Contribution from the Department of Chemistry,
Texas Christian University, Fort Worth, Texas 76129

Chemistry of [Bis(trimethylsilyl)amino]-*tert*-butylchloroborane: Synthesis of New Diborylamines and (Borylamino)phosphines[1]

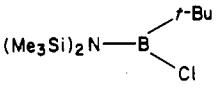
Bei-Li Li and Robert H. Neilson*

Received April 29, 1985

The title compound **1** reacts readily with $LiAlH_4$, $LiOCH_2CF_3$, MeMgBr, and excess NH_3 to form the nucleophilic substitution products $(Me_3Si)_2NB(t\text{-Bu})R$ [**2** (R = H), **3** (R = OCH_2CF_3), **4** (R = Me), **5** (R = NH_2)]. The amino compound **5**, in particular, is useful for further derivatization. Thus, the *N*-lithio derivative **5a**, prepared from **5** and *n*-BuLi, reacts with chloroboranes ClBXY to afford the stable diborylamines $(Me_3Si)_2NB(t\text{-Bu})N(H)BXY$ [**6** (X = Y = NMe_2), **7** (X = Ph, Y = Cl), **8** (X = Y = Cl)]. Likewise, treatment of **5a** with various chlorophosphines ClPXY yields the (borylamino)phosphines $(Me_3Si)_2NB(t\text{-Bu})N(H)PXY$ [**9** (X = Y = NMe_2), **10** (X = Y = Ph), **11** (X = $N(SiMe_3)_2$, Y = CH_2SiMe_3), **12** (X = $N(SiMe_3)_2$, Y = Cl), **13** (X = Ph, Y = Cl), **14** (X = Y = Cl)]. Compounds **8** and **14** are especially significant in being thermally stable species that contain the $-N(H)-ECl_2$ linkage [**8** (E = B), **14** (E = P)].

Introduction

In a recent paper,[2] we reported on the synthesis and stereochemistry of some alkyl(disilylamino)chloroboranes (e.g., **1**) and



1

their dimethylamino derivatives. One aspect of that study involved a comparison of the chemistry of **1** with that of the analogous (silylamino)phosphine. As a further extension of that work, we report here some additional substitution reactions of **1**, including the preparation of its B-NH_2 derivative. The latter compound, in turn, has proven to be a useful reagent for the synthesis of a variety of new diborylamines and (borylamino)phosphines. These systems are of interest as potential precursors, via silane elimination–condensation processes, to novel types of main-group element polymers and prepolymers.

Results and Discussion

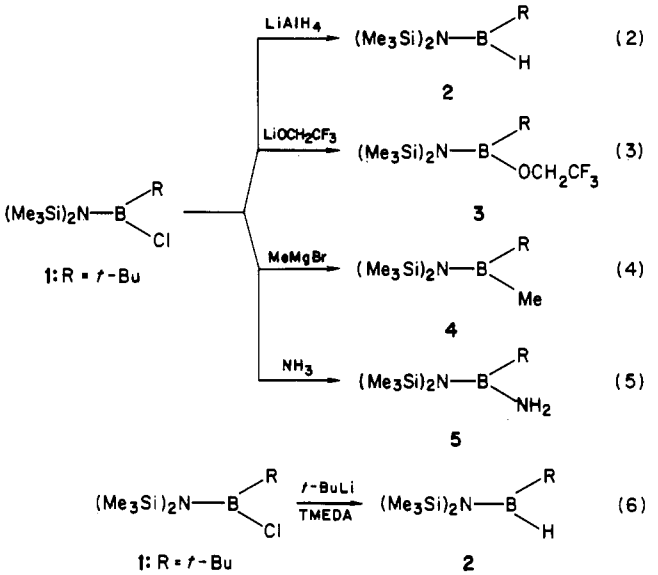
The chloroborane **1** was selected as the starting material in this study for three reasons: (1) it is prepared easily and in high yield directly from BCl_3 (eq 1);[2,3] (2) the bulky *tert*-butyl and di-

$$BCl_3 \xrightarrow{(Me_3Si)_2NLi} (Me_3Si)_2NBCl_2 \xrightarrow{t\text{-BuLi}} \mathbf{1} \qquad (1)$$

silylamino groups could provide kinetic stability to the B-N-B and B-N-P systems of interest; (3) the Si-N bonds are potential sites for further condensation reactions of such derivatives.

