Notes

Chemistry of Borabenzene: Efficient and General Synthesis of New Neutral Borabenzene−Ligand Complexes

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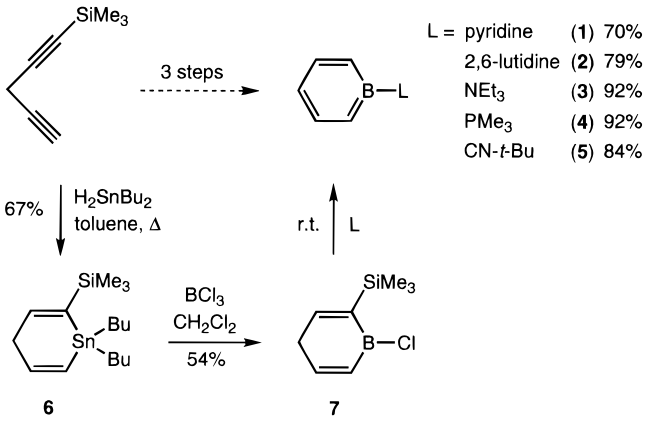
Received July 21, 1995[⊗]

Summary: An array of neutral borabenzene−ligand complexes (ligand = pyridine, 2,6-lutidine, NEt_3, PMe_3, CN-t-Bu) have been synthesized in three straightforward steps from commercially available 1-(trimethylsilyl)-1,4-pentadiyne. An X-ray crystal structure of borabenzene−PMe_3 is reported.

Although the chemistry of anionic borabenzene−ligand complexes ($[C_5H_5B-X]^-$) has been the focus of substantial interest,[1,2] the chemistry of neutral borabenzene−ligand complexes (C_5H_5B-L) has not yet been extensively explored.[3−5] This relatively low level of activity may be due in part to the absence of a facile route to this family of compounds. Indeed, only one neutral borabenzene−ligand complex, borabenzene−pyridine, has been fully characterized.[3a] In this paper, we report the generation of an array of new neutral borabenzene−ligand adducts by a straightforward three-step synthesis.

Our route (Scheme 1) parallels the pathway followed by Maier, Paetzold, and Schmid in their pioneering synthesis of borabenzene−pyridine (five steps from 1,4-pentadiyne[3a,6]). Treatment of commercially available 1-(trimethylsilyl)-1,4-pentadiyne with H_2SnBu_2 in refluxing toluene generates stannacycle **6**[7] in good yield. Exposure of **6** to BCl_3 leads to transmetalation, affording boracyclohexadiene **7**.[8] Reaction of **7** with pyridine at room temperature results in elimination of Me_3SiCl to provide borabenzene−pyridine (**1**).[9] By this route we have synthesized not only other nitrogen-bound Lewis acid−base complexes, including the sterically hindered 2,6-lutidine adduct (**2**)[10] and the triethylamine adduct (**3**), but also previously unknown phosphorus- (**4**) and carbon-bound (**5**) borabenzene−ligand complexes (Scheme 1).[11]

Scheme 1. Synthesis of Neutral Borabenzene−Ligand Complexes



The conversion of boracycle **7** to borabenzene−ligand complexes **1**−**5** likely proceeds via base-catalyzed isomer

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1996.

(1) (a) Herberich, G. E.; Greiss, G.; Heil, H. F. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 805−806. (b) Ashe, A. J.; Shu, P. *J. Am. Chem. Soc.* **1971**, *93*, 1804−1805.

(2) For leading references, see: (a) Herberich, G. E.; Ohst, H. *Adv. Organomet. Chem.* **1986**, *25*, 199−236. (b) Herberich, G. E.; Schmidt, B.; Englert, U. *Organometallics* **1995**, *14*, 471−480.

(3) (a) Borabenzene−pyridine: Boese, R.; Finke, N.; Henkelmann, J.; Maier, G.; Paetzold, P.; Reisenauer, H. P.; Schmid, G. *Chem. Ber.* **1985**, *118*, 1644−1654. See also: Boese, R.; Finke, N.; Keil, T.; Paetzold, P.; Schmid, G. *Z. Naturforsch., B* **1985**, *40*, 1327−1332. (b) IR evidence for borabenzene−N_2: Maier, G.; Reisenauer, H. P.; Henkelmann, J.; Kliche, C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 295−296.

