lithium and sodium indolyl form the same type of dimeric associates as described above, with  $M\text{--}N$  distances measuring  $2.004(7)$  and  $2.231(10)$  for  $M = \text{Li}$  and  $2.356(5)\text{--}2.481(5)$  Å for  $M = \text{Na}$ .<sup>15</sup> An array of  $\sigma$ -bonded carbazoyl sodium salts containing various ethers have been structurally characterized, with  $Na\text{--}N$  bond lengths situated between  $2.30$  and  $2.53$  Å.<sup>16</sup> Some of these structures contained  $[\text{Na}(\text{carbazole})]_2$  dimers similar to those observed in **2b**, and the  $Na\text{--}N$  distances for these compounds were situated at the higher end of the range, between  $2.40$  and  $2.34$  Å. It can therefore be concluded that the coordination behavior of the 1,2,4-triaza-3,5-diborolyl ligand toward alkali metals is very similar to that of its organic analogues, pyrrolyl, indolyl, and carbazoyl. These ligands coordinate to lithium and sodium in a  $\sigma$  fashion as well, and dimeric associates containing  $M_2N_2$  rhombs with  $M\text{--}N$  bonds very similar in length have been observed in some of their solid-state structures. A  $\pi$ -coordinating ligand ( $\eta^5$ ) was reported in the 1D polymeric structure of the sodium salt of the electron-rich tetramethylpyrrolyl in the solid state, but even there,  $Na\text{--}N$   $\sigma$  interactions were present ( $2.351(1)$  and  $2.411(2)$  Å), and the THF solutions contained dimeric, likely  $\sigma$ -bonded units.<sup>17</sup> Indolyl–metal  $\pi$  interactions have also been observed in the sodium and potassium salts, featuring a pendant macrocyclic ligand attached to the indolyl moiety.<sup>18</sup>

Lithium salts of 2,4,6-triorganoborazines crystallized with various Lewis bases have been structurally characterized, and all of them contained  $\sigma$  interactions between lithium and nitrogen.<sup>19</sup> Although dimers formed through  $Li_2N_2$  bridges, similar to those observed in **2a**, were present only in three out of nine structures, in six of the examples the deprotonated nitrogen in borazine was connected to two lithium ions, resulting in a distorted tetrahedral environment of the metal. In all of the derivatives, the  $Li\text{--}N$  bonds ranged between  $1.96$  and  $2.16$  Å. Upon deprotonation, an elongation of the borazine skeleton was observed in these compounds as a

(11) Heldt, I.; Behrens, U. *Z. Anorg. Allg. Chem.* **2005**, *631*, 749.

(12) Hacker, R.; Kaufmann, E.; Schleyer, P. v. R.; Mahdi, W.; Dietrich H. *Chem. Ber.* **1987**, *120*, 1533.

(13) Westerhausen, M.; Wieneke, M.; Nöth, H.; Seifert, T.; Pfitzner, A.; Schwarz, W.; Schwarz, O.; Weidlein J. *Eur. J. Inorg. Chem.* **1998**, 1175.

(14) Heldt, I.; Borrmann, T.; Behrens, U. *Z. Anorg. Allg. Chem.* **2003**, *629*, 1980.

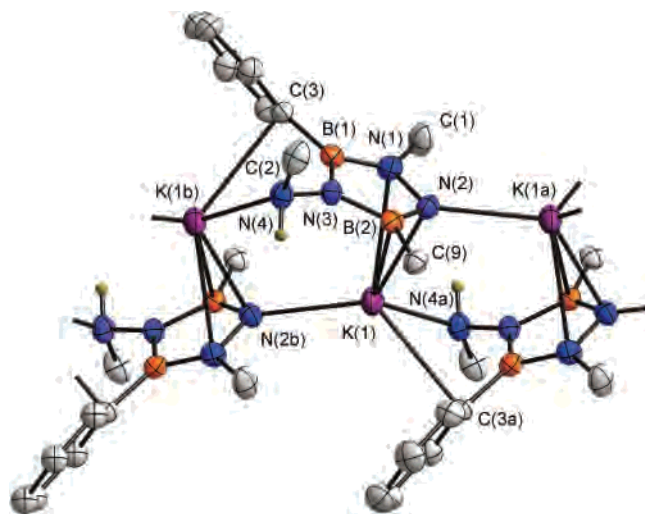
(15) Gregory, K.; Bremer, M.; Bauer, W.; Schleyer, P. v. R.; Lorenzen, N. P.; Kopf, J.; Weiss, E. *Organometallics* **1990**, *9*, 1485.

(16) (a) Bock, H.; Arad, C.; Näther, C.; Havlas, Z. *Helv. Chim. Acta* **1997**, *80*, 606. (b) Bock, H.; Arad, C.; Näther, C.; Havlas, Z. *J. Organomet. Chem.* **1997**, *548*, 115.

(17) Kuhn, N.; Henkel, G.; Kreutzberg, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1143.

(18) Hu, J.; Barbour, L. J.; Gokel, G. W. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5121.

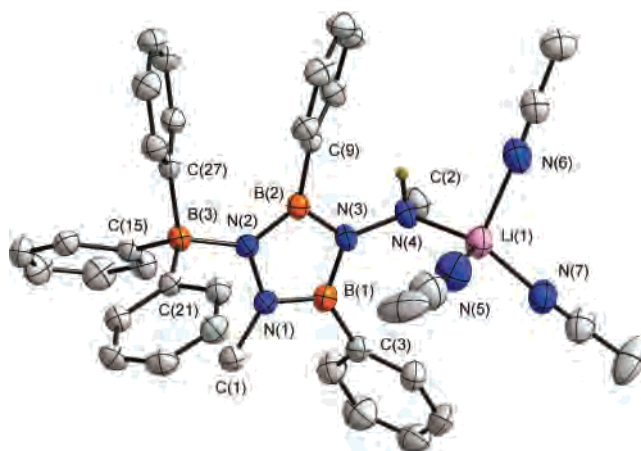
(19) (a) Nöth, H.; Rojas-Lima, S.; Troll, A. *Eur. J. Inorg. Chem.* **2005**, 1895. (b) Nöth, H.; Troll, A. *Eur. J. Inorg. Chem.* **2005**, 3524.