Reactivity of 1. Initially, a survey of some reactions of **1** with several simple nucleophiles was conducted (eq 2–5). The preparation of derivatives **2–5** in yields of 60–93% reinforced our earlier finding[2] that, despite the high degree of steric hinderance in **1**, the B-Cl bond is still susceptible to nucleophilic substitution. These new derivatives were obtained as thermally stable, distillable liquids and were characterized by NMR (Table I) and mass spectroscopy (see Experimental Section) in addition to elemental analysis (Table I).

The B-H compound **2** was also formed as the major product when **1** was treated with *t*-BuLi in the presence of tetramethylethylenediamine (TMEDA) (eq 6). Similar reductions, accompanied by β-elimination of olefins, have been observed in the reactions of chlorophosphines with bulky organometallic reagents.[4] The exactly analogous reaction of *t*-BuLi with $(Me_3Si)_2NP(t\text{-Bu})Cl$, however, yields a coupled (P-P) product.[5] When prepared by either method (eq 2 and 6), compound **2** could not be separated by fractional distillation from small amounts (ca. 5%) of an unidentified impurity. Thus, a satisfactory elemental analysis was not obtained. The presence of the B-H functional group, however, was confirmed by its intense stretching frequencies at 2350 and 2400 cm^{-1} in the IR spectrum.

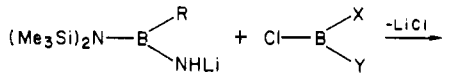


The amino compound **5** is of interest here since it provides an obvious entry into further derivative chemistry such as that described below. In addition to the expected NMR spectral data and elemental analysis, **5** exhibits the characteristic NH_2 bending vibration at 1590 cm^{-1} in the IR. The compound is thermally stable to distillation, and it shows no tendency to rearrange to the structural isomer $t\text{-BuB}(NHSiMe_3)_2$. A few other stable primary aminoboranes have been reported,[6] and as in the case of **5**, their stability is attributed to hindering groups on boron.

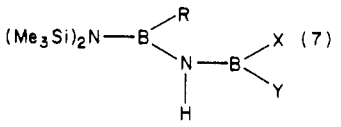
Diborylamines. Treatment of the primary aminoborane **5** with *n*-BuLi in either hexane or Et_2O solution affords the corresponding *N*-lithio derivative **5a** as a useful reactive intermediate. Subsequent reaction of the amide **5a** with chloroboranes provides a convenient synthesis of the new diborylamines **6–8** (eq 7) in yields of 68, 40, and 32%, respectively. The relatively low yields of **7** and **8** are

(1) Presented at the VIIth International Symposium on Organosilicon Chemistry, Kyoto, Japan, Sept 1984.
(2) Li, B.-L.; Goodman, M. A.; Neilson, R. H. *Inorg. Chem.* **1984**, *23*, 1368.
(3) Compounds similar to **1** have been previously prepared from alkyldichloroboranes. See, for example: (a) Paetzold, P.; von Plotho, C. *Chem. Ber.* **1982**, *115*, 2819. (b) Meier, H.-U.; Paetzold, P.; Schroder, E. *Ibid.* **1984**, *117*, 1954. (c) Paetzold, P.; von Plotho, C.; Schmid, G.; Boese, R.; Schrader, B.; Bougeard, D.; Pfeiffer, U.; Gleiter, R.; Schafer, W. *Ibid.* **1984**, *117*, 1089.
(4) O'Neal, H. R., Neilson, R. H. *Inorg. Chem.* **1983**, *22*, 814.
(5) Roy, A. H.; Neilson, R. H., unpublished results.
(6) See: Graham, D. M.; Bowser, J. R.; Moreland, C. G.; Neilson, R. H.; Wells, R. L. *Inorg. Chem.* **1978**, *17*, 2028 and references cited therein.