(4) (a) Pyridine− and triethylamine−2-boranaphthalene: Reference 3a. (b) (Dimethyl sulfide)−9-boraanthracene: Jutzi, P. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 838.

(5) For computational studies of free borabenzene and of neutral borabenzene−ligand complexes, see: (a) Schulman, J. M.; Disch, R. L.; Sabio, M. I. *J. Am. Chem. Soc.* **1982**, *104*, 3785−3788. (b) Raabe, G.; Heyne, E.; Schleker, W.; Fleischhauer, J. *Z. Naturforsch., A* **1984**, *39*, 678−681. (c) Raabe, G.; Schleker, W.; Heyne, E.; Fleischhauer, J. *Z. Naturforsch., A* **1987**, *42*, 352−360. (d) Schulman, J. M.; Disch, R. L. *Organometallics* **1989**, *8*, 733−737. (e) Cioslowski, J.; Hay, P. J. *J. Am. Chem. Soc.* **1990**, *112*, 1707−1710.

(6) 1,4-Pentadiyne is not commercially available. For preparations of this difficult-to-isolate compound, see: (a) Ben-Efraim, D. A.; Sondheimer, F. *Tetrahedron* **1969**, *25*, 2823−2835. (b) Verkruijsse, H. D.; Hasselaar, M. *Synthesis* **1979**, 292−293.

(7) Ashe, A. J., III; Chan, W.-T.; Smith, T. W.; Taba, K. M. *J. Org. Chem.* **1981**, *46*, 881−885.

(8) For a related reaction, see: Ashe, A. J., III; Meyers, E.; Shu, P.; Von Lehmann, T.; Bastide, J. *J. Am. Chem. Soc.* **1975**, *97*, 6865−6866. Treatment of **6** with BBr_3 produces the more reactive bromine analogue of **7**; preliminary results indicate that this compound also serves as a precursor to neutral borabenzene−ligand adducts.

(9) Compound **1** is identical (^1H, ^{11}B, and ^{13}C NMR) with borabenzene-pyridine reported by Schmid.[3a]

(10) However, we were not able to generate the borabenzene−(2,6-di-*tert*-butyl-4-methylpyridine) complex by this route. Amendola, M. C. Unpublished results.

(11) Using this procedure, we have synthesized, but not yet fully characterized, a number of other neutral borabenzene−ligand complexes (e.g., phosphite and arsine adducts).

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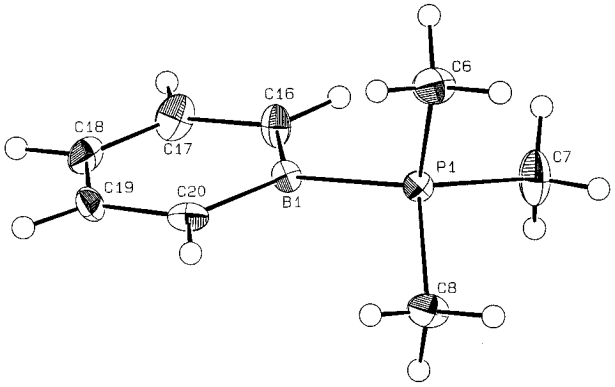
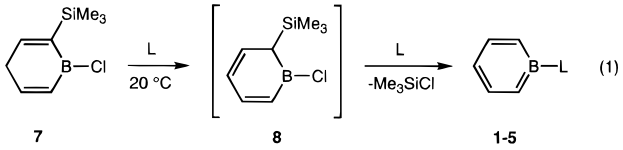


Figure 1.

