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Borabenzene Adducts of Ylidic Lewis Bases. Syntheses and Structures of 3,5-$Me_2C_5H_3BCH_2PPh_3$, 3,5-$Me_2C_5H_3BCH(SiMe_3)PPh_3$, and $C_5H_5BN(Ph)PPh_3$[1]

Xiaolai Zheng, Bing Wang, and Gerhard E. Herberich*

Institut für Anorganische Chemie, Technische Hochschule Aachen, D-52056 Aachen, Germany

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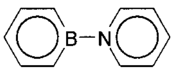
The methylenephosphorane Ph_3PCH_2 reacts with 1-chloro-3,5-dimethyl-2-(trimethylsilyl)-1,2-dihydroborinine (**2c**) (in a 2/1 ratio) at ambient temperature to produce (triphenylphosphonio)methanide−3,5-dimethylborabenzene, 3,5-$Me_2C_5H_3BCH_2PPh_3$ (**3**), with 1 equiv of $(Ph_3PCH_2SiMe_3)Cl$ (**4**), and (trimethylsilyl)(triphenylphosphonio)methanide−3,5-dimethylborabenzene, 3,5-$Me_2C_5H_3BCH(SiMe_3)PPh_3$ (**5**), with 1 equiv of $(PMePh_3)Cl$ (**6**). Both adducts **3** and **5** are yellow crystalline compounds. Treatment of the iminophosphorane Ph_3PNPh with an isomer mixture of 1-chloro(trimethylsilyl)dihydroborinines (**8**) produces *N*-(triphenylphosphonio)anilide−borabenzene $C_5H_5BN(Ph)PPh_3$ (**9**) as brown-yellow crystals. The reaction of PMe_3 with **2c** affords the colorless trimethylphosphine adduct 3,5-$Me_2C_5H_3BPMe_3$ (**10**). The structures of the new adducts **3**, **5**, and **9** are reported. They do not show conjugation between the two remote charge centers, even in the case of the iminophosphorane adduct **9**.

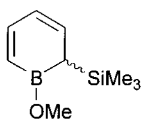
Introduction

The pyridine adduct of borabenzene, $C_5H_5NBC_5H_5$ (**1**), was described in 1985[3] and is the first example of a Lewis base borabenzene adduct.[4] Up to now 10 such borabenzene derivatives have been described, comprising 7 adducts of nitrogen bases,[5] 1 adduct of a phosphorus Lewis base, $Me_3PBC_5H_5$,[5a] 1 of an isocyanide, $Bu^tNCBC_5H_5$,[5a] and 1 of a carbene.[6]

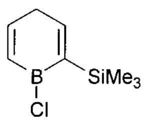


1

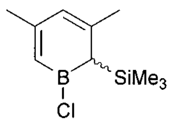
The known borabenzene adducts have been synthesized by treating the dihydroborinines **2a**−**c** with a Lewis base.[3,5a,6] In the case of the starting materials **2a**,**c** this reaction is presumably initiated by a reversible addition of the Lewis base at the boron center and subsequent elimination of Me_3SiOMe or Me_3SiCl to give the desired adduct; compound **2b** requires an additional proton shift. This speculation suggests that any uncharged nucleophile that can form an adduct with a compound of types **2a**−**c** should be able to produce the corresponding Lewis base adducts. Obvious new candidates to be tested are methylenephosphoranes or phosphoniomethanides[7] (traditionally called phosphonium ylides) and isoelectronically related iminophosphoranes or phosphonioamides,[7] examples of which are the subject of this paper. We also describe a further trimethylphosphine adduct.



2a



2b



2c

Results and Discussion

Syntheses of Methylenephosphorane Adducts. Compound **2c**[6] can readily be synthesized from Li(3,5-$Me_2C_5H_3BNMe_2$)[8] via silylation with Me_3SiCl and subsequent chlorodeamination with BCl_3. Treatment of the methylenephosphorane Ph_3PCH_2[9] with **2c** in a 2/1 ratio results in the formation of the two pairs of products, the yellow adduct **3** with 1 equiv of the phosphonium salt $(Ph_3PCH_2SiMe_3)Cl$ (**4**), and the yellow adduct **5** with

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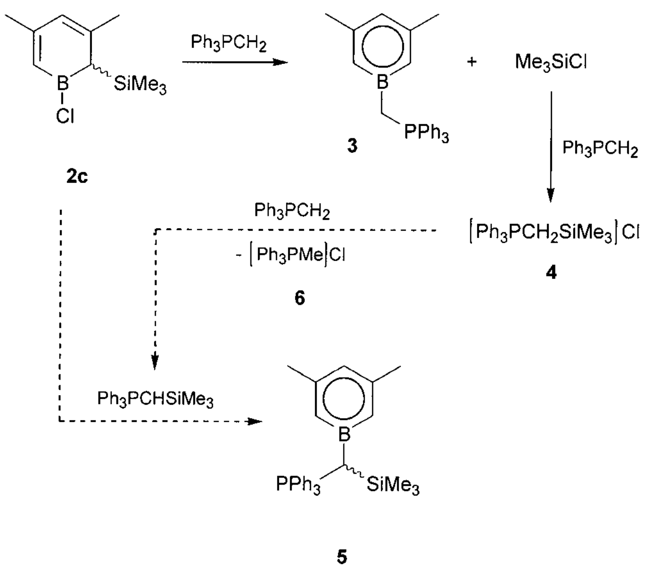
Scheme 1

