ultimately lead to clinically more effective antitumor drugs.

Acknowledgment. This work was supported by U.S. Public Health Service Grant CA 34992 from the National Cancer Institute. We thank the Engelhard Corp. for a loan of K_2PtCl_4, from which all platinum complexes were prepared. W.I.S. is grateful to the Whitaker Health Sciences Fund for a predoctoral fellowship. B.E.B. acknowledges the Canadian Natural Sciences and Engineering Research Council for a postgraduate scholarship. FAB mass spectra were obtained with the assistance of Dr. C. Costello at the facility supported by NIH Grant RR 00317 (Principal Investigator, Prof. K. Biemann) from the Biotechnology Resources Branch, Division of Research Resources.

Supplementary Material Available: Details of the synthesis of ligands and their precursors, tables reporting final hydrogen and non-hydrogen atom positional and thermal parameters and interatomic distances and angles, and figures showing the structures of **5** and **15** and the stereoviews of $[AO(CH_2)_6OH]I$ and $[AO(CH_2)_3OH]I$ (32 pages); tables of observed and calculated structure factors for **5**, **10**, and **15** (55 pages). Ordering information is given on any current masthead page.

Synthesis and Spectroscopic and X-ray Structural Characterization of Compounds Involving Boron–Phosphorus Multiple Bonds: Lithium Salts of Boryl Phosphides and Their Precursors

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Abstract: The synthesis and spectroscopic and structural characterization of several lithium salts of boryl phosphides and their precursors are described. Treatment of the lithium salt of a primary phosphane H_2PR' with R_2BX (X = F, Cl) affords the phosphinoboranes (borylphosphanes) R_2BPHR' (R/R′ = Ph/*t*-Bu (**1**), Mes/*t*-Bu (**2**), Trip/*t*-Bu (**3**), Mes/Ph (**4**), Mes/Cy (**5**), Mes/Mes (**6**) (Mes = 2,4,6-$Me_3C_6H_2$, Trip = 2,4,6-*i*-$Pr_3C_6H_2$, Cy = cyclohexyl)) in good yield. The reaction of compounds **1–6** with 1 equiv of *n*-BuLi or *t*-BuLi affords their corresponding lithium salts $[Li(Et_2O)_2PR'BR_2]$ (**7–12**). The addition of 2 equiv of 12-crown-4 to $Li(Et_2O)_2PR'BMes_2$ (R′ = Ph (**10**), Cy (**11**), Mes (**12**)) gives the solvent-separated salts $[Li(12\text{-crown-}4)_2][PR'BMes_2]\cdot THF$ (R′ = Ph (**13**), Cy (**14**), Mes (**15**)). Also, the reaction of Mes_2BF with $[Li(THF)_2P(SiMe_3)_2]_2$ gives $[Li(THF)_3P(SiMe_3)BMes_2]$ (**16**) with elimination of Me_3SiF rather than LiF. In addition, the reaction between $TripBBr_2$ and 2 equiv of LiPHMes gave the lithium salt $[Li(Et_2O)_2P(Mes)B(PMesH)Trip]$ (**17**), involving boron bound to two phosphorus centers through a single and a multiple bond. Apart from ^{11}B and ^{31}P NMR spectroscopic characterization, the X-ray structures of the dimeric compound **1**, the lithium salts $[Li(Et_2O)_2P(t\text{-Bu})BTrip_2]$ (**9**), $[Li(THF)_3P(SiMe_3)BMes_2]$ (**16**), and $[Li(Et_2O)_2P(Mes)B(PHMes)\ Trip]$ (**17**) are described. Compounds **10–12** and **13–15**, including the structures of **11**, **12**, and **15**, have been described in a preliminary communication. The lithium compounds **7–17** are of particular interest because they are the only structurally characterized compounds known to involve a high degree of multiple bonding between boron and phosphorus. Thus, compound **17** is also notable since it has the shortest B–P bond length, 1.810 (3) Å, reported to date. Crystal data with Mo Kα radiation (λ = 0.71069 Å) at 130 K: **1**, a = 10.291 (4) Å, b = 10.468 (3) Å, c = 14.767 (2) Å, α = 71.05 (2)°, β = 75.63 (2)°, γ = 82.49 (3)°, triclinic, space group $P\bar{1}$, Z = 2, R = 0.049; **9**, a = 10.378 (4) Å, b = 19.094 (6) Å, c = 21.995 (7) Å, orthorhombic $Pc2_1n$, Z = 4, R = 0.036; **16**, a = 10.331 (6) Å, b = 16.133 (5) Å, c = 10.647 (5) Å, β = 95.13 (4°), monoclinic, space group $P2_1$, Z = 2, R = 0.049; **17**, a = 13.543 (2) Å, b = 17.812 (3) Å, c = 17.475 (3) Å, β = 93.72 (1)°, monoclinic, space group $P2_1/n$, Z = 4, R = 0.063.

Lithium derivatives of the amide (NR_2) and phosphide (PR_2) ligands are the most important transfer agents for these species, and this has generated considerable interest in their structures. Usually they associate in the solid state to form oligomeric or polymeric species involving the nitrogen or phosphorus centers bridging two or more metals. However, the bridging tendency can be reduced by increasing the size of the substitutents on nitrogen or phosphorus. For example, when crystallized from Et_2O or THF, both $LiPPh_2$[1] and $LiP(C_6H_{11})_2$[1] have polymeric chain-like structures whereas $LiP(t\text{-Bu})_2$ is tetrameric[2] and $LiP\{CH(SiMe_3)_2\}_2$ exists as a dimer,[3] even in the absence of donor solvents. In both $LiPR_2$ compounds and their nitrogen counterparts there is a lone pair available on either phosphorus or nitrogen which facilitates their association. It seemed reasonable to assume that if the avilability of the lone pair were to be reduced by electronic rather than steric means, monomeric species might ensue owing to the lower tendency toward bridging. Recent work in this laboratory has shown that, for amide ligands, replacement of one of the alkyl or aryl substituents by the dimesitylboryl group ($BMes_2$) results in amide ligands that have little or no tendency to bridge or behave as π-donors.[4] The use of amide ligands such as $NRBMes_2$ (R = Ph or Mes) has allowed the facile synthesis of a range (d^4–d^8) of two-coordinate transition-metal complexes, for example, $M(NMesBMes_2)_2$ (M = Cr, Mn, Fe, Co, Ni).[5] In addition, the lithium salts $Li(Et_2O)_2NRBMes_2$ (R = Ph, Mes) are monomeric[4,5] even though bulky amide ligands are normally found to be as-