0020-1669/86/1325-0361$01.50/0



5a: R = *t*-Bu

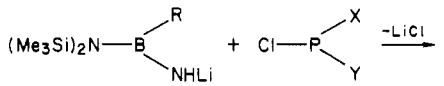


6: X = Y = NMe_2
7: X = Ph, Y = Cl
8: X = Y = Cl

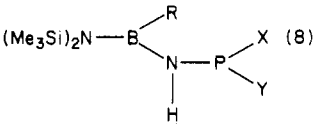
due to some decomposition, via elimination of Me_3SiCl, which occurs during their vacuum distillation at high temperature. Because of this moderate thermal instability, the dichloro compound **8** could not be obtained in analytically pure form. The crude products **7** and **8**, however, were both found by NMR to contain only small amounts (ca. 5–10%) of impurities prior to distillation.

Several types of diborylamines[7] have been reported in recent years although those bearing unsymmetrical substitution patterns are few in number. Compounds **7** and **8** are significant in being the first diborylamines that contain both B–Cl and Si–N bonds. Moreover, **8** appears to be only the second reported compound containing the $-N(H)BCl_2$ moiety, the other being [2,4,6-(*t*-Bu)$_3C_6H_2$]$N(H)BCl_2$.[8] The relatively high thermal stability of **7** and **8** must be due to the added steric protection afforded by the *tert*-butyl substituent since similar derivatives of other aminoboranes $(Me_3Si)_2NB(R)NH_2$[6] (R = Ph, NMe_2) could not be prepared.[9]

(Borylamino)phosphines. In light of the successful synthesis of these diborylamines, it seemed likely that the *N*-lithio derivative **5a** would be a useful reagent for preparing other boron–nitrogen–element element linkages including (borylamino)phosphines. Relatively few acyclic B–N–P compounds[10] are known, with the sterically unencumbered examples being prone to decomposition to borazenes. Thus, we investigated the reactions of **5a** with a series of chlorophosphines (eq 8) and, in this manner, were able to prepare six new (borylamino)phosphines (**9–14**).



5a: R = *t*-Bu



9: X = Y = NMe_2
10: X = Y = Ph
11: X = $N(SiMe_3)_2$, Y = CH_2SiMe_3
12: X = $N(SiMe_3)_2$, Y = Cl
13: X = Ph, Y = Cl
14: X = Y = Cl

With the exception of the PCl_2 derivative **14**, these compounds were obtained as thermally stable, distillable liquids (**9**, **11**, **13**) or crystalline solids (**10**, **12**).[11] The yields of these reactions ranged from 45 to 80%. Each of the phosphines gave a single ^{31}P NMR resonance with chemical shifts similar to those of appropriate model compounds. Interestingly, none of them displayed any indication of isomerization to the corresponding P–H-substituted phosphoranimine as has been observed for some other $-N(H)PR_2$ systems.[12]

Like its $-BCl_2$ analogue **8**, the dichlorophosphine **14** is especially noteworthy. Although it could not be distilled without decomposition, the compound was isolated in ca. 90% yield as a colorless liquid, which gave a satisfactory elemental analysis prior to distillation. Under an inert atmosphere, it is stable at room temperature for at least several days. To our knowledge, **14** is the only P(III) compound containing the $-N(H)PCl_2$ group that is even moderately stable toward HCl elimination. The thermal decomposition of the dichloro compounds **8** and **14**, in fact, occurs mainly via the elimination of Me_3SiCl rather than HCl. The nonvolatile and possibly polymeric products thus afforded are currently under investigation.

Conclusion. (Silylamino)boranes of the type $(Me_3Si)_2NB(t\text{-}Bu)X$ have a rich derivative chemistry as well as some interesting stereochemical[2] and structural[11] features. Compounds such as the aminoborane **5** are easily prepared and are useful reagents for attaching the B–N grouping to other elements [e.g., the (borylamino)phosphines] or for extending short B–N chains (e.g., the diborylamines).