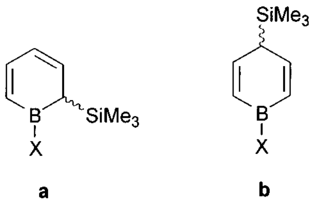


1 equiv of $(PMePh_3)Cl$ (**6**). The second pair of products, **5** and **6**, results from an intervening proton-transfer reaction (Scheme 1). Both the silylation of methylenephosphoranes[7,10] and the proton transfer or, in this context, transylidation reaction[11] are well-known transformations.

The preparative outcome of the reaction depends on the sequence of addition. When a solution of the phosphorane is added dropwise to a solution of **2c**, the products are essentially the simple adduct **3** and the salt **4**. With inverse addition, the phosphorane concentration in the reaction mixture is high, favoring the proton-transfer reaction. The silylated adduct **5** is now produced in appreciable quantities together with adduct **3** and the corresponding phosphonium chlorides.

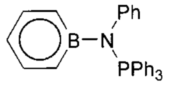
Most previously described borabenzene adducts have adjacent charge centers, as in **1**, or at least some conjugation between the charge centers which will stabilize the adducts to some extent. In contrast, the compounds **3** and **5** have only remote charge compensation and the methylene linker between the boron and the phosphorus atoms does not allow for any conjugation. It would therefore be justified to consider **3** and **5** as derivatives of 1-methylboratabenzene, and indeed, spectroscopic and structural comparisons (see below) lend support to this interpretation.

Synthesis of an Iminophosphorane Adduct. The dihydroborinine component **8a**,**b** was synthesized from $Li(TMEDA)(C_5H_5BNMe_2)$[12] in the usual two steps.



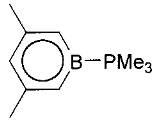
7a,**b**: X = NMe_2; **8a**,**b**: X = Cl

Treatment with Me_3SiCl gave a distillable isomer mixture **7a**,**b** of variable isomer ratio; after thermal equilibration (150 °C, 12 h) the isomer ratio amounts to 3/2.[12c] Subsequent treatment with BCl_3 produced the chloro compound **8a** with a small admixture of the isomer **8b**. The commercially available *N*-(phosphonio)anilide or triphenyl(phenylimino)phosphorane Ph_3PNPh[13] smoothly reacted with the chloro compounds **8a**,**b** at ambient temperature to form the adduct **9** as brown-yellow microcrystalline material and, of course, 1 equiv of Me_3SiCl.



9

Synthesis of a Phosphine Adduct. The single known phosphine adduct $Me_3PBC_5H_5$ has been synthesized via the 1,4-dihydroborinine **2b**.[5a] Dihydroborinines derived from **8a** or **8b** are, of course, equally suitable sources of the borabenzene ring. Thus, the dimethyl compound **2c** reacts smoothly with trimethylphosphine to give the 3,5-dimethyl derivative $3,5\text{-}Me_2C_5H_3BPMe_3$ (**10**) and 1 equiv of Me_3SiCl, as expected. We also learn



10

that the Lewis basicity of the attacking phosphine is crucial, since the much less basic phosphaferrocene $CpFe(3,4\text{-}Me_2C_4H_2P)$[14] failed to react. This negative result suggests that, for instance, a phosphinine–borabenzene adduct that would be a particularly attractive synthetic goal will not be easily accessible.

Crystal Structures. Crystals of **3** and **5** that were suitable for a single-crystal structural study were obtained from toluene; in the case of **5**, the crystals contained $^1/_2$ mol of cocrystallized toluene. The molecules of **3** and **5** (Table 1, Figures 1 and 2) consist of a planar borabenzene ring (maximum vertical deviation of 0.010(3) Å for **3** and of 0.011(2) Å for **5**), a triphenylphosphonio group, and a methylene or a (trimethylsilyl)methylene linker. The dihedral angle between the borabenzene plane and the plane (B,C1,P) amounts to 63.4(2)° for **3** and to 54.3(1)° for **5**. The angle C1–B–C11 (127.0(4)°) for **3** is larger than the angle C1–B–C15 (117.0(4)°), reflecting steric crowding and repulsion between the C11–H11 vertex of the borabenzene ring and the PPh_3 group. This effect is somewhat less pronounced in the sterically more crowded molecule **5** (with C1–B–C11 = 124.9(2)° and C1–B–C15 = 118.7(2)°).