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sociated as in $[Li(THF)_2N(SiMe_3)_2]_2$.[6]

The case of the modified phosphide ligands ($PR'BMes_2$) has proved to be more intriguing. The major reason for this is that boron–phosphorus compounds are, in general, poorly investigated in comparison to their nitrogen counterparts. Thus, although the preliminary report[7] on the synthesis and structures of the $Li(Et_2O)_2PR'BMes_2$ salts (R' = Ph, C_6H_{11}, Mes) showed that they were monomeric, there was the added novelty that the B–P bond was multiple in character with short B–P bond lengths of about 1.83 Å. Another feature of interest was the isoelectronic relationship between the B–P pairs and others such as C–Si[8] and N–Al,[9] which are of current interest from the point of view of multiple bonding. In addition, the $PR'BMes_2$ ligand itself should display only weak bridging characteristics in contrast to the strong bridging tendency of phosphide ligands that have bulky substituents, for example, $P(t\text{-}Bu)_2$.[10]

In this paper we provide details of the synthesis and spectroscopy of 17 boron–phosphorus compounds in connection with the synthesis of a range of lithium salts of the type $Li(Et_2O)_2PR'BR_2$. Four new structures are described that, in addition to those published in a preliminary communication,[7] provide important data for a wide range of different boryl phosphides. To our knowledge these represent the only known structurally characterized examples of compounds of the type $Li(Et_2O)_2PR'BR_2$, although species such as LiP(Ar)BR(tmp) (Ar = 2,4,6-*t*-$Bu_3C_6H_2$, R = Me or *t*-Bu, tmp = 2,2,6,6-tetramethylpiperidino) have been spectroscopically characterized.[11,12] Also, there are no prior reports for compounds of type **17**. In addition, the dimer **1** represents a rare example of a structure of a dimeric phosphinoborane. In this case the structure $(Ph_2PBI_2)_2$ seems to be the sole precedent.[13]

Experimental Section

All experiments were performed by using either modified Schlenk techniques under N_2 or a Vacuum Atmospheres HE 43-2 drybox under argon due to the air and moisture sensitivity of compounds **1–17**. Solvents were freshly distilled under N_2 from Na/K alloy–benzophenone ketyl and degassed twice immediately prior to use.

The reagents Mes_2BF,[14] $Trip_2BF$,[14] $TripBBr_2$,[15] $MesPH_2$,[16] *t*-$BuPCl_2$,[17] and $[Li(THF)_2P(SiMe_3)_2]_2$[18] were prepared according to the literature methods or modifications thereof. Ph_2BBr (Alfa), $CyPH_2$ (Alfa), $PhPH_2$ (Alfa), *n*-BuLi (Aldrich), and *t*-BuLi (Aldrich) were obtained commercially and used as received. *t*-$BuPH_2$ was prepared from *t*-$BuPCl_2$ by $LiAlH_4$ reduction in diglyme. 12-Crown-4 was obtained commerically (Strem) and distilled over Na under N_2 before use.

^{31}P and ^{11}B NMR data were obtained with a Nicolet NT-200 spectrometer operating at 81 and 64 MHz, respectively. All the ^{31}P spectra were referenced to external 85% H_3PO_4, and ^{11}B spectra were referenced to external $BF_3{\cdot}OEt_2$. The THF/C_6D_6 mixture was used as the solvent unless otherwise noted.

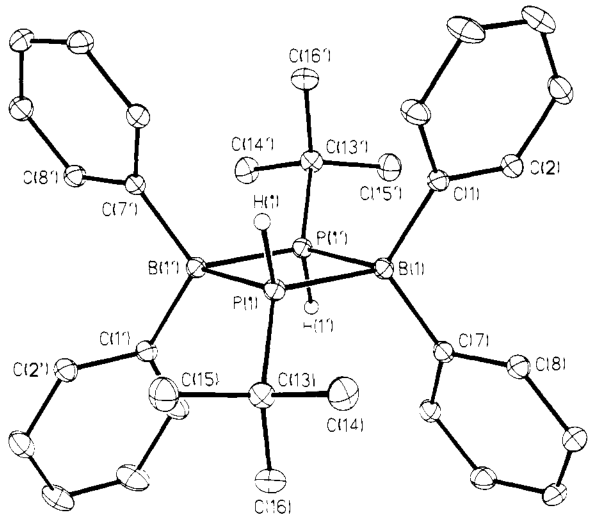

Figure 1. Computer-generated thermal ellipsoid plot of **1**.

Synthesis of Compounds 1–17. $[Ph_2BP(H)\text{-}t\text{-}Bu]_2$ (1). *t*-$BuPH_2$ (0.44 g, 4.9 mmol) in Et_2O (30 mL) at 0 °C was treated dropwise with *n*-BuLi (1.6 M, 3 mL). The solution was stirred for 30 min and Ph_2BBr (1.2 g, 4.9 mmol) in hexane (5 mL) was added dropwise. The reaction mixture was stirred for 3 h and filtered. The filtrate was concentrated to incipient crystallization and cooled at 0 °C to obtain pale yellow crystals of **1**. Yield 72%; mp >250 °C (turns dark yellow above 170 °C).

