Organometallics **1996,** *15,* 387−393

Aminoboratabenzenes. An Evaluation of the Exocyclic B−N Interaction

Arthur J. Ashe, III,* Jeff W. Kampf, Christian Müller, and Manuela Schneider

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109-1055

Received August 10, 1995[⊗]

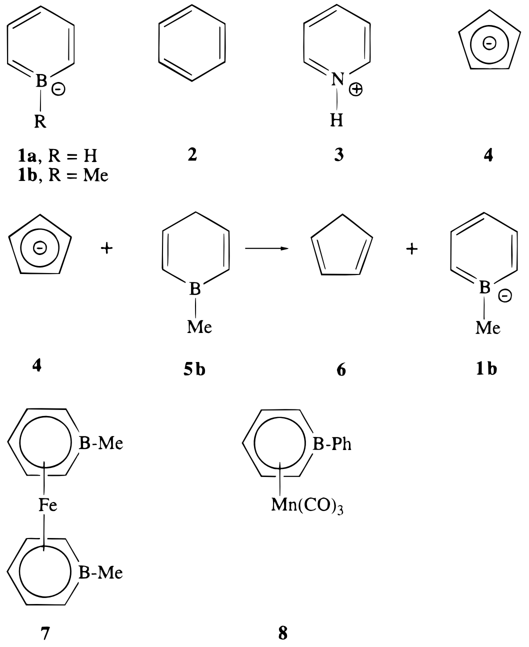
The reaction of 1-chloro-1-boracyclohexa-2,5-diene with diisopropylamine or *N*-benzyl-*N*-methylamine followed by reaction with LDA in THF affords lithium *N*,*N*-diisopropyl-1-aminoboratabenzene (**9b**) or lithium *N*-benzyl-*N*-methyl-1-aminoboratabenzene (**9c**), respectively. The reaction of **9b** with $FeCl_2$ affords bis(*N*,*N*-diisopropyl-1-aminoboratabenzene)iron (**18b**), while the reaction of **9b** or **9c** with $Mn(CO)_3(CH_3CN)_3PF_6$ affords tricarbonyl[*N*,*N*-diisopropyl-1-aminoboratabenzene)manganese (**19b**) or tricarbonyl-1-(*N*-benzyl-*N*-methylamino) boratabenzene manganese (**19c**), respectively. Photochemical displacement of CO by PMe_3 from **19b** affords dicarbonyl(trimethylphosphine) (*N*-benzyl-*N*-methyl-1-aminoboratabenzene)manganese (**20b**). The rates of bond rotation about the B−N bonds of **9c**, **18b**, **19b**,**c**, and **20b** have been determined using variable-temperature NMR spectroscopy. The rates depend markedly on the electron-withdrawing power of the coordinating metal group. The boron atom is weakly coordinated to manganese (B−Mn = 2.485(3) Å) and strongly bound to nitrogen (B−N = 1.417 (3) Å).

Introduction

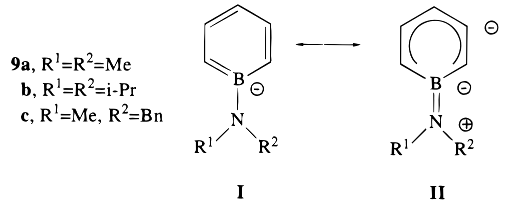
[1H]-Boratabenzene (**1a**) (see Chart 1) is an aromatic 6 π-electron ring which is isoelectronic with benzene (**2**) and pyridinium (**3**).[1−3] However since boratabenzenes are anionic, their chemistry is more analogous to that of cyclopentadienide (**4**). Thus 1-methylboracyclohexadiene (**5b**) is even more acidic than cyclopentadiene (**6**) in both the gas phase[4a] and in solution.[1b,4b] Similarly 1-substituted boratabenzenes can serve as anionic ligands toward transition metals.[1,3,5,6] A large number of complexes of both the sandwich (e.g. **7**)[3,5] and metal carbonyl (e.g. **8**) types are known. These complexes are closely analogous to the corresponding cyclopentadienyl metal complexes.

However boratabenzenes diverge from cyclopentadienyl in that exocyclic B-substituents may interact with boron to change the electronic character of the ring. Herberich et al. have argued that strong π-donation by the nitrogen lone pair in *N*,*N*-dimethyl-1-aminoboratabenzene (**9a**) saturates the boron and greatly attenuates the C−B ring delocalization.[1,7] In other words cyclohexadienyl resonance structure **II** dominates over aromatic resonance structure **I** (Scheme 1).

Chart 1. Structures 1−8



Scheme 1. Resonance Structures of Aminoboratabenzenes



In order to probe this question we have prepared and examined various metal derivatives of *N*,*N*-diisopropyl-1-aminoboratabenzene (**9b**) and *N*-benzyl-*N*-methyl-1-aminoboratabenzene (**9c**). The strength of exocyclic B−N π-bonding has been estimated by evaluating the barriers to rotation about these bonds. We propose that

---

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1995.

(1) (a) Herberich, G. E.; Greiss, G.; Heil, H. F. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 805. (b) Herberich, G. E.; Schmidt, B.; Englert, U. *Organometallics* **1995**, *14*, 471.

(2) (a) Ashe, A. J., III; Shu, P. *J. Am. Chem. Soc.* **1971**, *93*, 1804. (b) The ^{11}B NMR chemical shift reported for lithium 1-phenylboratabenzene in ref 2a is wrong. The correct value is $\delta = 32.2$.

(3) (a) Herberich, G. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A, Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 1, p 381. (b) Herberich, G. E.; Ohst, H. *Adv. Organomet. Chem.* **1986**, *25*, 199.

(4) (a) Sullivan, S. A.; Sandford, H.; Beauchamp, J. L.; Ashe, A. J., III. *J. Am. Chem. Soc.* **1978**, *100*, 3737. (b) Sandford, H. Ph.D. Dissertation, University of Michigan, 1979.