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Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for 3, 5·0.5(toluene), and 9·0.5(toluene)[a]

	3	**5**·0.5(toluene)	**9**·0.5(toluene)
	(a) Bond Distances (Å)		
B−X	1.617(6)	1.652(3)	1.533(3)
P−X	1.796(4)	1.769(2)	1.633(2)
B−C11	1.494(4)	1.495(3)	1.506(3)
B−C15	1.488(4)	1.508(3)	1.504(3)
C11−C12	1.372(5)	1.398(3)	1.390(3)
C12−C13	1.387(5)	1.403(3)	1.398(3)
C13−C14	1.386(6)	1.399(3)	1.396(3)
C14−C15	1.386(5)	1.389(3)	1.385(3)
	(b) Bond Angles (deg)		
P−X−B	118.5(3)	115.1(1)	123.4(2)
C11−B−X	127.0(4)	124.9(2)	119.7(2)
C15−B−X	117.0(4)	118.7(2)	123.9(2)
C11−B−C15	115.7(4)	116.4(2)	116.4(2)
C12−C11−B	119.6(4)	119.7(2)	118.6(2)
C14−C15−B	120.4(4)	120.2(2)	119.1(2)
C11−C12−C13	121.8(5)	120.4(2)	123.1(2)
C12−C13−C14	121.9(5)	123.1(2)	119.8(2)
C13−C14−C15	120.5(4)	120.1(2)	122.9(2)

[a] X represents the exocyclic atom attached to the boron atom: X = C1 for **3** and **5**·0.5(toluene), X = N for **9**·0.5(toluene).

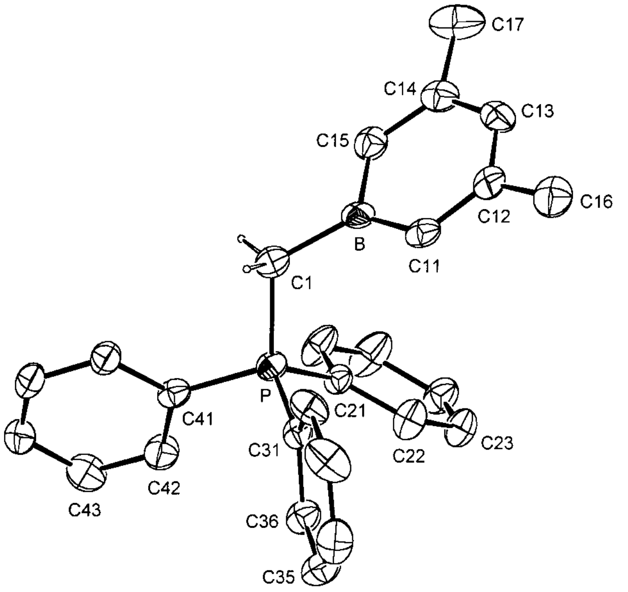

Figure 1. Platon plot[15] of **3** (at the 30% probability level).

The bond lengths of the B−C−P unit are particularly interesting. The bond length P−C1 for **3** (1.796(4) Å) is much longer than for the free methylenephosphorane Ph_3PCH_2 (1.693 Å (av) at 100 K;[9c] see also refs 9d and 16) and may be compared to P−C bonds in organophosphonium ions (P−C = 1.79−1.80 Å for P−C(alkyl) and 1.80−1.81 Å for P−C(Ph)).[16a] Since the coordination of the borabenzene ring largely removes the negative charge from the methylene C atom, the electrostatic attraction of this C atom and the positive P center is attenuated and similar to the situation in a phosphonium salt. On the other hand, the bond length C1−B (1.617(6) Å) is rather long and similar to that in $NMe_3Ph(C_5H_5BMe)$ (1.599(3) Å).[12b] The bonding picture that emerges from these structural details is that of a phosphonio-substituted 1-methylboratabenzene. Compound **3** is the first borabenzene adduct with two nonadjacent charge centers that are not conjugated; the methylene linker does not allow for resonance interactions between the charge centers. The situation in **5** is similar. The polarity of the bond Si−C1 increases the charge at C1 and gives rise to a somewhat shorter bond P−C1 (1.769(2) Å). The bond C1−B (1.652(3) Å) is remarkably long, presumably because of increased steric repulsion and reduced Lewis basicity of the trimethylsilyl-substituted methylenephosphorane. The simple adduct $Me_3PCH_2BH_3$ ($P-CH_2$ = 1.756(6) Å and CH_2-B = 1.655(11) Å) may be of interest for comparison and also shows a rather long C−B bond.[17]

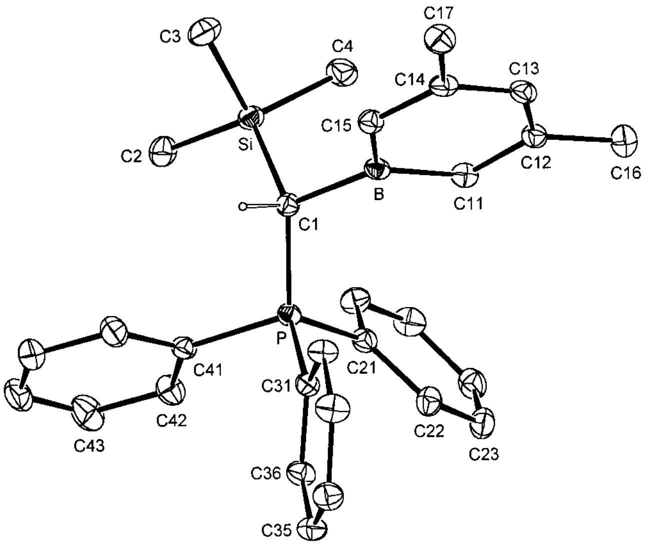

Figure 2. Platon plot[15] of **5** (at the 30% probability level).