In Situ Preparation of $Mes_2BP(H)R'$ (R' = *t*-Bu (2), Ph (4), Cy (5), Mes (6)). Solid Mes_2BF (0.81 g, 3 mmol) was added via a solid addition tube to an Et_2O (30 mL) solution of RPHLi (3 mmol), generated in situ from RPH_2 (3 mmol) and *n*-BuLi (1.6 M, 1.9 mL) at 0 °C. The resulting mixture was stirred for an additional hour at room temperature to obtain over 80% yield of **2** and **4–6**.

In Situ Preparation of $Trip_2BP(H)\text{-}t\text{-}Bu$ (3). Compound **3** was prepared by a method similar to that used for **2** using $Trip_2BF$ and *t*-BuPHLi. The **3** was obtained in >80% yield.

In Situ Preparation of $[Ph_2BP(t\text{-}Bu)Li(Et_2O)_2]$ (7). **1** (0.7 g) was dissolved in Et_2O and treated with *t*-BuLi (1 equiv) at −78 °C. After the mixxture warmed to room temperature, ^{31}P and ^{11}B NMR analysis indicated formation of **7** in over 80% yield. Attempts to grow crystals failed due to their ready decomposition in solution on standing.

$[Li(Et_2O)_2PR'BMes_2]$ (R' = *t*-Bu (8), Ph (10), Cy (11), Mes (12)). Treatment of $Mes_2BP(R')H$ with 1 equiv of *t*-BuLi in Et_2O (50 mL) at 0 °C resulted in a dark yellow solution. This was stirred for 1 h and the volume was reduced to incipient crystallization. The reaction mixture was filtered and cooled at −20 °C, affording ca. 60% yield of **8** (mp 179–183 °C (turns opaque around 108 °C)), **10** (mp 105–107 °C), **11** (mp 92–94 °C), or **12** (mp 118–121 °C).

$[Li(Et_2O)_2P(t\text{-}Bu)BTrip_2]$ (9). $Trip_2BF$ (0.875 g, 2 mol) in Et_2O (20 mL), cooled in an ice bath, was treated dropwise with a solution formed from *t*-$BuPH_2$ (0.185 g, 2 mmol) in Et_2O (20 mL) and 1.25 mL of a 1.6 M *n*-BuLi solution in hexane. The solution became yellow and was stirred for 1 h at ambient temperature. The volume was reduced to 15 mL under low pressure, and *n*-hexane was added to incipient crystallization. Filtration and reduction of the volume as necessary afforded the product as yellow crystals. Yield 0.75, 55%. The crystals became opaque at 98–100 °C and decompose at 280 °C.

$[Li(12\text{-}crown\text{-}4)_2][Mes_2BPR']{\cdot}THF$ (R' = Ph (13), Cy (14), Mes (15)). $Li(Et_2O)_2P(R')BMes_2$ (1 mmol) was dissolved in Et_2O (20 mL), and 2 equiv of 12-crown-4 was added at 0 °C. A yellow precipitate was obtained. This precipitate was recrystallized from 1:1 THF/Et_2O to give ca. 65% yield of **13** (mp 90–95 °C (dec)), **14** (mp 150–155 °C (dec)), or **15** (mp 127–135 °C).

$[Li(THF)_3P(SiMe_3)BMes_2]$ (16). Mes_2BF (0.97 g, 3.6 mmol) in Et_2O (20 mL) and THF (0.5 mL), cooled in an ice bath, was treated dropwise with $[\{Li(THF)_2P(SiMe_3)_2\}_2]$ (1.1 g, 1.8 mmol) in Et_2O (25 mL). The solution became yellow and after 30 min it was allowed to warm to room temperature and stirred for 2 h. The volatiles were removed under reduced pressure, and hexane was added with warming to 40 °C. Filtration and cooling in a −20 °C freezer gave the product as yellow-amber crystals. Yield 1.2 g, 55%. The crystals darken on heating, soften at 125 °C, and melt at 133–136 °C.

$[Li(Et_2O)_2P(Mes)B(PMesH)Trip]$ (17). $MesPH_2$ (1.2 g, 7.9 mmol) was lithiated in Et_2O (30 mL) with *n*-BuLi (1.6 M, 5.0 mL) at 0 °C. The solution was stirred for 20 min, and $TripBBr_2$ (1.35 g, 3.6 mmol) in hexane (15 mL) was added dropwise. The color became dark orange.

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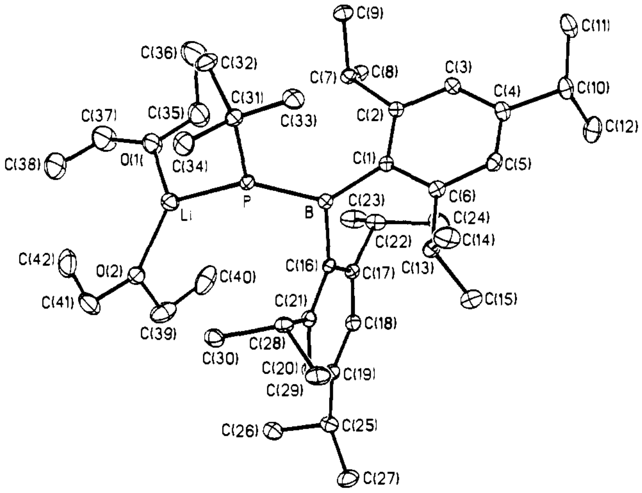

Figure 2. Computer-generated thermal ellipsoid plot of **9**.

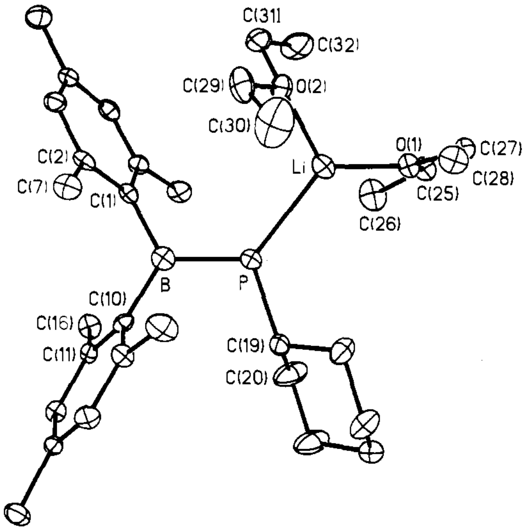

Figure 3. Computer-generated thermal ellipsoid plot of **11**.