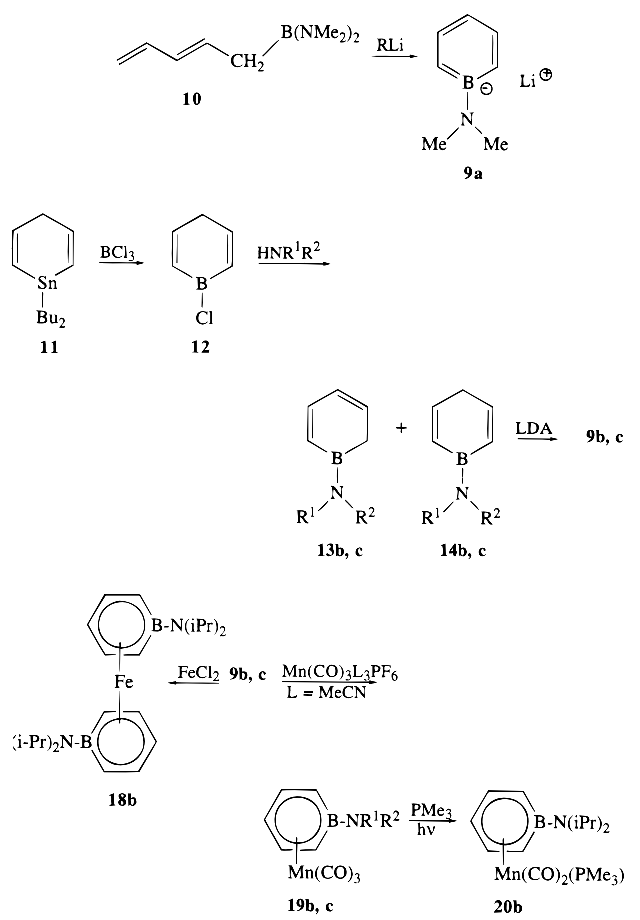
(5) Ashe, A. J., III; Meyers, E.; Shu, P., Von Lehmann, T.; Bastide, J. *J. Am. Chem. Soc.* **1975**, *97*, 6865.

(6) (a) Herberich, G. E.; Becker, H. J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 764. (b) Huttner, G.; Gartzke *Chem. Ber.* **1974**, *107*, 3786.

(7) Herberich, G. E.; Schmidt, B.; Englert, U.; Wagner, T. *Organometallics* **1993**, *12*, 2891.

0276-7333/96/2315-0387$12.00/0

Scheme 2. Synthesis of Compounds

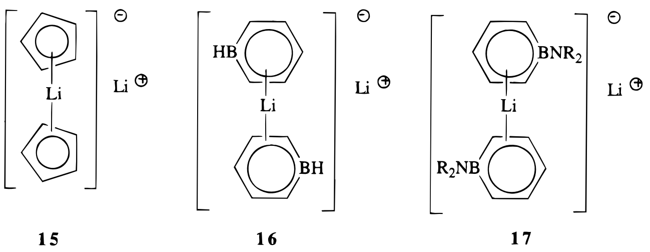


the relative importance of resonance structures **I** and **II** depends markedly on the electron-withdrawing power of the coordinating metal group.

Syntheses. Lithium *N*,*N*-dimethyl-1-aminoboratabenzene (**9a**) is easily prepared by the base-induced ring closure of bis(dimethylamino)-2,4-pentadienylborane (**10a**)[7] (Scheme 2). However since this method fails for bulky amine substituents, it was necessary to prepare **9b** and **9c** by the older organotin route.[2] The reaction of 1-chloroboracyclohexa-2,5-diene (**12**)[8] with excess *N*,*N*-diisopropylamine gives the corresponding aminoborane **14b**, which can be easily separated from insoluble hydrochloride of the amine. Treating **14b** with a trace of LDA in THF converts it to 1:1 mixture of **14b** and its conjugated isomer **13b**. On the other hand, the reaction of **12** with *N*-benzyl-*N*-methylamine always afforded a mixture of the conjugated and unconjugated isomers **13c** and **14c** in the ratio 55:45, respectively. The rather complicated ^{1}H NMR spectrum indicates that **13c** is a mixture of *E* and *Z* isomers. No attempt was made to separate the isomers.

Treating **14b** with LDA in THF-d_8 affords clean solutions of **9b**. Similar reaction of the mixed isomers **13c** and **14c** with LDA gives **9c**. The ^{1}H, ^{11}B, and ^{13}C NMR spectra of **9b**,**c** show typical boratabenzene patterns which closely resemble those reported for **9a.** The ^{7}Li NMR spectra show signals at −4.8 and −6.6 for **9b**,**c**, respectively. These chemical shift values are similar to those of the LiCp dimer **15**[9] ($\delta = -8.4$) (Chart 2) which has a bis-sandwich structure.[10] Since (1*H*-boratabenzene)lithium has a similar structure (**16**),[11] it seems highly likely that the THF solutions of **9a**−**c** also adopt this arrangement (**17**).

Chart 2



The reaction of **9b** with $FeCl_2$ affords the bis(boratabenzene)iron complex **18b** isolated as beautiful deep red plates. The compound is mildly oxygen sensitive in solution but air stable in crystalline form. Similarly the reaction of **9b** with $Mn(CO)_3(CH_3CN)_3\ PF_6$ affords **19b** as yellow crystals. Photochemical replacement of a carbonyl group by PMe_3 affords **20b**. In a similar manner **9c** was converted to **19c** for which we have obtained a crystal structure.

Results and Discussion

In general the B−N bonds of aminoboranes have double-bond character.[12] The barriers to rotation about B−N bonds in the range 10−24 kcal/mol have been evaluated using variable-temperature NMR spectroscopy.[13] The barriers depend upon both steric and electronic effects, and in particular π-donor substituents on boron lower the barriers by weakening the B−N π bond. Earlier work has involved examination of five-[14] and seven-membered[15] boron heterocycles with pendant amino groups. There is no prior report on the rotational barriers of aminoboratabenzenes.

We first examined **14c**. The ^{13}C NMR spectrum in $CDCl_3$ at 25 °C shows two signals (δ 147.88 and 147.75) for the carbon atoms β to boron. Thus B−N rotation must be slow on the NMR time scale. On warming of the sample to 122 °C, these signals coalesce from which a $\Delta G^\ddagger$ value of 20.7 kcal/mol can be derived in the usual manner. This value is only slightly higher than that obtained for the corresponding dihydroborepin ($\Delta G^\ddagger = 19.8$ kcal/mole).[15] Since the six-membered rings of the boratabenzenes must be similar in size to **14c**, this

---

[8] Maier, G.; Henkelmann; Reisenauer, H. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1065.

[9] (a) Cox, R. H.; Terry, H. W., Jr. *J. Magn. Reson.* **1974**, *14*, 317. (b) Paquette, L. A.; Bauer, W.; Sivik, M. R.; Bühl, M.; Feigel, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 8776.

[10] (a) Harder, S.; Prosenc, M. H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1744. (b) Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2168.

[11] Hoic, D. A.; Davis, W. M.; Fu, G. C. *J. Am. Chem. Soc.* **1995**, *117*, 8480.

[12] (a) Greenwood, N. N.; Thomas, B. S. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Ed.; Pergamon: Oxford, U.K., 1973; pp 925−935. (b) Pelter, A.; Smith, K. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, N. D., Eds.; Pergamon: Oxford, U.K., 1979; Vol. 3, pp 925−932.

[13] (a) Dewar, M. J. S.; Rona, P. *J. Am. Chem. Soc.* **1969**, *91*, 2259. (b) Imbery, D.; Jaeschke, A.; Friebolin, H. *Org. Magn. Reson.* **1970**, *2*, 271. Friebolin, H.; Rensch, R.; Wendel, H. *Org. Magn. Reson.* **1976**, *8*, 287. (c) Brown, C.; Cragg, R. H.; Miller, T. J.; Smith, D. O'N. *J. Organomet. Chem.* **1983**, *244*, 209 and earlier papers in this series.

