Contributions to the Chemistry of Boron, 214[1]

Synthesis and Reaction Chemistry of Aminophosphanylboranes

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Aminochlorophosphanylboranes, $(R_2N)B(Cl)P(SiMe_3)_2$ (**1a – d**) and $(R_2N)B(Cl)PH_2$ (**2a – d**), are obtained from elimination reactions between aminochloroboranes and $LiP(SiMe_3)_2$ and $LiPH_2$, respectively. Selected reaction chemistry of $(i\text{-}Pr_2N)B(Cl)[P(SiMe_3)_2]$ (**1a**) with NH_3, Me_3SiN_3, $Cr(CO)_5 \cdot NMe_3$, and $W(CO)_5 \cdot NMe_3$ is described. The azide $(i\text{-}Pr_2N)B(N_3)P(SiMe_3)_2$ (**12a**) is stable at 25°C; however, thermolysis at 80°C provides a novel six-membered ring compound $[(i\text{-}Pr_2N)BN(SiMe_3)P(SiMe_3)]_2$ (**13a**). The reaction of $(Ph_2N)B(Cl)P(SiMe_3)_2$ (**1b**) with $LiP(SiMe_3)_2$ produces the only isolable bis(phosphanyl)borane (**5b**), while combination of $(R_2N)B(Cl)PH_2$ with $LiPH_2 \cdot DME$ yields new diphosphadiboretanes **6** $\{(R_2N)BPH\}_2$ (R_2N = $i\text{-}Pr_2N$, Ph_2N and tmp = 2,2,6,6-tetramethylpiperidino) and triphosphatriborinanes **7** $\{(R_2N)BPH\}_3$ (R_2N = $(Me_3Si)_2N$, Me_2N and Et_2N). Two salts, $[(i\text{-}Pr_2N)BP(H)B(i\text{-}Pr_2N)PLi \cdot DME]_2$ (**8a**) and $[tmpBP(H)B(tmp)PLi \cdot DME]_2$ (**8c**) (DME = ethylene glycol dimethyl ether) are also isolated. The results of molecular structure determinations for $[(i\text{-}Pr_2N)Bn(SiMe_3)P(SiMe_3)]_2$ (**13a**), $[tmpBPH]_2$ (**4c**), $[tmpBPH]_2 \cdot Cr(CO)_5$ (**7c**), $\{[(Me_3Si)_2N]BPH\}_3$ (**4d**), $\{[(Me_3Si)_2N]BPH\}_3 \cdot Cr(CO)_5$ (**7d**), $(Ph_2N)B[P(SiMe_3)_2]_2$ (**5b**), and $[(i\text{-}Pr_2N)BP(H)B(i\text{-}Pr_2N)PLi \cdot DME]_2$ (**8a**) are discussed.

The formation of phosphanylboranes, R_2P-BX_2, from hydrogen or hydrogen halide elimination reactions between appropriate phosphane and borane reagents was examined intently for a number of years[2–21]. These studies led to the isolation and partial characterization of several molecular ring compounds $(R_2PBX_2)_n$ (n = 2, 3) as well as oligomeric species. Some of this chemistry has recently been revisited and extended in order to obtain monomeric boraphosphene species that contain a $-P=B-$ double bond and to define new classes of boron-phosphorus ring and cage compounds[22–50]. These results make it clear that there is considerable potential for the development of additional chemistry from phosphanylborane reagents. In that regard, we report here the use of several phosphanylboranes as reagents for the formation of more complex compounds as well as some aspects of their derivative chemistry.

Reactions

In the past, the majority of phosphanylborane chemistry has been developed with phosphide fragments that contain strongly bonded alkyl or aryl substituents. Relatively few compounds have been reported that possess potentially labile substituents, such as organosilyl groups or hydrogen. Pioneering work by Fritz and Hölderich[21] revealed that reactions of $LiP(SiMe_3)_2 \cdot 2\ THF$ with $(Me_2N)_2BCl$ and Me_2NBCl_2 produced $(Me_2N)_2BP(SiMe_3)_2$, $Me_2NB(Cl)P(SiMe_3)_2$, and $Me_2NB[P(SiMe_3)_2]_2$. Further, it was found that, when heated to 150°C, the bis(phosphanyl)borane $Me_2NB[P(SiMe_3)_2]_2$ released $P(SiMe_3)_3$, and a diphosphadiboretane, $[(Me_2N)BP(SiMe_3)]_2$, formed. Extending this early work, we have found that a family of reactive phosphanylboranes may be prepared by combination of aminohaloboranes with $LiP(SiMe_3)_2 \cdot 2\ THF$ or $LiPH_2 \cdot DME$[42–49], and in the present study several new examples are described as shown in eqs. (1)–(4). The aminochlorophosphanylboranes **1a – d** are obtained in good yields as distillable oils or crystalline solids. The compounds **2a – d** result as the dominant product from the 1:1 reactions of the respective aminodichloroboranes and $LiPH_2 \cdot DME$. It is important to note, however, that **2a – d** are accompanied by unreacted aminodichloroborane, aminobis(phosphanyl)boranes **3a – d**, and diphosphadiboretanes, **4a – c**. This chemistry is described in detail below.

We have previously noted that the silylphosphanylboranes **1a – c**, when combined with a second equivalent of $LiP(SiMe_3)_2$ in hexane or benzene, produce in good yield the corresponding diphosphadiboretanes[45], $[R_2NBP(SiMe_3)]_2$ (**6a – c**), and an equivalent of $P(SiMe_3)_3$, as illustrated in eq. (5). It was assumed that (diorganylamino)bis[(trimethylsilyl)phosphanyl]boranes, $R_2NB[P(SiMe_3)_2]_2$ (**5a – c**), were formed as intermediates in each case, but none were isolated due to the facile elimination of $P(SiMe_3)_3$. In the present study, one bis(phosphanyl)borane, **5b**, was prepared and isolated as outlined in eq. (5). However, the corresponding analogs **5a**, **5c**, and **5d** were not detected in NMR spectra recorded from 1:1 reaction mixtures prepared from **1a**, **1c**, and **1d** with $LiP(SiMe_3)_2$. It is therefore assumed

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that these bis(phosphanyl)boranes have only a fleeting existence under the reaction conditions employed.

$$R_2NBCl_2 + LiP(SiMe_3)_2 \xrightarrow{-LiCl} \underset{\mathbf{1a-1d}}{R_2NB(Cl)P(SiMe_3)_2} \qquad (1)$$

	1a	1b	1c	1d
R₂N	i-Pr₂N	Ph₂N	tmp	(Me₃Si)₂N

$$R_2NBCl_2 + LiPH_2{\cdot}DME \xrightarrow[-DME]{-LiCl} \underset{\mathbf{2a-2d}}{R_2NB(Cl)PH_2} \qquad (2)$$

	2a	2b	2c	2d
R₂N	i-Pr₂N	Ph₂N	tmp	(Me₃Si)₂N

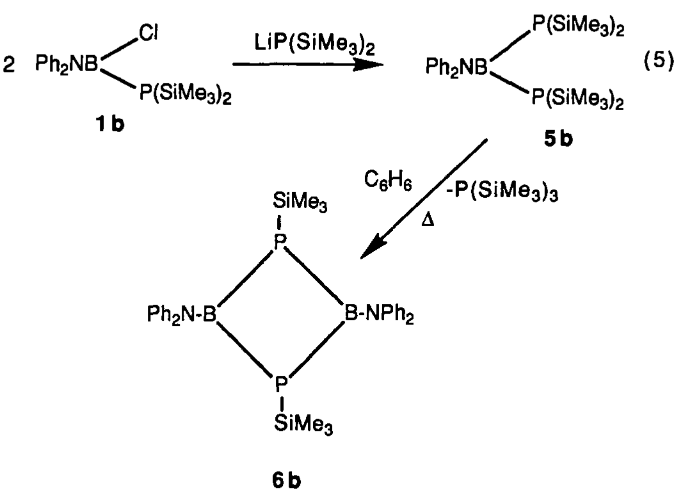
$$R_2NBCl_2 + 2LiPH_2{\cdot}DME \xrightarrow[-2DME]{-2LiCl} \underset{\mathbf{3a-3d}}{R_2NB(PH_2)_2} \qquad (3)$$

	3a	3b	3c	3d
R₂N	i-Pr₂N	Ph₂N	tmp	(Me₃Si)₂N

$$R_2NBCl_2 + 2LiPH_2{\cdot}DME \xrightarrow[-PH_3]{-2LiCl} \underset{\mathbf{4a-4f}}{1/n\ (R_2NBPH)_n} \qquad (4)$$

	4a	4b	4c	4d	4e	4f
R₂N	i-Pr₂N	Ph₂N	tmp	(Me₃Si)₂N	Me₂N	Et₂N
n	2	2	2	3	3	3

The key to the isolation of **5b** rests on utilizing hexane as the solvent in which the compound is relatively stable. However, when a solution of **5b** in benzene is refluxed, rapid formation of the previously reported[45] diphosphadiboretane **6b** occurs. It is important to point out that the diphosphadiboretanes **6a – d** are also available directly from combination of R_2NBCl_2 and two equivalents of $LiP(SiMe_3)_2$ in benzene without isolation of **1a – c**. Compound **6d** is also obtained from $(Me_3Si)_2NBCl_2$ and two equivalents of $LiP(SiMe_3)_2 \cdot 2\ THF$ in refluxing hexane.



Parallel chemistry for the formation of phosphanylboranes $R_2NB(Cl)PH_2$ appears more complex. We have previously reported that combination of a pentane solution of $tmpBCl_2$ and a diethyl ether solution of $LiPH_2 \cdot DME$ in a 1:2 ratio produces the diphosphadiboretane $(tmpBPH)_2$ (**4c**) in good yield, as described in eq. (4)[44]. Although $tmpB(PH_2)_2$ could not be isolated, it was proposed that the compound initially forms, as evidenced by NMR data: $\delta^{11}B = 53.4$; $\delta^{31}P = -183.6$ (t), $^1J_{PH} = 200$ Hz. Furthermore, it was found that **4c** under UV photolysis converts to a novel bicyclic compound $(tmpBP)_2$.

In the present study, the 1:1 reactions of R_2NBCl_2 with $LiPH_2 \cdot DME$ in hexane produce the species $R_2NB(Cl)PH_2$. However, the reaction rates and product distributions are sensitive to stoichiometry control, reaction conditions, and solvent. In each case, it is difficult to obtain **2** completely

Table 1. ^{11}B- and ^{31}P-NMR data for reactions of i-Pr_2NBCl_2 with $LiPH_2 \cdot DME$ at various stoichiometric ratios

Reactant Ratio i-Pr₂NBCl₂:LiPH₂	NMR Data ¹¹B{¹H}(δ)	³¹P{¹H}(δ)	Species	Relative Amount (%)
2:1	48.8	-192	**3a**	4
	39.9	-198	**2a**	22
	30.3	--	i-Pr₂NBCl₂	74
		-157	?	<1
1:1	48.8	-192	**3a**	32
	39.9	-198	**2a**	61
	30.3	--	i-Pr₂NBCl₂	7
		-157	?	<1
		-153	?	<1
		-183	?	<1
1:1.5	48.8	-192	**3a**	40
	39.9	-198	**2a**	48
	30.3	--	i-Pr₂NBCl₂	12
		-157	?	<1
		-153	?	<1
		-183	?	<1
1:2	*	-91	**8a**	
		-175	**8a**	15
	49.1	-151	?	82
	*	-162	**4a**	1
	*	-193	**3a**	1
	41	-13	(i-Pr₂NB)₃P₂	1
1:2.25	*	-91	**8a**	
		-175	**8a**	20
	49.1	-151	?	70
	*	-162	**4a**	1
	*	-193	**3a**	<1
	41	-13	(i-Pr₂NB)₃P₂	9
1:2.5		-91	**8a**	
	50.0	-175	**8a**	90
	*	-162	**4a**	10

* The ^{11}B resonances for **3a**, **4a**, and **8a** overlap with the resonance for the unidentified compound.

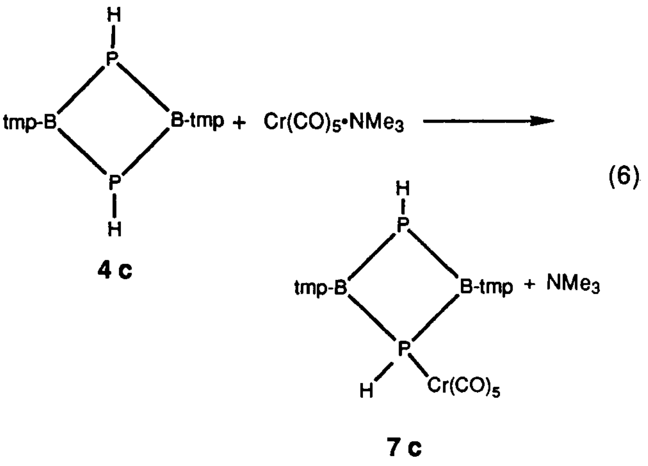
free of contaminants **3** and **4**. The primary contaminant in each of the 1:1 reactions is **3**. Further, with R_2N = Ph_2N, the products have relatively low solubility. For this reason, it has so far proven impossible to obtain reliable characterization data for **2b**, **3b**, and **4b**.

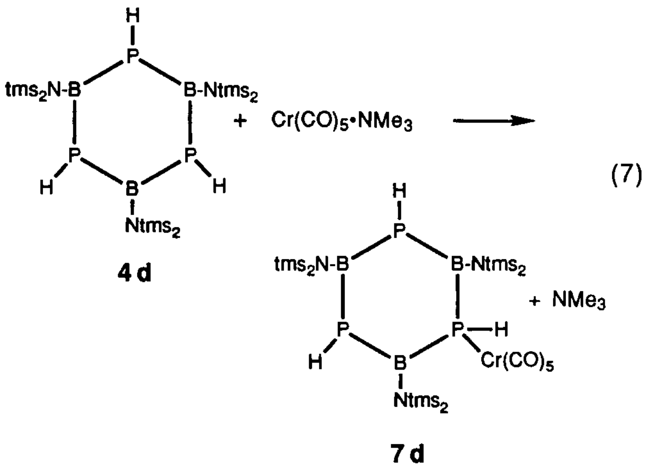
Since the initial studies of the 1:1 reactant combination showed considerable complexity, ^{11}B- and ^{31}P-NMR studies for mixtures containing reactant ratios i-Pr_2NBCl_2:$LiPH_2 \cdot$ DME = 2:1, 1:1, 1:1.5, 1:2, 1:2.25, and 1:2.5 were performed. The data, summarized in Table 1, show that three or four species are present at each stoichiometry. In the 2:1, 1:1, and 1:1.5 mixtures, the dominant species are **2a**, **3a**, and i-Pr_2NBCl_2. As the amount of $LiPH_2 \cdot$ DME employed increases, the yield of **3a** increases, while the amount of i-Pr_2NBCl_2 decreases. There is no evidence for formation of **4a** or **8a**, the lithium salt of **4a**, at these stoichiometries. Similar results are obtained for the same reaction stoichiometries of $tmpBCl_2$ and $LiPH_2 \cdot$ DME, although small (<10%) amounts of **4c** are found in each reaction mixture.

i-Pr_2NBCl_2 is completely consumed at the 1:2 reactant ratio. The Li salt **8a** is observed in a modest amount at this stoichiometry, and very small quantities of **3a**, **4a**, and the cage species $(i\text{-}Pr_2NB)_3P_2$[43] are detected. The dominant product in the 1:2 reaction mixture displays a broad $^{31}P\{^1H\}$-NMR resonance ($W_{1/2} \approx 650$ Hz) centered at $\delta = -151$; the identity of this species is presently unknown. The ^{31}P-NMR spectrum for the 1:2.25 reaction mixture indicates formation of the same species, although greater relative amounts of **8a** and $(i\text{-}Pr_2NB)_3P_2$ are present. The unidentified compound ($\delta = -151$) remains as the dominant product. The ^{31}P-NMR spectrum of the 1:2.5 reaction mixture shows the presence of **8a**, with a small amount of **4a**. These data show why attempts to obtain **2a**, **2c**, **2d**, **3a**, **3c**, and **3d** in analytically pure form failed. Nonetheless, each was obtained in good yield with sufficient purity to obtain reliable spectroscopic characterization data.