Table 1. Selected Bond Distances (Å) and Angles (deg)

P(1)−B(1)	1.900(8)	P(1)−C(6)	1.791(8)
P(1)−C(7)	1.788(8)	P(1)−C(8)	1.785(8)
B(1)−C(16)	1.47(1)	B(1)−C(20)	1.47(1)
C(16)−C(17)	1.39(1)	C(17)−C(18)	1.37(1)
C(18)−C(19)	1.39(1)	C(19)−C(20)	1.40(1)
C(6)−P(1)−C(7)	106.6(4)	C(6)−P(1)−C(8)	104.6(4)
C(7)−P(1)−C(8)	106.4(4)	C(6)−P(1)−B(1)	113.2(4)
C(7)-P(1)-B(1)	114.6(4)	C(8)-P(1)-B(1)	110.8(4)
C(17)-C(16)-B(1)	119.2(7)	C(19)-C(20)-B(1)	119.5(8)
C(16)-C(17)-C(18)	121.1(8)	C(17)-C(18)-C(19)	122.5(7)
C(18)-C(19)-C(20)	120.2(8)	C(16)−B(1)−C(20)	117.4(7)

ization of **7** to **8**,[12] followed by ligand-induced elimination of Me_3SiCl (eq 1). To provide support for this



pathway, we prepared boracycle **8** independently (via thermal isomerization of **7**) and demonstrated by treatment with PMe_3 that it is both a chemically and a kinetically competent intermediate in the formation of borabenzene−ligand adducts from **7**.

The results of an X-ray crystallographic study of borabenzene−PMe_3 (**4**) are illustrated in Figure 1 (see also Tables 1−3). The phosphorus-bound groups are disposed in a tetrahedral geometry about the central atom (bond angles range from 105 to 115°). As in the case of borabenzene−pyridine,[3a] the aromatic ring of borabenzene−PMe_3 is essentially planar (all torsion angles are less than 2°) and is slightly distorted from a regular hexagon (carbon−carbon bond distances, 1.37−1.40 Å; carbon−boron bond distances, 1.47 Å), presumably due in part to the larger covalent radius of boron as compared to carbon.[13] The boron−phosphorus bond length is 1.900(8) Å.[14]

In summary, we have developed an efficient synthetic route to neutral borabenzene−ligand adducts which provides, for the first time, ready access to a wide array of these complexes. Studies of their reactivity,[15] as well as efforts to extend this synthetic approach to other families of heterocycles, are underway.

Table 2. Crystallographic Data for Borabenzene−Trimethylphosphine (4)

empirical formula	$C_8H_{14}BP$
fw	151.98
cryst color, habit	colorless, prismatic
cryst dimens (mm)	0.340 × 0.380 × 0.420
cryst system	monoclinic
space group	*P*2/*c* (No. 13)
a (Å)	17.583(3)
b (Å)	6.286(1)
c (Å)	35.140(4)
β (deg)	102.93(2)
V (Å^3)	3785(1)
Z	16
ρ_{calc}	1.067
radiation	Mo Kα (λ = 0.710 69 Å)
temp (°C)	−86
μ(Mo Kα) (cm^{-1})	2.13
diffractometer	Enraf-Nonius CAD-4
scan type	$\omega-2\theta$
rate (deg min^{-1} in ω)	1.9−16.5
scan width (deg)	(0.80 + 0.35 tan θ)
$2\theta_{max}$	45.0
tot. reflcns	5674
unique reflcns	5467 (R_{int} = 0.177)
corrs	Lorentz−polarization; abs (transm factors: 0.33−1.69); secondary extinctn (coeff: 0.398 88 × 10^{-6})
struct soln, refinement	direct methods, full-matrix least squares
no. of observns ($I > 3.00\sigma(I)$)	2735
no. of variables	362
reflcn/param ratio	7.56
R; R_w	0.065; 0.073
goodness of fit	2.14

Experimental Section

General Methods. ^{1}H nuclear magnetic resonance spectra were recorded on Varian XL-300, Unity 300, or VXR 500 NMR spectrometers at ambient temperature, unless otherwise specified. ^{1}H data are reported as follows: chemical shift (δ scale), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and app = apparent), integration, and coupling constant (Hz). The spectra are referenced to residual solvent ($CDCl_3$, δ 7.25; C_6D_6, δ 7.15).

All ^{13}C NMR spectra were determined with complete proton decoupling on Varian XL-300 NMR (75 MHz) spectrometers and are referenced to residual solvent in ppm downfield from tetramethylsilane ($CDCl_3$, δ 77.0; C_6D_6, δ 128.0). ^{11}B NMR spectra were obtained on Varian XL-300 or Unity 300 NMR spectrometers (96 MHz) and are referenced to external neat BF_3−OEt_2 (δ 0.0). ^{31}P NMR spectra were obtained on Varian XL-300 or Unity 300 NMR spectrometers (121 MHz) and are referenced to external 85% H_3PO_4 (δ 0.0).