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without further purification: BCl_3, PCl_3, $PhPCl_2$, Ph_2PCl, $(Me_3Si)_2NH$, Me_3SiNMe_2, NH_3, CF_3CH_2OH, *n*-BuLi (hexane solution), *t*-BuLi (pentane solution), and ether solutions of MeMgBr and $LiAlH_4$. Hexane, ether, and TMEDA (tetramethylethylenediamine) were distilled from CaH_2 and stored over molecular sieves. The starting chloroborane **1** was routinely prepared in 0.5–1.0-mol quantities from *t*-BuLi and $(Me_3Si)_2NBCl_2$ by scale up of the published procedure.[2] Yields of 70–75%, based on starting BCl_3, were typically obtained. The published procedures were also used to prepare $PhBCl_2$,[13] $(Me_3Si)_2NPCl_2$,[14] and $(Me_3Si)_2NP(Cl)CH_2SiMe_3$.[15] Bis(dimethylamino)chloroborane was prepared by the addition of Me_3SiNMe_2 (0.4 mol in 40 mL of hexane) to a stirred solution of BCl_3 (0.2 mol in 200 mL of hexane) at −78 °C. Similarly, $(Me_2N)_2PCl$ was obtained from Me_3SiNMe_2 and PCl_3 in Et_2O solution at 0 °C. Yields of these simple Si–N bond cleavage reactions were 90–95%.

Proton NMR spectra were recorded on a Varian EM-390 spectrometer; ^{13}C and ^{31}P NMR spectra, both with ^1H decoupling, were obtained on a JEOL FX-60 instrument. Mass spectral data were obtained on a Finnigan OWA 1020 GC-MS system. Infrared spectra were recorded on a Beckman 4250 spectrophotometer using neat liquid samples. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The procedures described herein are typical of those used for the preparation of the new compounds in this study.

[Bis(trimethylsilyl)amino]-*tert*-butylborane (2). From $LiAlH_4$. A solution of $LiAlH_4$ (10.0 mL, 1.0 M in Et_2O) was added via syringe to a stirred solution of the chloroborane **1** (10.54 g, 40 mmol) in Et_2O (80 mL) at 0 °C. The mixture was allowed to warm to room temperature and was then stirred overnight. Solids were removed by filtration and/or decantation under nitrogen. After solvent removal under reduced pressure, fractional distillation through a 10-cm Vigreux column afforded **2** as a colorless liquid. A small amount (ca. 5%) of an unidentified impurity was evident in the ^1H NMR spectrum of the distillate. The impurity could not be completely removed by repeated distillation and a satisfactory elemental analysis of **2** was not obtained.

From *t*-BuLi. In a similar manner, **1** (40 mmol) in Et_2O (80 mL) and TMEDA (6.0 mL, 40 mmol) was treated with *t*-BuLi (22.2 mL, 1.8 M, 40 mmol) at 0 °C. After the mixture was stirred overnight at room temperature, workup as above gave **2** in 56% yield. The β-elimination byproduct $Me_2C{=}CH_2$ was observed by ^1H NMR spectroscopy to be present in the solvent fraction. Similar purification problems were en-

(7) See for example: (a) Gasparis, T.; Nöth, H.; Storch, W. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 326. (b) Storch, W.; Nöth, H. *Ibid.* **1976**, *15*, 235. (c) Nöth, H.; Storch, W. *Chem. Ber.* **1976**, *109*, 884.
(8) Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F.; Williams, H. D. *J. Chem. Soc., Chem. Commun.* **1984**, 662.
(9) Neilson, R. H.; Wells, R. L., unpublished results.
(10) (a) Storch, W.; Nöth, H. *Chem. Ber.* **1977**, *110*, 2607. (b) Maringgele, W.; Meller, A.; Nöth, H.; Schroen, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 673. (c) Cowley, A. H.; Kilduff, J. E.; Wilburn, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 1575.
(11) An incompletely-refined X-ray crystallographic structure of **10** confirms the conclusions of previous NMR studies in ref 2 concerning the molecular geometry of these (silylamino)boranes.
(12) O'Neal, H. R.; Neilson, R. H. *Inorg. Chem.* **1984**, *23*, 1372 and references cited therein.
(13) Jolly, W. L. "The Synthesis and Characterization of Inorganic Compounds"; Prentice-Hall: Englewood Cliffs, NJ, 1970; p 481.
(14) Neilson, R. H.; Wisian-Neilson, P. *Inorg. Chem.* **1982**, *21*, 3568.
(15) Neilson, R. H. *Inorg. Chem.* **1981**, *20*, 1679.