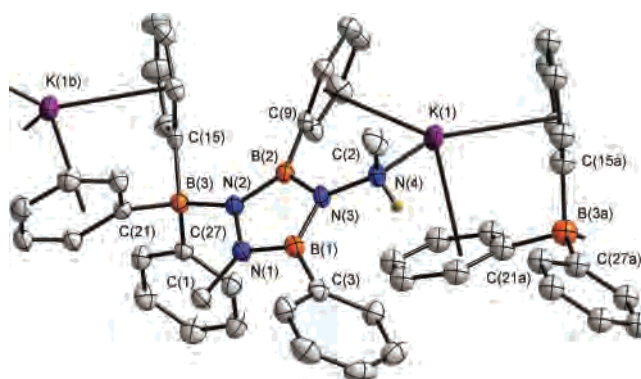
**Figure 3.** Fragment from the 1D polymeric structure of **2c** with 50% probability level thermal ellipsoids. For clarity, only the ipso carbon atom of the phenyl group on B(1) is represented, and all of the hydrogen atoms on the organic substituents have been omitted.

result of the reduction in the width of B–N–B and the opposite N–B–N angles. This was explained through the greater electronic repulsions between the B–N bonds and the  $\sigma$  lone pair on nitrogen, according to the VSEPR theory of bonding. A similar effect is observed upon deprotonation of the 1,2,4-triaza-3,5-diborole, with the N(1)–N(2)–B(2) angle contracting from 110 in the neutral ligand **1** to 105° in the alkali metal salts **2a**, **2b**, and **2c**.

Potassium salt **2c** features a 1D polymeric structure in the solid state, with the ligand coordinating in both  $\sigma$  and  $\pi$  fashions (Figure 3). The potassium ion is  $\sigma$ -coordinated by the amide nitrogen, N(2), and the nitrogen of the pendant methylamino group, N(4), of the successive ligand, with the K–N bonds measuring 2.681(3) and 2.889(3) Å, respectively, leading to the formation of linear chains. The potassium ion is additionally coordinated by the ipso carbon of a phenyl group in the ligand, with a K–C contact distance of 3.127 Å. Two such linear chains are connected by  $\eta^3$  interchain interactions involving the metal and the B(2)–N(2)–N(1) fragment in the B<sub>2</sub>N<sub>3</sub> ring. The B(2)–K, N(2)–K, and N(2)–K distances measure 3.149(3), 2.800(3), and 3.009(3) Å, respectively. The coordination environment of the potassium ion could be described as a three-legged piano stool. The polymeric double-stranded arrangement observed in **2c** is somewhat similar to the aforementioned structure of tetramethylpyrrolyl sodium<sup>17</sup> and to the structure of 2,3-dimethylindolyl potassium.<sup>20</sup> Exclusively,  $\sigma$  interactions between potassium and the pyrrolyl ring are rather rare and have been observed only for pyrrolyl and carbazolyl salts having a crown ether hosting the metal (K–N distance 2.712–(3), 2.774(2) Å).<sup>11,21</sup> More commonly, the pyrrolyl,<sup>22–24</sup>



**Figure 4.** Molecular structure of **3a**(CH<sub>3</sub>CN)<sub>3</sub> with 50% probability level thermal ellipsoids. Hydrogen atoms on the organic substituents have been omitted for clarity.



**Figure 5.** Fragment from the monodimensional polymeric structure of **3c** with 50% probability level thermal ellipsoids. Hydrogen atoms on the organic substituents have been omitted for clarity.

indolyl,<sup>18,20</sup> and carbazolyl<sup>25</sup> ligands coordinate to potassium in a similar fashion to that of the triazadiborolyl ligand in **2c**, through  $\sigma$  (K–N 2.676(3)–2.826(2) Å) and  $\pi$  interactions (potassium to ring plane distance 2.80–3.06 Å). By comparison, the distance between the potassium center and the plane of the B<sub>2</sub>N<sub>3</sub> ring in **2c** measures 2.79 Å.

The above results show that the alkali metal coordination chemistry of ligand **D** is dominated by  $\sigma$  interactions involving the amide ring nitrogen, just like the chemistry of the organic analogues pyrrole, indole, and carbazole. Attempting to enforce  $\pi$  coordination, the alkali metal salts **2a–c** were reacted with BPh<sub>3</sub> (Scheme 1). The involvement of the nonparticipating electron pair on nitrogen in a dative bond to boron was successful in ferrocene analogues incorporating pyrrolyl<sup>26,27</sup> and in lithium pyrrolyl salts.<sup>28</sup> The formation of the 1:1 adducts **3a–c** was immediate and quantitative, as indicated by the singlet resonance characteristic for a borate ion in the <sup>11</sup>B NMR spectra ( $\delta = -4$  to  $-7$ ). The singlet resonances corresponding to the two

(20) Evans, W. J.; Brady, J. C.; Ziller, J. W. *Inorg. Chem.* **2002**, *41*, 3340.

(21) Esbak, H.; Behrens, U. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1581.

(22) Reid, S. D.; Blake, A. J.; Wilson, C.; Love, J. B. *Inorg. Chem.* **2006**, *45*, 636.

(23) Love, J. B.; Blake, A. J.; Wilson, C.; Reid, S. D.; Novak, A.; Hitchcock, P. B. *Chem. Commun.* **2003**, 1682.

(24) Athimoolam, A.; Gambarotta, S.; Korobkov, I. *Can. J. Chem.* **2005**, *83*, 832.

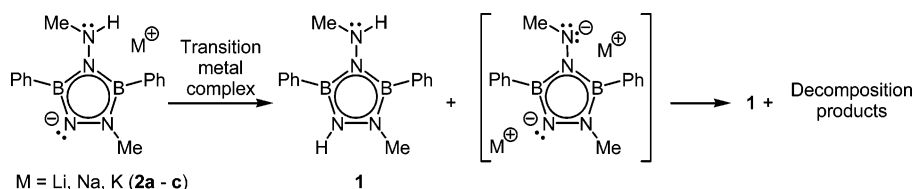
(25) Gregory, K.; Bremer, M.; Schleyer, P. v. R.; Klusener, P. A. A.; Brandsma, L. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1224.