[14] (a) Herberich, G. E.; Negele, M.; Ohst, H. *Chem. Ber.* **1991**, *124*, 25. (b) Siebert, W.; Full, R.; Edwin, J.; Kinberger, K.; Krüger, C. *J. Organomet. Chem.* **1977**, *131*, 1. (c) Herberich, G. E.; Ohst, H. *Chem. Ber.* **1985**, *118*, 4303. (d) Herberich, G. E.; Englert, U.; Hostalek, M.; Laven, R. *Chem. Ber.* **1991**, *124*, 17.

[15] Ashe, A. J., III; Klein, W.; Rousseau, R. *J. Organomet. Chem.* **1994**, *468*, 21.

barrier height should be an appropriate model for the B−N barrier without the electronic effects of boratabenzene.

At ambient temperature THF-d_8 solutions of **9c** show ^{1}H and ^{13}C NMR spectra with single signals for CH(2)/CH(6) and for CH(3)/CH(5). Thus B−N rotation must be fast on the NMR time scale. Cooling the solution of **9c** to −87 °C caused the signal for C(3)/C(5) to separate (δ 135.07, 134.85). T_c was at −72 °C from which a value of $\Delta G^\ddagger = 10.1$ kcal/mol can be derived. We believe that this nonequivalence is the consequence of slow B−N rotation, although the possibility that there may be slow exchange between different aggregations of the lithium salt cannot be excluded. However the observation that the N−CH$_3$ and N−CH$_2$ signals do not simultaneously separate makes the latter explanation less likely.

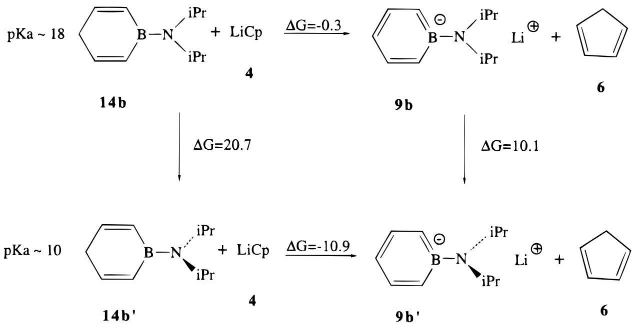
There is greater than a 10 kcal/mol decrease in the B−N π bonding in the boratabenzene (**9c**) compared with the boracyclohexadiene (**14c**). This indicates that incorporation of the boron atom into the aromatic boratabenzene ring greatly diminishes its ability to form an external π-bond to nitrogen.

The B−N π bonding in aminoboratabenzenes should affect the acidity of the corresponding boracyclohexadienes. Prior qualitative observations indicate that **5b** is a stronger acid than cyclopentadiene in THF[4b] and in water.[1b] However there are no prior measurements of the acidity of an aminoboracyclohexadiene.

We have chosen to measure the pK_a of **14b** in DMSO because of the large amount of comparable acidity data available in this solvent.[16] Treating a DMSO-d_6 solution of **14b** with 1 equiv of lithium cyclopentadienide gives a complicated mixture of **4**, **6**, **9b**, **13b**, and **14b** which can be analyzed by H NMR spectroscopy. On the basis of the pK_a(DMSO) = 18.0 for cyclopentadiene,[16] pK_a(DMSO) = 17.7 and 17.8 for **13b** and **14b**, respectively. Thus **13b** and **14b** are nearly equivalent in acidity to cyclopentadiene. On the other hand, **5b** is a much stronger acid. Treating **5b** in DMSO with either **4** or **9b** quantitatively converts it to **1b**. Similarly treating a DMSO solution of **5b** with 1 equiv of the much weaker base lithium pentaphenylcyclopentadienide converts it to **1b** and 1,2,3,4,5-pentaphenylcyclopentadiene (pK_a(DMSO) = 12.5).[16]

The data for the acidity of **14b** can be combined with the B−N rotational data for **14c** and **9c** in a self-consistent manner. (It will be assumed that the B−N rotational barriers are the same for **9b**,**c** and for **14b**,**c**.) The structure of the transition states for B−N rotation of aminoboranes have been evaluated computationally.[17] Relative to the planar aminoboranes the major changes involve a 90° rotation about the B−N bond, a lengthening of that bond, and pyramidalization of the nitrogen. Since the nitrogen lone pair is now orthogonal to the boron p_z orbital, π-bonding is absent. The transition states for B−N rotation of **14b** and **9b** are indicated as structures **14b′** and **9b′**, respectively. Scheme 3 illustrates the application of a Hess's law cycle to the acid−base reactions of **9b**, **9b′**, **14b**, and **14b′**. It can be seen that the pK_a(DMSO) of **14b′** is 10.2. Thus **14b′** is a considerably stronger acid than **14b**.

Scheme 3. Hess's Law Cycle for B−N Rotation and Acidity of *N,N*-Diisopropylaminoboracyclohexadiene with ΔG Values Expressed in kcal/mol



Since **5b** like **14b′** lacks π-bonding to the exocyclic substituent, its acidity should be similar. Indeed the experimental observation that **5b** is a stronger acid than pentaphenylcyclopentadiene indicates that its pK_a (<12.5) must approximate that of **14b′**. This result provides strong evidence that the B−N π-bonding of **9b** is much weaker than in its conjugate acid (**14b**).

It was also of interest to examine the B−N rotational barriers of transition metal coordinated boratabenzenes. The ^{1}H and ^{13}C NMR spectra of **19c** in CDCl$_3$ at ambident temperature show nonequivalence of H(2)/H(6) and C(3)/C(5). The carbon signals (δ 109.22, 108.97) coalesce at 51.5 °C indicating a B−N barrier of 16.6 kcal/mole. Thus coordination of the aminoboratabenzene moiety to the Mn(CO)$_3$ group in **19c** considerably enhances the barrier relative to the lithium salt.

It is particularly interesting to compare the behavior of **19c** with **19b**. In **19b** slow B−N rotation makes the pairs of methyl groups diastereotopic. The ^{1}H and ^{13}C NMR spectra in CD$_2$Cl$_2$ recorded at ambident temperature show two sets of nonequivalent methyl signals. On heating of the sample, the carbon signals (δ 22.79, 22.72) coalesce at 57 °C indicating a barrier height of 17.5 kcal/mole. Since this barrier is virtually identical to that found for **19c**, it is unquestionably due to B−N rotation. The similarity in values for **19b**,**c** show that there are no large steric differences in the requirements for rotation of the BN(i-Pr)$_2$ and BNMeBn groups. This observation seems particularly important since there are considerable data on interconversion of diastereotopic methyls of BN(i-Pr)$_2$ groups in other boron ring systems.[14] Thus our BNMeBn data can be placed in a broader context.