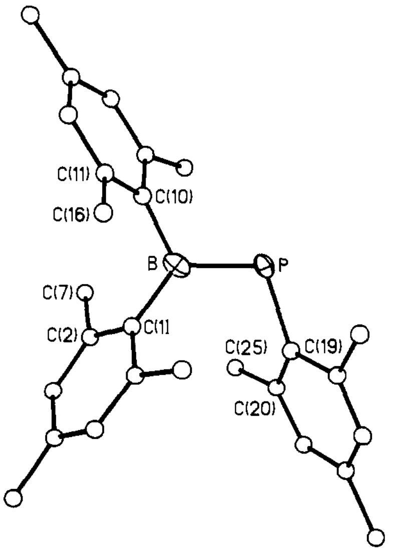

Figure 4. Computer-generated thermal ellipsoid plot of **13**.

The mixture was stirred for 15 min at 0 °C and allowed to warm to room temperature. After stirring for an additional 3 h, the solution was concentrated and cooled at −20 °C to give **17** in 29% yield. The crystals turned opaque around 120 °C and did not melt at <250 °C.

X-ray Crystallographic Studies. All X-ray data were collected on a Syntex $P2_1$ diffractometer equipped with a locally modified LT-1 device, Mo Kα radiation, and a graphite monochromator. Calculations were carried out on a Data General Eclipse computer using the SHEXTL, Version 5, programs. Absorption corrections were made with the program XABS.[19] Neutral-atom scattering factors and corrections for anomalous dispersions were from ref 20. Crystals of **1**, **9**, **16**, and **17** were grown as described above. Upon removal from the Schlenk tube, the crystals were covered with a hydrocarbon oil to protect them from decomposition in the air. A single crystal was selected under oil, mounted on a glass fiber with silicone grease, and immediately placed in the low-temperature N_2 stream. Further details are provided in the Supplmentary Material. Selected bond distances and angles are given in Table I. The structures of compounds **1**, **9**, **16**, and **17** are illustrated in Figures 1, 2, 5, and 6, respectively. Additional information is given below. For comparison, Table **II** lists selected bonding parameters for **9** and **11**, **12**,

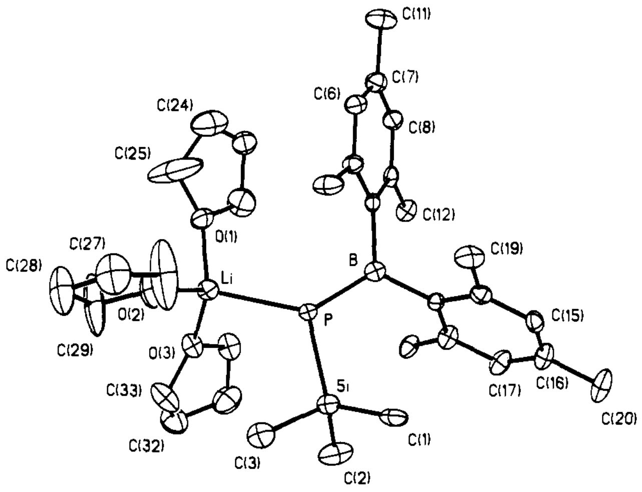

Figure 5. Computer-generated thermal ellipsoid plot of **16**.

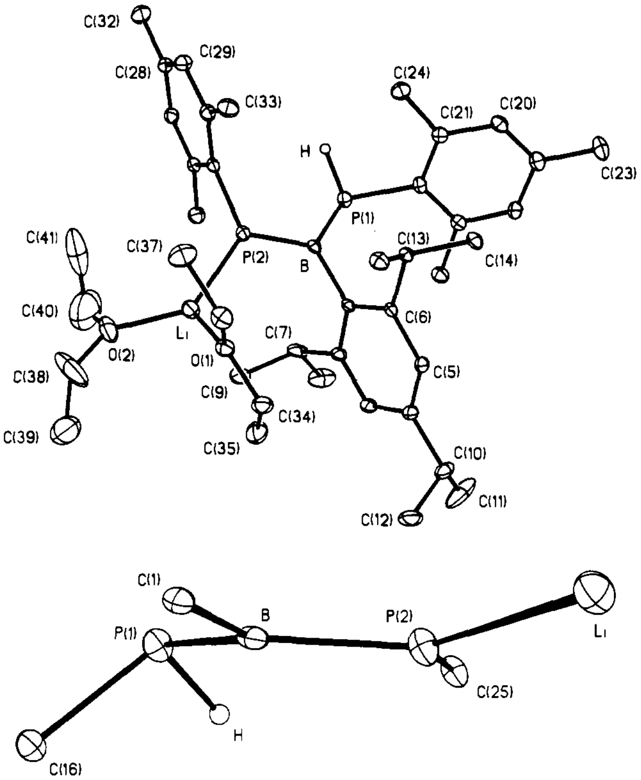

Figure 6. (Top) Computer-generated thermal ellipsoid plot of **17**. (Bottom) A view of the core atoms in **17**, showing the planar P(2) and pyramidal P(1) centers.