Troublesome impurities and, in some cases, low solubility have made unambiguous assignment of ring sizes of **4**, $(R_2NBPH)_n$, difficult. Nonetheless, the available data suggest that ring size is determined, in part, by the size of the *exo*-alkylamino groups[51]. For example, the appearance of appropriate parent ions in the mass spectra of **4e** (R_2N = Me_2N) and **4f** (R_2N = Et_2N) indicates that they exist as six-membered triphosphatriborinane[52] ring compounds (n = 3). The compound **4a**, with larger i-Pr_2N groups, is particularly hard to purify; however, it is obtained in pure form from an alternative synthetic approach[52]. A $^{31}P\{^1H\}$-NMR spectrum for pure **4a** shows a single resonance at $\delta = -162$, and single-crystal X-ray diffraction analysis confirms that the compound is a diphosphadiboretane (n = 2)[52]. It is possible that the broad $^{31}P\{^1H\}$ resonance ($\delta = -151$) in the 1:2 and 1:2.25 reaction mixtures (Table 1) corresponds to a trimeric ring (n = 3), and further attempts to isolate this species are in progress. The compounds with larger amino groups Ph_2N, **4b**, and tmp, **4c**, are identified as four-membered rings (n = 2) based on mass spectrometric data (**4b** and **4c**), cryoscopic molecular weight measurements (**4c**), and single-crystal X-ray analysis (**4c**) (vide infra). Somewhat surprisingly, compound **4d** with large amino groups $(Me_3Si)_2N$ is a triphosphatriborinane (n = 3) ring, as evidenced by mass spectrometric data, cryoscopic molecular weight data, and single-crystal X-ray analysis (vide infra). In summary, the chemistry described in equation (4) only provides pure samples of **4c** and **4d**. The compounds **4a**, **4b**, **4e**, and **4f** are obtained in an impure state; however, ring sizes have been deduced from the combined physical characterization data.

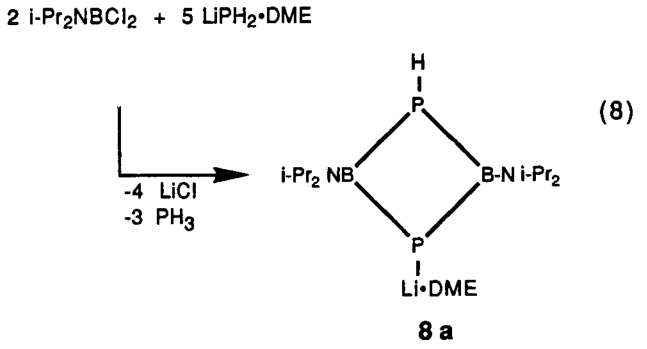
Some aspects of the coordination chemistry of the new ligands have been surveyed. For example, monometallic complexes of **4c** and **4d** are isolated in good yield, as shown in eq. (6) and (7) by combination of the ligands with $Cr(CO)_5 \cdot NMe_3$. The molecular structures of both complexes are confirmed by single-crystal X-ray diffraction analysis. Attempts to form dimetallic complexes by this approach were unsuccessful.

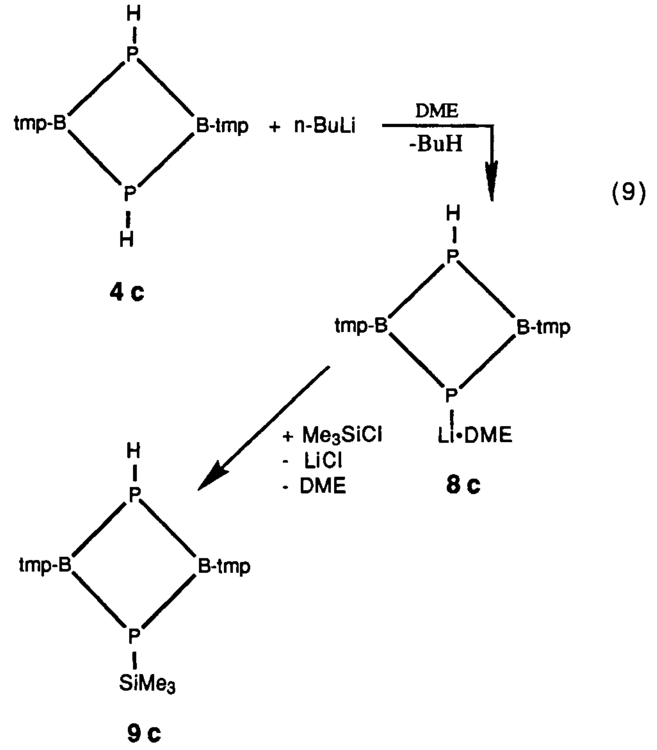




As mentioned above, the 1:2 reaction of i-Pr_2NBCl_2 with $LiPH_2 \cdot$ DME gave evidence for the formation of a Li salt of **4a**. Further study of the reaction with a reactant ratio of 1:2.5 gave high yields of crystalline solid **8a**, as described in eq. (8).

Efforts to obtain **8c** in a similar fashion gave low yields. The compound is obtained, however, in high yield, as depicted in eq. (9). Deprotonation of **4c** by n-BuLi in a THF/

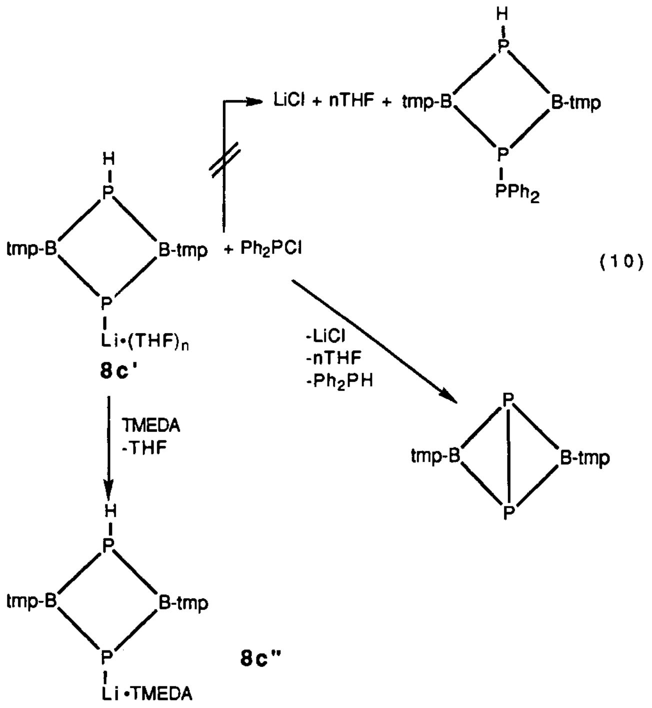




hexane mixture also stops at the monolithium salt, its Li atom being solvated by THF to produce **8c′**. Similarly, a crystalline TMEDA solvate **8c″** can be prepared. Combinations of the salts **8c** and **8c′** with Me_3SiCl led to formation of *P*-silyldiphosphadiboretane **9c** as shown in eq. (9). However, the reaction of **8c′** with Ph_2PCl does not proceed as described in eq. (10). Instead, the known bicyclic compound $(tmpBP)_2$[44] is formed.

Several substitution reactions of **1a** were studied, and the results are summarized in Scheme 1. As noted above, **5a** is not detected by NMR, but it is presumed to be an intermediate species in the formation of **6a**. We have previously noted that combination of **1a** and *i*-Pr_2NBCl_2 results in the formation of a novel cage compound[43] $P_2[B(N\text{-}i\text{Pr}_2)]_3$ (**10a**). Aminolysis of **1a** leads to **11a** in good yield. This white solid is stable at 100°C, and no evidence for cleavage of the $B-P(SiMe_3)_2$ group was found that would ultimately be expected to produce an aminoborazine, (*i*-$Pr_2NBNH)_3$ or $(H_2NBNH)_3$.

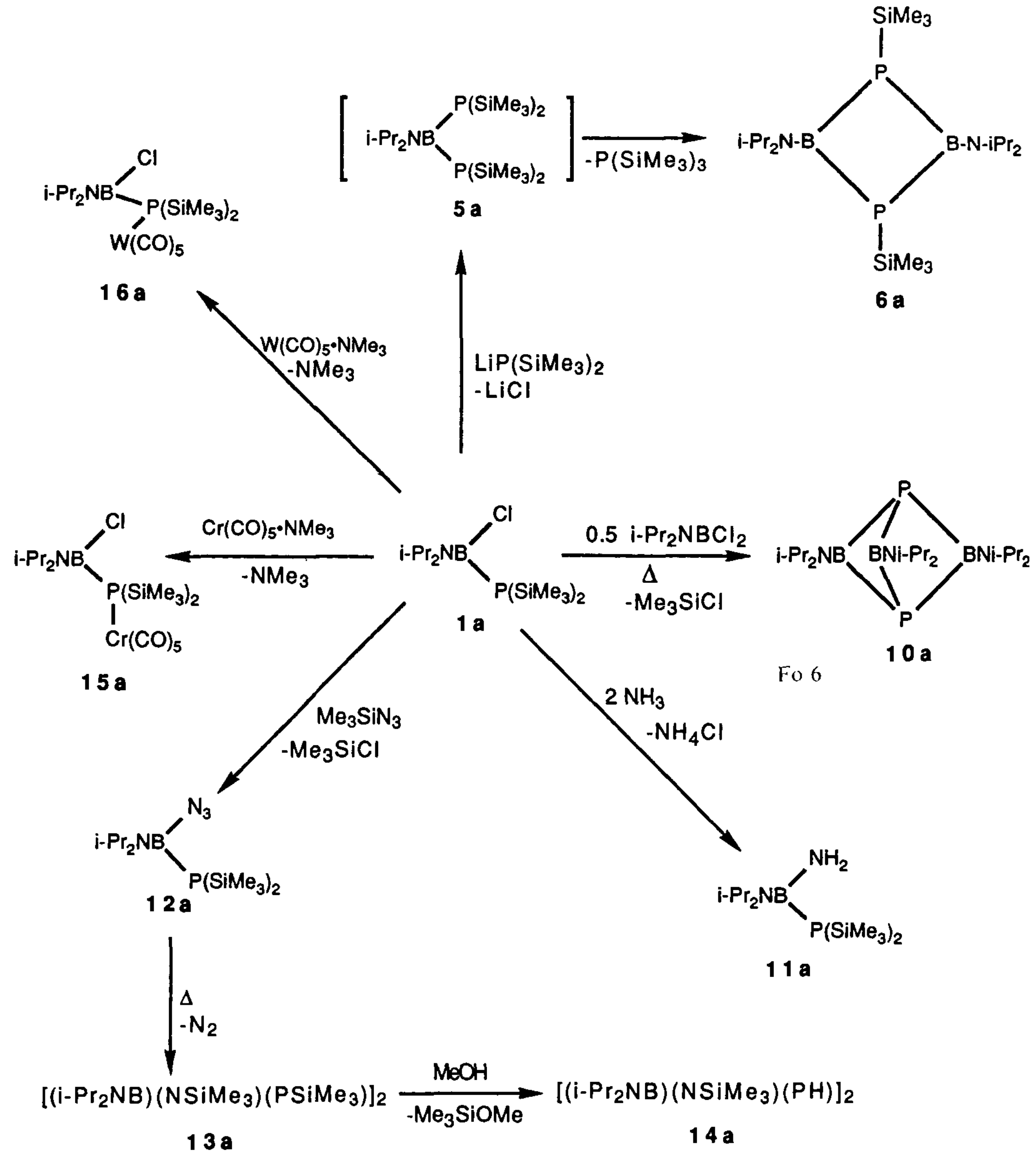
Many substitution reactions on B–Cl bonds are facilitated by utilization of Me_3SiX reagents. Indeed, combination of **1a** with Me_3SiN_3 leads to formation of *i*-Pr_2N-$B(N_3)P(SiMe_3)_2$ (**12a**) as a yellow oil. Thermolysis of **12a** at 80°C produces nitrogen and a white solid identified as [*i*-$Pr_2NBN(SiMe_3)P(SiMe_3)]_2$ (**13a**). This compound may arise from dimerization of a nitrene intermediate, *i*-$Pr_2NB(N{:})P(SiMe_3)_2$, followed by silyl group migration from phosphorus to nitrogen. This process would parallel the decomposition of azidodialkylboranes, R_2BN_3, reported by Paetzold[53] that produces borazines $(RBNR)_3$. Furthermore, the phosphanyl analog [*i*-$Pr_2NB(NSiMe_3)(PH)]_2$ (**14a**) is obtained by careful solvolysis of **13a** with MeOH. However, the reaction of Me_3SiCN with **1a** gave no evidence for the formation of a cyano derivative. The lone pair on the $P(SiMe_3)_2$ substituent of **1a** is also subject to nucleophilic addition, as evidenced by the displacement of Me_3N from $Cr(CO)_5 \cdot NMe_3$ and $W(CO)_5 \cdot NMe_3$. The resulting complexes, *i*-$Pr_2NB(Cl)P(SiMe_3)_2 \cdot Cr(CO)_5$ (**15a**) and *i*-$Pr_2NB(Cl)P(SiMe_3)_2 \cdot W(CO)_5$ (**16a**) are yellow oils.



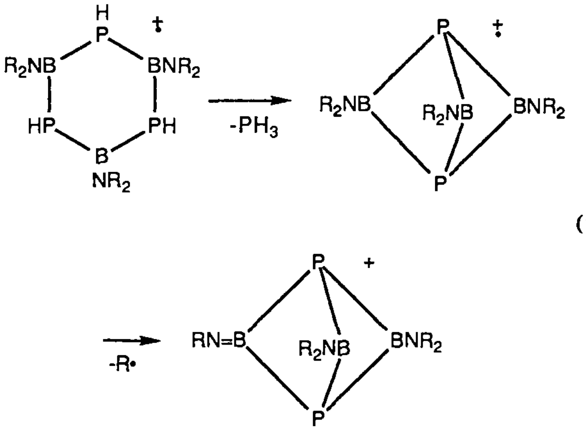
Spectra

Mass spectra were recorded for all isolated compounds except the short-lived **3a**–**d**, **4a**, and the Li salts **8a** and **8c**. A parent ion is observed for each compound except **1d**, **11a**, and the metal carbonyl compounds **15** and **16**. These data, together with elemental analyses, confirm the composition of each phosphanylborane. All spectra also show fragment ions consistent with the proposed structures, and comparison of the fragmentation of molecular ions $[R_2NBPH]_n^+$ reveals some diagnostic features. The four-membered rings readily lose a PH_2 radical and form a cation $[(R_2N)_2B_2P]^+$ of high relative intensity. Potential structures for this cation include the cyclic phosphenium ion $R_2N\overline{BB(NR_2)P}^+$ and $[R_2N=B=P=B=NR_2]^+$ with a linear array of two coordinated boron and phosphorus atoms. This kind of frag-

Scheme 1



mentation is ascertained by the observation of metastable peaks. In contrast, all six-membered $(R_2NBPH)_3$ species lose a PH_3 molecule, followed by loss of an R radical as described by eq. (11).