Cooling **19b** below −58 °C causes additional changes in the spectrum. The signals for C(2)/C(6), C(3)/C(5), and NCH split into two signals each while the methyl signals split into four peaks. This low-temperature process is likely due to restricted N−C rotation in the N(i-Pr)$_2$ group. In a number of similar cases it has been found that geminal isopropyl groups lock in a "gear mesh" fashion which restricts rotation.[18] The barriers for degearing are usually found in the range of 10−15 kcal/mole. Using the CH signals (δ 46.78, 42.65) which coalesce at −23.6 °C, a barrier of $\Delta G^\ddagger = 11.1$ kcal/mol is found.

Replacement of a carbonyl group of **19b** with the less electron-withdrawing PMe$_3$ is expected to make the Mn

---

(16) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

(17) (a) Dill, J. D.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3402. (b) Bentley, T. W. *J. Org. Chem.* **1982**, *47*, 60.

(18) Berg, U.; Liljefors, T.; Roussel, C.; Sandström, J. *Acc. Chem. Res.* **1985**, *18*, 80.

Table 1. Barriers to Rotation about B−N Bonds of Aminoboratabenzenes Determined by Variable-Temperature NMR Spectroscopy

compd	$\Delta G^{\ddagger}$ (kcal/mol)[a]	T_c (°C)	solvent
9c, $[(C_5H_5B)NMeBn]Li$	10.1	−72	THF-d_8
18b, $[(C_5H_5B)N(iPr)_2]_2Fe$	14.8	25	C_6D_6
20b, $[(C_5H_5B)N(iPr)_2]Mn(CO)_2PMe_3$	15.4	23	C_7D_8
19c, $[(C_5H_5B)NMeBn]Mn(CO)_3$	16.6	5	$CDCl_3$
19b, $[(C_5H_5B)N(iPr)_2]Mn(CO)_3$	17.5	57	CD_2Cl_2
14c, $C_5H_6BNMeBn$	20.7	122	$CDCl_3$

[a] ± 0.5 kcal/mol.

more negative in **20b**.[19] The decrease in the IR symmetric CO-stretching frequency of **20b** ($\nu = 1945$ cm^{-1}) from **19b** ($\nu = 2031$ cm^{-1}) confirms that the Mn group is less electron-withdrawing from the ring.[19b] We had also hoped that the small phosphine would minimize steric changes. The B−N rotational barrier was evaluated by observing coalescence of the signals for diastereotopic methyl groups (δ 1.322, 1.291) in ^{1}H NMR spectrum of a toluene-d_8 solution of **20b**. Coalescence at 23 °C gave $\Delta G^{\ddagger} = 15.4$ kcal/mol. There is a 2.1 kcal/mol difference between the barriers of **19c** and **20c**. Clearly electron-withdrawal by the metal group increases the B−N barrier.

Finally we have examined the B−N rotational barrier in **18b**. The diastereotopic methyl groups of **18b** show only single signals in both ^{1}H and ^{13}C NMR spectra when the spectra are recorded from $CDCl_3$ solution. However two different methyl signals (δ 1.285, 1.217) are observed in ^{1}H NMR spectrum of benzene solutions at 15 °C. Coalescence at 25 °C gives a barrier of 14.9 kcal/mole. The decrease in the barrier height of **18b** relative to **19b** is consistent with a smaller electron-withdrawal by the iron atom than by the $Mn(CO)_3$. This order is analogous to the change from Cp_2Fe to $CpMn(CO)_3$.[20]

In summary, the electron donation by the pendant amino substituent of boratabenzenes seems to depend markedly on the electron-withdrawing power of the coordinating metal. In the contact ion pairs of the lithium salts **9a-c** the metal is a rather poor acceptor. Hence the acceptor capacity of the boron atoms is saturated by the electron rich carbon atoms.[21] The resulting low π-bond character of the B−N bond is evidenced by the relative long B−N bond length of **9a** found by Herberich et al.[7] and the low B−N rotational barrier of **9c**. In contrast the strong acceptor ability of the $Mn(CO)_3$ group of **19b**,**c** removes electron density from the ring. The boron atom is now able to accept the electron pair proffered by the pendant nitrogen. The resulting high π-bond character of the B−N bond is evidenced by the high B−N rotational barriers of **19b**,**c**. The less electron-withdrawing $Mn(CO)_2PMe_3$ group of **18b** and $FeC_5H_5B(i\text{-}Pr)_2$ group of **20b** result in the observed lower B−N barriers. See Table 1.

Structure. It was of considerable interest to obtain a crystal structure of **19c**. Although there are a number of structures of transition metal complexes of boratabenzenes, e.g. **8**,[3] in no case do the boratabenzenes bear as strong a donor as in **19c**. A crystal structure has recently been reported for the TMEDA-stabilized lithium salt of **9a**.[1b] It seems probable that the aminoboratabenzene moiety of **9a** is similar to that of **9c**. Therefore a comparison of **9a** and **19c** should show the changes effected by complexation.

Table 2. Summary of Structure Determination for 19c

Crystal Data	
empirical formula	$C_{16}H_{15}BNO_3Mn$
fweight	335.04
cryst color and habit	yellow, flat needle
cryst dimens	0.62 × 0.22 × 0.44 mm
cryst system	monoclinic
space group	$P2_1/n$ (No. 14)
Z	4
unit cell dimens from 28 reflcns (10.2° ≤ 2θ ≤ 25.0°)	
a	9.432(1) Å
b	15.227(2) Å
c	10.688(1) Å
β	99.42(1)d
V	1514.3(3) Å^3
D(calc)	1.470 g cm^{-3}
F(000)	688 electrons
linear abs coeff (m)	8.81 cm^{-1}
Data Collection	
diffractometer	Siemens P4U, equipped with LT-2
radiation type	Mo $K\bar{\alpha}$, $\lambda = 0.710\ 73$ Å, Lp corrected, graphite monochromator
temp	178(2) K
scan type	$\theta/2\theta$ scan
2θ scan range	5−52°
octants used	$\pm h,+k,\pm l$ (h, $\bar{1}$/11, k, $\bar{1}$/18; l, $\bar{1}\bar{3}$/13)
scan rate (in ω)	3−20 deg per min, variable
scan width	0.55° below $K\alpha_1$ to 0.55° above $K\alpha_2$
bckgd scan ratio	0.5
std reflcns	3 measd every 97 reflcns, random variations <2%
no. of data collcd	3945
no. of unique reflcns	2969, $R_{int} = 0.0356$
abs corr	empirical
rel max/min transm	0.821/1.332
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	individual isotropic refinement
data/restraints/params	2967/0/259
final R indices ($I \geq 2\sigma(I)$)[a]	$R1 = 0.0395$, w$R2 = 0.1046$
R indices (all data)	$R1 = 0.0471$, w$R2 = 0.1081$
GOF	0.979
mean shift/error	<0.001
max shift/error	<0.001
secondary extinction	1 reflcn excluded from refinement
residual electron density	+0.355/−0.752 e/Å^3

[a] $R1 = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$; w$R2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w^{-1} = [\sigma^2(F_o)^2 + (0.0718P)^2$, $P = [\max(F_o^2,0) + 2F_c^2]/3$.