Table I. Preparative, Analytical, and NMR Spectroscopic Data[a]

no.	R	NMR spectra signal	^{1}H δ	^{13}C δ	preparative data bp, °C (*P*, mm)	% yield	anal.[b] % C	% H
2	H	$(Me_3Si)_2N$	0.08	4.39	75–82 (10)	67		
		t-Bu	0.80	27.57				
3	OCH_2CF_3	$(Me_3Si)_2N$	0.13	3.33	86–88 (4.8)	66	44.19 (44.03)	9.10 (8.93)
		t-Bu	0.90	28.30				
		CH_2	4.18[c]	62.33[c]				
		CF_3		124.10[c]				
4	Me	$(Me_3Si)_2N$	0.06	4.18	80–83 (6.5)	60	54.42 (54.29)	12.52 (12.43)
		t-Bu	0.84	28.30				
		Me	0.54					
5	NH_2	$(Me_3Si)_2N$	0.08	3.74	82–89 (6.5)	93	49.49 (49.18)	11.93 (11.89)
		t-Bu	0.84	29.68				
6	$N(H)B(NMe_2)_2$	$(Me_3Si)_2N$	0.11	4.51	114–115 (0.7)	68	49.18 (49.12)	11.46 (11.70)
		t-Bu	0.89	30.01				
		Me_2N	2.57	39.88				
7	N(H)B(Ph)Cl	$(Me_3Si)_2N$	0.17	4.03	131–133 (0.1)	40	52.46 (52.39)	9.18 (9.00)
		t-Bu	1.03	29.17				
		Ph	7.3–8.1[d]	128–134[d]				
8	$N(H)BCl_2$	$(Me_3Si)_2N$	0.14	3.82	114–117 (0.1)	32		
		t-Bu	0.89	28.99				
9	$N(H)P(NMe_2)_2$	$(Me_3Si)_2N$	0.08	3.70	108–114 (0.1)	45	46.42 (46.41)	10.95 (11.05)
		t-Bu	0.89	29.37				
		Me_2	2.39 (9.0)	37.72 (18.6)				
10	$N(H)PPh_2$	$(Me_3Si)_2N$	0.01	3.80	135–154 (0.05)	67	61.84 (61.68)	8.65 (8.88)
		t-Bu	0.94	29.50				
		Ph	7.4[d]	128–144[d]				
11	$N(H)P(CH_2SiMe_3)N(SiMe_3)_2$	$(Me_3Si)_2NB$	0.10	3.94	132–134 (0.03)	65	46.12 (46.06)	10.72 (10.94)
		$(Me_3Si)_2NP$	0.17	3.92 (7.9)				
			0.24					
		Me_3SiC	0.05	0.04				
		CH_2	1.3–1.5[d]	27.0 (51.9)				
		t-Bu	0.87	29.56				
12	$N(H)P(Cl)N(SiMe_3)_2$	$(Me_3Si)_2NB$	0.13	3.57	*e*	80	40.97 (40.89)	9.86 (9.80)
			0.17	3.83				
		$(Me_3Si)_2NP$	0.35 (1.8)	4.13 (8.8)				
		t-Bu	0.93	29.04				
13	N(H)P(Ph)Cl	$(Me_3Si)_2N$	0.08	3.64	140–142 (0.2)	52		
			0.11					
		t-Bu	0.91	28.85				
		Ph	7.3–7.8[d]	128–132[d]				
14	$N(H)PCl_2$	$(Me_3Si)_2N$	0.13	3.48	*f*	90	35.02 (34.78)	8.11 (8.11)
		t-Bu	0.90	28.39				

[a] Chemical shifts downfield from Me_4Si. Solvents: ^{1}H, CH_2Cl_2; ^{13}C, $CDCl_3$. Phosphorus couplings (Hz), J_{PH} and J_{PC}, are given in parentheses for **9–14**; ^{31}P chemical shifts (CH_2Cl_2 solution) downfield from H_3PO_4 are given in Experimental Section. [b] Calculated values in parentheses. [c] $^3J_{HF}$ = 9.9 Hz, $^2J_{CF}$ = 35.0 Hz, $^1J_{CF}$ = 278 Hz. [d] Complex multiplet. [e] Solid, not distilled. [f] Unstable to distillation.

countered as in the $LiAlH_4$ reduction.