Crystals of **9** were obtained by crystallization from toluene; as in the case of **5**, the crystals of **9** contained $^1/_2$ mol of cocrystallized toluene. The molecule of **9** (Table 1, Figure 3) consists of a planar borabenzene ring (maximum vertical deviation of 0.019(3) Å at boron), a triphenylphosphonio group, and a phenylimino linker. The dihedral angle between the borabenzene plane and the plane (B,N,P) amounts to 2.4(2)°.

The bond length P−N for **9** (1.633(2) Å) is longer than for the free (phenylimino)phosphorane Ph_3PNPh (1.602(3) Å).[13c] On the other hand, the bond length N−B (1.533(3) Å) is rather long. It may be compared to the N−B distances (i) in $Li(TMPDA)(C_5H_5BNMe_2)$ (1.448(2) Å),[12a] where the presence of considerable π interactions has been deduced from the structural data[12a] and from the presence of a marked barrier to internal rotation around the N−B bond (measured for $Li(C_5H_5BNMeCH_2Ph)$, $\Delta G^\ddagger$ = 10.1 kcal/mol),[18] and (ii) in **1** (1.558(3) Å)[3] with negligible π interactions.[19] This comparison leads to the conclusion that the nitrogen lone pair of **9** exerts little π interaction with the p_z

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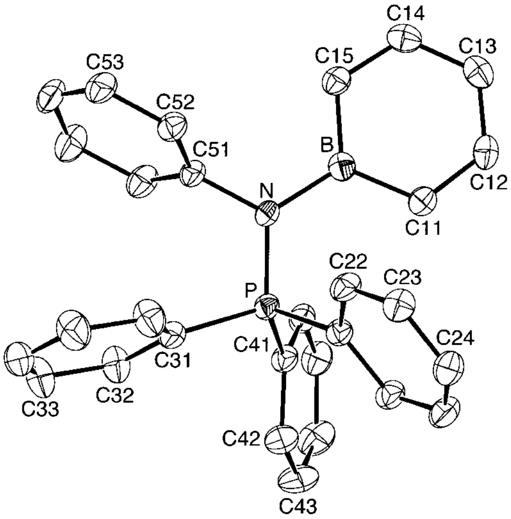

Figure 3. Platon plot[15] of **9** (at the 30% probability level).

orbital at boron. The atoms B, N, P, and C51 are located in a perfect plane (angle sum around the N atom 360.0°; B−N−P = 123.4(2)°, B−N−C51 = 118.6(2)°, P−N−C51 = 118.0(2)°). The planarity of such nitrogen centers is well-known and is caused by the stabilization of the nitrogen lone pair by the neighboring positive charge at the phosphorus center.[20] It is this same effect which also suppresses N−B π bonding.

Other properties of the compounds **3**, **5**, and **9** are consistent with the interpretation given here. The intraring C−B bond distances (1.491(4) Å (av) for **3**, 1.502(3) Å (av) for **5**, and 1.505(3) Å (av) for **9**) are close to those of $NMe_3Ph(C_5H_5BMe)$[12b] (1.501(3) Å (av)), while adducts with adjacent charge centers display markedly shorter bonds (1.473(4) Å (av) for **1** and 1.47(1) Å (av) for $Me_3PBC_5H_5$[5a]). For monosubstituted benzenes it is well established that ^{13}C chemical shift data of the para carbon atoms reflect the resonance contribution to the electron density distribution within the aromatic ring; the meta carbon atoms are not much affected at all, and the data for ortho carbon atoms are influenced both by resonance and by electrostatic effects. A similar situation seems to exist for bora- and boratabenzenes. Comparison of the ^{13}C chemical shifts of the borabenzene atoms C-4 (for 3,5-dimethyl compounds $\delta(^{13}C)$ 110.1 ppm for Li(3,5-$Me_2C_5H_3BMe$),[21] 114.8 ppm for **3**, 114.2 ppm for **5**, 127.9 ppm for the carbene adduct 3,5-$Me_2C_5H_3BC(NMeCMe)_2$,[6] and 122.3 ppm for **10**; 107.9 ppm for Li(C_5H_5BMe),[12b] 108.4 ppm for **9**, 116.6 ppm for **1**,[3,5a] and 120.7 ppm for $Me_3PBC_5H_5$[5a]) show that the borabenzene rings of the new adducts **3**, **5**, and **9** are similar to those of comparable boratabenzene ions but not to those of borabenzene adducts with adjacent charge centers.

Concluding Remarks

This paper presents the three new borabenzene adducts **3**, **5**, and **9** with remote charge compensation. The two opposite charge centers, i.e., that in the borabenzene ring and that of the phosphonio group, are not conjugated. This is so because the methylene linkers of **3** and **5** do not allow for conjugation. Compound **9** does not display appreciable conjugation either. In this case the positive charge of the phosphonio group stabilizes the nitrogen lone pair. This not only is the cause of the planarity around the nitrogen atom but also suppresses any appreciable shortening of the N−B bond by π interactions.

