Table I. Enthalpies and Entropies of Activation and 1 atm of Pressure Rate Constants[a]

anion	ΔH^*, kcal/mol	ΔS^*, cal/(mol deg)	$10^{-3}k_0$, $M^{-1}\ s^{-1}$
PF_6^-[b]	8.0 ± 0.3	−16.3 ± 0.8	1.6
ClO_4^-[c]	8.5 ± 0.2	−14.9 ± 0.3	1.7
BF_4^-[d]	8.4 ± 0.2	−15.2 ± 0.2	1.7

[a] Six points in the temperature range 20–70 °C; k_0 is for 20 °C. [b] $[Ru(cp)_2]$ = 16.7 mM; $[Ru(cp)_2Br]PF_6$ = 19.1 mM. [c] $[Ru(cp)_2]$ = 7.6 mM; $[Ru(cp)_2Br]ClO_4$ = 7.2 mM. [d] $[Ru(cp)_2]$ = 10.2 mM; $[Ru(cp)_2Br]BF_4$ = 9.3 mM.

Table II. Volume of Activation and 1 atm of Pressure Rate Constants

T, °C	no. of points[a]	ΔV^*, cm^3/mol	$10^{-3}k_0$, $M^{-1}\ s^{-1}$
33.5[b]	10	−2.9 ± 0.1	3.1
41.7[c]	8	−2.7 ± 0.4	5.2
41.9[b]	9	−2.9 ± 0.1	4.6
43.7[d]	9	−3.1 ± 0.2	5.0
54.7[d]	11	−3.3 ± 0.2	9.0

[a] Pressures in the range 0.1–200 MPa. [b] $[Ru(cp)_2]$ = 8.9 mM; $[Ru(cp)_2Br]PF_6$ = 8.4 mM. [c] $[Ru(cp)_2]$ = 8.6 mM; $[Ru(cp)_2Br]PF_6$ = 10.3 mM. [d] $[Ru(cp)_2]$ = 12.5 mM; $[Ru(cp)_2Br]PF_6$ = 8.8 mM.

The temperature-dependence data were fit to the Eyring equation. The errors were calculated from the standard deviation in k, the second-order rate constant. The volume of activation, $\Delta V^* = -RT(\partial \ln k/\partial P)_T$, was found by plotting ln k vs pressure (0–200 MPa). For all pressure-dependent data a simple linear fitting procedure could be used. The errors were derived from the scatter about the fit lines.

Results and Discussion

The results of the temperature and pressure dependences are summarized in Tables I and II. Activation enthalpies and entropies are similar to those obtained by Taube et al.,[1] 9.3 ± 1.1 kcal/mol and −12 ± 4 cal/(mol deg), by using CD_3NO_2 as the solvent and PF_6^- as the counterion. There is essentially no dependence on the counter ion, as might be expected in acetonitrile in which little ion pairing is expected. The volume of activation is −3.0 ± 0.2 $cm^3\ mol^{-1}$, independent of temperature in the range 34–55 °C.

The factors that control the volume of activation for an outer-sphere electron-transfer reaction involving a neutral reactant arise primarily from solvation contributions.[7,8] These can be considered within a Marcus theory formalism or more simply by a consideration of just the electrostriction of the solvent. An inner-sphere reaction should include the same solvation terms, but also requires consideration of any coordinated solvent that is displaced and the particular structure of the inner-sphere transition state. Since the system studied here does not involve coordinated solvent displacement and is of the simplest 0/+ charge type, it can be compared with the ferrocene–ferrocenium system with the added consideration for the inner-sphere transition-state structure. Our studies of that system to date suggest ΔV^* values of −5 to −8 $cm^3\ mol^{-1}$.[2] Only positive values can be predicted from simple solvent electrostriction arguments. A somewhat more negative value is predicted by the Marcus theory formalism, by using estimates of some of the solvent parameters. The similarity of the two measured values is probably fortuitous, but may indicate that reactant juxtaposition and charge type control ΔV^*. The ruthenium reaction is about 3 orders of magnitude slower, primarily because of a much greater enthalpy of activation. Also, it involves ring reorientation and the bridge bond formation. The iron case involves an especially rapid reaction, and it has been suggested[9] that the transition state involves a stacked ring geometry.