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Table I. Selected Bond Distances (Å) and Angles (deg) for **1**, **9**, **16**, and **17**

$[Ph_2BP(t\text{-}Bu)H]_2$ (**1**)	
P(1)–B(1) = 2.026 (2)	P(2)–B(2) = 2.035 (3)
P(1)–C(13) = 1.856 (2)	P(2)–C(29) = 1.858 (2)
P(4)–H(1) = 1.400 (18)	nP(2)–H(2P) = 1.400 (9)
P(1)–B(1′) = 2.026 (2)	P(2)–B(2′) = 2.021 (2)
B(1)–C(1) = 1.614 (3)	B(2)–C(17) = 1.614 (3)
B(1)–C(7) = 1.613 (3)	B(2)–C(23) = 1.620 (3)
B(1)–P(1)–C(13) = 121.3 (1)	B(2)–P(2)–C(29) = 127.6 (1)
B(1)–P(1)–B(1′) = 94.3 (1)	B(2)–P(2)–B(2′) = 94.6 (1)
B(1)–P(1)–H(1) = 111.3 (6)	B(2)–P(2)–H(2P) = 107.5 (9)
C(13)–P(1)–B(1′) = 122.4 (1)	C(29)–P(2)–B(2′) = 120.2 (1)
C(13)–P(1)–H(1) = 97.5 (8)	C(29)–P(2)–H(2P) = 97.0 (10)
B(1′)–P(1)–H(1) = 110.6 (9)	B(2′)–P(2)–H(2P) = 109.3 (9)
P(1)–B(1)–P(1′) = 85.7 (1)	P(2)–B(2)–P(2′) = 85.4 (1)
P(1)–B(1)–C(1) = 114.4 (1)	P(2)–B(2)–C(17) = 115.8 (2)
P(1)–B(1)–C(7) = 114.6 (1)	P(2)–B(2)–C(23) = 111.6 (1)
C(1)–B(1)–C(7) = 113.2 (2)	C(17)–B(2)–C(23) = 113.8 (2)
C(1)–B(1)–P(1′) = 111.8 (1)	C(17)–B(2)–P(2′) = 114.0 (1)
C(7)–B(1)–P(1′) = 114.4 (1)	C(23)–B(2)–P(2′) = 113.3 (1)
twist angle between P(1) and B(1) plane = 28.9	twist angle between P(2) and B(2) plane = 28.5
dihedral angle between Ph groups = 69.0	dihedral angle between Ph groups = 69.4
$[Li(Et_2O)_2P(t\text{-}Bu)BTrip_2]$ (**9**)	
P–B = 1.836 (2)	B–C(1) = 1.609 (3)
P–Li = 2.460 (4)	B–C(16) = 1.624 (3)
P–C(31) = 1.893 (2)	Li–O(1) = 1.960 (5)
	Li–O(2) = 1.925 (4)
B–P–Li = 122.6 (1)	P–B–C(16) = 111.1 (1)
B–P–C(31) = 116.2 (1)	C(1)–B–C(16) = 118.5 (2)
Li–P–C(31) = 117.3 (1)	P–Li–O(1) = 119.3 (2)
P–B–C(1) = 130.4 (2)	P–Li–O(2) = 123.0 (2)
	O(1)–Li–O(2) = 117.1 (2)
twist angle between P and B planes = 33.3	dihedral angle between Trip groups = 87.7
$[Li(THF)_3P(SiMe_3)BMes_2]$ (**16**)	
P–Si = 2.213 (2)	B–C(13) = 1.602 (8)
P–B = 1.833 (6)	Li–O(1) = 1.941 (11)
P–Li = 2.540 (10)	Li–O(2) = 1.898 (11)
B–C(4) = 1.608 (8)	Li–O(3) = 1.950 (10)
Si–P–B = 109.5 (2)	P–Li–O(1) = 114.2 (4)
Si–P–Li = 117.0 (2)	P–Li–O(2) = 111.3 (4)
B–P–Li = 131.2 (3)	P–Li–O(3) = 107.2 (4)
P–B–C(4) = 118.5 (4)	O(1)–Li–O(2) = 106.7 (5)
P–B–C(13) = 123.8 (4)	O(1)–Li–O(3) = 105.5 (5)
C(4)–P–C(13) = 117.7 (5)	O(2)–Li–O(3) = 111.9 (5)
twist angle between B and P planes = 22	dihedral angle between Mes groups = 110.8
$[Li(Et_2O)_2P(Mes)B(PHMes)Trip]$ (**17**)	
P(1)–B = 1.927 (3)	P(2)–Li = 2.476 (6)
P(1)–C(16) = 1.844 (3)	B–C(1) = 1.589 (4)
P(1)–H = 1.316 (32)	Li–O(1) = 1.907 (6)
P(2)–B = 1.810 (4)	Li–O(2) = 1.881 (7)
P(2)–C(25) = 1.846 (3)	
B–P(1)–C(16) = 108.1 (1)	P(1)–B–P(2) = 122.9 (2)
B–P(1)–H = 101.6 (13)	P(1)–B–C(1) = 117.6 (2)
C(16)–P(1)–H = 97.0 (14)	P(2)–B–C(1) = 119.0 (2)
B–P(2)–C(25) = 109.1 (1)	P(2)–Li–O(1) = 123.9 (3)
B–P(2)–Li = 122.2 (2)	P(2)–Li–O(2) = 122.2 (3)
C(25)–P(2)–Li = 128.1 (2)	O(1)–Li–O(2) = 113.2 (3)
twist angle between P(1) and B plane = 24.3	twist angle between P(2) and B plane = 18.6

and **15**, and Figures 3 and 4 illustrate compounds **11** and **15**.

Structural Descriptions

trans**-**$[\{Ph_2BP(t\text{-}Bu)H\}_2]$ **(1).** The asymmetric unit of **1** has two crystallographically independent, but chemically identical, trans dimers of the $Ph_2BP(t\text{-}Bu)H$ unit. Each dimer has a crystallographically imposed center of symmetry and thus a planar B_2P_2 core. The B–P bond lengths, 2.026 (2) Å, are identical in one of the dimers. In the other they are 2.035 (3) and 2.021 (2) Å, which give an average value of 2.028 Å. The internal angles at phosphorus average close to 94.5° and those at boron 85.5°. The B–C, P–C, and P–H distances (Table I) are consistent with those expected for bonding involving four-coordinate boron and phosphorus centers.

