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Intramolecular B−N Coordination in Boratabenzene Complexes

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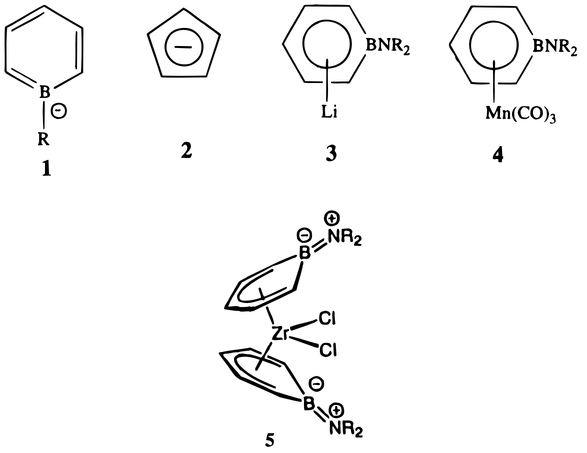
The reaction of 1-chloro-1-boracyclohexa-2,5-diene with (3-(dimethylamino)propyl)magnesium chloride followed by reaction with *tert*-butyllithium in ether affords lithium 1-(3-(dimethylamino)propyl)boratabenzene (**8**). The reaction of **8** with Mn(CO)$_3$(CH$_3$CN)$_3$PF$_6$ affords tricarbonyl[1-(3-(dimethylamino)propyl)boratabenzene]manganese(I) (**15B**). The crystal structure of **15B** shows that it exists in the intramolecularly B−N-coordinated form with a B−N bond distance of 1.716(5) Å. However in toluene-d_8 solution **15B** is in mobile equilibrium with its ring-opened isomer **15A**. Using ^{11}B NMR spectroscopy the equilibrium constants for **15B** → **15A** have been measured over the temperature range −35 to 48 °C, allowing evaluation of $\Delta H°$ (6.0 kcal/mol) and $\Delta S°$ (23 cal/mol K).

Introduction

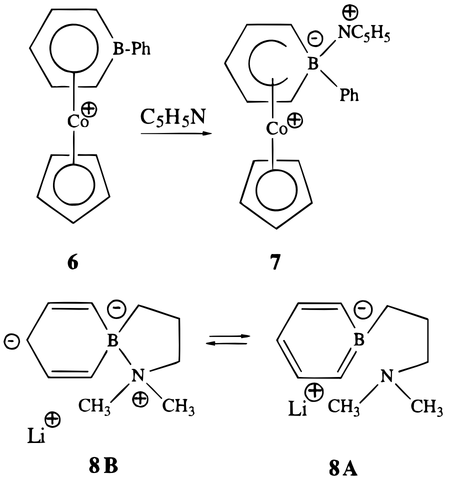
Although boratabenzenes (**1**) (Chart 1) have been known since 1970,[1,2] these aromatic anions have recently attracted renewed attention.[3−6a] A major interest is that these 6-π-electron ligands are good replacements for cyclopentadienyl (**2**) in important organometallic compounds.[6] However, unlike cyclopentadienyl, 1-substituted boratabenzenes can interact strongly with exocyclic substituents which can change the character of the ligand.[5]

In a recent study of aminoboratabenzenes we found that exocyclic B−N π-bonding is quite weak in the lithium complex **3**.[5] However B−N π-bonding increases in strength when the aminoboratabenzene is coordinated to an electron-withdrawing metal group. The strong acceptor Mn(CO)$_3$ removes electron density from the boratabenzene ring of **4**, allowing boron to accept π-electron density from the nitrogen lone pair. This results in a slip distortion of the metal away from boron. The extreme is reached in **5** where the highly electron withdrawing Zr(IV) is only η^5-coordinated to the five carbon atoms of each ring while there is very strong exocyclic B−N π-bonding.[6a]

Chart 1



Scheme 1



By analogy electron withdrawal by a coordinating metal should increase the Lewis acidity of boron. Indeed Herberich has demonstrated an enhanced Lewis acidity for the cationic boratabenzene complex **6**, which forms addition compound **7** by reaction with pyridine[7] (Scheme 1). In order to explore an intramolecular variant of this effect we have prepared metal derivatives of 1-(3-(dimethylamino)propyl)boratabenzene (**8**). B−N

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(2) (a) Ashe, A. J., III; Shu, P. *J. Am. Chem. Soc.* **1971**, *93*, 1804. (b) Ashe, A. J., III; Meyers, E.; Shu, P.; Von Lehmann, T.; Bastide, J. *J. Am. Chem. Soc.* **1975**, *97*, 6865.