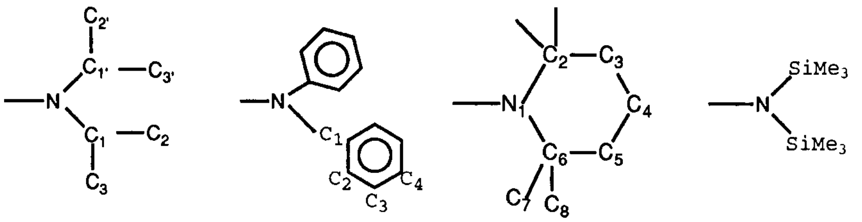
(11)

Infrared spectra were recorded for all compounds except **3a**–**d**, **4a**, **e**, **f**, and the data show absorptions in the expected fingerprint regions. The region 800–500 cm^{-1} typically associated with the B–P stretching frequency in phosphane– and phosphanylboranes is complicated, and no attempt was made to assign this frequency. Spectra of pure samples of **2a**–**d** should display two bands (A′ and A″) in the region 2400–2200 cm^{-1} due to antisymmetric and symmetric stretching motions of the PH_2 group. Although samples of these compounds are contaminated with small amounts of **3**, two bands at 2326 and 2310 cm^{-1} are resolved and can be confidently assigned to this group in **2a**. Only one band is resolved for **2b**, 2316, **2c**, 2316, and **2d**, 2313 cm^{-1}. Compounds **4a**–**d** and **14a** should show one PH stretching band, and samples of **4c**, **4d**, and **14a** reveal bands at 2267, 2277, and 2252 cm^{-1}, respectively. The metal carbonyl complexes **7c**, **7d**, **15a**, and **16a** contain an $M(CO)_5$ unit (M = Cr, W), and extensive studies of $M(CO)_5 \cdot L$ complexes suggest that three carbonyl stretching frequencies should appear in the region 2070–1900 cm^{-1}[54]. Indeed, three bands are resolved in the carbonyl region for each complex: **7c**: 2057, 1974, 1935; **7d**: 2060, 1981, 1940; **15a**: 2053, 1987, 1933; **16a**: 2064, 1954, and 1931 cm^{-1}. The value of the lowest frequency carbonyl stretch, ν_{CO} (E), in $Cr(CO)_5 \cdot L$ complexes is often used to assess the σ donor/π acceptor character of a ligand L. It is found that more electron-deficient phosphanes (poorer σ donors) act as better π accep-

Table 2. NMR data for phosphanylboranes

Compound[a,b]	δ $^{11}B\{^1H\}$	δ $^{31}P\{^1H\}$	δ ^1H	δ $^{13}C\{^1H\}$
$(i\text{-}Pr_2N)B(Cl)P(SiMe_3)_2$ **1a**	40.6	-213.3	1.3(Me2,3) 1.0(CH) 0.4($SiMe_3$)	53.0(1),48.0(1′) 23.3(2,3),22.0(2′,3′) 3.4($SiMe_3$)
$(Ph_2N)B(Cl)P(SiMe_3)_2$ **1b**	46.2	-211.6	7.3(Ph) 0.3($SiMe_3$)	148.9(1),128.2(2) 128.7(3),125.8(4) 3.1($SiMe_3$)
$(tmp)B(Cl)P(SiMe_3)_2$ **1c**	46.4	-179.5	1.6(7,8) 0.3($SiMe_3$)	57.3(2,6),36.0(3,5) 33.4(7,8),33.0(7′,8′) 14.8(4),3.4($SiMe_3$)
$[(Me_3Si)_2N]B(Cl)P(SiMe_3)_2$ **1d**	54.2	-175.8	0.38($SiMe_3$) 0.36($SiMe_3$)	
$(i\text{-}Pr_2N)B(Cl)PH_2$ **2a**	39.9	-197.9 -198.3	3.3(CH) 2.3(PH) 1.2(2,3),0.8(2′,3′)	52.1(1),47.9(1′) 22.8(2,3),21.4(2′,3′)
$(Ph_2N)B(Cl)PH_2$ **2b**	44.0	-204.0 -196.6	6.98(Ph) 2.25(PH)	131.2(3),130.6(1) 129.4(2),128.8(4)
$tmpB(Cl)PH_2$ **2c**	44.3	-184.1 -183.8	2.71(PH) 1.27(7,8)	
$[(Me_3Si)_2N]B(Cl)PH_2$ **2d**	52.1	-184.3		
$(i\text{-}Pr_2N)B(PH_2)_2$ **3a**	48.9	-191.7		
$tmpB(PH_2)_2$ **3c**	53.4	-181.3		
$[(Me_3Si)_2N]B(PH_2)_2$ **3d**	68.0	-174.1		
$[(i\text{-}Pr_2N)BPH]_2$ **4a**	47.1	-162.8	3.9(PH) 3.5(CH) 1.1(2,3)	51.6(1) 23.2(2,3)

[a] Abbreviations and Numbering Schemes



[b] Coupling Constants (Hz): **1a** $^3J_{CP}$ = 24.8 (C_1), $^2J_{CP}$ = 12.2 ($SiMe_3$), $^3J_{HH}$ = 7.0 (C_2), $^3J_{HH}$ = 6.8 (C_3), $^3J_{HP}$ = 4.8 ($SiMe_3$); **1b** $^2J_{CP}$ = 11.7 ($SiMe_3$), $^3J_{HP}$ = 4.7 ($SiMe_3$); **1c** $^3J_{CP}$ = 3.4 ($C_{2,6}$), $^2J_{CP}$ = 11.8 ($SiMe_3$), $^3J_{HP}$ = 4.5 ($SiMe_3$); **2a** $^1J_{PH}$ = 209.2; **2b** $^1J_{PH}$ = 216; **2c** $^1J_{PH}$ = 209.6; **3a** $^1J_{PH}$ = 205; **3c** $^1J_{PH}$ = 206; **3d** $^1J_{PH}$ = 206; **4a**: $^1J_{PH}$ = 111.0, $^3J_{HH}$ = 6.8; **4c** $^1J_{PH}$ = 230.0, $^3J_{PH}$ = 18.8, $^2J_{PP}$ = 117.8; **4d** $^1J_{PH}$ = 221.9, J_{PP} = 91.5; **7c** J_{PP} = 257, $^1J_{PH}$ = 242, $^3J_{PH}$ = 66; **7d** J_{PP} = 180; $^1J_{PH}$ = 240, $^3J_{PH}$ = 94; **8a** J_{PP} = 52, $^1J_{PH}$ = 146; **8c** J_{PP} = 66, $^1J_{PH}$ = 132; **9c** J_{PP} = 51.5, $^1J_{PH}$ = 169; **11a** $^2J_{CP}$ = 12.4 (SiMe), $^3J_{HH}$ = 6.9 (2,3), $^3J_{HP}$ = 4.5 (SiMe); **12a** $^3J_{CP}$ = 24.4 (C_1), $^2J_{CP}$ = 13.7 (SiMe), $^3J_{HH}$ = 6.7 (2,3), $^3J_{HH}$ = 6.7 (2′,3′), $^3J_{HP}$ = 5.3 (SiMe); **13a** $^4J_{HP}$ = 1.3, $^3J_{HP}$ = 4.5 **14a** $^1J_{PH}$ = 187, $^3J_{HH}$ = 6.9 (2,3), 6.7 (2′,3′), **15a** $^3J_{CP}$ = 7.1 (1), $^3J_{CP}$ = 2.7(1′), $^2J_{CP}$ = 7.6 (SiMe), $^3J_{HH}$ = 7.0 (2,3), $^3J_{HH}$ = 6.6 (2′,3′), $^3J_{HP}$ = 4.9 (SiMe), **16a** $^2J_{CP}$ = 12.5 (SiMe), $^3J_{HH}$ = 6.7 (2,3), $^3J_{HH}$ = 6.9 (2′,3′), $^3J_{HP}$ = 4.7 (SiMe).

Table 2 *(Continued)*

Compound[a,b]	δ $^{11}B\{^1H\}$	δ $^{31}P\{^1H\}$	δ ^1H	δ $^{13}C\{^1H\}$
$[tmpBPH]_2$ **4c**	50.8	-127.2	4.7(PH) 1.52(7,8)	58.2(2),40.9(3) 30.2(8),33.4(7) 16.5(4)
$[(Me_3Si)_2NBPH]_3$ **4d**	68.4	-68.3	3.8(PH) 0.35($SiMe_3$)	4.7($SiMe_3$)
$(Ph_2N)B[P(SiMe_3)_2]_2$ **5b**	56.7	-154.5	7.1(Ph) 0.3($SiMe_3$)	151.3(1),128.8(3) 128.5(2),124.3(4) 3.3($SiMe_3$)
$[Ph_2NBP(SiMe_3)]_2$ **6b**	58.2	-122.6	7.4(Ph) 0.2($SiMe_3$)	161.0(1),130.0(3) 128.4(2),126.0(4) 2.7($SiMe_3$)
$[(Me_3Si)_2NBP(SiMe_3)]_2$ **6d**	69.1	-63.3	0.44($SiMe_3$) 0.39($SiMe_3$)	5.1($SiMe_3$) 3.3($SiMe_3$)
$[tmpBPH]_2Cr(CO)_5$ **7c**	46.4	-108.2 -91.0		
$[(Me_3Si)_2NBPH]_3Cr(CO)_5$ **7d**	62.0	-91.0 -69.3	3.6(PH) 0.34($SiMe_3$) 0.29($SiMe_3$)	5.16($SiMe_3$) 4.76($SiMe_3$)
$i\text{-}Pr_2NBP(H)(i\text{-}Pr_2N)BPLi \cdot DME$ **8a**	50.0	-174.9 -91.2	4.41(PH) 4.12(1),3.78(1') 3.39(DME),3.2(DME) 1.45(2,3),1.38(2',3')	70.7(DME),59.4(DME) 50.6(1),49.3(1') 24.8(2,3),23.5(2',3')
$tmpBP(H)(tmp)BPLi \cdot DME$ **8c**	53.6	-138.3 -15.5	5.62(PH) 3.28,3.13(DME) 1.93,1.65(7,8)	71.8,58.8(DME) 57.0,44.5(7,8) 33.3,17.5
$tmpBP(H)(tmp)BPSiMe_3$ **9c**	50.7	-129.3 -108.8	5.7(PH) 1.6,1.4(7,8) 0.5($SiMe_3$)	59.9,42.4(1,1') 33.0,16.6 2.6($SiMe_3$)
$(i\text{-}Pr_2N)B(NH_2)P(SiMe_3)_2$ **11a**	31.2	-245.8	3.7(1) 2.4(NH) 1.0(2,3) 0.3($SiMe_3$)	47.4(1) 23.0(2,3) 3.6($SiMe_3$)
$(i\text{-}Pr_2N)B(N_3)P(SiMe_3)_2$ **12a**	34.3	-240.0	1.2(2,3),1.0(2',3') 0.4($SiMe_3$)	51.8(1),46.3(1') 24.0(2,3),21.8(2',3') 4.0($SiMe_3$)
$[(i\text{-}Pr_2N)B(NSiMe_3)(PSiMe_3)]_2$ **13a**	43.0	-57.0	4.5(1),3.2(1') 1.3(2,3) 0.5($NSiMe_3$) 0.4($PSiMe_3$)	
$[(i\text{-}Pr_2N)B(NSiMe_3)(PH)]_2$ **14a**	39.2	-62.6	5.0(PH) 4.3(1),3.1(1') 1.2(2,3),1.0(2',3') 0.5($NSiMe_3$)	
$[(i\text{-}Pr_2N)B(Cl)P(SiMe_3)_2]Cr(CO)_5$ **15a**	40.2	-189.9	1.3(2,3) 1.0(2,3) 0.4($SiMe_3$) 53	54.2(1),48.6(1') 23.0(2,3),21.6(2',3') 3.8($SiMe_3$)
$[(i\text{-}Pr_2N)B(Cl)P(SiMe_3)_2]W(CO)_5$ **16a**	39.4	-185.5	1.4(2,3),1.2(2',3') 0.5($SiMe_3$)	60.7(1),47.9(1') 23.2(2,3),21.8(2',3') 3.3($SiMe_3$)

tors, and ν_{CO} (E) is shifted to a higher frequency compared to a good σ donor phosphane[55]. For example, ν_{CO} (E) appears at 1986 cm^{-1} for $Cr(CO)_5 \cdot PBr_3$[56] and at 1942 cm^{-1} for $Cr(CO)_5 \cdot PH_3$[57]. The values of ν_{CO} (E) in **7c**, **7d**, and **15a** are 1935, 1940, and 1933 cm^{-1}, respectively, and these suggest that the borylphosphanes in these complexes are comparable or slightly better σ-donor ligands than PPh_3. The infrared data for **7c**, **7d**, **15a**, and **16a** also compare favorably with data for $Cr(CO)_5 \cdot PPh_2[B(NMe_2)_2]$ 2057, 1957, and 1934 cm^{-1} and for $W(CO)_5 \cdot PPh_2[B(NMe_2)_2]$ 2066, 1947, and 1933 cm^{-1} [40]. In addition, **7c** shows two weak bands in the P–H region at 2331 and 2321 cm^{-1}.

NMR data (^{11}B, ^{31}P, ^{13}C, and ^1H) for the new compounds are summarized in Table 2. Compounds **1a–d** display single ^{11}B and ^{31}P resonances in the ranges $\delta = 40$ to 50 and -215 to -179, respectively. The values compare favorably with data reported for several related compounds[21,45]. It was observed previously[45] that formation of diphosphadiboretanes results in deshielding of both boron and phosphorus atoms relative to the shifts for the parent aminochlorophosphanylboranes. This trend is also confirmed here. Further, it was noted that, for the compound pairs $R_2NB(Cl)P(SiMe_3)_2/[R_2NBPSiMe_3]_2$, $\Delta^{31}P$ is 70–90 ppm for examples containing amino groups with low steric demand[45]. For one sterically demanding group, tmp, $\Delta^{31}P$ was dramatically greater: ≈ 125 ppm. In the present study, the $(Me_3Si)_2N$ group also produces a large deshielding shift: $\Delta^{31}P = 112$ ppm between **1d** and **6d**. It is noteworthy that replacement of the Cl substituent in **1a** with NH_2 in **11a** and N_3 in **12a** results in increased shielding of both boron and phosphorus atoms. On the other hand, for **1b**, significant deshielding ($\Delta^{31}P \approx 60$ ppm) occurs with replacement of Cl by $P(SiMe_3)_2$ with formation of **5b**. A smaller low-field shift ($\Delta^{31}P \approx 32$ ppm) occurs when **5b** is converted to **6b**.

Compounds **2a–d** show singlets in the ^{11}B-NMR spectra; however, **2a** and **2c** display two closely spaced peaks in the $^{31}P\{^1H\}$-NMR spectra (40–65 Hz separation) with approximately the same intensities. Compound **2b** shows two resonances separated by ≈ 7 ppm. It is assumed that this feature arises from the presence of rotamers in solutions of these compounds. Alternatively, the "doublet" pattern may arise from an intermediate P–B coupling condition where only two of the expected four peaks of the 1:1:1:1 quartet are resolved[58]. The large separation of the "doublet" in **2b** seems to argue against this interpretation. Only one resonance is resolved in the $^{31}P\{^1H\}$-NMR spectrum of **2d**. These compounds also show ^{11}B and ^{31}P deshielding trends similar to those described above. For example, replacement of Cl in **2a**, **c**, and **d** with PH_2, resulting in **3a**, **c**, and **d**, produces deshielding of both boron and phosphorus nuclei, although the $\Delta^{31}P$'s are much smaller (10 ppm or less). In the present study, the $^{31}P\{^1H\}$ shift for **3c** appears at $\delta = -181.3$, and restoration of proton coupling gives a triplet pattern with $J_{PH} = 206$ Hz. Conversion of the transient bis(phosphanyl)boranes **3a** and **3c** to the respective diphosphadiboretanes **4a** and **4c** has no significant effect on the ^{11}B-NMR spectra, while the ^{31}P-NMR spectra show large deshielding shifts: $\Delta^{31}P \approx 35$ to ≈ 60 ppm. The triphosphatriborinane **4d** is characterized by an ^{11}B-NMR resonance at δ 68.4 and a ^{31}P-NMR resonance at δ -68.3. Further evidence in support of the six-membered ring structure of **4d** is provided by the proton-coupled ^{31}P-NMR spectrum that shows a triplet ($^3J_{PH} = 91.5$ Hz) of doublets ($^1J_{PH} = 140.4$ Hz).

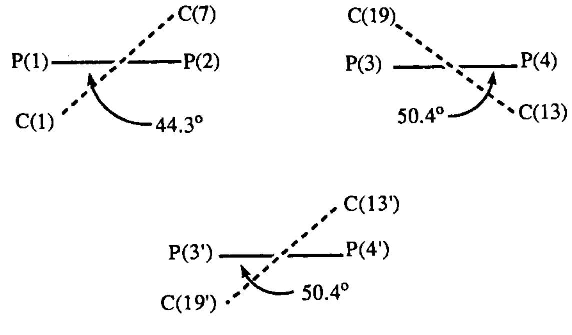
The ^{13}C- and ^1H-NMR data are in agreement with the proposed structural assignments, and they are similar to spectra reported previously for several related compounds[21,45].

Crystal and Molecular Structures

The molecular structures for $Ph_2NB[P(SiMe_3)_2]_2$ (**5b**), $[i\text{-}Pr_2NBN(SiMe_3)P(SiMe_3)]_2$ (**13a**), and $(tmpBPH)_2$ (**4c**), $[(Me_3Si)_2NBPH]_3$ (**4d**), $(tmpBPH)_2 \cdot Cr(CO)_5$ (**7c**), $[(Me_3Si)_2NBPH]_3 \cdot Cr(CO)_5$ (**7d**), and $[i\text{-}Pr_2NBP(H)B(N-iPr_2)PLi \cdot DME]_2$ [(**8a**)$_2$] have been determined by single-crystal X-ray diffraction analyses. Views of the molecules are shown in Figures 1–7, and selected bond distances and angles are listed in Tables 3, 4.

The aminobis(silylphosphanyl)borane **5b** (Figure 1) crystallizes with two unique molecules in the unit cell that differ by the orientation of the NPH_2 "propeller blades," as schematically shown in Scheme 2.