(26) Kuhn, N.; Schulten, M.; Zauder, E.; Augart, N.; Boese, R. *Chem. Ber.* **1989**, *122*, 1891.

(27) Kuhn, N.; Horn, E.-M.; Boese, R.; Augart, N. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 342.

(28) Kehr, G.; Roesmann, R.; Fröhlich, R.; Holst, C.; Erker, G. *Eur. J. Inorg. Chem.* **2001**, 535.

Scheme 2



inequivalent ring borons overlap into a broad signal at 25–27 ppm. Except for the additional signals corresponding to the BPh<sub>3</sub> moiety, the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the adducts are not significantly different from the corresponding spectra of the alkali metal salts **2a–c**.

The crystallographic analysis of **3a**(CH<sub>3</sub>CN)<sub>3</sub> reveals a monomeric structure featuring the BPh<sub>3</sub> unit coordinated to the amide ring nitrogen, N(2), of the 1,2,4-triaza-3,5-diborolylium ligand and the lithium ion  $\sigma$ -coordinated by the nitrogen atom of the pendant methylamino group (Figure 4). The distorted tetrahedral coordination sphere of the lithium ion is completed by three acetonitrile molecules, and no  $\pi$  interactions between the metal and the cyclic ligands are present. The metric parameters of the ligand do not suffer considerable changes upon the coordination of the triphenyl borane. As expected for a tetracoordinated boron, the extraannular B–N bond (1.579(3) Å) is significantly longer than the intraannular B–N bonds (1.412(4)–1.452(4) Å). The Li–N distances fall in a narrow range, between 1.979(6) and 2.072(6) Å, comparable to the corresponding distances observed in **2a**.

The crystal structure of **3c** features polymeric chains containing potassium ions alternating with triphenylborane moieties and triaza-diborolylium ligands (Figure 5). As observed in **3a**, the triphenylborane molecule is coordinated by the amide nitrogen of the cyclic ligand through a long B(3)–N(2) bond (1.576(2) Å), and this coordination induces little change in the metric parameters of the triaza-diborolylium ligand. The potassium center is  $\sigma$ -coordinated by the pendant amino group (K–N distance 2.8334(18) Å) and  $\pi$ -coordinated by three phenyl groups, one belonging to the ligand and two belonging to the phenylborane moiety. The distances between potassium and the phenyl planes measure 2.84 Å for the ligand phenyl and 2.91 and 2.99 Å for the phenyl groups in triphenylborane, with the shortest K $\cdots$ C contacts involving the ipso (3.04), ortho (2.99), and ipso (3.11 Å) carbon atoms, respectively. Such  $\pi$  coordination by aryl groups is typical for potassium and is encountered in K[BPh<sub>4</sub>], which is used for the selective precipitation of this ion from aqueous solutions.<sup>29</sup> The K $\cdots$ C contacts observed in **3c** are short; for comparison, the distances between potassium and the aryl planes measure 2.98 in K[BPh<sub>4</sub>] and range between 2.92 and 3.02 Å in K[B(C<sub>6</sub>H<sub>4</sub>OC<sub>6</sub>H<sub>5</sub>)<sub>4</sub>].<sup>30,31</sup>

The transition-metal coordination chemistry of the triaza-diborolylium ligand was investigated using the alkali metal

derivatives described above as starting materials. Various transition-metal reagents were employed, such as FeCl<sub>2</sub>(thf)<sub>2</sub>, [Cp\*<sup>+</sup>RuCl]<sub>4</sub>, and CuBr. The major product of most reactions between the alkali metal salts **2a–c** and the transition-metal reagent was **1**, along with a complex mixture of byproducts that was not further investigated. With the most likely source of protons necessary for the regeneration of **1** being the pendant methylamino group of the ligand itself, it is possible that the presence of transition-metal reagents promotes a disproportionation of the monoanionic salts **2** to **1** and the dianionic analogues (Scheme 2). The doubly deprotonated form of **1** is indeed not isolable (vide supra), and the driving force for the process could be the formation of transition-metal methylhydrazides.

The reaction of **2a** with [Rh(cod)Cl]<sub>2</sub> in THF, however, gave **4** in a moderate yield. The <sup>1</sup>H and <sup>13</sup>C NMR spectra indicated that **4** consisted of Rh(cod) fragments and triaza-diborolylium ligands (L) in a ratio of 1:1, and the heaviest ion featured in the electron-impact mass spectrum corresponded to the formulation Rh(cod)L. Only one broad resonance was observed in the <sup>11</sup>B NMR spectrum, but the <sup>1</sup>H and <sup>13</sup>C NMR spectra displayed signals for two sets of nonequivalent cyclooctatetraene vinyl and methylene groups. Single-crystal X-ray diffractometry revealed that **4** has a centrosymmetric dimeric structure [Rh(cod)L]<sub>2</sub> in the solid state, with two ligands bridging two Rh(cod) fragments through the amide nitrogen N(2) (Figure 6). The plane of the Rh<sub>2</sub>N<sub>2</sub> rhomb is practically perpendicular to the planes of the planar B<sub>2</sub>N<sub>3</sub> rings (dihedral angle 88.4°). The only mentionable changes in the metric parameters of the triaza-diborolylium are the slight lengthening of the B(2)–N(2) bond and the shortening of the B(2)–N(3) bond, and as a consequence, the ligand is better described by resonance structure **F**. The lengths of the Rh–N bonds (2.141(2) and 2.168(2) Å) fall in the same range observed for cyclooctadienerhodium complexes containing 2-aminomethylpyrrolidines<sup>32</sup> and 2-aminomethylpyrrolyl,<sup>33</sup> and the Rh–N–Rh and N–Rh–N angles measure 98.33(9) and 81.67(9)°, respectively. The cyclooctadiene ligand is oriented with the C=C bonds coordinating to the metal trans to the amide ring nitrogen in a pseudo-square planar geometry, and the Rh–C distances measure 2.115(3)–2.168(2) Å. This type of geometry is common for molecules containing the Rh(cod)N<sub>2</sub> moiety, such as 2-ami-