A crystal of **19c** suitable for X-ray diffraction was obtained by recrystallization from pentane. Crystal data and data collection and refinement parameters are summarized in Table 2. An ORTEP plot of the molecular structure of **19c** which shows the numbering scheme used in the refinement is illustrated in Figure 1. Table 3 gives the positional values, while Table 4 gives the more important bond distances and angles for non-hydrogen atoms.

---

[19] (a) Le Plouzennec, M.; Le Moigne, F.; Dabard, R. *J. Organomet. Chem.* **1977**, *132*, 409. (b) Morris, R. H.; Earl, K. A.; Luck, R. L.; Lazarowch, N. J.; Stella, A. *Inorg. Chem.* **1987**, *26*, 2674.

[20] Watts, W. E. In *Comprehensive Organometallic Chemistry*, Vol. 8 Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 8, p 1016.

[21] For discussion of similar effects in aminoborirenes see: Budzelaar, P. H. M.; Kos, A. J.; Clark, T.; Scheyler, P. v. R. *Organometallics* **1985**, *4*, 429.

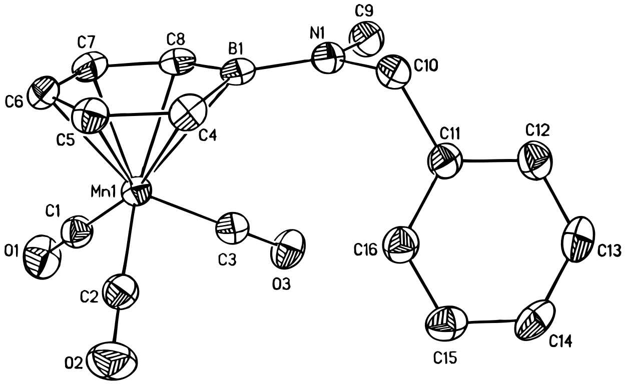


Figure 1. ORTEP drawing of the solid-state structure of **19c**, with thermal ellipsoids at the 50% probability level.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotopic Displacement Parameters ($Å^2 \times 10^3$) for 19c

	x	*y*	*z*	*U*(eq)[a]
Mn(1)	2477(1)	262(1)	1915(1)	22(1)
O(1)	2700(2)	481(1)	−783(2)	47(1)
O(2)	−406(2)	1065(1)	1489(2)	37(1)
O(3)	1305(2)	−1532(1)	1498(2)	37(1)
N(1)	3328(2)	−1215(1)	4626(2)	27(1)
B(1)	3533(3)	−433(2)	3959(3)	25(1)
C(1)	2631(3)	392(2)	272(2)	30(1)
C(2)	729(3)	760(2)	1638(2)	30(1)
C(3)	1742(3)	−833(2)	1668(2)	28(1)
C(4)	2671(3)	410(2)	4031(2)	26(1)
C(5)	3019(3)	1198(2)	3474(2)	27(1)
C(6)	4059(3)	1228(2)	2657(2)	28(1)
C(7)	4788(2)	459(2)	2407(2)	29(1)
C(8)	4510(2)	−355(2)	2936(2)	26(1)
C(9)	3953(3)	−2055(2)	4369(3)	36(1)
C(10)	2349(3)	−1270(2)	5557(2)	31(1)
C(11)	934(2)	−1722(2)	5049(2)	27(1)
C(12)	581(3)	−2532(2)	5517(2)	33(1)
C(13)	−706(3)	−2945(2)	5036(3)	37(1)
C(14)	−1661(3)	−2555(2)	4083(3)	36(1)
C(15)	−1329(3)	−1752(2)	3608(3)	34(1)
C(16)	−44(3)	−1338(2)	4084(2)	30(1)

[a] *U*(eq) is defined as 1/3 of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for 19c

Mn(1)−C(2)	1.794(2)	O(3)−C(3)	1.145(3)
Mn(1)−C(1)	1.797(3)	N(1)−B(1)	1.417(3)
Mn(1)−C(3)	1.809(3)	N(1)−C(9)	1.453(3)
Mn(1)−C(6)	2.152(2)	N(1)−C(10)	1.466(3)
Mn(1)−C(7)	2.178(2)	N(1)−C(4)	1.528(3)
Mn(1)−C(5)	2.189(2)	B(1)−C(8)	1.546(3)
Mn(1)−C(4)	2.250(3)	C(4)−C(5)	1.403(3)
Mn(1)−C(8)	2.251(2)	C(5)−C(6)	1.417(3)
Mn(1)−B(1)	2.485(3)	C(6)−C(7)	1.406(4)
O(1)−C(1)	1.148(3)	C(7)−C(8)	1.405(3)
O(2)−C(2)	1.154(3)		
B(1)−N(1)−C(9)	123.5(2)	C(4)−C(5)−C(6)	121.5(2)
B(1)−N(1)−C(10)	122.8(2)	C(5)−C(4)−B(1)	122.3(2)
C(9)−N(1)−C(10)	113.4(2)	C(7)−C(6)−C(5)	120.0(2)
N(1)−B(1)−C(4)	124.3(2)	C(7)−C(8)−B(1)	121.6(2)
N(1)−B(1)−C(8)	124.5(2)	C(8)−C(7)−C(6)	122.0(2)
C(4)−B(1)−C(8)	110.8(2)		

The structure of **19c** shows the aminoboratabenzene ligand η^6-coordinated to the $Mn(CO)_3$ unit in a manner similar to that shown by the phenyl compound **8**.[6] The corresponding ring C−C and B−C bond lengths are identical within experimental error. The major difference between the two compounds is that the Mn−B distance is 0.1 Å longer in **19c** (2.48 Å vs 2.38 Å). Since the corresponding Mn−C distances are essentially the same, the B atom is markedly displaced away from Mn out of the ring plane by 0.18 Å. The ring is folded along atoms C(4)−C(8) so that the plane of the five carbon atoms intersects the C(4)BC(8) plane at 12°. Although similar distortions are found in the structures of most complexed boron heterocycles,[3] the boron displacement is larger than in other (boratabenzene) metal complexes. Clearly the boron atom of **19c** is only weakly coordinated to the metal.

Heterocycle−$M(CO)_3$ complexes show a strong preference for conformations in which carbonyl groups eclipse the more positive weaker coordinated atoms.[22] In almost all cases of complexed boron heterocycles one of the carbonyl groups eclipses a boron atom.[3] However the conformation that **19c** populates in the solid state shows the $Mn(CO)_3$ group displaced from perfect eclipsing by 15° toward the NMe group. It seems likely that this displacement is due to the unsymmetrical nature of the pendant group.