Scheme 2



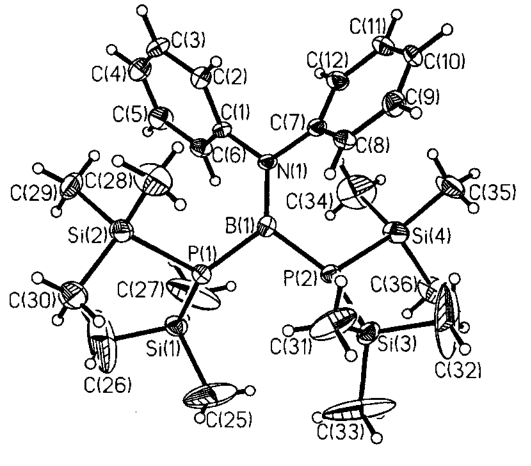


Figure 1. Molecular structure and atom labelling scheme for (diphenylamino)bis[bis(trimethylsilyl)phosphanyl]borane (**5b**). Thermal ellipsoids represent 20% probability

Table 3. Selected bond lengths [Å] for phosphanylboranes

5b molecule 1	5b molecule 2	13a	4c	7c
1.895(7) B(1)-P(1)	1.884(8) B(2)-P(3)	1.950(3) B-P	1.913(4) B'-P	1.967(5) B(2)-P(1)
1.893(7) B(1)-P(2)	1.913(8) B(2)-P(4)		1.934(4) B-P	1.963(5) B(1)-P(1)
				1.938(5) B(1)-P(2)
				1.939(5) B(2)-P(2)
1.465(8) B(1)-N(1)	1.462(8) B(2)-N(2)	1.475(3) B-N(1)	1.405(5) B-N	1.388(6) B(1)-N(1)
		1.407(4) B-N(2)		1.382(6) B(2)-N(2)
		1.753(2) P-N(1')		
2.238(3) P(1)-Si(1)	2.247(3) P(3)-Si(5)	2.272(1) P-Si(1)		
2.235(3) P(1)-Si(2)	2.253(3) P(3)-Si(6)			
2.231(3) P(2)-Si(3)	2.248(3) P(4)-Si(7)			
2.226(3) P(2)-Si(4)	2.244(3) P(4)-Si(8)			
		1.757(2) N(1)-Si(2)		
				Cr-P 2.458(2)

4d	7d	8a
1.924(10) B(1)-P(1)	1.965(8) B(1)-P(1)	1.897(6) P(1)-B(1)
1.921(9) B(3)-P(1)	1.983(8) B(3)-P(1)	1.953(6) P(2)-B(1)
1.939(8) B(1)-P(2)	1.920(8) B(1)-P(2)	1.905(6) P(3)-B(2)
1.925(10) B(2)-P(2)	1.906(8) B(2)-P(2)	1.946(6) P(4)-B(2)
1.932(9) B(3)-P(3)	1.903(8) B(3)-P(3)	
1.929(10) B(2)-P(3)	1.953(8) B(2)-P(3)	
1.427(11) B(1)-N(1)	1.410(9) B(1)-N(1)	1.402(7) B(1)-N(1)
1.425(9) B(2)-N(2)	1.412(10) B(2)-N(2)	1.398(8) B(2)-N(2)
1.436(1) B(3)N(3)	1.417(10) B(3)-N(3)	
1.775(5) N(1)-Si(1)	1.793(6) N(1)-Si(1)	2.539(16) P(1)-Li(1)
1.763(6) N(1)-Si(2)	1.773(6) N(1)-Si(2)	
1.781(7) N(2)-Si(3)	1.772(6) N(2)-Si(3)	2.539(11) P(1)-Li(2)
1.758(7) N(2)-Si(4)	1.778(6) N(2)-Si(4)	2.664(15) P(3)-Li(2)
1.780(5) N(3)-Si(5)	1.774(6) N(3)-Si(5)	2.549(13) P(3)-Li(1)
1.750(6) N(3)-Si(6)	1.788(6) N(3)-Si(6)	

The boron and nitrogen atoms in both molecules have planar geometries, with an average B – N bond distance of 1.464 Å. This distance is relatively long for monoaminoborane fragments, which typically have B – N distances in the range 1.36 – 1.40 Å[42]. In particular, the B – N bond distance in Ph_2NBCl_2 is 1.380(6) Å[59].

The average B – P bond distance in **5b**, 1.896 Å, is comparable to the B – P distances in most four- and three-coordinate phosphane – and phosphanylboranes[42,45] and as expected, the average P – B – P angle, 111.4°, in **5b** is more compressed than the average P – B – N angle, 124.3°. This may either be an indication of B – P π-bonding or a change in hybridization at the P atom. The latter seems more likely since the sums of the bond angles about the pyramidal phosphorus centers in **5b**, 343.3 – 339.3°, are larger than encountered in most phosphanes: 310°. For comparison, B – P distances in four-coordinate $X_3B \cdot PY_3$ complexes and $(X_2BPY_2)_n$ ring compounds appear in a range 1.92 – 2.08 Å[2,45], while B – P distances in diphosphadiboretanes typically fall in a range 1.91 – 1.97 Å[42,45]. It is appropriate to compare the parameters in **5b** with the only other bis(phosphanyl)borane, $MesB(PPh_2)_2$[27], for which the structure has been determined. In this case, the B – P distances are 1.879(2) and 1.901(2) Å, and the sums of the angles at the phosphorus atoms are 324.5 and 318.8°. Further useful comparison may be found in the data for monomeric Mes_2BPPh_2[25]: B – P 1.859(3) Å and sum of the phosphorus bond angles 339.4°. It is also noteworthy that the PSi_2 planes are twisted with respect to each other: molecule 1: 84.8°; molecule 2: 79.1°.

The structure of **13a** (Figure 2) demonstrates that the gentle thermolysis of the boron azide **12a** generates an interesting six-membered ring compound with a boat conformation in which the endocyclic nitrogen atoms occupy the prow positions. There is one substituent on each ring atom: an *i*-Pr_2N group on the boron atoms and an Me_3Si group on each nitrogen and phosphorus atom. The phosphorus atoms are pseudo-tetrahedral (sum of angles 328.4°), while the boron and nitrogen atoms are trigonal (sums of angles 359.2 and 358.3°, respectively). The Me_3Si groups on the phosphorus atoms are directed below the ring. The *i*-Pr_2N group is twisted by only 5.1° out of the PBN(1) plane,

Table 4. Selected bond angles [°] for phosphanylboranes

5b		**13a**	**4c**
molecule 1	molecule 2		
110.1(4)	112.6(4)		90.6(2) P-B-P'
			89.4(2) B-P-B'
124.4(5) P(2)-B(1)-N(1)	123.1(5) P(3)-B(2)-N(2)	114.7(2) P-B-N(1)	133.7(3) P-B-N
125.4(5) P(1)-B(1)-N(1)	124.3(5) P(4)-B(2)-N(2)	120.5(2) P-B-N(2)	135.6(3) N-B-P'
117.4(2) B(1)-P(1)-Si(2)	115.0(3) B(2)-P(3)-Si(6)	118.0(1) B-P-Si(1)	
113.2(3) B(1)-P(1)-Si(1)	114.6(3) B(2)-P(3)-Si(5)		
117.4(2) B(1)-P(2)-Si(4)	113.1(3) B(2)-P(4)-Si(8)	105.0(1) B-P-N(1)	
113.3(3) B(1)-P(2)-Si(3)	116.4(2) B(2)-P(4)-Si(7)	119.5(2) B-N(1)-P'	
		124.0(3) N(1)-B-N(2)	
112.9(1) Si(1)-P(1)-Si(2)	109.7(1) Si(5)-P(3)-Si(6)		
112.6(1) Si(3)-P(2)-Si(4)	112.2(1) Si(7)-P(4)-Si(8)		
112.1(4) B(1)-N(1)-C(1)	121.7(4) B(2)-N(2)-C(19)		
122.0(4) B(1)-N(1)-C(7)	121.7(5) B(2)-N(2)-C(13)		
115.9(5) C(1)-N(1)-C(7)	116.6(5) C(13)-N(2)-C(19)		

7c	**4d**	**7d**	**8a**
89.0(2) P(1)-B(1)-P(2)	111.5(5) P(1)-B(1)-P(2)	110.7(4) P(1)-B(1)P(2)	97.3(3) P(1)-B(1)-P(2)
88.8(2) P(1)-B(2)-P(2)	111.7(4) P(2)-B(2)-P(3)	112.4(4) P(2)-B(2)-P(3)	98.3(3) P(3)-B(2)-P(4)
	111.1(4) P(1)-B(3)-P(3)	109.6(4) P(1)-B(3)-P(3)	
81.2(2) B(1)-P(1)-B(2)	106.6(4) B(1)-P(1)-B(3)	106.2(3) B(1)-P(1)-B(3)	81.3(4) B(1)-P(1)-B(1')
82.5(2) B(1)-P(2)-B(2)	107.5(3) B(1)-P(2)-B(2)	109.2(3) B(1)-P(2)-B(2)	78.5(4) B(1)-P(2)-B(1')
	106.9(4) B(2)-P(3)-B(3)	107.3(3) B(2)-P(3)-B(3)	79.1(4) B(2)-P(3)-B(2')
			77.2(4) B(2)-P(4)-B(2')
135.1(4) P(2)-B(1)-N(1)	123.7(6) P(1)-B(1)-N(1)	124.2(5) P(1)-B(1)-N(1)	131.2(4) P(1)-B(1)-N(1)
135.9(4) P(1)-B(1)-N(1)	124.1(6) P(2)-B(1)-N(1)	124.7(5) P(2)-B(1)-N(1)	131.5(4) P(2)-B(1)-N(1)
135.4(3) P(2)-B(2)-N(2)	124.0(6) P(2)-B(2)-N(2)	122.6(5) P(2)-B(2)-N(2)	134.1(4) P(3)-B(2)-N(2)
135.8(4) P(1)-B(2)-N(2)	123.6(6) P(3)-B(2)-N(2)	124.1(6) P(3)-B(2)-N(2)	127.7(4) P(4)-B(2)-N(2)
	124.5(6) P(1)-B(3)-N(3)	124.0(5) P(1)-B(3)-N(3)	
	123.4(6) P(3)-B(3)-N(3)	126.4(6) P(3)-B(3)-N(3)	
	119.3(4) B(1)-N(1)-C(1)		104.7(5) P(1)-Li(1)-P(3)
	124.7(4) B(1)-N(1)-C(4)		101.4(5) P(1)-Li(2)-P(3)
	121.6(4) B(2)-N(2)-C(7)		
	123.3(4) B(2)-N(2)-C(10)		78.2(4) Li(1)-P(1)-Li(2)
			75.7(4) Li(1)-P(3)-Li(2)
	115.9(4) C(1)-N(1)-C(4)		
	114.9(4) C(7)-N(2)-C(10)		

and this suggests good B – N π overlap between the boron atom and the nitrogen atom of the exocyclic amide group. Consistent with this, the exocyclic B – N(2) bond distance, 1.407(4) Å, is significantly shorter than the endocyclic B – N(1) bond distance, 1.475(3) Å. The B – N(1) distance is also longer than the endocyclic BN distance in the borazine derivative $(Me_2NBNH)_3$, 1.434(8) Å[60].

The B – P bond distance in **13a**, 1.950(3) Å, is comparable to the bond distance in the six-membered phosphanyl borane ring[61] $(Me_2PBH_2)_3$, 1.935(2) Å, and to distances in a number of four-membered diphosphadiboretanes, 1.91 – 1.97 Å[45]. The P – N bond distance, 1.753(2) Å, is relatively long compared to distances in aminophosphanes where a nitrogen substituent typically acts as an electron donor to the phosphorus atom, e.g., $Cl\overline{P(t\text{-}BuN)_2P}Cl$, 1.687(9) Å[62]. These distances, as well as the internal ring angles and boat conformation, indicate that there is little π interaction between the ring atoms.

The molecular structure determination for **4c** (Figure 3) unambiguously confirms that the compound is a diphosphadiboretane, and it is closely related to the structures of related planar B_2P_2 four-membered rings that carry *exo*-amino groups on the boron atoms and alkyl, aryl, or silyl groups on the phosphorus atoms[23,42,45]. The B_2P_2 rhombus has a crystallographically imposed center of inversion, and as a result, the P – H bonds must be oriented in a *trans* arrangement. The nitrogen atoms in the tmp groups lie in the B_2P_2 plane, and the boron and nitrogen atoms have trigonal-planar geometries. The P – B – P′ angle, 90.6(2)°, is on the small end of the range of angles found for related compounds, while the B – P – B′ angle, 89.4(2)°, is on the more open end of the range. the B – P and B – N bond distances are closely comparable with the average of the distances reported for other B_2P_2 rings.

The structure of the coordination compound $[tmpBPH]_2 \cdot Cr(CO)_5$ **7c** (Figure 4) provides an opportunity to compare

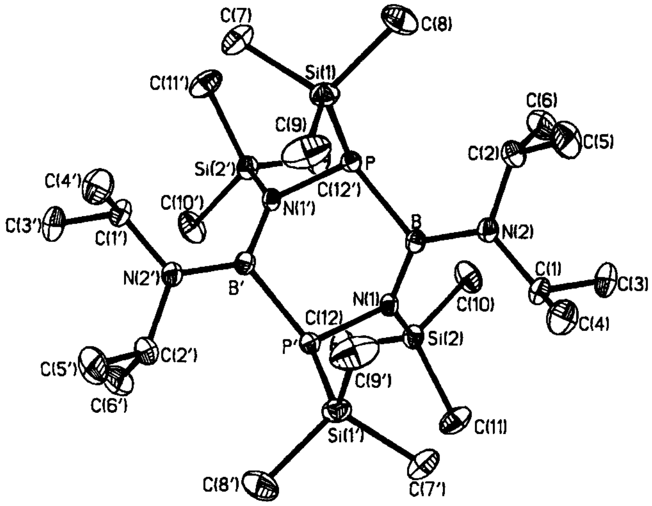


Figure 2. Molecular structure and atom labelling scheme for 3,6-(diisopropylamino)-1,2,4,5-tetrakis(trimethylsilyl)-1,4,2,5,3,6-diazadiphosphadiborinane (**13a**). Thermal ellipsoids represent 20% probability

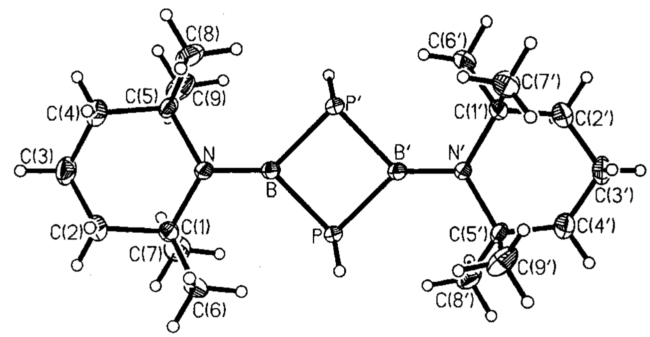


Figure 3. Molecular structure and atom labelling scheme for 2,4-bis(2,2,6,6-tetramethylpiperidino)-1,3,2,4-diphosphadiboretane (**4c**). Thermal ellipsoids represent 20% probability

the metrical parameters of a ligand, **4c**, and its complex. The structure of the complex shows a folded P_2B_2 ring (fold angle along the P···P' vector: 46.7°), with the hydrogen atoms in *trans* positions. The P–B bond distances, as expected, differ significantly for the four-coordinate phosphorus atom [P(1)–B(1) 1.963(5), P(1)–B(2) 1.967(5) Å] and the three-coordinate phosphorus atom [P(2)–B(1) 1.938(5), P(2)–B(2) 1.939(5) Å]. As expected, the four-coordinate P–B bonds are lengthened with respect to the distances in **4c**. The internal B–P–B angles, on the other hand, are only slightly different [B(1)–P(1)–B(2) 81.2(2)° and B(1)–P(2)–B(2) 82.5(1)°] and both are compressed in comparison to the angle in **4c**. The internal P–B–P angles, 88.8(2) and 89.0(2)°, are identical and comparable with the angle in **4c**. The boron and nitrogen atoms retain their trigonal planar geometry, and the average B–N bond distance, 1.385 Å, is slightly shorter than the distance in the free ligand because of the inductive effect exerted by the formal $>\overset{+}{P}<$ center.