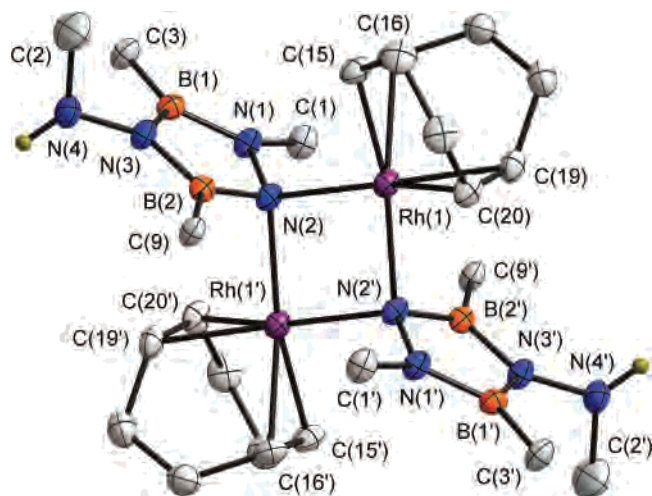
(29) (a) Wittig, G.; Keicher, G.; Rückert, A.; Raff, P. *Liebigs Ann.* **1949**, 563, 110. (b) Wittig, G. *Angew. Chem.* **1950**, 62, 231. (c) Cassaretto, F. P.; McLafferty, J. J.; Moore, C. E. *Anal. Chim. Acta* **1965**, 32, 376.

(30) Hoffmann, K.; Weiss, E. *J. Organomet. Chem.* **1974**, 67, 221.

(31) Alaviuhkola, T.; Bobacka, J.; Nissinen, M.; Rissanen, K.; Ivaska, A.; Pursiainen, J. *Chem.—Eur. J.* **2005**, 11, 2071.

(32) (a) Raja, R.; Thomas, J. M.; Jones, M. D.; Johnson, B. F. G.; Vaughan, D. E. W. *J. Am. Chem. Soc.* **2003**, 125, 14982. (b) Jones, M. D.; Raja, R.; Thomas, J. M.; Johnson, B. F. G.; Lewis, D. W.; Rouzaud, J.; Harris, K. D. M. *Angew. Chem., Int. Ed.* **2003**, 42, 4326. (c) Rouzaud, J.; Jones, M. D.; Raja, R.; Thomas, J. M.; Johnson, B. F. G.; Thomas, J. M.; Duer, M. J. *Helv. Chim. Acta* **2003**, 86, 1753.

(33) de Bruin, B.; Kicken, R. J. N. A. M.; Suos, N. F. A.; Donners, M. P. J.; den Reijer, C. J.; Sandee, A. J.; de Gelder, R.; Smits, J. M. M.; Gal, A. W.; Spek, A. L. *Eur. J. Inorg. Chem.* **1999**, 1581.



**Figure 6.** Molecular structure of **4** with 50% probability level thermal ellipsoids. For clarity, only the ipso carbon atom of the phenyl group on boron is represented, and all of the hydrogen atoms on the organic substituents have been omitted.

nomethylpyrrolidines<sup>31</sup> and 2-aminomethylpyrrolyl.<sup>32</sup> The structure reveals the reason for the nonequivalence of the methylene and vinyl groups in the coordinated cyclooctatetraene, which occupy different positions with respect to the asymmetric triazadiborolyl ligand. It is worth mentioning that, although transition-metal complexes featuring  $\pi$ -coordinating pyrrazolyl-type ligands are not uncommon, no such derivatives of rhodium have been reported, and hence  $\sigma$ -bonded **4** is not an exception.

## Conclusions

1-methyl-3,5-diphenyl-4-methylamino-1,2,4-triaza-3,5-diborole **1** can be selectively deprotonated at the ring nitrogen, yielding salts that have polymeric bidimensional (lithium, **2a**, and sodium, **2b**) and monodimensional (potassium, **2c**) solid-state structures dominated by  $\sigma$  M–N interactions between the carbon-free cyclopentadienyl analogue and the alkali metals. In the potassium derivative,  $\pi$  interactions involving the metal and the B<sub>2</sub>N<sub>3</sub> ring are present as well. The coordination site at the amido ring nitrogen can be conveniently blocked using triphenylborane, and this change does not induce  $\pi$  coordination through the B<sub>2</sub>N<sub>3</sub> ring in the resulting alkali metal derivatives. Instead, the lithium ion is coordinated by the pendant methylamino group of the ligand and three acetonitrile molecules in **3a**(CH<sub>3</sub>CN)<sub>3</sub>, whereas the potassium ion is coordinated by the pendant methylamino group of the ligand and three phenyl groups in **3c**. Reaction of the alkali metal salts **2a–c** with most transition-metal reagents led to reprotonation of the ligand in a potential disproportionation process that also produced an intractable mixture of byproducts. However, [Rh(cod)Cl]<sub>2</sub> reacted with **2a** and yielded dimeric **4**, featuring Rh(cod) fragments bridged by  $\sigma$ -coordinating 1,2,4-triaza-3,5-diborolyl moieties. The B<sub>2</sub>N<sub>3</sub> ring is planar in all of the compounds described herein, and its metric parameters indicate that the most-accurate descriptions of the bonding in this ligand are provided by resonance structures **E** and **F**.

The coordination behavior of the investigated 1,2,4-triaza-3,5-diborolyl ligand strongly resembles the coordination behavior of its organic analogues pyrrolyl, indolyl, and carbazolyl. All of these carbon-based nitrogen ligands feature  $\sigma$ -coordination modes in their alkali metal salts and  $\pi$ -coordination modes in many of their transition-metal complexes. It can be therefore concluded that the 1,2,4-triaza-3,5-diborolyl ligands are promising candidates for the formation of inorganic sandwich compounds, as claimed by Nöth four decades ago.<sup>4c</sup> The pendant amino group in **1** provides an additional binding site, allowing for a more-varied coordination chemistry. According to our investigations, the replacement of the active hydrogen of the pendant methylamino group with a less-reactive organic group is a mandatory condition for the successful use of heterocycles derived from **1** as  $\pi$  ligands in transition-metal chemistry.