(3) (a) Herberich, G. E.; Schmidt, B.; Englert, U.; Wagner, T. *Organometallics* **1993**, *12*, 2891. (b) Herberich, G. E.; Schmidt, B.; Englert, U. *Organometallics* **1995**, *14*, 471. (c) Herberich, G. E.; Englert, U.; Schmidt, M. U.; Standt, R. *Organometallics* **1996**, *15*, 2707.

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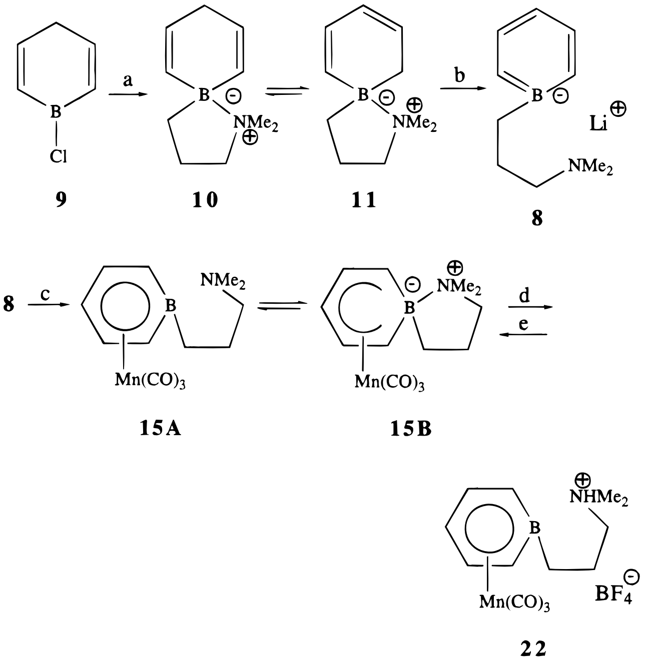
S0276-7333(96)00738-8 CCC: $14.00

Scheme 2. Synthesis of Compounds[a]



[a] Key: (a) $Me_2NCH_2CH_2CH_2MgCl$; (b) *tert*-BuLi; (c) $Mn(CO)_3(CH_3CN)_3PF_6$; (d) HBF_4; (e) CH_3SOCH_2Li/DMSO.

σ-bond formation was detected by ^{11}B NMR spectroscopy and by an X-ray structural determination.

Results and Discussion

Alkylation of 1-chloro-1-boracyclohexa-2,5-diene (**9**)[8] with (3-(dimethylamino)propyl)magnesium chloride affords **10** in 68% yield (Scheme 2). On standing for several hours at room temperature, **10** isomerizes to a 2:1 mixture of **10** and its conjugated isomer **11**. Although these compounds could not be separated, they are easily characterized by using their unambiguous ^1H and ^{13}C NMR spectra. The ^{11}B NMR chemical shifts for **10** and **11** are at δ −1.6 and −3.2, respectively. These values are far upfield from the chemical shift values of trivalent boranes, e.g. δ 52 for 1-methyl-1-boracyclohexa-2,5-diene (**12**),[2b] and are typical of those observed for four-coordinate boron.[10] They provide strong evidence that **10** and **11** have the assigned spiro structure.

Treating a mixture of **10** and **11** with *tert*-butyllithium in ether gave the lithium boratabenzene **8**, which was isolated as a white solid after removal of solvent. The ^1H, ^{11}B, and ^{13}C NMR chemical shift values for the ring atoms of **8** are compared with those of lithium 1-methylboratabenzene (**13**)[3b] and lithium 6,6-dimethylcyclohexadienide (**14**)[11] in Figure 1. The chemical shift values of **8** and **13** are virtually identical and are typical of lithium boratabenzenes.[3b,5] The ^{11}B NMR shift of **8** at δ 36.6 is far downfield from those of its conjugate acids **10** and **11** indicating that the pendant dimethylamino group is not coordinated to boron as in structure **8B**. It is reasonable to expect that the heterocyclohexadienide structure **8B** would show ^1H and ^{13}C NMR spectra similar to those of cyclohexadienide **14**. The marked divergence of the spectra of **8** and **13** from those of **14** conclusively demonstrates that the NMe_2 group is not coordinated to the boron of **8**.