Comparison of the boratabenzene rings of **9a** and **19c** shows that the C−C and C−B bond lengths uniformly lengthen by 0.02 Å on complexation. This suggests a rather even removal of electron density from the boratabenzene by $Mn(CO)_3$. The exocyclic B−N bond shrinks by 0.03 Å on complexation. The B−N distance of **19c** (1.417 Å) is only slightly larger than the usual values found for aminoboranes (1.41 Å).[23] Thus the π-bond character of the B−N bond in **19c** is normal. On the other hand, the rather long B−N bond of **9a** (1.448 Å) suggests that it has only weak π-bond character.[7] Thus the structural comparison of **9a** with **19c** is consistent with the higher B−N rotational barrier found for **19c** than for **9c**.

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 either a Bruker WH-500, WH-360 or AM-300 spectrometer. The ^1H NMR and ^{13}C NMR spectra were calibrated by using signals from the solvents referenced to Me_4Si. The ^7Li NMR spectra were referenced to an external 1 m aqueous solution of LiCl, while the ^{11}B NMR spectra were referenced to external $BF_3{\cdot}OEt_2$ and the ^{31}P NMR spectrum was referenced to 85% H_3PO_4. The combustion analyses were determined by the Analytical Services Department of the Department of Chemistry, University of Michigan.

***N,N*-Diisopropyl-1-aminoboracyclohexa-2,5-diene (14b).** Diisopropylamine (0.58 g, 5.7 mmol) was added dropwise with stirring to a solution of 1-chloroboracyclohexa-2,5-diene (0.32 g, 2.85 mmol) in 15 mL of pentane at 25 °C. Filtration and removal of solvent in vacuo gave 0.47 g (93%) of **14b** as an air-sensitive colorless oil. Attempts to distill **14b** lead to decomposition.

^1H NMR ($CDCl_3$, 360 MHz): δ 6.81 (br dd, $J = 12.8$, 3 Hz, *H(3,6)*, 6.44 (dd, $J = 12.8$, 1.8 Hz, *H(2,6)*, 3.81 (sept, $J = 6.8$ Hz, *NCH*), 2.96 (m, *H(4)*), 1.21 (d, $J = 6.8$ Hz, CH_3). ^{13}C NMR ($CDCl_3$, 76.5 MHz): δ 145.7(*C(3,5)*, 135.1 (br, *C(2,6)*), 46.7 (*NCH*), 34.1 (C(4)), 23.6 (CH_3). ^{11}B NMR ($CDCl_3$, 115.6 MHz): δ 39.3. MS(EI) [*m/z* (intensity)]: 177(23, M^+, calcd

---

(22) (a) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546. (b) Albright, T. A.; Hoffmann, R. *Chem. Ber.* **1978**, *111*, 1578. (c) Albright, T. *Acc. Chem. Res.* **1982**, *15*, 149.

(23) Paetzold, P. *Adv. Inorg. Chem.* **1987**, *31*, 123.

for $C_{11}H_{20}BN$), 162 (100). MS(EI) exact mass (*m/z*): calcd for $C_{11}H_{20}BN$: 177.1689; found, 177.1696.

Equilibration of 13b and 14b. A sample of **14b** (10 mg, 0.05 mmol) was dissolved in 0.5 mL of THF-*d*$_8$. LDA (1 mg) was added and the sample was allowed to stand at 25 °C for 1 day. The ^{1}H NMR spectrum showed a 1:1 mixture of **14b** and **13b**.

13b. ^{1}H NMR (THF-*d*$_8$, 300 MHz): δ 1.12 (d, $J = 6.8$ Hz, CH_3), 1.27 (d, $J = 7.1$ Hz, CH_3), 1.86 (br m, H(6)), NCH peak obscured by residual THF, 6.0, 6.1 (m, H(4,5)), 6.32 (d, $J = 12.6$ Hz, H(2)), 6.73 (m, H(3)).

***N*-Benzyl-*N*-methyl-1-aminoboracyclohexadienes (13c, 14c).** *N*-Benzyl-*N*-methylamine (1.0 g, 8.3 mmol) in 8 mL of pentane was added dropwise with stirring to a solution of 1-chloroboracyclohexa-2,5-diene (510 mg, 4.5 mmol) in 15 mL of pentane at −78 °C. A white precipitate formed immediately. After being stirred for 4 h at 25 °C, the suspension was filtered to give a clear solution which after removal of the solvent under reduced pressure afforded 640 mg (78%) of a light yellow air-sensitive oil. The ^{1}H NMR spectrum indicated the product was a mixture of 40% **14c** and 60% the two isomers of **13c** in the ratio of 2:3.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.95 (m, H(6), **13c**), 2.62, 2.80 (s, s, NCH_3, **13c**), 2.82 (s, NCH_3 **14c**), 3.06 (m, H(4), **14c**), 4.22, 4.37 (s, s, NCH_2, **13c**), 4.41 (s, NCH_2, **14c**), 6.15, 6.25, 6.40 (m, m, m, H(2), H(4) H(5) **13c**, H(2), **14c**), 6.95 (m, H(3), 14c, **13c**), 7.3 (m, Ph). ^{13}C NMR ($CDCl_3$, 90.6 MHz, 25 °C): δ 34. 8 (C(4), **14c**), 36.4, 36.5 (CH_3), 55.0, 55.3 (CH_2), 125.5, 127.0, 127.2, 127.5, 128.5, 128.6, 134.6, 144.60, 144.6, 144.7 and 147.75 (C(3), **14c**), 147.88 (C(3), **14c**). On heating of the sample to 122 °C, the peaks for C(3) of **14c** coalesce to a singlet δ 147.81. ^{11}B NMR ($CDCl_3$, 115.6 MHz): δ 40.6. MS (EI) exact mass (*m/z*): calcd for $C_{13}H_{16}BN$, 197.1376; found, 197.1373.

(*N,N*-Diisopropyl-1-aminoboratabenzene)lithium (9b). In a typical NMR tube experiment *N,N*-diisopropyl-1-aminoboracyclohexa-2,5-diene (**14b**) was dissolved in 0.5 mL of THF-*d*$_8$, and a small amount of LDA was added. The NMR spectra of the orange solution showed the generation of the anion **9b**.

In the same manner **9b** could be generated in DMSO-*d*$_6$, affording a brown solution.

^{1}H NMR (THF-*d*$_8$, 360 MHz): δ 1.11 (d, $J = 6.8$ Hz, CH_3), 3.62 (m, NCH), 5.34 (t, $J = 6.6$ Hz, H(4)), 5.63 (d, $J = 10.6$ Hz, H(2,6)), 6.90 (dd, $J = 9.4$, 7.0 Hz, H(3,5)). ^{1}H NMR (DMSO-*d*$_6$, 360 MHz): δ 1.10 (d, $J = 6.7$ Hz, CH_3), 3.58 (m, NCH), 5.17 (t, $J = 6.6$ Hz, H(4)), 5.35 (d, $J = 10.6$ Hz, H(2,6)), 6.64 (dd, $J = 10.5$, 6.6 Hz, H(3,5)). ^{13}C NMR (THF-*d*$_8$, 90.6 MHz): δ 23.7 (CH_3), 46.4 (NCH), 98.9 (C(4)), 113.8 (C(2,6)), 134.3 (C(3,5)). ^{11}B NMR (THF, 115.6 MHz): δ 31.0. ^{7}Li NMR (THF, 140.0 MHz): δ −4.82.