The ruthenocene–haloruthenocene system is particularly interesting because it involves multiple electron and halogen transfer and it is amenable to study. We are pursuing further studies on it and the decamethyl derivative. Solvent and halogen variation may prove especially interesting since bromoruthenocene is soluble and stable only in solvents of moderate dielectric constant and high acceptor ability. This indicates a significant influence of the bromine atom on the solvation, and this atom must be desolvated for electron-transfer bridge formation. Studies of ion pairing through the use of high anion concentrations or lower dielectric solvents will establish whether this class of reactions behaves as do outer-sphere processes.

Acknowledgment. We acknowledge the assistance of Don Appel with the NMR measurements. This work was supported by the National Science Foundation and by the Boeing Co. through funds for the purchase of the Nicolet instrument.

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Reactions of an Azidoborane with Phosphines: Synthesis of (Borylimino)phosphoranes

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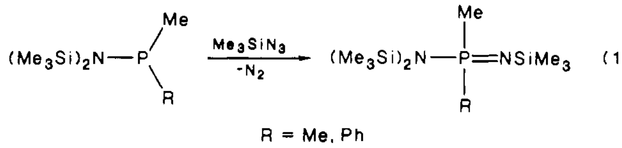
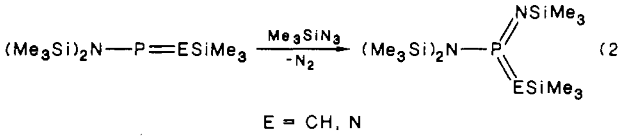
Received July 22, 1988

The oxidation of organophosphines with covalent azides, the well-known Staudinger reaction,[1,2] is a very useful method for preparing the pentavalent iminophosphorane derivatives ($R_3P{=}NR$). The high thermal stability and ready availability of silyl azides[3] makes this method particularly useful for the synthesis of *N*-silylphosphoranimines such as those derived from either the (silylamino)phosphines (eq 1)[4] or the two-coordinate methylene-[5] and iminophosphines[6] (eq 2).



$$(Me_3Si)_2N{-}P(Me)R \xrightarrow[-N_2]{Me_3SiN_3} (Me_3Si)_2N{-}P(Me)(R){=}NSiMe_3 \quad (1)$$

R = Me, Ph



$$(Me_3Si)_2N{-}P{=}ESiMe_3 \xrightarrow[-N_2]{Me_3SiN_3} (Me_3Si)_2N{-}P({=}NSiMe_3)({=}ESiMe_3) \quad (2)$$

E = CH, N

Much of our recent work has involved the preparative chemistry of new Si–N–P,[7] Si–N–B,[8,9] and B–N–P[10] compounds as possible

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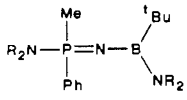
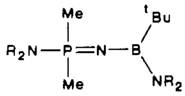
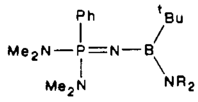
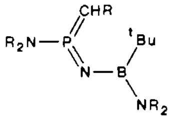
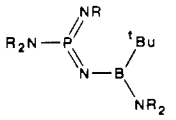
Table I. NMR Spectroscopic Data[a,b]

compd (R = Me_3Si)	signal	^1H NMR		^{13}C NMR		
		δ	U_{PH}	δ	J_{PC}	δ
 **2**	R_2NB	0.08		4.74		0.7
	R_2NP	0.24		5.69		
	${}^tBu$	0.90		30.77		
	PMe	1.79	13.1	23.69	77.8	
	Ph	7.3–7.7[c]		141.79 (C^1)	122.2	
				131.12 ($C^{2,6}$)	11.2	
				128.12 ($C^{3,5}$)	13.0	
				130.44 (C^4)	2.9	
 **3**	R_2NB	0.10		4.90		8.9
	R_2NP	0.33		6.03	1.8	
	${}^tBu$	0.86		30.75		
	PMe_2	1.62	12.9	24.35	79.2	
 **4**	R_2NB	0.15		4.03		3.6
	${}^tBu$	0.91		30.34		
	Me_2N	2.59	11.2	37.16	3.9	
	Ph	7.4–7.6[c]		127–142[c]		
 **5**	R_2NB	0.25		4.34		56.3
	R_2NP	0.12		2.92	5.4	
	CH*R*	0.05		1.60	4.1	
	${}^tBu$	0.86		29.92		
	*CH*R	1.00	13.0	27.30	78.4	
 **6**	R_2NB	0.28		4.36		3.6
	R_2NP	0.12		3.47	2.9	
	NR	0.33		7.15	1.8	
	${}^tBu$	1.03		29.23		