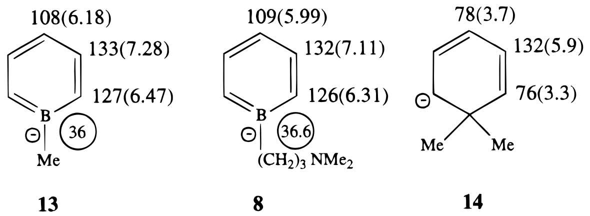


Figure 1. Comparison of the ^{13}C NMR, ^1H NMR (in parentheses), and ^{11}B NMR (circled) chemical shift values of **8** with **13** and **14**.

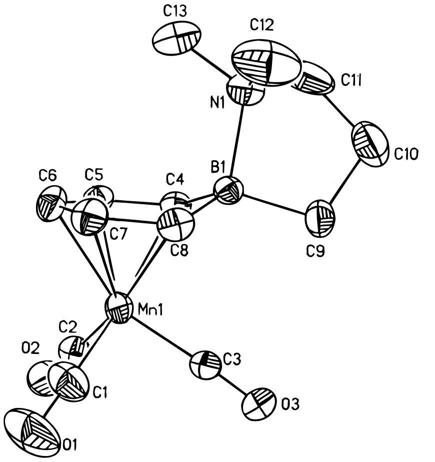


Figure 2. ORTEP drawing of the molecular structure of **15B**, with thermal ellipsoids at the 50% probability level.

The B−N σ-coordination in **10** and **11** should affect their acidity relative to 1-methylboracyclohexadiene (**12**) (pK_a < 12.5 in DMSO).[5] In DMSO the acidities of **10** and **11** have been bracketed between cyclopentadiene (pK_a = 18.0)[12] and 1,2,3-triphenylindene (pK_a = 15.2)[12] with an estimated value of 17.1 ± 0.7. Thus **10** and **11** are less acidic than **12** by at least 4.5 pK_a units. This diminished acidity must be due to the energetic cost of breaking the B−N σ-bond to form **8**.

The reaction of **8** with $Mn(CO)_3(CH_3CN)_3PF_6$ gave **15B** as yellow crystals in 49% yield. We have obtained an X-ray structure which indicates that the compound has the B−N ring closed form. The molecular structure of **15B** is illustrated in Figure 2.

The structure involves a $Mn(CO)_3$ unit which is η^5-coordinated to the five ring carbon atoms of the boratacyclohexadienyl unit. In this respect there is a very close resemblance to the structure of cyclohexadienyltricarbonylmanganese (**16**) (Chart 2).[13] In both **15B** and **16** the five coordinated carbon atoms lie in a common plane while the uncoordinated tetrahedral ring atoms lie above this plane (0.49 Å for **15B** and 0.64 Å for **16**) away from $Mn(CO)_3$. The intra-ring B−C bonds of **15B** (1.585, 1.595 Å) are much longer than 1.52 Å found in η^6-(1-phenylboratabenzene)$Mn(CO)_3$ (**17**).[14] The longer B−C distances are inconsistent with B−C π-bonding in **15B**.

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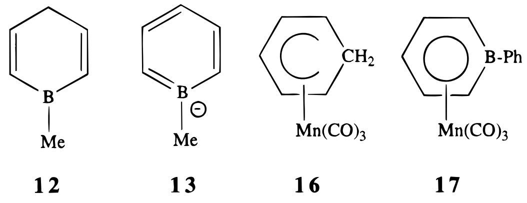
Chart 2



The length of the B−N bond **15B** is 1.716(5) Å. There are very few structural data on trialkylborane−trialkylamine adducts available for comparison. The B−N bond length of 1.698(10) Å for the adduct of trimethylamine with trimethylborane (**18**)[15] was determined in the gas phase by microwave spectroscopy. The B−N bond lengths of 1.746(3) and 1.764(2) Å were found from the X-ray structures of **20B** and **21B**, respectively.[16] Although these compounds have nearly the same (CCCBN)-ring, the longer B−N bonds may be a consequence of the greater steric bulk of the 9-BBN group. Indeed the increase in B−N bond lengths in the series **18** < **15B** < **20B** < **21B** parallels the increase in steric hindrance.