Table II. Selected Structural Parameters for the Lithium Salts of Boryl Phosphides

	$Li(Et_2O)_2PR'BR_2$			$[R'P{=}BR_2]^-$
parameter	t-Bu/Trip[a] **9**	Cy/Mes[a] **11**	Mes/Mes[a] **12**	Mes/Mes[a] **15**
B–P, Å	1.836 (2)	1.832 (6)	1.823 (7)	1.835 (13)
Li–P, Å	2.460 (4)	2.454 (9)	2.451 (14)	
P–C, Å	1.893 (2)	1.871 (6)	1.850 (10)	1.863 (10)
B–C, Å	1.609 (3)	1.598 (8)	1.604 (14)	1.582 (15)
B–C, Å	1.624 (3)	1.593 (7)	1.598 (11)	1.619 (15)
BPC, deg	116.2 (1)	108.2 (3)	111.7 (4)	108.2 (5)
twist angle between B and P planes, deg	33.3	3.8	11.7	0

[a] R′/R in the complex.

$[\mathbf{Li(Et_2O)_2P(}\boldsymbol{t}\mathbf{\text{-}Bu)BTrip_2}]$ **(9).** Compound **9** crystallizes as discrete units of formula $Li(Et_2O)_2P(t\text{-}Bu)BTrip_2$ with no close intermolecular contacts. The compound is structurally similar to complexes **11** and **12**, which were described in a preliminary communication. The major structural features concern the short B–P distance of 1.836 (2) Å and the somewhat long B–C and P–C distances of 1.609 (3), 1.624 (3), and 1.893 (2) Å. Also, the BPC(31) angle, 116.2 (1)° is wide and the dihedral angle between the B and P planes is 33.3°. Both Trip groups lie almost perpendicular to the plane at boron. The Li–P and Li–O distances may be considered to be normal; however, it is notable that the dihedral angle between the LiPO(1)O(2) plane and that formed by BPC(31) is 72.9°.

$[Li(THF)_3\mathbf{P(SiMe_3)BMes_2}]$ **(16).** The structure consists of discrete units of the title compound. The major difference between **16** and **9**, **11**, or **12** involves the solvation of Li by three THF donors and the substitution of a silyl group rather than an organo group on phosphorus. These changes, however, have little effect on the B–P bond length, 1.833 (6) Å. As expected, the Li–P and Li–O distances are somewhat lenghtened owing to the higher coordination number at lithium. As in **9** the B–C distances are somewhat longer than expected. Also, the twist angle between the B and P planes is high at 22°. The P–Si bond length is 2.213 (2) Å. This is slightly less than the sum of their atomic radii. The bond distances and angles within the mesityl and $SiMe_3$ groups are normal.

$[\mathbf{Li(Et_2O)_2P(Mes)B(PMesH)Trip}]$ **(17).** The structure consists of discrete molecules of the title compound. They involve a planar boron center substituted by the three groups, Trip, PHMes, and $P(Mes)Li(Et_2O)_2$. The phosphorus substituent bearing the $Li(Et_2O)_2$ group is planar whereas the PHMes group is pyramidal, with the sum of the angles at P(1) being 306.7°. The P(1)–B bond is 1.927 (3) Å whereas P(2)–B, involving the planar phosphorus center, is 1.810 (4) Å, which is the shortest B–P bond reported to date. The dihedral angle between the B and P(2) planes is 18.6°. There are no unusual B–C, P–C, or P–H bond lengths, and the Li–P and Li–O distances are within the expected ranges.

Discussion

Compounds **1–17** may be conveniently divided into four different classes for the purposes of this discussion. The phosphinoboranes **1–6** can be most simply treated as secondary phosphanes in which one of the substituents is a diarylboryl group. These serve as precursors for the ether-solvated lithium salts **7–12**. The addition of 12-crown-4 to **10–12** affords their closely related ionic species **13–15** in which the lithium ion has been separated via coordination to 12-crown-4. The remaining compounds **16** and **17** are treated separately because in the case of **16** the product is unexpected and **17** is unique in that it involves two very different phosphorus centers bonded to boron.

Compounds 1–6. With the exception of the dimer **1**, the compounds were synthesized in situ, characterized on the basis of ^{11}B and ^{31}P NMR, and used without further purification. They may be isolated as yellow oils or solids. However, attempts at puri-

Table III. ^{11}B and ^{31}P NMR Chemical Shift Data (ppm) for Compounds **1–17**

compd	^{11}B	^{31}P (J_{P-H}, Hz)
$[Ph_2BP(t\text{-}Bu)H]_2$ (**1**)	−5.7	−28.0 (255)
$Mes_2BP(t\text{-}Bu)H$ (**2**)	83.8	−4.0 (270)
$Trip_2BP(t\text{-}Bu)H$ (**3**)	79.7	−1.6 (269)
$Mes_2BP(Ph)H$ (**4**)		−41.5 (254)
$Mes_2BP(Cy)H$ (**5**)		−20.0 (264)
$Mes_2BP(Mes)H$ (**6**)		−66.0 (301)
$[Li(Et_2O)_2P(t\text{-}Bu)BPh_2]$ (**7**)	64.8	97.6
$[Li(Et_2O)_2P(t\text{-}Bu)BMes_2]$ (**8**)	62.5	104.3
$[Li(Et_2O)_2P(t\text{-}Bu)BTrip_2]$ (**9**)	58.9	113.2
$[Li(Et_2O)_2P(Ph)BMes_2]$ (**10**)	65.4	73.1
$[Li(Et_2O)_2P(Cy)BMes_2]$ (**11**)	65.6	70.1
$[Li(Et_2O)_2P(Mes)BMes_2]$ (**12**)	63.7	55.5
$[Li(12\text{-crown-}4)_2][PhPBMes_2]$ (**13**)	close to Li compd **10–12**	103.6
$[Li(12\text{-crown-}4)_2][CyPBMes_2]$ (**14**)		113.6
$[Li(12\text{-crown-}4)_2][MesPBMes_2]\cdot THF$ (**15**)		91.3
$[Li(THF)_3P(SiMe_3)BMes_2]$ (**16**)	71.6	−49.2
$[Li(Et_2O)_2P(Mes)B(PHMes)Trip]$ (**17**)	64.0	32.0 −117.0 (247)

fication via recrystallization did not result in material suitable for X-ray crystallography.