[Bis(trimethylsilyl)amino]-*tert*-butyl(trifluoroethoxy)borane (3). A solution of $LiOCH_2CF_3$ was prepared by the slow addition of *n*-BuLi (16 mL, 2.5 M, 40 mmol) to CF_3CH_2OH (3.1 mL, 40 mmol) in Et_2O (60 mL) at 0 °C. This solution was transferred to an addition funnel and then added to **1** (10.54 g, 40 mmol) in Et_2O (80 mL) with stirring at 0 °C. After removal of solids and solvent, distillation gave **3** as a colorless liquid that solidified in the receiving flask.

[Bis(trimethylsilyl)amino]-*tert*-butylmethylborane (4). Similarly, **1** (26.4 g, 0.10 mol) in Et_2O (200 mL) was treated with MeMgBr (36 mL, 3.2 M, 0.12 mol) at 0 °C. After the mixture was stirred overnight at room temperature, most of the Et_2O was removed and hexane (200 mL) was added. Following filtration and solvent removal, compound **4** was isolated by distillation as a colorless liquid.

Amino[bis(trimethylsilyl)amino]-*tert*-butylborane (5). Ammonia (9.0 mL, 0.43 mol), measured as a liquid at −78 °C, was allowed to bubble through a stirred solution of **1** (39.5 g, 0.15 mol) in hexane (300 mL) at −78 °C. After being warmed to room temperature, the mixture was stirred for a few hours and then filtered. Following solvent removal, distillation afforded **5** as a colorless liquid.

([Bis(trimethylsilyl)amino]-*tert*-butylboryl)[bis(dimethylamino)boryl]amine (6). A solution of the *N*-lithio derivative **5a** was prepared by the slow addition of *n*-BuLi (16 mL, 2.5 M, 40 mmol) to a stirred solution of **5** (9.76 g, 40 mmol) in hexane (60 mL) at 0 °C. The mixture was allowed to warm to room temperature and was stirred for 1 h. After the solution of **5a** was recooled to 0 °C, $(Me_2N)_2BCl$ (5.5 mL, 40 mmol) was added via syringe and the mixture was stirred overnight at room temperature. Following filtration and solvent removal, distillation through a 5-cm column afforded **6** as a colorless, viscous liquid.

([Bis(trimethylsilyl)amino]-*tert*-butylboryl)(phenylchloroboryl)amine (7). In the same manner as described above for the preparation of **6** the amide **5a** (30 mmol) was treated with $PhBCl_2$ (30 mmol). Distillation through a short-path apparatus gave **7** as a colorless liquid. Approximately 50% of the product remained in the distillation flask as a thick orange residue. The ^{1}H NMR spectrum of this material showed the ratio of Me_3Si to *t*-Bu signals to be ca. 1:1, indicating that some loss of Me_3SiCl probably occurred during the distillation.

([Bis(trimethylsilyl)amino]-*tert*-butylboryl)(dichloroboryl)amine (8). Trichloroborane (2.6 mL, 30 mmol), measured as a liquid at −78 °C, was allowed to condense slowly into a stirred suspension of the amide **5a** (30 mmol) in hexane (50 mL) at −78 °C. Workup as described for **7** afforded **8** as a colorless liquid, with the distillation again being accompanied by some decomposition.

[([Bis(trimethylsilyl)amino]-*tert*-butylboryl)amino]bis(dimethylamino)phosphine (9). By means of the same procedure as described above for **6**, the amide **5a** was treated with $(Me_2N)_2PCl$ on a 40-mmol scale. Distillation through a short-path apparatus afforded **9** as a colorless liquid. ^{31}P NMR: δ 102.4.