## Experimental Section

**General Considerations.** All of the operations were performed under an argon atmosphere using standard Schlenk and glove-box techniques. Solvents were dried and deoxygenated prior to use and methylhydrazine was dried over CaH<sub>2</sub>. Methylated hydrazines are highly toxic and probable carcinogens, and their handling requires special precautions; all of the residues were neutralized using commercial bleach solution. 1-methyl-4-methylamino-triaza-3,5-diphenyldiborole **1** was prepared according to a reported procedure.<sup>7b</sup> NMR spectra were recorded on Bruker Advance DRX-400 and AMX-300 spectrometers and calibrated with respect to CDHCl<sub>2</sub> (<sup>1</sup>H, 5.32), THF-d<sub>7</sub> (<sup>1</sup>H, 3.58), CD<sub>2</sub>Cl<sub>2</sub> (<sup>13</sup>C, 54.00), THF-d<sub>8</sub> (<sup>13</sup>C, 67.57), and BF<sub>3</sub>·Et<sub>2</sub>O (<sup>11</sup>B, 0 ppm). The mass spectrum of **2** was performed by the Analytical Instrumentation Laboratory, Department of Chemistry, University of Calgary, using a Micromass VG7070F instrument.

**3,5-Diphenyl-1-methyl-4-methylamino-1,2,4-triaza-3,5-diborole, 1.**<sup>7b</sup> <sup>1</sup>H NMR (400 MHz, THF-d<sub>8</sub>, 25 °C):  $\delta$  = 2.45 (d, 3H, <sup>3</sup>J<sub>HH</sub> = 6.2 Hz, HNCH<sub>3</sub>), 3.21 (s, 3H, BNCH<sub>3</sub>), 4.14 (q, 1H, <sup>3</sup>J<sub>HH</sub> = 6.2 Hz, HNCH<sub>3</sub>), 7.27–7.36 (m, 6H, C<sub>6</sub>H<sub>5</sub>), 7.49 (s, br, HNB), 7.60 (d, 2H, *o*-C<sub>6</sub>H<sub>5</sub>), 7.93 (d, 2H, *o*-C<sub>6</sub>H<sub>5</sub>); <sup>13</sup>C NMR (100 MHz, THF-d<sub>8</sub>, 25 °C):  $\delta$  = 35.6 (s, BNCH<sub>3</sub>), 43.3 (s, HNCH<sub>3</sub>), 128.3 (s, *m*-C<sub>6</sub>H<sub>5</sub>), 128.7 (s, *m*-C<sub>6</sub>H<sub>5</sub>), 129.0 (s, *p*-C<sub>6</sub>H<sub>5</sub>), 129.3 (s, *p*-C<sub>6</sub>H<sub>5</sub>), 134.3 (s, *o*-C<sub>6</sub>H<sub>5</sub>); <sup>11</sup>B NMR (128 MHz, THF-d<sub>8</sub>, 25 °C):  $\delta$  = 27.5 (s, br, LW<sub>1/2</sub> = 330 Hz). The NMR data was in good agreement with the reported values.<sup>7b</sup>

**3,5-Diphenyl-1-methyl-4-methylamino-1,2,4-triaza-3,5-diborolylithium, 2a.** A yellow solution of lithium 2,2,6,6-tetramethylpiperidide, LiTMP, was prepared from *n*-butyllithium in hexane (3.11 mL, 1.6 M, 4.99 mmol) and tetramethylpiperidine, HTMP, (0.704 g, 4.99 mmol) in THF (3 mL). Solutions of **1** (1.32 g, 4.99 mmol) in THF (3 mL) and LiTMP were pre-cooled to –35 °C, mixed and kept at this temperature for 2 h. The resulting yellow solution was allowed to warm to room temperature overnight, and the solvent was removed under a vacuum, leaving behind a yellow residue that was washed twice with hexane (30 mL) and dried under a vacuum. The product was obtained as a colorless powder (1.24 g, 92.1%). <sup>1</sup>H NMR (400 MHz, THF-d<sub>8</sub>, 25 °C):  $\delta$  = 2.36 (d, 3H, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, HNCH<sub>3</sub>), 3.22 (s, 3H, BNCH<sub>3</sub>), 3.75 (q, 1H, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, HNCH<sub>3</sub>), 7.05–7.23 (m, 6H, *m*- and *p*-C<sub>6</sub>H<sub>5</sub>), 7.60 (d, 2H, *o*-C<sub>6</sub>H<sub>5</sub>), 7.77 (d, 2H, *o*-C<sub>6</sub>H<sub>5</sub>); <sup>13</sup>C NMR (100 MHz, THF-d<sub>8</sub>, 25 °C):  $\delta$  = 39.0 (s, BNCH<sub>3</sub>), 44.0 (s, HNCH<sub>3</sub>), 125.9 (s, *p*-C<sub>6</sub>H<sub>5</sub>), 126.7 (s, *p*-C<sub>6</sub>H<sub>5</sub>), 127.5 (s, *m*-C<sub>6</sub>H<sub>5</sub>), 127.9 (s, *m*-C<sub>6</sub>H<sub>5</sub>), 134.5 (s, *o*-C<sub>6</sub>H<sub>5</sub>), 134.6 (s, *o*-C<sub>6</sub>H<sub>5</sub>), 139.9 (s, br, *i*-C<sub>6</sub>H<sub>5</sub>), 144.0 (s, br, *i*-C<sub>6</sub>H<sub>5</sub>); <sup>11</sup>B

NMR (128 MHz, THF- $d_8$ , 25 °C):  $\delta$  = 24.2 (s, br), 27.8 (s, br);  $^7\text{Li}$  NMR (155 MHz, THF- $d_8$ , 25 °C):  $\delta$  = -1.24 (s); MS (EI+, 70 eV):  $m/z(\%)$ : 264(36)  $[\text{M} - \text{Li} + \text{H}]^+$ , 179.2(100)  $[\text{M} - \text{Li} - \text{Me} + \text{H}]^+$ . Colorless crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a THF solution of **2a**.