The ^{11}B NMR spectra (Table III) of **2** and **3** exhibit broad (300–500 Hz) signals around 80 ppm. These values indicate the presence of three-coordinate rather than four-coordinate boron.[21] In sharp contrast, the ^{11}B chemical shift of **1** is −5.7 ppm. This value is consistent with the four-coordinate boron seen in the X-ray crystal structure. The dimeric nature of **1** is mainly a result of the reduced steric requirements of the phenyl groups at the boron center which allow bridge bonding to two phosphorus groups.

The ^{31}P chemical shifts of **1–6** are all negative. The observed shifts are comparable to those normally seen for secondary phosphines, suggesting that the interaction of the phosphorus lone pair with boron has little effect on the deshielding of the ^{31}P nucleus. However, it is notable that the J_{P-H} values 254–301 Hz are significantly higher than the typical P–H coupling constants (180–220 Hz) observed for secondary phosphanes. This increase can be accounted for in terms of the changed hybridization of the P–H bond. In essence, the interaction between the phosphorus lone pair orbital and the empty p orbital on boron results in wider angles at phosphorus with increased s-orbital character (somewhere between sp^2 and sp^3) in the σ-bonds to phosphorus, resulting in a higher P–H coupling constant.

The centrosymmetric structure of the trans dimer **1** merits little further comment. The average B–P bond distances, 2.026 (2) and 2.028 (2) Å, are the most notable feature. These are comparable to the B–P bond length, 2.01 Å, in $[(Ph_2PBI_2)_2]$.[13] Presumably, the four-coordinate nature of both boron and phosphorus, the somewhat strained angles in the planar B_2P_2 ring, and the presence of a total of six fairly large organic goroups on the ring combine to give the long B–P bonds. These distances are significantly larger than those in boron phosphide itself[22] (1.96 Å) or the adducts H_3PBH_3[23] and Me_3PBH_3,[23] which have B–P bonds of about 1.93 Å. However, none of the latter involve strained rings or are encumbered by organic substituents of significant size.

Ether-Solvated Lithium Salts $Li(Et_2O)_2PR'BR_2$ (7–12). Compounds **1–6** react quantitatively and smoothly with either *n*-BuLi or *t*-BuLi in ether solution to give the various ether-solvated lithium derivatives **7–12**. Compounds **8** and **9** have been structurally characterized, and the X-ray structures of **11** and **12** have been described in a preliminary communication. The ^{11}B NMR spectra of all compounds show broad singlets that have remarkably constant chemical shifts. The most notable datum concerns compound **7**, whose ^{11}B chemical shift of 64.8 ppm is very similar to those of the others and consistent with the presence of three-coordinate boron. Similarly, the ^{31}P chemical shift of **7** is close to the values found for the two other *t*-Bu derivatives **8** and **9**. This leads to the conclusion that the metalation of the dimer **1** with *t*-BuLi leads to a monomeric product **7**, which presumably has a very similar structure to those of **8**, **9**, **11**, and **12**. However, it is notable that this compound is unstable and decomposes in solution at room temperature over a period of hours. This instability may be due to an oligomerization, as a result of the lower steric requirements at boron which make it more vulnerable to attack. Overall, the ^{31}P NMR chemical shifts, which range from 55.5 to 113.2 ppm, are more variable than the ^{11}B values. They are significantly (60–120 ppm) more positive than the shifts for their precursors **1–6**. The decreased shielding may be accounted for in terms of the increased degree of removal of electron density from the phosphorus onto boron, which is consistent with the short B–P bonds (ca. 1.83 Å) seen in the X-ray structures. Also, the ease with which the Li^+ ion can be removed by 12-crown-4 and the relatively long Li–P interactions suggest that the association between Li and P is quite weak. Thus, the P center can be regarded as incipiently two-coordinated, which results in the observed downfield shifts. Downfield shifts are also observed when "normal" secondary phosphanes are treated with *n*-BuLi.[24]

The major structural features of **9**, **11**,[7] and **12**[7] involve a short B–P bond distance, which varies between 1.823 (7) Å for **12**[7] and 1.836 (2) Å for **9**, and an array of P, B, their substituent carbon atoms, and lithium, which show variable deviation from planarity. These data point to a significant overlap between the boron p orbital and the lone pair on the approximately sp^2-hybridized phosphorus, resulting in a high degree of double-bond character for the B–P bond. The B–C and P–C distances are normal in compounds **11** and **12**. In **9**, however, the B–C and P–C distances are significantly longer than those in **11** and **12**. Also, the dihedral angle 33.3° between the B and P planes in **9** is a lot larger than those in **11** (3.8°) or **12** (11.7°) (see Table II). These data, along with the almost 90° dihedral angles for the Trip ring planes, point to significantly more steric congestion in **9** compared to **11** or **12**. A final aspect of the structures of **9**, **11**, and **12** concern their unassociated nature. Most dialkyl and diaryl phosphides,[1,2] even the very bulky species $LiP\{CH(SiMe_3)_2\}_2$,[3] are found to be associated in the solid. The monomeric structures of **7–12** are thus mainly a consequence of the reduced bridging tendency of the phosphorus center as a result of its multiple bonding to boron.