Although compound **15B** has the ring-closed structure in the solid state, the ^{11}B NMR spectra in toluene-d_8 indicate that **15B** is in mobile equilibrium with the ring-opened form **15A**. The ^{11}B NMR spectrum shows a single broad peak which is highly temperature dependent (range: δ -5.0 at −72 °C to δ 25.3 at 97 °C). The ^{1}H and ^{13}C NMR spectra are also temperature dependent, but the shifts are small. Since ^{11}B NMR chemical shifts values are very sensitive to the coordination number of boron,[10] it seems likely that isomer **15B** is the predominant form at low temperature, while isomer **15A** is preferentially populated at high temperature. The observed chemical shift represents a concentration-weighted average[17] of **15A** and **15B**, which are interconverting rapidly on the NMR time scale.

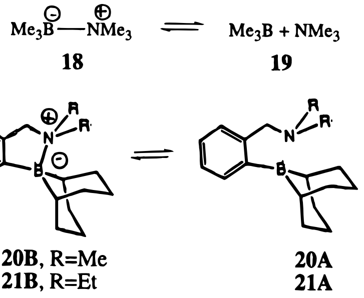
Treating a DMSO-d_6 solution of **15** with 1 equiv of fluoroboric acid converted it to its ammonium salt **22**, which re-forms **15** on addition of base. The ^{11}B NMR spectrum of **22** shows a signal for the ring boron at δ 26.6, which is a typical value for η^6-boratabenzene transition metal complexes.[1b] For example, **6** shows a signal at δ 23.4, while **17** shows a signal at δ 24.6.[1b] Since these chemical shift values are close to the signal observed for **15** at 97 °C, they provide additional evidence that **15A** is the high-temperature species. Similarly the ^{11}B NMR signal for **7** (δ −6.8) is close to the low-temperature signal for **15**,[6] assigned to **15B**. Assuming pure **15B** has δ −6.0 and pure **15A** has δ 27.0, the equilibrium constants for **15B** $\rightleftharpoons$ **15A** can be calculated (Table 1). The temperature dependence of K allows determination of $\Delta H° = 6.0$ kcal/mol and $\Delta S° = 22$ cal/mol K ($r = 0.998$).

It is useful to compare these thermodynamic functions with available data for dissociations of trialkylamine−trialkylborane adducts. For **18** in the gas phase $\Delta H° = 17.6$ kcal/mol and $\Delta S° = 46$ cal/mol K.[18] In this case the large positive entropy term is due to the increase in molecularity of the products. More comparable are data on the averaging of ^{1}H and ^{13}C NMR signals due to the exchange of diasterotopic groups of **20B** and **21B**[19] (Scheme 3). Oki and Toyota have argued that this process involves a rate-determining B−N bond dissociation followed by faster rotation about the N−C bond and recombination to re-form the B−N bond. In toluene-d_8 $\Delta H^‡ = 23.7(5)$, 18.9(5) kcal/mol and $\Delta S^‡ = 16.6(14)$, 14.9(16) cal/mol K for **20B** and **21B**, respectively.[19] These $\Delta S^‡$ values and those of other similar ring-opening reactions[20] indicate that our $\Delta S°$ value is appropriate for the reaction **15B** → **15A**.

Table 1. Equilibrium Constants (*K*) for 15B $\rightleftharpoons$ 15A in Toluene-d_8 in the Temperature Range 48 to −35 °C

T (°C)	obsd ^{11}B NMR δ	K	*T* (°C)	obsd ^{11}B NMR δ	K
48	21.7	0.19	2.2	10.3	1.02
37.4	19.7	0.28	−6.2	7.3	1.48
29	18.7	0.33	−15	4.6	2.11
17.2	15.1	0.56	−24	1.9	3.18
9.1	12.2	0.81	−34.7	−0.1	4.48

