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A Boron Analogue of Furan. The Synthesis and Coordination Chemistry of 2-Substituted-1,2-Oxaborolides

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*Summary: Two general methods have been developed for the synthesis of alkali metal salts of 2-substituted-1,2-oxaborolides (**6**). 2-Phenyl-1,2-oxaborolide (**6b**) has been converted to RuCp* complex **11b** and to Mn(CO)$_3$ complex **12b**, in which the metals are η^5-bound to the ligand.*

Although thiophene (**1**), pyrrole (**2**), and furan (**3**) are the best known and most important five-membered ring aromatic heterocycles,[1] they are not particularly good η^5-ligands toward transition metals. Thiophene[2] and pyrrole[3] form few stable π-coordinated transition metal complexes. To the best of our knowledge only one complex containing an η^5-furan ligand has been reported: the very labile [Cp*Ru(η^5-C_4H_4O)]Cl.[4−6] We have been interested in anionic aromatic ligands, in which a CH group of a neutral aromatic is replaced by the isoelectronic BH^- group.[7−14] In this manner **1**, **2**, and **3** are converted to 1,2-thiaborolide (**4**),[10] 1,2-azaborolide (**5**),[11−14] and 1,2-oxaborolide (**6**), respectively. **4** and **5** are good ligands, which have been used to prepare Cp-like transition metal complexes.[10−14] Of particular significance is the observation that zirconium(IV) derivatives of **4**[10] and **5**[14] have high activity for the polymerization of olefins. Thus it is of considerable interest to prepare **6** so that its coordination chemistry can be explored. We now wish to report the first synthesis of the 1,2-oxaborolide ring system and on its facile conversion to late transition metal complexes.

The precursors to **6**, 2-substituted-2,5-dihydro-1,2-oxaboroles (**9**), may be easily prepared by either of two syntheses summarized in Scheme 2. (Allyloxy)(*N*,*N*-diisopropylamino)vinylborane (**8**) was prepared in 87% yield by treatment of (*N*,*N*-diisopropylamino)vinylboron chloride (**7**)[10b] with lithium alloxide in THF. Upon addition of 2 mol % of Grubbs catalyst to **8** in methylene chloride, cyclization took place smoothly to give **9a** in 92% yield. Alternatively the reaction of 2,2-dibutyl-2,5-dihydro-1,2-oxastannole (**10**)[15] with $PhBCl_2$ afforded **9b** in 83% yield. Since **10** is available in large quantities from the reaction of Bu_2SnH_2 with propargyl alcohol, the latter preparation is particularly facile.

The reaction of **9a** with t-BuLi in pentane at −78 °C gave a yellow powder, which after washing with excess pentane afforded pure Li-**6a** in 53% yield. Alternatively treatment of **9b** in ether with $KN(SiMe_3)_2$ gave a 86% yield of K-**6b**. The ^1H NMR spectra of **6a** and **6b** in THF-d_8 or DMSO-d_8 show first-order patterns, which are consistent with the assigned structures.

Of particular significance is the observation that the ^1H, ^{11}B, and ^{13}C NMR spectra of **6b** are extremely similar to those of **5b**, as is illustrated in Figure 1. The spectra exhibit high-field ^{11}B chemical shift values, which are consistent with strong stabilization by π-bonding to boron.[16] The high-field ^{13}C NMR shifts for C(3) are consistent with appreciable carbanionic character,

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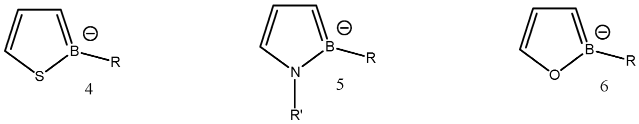
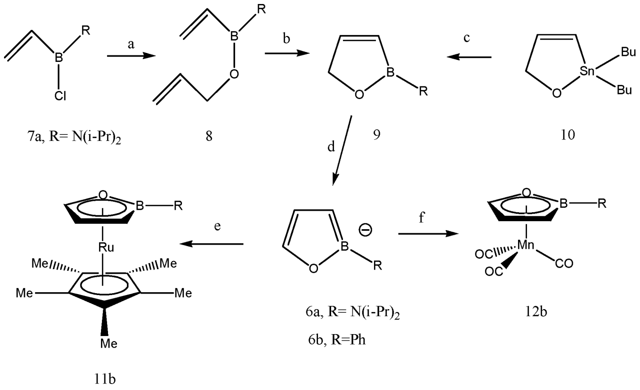
Scheme 1