**3,5-Diphenyl-1-methyl-4-methylamino-1,2,3-triaza-3,5-diborolylium, 2b.** A solution of **1** (340 mg, 1.28 mmol) in THF (20 mL) was added to a stirring solution of sodium bis(trimethylsilyl)amide, NaHMDS, (236 mg, 1.28 mmol) in THF (15 mL). The resulting yellow mixture was stirred at ambient temperature for 3 h to ensure completion of the reaction. The solvent was removed under a vacuum, leaving behind a light-yellow residue that was washed twice with hexane (30 mL) and dried under a vacuum. The product was obtained as a colorless powder (340 mg, 92.4%).  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ , 25 °C):  $\delta$  = 2.35 (d, 3H,  $^3J_{\text{HH}}$  = 6.4 Hz,  $\text{HNCH}_3$ ), 3.25 (s, 3H,  $\text{BNCH}_3$ ), 3.80 (q, 1H,  $^3J_{\text{HH}}$  = 6.4 Hz,  $\text{HNCH}_3$ ), 7.08–7.28 (m, 6H, *m*- and *p*- $\text{C}_6\text{H}_5$ ), 7.56 (d, 2H,  $^3J_{\text{HH}}$  = 6.6 Hz, *o*- $\text{C}_6\text{H}_5$ ), 7.83 (d, 2H,  $^3J_{\text{HH}}$  = 6.6 Hz, *o*- $\text{C}_6\text{H}_5$ );  $^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ , 25 °C):  $\delta$  = 39.5 (s,  $\text{BNCH}_3$ ), 44.0 (s,  $\text{HNCH}_3$ ), 126.6 (s, *p*- $\text{C}_6\text{H}_5$ ), 127.1 (s, *p*- $\text{C}_6\text{H}_5$ ), 128.1 (s, *m*- $\text{C}_6\text{H}_5$ ), 128.2 (s, *m*- $\text{C}_6\text{H}_5$ ), 133.9 (s, *o*- $\text{C}_6\text{H}_5$ ), 134.4 (s, *o*- $\text{C}_6\text{H}_5$ ), 139.3 (s, br, *i*- $\text{C}_6\text{H}_5$ ), 142.7 (s, br, *i*- $\text{C}_6\text{H}_5$ );  $^{11}\text{B}$  NMR (128 MHz, THF- $d_8$ , 25 °C):  $\delta$  = 24.7 (s, br), 27.4 (s, br). Colorless crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a THF solution of **2b**.

**3,5-Diphenyl-1-methyl-4-methylamino-1,2,3-triaza-3,5-diborolylium, 2c.** A solution of **1** (1.50 g, 5.68 mmol) in THF (30 mL) was added slowly under stirring to a suspension of potassium hydride (0.228 g, 5.68 mmol) in THF (20 mL). The hydride dissolved with concomitant evolution of gas, yielding a yellow solution. The mixture was stirred at ambient temperature for 3 h to ensure completion of the reaction, and the solvent was subsequently removed under a vacuum. The yellow residue was washed twice with hexane (30 mL) and dried under a vacuum, yielding a light yellow powder (1.68 g, 98%).  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ , 25 °C):  $\delta$  = 2.40 (d, 3H,  $^3J_{\text{HH}}$  = 6.4 Hz,  $\text{HNCH}_3$ ), 3.27 (s, 3H,  $\text{BNCH}_3$ ), 3.87 (q, 1H,  $^3J_{\text{HH}}$  = 6.4 Hz,  $\text{HNCH}_3$ ), 7.06–7.27 (m, 6H, *m*- and *p*- $\text{C}_6\text{H}_5$ ), 7.56 (d, 2H,  $^3J_{\text{HH}}$  = 6.6 Hz, *o*- $\text{C}_6\text{H}_5$ ), 7.89 (d, 2H,  $^3J_{\text{HH}}$  = 6.6 Hz, *o*- $\text{C}_6\text{H}_5$ );  $^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ , 25 °C):  $\delta$  = 39.4 (s,  $\text{BNCH}_3$ ), 44.0 (s,  $\text{HNCH}_3$ ), 126.3 (s, *p*- $\text{C}_6\text{H}_5$ ), 127.1 (s, *p*- $\text{C}_6\text{H}_5$ ), 128.2 (s, *m*- $\text{C}_6\text{H}_5$ ), 128.3 (s, *m*- $\text{C}_6\text{H}_5$ ), 133.5 (s, *o*- $\text{C}_6\text{H}_5$ ), 134.4 (s, *o*- $\text{C}_6\text{H}_5$ ), 139.0 (s, br, *i*- $\text{C}_6\text{H}_5$ ), 143.1 (s, br, *i*- $\text{C}_6\text{H}_5$ );  $^{11}\text{B}$  NMR (128 MHz, THF- $d_8$ , 25 °C):  $\delta$  = 26.6 (s, br). Yellow crystals suitable for single-crystal X-ray diffraction were obtained by slow diffusion of hexane in a THF solution of **2c**.