Scheme 3



The average value of the enthalpy of dissociation of trialkylamine−trialkylborane adducts (**18**, **20B**, **21B**) is 20 kcal/mol. This exceeds the $\Delta H°$ of **15B** → **15A** by 14 kcal/mol, indicating that the B−N bond of **15B** is unusually weak. The major factor weakening the B−N bond of **15B** must be the formation of the delocalized boratabenzene of **15A**. Therefore it seems reasonable to estimate that the delocalization energy of the Mn(CO)$_3$-coordinated boratabenzene of **15A** is approximately 14 kcal/mol. Since we were unable to detect the ring-closed isomer **8B** of **8A**, the delocalization energy of **8A** must be even greater than **15A**. These arguments confirm that boratabenzene has a large π-delocalization energy as had previously been determined from acidity data on **12**.[21]

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of nitrogen. Solvents were dried by using standard procedures. The IR spectra were recorded using a Nicolet 5 DXB FT-IR spectrometer. The mass spectra were determined by using a VG-70-S spectrometer, while the NMR spectra were obtained by using a Bruker WH-360, AM-300, or AM-200 spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were calibrated by using signals from the solvents referenced to Me$_4$Si. The ^{7}Li NMR spectra were referenced to an external 1 M aqueous solution of LiCl, while the ^{11}B NMR spectra were referenced to external BF$_3$·OEt$_2$. The combustion analyses were determined by the Analytical Services Department of the

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[17] For a similar case based on concentration differences see: Brown, H. C.; Soderquist, J. A. *J. Org. Chem.* **1980**, *45*, 846.

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[19] Toyota, S.; Oki, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1554.

[20] Toyota, S.; Oki, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1564 and the other papers in this series.

[21] Sullivan, S. A.; Sandford, H.; Beauchamp, J. L.; Ashe, A. J., III. *J. Am. Chem. Soc.* **1978**, *100*, 3737.

Department of Chemistry, University of Michigan. 1-Chloro-1-boracyclohexa-2,5-diene,[8] (3-(dimethylamino)propyl)magnesium chloride,[9] and $Mn(CO)_3(CH_3CN)_3PF_6$[22] were prepared by literature procedures. All other compounds are commercially available.

1-(3-(Dimethylamino)propyl)-1-boracyclohexa-2,5-diene (10) and 1-(3-(Dimethylamino)propyl)-1-boracyclohexa-2,4-diene (11). A solution of (3-(dimethylamino)propyl)magnesium chloride (10.0 mmol) in 20 mL of THF was added dropwise with stirring to a solution of 1-chloro-1-boracyclohexa-2,5-diene (1.10 g, 10.0 mmol) in 40 mL of pentane at −78 °C. The reaction mixture was allowed to warm to 25 °C and was stirred for 7 h, during which a white precipitate formed. The volatile materials were then removed in vacuum leaving a residue which was extracted with pentane (3 × 30 mL). After filtration through glass wool, solvent was removed in vacuum leaving **10** as a colorless oil (1.05 g, 64% yield).

^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.31 (br d, J = 12.8 Hz, *H*(3,5)), 5.83 (d, J = 12.7 Hz, *H*(2,6)), 2.79 (t, J = 7.4 Hz, CH_2N), 2.72 (m, *H*(4)), 2.32 (s, NMe_2), 1.84 (m, CH_2CH$_2$N), 0.65 (br m, BCH_2). ^{13}C NMR ($CDCl_3$, 90.6 MHz): δ 138 (br, *C*(2,6)), 134.8 (*C*(3,5)), 62.2 (*C*H$_2$N), 45.7 (N*Me*$_2$), 32.7 (*C(4)*), 21.0 (CH_2), 19 (br, *C*H$_2$B). ^{11}B NMR ($CDCl_3$, 115.5 MHz): δ −1.6. MS (EI) exact mass (*m/z*): calcd for $C_{10}H_{18}{}^{11}BN$, 163.1532; found, 163.1528.

On standing **10** equilibrates with **11** reaching an equilibrium ratio of 2.2/1 (**10**/**11**). NMR spectra for **11** may be assigned from spectra the mixture of **10** and **11**: ^{1}H NMR ($CDCl_3$, 360 MHz): δ 6.31 (dd, J = 13.5, 5.4 Hz, *H(3)*), 5.83 (m, H(4)), 2.34 (s, N*Me*$_2$), 1.68(m, CH_2) 1.27 (br m, CH_2B), other peaks obscured by signals of **10**. ^{13}C NMR ($CDCl_3$, 90.6 MHz): δ 137 (br, C(2)), 132.9, 131.3, 125.2 (C(3,4,5)), 61.5 (*C*H$_2$N), 45.2 (N*Me*$_2$), 20.6 (CH_2), 17 (br, B*C*H$_2$, *C*(6)?). ^{11}B NMR ($CDCl_3$, 115.5 MHz): δ −3.2.