Infrared spectra were obtained on a Perkin-Elmer Series 1600 FT-IR spectrophotometer and are reported in cm^{-1}. Mass spectra (*m*/*e*) were recorded on a Finnegan MAT System 8200 spectrometer.

Benzene, diethyl ether, hexane, pentane, and THF were distilled from sodium/benzophenone. Toluene was distilled from sodium. Methylene chloride was distilled from CaH_2. Pyridine, triethylamine, and trimethylphosphine were distilled from Na/benzophenone. *tert*-Butyl isocyanide was purchased from Aldrich Chemical Co. and used without further purification.

(12) The thermal, photochemical, and base-induced isomerization of related compounds has been reported: (a) Maier, G.; Henkelmann, J.; Reisenauer, H. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1065−1066. (b) Maier, G. *Pure Appl. Chem.* **1986**, *58*, 95−104.

(13) Covalent radii: boron, 0.82 Å; carbon, 0.77 Å. Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972; pp 82−83.

(14) Boron−phosphorus bond lengths for BX_3-PMe_3: X = Cl, 1.957-(5) Å; X = Br, 1.924(12) Å; X = I, 1.918(15) Å. Black, D. L.; Taylor, R. C. *Acta Crystallogr., Sect. B* **1975**, *31*, 1116−1120.

(15) Hoic, D. A.; Davis, W. M.; Fu, G. C. *J. Am. Chem. Soc.* **1995**, *117*, 8480−8481.

Table 3. Positional Parameters for Borabenzene−Trimethylphosphine (4)

atom	*x*	*y*	*z*
P(1)	0.9123(1)	0.1241(3)	0.30548(5)
P(2)	0.4114(1)	0.3818(4)	0.55638(5)
P(3)	0.6080(1)	0.1291(4)	0.70488(5)
P(4)	0.8954(1)	0.3847(3)	0.04346(5)
C(1)	0.5453(4)	0.092(1)	0.5572(2)
C(2)	0.5786(5)	0.462(1)	0.5846(2)
C(3)	0.6250(6)	0.054(1)	0.5644(3)
C(4)	0.6790(4)	0.208(2)	0.5798(2)
C(5)	0.6571(4)	0.407(2)	0.5901(2)
C(6)	0.8856(5)	−0.040(1)	0.2630(2)
C(7)	0.8447(4)	0.341(1)	0.2986(2)
C(8)	0.8912(5)	−0.034(1)	0.3441(2)
C(9)	0.3823(5)	0.550(1)	0.5147(2)
C(10)	0.3466(5)	0.161(2)	0.5484(3)
C(11)	0.6707(4)	0.217(1)	0.7877(2)
C(12)	0.6155(4)	−0.155(1)	0.7734(2)
C(13)	0.6352(5)	−0.191(1)	0.8137(2)
C(14)	0.6688(5)	−0.037(1)	0.8400(2)
C(15)	0.3875(5)	0.523(2)	0.5957(2)
C(16)	1.0455(4)	0.416(1)	0.3064(2)
C(17)	1.1250(5)	0.459(1)	0.3141(3)
C(18)	1.1789(4)	0.310(2)	0.3311(2)
C(19)	1.1578(4)	0.110(2)	0.3419(2)
C(20)	1.0791(5)	0.054(1)	0.3357(2)
C(21)	0.5259(4)	0.304(1)	0.6922(2)
C(22)	0.5866(6)	−0.090(2)	0.6723(2)
C(23)	0.6865(4)	0.269(2)	0.6916(2)
C(24)	0.8772(4)	0.346(1)	−0.0414(2)
C(25)	0.8509(4)	0.420(1)	−0.0797(2)
C(26)	0.8215(4)	0.622(1)	−0.0875(2)
C(27)	0.8140(4)	0.761(1)	−0.0580(2)
C(28)	0.8380(4)	0.702(1)	−0.0186(2)
C(29)	0.8127(4)	0.256(1)	0.0555(2)
C(30)	0.9249(5)	0.586(1)	0.0802(2)
C(31)	0.9710(4)	0.187(1)	0.0513(2)
C(32)	0.6860(4)	0.162(1)	0.8275(2)
B(1)	1.0190(4)	0.206(1)	0.3168(2)
B(2)	0.5186(4)	0.302(1)	0.5673(2)
B(3)	0.6321(5)	0.054(2)	0.7589(2)
B(4)	0.8700(5)	0.489(1)	−0.0092(2)