Scheme 2. Synthesis[a]



[a] Key: (a) $LiOC_3H_5$/THF; (b) $(Cy_3P)_2(PhCH)RuCl_2$; (c) $PhBCl_2$; (d) t-BuLi or $KN(SiMe_3)_2$; (e) $[Cp^*RuCl]_4$; (f) $(AN)_3Mn(CO)_3PF_6$.

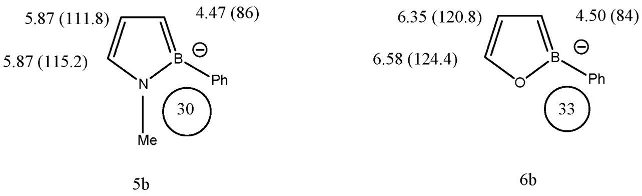


Figure 1. Comparison of the ^1H NMR, ^{13}C NMR (in parentheses), and ^{11}B NMR (in circles) chemical shift values of **5b** and **6b** in THF-d_8.

while the lower field chemical shift values of C(4) and C(5) suggest that these atoms bear little negative charge.[17] Overall the great similarity in spectra implies a similarity in the electronic structure of **5b** and **6b**.

Like 1,2-azaborolides, 1,2-oxaborolides readily form transition metal complexes. The reaction of **6b** with $[Cp^*RuCl]_4$ gave **11b** as bright amber crystals in 70% yield. The crystal structure of **11b** shows that it is a diheteroruthenocene in which the oxaborolyl ring is η^5-bond to Ru in the same manner found for the corresponding complex of **4a**. See Figure 2.

Unfortunately, a partial disorder limits the accuracy of the bond distances. **11b** is more robust than the isoelectronic furan complex, $[Cp^*Ru(\eta^5\text{-}C_4H_4O)]Cl$, which was reported to be stable only in solutions of noncoordinating solvents.[4]

The reaction of **6b** with $Mn(CO)_3(AN)_3PF_6$ in THF afforded **12b** as a yellow crystalline solid in 63% yield. On recrystallization from pentane, **12b** was subject to single-crystal X-ray analysis. The molecular structure of **12b**, illustrated in Figure 3, shows that the near planar oxaborolyl ring is η^5-bound to the $Mn(CO)_3$ group in a typical piano-stool fashion. The oxaborolyl ring shows a small deviation from planarity in that the boron atom is displaced away from Mn out of the plane defined by C(1)C(2)C(3)O(1) by 0.12(2) Å. The B–Mn distance (2.301(1) Å) is somewhat longer than the C–Mn distances (2.06–2.21 Å) and the Mn–O distance (2.111(1) Å). These observations are consistent with a somewhat weaker coordination to boron, and they conform to the pattern shown by complexes of other heterocyclic boron ligands.[7-12]