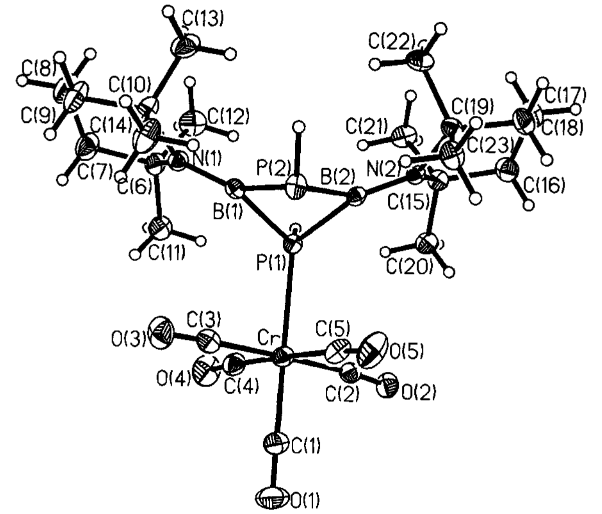


Figure 4. Molecular structure and atom labelling scheme for [2,4-bis(2,2,6,6-tetramethylpiperidino)-1,3,2,4-diphosphadiboretane]pentacarbonylchromium (**7c**). Thermal ellipsoids represent 20% probability

The $Cr(CO)_5P$ unit is pseudooctahedral, with no large distortions induced in the $Cr(CO)_5$ unit by the phosphanylborane ligand. The P–Cr–C(1) angle is 177.8(2)°, and the two equatorial CO ligands [C(3) and C(5)] are pushed slightly toward the phosphorus atom, while the remaining two equatorial carbonyls [C(2) and C(4)] are pushed slightly away. Grim and co-workers[54] have reported a correlation between Cr–P bond distance and ν_{CO} (E) in $Cr(CO)_5 \cdot PX_3$ complexes. From the correlation, it can be deduced that Cr–P bond distances typically increase with increasing σ-donor (decreasing π-acceptor) strength of the phosphane. Based on the infrared data presented above, the Cr–P bond distance in **7c** would be predicted to be slightly longer than in $Cr(CO)_5 \cdot PPh_3$. Indeed, the Cr–P bond distance, 2.458(2) Å, is longer than that reported for $(CO)_5Cr \cdot PPh_3$, 2.422(1) Å[57], and much longer than the distances in $(CO)_5Cr \cdot P(OPh)_3$, 2.309(1) Å[58], $(CO)_5Cr \cdot P(CH_2CH_2CN)_3$, 2.364(1) Å[63], and $(CO)_5CrPBr_3$, 2.263(3) Å[56]. The Cr–C bond distances should also be affected by the σ-donor/π-acceptor character of the phosphane, with the $M-CO_{ax}$ distance being most affected. In comparison with the series of complexes listed above, the Cr–C distances in **7c** are most nearly similar to those of $(CO)_5Cr \cdot PPh_3$: **7c**: $Cr-CO_{ax}$ 1.847 Å, avg. $Cr-CO_{eq}$ 1.898 Å; $(CO)_5Cr \cdot PPh_3$: $Cr-CO_{ax}$ 1.845 Å; avg. $Cr-CO_{eq}$ 1.880 Å. Further, the long Cr–P bond distance and short $Cr-CO_{ax}$ bond distance confirm that **4c** acts more as a σ-donor than as a π-acceptor ligand.

Despite the presence of the large $(Me_3Si)_2N$ groups at the boron atoms, the molecular structure determination for **4d** (Figure 5) confirms that this molecule exists as a trimeric, six-membered, chair-shaped ring with the phosphane hydrogens in equatorial positions. The planar $(Me_3Si)_2N$ groups are slightly inclined from the plane formed by the associated BP_2 planes, and they are twisted in the same sense in relation to each other. The average B–P bond distance, 1.928 Å, is comparable to B–P bond distances in $(Me_2PBH_2)_3$[60], 1.935(2) Å, and in several diphosphadiboretanes mentioned above. The average P–B–P and

B–P–B angles, 111.4 and 107.0°, are more obtuse than those in the diphosphadiboretanes. The average *exo*-B–N bond distance, 1.429 Å, falls in a range expected for aminoborane fragments, and it is also comparable with the *exo*-B–N bond distance in $(Me_2NBNH)_3$, 1.434(8) Å[59].

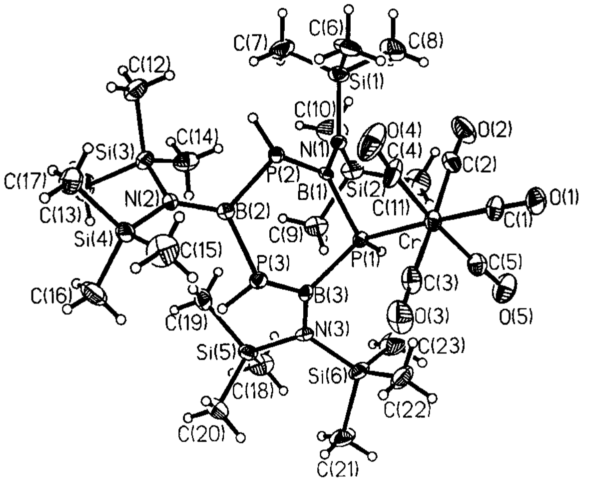


Figure 5. Molecular structure and atom labelling scheme for 2,4,6-tris[bis(trimethylsilyl)amino]-1,3,5,2,4,6-triphosphatriborinane (**4d**). Thermal ellipsoids represent 20% probability

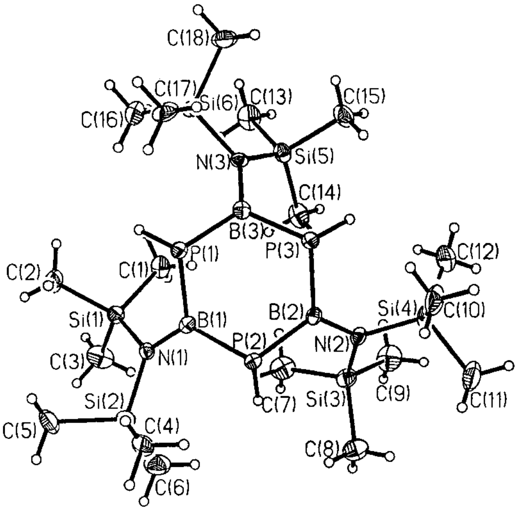


Figure 6. Molecular structure and atom labelling scheme for pentacarbonyl{2,2,6-tris[bis(trimethylsilylamino]-1,3,5,2,4,6-triphosphatriborinane}chromium (**7d**). Thermal ellipsoids represent 20% probability

The coordination complex **7d** (Figure 6) shows little variation in shape or metrical parameters when compared to **4d**. The chair conformation of the ring is retained, and the $Cr(CO)_5$ group occupies an axial position on P(1). All P–H bonds remain in equatorial positions. The B–P bond distances show greater variation than in **4d**. The B–P distances associated with the coordinated phosphorus atom P(1) are longer, 1.965(8) and 1.983(8) Å, than the distances in **4d**, while the average value of the remaining B–P bonds, 1.902 Å (range 1.903 to 1.953 Å), is comparable to the average B–P distance in the free ligand. The average B–N bond length is 1.413 Å, and the Cr–P bond distance, 2.476(2) Å, is similar to that found in **7c**.

The monolithium salt **8a** (Figure 7) has a dimeric structure whose P_2Li_2 core resembles the cores in the dimeric structures of $[(Me_3Si)_2PLi \cdot DME]_2$[64] and $[(i\text{-}Pr_2N)_2BPHLi \cdot DME]_2$[50]. Two nonplanar monophosphido rings, $i\text{-}Pr_2NBP(H)B(N-iPr_2)P^-$, are asymmetrically bonded through the phosphido P atoms to two $[Li \cdot DME]^+$ units. The central P_2Li_2 ring is planar, and the Li · DME chelate rings are held in an approximately perpendicular orientation to the P_2Li_2 ring.

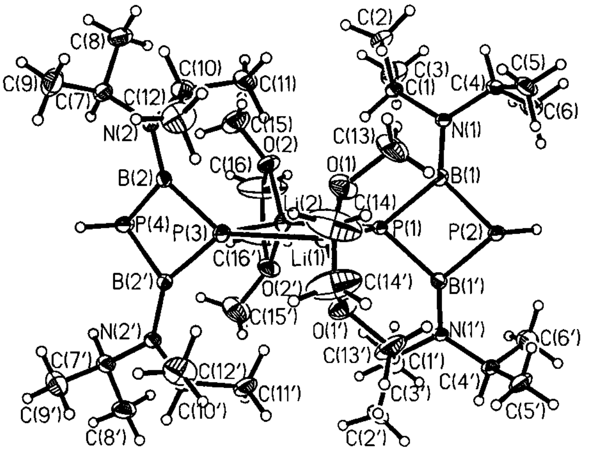


Figure 7. Molecular structure and atom labelling scheme for 2,4-bis(diisopropylamino)-1-(lithio · DME)-1,3,2,4-diphosphadiboretane (**8a**). Thermal ellipsoids represent 20% probability

The P_2Li_2 ring in **8a** is more asymmetric, particularly about Li(2) and P(3), than are the P_2Li_2 rings in the other two dimeric salts. In particular, three of the Li–P distances in **8a** are identical within experimental error, 2.539(16), 2.539(11), and 2.549(13) Å, while one distance is relatively longer, 2.664(15) Å. The first three distances compare favorably with the Li–P distances in $[(Me_3Si)_2PLi \cdot DME]_2$, 2.559(4) Å, and in $[(i-Pr_2N)_2BPHLi \cdot DME]_2$, 2.535(7) and 2.554(7) Å. The internal ring angles in **8a**, P(1)–Li(1)–P(3) 104.7(5)°, P(1)–Li(2)–P(3) 101.4(5)°, Li(1)–P(1)–Li(2) 78.2(4)°, and Li(1)–P(3)–Li(2) 75.7(4)°, are also comparable with the values in $[(Me_3Si)_2PLi \cdot DME]_2$, P–Li–P 104.3(2), Li–P–Li 75.7(2)°, and in $[(i\text{-}Pr_2N)_2BPHLi \cdot DME]_2$, P–Li–P 104.8(3), Li–P–Li 75.2(3)°. It is generally accepted that the steric bulk of the substituents at the P atoms in these rings is responsible for the adoption of the dimeric structures[64].

The P_2B_2 rings may be viewed as folded along the P···P vectors (e.g., $P_1 \cdots P_2$) with internal fold angles 151.8° [P(1)–B(1) ring] and 149.1° [P(3)–B(2) ring]. As expected, the P–B bonds in the P_2B_2 rings are asymmetric; the bonds involving the phosphide phosphorus atoms [P(1) and P(3)] are much shorter than those involving the phosphane phosphorus atoms, P(2) and P(4): P(1)–B(1), 1.897(1) and P(3)–B(2), 1.905(2) Å; P(2)–B(1), 1.953(1) and P(4)–B(2), 1.946(2) Å. The P–B distances involving P(1) and P(3) are also comparable with the P–B distance in $[(i\text{-}Pr_2N)_2BPHLi$

· DME], 1.901(5) Å. All of these distances are longer than that reported by Power for monomeric lithium salts of organo-substituted boryl phosphide (avg. 1.83 Å)[30]. In addition, internal P_2B_2 ring bonds vary in a predictable fashion: B(1)–P(1)–B(1′) 81.3(4)°, B(2)–P(3)–B(2′) 79.1(4)°; B(1)–P(2)–B(1′) 78.5(4)°, B(2)–P(4)–B(2′) 77.2(4)°. These angles are smaller than the P–B–P angles: 97.3(3) and 98.3(3)°.

This work was supported by the *National Science Foundation* (R.T.P.) and the *Fonds der Chemischen Industrie* (H.N.). A *NATO* grant, which allowed the cooperation of our research groups, is gratefully acknowledged.

Experimental

All manipulations of the compounds were performed under dry nitrogen, argon, or in vacuo. – IR: Nicolet FTIR Model 6000 spectrometer. – MS: Finnegan GC/MS or Varian CH7 spectrometers. – NMR: Varian FT-80, JEOL FX90 and GSX-400, and Bruker WP 250 instruments. – X-ray: Syntex P3/R3 diffractometer, SHELXTL programs for structure solutions. – Elemental analyses: Galbraith Laboratories and the UNM microanalytical facility. Most of the compounds gave satisfactory C, H, and N analyses, several compounds gave unreliable data as a result of impurities. – Cryoscopic molecular weights: benzene solutions, values are an average of three measurements.

[Bis(trimethylsilyl)phosphanyl](diisopropylamino)boron Chloride (**1a**): A solution containing 1.81 g (10 mmol) of $(i\text{-}Pr_2N)BCl_2$[65] in 15 ml of dry hexane was cooled to –78°C, and 3.28 g (10 mmol) of $LiP(SiMe_3)_2 \cdot 2\,THF$[66] in 40 ml of hexane was added slowly. The mixture was stirred at –78°C for 2 h and then warmed to 25°C. After 4 h at 25°C, the resulting slurry was filtered under nitrogen, and the solvent was evaporated from the filtrate. Isolation by distillation: 65–70°C/10^{-3} Torr. Yield: 2.9 g of **1a** (90%), colorless liquid. – MS (55 eV), *m/z* (%): 323.5 (30) [M^+], 280 (85) [M – $C_3H_7^+$], 172 (100), 110 (10), 73 (90), 43 (30). – IR (neat, cm^{-1}): ṽ = 2999 (m), 2969 (s), 2933 (m), 1473 (m), 1462 (m), 1444 (s), 1401 (w), 1368 (s), 912 (w), 882 (sh, s), 855 (vs), 838 (vs), 758 (m), 689 (m), 626 (s), 576 (w).

$C_{12}H_{32}BClNPSi_2$ (323.7) Calcd. C 44.52 H 9.89 N 4.33
Found C 44.86 H 9.84 N 4.31

[Bis(trimethylsilyl)phosphanyl](diphenylamino)boron Chloride (**1b**): Prepared in analogy to **1a** from 6.56 g (20 mmol) of $LiP(SiMe_3)_2 \cdot 2\,THF$ and 4.89 g (20 mmol) of $(Ph_2N)BCl_2$[67] in a total of 80 ml of hexane. A yellow oil was obtained from the evaporated filtrate, which crystallized slowly. The yellow solid was washed with cold hexane. Yield: 4.3 g of **1b** (55%), m.p. 107–109°C. – MS (70 eV), *m/z* (%): 391.1 (100) [M^+], 319 (8), 284 (35), 179 (25), 169 (20), 73 (100). – IR (hexane, cm^{-1}): ṽ = 3069 (w), 1592 (m), 1492 (s), 1401 (m), 1379 (m), 1340 (s), 1300 (m), 1246 (s), 1098 (w), 1074 (w), 1029 (m), 961 (w), 942 (m), 989 (w), 861 (sh), 841 (s), 752 (m), 723 (w), 696 (s), 627 (m), 601 (w).

$C_{18}H_{28}BClNPSi_2$ (391.85) Calcd. C 55.18 H 7.20 N 3.57
Found C 51.72 H 8.74 N 2.91

[Bis(trimethylsilyl)phosphanyl](2,2,6,6-tetramethylpiperidino)boron Chloride (**1c**): Prepared by analogy to **1a** from 2.56 g (7.6 mmol) of $LiP(SiMe_3)_2 \cdot 2\,THF$ and 1.76 g (7.6 mmol) of $tmpBCl_2$[68] in a total of 60 ml of hexane. The yellow filtrate was evaporated, leaving a pale yellow liquid. Isolation of **1c** by distillation: 103°C/10^{-3} Torr. Yield: 1.74 g of **1c** (63%). – MS (40 eV), *m/z* (%): 363.6 (5) [M^+], 290 (5), 254 (2), 178 (100), 73 (60). – IR (neat, cm^{-1}): ṽ = 2961 (s), 2950 (s), 2896 (s), 1470 (m), 1400 (m), 1385 (s), 1365 (s), 1323 (s), 1283 (s), 1244 (s), 1214 (w), 1169 (s), 1126 (m), 1039 (w), 992 (m), 970 (s), 840 (s), 779 (s), 756 (m), 688 (m), 625 (s), 578 (w), 515 (w).

$C_{15}H_{36}BClNPSi_2$ (363.9) Calcd. C 49.51 H 9.97 N 3.85
Found C 48.75 H 9.77 N 3.93

[Bis(trimethylsilyl)amino][bis(trimethylsilyl)phosphanyl]boron Chloride (**1d**): Prepared by analogy with **1a** from combination of 1.2 g (5.0 mmol) of $(Me_3Si)_2NBCl_2$ in 25 ml of hexane with 1.6 g (5.0 mmol) of $LiP(SiMe_3)_2 \cdot 2\,THF$ in 25 ml of hexane at –78°C. The mixture was stirred for 2 h at –78°C and for 12 h at 25°C. The cloudy mixture was filtered and the solvent removed by vacuum evaporation, leaving a slightly yellow oil. Isolation by distillation: 65–70°C/10^{-3} Torr. Yield: 1.31 g of **1d** (68%), colorless oil. – MS (30 eV), *m/z* (%): 250 (50), 147 (60), 73 (100). – IR (neat, cm^{-1}): ṽ = 2967–2893 (m), 1404 (w), 1249 (s), 1224 (s), 907 (s), 847 (vs), 689 (w), 626 (w).

$C_{12}H_{36}BClNPSi_4$ (384.0) Calcd. C 37.53 H 9.45 N 3.65
Found C 38.77 H 9.82 N 3.99

(Diisopropylamino)phosphanylboron Chloride (**2a**): A solution containing 1.82 g (10 mmol) of $i\text{-}Pr_2NBCl_2$ in 20 ml of hexane was combined with 1.3 g (10 mmol) of solid $LiPH_2 \cdot DME$[69] at 0°C. The solution was warmed to 23°C, stirred for 2 h, and filtered. The volatiles were removed from the filtrate, leaving a colorless oil. Yield: 1.7 g of **2a** (95%). **2a** decomposes upon heating above 100°C. Samples prepared in this fashion also contain small amounts of **3a** and minute quantities of **4a**. – MS (30 eV), *m/z* (%): 179 (8) [M^+], 164 (3), 146 (30), 144 (12), 104 (63), 86 (100), 68 (54). – IR (neat, cm^{-1}): ṽ = 2970 (vs), 2929 (s), 2871 (m), 2759 (w), 2722 (w), 2489 (w), 2326 (m), 2310 (m), 1476 (s), 1447 (s), 1368 (s), 1319 (s), 1185 (s), 1140 (s), 1117 (w), 1072 (w), 1006 (m), 919 (w), 886 (m), 826 (w), 805 (w), 781 (w), 717 (w), 573 (m). – Attempts to obtain reliable analytical data for this compound were particularly unsuccessful due to the presence of small amounts of **3a**.