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware inside a Vacuum Atmospheres HE-43-2 glovebox or under argon using standard Schlenk techniques. All reported yields are the average of two runs.

1,1-Di-*n*-butyl-2-(trimethylsilyl)stannacyclohexa-2,5-diene (6).[16] A solution containing 1-(trimethylsilyl)-1,4-pentadiyne (5.00 g, 36.8 mmol; Farchan) and dibutyltin dihydride[17] (8.64 g, 36.8 mmol) in 18 mL of toluene was refluxed for 8 h. The toluene was then removed in vacuo, and stannacycle **6** was distilled under reduced pressure, providing a clear oil (bp 95−110 °C, 400 mTorr). Redistillation yielded 9.0 g (66%) of stannacycle **6** as a slightly air-sensitive colorless oil. ^{1}H NMR (C_6D_6): δ 6.84 (t, 1H, J = 3; $J_{H-^{119}Sn}$ = 35.4; $J_{H-^{117}Sn}$ = 34.5), 6.56 (dtd, 1H, J = 1.2, 4.0, 14.0), 6.29 (dtd, 1H, J = 0.9, 1.9, 13.9; $J_{H-^{119}Sn}$= 66.6; $J_{H-^{117}Sn}$= 63.5), 2.95 (m, 2H), 1.58 (m, 4H), 1.36 (m, 4H), 1.02 (m, 4H), 0.90 (t, 6H, J = 7.2), 0.15 (s, 9H). Coupling to tin was resolved at 500 MHz. ^{13}C NMR (C_6D_6): δ 151.7, 145.0, 140.4, 126.4, 38.6, 29.7, 27.7, 13.9, 11.5, 0.4. IR (neat): 2956, 2929, 2871, 2852, 2175, 1824, 1602, 1566, 1463, 1399, 1245, 928, 836, 747, 687. HRMS: Calcd for $C_{16}H_{32}SiSn$, 372.1295; found, 372.1293.

1-Chloro-2-(trimethylsilyl)boracyclohexa-2,5-diene (7). BCl_3 (15.0 mL, 15.0 mmol; 1.0 M in CH_2Cl_2, Aldrich) was added dropwise to a −78 °C solution of stannacycle **6** (5.57 g, 15.0 mmol) in CH_2Cl_2. The reaction mixture immediately turned cloudy, canary yellow. Upon completion of the addition, the reaction was warmed to room temperature, at which point it was homogeneous, and stirred overnight. CH_2Cl_2 was distilled from the resulting clear gold solution at ambient pressure. Distillation of the residue[18] (bp 40−75 °C, 200 mTorr; oil bath temperature 105 °C) afforded 1.9 g (70%) of product (>85% pure by NMR) as a clear, pale yellow oil. Redistillation (bath temperature 50 °C; 180 mTorr) afforded 1.53 g (56%) of clear, colorless boracycle **7**. ^{1}H NMR (C_6D_6): δ 7.22 (br s, 1H), 6.77 (br d, 1H, J = 11.7), 6.58 (dt, 1H, J = 11.7, 1.3), 2.47 (m, 2H), 0.31 (s, 9H). ^{13}C NMR (C_6D_6): δ 164.2, 155.5, 144.5 (br), 134.5 (br), 38.0, −0.6. ^{11}B NMR (C_6D_6): δ 53.6. IR (neat): 3009, 2959, 2900, 1599, 1397, 1354, 1329, 1246, 1196, 1014, 999, 965, 838. EIMS: 169, 112, 93, 73. HRMS ($M^+ - CH_3$): Calcd for $C_7H_{11}BClSi$, 169.0416; found, 169.0410.