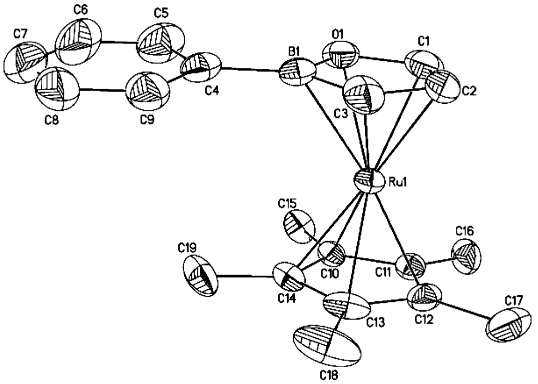


Figure 2. Solid-state Structure of **11b** (ORTEP). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances (Å): B(1)–C(3), 1.468(2); B(1)–O(1), 1.427(2); C(1)–C(2), 1.382(2); C(2)–C(3), 1.416(2); C(1)–O(1), 1.422(2); B(1)–Ru(1), 2.278(2); C(1)–Ru(1), 2.149(2); C(2)–Ru(1), 2.193(2); C(3)–Ru(1), 2.230(2); O(1)–Ru(1), 2.217(1); C(Cp)–Ru(1), 2.148(2)–2.186(2).

The intra-ring C–C and B–C distances of the 1,2-oxaborolyl ligand of **12b** are typical of those found for similarly coordinated heteroaromatic ligands. The C–C bond distances (1.43–1.39 Å) of **12b** are only slightly different than those shown by (1-phenylboratabenzene)-$Mn(CO)_3$ (**13**) (1.42–1.40 Å).[18] The intra-ring B–C distance of **12b** (1.514(2) Å) is identical to that shown by **13**. However it is more difficult to draw conclusions about the B–O and C–O bonds due to the dearth of compounds with coordination similar to that of **12b**. The C–O bond of **12b** (1.404(2) Å) is somewhat longer than that of furan (1.368 Å).[19] On the other hand the B–O bond of **12b** (1.456(2) Å) is well outside the range of the B–O bonds (1.34–1.38 Å) found for esters of borinic acids (R_2BOR') (**14**).[20] We speculate that hypothetical metal coordination to **3** or **14** might reasonably be expected to expand these bonds.

Finally we note that the CO stretching frequencies in the IR spectrum of **12b** in hexane are 2039, 1966, and 1948 cm^{-1}, which are virtually identical to those of **13** (2039, 1974, 1960 cm^{-1}),[21] but are slightly shifted from those of $CpMn(CO)_3$ (2028, 1944 cm^{-1}). This suggests that the boron heterocycles are weaker donors but better acceptors than Cp.[8b]

In summary, we have developed two efficient syntheses of 1,2-oxaborolides from readily available starting materials. 1,2-Oxaborolides are diheterocyclopentadienides, which are also anionic boron analogues of furan.

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They are good ligands toward late transition metals. The way is now open for the development of new coordination chemistry of this Cp surrogate.

Experimental Section

General Methods. ^{1}H, $^{11}B\{^{1}H\}$, and $^{13}C\{^{1}H\}$ NMR spectra were recorded on Varian INOVA-400 or 500 MHz spectrometers. The solvents used were chloroform-d_1 ($CDCl_3$), benzene-d_6 (C_6D_6), methyl sulfoxide (DMSO-d_6), or tetrahydrofuran-d_8 (THF-d_8), as indicated. Chemical shifts (δ) are reported in parts per million (ppm). Proton and carbon chemical shifts are relative to respective solvent internal standards: 7.27 (for proton), 77.23 (for carbon) ($CDCl_3$); 7.16, 128.39 (C_6D_6); 2.50, 39.70 (DMSO-d_6); 3.58, 67.40 (THF-d_8). Boron-11 chemical shifts are relative to prospective external reference: δ 0.00 (BF_3/Et_2O 1.0 M LiCl in D_2O). The coupling constants (J) are reported in Hz. The following abbreviations are used to describe peak patterns: "s" for singlet, "d" for doublet", "t" for triplet, "q" for quartet, "m" for multiplet, and "br" for broad peak. Data are presented as follows: chemical shift (multiplicity, integrated intensity, coupling constant, and assignment). Infrared (IR) spectra were recorded on a Nicolet Mode 5-DX FT-IR spectrometer using thin films in hexane. Data are reported in wavenumber (cm^{-1}). High-resolution mass spectra (HRMS) were recorded on a VG-250S spectrometer with electron-impact spectra at 70 eV. Elemental analysis was conducted on a Perkin-Elmer 240 CHN analyzer by the analytical service in the Department of Chemistry at the University of Michigan, Ann Arbor. Melting points were recorded on a Laboratory Devices MEL-TEMP melting point apparatus with an uncorrected thermometer.