The NMR studies of the reactions of $i\text{-}Pr_2NBCl_2$ with $LiPH_2 \cdot DME$ were accomplished by combination of the reagents at –78°C in hexane solution. The mixture were stirred for 2 h, warmed to 23°C, and stirred for another 2 h. The LiCl was removed by filtration, and the product mixture was recovered from the filtrate by vacuum evaporation. The residue was then redissolved in C_6D_6 for NMR analysis.

(Diphenylamino)phosphanylboron Chloride (**2b**): A 0.55-g (4.23-mmol) sample of solid $LiPH_2 \cdot DME$ was added to 1.06 g (4.23 mmol) of Ph_2NBCl_2 in 20 ml of hexane at –78°C, and the mixture was stirred for 1 h. The solution was warmed to 23°C, filtered, and volatiles were removed from the filtrate by vacuum evaporation. Attempts to redissolve the resulting yellow solid revealed that the compound is only sparingly soluble in THF, toluene, and benzene. Samples prepared in this fashion also contain very small amounts of **4b**. Yield: 0.96 g of **2b** (92%). – MS (20 eV), *m/z* (%): 247 (100) [M^+], 214 (61) [M – Ph_2^+], 212 (35) [M – Cl^+], 178 (58), 169 (23). – IR (hexane, cm^{-1}): ṽ = 2950 (vs), 2870 (vs), 2316 (m), 1492 (m), 1464 (s), 1378 (s), 1305 (m), 1249 (m), 1194 (w), 1134 (m), 1114 (m), 1075 (m), 1064 (m), 1029 (m), 1000 (m), 971 (m), 952 (m), 902 (m), 885 (m), 867 (m), 855 (w), 813 (w), 754 (m), 724 (m), 698 (s), 619 (m), 597 (m).

$C_{12}H_{12}BClNP$ (247.5) Calcd. C 58.24 H 4.89 N 5.66
Found C 60.12 H 4.90 N 5.50

Phosphanyl(2,2,6,6-tetramethylpiperidino)boron Chloride (**2c**): Prepared in analogy to **2b** from 2.2 g (17 mmol) of $LiPH_2 \cdot DME$ and 3.8 g (17 mmol) of $tmpBCl_2$ in 30 ml of hexane. Filtration after

1 h and vacuum evaporation of volatiles leaves a yellow oil. Isolation by distillation (some decomposition): 62°C/10^{-3} Torr, pale yellow oil. Yield: 3.5 g of **2c** (95%) (without distillation). Samples prepared in this fashion also contain small amounts of **3c** and **4c**. – MS (50 eV), *m/z* (%): 219 (3) [M$^+$], 204 (22), 186 (23), 170 (11). – IR (neat, cm^{-1}): $\tilde{\nu}$ = 2993 (s), 2966 (s), 2948 (s), 2938 (s), 2316 (m), 2270 (w), 1467 (m), 1374 (s), 1346 (s), 1303 (m), 1287 (m), 1253 (m), 1171 (m), 1128 (m), 1083 (w), 993 (m), 973 (m), 858 (w).

$C_9H_{20}BClNP$ (219.5) Calcd. C 49.25 H 9.18 N 6.38
Found C 49.44 H 9.10 N 6.52

[Bis(trimethylsilyl)aminophosphanylboron Chloride (**2d**): Prepared in analogy to **2b** from 1.45 g (11.2 mmol) of $LiPH_2 \cdot DME$ and 2.7 g (11.2 mmol) of $(TMS_2N)BCl_2$ in 20 ml of hexane. Isolation by vacuum evaporation of the volatiles. Yield: 1.17 g of **2d** (75%), colorless oil. Samples prepared in this fashion also contain small amounts of **3d** and **4d**. – MS (40 eV), *m/z* (%): 238 (1) [M$^+$], 206 (86), 204 (100), 187 (31), 146 (14), 98 (97). – IR (neat, cm^{-1}): $\tilde{\nu}$ = 2956 (s), 2900 (m), 2323 (m), 1408 (s), 1374 (s), 1348 (s), 1280 (vs), 1254 (vs), 1149 (m), 1114 (m), 1080 (m), 915 (s), 870 (s), 864 (s), 845 (vs), 766 (m), 734 (m), 683 (m).

2,4-Bis(diisopropylamino)-1,3,2,4-diphosphadiboretane (**4a**)

a) A 0.57-g (3.1-mmol) sample of $i\text{-}Pr_2NBCl_2$ in 25 ml of dry hexane was combined with 0.81 g (6.2 mmol) of $LiPH_2 \cdot DME$ at −78°C, and the mixture was stirred for 10 h. The mixture was then warmed to 23°C and stirred for 15 h. The cloudy solution was filtered and the solvent removed from the filtrate by vacuum evaporation. A colorless oil was recovered. Yield: 85%. Attempts to obtain reliable analytical data for this compound were frustrated by the presence of **8a**.

b) A suspension of 2.96 g (22.8 mmol) of $LiPH_2 \cdot DME$ in 50 ml of diethyl ether was slowly added at ambient temp. to a stirred solution of 2.07 g (11.4 mmol) of $i\text{-}Pr_2NBCl_2$ in 50 ml of pentane. The PH_3 formed was swept away by a slow stream of N_2. The insoluble material was removed by filtration and the solvents vacuum-evaporated (0.1 Torr). 1.43 g of a solid containing **4a** remained, m.p. 100–102°C (dec.), which could not be separated into its components by fractional crystallization from pentane, toluene, or a mixture of these solvents.

2,4-Bis(2,2,6,6-tetramethylpiperidino)-1,3,2,4-diphosphadiboretane (**4c**)

a) Samples of **4c** were prepared by a slight modification of the previously described method[45]. A 3.8-g (29.2-mmol) sample of $LiPH_2 \cdot DME$ suspended in 30 ml of hexane was cooled to −78°C, and a solution containing 3.24 g (14.6 mmol) of $tmpBCl_2$ in 20 ml of hexane was added dropwise. After 1 h, the mixture was warmed to 23°C, and at ≈ −20°C PH_3 formation of **3c** was detected by IR analysis. The solution was stirred at 23°C until PH_3 evolution ceased (≈ 4 h). The mixture was filtered and the volatiles removed from the filtrate. The residue was recrystallized from warm hexane cooled to 0°C. Yield: 2.2 g of **4c** (82%), m.p. 169–171°C, light yellow-green crystals. Molecular weight (benzene): 349. – MS (50 eV), *m/z* (%): 366 (51) [M$^+$], 333 (100) [M − PH_2^+], 213 (14), 182 (7). – IR (cyclohexane, cm^{-1}): $\tilde{\nu}$ = 2277 (w), 2260 (w), 1468 (w), 1449 (s), 1442 (w), 1382 (m), 1373 (s), 1330 (s), 1302 (w), 1170 (w), 990 (w), 727 (w).

$C_{18}H_{38}B_2N_2P_2$ (366.1) Calcd. C 59.06 H 10.46 N 7.65
Found C 58.85 H 10.55 N 7.54

b) In a similar procedure, a suspension of 2.57 g (19.8 mmol) of $LiPH_2 \cdot DME$ in 50 ml of diethyl ether was combined at −78°C within 40 min with 2.20 g (9.9 mmol) of $tmpBCl_2$ dissolved in 50 ml of pentane. This suspension was slowly (2 h) warmed to ambient temp. The solution then contained mainly $tmpB(PH_2)_2$, as shown by $\delta^{11}B$ = 53.4, $\delta^{31}P$ = −183.6 t, $^1J(PH)$ = 200 Hz, besides some PH_3 and **4c**. After the solids had been removed, PH_3 evolution increased as the solution was concentrated. Removal of all volatiles in vacuo left behind 1.80 g of **4c** (99%) as a pale yellow powder.

2,4,6-Tris[bis(trimethylsilyl)amino]-1,3,5,2,4,6-triphosphatriborinane (**4d**): A 0.5-g (2.1-mmol) sample of $(Me_3Si)_2NBCl_2$ in 25 ml of dry hexane was combined with 0.54 g (4.2 mmol) of $LIPH_2 \cdot DME$ at −78°C, and the mixture was stirred for 10 h. This mixture was warmed to 23°C and stirred for an additional 12 h. The resulting mixture was filtered and the solvent evaporated, leaving a yellow oil that solidified upon standing. Further vacuum evaporation of volatiles, followed by recrystallization from hexane, left a colorless solid. Yield: 0.38 g of **4d** (60%), m.p. 138–140°C. Molecular weight (benzene): 614. – MS (30 eV), *m/z* (%): 609 (1) [M$^+$], 576 (10), 406 (22), 373 (100), 260 (12), 204 (20), 188 (10), 172 (12), 98 (41), 73 (13). – IR (neat, cm^{-1}): $\tilde{\nu}$ = 2946 (m), 2895 (w), 2362 (w), 1322 (vs), 1298 (m), 1195 (m), 928 (s), 880 (vs), 860 (vs), 750 (w), 690 (w), 610 (w).

$C_{18}H_{57}B_3N_3P_3Si_6$ (609.6) Calcd. C 35.47 H 9.42 N 6.89
Found C 35.05 H 9.52 N 7.01

2,4,6-Tris(dimethylamino)-1,3,5,2,4,6-triphosphatriborinane (**4e**): A suspension of 2.13 g (16.4 mmol) of $LiPH_2 \cdot DME$ in 50 ml of *n*-pentane was dripped within 20 min into a stirred pentane solution of 1.02 g (8.2 mmol) of Me_2NBCl_2. Slow warming of the reaction mixture to ambient temp. resulted in the evolution of PH_3 gas, which was absorbed into an aqueous solution of $CuSO_4$. After 3 h of stirring, a single ^{11}B-NMR signal (δ = 50.9) was recorded for the solution. The insoluble material was then removed by filtration through a sintered glass disk (G3 pore size), and all volatiles were distilled off at 10^{-1} Torr and 20°C. Crystallization of the solid residue from diethyl ether/pentane (≈1:1) produced 0.56 g of **4e** (26%) as small cubes, m.p. 95–96°C, which were very sensitive to moisture. – MS: *m/z* 261 (M$^+$ with correct isotope pattern for three B atoms).

$C_6H_{21}B_3N_3P_3$ (260.6) Calcd. C 27.65 H 8.12 N 16.12
Found C 26.60 H 7.83 N 14.02

2,4,6-Tris(diethylamino)-1,3,5,2,4,6-triphosphatriborinane (**4f**)

a) To a stirred suspension of 3.32 g (25.5 mmol) of $LiPH_2 \cdot DME$ at −60°C in 70 ml of light petroleum ether was added, within 30 min, a solution of 1.96 g (12.7 mmol) of Et_2NBCl_2 in 20 ml of petroleum ether. ^{11}B-NMR spectra showed the reaction to be completed within 2 h at ambient temp. Removal of the solid from the suspension and the solvent from the filtrate left an oily yellow residue (1.18 g of **4f**, 86%). This was dissolved in 10 ml of pentane. From the solution, **4f** separated at −20°C in the form of sticky crystals. NMR and MS showed it to be almost pure, but poor elemental analyses were obtained from the hydrolytically and oxidatively sensitive material.

$C_{12}H_{33}B_3N_3P_3$ (344.8) Calcd. C 41.77 H 9.65 N 12.19
Found C 36.09 H 8.78 N 9.80

b) Similarly, 1.74 g (13.4 mmol) of $LiPH_2 \cdot DME$ in 60 ml of hexane were treated with 1.62 g (6.7 mmol) of Et_2NBBr_2 dissolved in 20 ml of hexane at −68°C. PH_3 evolution commenced at 20°C. Workup of the suspension began 2 d after mixing the reactants. A yellow oil remained after removal of all volatiles, and crystals of **4f** grew from a pentane solution within 3 months. The crystal started to melt at 81°C, with the production of a material that did not melt at 300°C. The yield was not determined, and analysis (Found C 33.92 H 8.2 N 9.0) was unsatisfactory despite its excellent spectroscopic purity.

Bis[bis(trimethylsilyl)phosphanyl](diphenylamino)borane (**5b**): A solution containing 0.33 g (1 mmol) of $LiP(SiMe_3)_2 \cdot 2$ THF in 30 ml of hexane was added to a solution of **1b** (0.39 g, 1 mmol) in 100 ml of hexane. The mixture was stirred at 23 °C for 2 h, and the resulting cloudy mixture was filtered. Vacuum evaporation of the solvent left a bright yellow solid that required no further purification. Yield: 0.4 g of **5b** (75%), m.p. 140–142 °C. – MS (70 eV), *m/z* (%) = 533.6 (5) [M^+], 460 (35), 356 (15), 281 (15), 250 (15), 73 (100). – IR (benzene, cm^{-1}): $\tilde{\nu}$ = 1587 (w), 1447 (m), 1350 (w), 1319 (w), 1245 (s), 1133 (w), 1074 (w), 1041 (w), 916 (w), 839 (vs), 800 (s), 749 (m), 696 (m), 629 (m).

$C_{24}H_{46}BNP_2Si_4$ (533.7) Calcd. C 54.06 H 8.63 N 2.63
Found C 54.28 H 8.73 N 2.80

2,4-Bis(diphenylamino)-1,3-bis(trimethylsilyl)-1,3,2,4-diphosphadiboretane (**6b**): A 0.26.g (0.5 mmol) sample of **5b** was dissolved in 30 ml of benzene. The solution was frozen, the flask evacuated, and the solution subsequently refluxed for 2 h. The solvent was then vacuum-evaporated, leaving a yellow solid and liquid. The liquid was removed with a cold hexane wash, leaving a colorless solid. Yield: 0.66 g of **6b** (47%). – MS (55 eV), *m/z* (%): 566 (20) [M^+], 493 (10), 283 (5), 73 (100). – IR (benzene, cm^{-1}): $\tilde{\nu}$ = 1593 (m), 1509 (m), 1491 (s), 1466 (m), 1391 (m), 1376 (m), 1339 (s), 1297 (s), 1286 (m), 1246 (m), 840 (s), 796 (w), 749 (m), 628 (m).

$C_{30}H_{38}B_2N_2P_2Si_2$ (566.4) Calcd. C 63.63 H 6.72 N 4.95
Found C 63.36 H 7.34 N 4.86

2,4-Bis[bis(trimethylsilyl)amino]-1,3-bis(trimethylsilyl)-1,3,2,4-diphosphadiboretane (**6d**): A solution of $(Me_3Si)_2NBCl_2$ (0.70 g, 2.9 mmol) in 25 ml of dry hexane was combined with $LiP(SiMe_3)_2 \cdot 2$ THF (1.9 g, 5.8 mmol) dissolved in hexane (25 ml) at −78 °C. The solution was stirred at −78 °C for 1 h and then warmed to 23 °C and stirred for 20 h. The resulting yellow cloudy solution was filtered. The solvent was removed by vacuum evaporation, leaving a yellow oil. The $P(SiMe_3)_3$ was removed into a cold trap by vacuum distillation. The yellow oily product needs no further purification. Yield: 0.48 g of **6d** (87%). – MS (30 eV), *m/z* (%): 550 (2) [M^+], 275 (30), 147 (29), 98 (45), 73 (100). – IR (neat, cm^{-1}): $\tilde{\nu}$ = 2953 (m), 2895 (w), 1248 (s), 1196 (s), 916 (s), 837 (vs), 686 (w), 627 (w).

$C_{18}H_{54}B_2N_2P_2Si_6$ (550.7) Calcd. C 39.26 H 9.88 N 5.09
Found C 40.13 H 10.40 N 3.66

[2,4-Bis(2,2,6,6-tetramethylpiperidino)-1,3,2,4-diphosphadiborethane-P]pentacarbonylchromium (**7c**): A 0.48-g (1.3-mmol) sample of **4c** was dissolved in 50 ml of hexane and added to 0.33 g (1.3 mmol) of $Cr(CO)_5 \cdot NMe_3$ in 25 ml of hexane. The mixture was stirred at 23 °C for 12 h and the solvent removed by vacuum evaporation, leaving a brown solid. This was recrystallized from hexane, and yellow-green crystals were obtained. Yield: 0.60 g of **7c** (83%), m.p. 130–132 °C. – IR (cyclohexane, cm^{-1}): $\tilde{\nu}$ = 2331 (w), 2321 (w), 2057 (m), 1974 (w), 1935 (vs), 1461 (m), 1379 (w), 1343 (w), 1169 (w), 726 (w), 671 (m).