**3,5-Diphenyl-1-methyl-4-methylamino-2-triphenylboryl-1,2,3-triaza-3,5-diborolyllithium, 3a.** A solution of  $\text{BPh}_3$  (475 mg, 1.96 mmol) in THF (15 mL) was added dropwise to a stirred-yellow solution of **2a** (530 mg, 1.96 mmol) in THF (20 mL), and the pale-yellow mixture was stirred at ambient temperature for 12 h. Subsequent removal of the volatiles in vacuo left behind a colorless solid that was washed with hexane and dried under a vacuum, yielding a colorless powder (930 mg, 93%).  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ , 25 °C):  $\delta$  = 2.22 (d, 3H,  $^3J_{\text{HH}}$  = 6.4 Hz,  $\text{HNCH}_3$ ), 2.69 (s, 3H,  $\text{BNCH}_3$ ), 3.56 (q, 1H,  $^3J_{\text{HH}}$  = 6.4 Hz,  $\text{HNCH}_3$ ), 6.62 (t, 3H, *p*- $\text{B}(\text{C}_6\text{H}_5)_3$ ), 6.75 (t, 6H, *m*- $\text{B}(\text{C}_6\text{H}_5)_3$ ), 7.39 (d, 6H, *o*- $\text{B}(\text{C}_6\text{H}_5)_3$ ), 6.71 (m, 3H, *p*- and *m*- $\text{BC}_6\text{H}_5$ ), 6.96 (m, 2H, *o*- $\text{BC}_6\text{H}_5$ ), 7.13 (t, 1H, *p*- $\text{BC}_6\text{H}_5$ ), 7.21 (t, 2H, *m*- $\text{BC}_6\text{H}_5$ ), 7.66 (d, 2H, *o*- $\text{BC}_6\text{H}_5$ );  $^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ , 25 °C):  $\delta$  = 37.1 (s,  $\text{BNCH}_3$ ), 43.6 (s,  $\text{HNCH}_3$ ), 122.6 (s, *p*- $\text{B}(\text{C}_6\text{H}_5)_3$ ), 125.7 (s, *m*- $\text{B}(\text{C}_6\text{H}_5)_3$ ), 124.8 (s, *p*- $\text{BC}_6\text{H}_5$ ), 126.6 (s, *m*- $\text{BC}_6\text{H}_5$ ), 127.1 (s, *p*- $\text{BC}_6\text{H}_5$ ), 127.6 (s, *m*- $\text{BC}_6\text{H}_5$ ), 134.1 (s, *o*- $\text{BC}_6\text{H}_5$ ), 135.1 (s, *o*- $\text{BC}_6\text{H}_5$ ), 136.6 (s, *o*- $\text{B}(\text{C}_6\text{H}_5)_3$ ), 138.9 (s, br, *i*- $\text{BC}_6\text{H}_5$ ), 142.1 (s,

*br*, *i*- $\text{BC}_6\text{H}_5$ ), 162.9 (s, br, *i*- $\text{B}(\text{C}_6\text{H}_5)_3$ );  $^{11}\text{B}$  NMR (128 MHz, THF- $d_8$ , 25 °C):  $\delta$  = -4.60 (s, br,  $\text{BPh}_3$ ), 27.3 (s, br,  $\text{BPh}$ ). Colorless crystals of **3a**( $\text{CH}_3\text{CN}$ ) $_3$  suitable for single-crystal X-ray diffraction were obtained by cooling a concentrated solution of **3a** in a mixture of acetonitrile and hexane to -30 °C.

**3,5-Diphenyl-1-methyl-4-methylamino-2-triphenylboryl-1,2,3-triaza-3,5-diborolylium, 3b.** A colorless solution of  $\text{BPh}_3$  (150 mg, 0.619 mmol) in THF (15 mL) was added dropwise to a stirred-yellow solution of **2b** (177 mg, 0.619 mmol) in THF (20 mL). The pale-yellow mixture was stirred at ambient temperature for 12 h, and the volatiles were subsequently removed in vacuo. The residue was washed twice with hexane and dried under a vacuum, yielding the desired product as a colorless powder (280 mg, 85.9%).  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ , 25 °C):  $\delta$  = 2.19 (d, 3H,  $^3J_{\text{HH}}$  = 6.4 Hz,  $\text{HNCH}_3$ ), 2.71 (s, 3H,  $\text{BNCH}_3$ ), 3.54 (q, 1H,  $^3J_{\text{HH}}$  = 6.4 Hz,  $\text{HNCH}_3$ ), 6.62 (t, 3H, *p*- $\text{B}(\text{C}_6\text{H}_5)_3$ ), 6.74 (t, 6H, *m*- $\text{B}(\text{C}_6\text{H}_5)_3$ ), 7.39 (d, 6H, *o*- $\text{B}(\text{C}_6\text{H}_5)_3$ ), 6.70 (m, 3H, *p*- and *m*- $\text{BC}_6\text{H}_5$ ), 6.96 (m, 2H, *o*- $\text{BC}_6\text{H}_5$ ), 7.13 (t, 1H, *p*- $\text{BC}_6\text{H}_5$ ), 7.21 (t, 2H, *m*- $\text{BC}_6\text{H}_5$ ), 7.66 (d, 2H, *o*- $\text{BC}_6\text{H}_5$ );  $^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ , 25 °C):  $\delta$  = 37.1 (s,  $\text{BNCH}_3$ ), 43.7 (s,  $\text{HNCH}_3$ ), 122.6 (s, *p*- $\text{B}(\text{C}_6\text{H}_5)_3$ ), 125.7 (s, *m*- $\text{B}(\text{C}_6\text{H}_5)_3$ ), 124.7 (s, *p*- $\text{BC}_6\text{H}_5$ ), 127.1 (s, *p*- $\text{BC}_6\text{H}_5$ ), 126.6 (s, *m*- $\text{BC}_6\text{H}_5$ ), 127.7 (s, *m*- $\text{BC}_6\text{H}_5$ ), 134.1 (s, *o*- $\text{BC}_6\text{H}_5$ ), 135.1 (s, *o*- $\text{BC}_6\text{H}_5$ ), 136.7 (s, *o*- $\text{B}(\text{C}_6\text{H}_5)_3$ ), 138.9 (s, br, *i*- $\text{BC}_6\text{H}_5$ ), 142.5 (s, br, *i*- $\text{BC}_6\text{H}_5$ ), 162.9 (s, br, *i*- $\text{B}(\text{C}_6\text{H}_5)_3$ );  $^{11}\text{B}$  NMR (128 MHz, THF- $d_8$ , 25 °C):  $\delta$  = -6.45 (s, br,  $\text{BPh}_3$ ), 25.0 (s, br,  $\text{BPh}$ ).