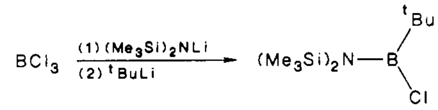
[a] Chemical shifts relative to Me_4Si for ^1H and ^{13}C spectra and to H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: $CDCl_3$ or CH_2Cl_2. [b] The ^{11}B NMR spectra of compounds **2–6** all consist of broad singlets in the range of 40–43 (i.e., downfield relative to $BF_3{\cdot}OEt_2$). [c] Complex multiplet.

Table II. Preparative and Analytical Data

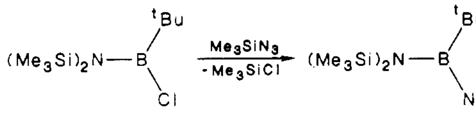
compd	yield, %	bp, 0 °C [*P*, mm Hg]	anal.[a] % C	anal.[a] % H
2	70	(117–120)[b]	52.81	10.02
			(52.57)	(10.10)
3	25	120–124 [0.03]	47.17	10.98
			(46.65)	(11.02)
4	71	140–147 [0.1] (64–65)[b]	54.53	9.94
			(54.79)	(10.05)
5	68	122–125 [0.01]	46.14	10.56
			(46.24)	(10.60)
6	72	(133–136 dec)[b]	43.62	10.29
			(43.85)	(10.38)

[a] Calculated values in parentheses. [b] Melting points in parentheses.

precursors to and/or model systems for new inorganic polymers. For example, we have reported the synthesis of the stable azidoborane **1** (eq 3 and 4) by a straightforward route starting from BCl_3.



(3)



(4)

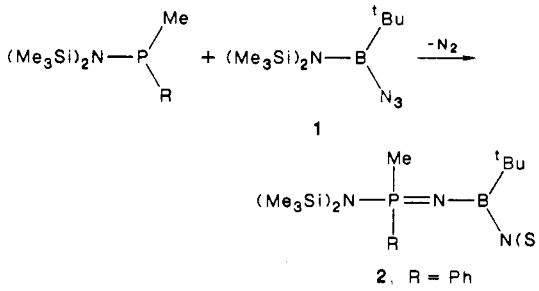
1

As a continuation of these earlier studies, and in an effort to develop new synthetic routes to B–N–P compounds,[11] we report here a series of reactions of the azidoborane **1** with some representative aminophosphines of both the two- and three-coordinate variety.

Results and Discussion

The azidoborane **1** was selected for this study because (1) it is easily prepared (eq 3 and 4) and isolated in high purity, (2) it is thermally stable to distillation and can be conveniently stored as a solution in hexane, and (3) its sterically bulky substituents should help to stabilize the products of its reactions with low-coordinate phosphorus species.

The oxidation of (silylamino)phosphines with **1** (eq 5) occurred smoothly in hexane solution at ca. 50–65 °C. The reactions were easily monitored by ^{31}P NMR spectroscopy, which indicated



(5)

2, R = Ph
3, R = Me

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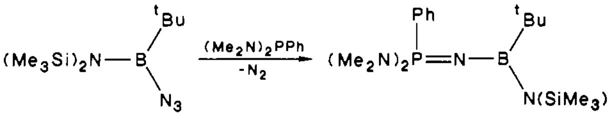
quantitative conversion to the (borylimino)phosphoranes **2** and **3** over a period of several hours. The *P*-phenyl derivative **2** (a white solid) was obtained in 65–70% yields, whereas the *P*-methyl analogue **3** (a colorless liquid) always underwent significant thermal decomposition during distillation. This reduced the distilled yields of **3** to 20–30%, although the crude product was essentially pure (on the basis of NMR spectroscopy). Although the exact decomposition pathway is uncertain, the ^{31}P NMR spectral data indicate that one of the decomposition products is the *N*-silylphosphoranimine $(Me_3Si)_2NPMe_2{=}NSiMe_3$.[4]