$C_{23}H_{38}B_2CrN_2O_5P_2$ (558.1) Calcd. C 49.50 H 6.86 N 5.02
Found C 49.49 H 7.03 N 5.19

Pentacarbonyl{2,4,6-tris[bis(trimethylsilyl)amino]-1,3,5,4,6-triphosphatriboretane-P}chromium (**7d**): A solution of **4d** (0.2 g, 0.33 mmol in 25 ml of dry hexane was combined with $Cr(CO)_5 \cdot NMe_3$ (0.082 g, 0.33 mmol) dissolved in 25 ml of hexane at 23 °C. The solution was stirred for 24 h, and the solvent was removed by vacuum evaporation. The resulting brown residue was evacuated for 2 h to remove all volatile by-products and was recrystallized from hexane, leaving yellow-orange crystals. Yield: 0.20 g of **7d** (76%), m.p. 152–155 °C (dec). – MS (30 eV), *m/z* (%): 598 (1), 458 (18), 372 (28), 255 (30), 172 (30), 147 (35), 98 (100), 73 (55). – IR (cyclohexane, cm^{-1}): $\tilde{\nu}$ = 2355 (w), 2344 (w), 2060 (m), 1981 (w), 1940 (vs), 1923 (s), 1379 (m), 1253 (m), 952 (m), 847 (m).

$C_{23}H_{57}B_3CrN_3O_5P_3Si_6$ (801.6) Calcd. C 34.56 H 7.57 N 5.36
Found C 34.46 H 7.17 N 5.24

2,4-Bis(diisopropylamino)-1-(lithio · DME)-1,3,2,4-diphosphadiboretane (**8a**): A 2.9-g (22.0-mmol) sample of $LiPH_2 \cdot DME$ sus-

Table 5. Crystallographic data for phosphanylboranes **5b**, **13a**, **4c**, **7c**, **4d**, **7d**, and **8a**

	5b $C_{24}H_{46}BNSi_4P_2$	**13a** $C_{24}H_{64}B_2N_4Si_4P_2$	**4c** $C_{18}H_{38}B_2N_2P_2$	**7c** $C_{23}H_{38}B_2CrN_2O_5P_2$	**4d** $C_{18}H_{57}B_3N_3P_3Si_6$	**7d** $C_{23}H_{57}B_3CrN_3O_5P_3Si_6$	**8a** $C_{16}H_{39}B_2LiN_2O_2P_2$
Mol. mass	533.7	604.85	366.1	558.1	609.6	801.6	382.0
a [Å]	9.929(2)	18.056(5)	6.679(1)	14.701(3)	13.761(2)	11.803(4)	10.042(3)
b [Å]	18.297(5)	15.738(4)	14.791(3)	11.920(2)	21.115(6)	18.003(6)	22.877(4)
c [Å]	20.387(7)	13.397(4)	11.265(3)	16.871(3)	13.786(2)	21.448(7)	21.115(3)
α [°]	67.63(3)						
β [°]	76.26(3)	99.66(2)	99.99(3)	91.08(3)	106.87(1)		
γ [°]	86.09(3)						
V [$Å^3$]	3226(2)	3753(2)	1095.9(3)	2955.8(9)	3833.2(2)	4557.5	4850.8
d_r [g cm^{-3}]	1.07	1.07	1.11	1.25	1.06	1.17	1.05
Z	4	4	2	4	4	4	8
Space group	$P\bar{1}$	$C2/c$	$P2_1/c$	$P2/c$	$P2_1/n$	$P2_12_12_1$	$Pbcm$
μ [Mo-K_α mm^{-1}]	0.28	0.26	0.20	0.50	0.35	0.53	0.18
F(000)	1152	1328	400	1176	1320	1696	1664
Crystal size [mm]	0.09 × 0.21 × 0.69	0.3 × 0.3 × 0.5	0.18 × 0.21 × 0.74	0.09 × 0.30 × 0.51	0.09 × 0.25 × 0.58	0.32 × 0.46 × 0.53	0.16 × 0.46 × 0.81
Temperature [°C]	20	20	20	20	20	20	−20
Reciprocal space	$\pm h, \pm k, \pm l$	$\pm h, \pm k, +l$	$-h, -k, \pm l$	$\pm h, \pm k, +l$	$\pm h, +k, +l$	$-h, +k, \pm l$	$-h, +k, -22 \leqslant l \leqslant 9$
2Θ range [°]	2–45	2–55	2–50	2–50	2–47	2–50	2–45
Scan mode	ω	Θ–2Θ	ω	Θ–2Θ	ω	ω	ω
Scan speed (° min^{-1})	6–30	4–30	6–30	6–30	5–30	6–30	7–30
Reflections measured	12438	11450	4304	11428	6129	8737	5457
Unique reflections	6233	4350	1933	5242	5673	8006	3284
Observed reflections [3σ(*F*)]	4854	3197	1529	3791	3013	5174	2183 ($F > 2\sigma F$)
Parameters refined	577	163	112	328	307	406	239
R [%]	6.86	7.24	7.19	7.51	7.18	6.58	8.20
R_w [%]	5.88	4.77	9.02	6.76	5.68	5.96	7.10

pended in 30 ml of hexane was cooled to $-78\,^{\circ}C$, and a solution of 1.6 g (8.8 mmol) of *i*-Pr_2NBCl_2 in 20 ml of hexane was added dropwise. The resulting mixture was warmed to 23 °C and stirred for 15 h. At about 0 °C, PH_3 was evolved and detected by IR. The solution was filtered, and colorless crystals formed in the filtrate at $-10\,^{\circ}C$. Yield: 1.30 g of **8a** (77%), m.p. 144 °C (dec). – IR (nujol, cm^{-1}): $\tilde{\nu} = 2277$.

$C_{16}H_{39}B_2LiN_2O_2P_2$ (382.0) Calcd. C 50.31 H 10.29 N 7.33
Found C 53.00 H 10.15 N 7.05

Table 6. Atomic coordinates ($\cdot 10^4$) and equivalent isotropic thermal parameters U_{eq} ($Å \cdot 10^3$) for **5b**. Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x/a	y/b	z/c	U_{eq}
B(1)	2271(7)	7617(4)	2603(4)	40(3)
P(1)	2867(2)	7013(1)	3466(1)	49(1)
Si(1)	3123(2)	5734(1)	3633(1)	64(1)
C(25)	4900(9)	5566(5)	3232(7)	216(11)
C(26)	2883(16)	5147(5)	4573(5)	292(13)
C(27)	2019(11)	5361(5)	3254(7)	217(11)
Si(2)	1800(2)	7198(1)	4485(1)	69(1)
C(28)	1602(9)	8282(5)	4208(5)	124(6)
C(29)	94(7)	6681(5)	4990(4)	109(5)
C(30)	3019(7)	6873(5)	5111(4)	105(5)
P(2)	3585(2)	7570(1)	1779(1)	50(1)
Si(3)	5617(2)	8152(1)	1595(1)	66(1)
C(31)	5645(8)	8618(6)	2229(5)	138(7)
C(32)	6059(14)	8887(9)	710(6)	391(16)
C(33)	6937(9)	7436(6)	1663(9)	279(16)
Si(4)	2867(2)	7869(2)	755(1)	80(1)
C(34)	1172(9)	7316(6)	1044(6)	167(9)
C(35)	2663(9)	8909(5)	204(4)	126(6)
C(36)	4190(9)	7464(5)	173(4)	138(7)
N(1)	955(5)	8029(3)	2572(3)	42(3)
C(1)	-322(6)	7676(4)	3060(3)	45(3)
C(2)	-1274(8)	8111(4)	3369(4)	65(4)
C(3)	-2536(8)	7752(6)	3829(4)	78(5)
C(4)	-2815(8)	6988(6)	3967(4)	87(5)
C(5)	-1889(8)	6558(5)	3664(4)	78(4)
C(6)	-641(7)	6913(4)	3206(4)	56(4)
C(7)	866(6)	8804(4)	2039(3)	44(3)
C(8)	1830(7)	9386(4)	1890(4)	51(4)
C(9)	1734(8)	10137(5)	1391(4)	72(4)
C(10)	666(9)	10316(5)	1045(4)	75(4)
C(11)	-295(8)	9746(5)	1187(4)	75(4)
C(12)	-201(7)	8996(4)	1680(4)	60(4)
B(2)	2803(7)	7390(4)	7531(4)	41(3)
P(3)	4588(2)	7888(1)	7274(1)	45(1)
Si(5)	4541(2)	9101(1)	7313(1)	53(1)
C(37)	4208(7)	9947(4)	6512(4)	78(4)
C(38)	3231(8)	9052(4)	8147(4)	86(4)
C(39)	6291(7)	9290(4)	7419(5)	101(5)
Si(6)	5950(2)	7913(1)	6210(1)	56(1)
C(40)	5401(8)	8624(5)	5398(4)	113(5)
C(41)	6021(8)	6924(4)	6161(4)	95(5)
C(42)	7720(7)	8213(5)	6170(5)	118(6)
P(4)	2909(2)	6297(1)	7731(1)	49(1)
Si(7)	919(2)	6556(1)	7896(1)	62(1)
C(43)	19(7)	6319(4)	7192(4)	80(4)
C(44)	-245(7)	5358(4)	8825(4)	85(4)
C(45)	1399(8)	4767(4)	7680(5)	116(6)
Si(8)	4063(2)	5652(1)	8600(1)	66(1)
C(46)	3725(9)	4593(4)	8901(5)	147(7)
C(47)	3567(11)	5935(6)	9385(5)	185(8)
C(48)	5948(7)	5817(5)	8237(5)	137(6)
N(2)	1506(5)	7815(3)	7584(3)	41(3)
C(13)	400(7)	7547(4)	8217(4)	48(4)
C(14)	664(8)	7269(4)	8892(5)	66(4)
C(15)	-408(11)	7028(5)	9520(4)	91(5)
C(16)	-1747(11)	7080(5)	9445(6)	105(6)
C(17)	-2053(8)	7354(5)	8788(6)	94(5)
C(18)	-990(8)	7590(4)	8161(4)	67(4)
C(19(	1280(6)	8514(4)	7006(4)	42(4)
C(20)	544(6)	9134(4)	7137(4)	56(4)
C(21)	293(7)	9794(4)	6574(5)	72(5)
C(22)	788(8)	9864(4)	5869(5)	74(5)
C(23)	1532(8)	9257(5)	5725(4)	70(4)
C(24)	1751(6)	8580(4)	6294(4)	54(4)

1-(Lithio · DME)-2,4-bis(2,2,6,6-tetramethylpiperidino)-1,3,2,4-diphosphadiboretane (**8c**): A solution of **4c** (2.0 g, 5.5 mmol) in 50 ml of dry DME was cooled to $-78\,^{\circ}C$, and 3.4 ml of *n*-BuLi (1.6 M, 5.5 mmol) was added by syringe. The red solution was stirred at $-78\,^{\circ}C$ for two h, then warmed to 23 °C and stirred for 12 h. The solvent was removed by vacuum evaporation, leaving a thick oil. Upon addition of 25 ml of hexane, the oil turned into a brown powder, which was isolated by filtration. Yield: 2.03 g of **8c** (80%), m.p. 138–140 °C. – IR (nujol, cm^{-1}): $\tilde{\nu}$ = 2171 (w), 1363 (m), 1274 (m), 1164 (m).

$C_{22}H_{47}B_2LiN_2O_2P_2$ (462.1) Calcd. C 57.18 H 10.25 N 6.06
Found C 54.89 H 10.52 N 6.18

2,4-Bis(2,2,6,6-tetramethylpiperidino-1-(trimethylsilyl)-1,3,2,4-diphosphadiboretane (**9c**): To a sample of **8c** (0.4 g, 0.87 mmol) suspended in 25 ml of dry hexane was added excess Me_3SiCl (0.1 g, 1.4 mmol) at 0 °C. The solution was stirred for 1 h, warmed to 23 °C, and stirred for 15 h. The resulting cloudy, yellow solution was filtered, and the solvent was removed by vacuum evaporation, leaving a yellow oil. Yield: 0.30 g of **9c** (80%). The yellow oil forms a tacky solid upon standing. – MS (30 eV), *m/z* (%): 438 (40) [M^+], 333 (73), 254 (18), 73 (100). – IR (neat, cm^{-1}): $\tilde{\nu}$ = 2958–2871 (vs), 2229 (s), 1464 (s), 1380 (s), 1363 (s), 1321 (vs), 1299 (s), 1242 (s), 1192 (m), 1165 (s), 1129 (s), 1087 (m), 1068 (m), 1042 (m), 989 (m), 905 (m), 844 (m), 750 (m), 705 (m), 688 (m), 629 (m), 571 (m).

$C_{21}H_{46}B_2N_2P_2Si$ (438.3) Calcd. C 57.55 H 10.58 N 6.39
Found C 55.79 H 10.75 N 6.52

Amino[bis(trimethylsilyl)phosphanyl](diisopropylamino)borane (**11a**): A 0.66-g (2.0-mmol) sample of **1a** was dissolved in 40 ml of hexane, the solution cooled to $-78\,^{\circ}C$, and ammonia (4 mmol) was condensed into the flask. The mixture was stirred for 1 h and then slowly warmed to 23 °C. The volatiles were removed by vacuum evaporation, and a white solid was obtained. Yield: 0.43 g of **11a**

Table 7. Atomic coordinates ($\cdot 10^4$) and equivalent isotropic thermal parameters U_{eq} ($Å \cdot 10^3$) for **13a**. Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x/a	y/b	z/c	U_{eq}
P	4171.7(4)	2333.2(5)	1596.0(6)	36.2(2)
Si(1)	3508.5(5)	3565.1(6)	1508.3(7)	48.9(3)
Si(2)	6228.7(5)	1019.7(5)	2044.4(6)	40.8(3)
B	5206(2)	2381(2)	1352(2)	33(1)
N(1)	5762(1)	1986(1)	2149(2)	31(1)
N(2)	5364(1)	2645(1)	408(2)	40(1)
C(1)	6146(2)	2743(2)	214(2)	49(1)
C(2)	4722(2)	2820(2)	-422(2)	60(1)
C(3)	6317(2)	2318(2)	-744(2)	75(1)
C(4)	6419(2)	3671(2)	256(3)	75(2)
C(5)	4777(2)	3652(2)	-1001(3)	91(2)
C(6)	4522(2)	2067(2)	-1117(3)	89(2)
C(7)	2675(2)	3357(2)	2137(3)	68(1)
C(8)	3097(2)	3841(2)	168(3)	94(2)
C(9)	4030(2)	4506(2)	2101(3)	84(2)
C(10)	5847(2)	513(2)	817(3)	70(1)
C(11)	7263(1)	1139(2)	2131(3)	71(2)
C(12)	6096(2)	266(2)	3066(3)	69(1)

(71%), m.p. 48–50°C. – MS (55 eV), *m/z* (%): 304 (25) [M$^+$], 262 (20), 127 (100), 73 (50). – IR (hexane, cm^{-1}): $\tilde{\nu}$ = 3535 (w), 3449 (w), 1590 (m), 1449 (w), 1430 (m), 1414 (w), 1401 (w), 1367 (w), 1330 (w), 1312 (s), 1260 (m), 1245 (s), 1226 (w), 1208 (s), 1190 (w), 1156 (w), 1130 (w), 1112 (w), 1042 (w), 1021 (w), 856 (s), 835 (vs), 749 (w), 686 (w), 628 (m), 594 (w).