Solvents were freshly distilled prior to use. THF and diethyl ether were distilled from sodium and benzophenone ketyl under N_2. Pentane and hexane were distilled from sodium metal. Dibutyltin dihydride was prepared by reaction of dibutyltin dichloride with lithium aluminum hydride followed by vacuum distillation. Tricarbonyl tris(acetonitrile) manganese hexafluorophosphate and 2-phenyl-1,2-dihydro-1,2-oxastannole[15] were prepared according to literature procedures. All other reagents were purchased from the commercial vendors and were used as received or distilled if necessary. All reactions were conducted under an inert atmosphere of argon or in the glovebox under nitrogen unless otherwise specified.

Synthesis of 2,5-Dihydro-2-phenyl-1,2-oxaborole (9b). A solution of dichlorophenylborane (7.87 g, 50 mmol) in 25 mL of pentane was added via cannula technique to a solution of 2,2-dibutyl-2,5-dihydro-1,2-oxastannole (14.45 g, 50 mmol), prepared according to literature procedure, in 60 mL of pentane at −78 °C. Upon the addition, the white oxastannole slurry dissolved and the solution turned light brown. The reaction mixture was gradually warmed and stirred at room temperature overnight. The solvent was removed under reduced pressure, and the product was obtained via vacuum distillation (bp 35−38 °C at 0.025 Torr) with a yield of 5.95 g (82.6%) as a colorless liquid. ^{1}H NMR (C_6D_6, 400 MHz): δ 8.13 (m, 2H, ArH), 7.28 (m, 3H, ArH), 7.01 (d, 1H, $J = 8$ Hz, H_3), 6.48 (d, 1H, $J = 8$ Hz, H_4), 4.44 (m, 2 H, H_5). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 158.94 (C_3), 136.29, 132.12, 128.63, 78.85 (C_5). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00 (m, 2H, ArH), 7.64 (d, 1H, $J = 8$ Hz, H_3), 7.54−7.45 (m, 3H, ArH), 6.68 (d, 1H, $J = 8$ Hz, H_4), 4.98 (d, 2H, $J = 1.2$ Hz, H_5). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 158. 54 (C_3), 135.56, 131.67, 128.14, 78.82 (C_5). ^{11}B NMR (C_6D_6, 160.4 MHz): δ 46.5. HRMS (EI, m/z): calcd for $C_9H_9{}^{11}BO$ (M^+), 144.0746; found, 144.0739. Anal. Calcd for C_9H_9BO: C, 75.08; H, 6.30. Found: C, 74.72; H, 6.28.

Potassium 2-Phenyl-1,2-oxaborolide (6b). A solution of potassium bis(trimethylsilyl)amide (5.95 g, 41.3 mmol) in 35 mL of diethyl ether was added slowly via cannula to a solution of **9b** (9.11 g, 43.4 mmol) in 15 mL of diethyl ether at −78 °C. Upon completion of addition, the solution turned light yellow. The reaction mixture was kept at −78 °C for 1 h and then slowly warmed to room temperature and stirred for 4 h. The liquid was removed via cannula filtration, and the residue was washed with diethyl ether (3 × 5 mL) to obtain the product (6.46 g, 85.9%) as a light yellow powder. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.48 (m, 2H, ArH), 7.03 (m, 2H, ArH), 6.82 (m, 1H, ArH), 6.47 (t, 1H, $J = 1.6$ Hz, H_5), 6.11 (dd, 1H, $J = 1.6$ Hz, $J = 4.4$ Hz, H_4), 4.30 (d, 1H, $J = 4.4$ Hz, H_3). ^{13}C NMR (DMSO-d_6, 100.6 MHz): δ 130.85, 126.23, 126.59, 122.55, 118.78, 85.50 (br). ^{11}B NMR (DMSO-d_6, 160.4 MHz): δ 33.34. ^{1}H NMR (THF-d_8, 500 MHz): δ 7.61 (d, 2H, $J = 9.5$ Hz, ArH), 7.02 (t, 2H, $J = 9.0$ Hz, ArH), 6.84 (t, H, $J = 9.0$ Hz, ArH), 6.58 (s, 1H, H_5), 6.35 (d, 1H, $J = 4.5$ Hz, H_4), 4.50 (d, 1H, $J = 4.5$ Hz, H_3). ^{13}C NMR (THF-d_8, 100.6 MHz): δ 132.46, 128.72, 127.61, 124.44, 120.77, 84.19.