Transition-metal complexes of borabenzene adducts all still quite rare. The known examples contain $Cr(CO)_3$ groups[22,23] and, in single examples, also $Mo(CO)_3$,[23] $W(CO)_3$,[23] and $Co(C_4Me_4)$[2] groups. The fact that the borabenzene rings of the new adducts **3**, **5**, and **9** are electronically close to boratabenzene ions suggests that these adducts should be excellent ligands to a wide range of transition metals.

Experimental Section

General Procedures. Reactions were carried out under an atmosphere of nitrogen by means of conventional Schlenk techniques. Hexane was distilled from sodium/potassium alloy, toluene from sodium, diethyl ether from sodium/benzophenone, and methylene dichloride from calcium dihydride. Elemental analyses were performed by Analystische Laboratorien, D-51779 Lindlar, Germany.

Mass spectra were recorded on a Finnigan MAT-95 at a nominal electron energy of 70 eV. NMR spectra were recorded on a Varian Unity 500 (^1H, 500 MHz; ^{13}C, 125.7 MHz; ^{11}B, 160.4 MHz) spectrometer. Chemical shifts are referenced to TMS for ^1H and ^{13}C, to $BF_3{\cdot}OEt_2$ for ^{11}B, and to H_3PO_4 (84%) for ^{31}P. Assignments of NMR signals are based on $^1H,^1H$-COSY and HMQC techniques.

Synthesis of (Triphenylphosphonio)methanide−3,5-Dimethylborabenzene (3) and (Trimethylsilyl)(triphenylphosphonio)methanide−3,5-Dimethylborabenzene (5). Method A. Addition of Ph_3PCH_2 to 2c. A solution of Ph_3PCH_2[9] (0.696 g, 2.52 mmol) in ether (10 mL) was added dropwise to 1-chloro-3,5-dimethyl-2-(trimethylsilyl)-1,2-dihydroborinine[6] (**2c**; 0.268 g, 1.26 mmol) in ether (10 mL). A yellow precipitate formed immediately. After the reaction mixture was stirred at ambient temperature for 2 h, the precipitate was collected by filtration and washed with ether (5 mL). The yellow solid obtained was suspended in toluene (20 mL), and the mixture was stirred vigorously at 100 °C for 10 min. A white solid of phosphonium chlorides was removed by fast filtration of the hot suspension and was washed with toluene (2 × 10 mL). The combined yellow filtrate, after being concentrated to ca. 20 mL, was stored at 4 °C to give **3** (0.290 g, 61%) as yellow needles, which were sensitive to air and moisture.

Method B. Inverse Addition. A solution of **2c** (0.198 g, 0.93 mmol) in ether (5 mL) was added slowly to Ph_3PCH_2[9] (0.542 g, 1.86 mmol) in ether (10 mL). The solution turned orange, and a yellow precipitate formed almost immediately. After the reaction mixture was stirred for 2 h, the solid was collected by filtration and washed with ether (5 mL). (a) The combined orange filtrate was concentrated to dryness under vacuum, and the residue was crystallized from toluene to give the (trimethylsilyl)methanide adduct **5** as the toluene solvate **5**·0.5(toluene) (0.088 g, 19% based on **2c**) as air- and moisture-sensitive yellow platelets. (b) The yellow powder obtained from the above filtration was extracted with toluene (20 mL) at 100 °C for 10 min. A fast filtration of the hot suspension removed

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[20] See ref 7, p 413.

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a white solid of phosphonium chlorides. The yellow filtrate, after being concentrated under vacuum, was stored at 4 °C to give yellow needles of **3** (0.085 g, 24%).

Data for 3. Anal. Calcd for $C_{26}H_{26}BP$: C, 82.12; H, 6.89. Found: C, 81.58; H, 7.12. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.83 (s, 1H, 4-H), 5.57 (s, 2H, 2-/6-H), 2.05 (s, 6H, 3-/5-Me); signals for Ph_3PCH_2 moiety δ 7.68−7.75 (m, 9H, 2′-/4′-/6′-H), 7.57 (m, 6H, 3′-/5′-H), 2.93 (d, $^{2}J(^{31}P-^{1}H)$ = 17.7 Hz, 2H, PCH_2)). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 141.5 (d, $^{4}J(^{31}P-^{13}C)$ = 1.1 Hz, C-3,5), 125.6 (br, C-2,6), 114.8 (C-4), 25.4 (3-/5-Me); signals for Ph_3PCH_2 moiety: 134.1 (d, $^{2}J(^{31}P-^{13}C)$ = 9.3 Hz, C-2′,6′), 133.9 (d, $^{4}J(^{31}P-^{13}C)$ = 2.8 Hz, C-4′), 129.6 (d, $^{3}J(^{31}P-^{13}C)$ = 12.1 Hz, C-3′,5′), 123.7 (d, $^{1}J(^{31}P-^{13}C)$ = 85 Hz, C-1′), 13.7 (br, PCH_2). $^{11}B\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, external $BF_3{\cdot}OEt_2$): δ 28.5. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, external H_3PO_4): δ 24.4. MS (70 eV): m/z (I_{rel}) 380 (11, M^+), 365 (4, $M^+ - Me$), 275 (42, Ph_3PCH^+), 262 (100, PPh_3^+), 185 (18, PPh_2^+), 108 (20, $M^+ - PPh_3$).