$C_{12}H_{34}BN_2PSi_2$ (304.3) Calcd. C 47.37 H 11.19 N 9.21
Found C 48.12 H 11.10 N 8.80

Table 8. Atomic coordinates (· 10^4) and equivalent isotropic thermal parameters U_{eq} (Å · 10^3) for **4c**. Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x/a	y/b	x/c	U_{eq}
P	368(2)	5889(1)	-216(1)	52(1)
B	1102(6)	4741(3)	-842(3)	39(1)
N	2163(4)	4495(2)	-1765(2)	39(1)
C(1)	3083(6)	5209(2)	-2452(3)	46(1)
C(2)	4709(8)	4828(3)	-3127(4)	72(2)
C(3)	4051(9)	4005(3)	-3857(4)	76(2)
C(4)	3598(9)	3303(3)	-3012(4)	78(2)
C(5)	1962(6)	3531(2)	-2261(3)	44(1)
C(6)	4197(7)	5915(3)	-1582(4)	65(2)
C(7)	1435(8)	5684(3)	-3329(4)	73(2)
C(8)	2333(9)	2850(3)	-1248(5)	76(2)
C(9)	-128(8)	3405(4)	-2993(5)	86(2)

Table 9. Atomic coordinates (· 10^4) and equivalent isotropic thermal paramters U_{eq} (Å · 10^3) for **7c**. Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x/a	y/b	z/c	U_{eq}
Cr	2660(1)	1436(1)	590(1)	48(1)
C(1)	3064(4)	2798(5)	210(4)	69(2)
O(1)	3306(3)	3651(4)	-26(3)	106(2)
C(2)	1458(4)	1885(4)	332(3)	53(2)
O(2)	753(3)	2202(3)	144(2)	70(2)
C(3)	3882(4)	978(5)	790(3)	60(2)
O(3)	4622(3)	714(4)	889(3)	86(2)
C(4)	2731(4)	824(5)	-436(3)	64(2)
O(4)	2784(3)	485(4)	-1068(2)	104(2)
C(5)	2604(4)	2109(4)	1621(3)	61(2)
O(5)	2569(3)	2547(4)	2216(3)	95(2)
P(1)	2150(1)	-357(1)	1146(1)	41(1)
B(1)	3109(3)	-1264(5)	1657(3)	40(2)
N(1)	3656(2)	-2157(3)	1435(2)	45(1)
C(6)	3463(3)	-2782(4)	660(3)	52(2)
C(7)	4258(4)	-3528(5)	412(3)	80(2)
C(8)	4664(5)	-4229(5)	1068(4)	90(2)
C(9)	4999(4)	-3452(5)	1691(4)	84(3)
C(10)	4278(3)	-2719(4)	2067(3)	57(2)
C(11)	3321(4)	-1941(5)	-20(3)	68(2)
C(12)	2606(4)	-3488(5)	753(3)	75(2)
C(13)	3695(4)	-3421(5)	2617(3)	78(2)
C(14)	4798(4)	-1808(5)	2527(4)	83(3)
P(2)	2953(1)	-408(1)	2621(1)	48(1)
B(2)	1702(3)	-336(4)	2238(3)	39(2)
N(2)	858(2)	-326(3)	2585(2)	38(1)
C(15)	-7(3)	-520(4)	2091(3)	45(2)
C(16)	-878(3)	-203(5)	2528(3)	64(2)
C(17)	-914(3)	-644(5)	3360(3)	66(2)
C(18)	-131(3)	-139(5)	3810(3)	63(2)
C(19)	806(3)	-438(4)	3491(3)	47(2)
C(20)	3(3)	228(5)	1353(3)	59(2)
C(21)	-46(3)	-1747(4)	1835(3)	59(2)
C(22)	1037(4)	-1650(4)	3730(3)	59(2)
C(23)	1473(3)	388(4)	3889(3)	58(2)

Azido[bis(trimethylsilyl)phosphanyl](diisopropylamino)borane (**12a**): A 1.6-g (5.0-mmol) sample of **1a** was dissolved in 40 ml of hexane, and 1.2 g (10 mmol) of Me_3SiN_3 was added by syringe. The mixture was stirred at 23°C for 48 h. During this time the solution changed from colorless to yellow. The volatiles were removed by vacuum evaporation, leaving a yellow oil. Yield: 1.57 g of **12a** (95%). – IR (neat, cm^{-1}): $\tilde{\nu}$ = 2967 (vs), 2931 (s), 2896 (s), 2873 (m), 2137 (vs), 1473 (s), 1462 (s), 1443 (s), 1401 (m), 1365 (s), 1305 (vs), 1246 (vs), 1186 (s), 1150 (s), 1138 (s), 1116 (m), 1084 (w), 1021 (m), 1004 (m), 968 (m), 909 (m), 881 (s), 836 (vs), 777 (w), 751 (m), 688 (m), 627 (s), 580 (w), 460 (w), 447 (m).

$C_{12}H_{32}BN_4PSi_2$ (330.3) Calcd. C 43.67 H 9.70 N 16.98
Found C 44.31 H 9.95 N 16.19

Table 10. Atomic coordinates (· 10^4) and equivalent isotropic thermal parameters U_{eq} (Å · 10^3) for **4d**. Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x/a	/b	z/c	U_{eq}
P(1)	-781(1)	1769(1)	5677(2)	42(1)
P(2)	-118(2)	3164(1)	5235(2)	46(1)
P(3)	-2148(2)	2949(1)	5864(2)	45(1)
Si(1)	-242(2)	1387(1)	3369(2)	48(1)
Si(2)	1557(2)	2280(1)	4178(2)	54(1)
Si(3)	-1757(2)	4153(1)	3299(2)	63(1)
Si(4)	-2634(2)	4519(1)	5027(2)	70(1)
Si(5)	-4141(2)	1984(1)	4262(2)	54(1)
Si(6)	-3032(2)	929(1)	5689(2)	56(1)
N(1)	340(4)	2019(2)	4178(4)	39(2)
N(2)	-1921(4)	3996(3)	4511(4)	44(2)
N(3)	-3035(4)	1686(3)	5169(4)	40(2)
B(1)	-165(6)	2277(4)	4858(7)	41(3)
B(2)	-1493(6)	3439(4)	5051(7)	42(4)
B(3)	-2144(6)	2078(4)	5438(6)	42(3)
C(1)	-1643(5)	1463(3)	2998(6)	61(3)
C(2)	159(6)	603(3)	3968(6)	71(4)
C(3)	75(6)	1428(4)	2157(6)	92(5)
C(4)	2224(5)	2686(4)	5381(6)	69(4)
C(5)	2341(5)	1566(4)	4102(7)	89(5)
C(6)	1505(7)	2838(4)	3128(7)	94(5)
C(7)	-1539(7)	3426(4)	2641(6)	84(4)
C(8)	-708(6)	4719(4)	3365(7)	93(5)
C(9)	-2975(6)	4468(4)	2448(6)	101(5)
C(10)	-2204(7)	4486(4)	6431(6)	96(5)
C(11)	-2386(7)	5359(4)	4715(7)	104(5)
C(12)	-4020(6)	4354(4)	4576(8)	107(6)
C(13)	-4833(6)	1322(4)	3456(6)	85(4)
C(14)	-3816(6)	2542(4)	3359(6)	74(4)
C(15)	-5013(5)	2383(4)	4889(7)	77(4)
C(16)	-2860(6)	300(4)	4825(7)	83(5)
C(17)	-2017(6)	857(4)	6900(6)	76(4)
C(18)	-4260(6)	799(4)	5990(6)	82(4)

3,6-(Diisopropylamino)-1,2,4,5-tetrakis(trimethylsilyl)-1,4,2,5,3,6-diazadiphosphadiboretane (**13a**): A 1.65-g (5-mmol) sample of **12a** was heated at 80°C while removing the evolved nitrogen. The yellow oil darkened and deposited a white solid. The mixture was washed with cold hexane, and a white solid was collected. Yield: 0.41 g of **13a** (27%), m.p. 199–200°C. – MS (70 eV), *m/z* (%): 604.6 (10) [M$^+$], 532 (2), 406 (90), 229 (10), 98 (15), 73 (100). – IR (CH_2Cl_2, cm^{-1}): $\tilde{\nu}$ = 2959 (s), 2930 (m), 2872 (m), 1468 (w), 1439 (m), 1417 (w), 1401 (w), 1379 (w), 1364 (w), 1305 (m), 1249 (m), 1205 (m), 1190 (m), 1142 (m), 1116 (w), 1095 (m), 1084 (m), 1051 (w), 1018 (m), 1009 (m), 865 (s), 842 (s).

$C_{24}H_{64}B_2N_4P_2Si_4$ (604.6) Calcd. C 47.69 H 10.60 N 9.27
Found C 46.63 H 10.70 N 8.88

3,6-Bis(diisopropylamino)-1,4-bis(trimethylsilyl)-1,4,2,5,3,6-diazadiphosphadiborinane (**14a**): A solution of 0.30 g (0.5 mmol) of **13a** in 50 ml of CH_2Cl_2 was cooled to 0°C. A solution containing 0.06 g (2 mmol) of CH_3OH in 10 ml of CH_2Cl_2 was added and the mixture stirred for 1 h. The volatiles were removed by vacuum evaporation, leaving a colorless solid. – MS (55 eV), *m/z* (%): 459.6 (28) [M^+], 262 (70), 229 (30), 199 (100), 141 (10), 98 (50), 73 (60). – IR (hexane, cm^{-1}): $\tilde{\nu}$ = 2252 (m), 1439 (m), 1364 (m), 1319 (m), 1303 (s), 1260 (m), 1248 (m), 1191 (m), 1145 (m), 1085 (m), 1031 (w), 889 (s), 862 (s), 842 (s), 738 (m).

{[Bis(trimethylsilyl)phosphanyl]chloro(diisopropylamino)boron-P}pentacarbonylchromium (**15a**): A solution of 0.32 g (1 mmol) of **1a** in 40 ml of hexane was added to 0.25 g (1 mmol) of $Cr(CO)_5 \cdot NMe_3$ in 20 ml of hexane. The mixture was stirred at 23°C for 12 h and the solvent removed by vacuum evaporation, leaving a bright yellow oil. Yield: 0.39 g of **15a** (75%). – MS (40 eV), *m/z* (%): 403 (30) [$Cr(CO)L^+$], 375 (50) [CrL^+]. – IR (neat, cm^{-1}): $\tilde{\nu}$ = 2972 (m), 2936 (m), 2902 (w), 2877 (w), 2054 (s), 1971 (s), 1929 (vs), 1910 (vs), 1478 (m), 1466 (m), 1449 (m), 1407 (w), 1386 (w), 1371 (m), 1313 (m), 1252 (s), 1183 (w), 1148 (m), 1116 (w), 999 (m), 912 (w), 876 (m), 846 (s), 831 (s), 803 (m), 756 (w), 690 (w), 673 (s), 654 (vs), 625 (s), 585 (w), 566 (w), 487 (w).

$C_{17}H_{32}BClCrNO_5PSi_2$ (515.9) Calcd. C 39.59 H 6.21 N 2.72
Found C 40.22 H 6.31 N 2.74

Table 11. Atomic coordinates (· 10^4) and equivalent isotropic thermal parameters U_{eq} (Å · 10^3) for **7d**. Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x/a	y/b	z/c	U_{eq}
Cr	5300(1)	926(1)	1281(1)	51(1)
C(1)	4037(8)	1472(5)	1491(4)	64(3)
O(1)	3250(5)	1817(4)	1607(3)	91(3)
C(2)	4360(7)	70(6)	1160(4)	69(4)
O(2)	3783(6)	-409(4)	1081(4)	116(4)
C(3)	6240(8)	1760(5)	1427(4)	69(4)
O(3)	6766(6)	2272(4)	1515(4)	113(4)
C(4)	5483(8)	683(6)	2119(4)	87(4)
O(4)	5502(7)	590(5)	2659(3)	139(4)
C(5)	4979(7)	1220(5)	453(4)	63(3)
O(5)	4732(7)	1397(4)	-36(3)	107(3)
P(1)	6913(2)	186(1)	882(1)	37(1)
B(1)	6884(6)	-771(4)	1323(3)	36(3)
P(2)	7510(2)	-672(1)	2145(1)	42(1)
B(2)	9026(7)	-313(4)	2083(4)	38(3)
P(3)	9116(2)	635(1)	1643(1)	46(1)
B(3)	8529(7)	480(4)	827(4)	37(3)
N(1)	6348(5)	-1415(3)	1094(2)	43(2)
Si(1)	5577(2)	-2030(1)	1597(1)	65(1)
C(6)	5059(8)	-1553(6)	2307(4)	97(4)
C(7)	6451(9)	-2832(5)	1819(5)	109(5)
C(8)	4263(8)	-2343(5)	1206(4)	99(4)
Si(2)	6482(2)	-1648(1)	294(1)	64(1)
C(9)	7902(7)	-1348(5)	0(4)	75(4)
C(10)	6512(10)	-2684(5)	191(5)	117(5)
C(11)	5314(9)	-1260(6)	-176(4)	105(5)
N(2)	9936(5)	-637(3)	2412(3)	44(2)
Si(3)	10143(2)	-1612(1)	2400(1)	62(1)
C(12)	9463(8)	-2085(5)	3084(4)	87(4)
C(13)	11674(8)	-1817(6)	2371(5)	110(5)
C(14)	9590(8)	-2030(4)	1670(4)	83(4)
Si(4)	10863(2)	-70(2)	2859(1)	67(1)
C(15)	10153(10)	811(5)	3080(4)	117(5)
C(16)	12189(8)	147(7)	2439(5)	113(5)
C(17)	11197(9)	-529(6)	3613(4)	113(5)
N(3)	9114(5)	595(3)	258(3)	45(2)
Si(5)	10522(2)	268(1)	165(1)	59(1)
C(18)	10661(8)	-140(5)	-644(4)	93(4)
C(19)	10817(6)	-529(4)	691(4)	69(3)
C(20)	11590(8)	1001(6)	302(5)	110(5)
Si(6)	8495(2)	1117(1)	-364(1)	66(1)
C(21)	9591(9)	1614(5)	-816(4)	110(5)
C(22)	7609(9)	1860(5)	-26(5)	102(5)
C(23)	7649(10)	536(6)	-906(4)	124(6)

{[Bis(trimethylsilylphosphanyl]chloro(diisopropylamino)boron-P}pentacarbonyltungsten (**16a**) was prepared as described for **15a** except $W(CO)_5 \cdot NMe_3$ was used, and the reaction mixture was heated to 40°C. A yellow oil was obtained. Yield: 40%. – MS (70 eV), *m/z* (%): 365 (90), 354 (90), 295 (10), 269 (10), 110 (10), 73 (35), 43 (100). – IR (hexane, cm^{-1}): $\tilde{\nu}$ = 2066 (w), 1983 (s), 1953 (s), 1931 (s), 1900 (w), 1482 (w), 1433 (w), 1400 (w), 1370 (w), 1344 (w), 1322 (w), 1307 (w), 1247 (w), 1182 (w), 1139 (w), 1002 (w), 883 (w), 839 (m), 626 (w), 602 (w).

X-ray Structure Determinations: Crystals were sealed under argon in glass capillary tubes. Data were collected by using Mo-K_α radiation, a scintillation counter, highly oriented graphite crystal monochromator, and pulse-height analyzer. The structures were solved by Direct Methods (**4c**, **4d**, **5b**, **7d**, **8a**, and **13a**) or heavy-atom methods (**7c**). Non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically with U_i = 1.2 U_{eq} of the parent atom. A summary of crystallographic data and information on data collection and refinement is given in Table 5. Tables 6–12 contain atomic coordinates of the nonhydrogen atoms[70].

Some specific additional comments are outlined. There are two independent molecules in the unit cell for **5b**, and the silyl methyl group carbon atoms display large anisotropic thermal motions. The metrical parameters do not differ significantly between the two molecules. The function minimized in refinements was $\Sigma w(F_o - F_c)^2$, $w^{-1} = \sigma(F)^2 + 0.0003\ F^2$. For **13a**, refinement in *Cc* is not as well behaved as in *C*2/*c*. Weights were defined as $w^{-1} = \sigma^2(F)$. The functions minimized in refinements of **7c**, **4c**, and **8a** were

Table 12. Atomic coordinates (· 10^4) and equivalent isotropic thermal parameters U_{eq} (Å · 10^3) for **8a**. Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x/a	y/b	z/c	U_{eq}
P(1)	1153(3)	4080(1)	7500	48(1)
P(2)	857(3)	2823(1)	7500	56(1)
B(1)	714(7)	3482(2)	6915(3)	39(2)
N(1)	393(4)	3506(2)	6269(2)	35(2)
C(1)	445(6)	4063(2)	5942(3)	48(2)
C(2)	1357(6)	4047(3)	5364(3)	72(3)
C(3)	-895(7)	4298(3)	5769(3)	92(3)
C(4)	-88(6)	3008(2)	5894(3)	47(2)
C(5)	942(6)	2525(2)	5863(3)	74(3)
C(6)	-1423(6)	2782(3)	6121(3)	84(3)
P(3)	3961(2)	5338(1)	7500	47(1)
P(4)	3557(3)	6598(1)	7500	50(1)
B(2)	4096(6)	5977(2)	6925(3)	35(2)
N(2)	4474(5)	6029(2)	6291(2)	41(2)
C(7)	4492(7)	6598(2)	5968(3)	54(2)
C(8)	3667(6)	6597(3)	5357(3)	73(3)
C(9)	5893(7)	6809(3)	5845(3)	94(3)
C(10)	4964(6)	5536(3)	5910(3)	59(3)
C(11)	3897(7)	5080(2)	5810(3)	78(3)
C(12)	6231(7)	5277(3)	6176(4)	100(3)
C(13)	4440(9)	3375(3)	6464(3)	116(4)
O(1)	4851(5)	3809(2)	6870(2)	82(2)
C(14)	6032(9)	3673(5)	7202(4)	179(6)
C(15)	628(8)	5925(3)	6362(3)	109(4)
O(2)	215(5)	5607(2)	6873(2)	68(2)
C(16)	-764(9)	5898(5)	7211(4)	191(6)
Li(1)	3658(16)	4232(6)	7500	58(6)
Li(2)	1330(14)	5187(5)	7500	50(5)

$\Sigma w(F_o - F_c)^2$, with $w^{-1} = \sigma(F)^2 + 0.0006\ F^2$, $w^{-1} = \sigma(F)^2 + 0.0012\ F^2$, and $w^{-1} = \sigma^2(F) + 0.0005\ F^2$, respectively.

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