[η^5-Pentamethylcyclopentadienyl][η^5-2-phenyl-1,2-oxaborolyl]ruthenium(II) (11b). A 40 mL portion of THF was added to a mixture of potassium 2-phenyl-1,2-oxaborolide (0.728 g, 4.0 mmol) and $[Cp^*RuCl]_4$ (1.087 g, 4.0 mmol) at −78 °C with magnetic stirring. The mixture was stirred at −78 °C for 2 h and allowed to warm to and maintained at room temperature for 20 h. The solvent was removed under reduced pressure, and the residue was dried in vacuo. The solid residue was then extracted with pentane (100 mL). The product was obtained as amber crystals (1.06 g, 70%) by cooling the extracts to −30 °C and slowly removing the solvent by vacuum. Mp = 84.7 °C (dec). ^{1}H NMR (C_6D_6, 400 MHz): δ 7.84 (m, 2H, ArH), 7.32 (m, 2H, ArH), 7.22 (m, 1H, ArH), 6.31 (s, 1H, H_5), 4.64 (d, 1H, $J = 4.8$ Hz, H_4), 4.10 (d, 1H, $J = 4.8$ Hz, H_3), 1.61 (s, 15H, Cp*Me). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 132.79, 128.01, 127.69, 99.10, 85.32, 83.98, 11.30. ^{11}B NMR (C_6D_6, 160.4 MHz): δ 19.72. HRMS (EI, m/z): calcd for $C_{19}H_{23}{}^{11}BO^{102}Ru$ (M^+), 380.0885; found, 380.0886. Anal. Calcd for C_9H_9BO: C, 60.17; H, 6.11. Found: C, 59.77; H, 5.98.

Tricarbonyl[η^5-2-phenyl-1,2-oxaborolyl]manganese(I) (12b). THF (50 mL) was added to a mixture of potassium 2-phenyl-1,2-oxaborolide (1.288 g, 7.0 mmol) and $Mn(CO)_3(NCCH_3)_3$ PF_6 (3.0 g, 7.0 mmol) at −78 °C with magnetic stirring. The mixture was stirred at −78 °C for 2 h and allowed to warm to and maintained at room temperature for 12 h. The solvent was removed under reduced pressure, and the residue was dried in vacuo. The solid residue was then extracted with pentane (100 mL). The product was obtained by recrystallization from pentane at −30 °C as yellow crystals (1.25 g, 62.5%). Mp = 64 °C. IR (hexane, film): 2039, 1966, 1948 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.56 (m, 2H, ArH), 7.17 (m, 3H, ArH), 5.79 (s, 1H, H_5), 4.65 (d, 1H, $J = 4.8$ Hz, H_4), 3.60 (d, 1H, $J = 4.8$ Hz, H_3). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 222.43, 134.24, 131.31, 128.71, 102.98, 98.23, 65.78. ^{11}B NMR (C_6D_6, 160.4 MHz): δ 24.68. HRMS (EI, m/z): calcd for $C_{12}H_8{}^{11}BOMn$ (M^+), 281.9896; found, 281.9902. Anal. Calcd for $C_{12}H_8BMnO_4$: C, 51.12; H, 2.86. Found: C, 51.49; H, 2.86.