Data for 5·0.5(toluene). Anal. Calcd for $C_{32.5}H_{38}BPSi$: C, 78.30; H, 7.68. Found: C, 77.92; H, 7.77. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 5.81 (s, 1H, 4-H), 5.45 (s, 2H, 2-/6-H), 2.05 (s, 6H, 3-/5-Me); signals for $Ph_3PCH(SiMe_3)$ moiety δ 7.74 (m, 6H, 2′-/6′-H), 7.64 (m, 3H, 4′-H), 7.51 (m, 6H, 3′-/5′-H), 2.53 (d, $^{2}J(^{31}P-^{1}H)$ = 21.4 Hz, 1H, PCH), −0.05 (s, 9H, $SiMe_3$); signals for toluene 7.24 (m), 7.17 (m), 7.14 (m), 2.34 (s). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2): δ 141.1 (s, C-3,5), 127.2 (b, C-2,6), 114.2 (s, C-4), 25.5 (s, 3-/5-Me); signals for $Ph_3PCH(SiMe_3)$ moiety δ 134.5 (d, $^{2}J(^{31}P-^{13}C)$ = 9.4 Hz, C-2′,6′), 133.3 (d, $^{4}J(^{31}P-^{13}C)$ = 2.8 Hz, C-4′), 129.2 (d, $^{3}J(^{31}P-^{13}C)$ = 11.5 Hz, C-3′,5′), 126.0 (d, $^{1}J(^{31}P-^{13}C)$ = 85 Hz, C-1′), 14.2 (br, PCH), 1.9 (d, $^{3}J(^{31}P-^{13}C)$ = 2.7 Hz, $SiMe_3$), and signals for toluene. $^{11}B\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, external $BF_3{\cdot}OEt_2$): δ 29.3. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, external H_3PO_4): δ 25.0. MS (70 eV)): m/z (I_{rel}) 452 (2, M^+), 379 (22, $M^+ - SiMe_3$), 262 (100, PPh_3^+), 185 (18, PPh_2^+), 73 (12, $SiMe_3^+$).

Synthesis of 1-(Dimethylamino)-2-(trimethylsilyl)-1,2-dihydroborinine (7a) and 1-(Dimethylamino)-4-(trimethylsilyl)-1,4-dihydroborinine (7b). Me_3SiCl (27.2 g, 250 mmol) in ether (50 mL) was added dropwise to a suspension of $Li(C_5H_5BNMe_2)(TMEDA)$[12a] (38.2 g, 157 mmol) in ether (250 mL) at −40 °C. After the addition was complete, the reaction mixture was stirred at ambient temperature for 2 h. The excess Me_3SiCl and the solvent were pumped off under vacuum. Hexane (200 mL) was added to the residue, and a white precipitate of LiCl was filtered off. The filtrate was concentrated under reduced pressure to remove all volatiles. Vacuum distillation (95−100 °C, 10 mbar) of the residue using a Vigreux column (10 cm) afforded the isomer mixture **7** (19.1 g, 63%; the isomer ratio **a**/**b** was 85/15, and is 3/2 after thermal equilibration at 150 °C) as an air- and moisture-sensitive pale yellow oil. Anal. Calcd for $C_{10}H_{20}BNSi$: C, 62.18; H, 10.44; N, 7.25. Found: C, 62.05; H, 10.37; N, 7.41.

Data for 7a. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.88 (dd, J = 12.2, 5.5 Hz, 1H, 5-H), 6.30 (dd, J = 9.0, 6.1 Hz, 1H, 3-H), 6.17 (d, J = 12.2 Hz, 1H, 6-H), 6.05 (dd, J = 9.0, 5.5 Hz, 1H, 4-H), 2.83 (s, 3H, NMe), 2.70 (s, 3H, NMe), 2.49 (d, J = 6.1 Hz, 1H, 2-H), −0.01 (s, 9H, $SiMe_3$). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 142.9 (C-5), 137.2 (C-3), 127.7 (br, C-6), 121.9 (C-4), 39.8 (NMe), 38.5 (NMe), 34.4 (br, C-2), −0.8 ($SiMe_3$). ^{11}B NMR (160 MHz, $CDCl_3$, external $BF_3{\cdot}OEt_2$): δ 40.5.

Data for 7b. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.92 (dd, J = 12.2, 3.8 Hz, 2H, 3-/5-H), 6.27 (d, J = 12.2 Hz, 2H, 2-/6-H), 3.07 (d, J = 3.8 Hz, 1H, 4-H), 2.87 (s, 6H, NMe_2), 0.01 (s, 9H, $SiMe_3$). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 148.1 (C-3,5), 127.7 (br, C-2,6), 43.9 (C-4), 38.7 (NMe_2), −2.9 ($SiMe_3$). ^{11}B NMR (160 MHz, $CDCl_3$, external $BF_3{\cdot}OEt_2$): δ 31.8.