Borabenzene−Pyridine (1). Pyridine (97 mg, 99 μL, 1.2 mmol) was added in a slow stream to a solution of boracycle **7** (225 mg, 1.22 mmol) in 1.5 mL of Et_2O. After 5 min, the Et_2O was removed in vacuo, and the resulting orange solid was recrystallized from CH_2Cl_2/Et_2O/hexane, yielding 128 mg (67%) of borabenzene−pyridine (**1**), a crystalline yellow solid. The ^{1}H and ^{13}C NMR spectra (CD_3CN) of this compound were identical with those previously reported for borabenzene−pyridine.[3a] ^{1}H NMR ($CDCl_3$): δ 9.04 (m, 2H), 8.07 (m, 1H), 7.74 (m, 2H), 7.57 (m, 2H), 6.72 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 144.3, 140.1, 135.4, 126.3, 119 (br), 116.6. Anal. Calcd for $C_{10}H_{10}BN$: C, 77.49; H, 6.50. Found: C, 77.26; H, 6.66.

Borabenzene−2,6-Lutidine (2). 2,6-Lutidine (140 μL, 1.2 mmol) was added dropwise to a solution of boracycle **7** (204 mg, 1.09 mmol) in 2.4 mL of hexane, resulting in the immediate precipitation of a yellow solid. The crystalline solid was collected, washed several times with hexane, and then dried, affording 160 mg (80%) of borabenzene−2,6-lutidine (**2**; mp 162−164 °C). ^{1}H NMR ($CDCl_3$): δ 7.89 (t, 1H, J = 7.8), 7.53 (t, 2H, J = 8.5), 7.43 (d, 2H, J = 8.0), 6.60 (td, 1H, J = 6.8, 1.0), 6.18 (dd, 2H, J = 9.5, 1.0), 2.65 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 156.7, 140.4, 134.7, 124.3, 118.5 (br), 113.9, 25.9. ^{11}B NMR ($CDCl_3$): δ 33.4. IR (KBr): 3058, 3004, 2979, 2918, 1618, 1533, 1480, 1412, 1376, 1286, 1147, 1054, 959, 792, 714. HRMS: Calcd for $C_{12}H_{14}BN$, 183.1219; found, 183.1218. Anal. Calcd for $C_{12}H_{14}BN$: C, 78.73; H, 7.71. Found: C, 78.57; H, 7.93.

Borabenzene−Triethylamine (3). Triethylamine (126 mg, 174 μL, 1.25 mmol) was added in a stream to a solution of boracycle **7** (208 mg, 1.13 mmol) in 2.4 mL of heptane, resulting in the precipitation of a white solid. After the mixture was stirred for 5 min, the supernatant was decanted, and the solids were washed with heptane. Additional white solid precipitated from the heptane. The solids were combined and dried, affording 183 mg (92%) of borabenzene−triethylamine (**3**; mp 86−88 °C). ^{1}H NMR (C_6D_6): δ 8.03 (br t, 2H, J = 8.7), 7.13 (t, 1H, J = 7.3), 6.45 (d, 2H, J = 10.2), 2.55 (q, 6H, J = 7.2), 0.51 (t, 9H, J = 6.9). ^{13}C NMR (C_6D_6): δ 135.3, 116.5 (br), 114.7, 50.2, 8.0. ^{11}B NMR (C_6D_6): δ 34.0. IR ($CDCl_3$): 3013, 2989, 2943, 1537, 1421, 1008, 938. EIMS 177, 162, 148, 134, 86, 77. HRMS: Calcd for $C_{11}H_{20}BN$, 177.1689; found, 177.1688. Anal. Calcd for $C_{11}H_{20}BN$: C, 74.60; H, 11.38. Found: C, 74.71; H, 11.53.