(1-(3-(Dimethylamino)propyl)boratabenzene)lithium (8). A solution of *tert*-butyllithium (4.72 mmol) in 2.8 mL pentane was added dropwise with stirring to a solution of **10** and **11** (0.77 g, 4.722 mmol) in 12 mL of ether at −78 °C. On warming to 25 °C the initially colorless solution changed to orange. The solvent was removed under high vacuum leaving a whitish solid which was washed with pentane (2 × 10 mL) affording **8** as a white solid (0.56 g, 70%).

^{1}H NMR (THF-d_8, 300 MHz): δ 7.11 (dd, J = 10.2, 7.0 Hz, *H(3,5)*), 6.31 (d, J = 10.2 Hz, *H(2,6)*), 5.99 (t, J = 6.9 Hz, H(4)); 2.25 (t, J = 9.2 Hz, CH_2N), 2.13 (s, *NMe*$_2$), 1.65 (m, CH_2), 1.06 (t, J = 7.0 Hz, BCH_2). ^{13}C NMR (THF-d_8, 75.5 MHz): δ 133.2 (*C(3,5)*), 126 (br, C*(2,6)*), 108.6 (*C(4)*), 65.2, 46.3, 28.8, 20 br. ^{11}B NMR (C_6D_6, 115.5 MHz): δ 36.6. ^{7}Li NMR (C_6D_6, 140 MHz): δ −9.16.

Tricarbonyl(1-(3-(dimethylamino)propyl)boratabenzene)manganese(I) (15B). A solution of *tert*-butyllithium (1.93 mmol) in 1 mL of pentane was added to a solution of **10** and **11** (315 mg, 1.93 mmol) in 30 mL of ether at −78 °C. The mixture was allowed to warm to 25 °C with stirring over 1 h. The resulting solution was added to a suspension of $Mn(CO)_3(CH_3CN)_3PF_6$ (786 mg, 1.93 mmol) in 20 mL of ether at −78 °C. The mixture was allowed to warm to 25 °C and was stirred for 4 h. Removal of solvents in vacuum left a residue which was extracted with pentane (5 × 10 mL) affording a bright yellow solution. The solution was concentrated by partial removal of solvent in vacuum. On cooling to −78 °C 282 mg (49%) of **15B** was obtained as a bright yellow solid, mp 64−65 °C.

Table 2. Structure Determination Summary

Crystal Data	
compd	**15B**
empirical formula	$C_{13}H_{17}BNO_3Mn$
fw	301.03
cryst color and habit	orange rectangular blocks
cryst dimens	0.28 × 0.22 × 0.20 mm
cryst system	monoclinic
space group	*C*2/*c* (No. 15)
Z	8
unit cell dimens from 25 reflcns	(2θ > 20.2°)
a	25.847(5) Å
b	7.318(1) Å
c	18.252(3) Å
b	126.44(1)°
V	2777.3(9) Å^3
D(calc)	1.440 g cm^{-3}
F(000)	1248 e
linear abs coeff (μ)	9.52 cm^{-1}
Data Collection	
diffractometer	Siemens P4u, equipped with LT-2
radiation type	Mo K$\bar{\alpha}$ λ = 0.710 73 Å, *Lp* corrected, graphite monochromator
temp	178(2) K
scan type	ω scan
2θ scan range	5−52°
octants used	$\pm h,+k,+l$ (h, $\overline{31}$/25; k, $\bar{1}$/9; l, $\bar{1}$/22)
scan rate	2−20° per min, variable
scan width	0.7° below Kα_1 to 0.7° above Kα_2
bckgd/scan ratio	0.5
std reflcns	3 measd every 97 reflcns, random variations <4%
no. of data collcd	3626
no. of unique reflcns	2721, R_{int} = 0.0688
abs corr	empirical, XABS2[a]
rel max/min transm	1.214/0.864
Solution and Refinement	
system used	Siemens SHELXTL PLUS, SHELXL-93, VAXStation 3500
solution	direct methods
refinement method:	full-matrix least squares on F^2
function minimized	$\sum w(\lvert F_o^2 - F_c^2\rvert)^2$
H atoms	riding model, common *U*(H) refined
data/restraints/params	2719/0/203
final *R* indices ($I \geq 2\sigma I$)[b]	$R1 = 0.0532$, w$R^2 = 0.1516$
R indices (all data)[b]	$R1 = 0.0650$, w$R^2 = 0.1578$
GOF	1.099
mean shift/error	<0.001
max shift/error	0.001
secondary extinction	no corr applied
resid electron density	+1.29/−0.62 e/Å^3