Compounds 13–15. The addition of 2 equiv of 12-crown-4 to **10–12** results in compounds **13–15**, which exist as ion pairs. Satisfactory X-ray data have only been obtained in the case of **15**. These show that the cation is formed from a Li^+ ion sandwiched between two 12-crown-4 donors. The coordination symmetry at Li^+ is approximately D_{4d} owing to the staggered nature of the 12-crown-4 rings. The Li–O distances range from about 2.3 to 2.5 Å, which represent a reasonable extrapolation of the Shannon–Prewitt[25] data from lower coordinate Li^+ ions. The $[Mes_2BPMes]^-$ anion has very similar structural parameters to the Li complexes **9**, **11**, and **12**. The most important feature, the B–P bond length, 1.835 (13) Å, shows little change from its complexed precursor **12**. In fact, all the interatomic distances show only insignificant changes upon removal of the Li^+ ion by complexation.

In contrast, downfield shifts of 30–35 ppm are seen in the ^{31}P NMR when 12-crown-4 is added to THF solutions of **10**, **11**, or **12** to give **13**, **14**, or **15**. The nature of this shift parallels our observations[24] for normal lithium secondary phosphide solutions, which in many instances show shifts to more positive values upon treatment with 12-crown-4. The more deshielded nature of the phosphorus centers is consistent with its low coordination number. The ^{11}B spectra of **13–16** show negligible changes from the

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corresponding data for **10–12**. This result is consistent with the very few changes in the structural parameters surrounding the boron centers as demonstrated by the structure of **12**.

Compounds 16 and 17. Compound **16** technically falls into the same class as **7–12**. However, the method of synthesis is different. The synthetic route is as shown in eq 1 and involves the elimination

$$\mathrm{Li(THF)_2P(SiMe_3)_2 + FBMes_2 \xrightarrow{THF} Me_3SiF + Li(THF)_3P(SiMe_3)BMes_2} \quad (1)$$

of Me_3SiF rather than LiF as was the case in the other compounds. Presumably, the relatively weak P–Si bond and the energetically favorable Si–F bonds as well as the greater degree solvation of the Li^+ ion provide a sufficient incentive for Me_3SiF elimination over the more conventional elimination of LiF. The structure has many characteristics in common with those of **8**, **11**, and **12**. The planar core, the B–P bond length, 1.833 (6) Å, and the angles and distances surrounding boron are very similar to those mentioned in the previous sections. The Li–P distance, 2.540 (10) Å, is somewhat longer owing to the higher coordination number (four) at lithium. On the other hand, the P–Si bond (2.213 (2) Å) may be regarded as longer than expected. For example, it is marginally longer than the values in $[\{Li(THF)_2P(SiMe_3)_2\}_2]$ (2.195 (5) Å) and very similar to the values (average 2.21 Å) seen in $[Li_4\{\mu_2\text{-}P(SiMe_3)_2\}\{\mu_3\text{-}P(SiMe_3)_2\}_2(THF)_2]$[26] even though the phosphorus centers in both these complexes are four-coordinate. The ^{11}B spectrum reveals a broad singlet at 71.6 ppm and this is a little higher than the normal range. The ^{31}P spectrum, however, affords a singlet at −49.2 ppm, which is much further upfield than the signals observed for **7–15**. We attribute this to a replacement of the carbon substituent on phosphorus by the more electropositive silicon.

Complex **17** is unique in the sense that it involves two very different phosphorus centers attached to a common boron center. The ^{31}P ^1H-decoupled NMR spectrum reveals singlets at 32 and −117 ppm. In the absence of decoupling, a doublet with a J_{P-H} of 247 Hz is seen for the upfield signal. The larger P–H coupling for the P(H)Mes group is consistent with the increased values noted earlier. However, it is notable that 247 Hz is the lowest of the values observed, suggesting a quite pyramidal phosphorus center. Also, the large upfield shift is consistent with a reduced delocalization of the phosphorus lone pair onto this particular boron center. However, it is clear from the X-ray structure (see Figure 6, bottom) that the lone pair on P(1) remains aligned correctly for overlap with the boron p orbital so that there is probably some residual interaction. Nevertheless ^{31}P data are in agreement with the high degree of pyramidicity, $\sum$[angles at P(1)] = 306.7°, and the long B–P(1) bond, 1.927 (3) Å. The other phosphorus center appears at 32 ppm. This is consistent with the very short B–P(2) bond length of 1.810 (5) Å, which suggests a strong B–P interaction. The B–P(2) bond is, in fact, the shortest B–P bond known at present. The upfield (compared to compounds **7–15**) ^{31}P NMR chemical shift value, 32 ppm, is probably due to the replacement of one of the boron aromatic groups by the less electronegative PHMes substituent in compound **17**. This explanation is also supported by a related case where ^{31}P chemical shifts of 30.1 and −0.01 ppm are observed for Mes_2BPPh_2[27] and $MesB(PPh_2)_2$.[28] The P–Li and Li–O bonds are comparable to those seen in the structures of **9**, **11**, **12**, and **17**. Apart from the latter, the most closely related structure to **17** involves the compound $MesB(PPh_2)_2$.[28] In this case, there is only a slight asymmetry in the B–P bonds, 1.879 (2) and 1.901 (2) Å, which is also reflected in the slightly different degrees of pyramidicity, 318.8° and 324.8° in each. The much larger asymmetry in **17** is a result of the different amounts of electron density available at the phosphorus atoms. In fact, the difference between P(1) and P(2) is comparable to that which exists between the phosphorus centers in **4–6** and **7–9**. Although there are no structural data available for **4–6**, it seems reasonable to suggest that the B–P bond length in these compounds may be close to 1.9 Å.[29]

An interesting aspect of the stoichiometry of **17** concerns its significance in the sequence of reactions leading to boraphosphabenzenes. However, this and related mechanistic investigations will be described in another publication.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8618739) and the A. P. Sloan Foundation for financial support.

Supplementary Material Available: Full tables of crystallographic data and summary of data collection and refinement, solution notes, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates for **1**, **9**, **16**, and **17** (27 pages). Ordering information is given on any current masthead page.

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