Synthesis of 1-Chloro-2-(trimethylsilyl)-1,2-dihydroborinine (8a) and 1-Chloro-4-(trimethylsilyl)-1,4-dihydroborinine (8b). A CH_2Cl_2 solution of boron trichloride (1.5 M, 78 mL, 117 mmol) was added dropwise to **7** (18.8 g, 97.5 mmol) in CH_2Cl_2 (60 mL) at −78 °C. The reaction mixture was slowly warmed to 0 °C, and stirring was continued for 2 h. After all volatiles were removed under reduced pressure, condensation (45 °C, 0.01 mbar) of the residue afforded the isomer mixture **8** (14.3 g, 80%, isomer ratio **a**/**b** ca. 95/5) as an air- and moisture-sensitive pale yellow oil. Anal. Calcd for $C_8H_{14}BSiCl$: C, 52.07; H, 7.65. Found: C, 52.39; H, 7.71.

Table 2. Crystal Data, Data Collection Parameters, and Convergence Results for 3, 5·0.5(toluene), and 9·0.5(toluene)

	3	**5**·0.5(toluene)	**9**·0.5(toluene)
empirical formula	$C_{26}H_{26}BP$	$C_{29}H_{34}BPSi{\cdot}0.5C_7H_8$	$C_{29}H_{25}BNP{\cdot}0.5C_7H_8$
fw	380.28	498.53	475.38
cryst syst	monoclinic	triclinic	triclinic
space group (No.)	$P2_1/n$ (14)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
radiation (λ, Å)	Mo Kα (0.710 73)	Cu Kα (1.541 84)	Cu Kα (1.541 84)
a, Å	9.498(2)	9.141(2)	9.217(2)
b, Å	12.950(3)	10.733(1)	12.037(5)
c, Å	17.303(5)	14.701(2)	12.448(3)
α, deg		84.889(8)	81.27(2)
β, deg	93.04(3)	82.61(1)	83.57(2)
γ, deg		81.40(1)	74.77(2)
V, Å^3	2125.2(9)	1410.7(4)	1313.3(7)
Z	4	2	2
d_{calcd}, g cm^{-3}	1.19	1.17	1.20
F(000)	808	534	502
μ, cm^{-1}	1.33	13.92	10.56
θ range, deg	2.4−26.0	4.2−69.9	3.6−74.9
temp, K	223	180	150
cryst dimens, mm^3	0.95 × 0.25 × 0.20	0.65 × 0.40 × 0.35	0.54 × 0.40 × 0.26
abs cor	none	empirical	numerical
max/min transmissn		0.998/0.876	0.786/0.554
no. of rflns	9050	7731	8346
no. of indep rflns	4165	5321	5412
no. of indep obsd rflns	1419 ($I > 2\sigma(I)$)	4200 ($I > 2\sigma(I)$)	4109 ($I > 2\sigma(I)$)
no. of variables	357	489	433
R1,[a] obsd (all data)	0.062 (0.195)	0.051 (0.067)	0.057 (0.076)
wR2,[b] obsd (all data)	0.086 (0.105)	0.121 (0.128)	0.140 (0.149)
GOF	0.704	1.038	1.060
max resd density, e Å^{-3}	0.18	0.67	0.71

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$.

Data for 8a. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (br, 1H, 5-H), 6.86 (br, 1H, 3-H), 6.53 (t, J = 7.6 Hz, 1H, 4-H), 6.51 (br, 1H, 6-H), 3.64 (br, 1H, 2-H), 0.12 (s, 9H, $SiMe_3$). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 150.4 (br, C-5), 143.7 (br, C-3), 132.8 (br, C-6), 123.3 (C-4), 54.2 (br, C-2), −0.6 ($SiMe_3$). ^{11}B NMR (160 MHz, $CDCl_3$, external $BF_3{\cdot}OEt_2$): δ 57.8.

Data for 8b. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (dd, J = 11.9, 3.7 Hz, 2H, 3-/5-H), 6.65 (d, J = 11.9 Hz, 2H, 2-/6-H), 3.85 (t, J = 3.7 Hz, 1H, 4-H), 0.08 (s, 9H, $SiMe_3$). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 157.2 (C-3,5), 132.3 (br, C-2,6), 51.7 (C-4), −2.2 ($SiMe_3$). ^{11}B NMR (160 MHz, CD_2Cl_2, external $BF_3{\cdot}OEt_2$): δ 49.0.

Synthesis of *N*-(Triphenylphosphonio)anilide−Borabenzene (9). A solution of **8** (0.298 g, 1.61 mmol) in ether (10 mL) was added slowly to *N*-(triphenylphosphonio)anilide (Aldrich, 0.522 g, 1.48 mmol) in ether (20 mL). A brown precipitate appeared immediately. After the reaction mixture was stirred at room temperature for 2 h, the solid was collected by filtration, washed with hexane (5 mL), and dried under high vacuum to give **9** (0.52 g, 82%) as shiny air- and moisture-sensitive brown-yellow microcrystals. Crystallization of **9** from hot toluene afforded the toluene solvate **9**·0.5(toluene) as platelets suitable for an X-ray diffraction study.