[([Bis(trimethylsilyl)amino]-*tert*-butylboryl)amino]diphenylphosphine (10). The same procedure as described above for **6** was followed with 24-mmol quantities of **5a** and Ph_2PCl used. The (borylamino)phosphine **10** was isolated by distillation through a short-path apparatus as a very viscous product that crystallized in the receiving flask. Recrystallization from a minimal amount of hexane gave white crystals of **10**, mp 129–130 °C. ^{31}P NMR: δ 17.4.

[([Bis(trimethylsilyl)amino]-*tert*-butylboryl)amino][bis(trimethylsilyl)amino][(trimethylsilyl)methyl]phosphine (11). The same procedure as described for **6** was followed with 30-mmol quantities of **5a** and

$(Me_3Si)_2NP(Cl)CH_2SiMe_3$ used. Compound **11** was isolated by short-path distillation as a very viscous colorless liquid. Two redistillation were required to produce an analytically pure sample of **11**. ^{31}P NMR: δ 75.5.

[([Bis(trimethylsilyl)amino]-*tert*-butylboryl)amino][bis(trimethylsilyl)amino]chlorophosphine (12). A solution of the amide **5a** (30 mmol) in hexane (50 mL) was added to a stirred solution of $(Me_3Si)_2NPCl_2$[14] [30 mmol, freshly prepared from PCl_3 and $(Me_3Si)_2NLi$] in Et_2O (30 mL) at 0 °C. The mixture was allowed to warm to room temperature and was stirred overnight. Filtration and solvent removal left a partially solid residue, which was dissolved in a minimal amount of hexane. Cooling the solution to 0 °C produced **12** as a white crystalline solid, mp 65-67 °C. ^{31}P NMR: δ 151.2.

[([Bis(trimethylsilyl)amino]-*tert*-butylboryl)amino]phenylchlorophosphine (13). The same procedure described above for **6** was followed with 30-mmol quantities of **5a** and $PhPCl_2$ used. Compound **11** was isolated by short-path distillation as a high boiling, viscous liquid. ^{31}P NMR: δ 108.1.

[([Bis(trimethylsilyl)amino]-*tert*-butylboryl)amino]dichlorophosphine (14). By use of the same procedure as described above for **12**, a solution of the amide **5a** (30 mmol) in hexane (50 mL) was added to PCl_3 (2.6 mL, 30 mmol) in Et_2O (50 mL) at -78 °C. After being stirred overnight at room temperature, the mixture was filtered and freed of solvent and other volatile materials. At this point, the dichlorophosphine derivative **14** remained as a colorless liquid, which gave a satisfactory elemental analysis without any further purification. ^{31}P NMR: δ 166.0.

Mass Spectra. The new compounds prepared in this study gave reasonable mass spectral fragmentation patterns and correct molecular ion peaks. Typically, the following significant peaks were observed with relative intensities in the indicated ranges: M^+ (2%), $M^+ - CH_3$ (5-20%), $M^+ - C(CH_3)_3$ (30-100%), $M^+ - Si(CH_3)_3$ (5-20%).

Acknowledgment. The authors thank the Robert A. Welch Foundation and the Texas Christian University Research Fund for financial support of this research.

Registry No. **1**, 89487-06-9; **2**, 99748-65-9; **3**, 99748-66-0; **4**, 99748-67-1; **5**, 99748-68-2; **5a**, 99748-76-2; **6**, 99748-69-3; **7**, 99748-70-6; **8**, 99748-71-7; **9**, 99766-97-9; **10**, 99748-72-8; **11**, 99748-73-9; **12**, 99748-77-3; **13**, 99748-74-0; **14**, 99748-75-1.