**3,5-Diphenyl-1-methyl-4-methylamino-2-triphenylboryl-1,2,3-triaza-3,5-diborolylium, 3c.** A colorless solution of  $\text{BPh}_3$  (160 mg, 0.662 mmol) in THF (10 mL) was added dropwise to a stirred-yellow solution of **2c** (200 mg, 0.662 mmol) in THF (15 mL). The pale-yellow mixture was stirred at ambient temperature for 12 h, and the volatiles were subsequently removed in vacuo. The colorless solid residue was washed with hexane and dried under a vacuum, yielding a colorless powder (300 mg, 83%).  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ , 25 °C):  $\delta$  = 2.24 (d, 3H,  $^3J_{\text{HH}}$  = 6.4 Hz,  $\text{HNCH}_3$ ), 2.69 (s, 3H,  $\text{BNCH}_3$ ), 3.56 (q, 1H,  $^3J_{\text{HH}}$  = 6.4 Hz,  $\text{HNCH}_3$ ), 6.65 (t, 3H, *p*- $\text{B}(\text{C}_6\text{H}_5)_3$ ), 6.78 (t, 6H, *m*- $\text{B}(\text{C}_6\text{H}_5)_3$ ), 7.43 (d, 6H, *o*- $\text{B}(\text{C}_6\text{H}_5)_3$ ), 6.72 (m, 3H, *p*- and *m*- $\text{BC}_6\text{H}_5$ ), 6.70 (m, 2H, *o*- $\text{BC}_6\text{H}_5$ ), 7.15 (t, 1H, *p*- $\text{BC}_6\text{H}_5$ ), 7.23 (t, 2H, *m*- $\text{BC}_6\text{H}_5$ ), 7.65 (d, 2H, *o*- $\text{BC}_6\text{H}_5$ );  $^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ , 25 °C):  $\delta$  = 37.1 (s,  $\text{BNCH}_3$ ), 43.6 (s,  $\text{HNCH}_3$ ), 122.6 (s, *p*- $\text{B}(\text{C}_6\text{H}_5)_3$ ), 125.7 (s, *m*- $\text{B}(\text{C}_6\text{H}_5)_3$ ), 124.8 (s, *p*- $\text{BC}_6\text{H}_5$ ), 127.1 (s, *p*- $\text{BC}_6\text{H}_5$ ), 126.6 (s, *m*- $\text{BC}_6\text{H}_5$ ), 127.6 (s, *m*- $\text{BC}_6\text{H}_5$ ), 134.1 (s, *o*- $\text{BC}_6\text{H}_5$ ), 135.1 (s, *o*- $\text{BC}_6\text{H}_5$ ), 136.6 (s, *o*- $\text{B}(\text{C}_6\text{H}_5)_3$ ), 138.9 (s, br, *i*- $\text{BC}_6\text{H}_5$ ), 142.1 (s, br, *i*- $\text{BC}_6\text{H}_5$ ), 162.9 (s, br, *i*- $\text{B}(\text{C}_6\text{H}_5)_3$ );  $^{11}\text{B}$  NMR (128 MHz, THF- $d_8$ , 25 °C):  $\delta$  = -6.58 (s, br,  $\text{BPh}_3$ ), 25.3 (s, br,  $\text{BPh}$ ). Colorless crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a solution of **3c** in a mixture of THF and  $\text{Et}_2\text{O}$ .

**3,5-Diphenyl-1-methyl-4-methylamino-1,2,3-triaza-3,5-diborolyrhodiumcyclooctadiene Dimer, 4.** A solution of the **2a** (100 mg, 0.370 mmol) and  $[\text{Rh}(\text{cod})\text{Cl}]_2$  (91 mg, 0.185 mmol) in THF (10 mL) was stirred for 2 h at ambient temperature. The bright-red solution was concentrated in vacuo to 3 mL and subsequently cooled to -35 °C for 2 days to afford a yellow-crystalline solid that was separated by decantation, washed with pentane, and dried under a vacuum (42%). Yellow, thin-prismatic crystals were obtained by cooling a concentrated solution of **4** in a mixture of hexane and THF to -35 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C):  $\delta$  = 1.30 (m, 2H,  $\text{CH}_2$ ), 1.89 (m, 2H,  $\text{CH}_2$ ), 2.20 (s, 3H,  $\text{HNCH}_3$ ), 2.23 (m, 2H,  $\text{CH}_2$ ), 2.77 (m, 2H,  $\text{CH}_2$ ), 2.90 (s, 3H,  $\text{BNCH}_3$ ), 3.30 (q, br, 2H,  $\text{CHCH}_2$ ), 3.46 (t, br, 2H,  $\text{CHCH}_2$ ), 3.63 (s, br, 1H,  $\text{HNCH}_3$ ), 7.24–7.35 (m, 5H,  $\text{BC}_6\text{H}_5$ ), 7.55 (t, 1H, *p*- $\text{BC}_6\text{H}_5$ ), 7.67 (t, 2H, *m*- $\text{BC}_6\text{H}_5$ ), 8.86 (d, 2H, *o*- $\text{BC}_6\text{H}_5$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ,



### *1,2,4-Triaza-3,5-diborolyl Ligand*

25 °C):  $\delta$  = 28.9 (2, CH<sub>2</sub>), 32.8 (s, CH<sub>2</sub>), 39.3 (s, BNCH<sub>3</sub>), 43.3 (s, HNCH<sub>3</sub>), 76.6 (d, <sup>1</sup>J<sub>RhC</sub> = 13.0 Hz, CHCH<sub>2</sub>), 84.3 (d, <sup>1</sup>J<sub>RhC</sub> = 13.0 Hz, CHCH<sub>2</sub>), 127.9 (s, *m*-BC<sub>6</sub>H<sub>5</sub>), 128.0 (s, *m*-BC<sub>6</sub>H<sub>5</sub>), 128.5 (s, *p*-BC<sub>6</sub>H<sub>5</sub>), 128.8 (s, *p*-BC<sub>6</sub>H<sub>5</sub>), 133.8 (s, *o*-BC<sub>6</sub>H<sub>5</sub>), 135.2 (s, *o*-BC<sub>6</sub>H<sub>5</sub>); <sup>11</sup>B NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$  = 30.6 (s, br); MS (EI<sup>+</sup>, 70 eV): m/z(%): 474 (10) [(cod)RhL]<sup>+</sup>, 364 (5) [RhL-2H]<sup>+</sup>, 264 (100) [L + H]<sup>+</sup>.

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**Supporting Information Available:** Complete crystallographic data in table format. This material is available free of charge via the Internet at <http://pubs.acs.org>. CIF files are available online from the Cambridge Crystallographic Data Centre (CCDC Nos. 645592 (**2a**), 645593 (**2b**), 645594 (**2c**), 645595 (**3a**), 645596 (**3c**), and 645597 (**4**)).

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