Data for 9. Anal. Calcd for $C_{29}H_{25}BNP$: C, 81.13; H, 5.87; N, 3.26. Found: C, 80.82; H, 6.08; N, 2.91. ^{1}H NMR (500 MHz,

CD_2Cl_2): δ 6.87 (dd, J = 10.4, 7.0 Hz, 2H, 3-/5-H), 5.83 (t, J = 7.0 Hz, 4-H), 5.26 (d, J = 12.4 Hz, 2H, 2-/6-H); signals for Ph_3PNPh moiety δ 7.77 (m, 6H, 2′-/6′-H, PPh_3), 7.67 (m, 3H, 4′-H, PPh_3), 7.51 (m, 6H, 2′-/6′-H, PPh_3), 6.95−7.10 (m, 5H, NPh). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 133.5 (C-3,5), 117.5 (br, C-2,6), 108.4 (C-4); signals for Ph_3PNPh moiety δ 143.9 (C-1″, NPh), 133.1 (d, $^2J(^{31}P-^{13}C)$ = 9.5 Hz, C-2′,6′, PPh_3), 132.5 (C-4′, PPh_3), 129.1 (d, $^3J(^{31}P-^{13}C)$ = 12.1 Hz, Ph_3P, C-3′,5′, PPh_3), 129.0 (d, $^1J(^{31}P-^{13}C) \approx$ 100 Hz, C-1′), 128.9 (C-3″,5″, NPh), 123.6 (d, $^3J(^{31}P-^{13}C)$ = 16.5 Hz, C-2”,6”, NPh), 118.4 (C-4″, NPh). $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, external $BF_3{\cdot}OEt_2$): δ 33.5. $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, external H_3PO_4): δ 34.5. MS (70 eV): m/z (I_{rel}) 429 (2, M^+), 262 (100, PPh_3^+), 185 (25, PPh_2^+).

Trimethylphosphine−3,5-Dimethylborabenzene (10). Trimethylphosphine (0.426 g, 5.60 mmol) in hexane (10 mL) was added to a solution of 1-chloro-3,5-dimethyl-2-(trimethylsilyl)-1,2-dihydroborinine (**2c**; 1.18 g, 5.54 mmol) in hexane (20 mL) at room temperature. The reaction mixture was stirred for 6 h, and a white precipitate formed during this time. The solid was collected by filtration, washed with hexane (2 × 10 mL), and dried under high vacuum to give **10** (0.93 g, 93%) as an air- and moisture-sensitive white powder. Crystallization of **10** from toluene at 30 °C afforded large colorless prisms.

Data for 10. Anal. Calcd for $C_{10}H_{18}BP$: C, 66.71; H, 10.08. Found: C, 66.86; H, 9.95. ^1H NMR (500 MHz, CD_2Cl_2): δ 6.50 (dm, $^2J(^{31}P-^1H) \approx$ 9 Hz, 2H, 2-/6-H), 6.38 (s, 1H, 4-H), 2.27 (s, 6H, 3-/5-Me), 1.61 (d, $^2J(^{31}P-^1H)$ = 11.6 Hz, 9H, PMe_3). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 142.4 (d, $^3J(^{31}P-^{13}C)$ = 8.2 Hz, C-3,5), 125.7 (br, C-2,6), 122.3 (s, C-4), 25.1 (d, $^4J(^{31}P-^{13}C)$ = 1.6 Hz, 3-/5-Me), 11.7 (d, $^1J(^{31}P-^{13}C)$ = 42.8 Hz, PMe_3). $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, external $BF_3{\cdot}OEt_2$): δ 21.8 (d, $^1J(^{31}P-^{11}B)$ = 110 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, external H_3PO_4): δ −22.3 (q, $^1J(^{31}P-^{11}B)$ = 110 Hz).

Crystal Structure Determinations. The data collections were performed on ENRAF-Nonius CAD4 diffractometers equipped with graphite monochromators using the $\omega-2\theta$ scan mode. Crystal data, data collection parameters, and convergence results are collected in Table 2. The structures were solved by direct methods and refined on reflection intensities (F^2) with the SHELXL-97 program.[24] Before merging over symmetry-related reflections, absorption corrections[25] were applied to the data sets collected with Cu Kα radiation.

In both the structures of **5**·0.5(toluene) and of **9**·0.5(toluene), the toluene molecules were disordered with respect to crystallographic inversion centers. The structural parameters of this solvent molecule were refined with the restraint that all six intra-ring C−C bond distances are taken to be equal within a standard deviation of 0.02 Å. Except for the disordered atoms, all non-hydrogen atoms were assigned with anisotropic displacement parameters, whereas the hydrogen atoms were refined isotropically.[26]

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Supporting Information Available: Tables giving X-ray crystallographic data for the structure determinations of **3**, **5**·0.5(toluene), and **9**·0.5(toluene) and files, in CIF format, for these same compounds.[26] This material is available free of charge via the Internet at http://pubs.acs.org.

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[26] Crystallographic data (excluding structure factors) for the structures reported in this paper are also available free of charge from the Cambridge Crystallographic Data Centre, on quoting the depository numbers CCDC-175679 for **3**, CCDC-175680 for **5**·0.5(toluene), and CCDC-175681 for **9**·0.5(toluene).