(*N*-Benzyl-*N*-methyl-1-aminoboratabenzene)lithium (9c). The mixed isomers **13c** and **14c** (15 mg, 0.076 mmol) were dissolved in 0.5 mL of THF-*d*$_8$ and treated with LDA (0.094 mmol), affording an orange solution of the anion **9c**.

^{1}H NMR (THF-*d*$_8$, 300 MHz): δ 2.67 (s, CH_3), 4.25 (s, CH_2), 5.54 (tt, $J = 6.4$, 1.2 Hz, H(4)), 5.74 (dd, $J = 10.9$, 1.1 Hz, H(2,6)), 7.05−7.29 (m, H(3,5), Ph.

^{13}C NMR (THF-*d*$_8$, 90.6 MHz, 25 °C): δ 37.1 (CH_3), 56.7 (CH_2), 100.3 (C(4)), 110.0 (br, C(2,6)), 126.2−129.1 (o, m, p-Ph), 134.9 (C(3,5)), 145.0 (ipso-C, Ph). At −87 °C the peak for C(3,5) splits into two peaks at δ 135.07, 134.85. $T_c = -72$ °C. ^{11}B NMR (THF, 115.6 MHz): δ 32.2. ^{7}Li NMR (THF, 140.0 MHz): δ −6.55.

Tricarbonyl(*N,N*-diisopropyl-1-aminoboratabenzene)-manganese (I) (19b). A solution of LDA (1.5 mmol) in 10 mL of ether, freshly prepared from 0.5 g of diisopropylamine and 0.6 mL of 2.5 M BuLi/hexane solution in ether at −78 °C, was added dropwise with stirring to a solution of **14b** (250 mg, 1.41 mmol) in 10 mL of ether at −78 °C. The color turned to light yellow. The reaction mixture was allowed to warm to 25 °C, and stirring was continued for 2.5 h. During this time the color changed to deep yellow and a white precipitate formed. The suspension was added dropwise with stirring to a suspension of $Mn(CO)_3(CH_3CN)_3PF_6$ (0.58 g, 1.41 mmol) in 15 mL of ether at −78 °C. The reaction mixture was allowed to warm to 25 °C, and the color changed from deep yellow to brown red. After the mixture was stirred for 6 h, the solvent was removed under reduced pressure and the brown red solid was extracted 4 times with 10 mL of pentane affording a deep yellow solution after filtration. Two-thirds of pentane was removed under vacuum. On cooling of the solution to −78 °C, 220 mg (0.7 mmol, 50%) of **19b** was obtained as yellow crystals, mp 61−3 °C.

^{1}H NMR (CD_2Cl_2, 360 MHz, T = 25 °C): δ 1.34 (d, $J = 6.7$ Hz, CH_3), 1.35 (d, $J = 6.7$ Hz, CH_3), 3.74 (m, NCH), 3.80 (d, $J = 9.4$ Hz, H(2,6)), 5.32 (t, $J = 5.2$ Hz, H(4)), 5.91 (dd, $J = 9.4$, 5.7 Hz, H(3,5)). ^{13}C NMR (CD_2Cl_2, 90.6 MHz, T = 25 °C): δ 22.72 (CH_3), 22.79 (CH_3), 46.5 (NCH), 77.8 (br, C(2,6)), 77.2 (C(4)), 109.0 (C(3,5)). At 57 °C the CH_3 signals coalesce (δ 22.74). At −58 °C the signals for C(2,6), C(3,5), and NCH split into doublets and the methyl signal splits into four peaks. T_c for the NCH signals is −23.6 °C and for the CH_3 signals −33.5 °C.

^{11}B NMR ($CDCl_3$, 115.6 MHz): δ 24.9. Anal. Calcd for $C_{14}H_{19}BMnNO_3$: C, 53.37; H, 6.08; N, 4.45. Found: C, 52.99, 53.10; H, 6.47, 6.42; N, 4.14, 4.16. MS (EI) exact mass (*m/z*): calcd for $C_{14}H_{19}BMnNO_3$, 315.0838; found, 315.0864. IR (hexane) (ν(CO)): 2031, 1953, 1947 cm^{-1}.

Tricarbonyl(*N*-benzyl-*N*-methyl-1-aminoboratabenzene)manganese(I) (19c). A solution of 2.5 mmol of LDA in 5 mL of ether, freshly prepared from 0.5 g of diisopropylamine and 1 mL of 2.5 M BuLi/hexane solution in ether at −78 °C, was added dropwise with stirring to a solution of 500 mg (2.5 mmol) of **13c** and **14c** in 20 mL of ether at −78 °C. The reaction mixture was allowed to warm to 25 °C. The color changed from light yellow to orange, and a white precepitate formed. Stirring was continued for 2.5 h. The suspension was added dropwise to a suspension of 1 g (2.5 mmol) of $Mn(CO)_3(CH_3CN)_3PF_6$ in 10 mL of ether at −78 °C, and the reaction mixture was allowed to warm to 25 °C. After stirring for 5 h the color changed from orange to brown red. The solvent was removed under reduced pressure affording a brown red solid which was extracted 5 times with 10 mL of pentane. After filtration two-thirds of pentane was removed under vacuum. On cooling of the solution to −78 °C, 480 mg (1.43 mmol, 57%) of **19c** was obtained as deep yellow crystals, mp 60−2 °C.

^{1}H NMR ($CDCl_3$, 300 MHz, $T = 25$ °C): δ 2.66 (s, CH_3), 3.72 (m, H(2,6)), 4.01 (d, $J = 15.4$ Hz, CH_2), 4.41 (d, $J = 15.4$ Hz, CH_2), 5.18 (t, $J = 5.7$ Hz, H(4)), 5.81 (m, H(3,5)), 7.78 (m, Ph). ^{13}C NMR ($CDCl_3$, 90.6 MHz, $T = 25$ °C): δ 35.9 (CH_3), 54.8 (CH_2), 74.8 (C(2,6)), 77.3 (C(4)), 109.22 (C(3,5)), 108.97 (C(3,5)), 126.9, 127.7, 128.5, 140.6 (Ph). On heating of the sample to 60 °C the signal for C(3,5) broadened and became a singlet at δ 109.34, $T_c = 51.4$ °C.