Borabenzene−Trimethylphosphine (4). PMe_3 (773 μL, 7.47 mmol) was added dropwise by pipet to a solution of boracycle **7** (1.37 g, 7.47 mmol) in hexane (15 mL), resulting in an exothermic reaction and the precipitation of a white solid. The reaction was stirred for 11 h, during which time additional white solid precipitated from the reaction mixture. The solution was decanted, and the remaining solids were washed twice with hexane and then dried, providing 1.04 g (92%) of borabenzene−trimethylphosphine (**4**; mp 135−139 °C). ^{1}H

(16) Ashe, A. J., III; Chan, W.-T.; Smith, T. W.; Taba, K. M. *J. Org. Chem.* **1981**, *46*, 881−885. These workers effect the same cyclization under somewhat different conditions (refluxing heptane, 16 h) and observe a 34% yield of stannacycle **6**.

(17) ***CAUTION!*** Dialkyltin dihydrides can evolve H_2 in the presence of metallic tin or other adventitious impurities (Kuivila, H. G. *Adv. Organomet. Chem.* **1964**, *1*, 47−87). We recommend that dibutyltin dihydride be prepared (Hayashi, K.; Iyoda, J.; Shiihara, I. *J. Organomet. Chem.* **1967**, *10*, 81−94) immediately prior to use.

(18) If the product is not distilled quickly, some isomerization to boracycle **8** is observed.

NMR (C_6D_6): δ 8.05 (br s, 2H), 7.42 (br t, 1H, $J = 8$), 7.23 (br t, 2H, $J = 8$), 0.64 (9H, d, $J_{P-H} = 9$). ^{13}C NMR (C_6D_6): δ 133.6 (d, $J_{C-P} = 17.5$), 128 (br), 120.7, 10.6 ($J_{C-P} = 42.0$). ^{11}B NMR (C_6D_6): δ 20.8 (d, $J_{P-B} = 110$). ^{31}P NMR (C_6D_6; referenced to PPh_3 in C_6D_6 at δ −5.95): δ −16.4 (q, $J_{P-B} = 102.6$). IR (KBr): 3059, 3006, 2982, 2908, 1528, 1420, 1411, 1289, 1152, 1022, 951, 860, 762, 703. EIMS: 152, 109, 91, 76, 61. HRMS: Calcd for $C_8H_{14}BP$, 152.0926; found, 152.0927. Anal. Calcd for $C_8H_{14}BP$: C, 63.22; H, 9.28. Found: C, 63.05; H, 9.26.

Borabenzene−(*tert*-Butyl Isocyanide) (5). *tert*-Butyl isocyanide (61 mg, 0.73 mmol) was added dropwise to a solution of boracycle **7** (134 mg, 0.730 mmol) in 3.5 mL of benzene. The solution was stirred for 3 h, after which time the volatiles were removed in vacuo, leaving a brown solid. The solid was washed three times with pentane and dried, affording 101 mg (87%) of borabenzene−(*tert*-butyl isocyanide) (**5**), a light brown solid (mp 80−82 °C). ^1H NMR (C_6D_6): δ 8.01 (app d, 4H, $J = 3.6$), 7.48 (app quintet, 1H, $J = 4.3$), 0.58 (s, 9H). ^{13}C NMR (C_6D_6): δ 138.0 (br q, $J_{C-B} = 71.2$), 133.8, 123.3, 59.0 (t, $J_{C-N} = 4.6$), 28.6. ^{11}B NMR (C_6D_6): δ 11.9. IR (CD_2Cl_2): 3340, 3122, 3011, 2992, 2302, 2233, 2197, 1750, 1388. EIMS: 159, 103, 76, 57. HRMS: Calcd for $C_{10}H_{14}BN$, 159.1219; found, 159.1222. Anal. Calcd for $C_{10}H_{14}BN$: C, 75.52; H, 8.87. Found: C, 75.25; H, 8.61.

Acknowledgment. Support has been provided by the Camille and Henry Dreyfus Foundation (New Faculty Award in Chemistry), the National Science Foundation (Young Investigator Award, with funding from Amoco, Berlex, Hoechst Celanese, Merck, Pfizer, Procter & Gamble, Rohm & Haas, and Upjohn), and the American Cancer Society (Junior Faculty Research Award). Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We gratefully acknowledge Marcus C. Sarofim and Michael C. Amendola for technical assistance.

Supporting Information Available: NMR and IR spectra for all compounds, and full X-ray data for **4** including tables of complete positional and thermal parameters and bond distances and angles and ORTEP diagrams (62 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

OM9505569