Contribution from the Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706

Reactions of Boron Hydrides with the Iminium Salt $[Me_2NCH_2]I$. Synthesis and Characterization of 1-X-μ-$(Me_2NCH_2)B_5H_7$ (X = H, C_2H_5, Br), a New Class of Bridge-Substituted Pentaborane Derivatives

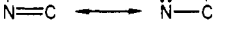
Donald F. Gaines* and Darrell E. Coons

Received June 14, 1985

Reactions of $[Me_2NCH_2]I$ (**1**) with salts of the $B_5H_8^-$, 1-$(C_2H_5)B_5H_7^-$, and 1-$BrB_5H_7^-$ anions produce the μ-((dimethylamino)-methyl)pentaborane derivatives μ-$(Me_2NCH_2)B_5H_8$, 1-(C_2H_5)-μ-$(Me_2NCH_2)B_5H_7$, and 1-Br-μ-$(Me_2NCH_2)B_5H_7$, respectively, in good yields. A structure for these compounds is proposed in which a bridging hydrogen atom of B_5H_9 has been replaced by a C-N two-atom bridge, the Me_2NCH_2 group. These clusters are analogues of the *arachno*-$B_5H_{10}^-$ anion, and there is no evidence of direct bonding between the Me_2NCH_2-bridged boron atoms. Reaction of **1** with $NaBH_4$ forms $Me_3N{\cdot}BH_3$, while reaction with $[Me_4N][B_3H_8]$ produces a variety of products including $Me_3N{\cdot}BH_3$, $Me_3N{\cdot}B_3H_7$, B_2H_6, and B_5H_9. Attack of **1** on B_5H_9 occurs slowly at 65 °C, forming $Me_3N{\cdot}BH_3$ and $Me_3N{\cdot}B_3H_7$.

Introduction

The organic chemistry of methyleneaminium (methaniminium) salts has been reviewed.[1] These species are powerful electrophiles, reacting with a wide range of nucleophiles through the methylene carbon, upon which the lowest unoccupied molecular orbital (of π symmetry) is primarily localized.[2] In valence bond terms the electrophilic nature of the methylene carbon results from the predominance of the resonance form in which the carbon atom bears the positive charge:

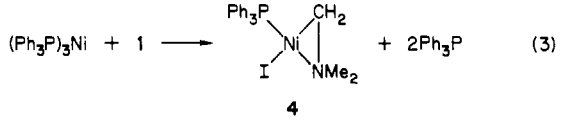


The reactions of methyleneaminium salts with organic nucleophiles generally result in aminomethylation or, in some cases, hydride abstraction.

The organometallic chemistry of iminium salts has received considerable recent attention. The reactions of commerically available $[Me_2NCH_2]I$ (Eschenmoser's salt, **1**) illustrated in eq 1-3, are typical of the reactivity that has been observed for iminium salts with different types of organometallic complexes. Reactions of **1** with organometallic nucleophiles (eq 1) result in a metathesis giving η^1-aminomethyl complexes such as **2**.[3] Loss of carbon monoxide from **2** occurs on heating to give the η^2-aminomethyl complex **3** (eq 2).[3] Reactions of **1** with neutral complexes (eq 3) usually result in oxidative addition with spontaneous loss of ligands from the metal to give η^2-aminomethyl

$$\mathrm{Na[(\eta^5\text{-}C_5H_5)Mo(CO)_3]} + \underset{\mathbf{1}}{[Me_2NCH_2]I} \rightarrow \underset{\mathbf{2}}{(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2NMe_2} + NaI \quad (1)$$

$$\mathbf{2} \xrightarrow{80\ ^\circ C} \underset{\mathbf{3}}{(\eta^5\text{-}C_5H_5)(CO)_2Mo(\eta^2\text{-}CH_2NMe_2)} + CO \quad (2)$$



(3)

4

(1) See, for example: Böhme, H.; Haake, M. *Adv. Org. Chem.* **1976**, *9*, 107-223 (Part 1).
(2) Kollman, P. A. *Adv. Org. Chem.* **1976**, *9*, 1-8 (Part 1).
(3) Fong, C. W.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1975**, 1100-1104.
(4) Barefield, E. K.; Carrier, A. M.; Sepelak, D. J.; Van Derver, D. G. *Organometallics* **1982**, *1*, 103-110.

0020-1669/86/1325-0364$01.50/0