(*N,N*-Diisopropylamino)allyloxyvinylborane (8). A solution of *N,N*-diisopropylvinylboron chloride (21 g, 121 mmol) in 30 mL of THF was treated with a solution of lithium allyloxide (1.0 equiv) in 20 mL of THF at −78 °C. The mixture was stirred at −78 °C for 2 h and at 25 °C for 3 h. A white solid formed gradually. After filtration and removal of the solvent the residue was vacuum distilled to give the product as a clear colorless liquid (20.5 g, 87%), bp 32−34 °C at 0.05 Torr. ^{1}H NMR (C_6D_6, 400 MHz): δ 6.03 (dd, 1H, $J = 20.5$, 15.0 Hz, vinyl), 5.84 (m, 1H, vinyl), 5.34 (dq, 1H, $J = 15.4$, 2.2 Hz, vinyl), 5.04 (dq, 1H, $J = 10.6$, 1.8 Hz, vinyl), 135.7 (br, vinyl), 126.9 (vinyl), 113.7 (vinyl), 66.4 (CH_2O), 48.2 (NC), 44.2 (NC), 23.9 (Me), 22.9 (Me). ^{11}B NMR (C_6D_6, 115.5 MHz): δ 29.9. HRMS (EI, m/z): calcd for $C_{11}H_{22}{}^{11}BNO$ (M^+), 195.1794; found, 195.1785. Anal. Calcd for $C_{11}H_{22}BNO$: C, 67.72; H, 11.36; N, 7.18. Found: C, 67.54; H, 11.52; N, 7.01.

***N,N*-Diisopropyl-2-amino-2,5-dihydro-1,2-oxaborole (9a).** A solution of **8** (16.7 g, 85.6 mmol) in 120 mL of CH_2Cl_2 was added to a solution of bis(tricyclohexylphosphine)benzylidene

Table 1. Crystal and Data Collection Parameters for 11b and 12b

	11b	12b
empirical formula	$C_{19}H_{23}BORu$	$C_{12}H_8BMnO_4$
fw	379.25	281.93
temp,K	293(2)	150(2)
wavelength, Å	0.71073	0.71073
cryst syst	monoclinic	monoclinic
space group	*P*2(1)/*n*	*P*2(1)/*c*
a, Å	8.7654(13)	8.4249(7)
b, Å	14.136(2)	17.0274(14)
c, Å	13.820(2)	8.2670(7)
β, deg	94.583(4)	98.110(2)
V, Å^3, *Z*	1706.9(4), 4	1174.07(17), 4
calcd density, Mg/m^3	1.476	1.595
abs coeff, mm^{-1}	0.917	1.124
F(000)	776	568
cryst size, mm	0.36 × 0.12 × 0.12	0.74 × 0.72 × 0.36
limiting indices	$-11 \leq h \leq 11$, $-18 \leq k \leq 18$, $-18 \leq l \leq 18$	$-11 \leq h \leq 11$, $-22 \leq k \leq 22$, $-11 \leq l \leq 11$
no. of reflns collected/ unique	23 160/22 728	13 720/2900
abs corr	semiempirical fr equivalents	semiempirical fr equivalents
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/ params	22 728/0/206	2900/0/163
GOF on F^2	1.043	1.058
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0350, wR2 = 0.0784	R1 = 0.0225, wR2 = 0.0634
R indices (all data)	R1 = 0.0534, wR2 = 0.0830	R1 = 0.0236, wR2 = 0.0641
largest diff peak and hole, e/A^3	0.772 and −0.790	0.377 and −0.282