^{11}B NMR ($CDCl_3$, 115 MHz): δ 24.6. Anal. Calcd for $C_{16}H_{15}BMnNO_3$: C, 57.36; H, 4.51; N, 4.18. Found: C, 57.43, 57.09; H, 4.69, 4.80; N, 4.15, 4.09. MS (EI) exact mass (*m/z*): calcd for $C_{16}H_{15}BMnNO_3$, 335.0525, found, 335.0532. IR (hexane) (ν(CO)): 2032, 1956, 1949 cm^{-1}.

Dicarbonyl(trimethylphosphine)(*N,N*-diisopropyl-1-aminoboratabenzene)manganese(I) (20b). A quartz cuvette was filled with a solution of **19b** (150 mg, 0.48 mmol) in 20 mL of benzene. Trimethylphosphine (44 mg, 0.58 mmol) was added, and the solution was irradiated for 4 h using a Hanovia lamp. The color changed from red to orange, and a fine precipitate formed. The solution was filtered, and the solvent was removed under reduced pressure. The residue was dissolved in 5 mL of pentane. Cooling to −78 °C afforded 90 mg (0.25 mmol), 52%) of **20b** as yellow crystals, mp 105−6 °C.

^{1}H NMR ($CDCl_3$, 300 MHz, $T = 25$ °C): δ 1.20 (d, $J = 6.8$ Hz, $C(CH_3)_2$), 1.33 (d, $J = 8.8$ Hz, PMe_3), 3.40 (d, $J = 9.3$ Hz, H(2,6)), 3.58 (m, NCH), 4.77 (t, $J = 5.2$ Hz, H(4)), 5.36 (dd, $J = 9.3$, 5.2 Hz, H(3,5)). ^{1}H NMR (toluene-*d*$_8$, 300 MHz, $T = 25$

°C): δ 0.84 (d, J = 8.6 Hz, PMe$_3$), 1.30 (s br, C(CH$_3$)$_2$), 3.34 (d, J = 9.1 Hz, H(2,6)), 4.36 (t br, H(4)), 5.02 (dd br, H(3,5). The broad signal at δ 1.30 splits into a doublet (J = 6.7 Hz) on heating to 32 °C. On cooling of the sample to 9.5 °C, the δ 1.30 signal becomes two doublets (δ 1.32 (J = 6.8 Hz), 1.29 (J = 6.1 Hz). T_c = 23 °C. ^{13}C NMR (C$_6$D$_6$, 75.5 MHz, T = 25 °C): δ 20.3 (d, J = 26.3 Hz, PC), 23.2 (CH$_3$), 46.4 (NCH), 75.7 (C(4)), 107.09 (C(3,5)), C(2,6) not observed. ^{11}B NMR (CDCl$_3$, 115.6 MHz): δ 23.4. ^{31}P NMR (CDCl$_3$, 145.8 MHz) δ 45.8. Anal. Calcd for $C_{16}H_{28}BMnNO_2P$: C, 52.92; H, 7.77; N, 3.86. Found: C, 52.73, 52.64; H, 7.56, 7.67; N, 3.49, 3.58. MS (EI) exact mass (m/z): calcd for $C_{16}H_{28}BMnNO_2P$, 363.1331; found, 363.1329. IR (hexane) (ν(CO)): 1945, 1885 cm^{-1}.

Bis(*N*,*N*-diisopropyl-1-aminoboratabenzene)iron (18b). A solution of 2.8 M butyllithium (2.6 mL, 7.2 mmol) in hexane was added dropwise with stirring to a solution of **14b** (1.28 g, 7.2 mmol) in 20 mL of THF at −78 °C. The color changed to bright purple on addition. After 10 min at −78 °C the reaction mixture was allowed to warm to 25 °C for 1 h. After recooling of the mixture to −78 °C, a suspension of FeCl$_2$ (0.45 g, 3.6 mmol) in 10 mL of THF was added slowly. The mixture was allowed to warm to 25 °C and was stirred for 12 h. The solvent was removed under reduced pressure, and the residue was recrystallized from pentane yielding 2.0 g (68%) of red plates, mp 114−115 °C.

^{1}H NMR (CDCl$_3$, 360 MHz, T = 25 °C): δ 5.26 (dd, J = 9.2, 5.5 Hz, *H(3, 5)*), 4.96 (t, J = 5.5 Hz, *H(4)*), 3.64 (sept, J = 6.8 Hz, *NCH*), 3.54 (d, J = 9.2 Hz, *H(2, 6)*), 1.20 (d, J = 6.8 Hz, *CH$_3$*). ^{1}H NMR (C$_6$D$_6$, 500 MHz, T = 45 °C): δ 5.07 (dd, J = 9.3, 5.5 Hz); 4.68 (t, J = 5.5 Hz) 3.68 (sept, J = 6.8 Hz); 3.55 (d, J = 9.2 Hz); 1.25 (d, J = 6.8 Hz). At 15 °C the high-field doublet splits at δ 1.285, 1.217. T_c = 25 °C. ^{11}B NMR (CDCl$_3$, 115.6 MHz): δ 20.5. ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ 92.8 (*C-(3,5)*; 73.9 (C(4)), 64.5 (br, *C(2,6)*), 45.9 (*NCH*), 23.3 (*CH$_3$*). MS (EI) exact mass (m/z): calcd for $C_{22}H_{38}B_2FeN_2$, 408.2570; found, 408.2571. Anal. Calcd for $C_{22}H_{38}B_2FeN_2$: C, 64.76; H, 9.39; N, 6.86. Found: C, 64.57; H, 9.21; N, 6.78.

Relative Acidities in DMSO-*d*$_6$. (a) 14b and CpLi. In each of the three NMR tubes **14b** (10 mg, 0.085 mmol) was dissolved in 0.5 mL of dry DMSO-d_6. Small variable amounts of LiCp (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, **14b**, **13b**, and **9b**. The relative concentrations were determined by integration of the appropriate signals. The pK_a's of **14b** = 17.8 and **13b** = 17.7 were determined relative to that for CpH = 18.0. Agreement between different runs was ±10%.

(b) 5b and CpLi. In the same manner as above mixtures of **5b** and CpLi showed complete conversion to CpH and **1b**.

(c) 5b and (1,2,3,4,5-Pentaphenylcyclopentadienyl)-lithium. In the same manner mixtures of **5b** and Ph$_5$CpLi showed complete conversion to Ph$_5$CpH and **1b**.

(d) 5b and 9b. In the same manner **9b** was prepared by adding 1 equiliv of LDA. Addition of **5b** showed complete conversion to **1b** and a mixture of **13b** and **14b**.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE-9224967) for generous financial support. C.M. and M.S. thank the Deutsche Akademische Austauschdienst for fellowships. We also thank Professor Gregory C. Fu for providing us with a copy of his paper on the structure of (1*H*-boratabenzene)lithium prior to publication.

Supporting Information Available: Tables of the anisotropic thermal parameters of the non-hydrogen atoms and positional and thermal parameters of the hydrogen atoms (1 page). Ordering information is given on any current masthead page.

OM9506330