[a] XABS2, An empirical absorption correction program. Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53−56. [b] $R1 = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$; w$R^2 = [\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)^2]^{1/2}$; $w^{-1} = [\sigma^2(F_o)^2 + (0.0928P)^2 + 4.20P]$, $P = [\max(F_o^2,0) + 2F_c^2]/3$.

^{1}H NMR (C_6D_6, 300 MHz): δ 5.03 (dd, J = 9.3, 7.3 Hz, *H(3,5)*), 4.46 (t, J = 7.3 Hz, *H(4)*), 3.36 (d, J = 9.3, *H(2,6)*), 2.11 (m, CH_2N), 1.73 (s, NMe$_2$), 1.61 (m, CH_2), 1.27 (m, BCH_2). ^{13}C NMR (C_6D_6, 75.4 MHz): δ 222.0 (*CO*), 107.9 (*C(3,5)*), 84 (br, *C(2,6)*), 80.7 (*C(4)*), 62.3 (CH_2N), 45.0 (N*Me*$_2$), 24.5 (CH_2), 17 (br, BCH_2). ^{11}B NMR (toluene-d_8, 115 MHz): 25.3 (T = 97 °C), 18.7 (T = 27 °C), −5.0 (T = −72 °C). IR (KBr) (ν(CO)): 2002, 1913, 1897 cm^{-1}. IR (hexane) ν(CO): 2037, 1961, 1942 cm^{-1}. MS (EI) exact mass (*m/z*): calcd for $C_{13}H_{17}{}^{11}BMnNO_3$, 301.0682; found, 301.0681. Anal. Calcd for $C_{13}H_{17}BMnNO_3$: C, 51.87, H, 5.69, N, 4.65. Found: C, 52.03, 51.80; H, 5.72, 5.49; N, 4.58, 4.64.

Tricarbonyl(1-(3-(dimethylammonio)propyl)boratabenzene)manganese(I) Tetrafluoroborate (22). To a solution of **15B** (30 mg, 100 μmol) in 400 μL of DMSO-d_6 in an NMR tube was added 1 equiv of fluoroboric acid (14 μL, 100 μmol, 54% in Et_2O) at 25 °C. The NMR spectra showed quantitative formation of the salt. ^{1}H NMR (DMSO-d_6, 360 MHz): δ 9.17 (br, NH), 6.22 (dd, J = 8.6, 6.0 Hz, *H(3,5)*), 5.74 (t, J = 5.6 Hz, *H(4)*), 4.30 (d, J = 9.1 Hz, *H(2,6)*, 3.07 (m, CH_2N), 2.77 (d, J = 4.7 Hz, HN*Me*$_2$), 1.77 (m, CH_2), 1.10 (t, J = 9.0 Hz, CH_2B). ^{13}C NMR (DMSO-d_6, 90 MHz): δ 221.2 (CO), 110.1 (*C(3,5)*), 90 (br, *C(2,6)*), 83.9 (*C(4)*), 59.1 (*C*H$_2$N), 42.0 (N*ME*$_2$), 21.2 (CH_2), 14 (br, CH_2). ^{11}B NMR (3:1 C_6D_6/DMSO-d_6, 115.5 MHz): δ 26.6, 0.

A solution of (dimsyl-d_5)-lithium in DMSO-d_6 was prepared by adding 0.6 mL of *n*-butyllithium (2.5 M in hexane) to DMSO-d_6 (1.5 mL) at 25 °C followed by removal of hexane in

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(22) Reimann, R. H.; Singleton, E. *J. Chem. Soc., Dalton Trans.* **1974**, 808.

vacuo. This solution was added in portions to the ammonium salt above. The ^{1}H-NMR spectrum was observed after each addition. Initially the solution showed broad peaks at frequencies intermediate between those of **15B** and **22**. Addition of 1 equiv of dimsyllithium afforded a solution of **15B**.