ruthenium(IV) dichloride (Grubb's catalyst) (1.4 g, 2 mol %) in 20 mL of CH_2Cl_2 at 25 °C for 10 h, after which the color had changed from purple-red to dark brown. The solvent was removed in vacuo at 0 °C, and the product (13.2 g, 92%) was obtained as a clear colorless liquid, bp 28 °C at 0.05 Torr. ^{1}H NMR (C_6D_6, 400 MHz): δ 6.78 (d, 1H, J = 7.7 Hz), 6.06 (d, 1H, J = 7.7 Hz), 4.40 (m, 2H), 3.64 (sept, 1H), 3.46 (sept, 1H, J = 6.6 Hz), 1.27 (d, 6H, J = 6.6 Hz), 1.09 (d, 6H, J = 6.6 Hz). ^{13}C NMR (C_6D_6, 100.5 MHz): δ 152.2 (C=C), 53.3 (CH_2O), 47.2 (NCH), 45.2 (NCH), 24.0 (CH_3), 23.3 (CH_3). ^{11}B NMR (C_6D_6, 115.5 MHz): δ 33.2. HRMS (EI, *m*/*z*): calcd for $C_9H_{18}{}^{11}BNO$, 167.1481; found, 167.1490. Anal. Calcd for $C_9H_{18}BNO$: C, 64.71; H, 10.86; N, 8.38. Found: C, 64.90; H, 10.78; N, 7.84.

Lithium *N*,*N*-Diisopropyl-2-amino-1,2-oxaborolide (6a). A solution of **9** (0.52 g, 3.11 mmol) in 12 mL of pentane was treated with a solution of t-BuLi (1.7 M, 1.8 mL) in pentane at −78 °C. The mixture was stirred at −78 °C for 1 h and at 25 °C for 15 min. A white solid formed gradually. After removal of the solvent and washing with cold pentane the residue was dried under vacuum to give the product as a light yellow powder (0.28 g, 53%). ^{1}H NMR (THF-d_8, 400 MHz): δ 6.2 (s, 1H, H_5), 6.04 (d, 1H, J = 4.8 Hz, H_4), 3.44 (sept, 2H, J = 6.6 Hz, NCH), 2.44 (d, 1H, J = 4.7 Hz, H_3), 1.11 (d, 12H, J = 6.6 Hz, Me). ^{13}C NMR (THF-d_8, 100.6 MHz): δ 122.0, 118.8, 58 (br, C(3)), 46.3 (NC), 23.9 (Me). ^{11}B NMR (THF-d_8, 115.5 MHz): δ 37.0.

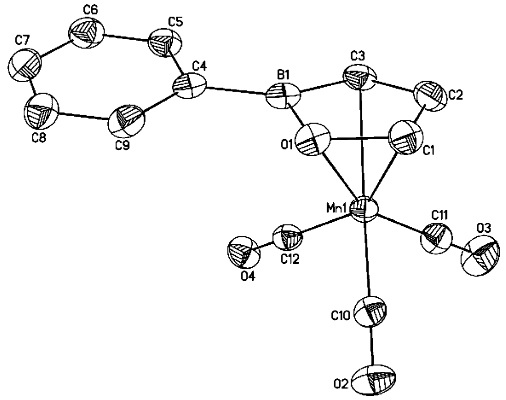

Figure 3. Solid-state structure of **12b** (ORTEP). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances (Å): B(1)−C(3), 1.514(2); B(1)−O(1), 1.456(2); C(1)−C(2), 1.392(2); C(2)−C(3), 1.427(2); C(1)−O(1), 1.404(2); B(1)−Mn(1), 2.301(2); C(1)−Mn(1), 2.057(2); C(2)−Mn(1), 2.154(1); C(3)−Mn(1), 2.210(1); O(1)−Mn(1), 2.111(1).

Single-Crystal X-ray Crystallography. Crystals of **11b** and **12b** suitable for X-ray diffraction were obtained by recrystallization from ether/hexane and pentane, respectively. Crystallographic and data collection parameters are collected in Table 1. ORTEP drawings of **11b** and **12b** showing the atom-numbering scheme used in the refinements are illustrated in Figures 2 and 3, respectively. Additional crystallographic data are available in the Supporting Information.

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Supporting Information Available: X-ray characterization of **11b** and **12b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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