Measurement of the Equilibrium Constant (*K*) for 15B $\rightleftharpoons$ 15A. The ^{11}B NMR spectrum of **15** in toluene-d_8 was recorded at approximately 10 °C intervals over the range $T = 97$ to -72 °C. A plot of the chemical shift δ_{obs} vs $1/T$ K showed that at high and low temperature δ_{obs} approached asymptotic values of δ 27 and -6, respectively. The equilibrium constants were set equal to $(27 - \delta_{\mathrm{obs}})/(6 + \delta_{\mathrm{obs}})$. Only values $0.05 < K < 5$ were used to find $\Delta H°$ and $\Delta S°$.

Relative Acidities in DMSO-d_6. (a) 10, 11, and CpLi. In each of the three NMR tubes a mixture of **10** and **11** (10 mg, .06 mmol) was dissolved in 0.5 mL of dry DMSO-d_6. Small variable amounts of CpLi (10−15 mg, 0.14−0.21 mmol) were added to each tube. The ^{1}H NMR spectra were recorded initially and after 18 h showing equilibration between CpLi, CpH, **10**, **11**, and **8**. The relative concentrations were determined by integration of appropriate signals.

(b) 10, 11, and (1,2,3-triphenylindenyl)lithium. In the same manner as above the concentrations were determined by ^{1}H NMR.

X-ray Structure Determination. Crystals of **15B** suitable for X-ray diffraction were obtained by recrystallization from pentane. Crystallographic data are collected in Table 2. An ORTEP plot of the molecular structure of **15B** showing the numbering scheme used in refinement is illustrated in Figure 2. Table 3 gives the more important distances and bond angles for non-hydrogen atoms. A list of observed and calculated structural factors is available from A.J.A. on request.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 15B

Mn(1)−C(2)	1.791(4)	N(1)−C(12)	1.479(6)
Mn(1)−C(1)	1.792(4)	N(1)−C(13)	1.508(6)
Mn(1)−C(3)	1.797(4)	N(1)−B(1)	1.716(5)
Mn(1)−C(6)	2.125(4)	B(1)−C(8)	1.585(5)
Mn(1)−C(5)	2.153(3)	B(1)−C(4)	1.595(5)
Mn(1)−C(7)	2.160(3)	B(1)−C(9)	1.635(5)
Mn(1)−C(8)	2.254(4)	C(4)−C(5)	1.399(5)
Mn(1)−C(4)	2.267(3)	C(5)−C(6)	1.423(5)
O(1)−C(1)	1.154(5)	C(6)−C(7)	1.420(5)
O(2)−C(2)	1.163(5)	C(7)−C(8)	1.400(5)
O(3)−C(3)	1.160(4)	C(9)−C(10)	1.545(6)
N(1)−C(11)	1.444(6)	C(10)−C(11)	1.624(9)

C(11)−N(1)−C(12)	114.9(4)	C(4)−B(1)−N(1)	110.2(3)
C(11)−N(1)−C(13)	109.3(4)	C(9)−B(1)−N(1)	98.1(3)
C(12)−N(1)−C(13)	104.1(4)	C(5)−C(4)−B(1)	121.7(3)
C(11)−N(1)−B(1)	104.0(3)	C(4)−C(5)−C(6)	121.3(3)
C(12)−N(1)−B(1)	109.9(3)	C(7)−C(6)−C(5)	119.2(3)
C(13)−N(1)−B(1)	115.0(3)	C(8)−C(7)−C(6)	121.2(3)
C(8)−B(1)−C(4)	103.5(3)	C(7)−C(8)−B(1)	121.7(3)
C(8)−B(1)−C(9)	118.1(3)	C(10)−C(9)−B(1)	107.1(3)
C(4)−B(1)−C(9)	116.2(3)	C(9)−C(10)−C(11)	105.4(4)
C(8)−B(1)−N(1)	110.7(3)	N(1)−C(11)−C(10)	100.5(4)

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Supporting Information Available: Tables of complete positional and *U* values and anisotropic thermal parameters of the non-hydrogen atoms for **15B** (3 pages). Ordering information is given on any current masthead page.

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