The (borylimino)phosphoranes **2** and **3** were readily characterized by NMR spectroscopy (Table I) and elemental analyses (Table II). Both the ^{1}H and ^{13}C NMR spectra contain two distinct resonances for the $(Me_3Si)_2N$ substituents attached to boron and phosphorus, in addition to the expected ^{t}Bu, P–Me, and phenyl signals. The large $^1J_{PC}$ and $^2J_{PH}$ values observed for the P–Me groups are particularly diagnostic of the P^V oxidation state in Si–N–P compounds.[4] The ^{31}P chemical shifts, which are upfield relative to those of the starting phosphines, are also indicative of an oxidized product, while the low-field ^{11}B NMR signals (δ ca. 40–43) are consistent with a three-coordinate boron environment.

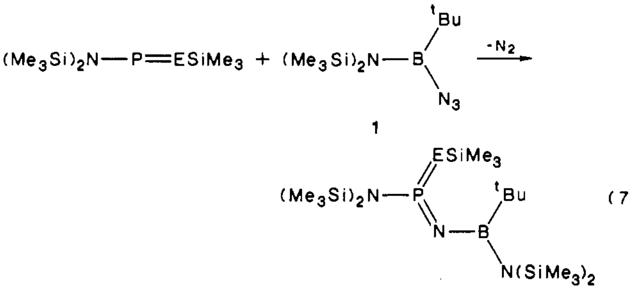
In addition to the reactions of the azidoborane **1** with (silylamino)phosphines, we also conducted a series of small-scale, "NMR tube" experiments involving the (dimethylamino)phosphines $(Me_2N)_nPPh_{3-n}$ (n = 1–3). In each case, the reaction was found to be complete under conditions similar to those described above. A typical example (eq 6) was then carried out on a preparative scale, and the (borylimino)phosphorane **4** was isolated in 71% yield as a distillable liquid that solidified upon standing.



(6)

1 4

The oxidation of phosphines by the azidoborane **1** is not limited to simple three-coordinate P^{III} centers. Indeed, we found that the two-coordinate methylene- and iminophosphines were both readily oxidized by **1** to give the novel three-coordinate P^V derivatives **5** and **6** (eq 7). Compounds **5** and **6** are both thermally stable products that were isolated in good yields by distillation (**5**) or recrystallization (**6**) and fully characterized by NMR spectroscopy (Table I), elemental analyses (Table II), and mass spectroscopy. The mass spectra of both compounds contained small (ca. 1% relative intensity) molecular ion peaks, large $M^+ - CH_3$ (ca. 30%) peaks, and base peaks corresponding to $M^+ - {}^tBu$. Interestingly, the ^{31}P NMR chemical shifts of **5** (δ 56.3) and **6** (δ 3.5) occur ca. 50 ppm upfield relative to those of their NSiMe$_3$ analogues $(Me_3Si)_2NP({=}ESiMe_3){=}NSiMe_3$ (E = CH (δ 103);[5] E = N (δ 55)[6]). The reason for such unusually high field chemical shifts is not readily apparent, but they are probably due to increased shielding of the phosphorus by the sterically bulky $-B(^tBu)N(SiMe_3)_2$ substituent on the P=N nitrogen. Various trends in the ^{31}P shifts of other three-coordinate phosphoranes have been summarized recently.[12]



(7)

5, E = CH
6, E = N

In summary, this work has demonstrated that the azidoborane **1** is a useful reagent for the oxidation of both two- and three-coordinate phosphines to afford new (borylimino)phosphoranes. These results suggest that similar phosphorus derivative chemistry of other, less hindered, azidoboranes should be explored.

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without further purification: $PhPCl_2$, Me_3SiN_3, and Me_3SiNMe_2. Hexane and ether were distilled from CaH_2 prior to use. Bis(dimethylamino)phenylphosphine, $(Me_2N)_2PPh$,[13] was prepared by the addition of 2 molar equiv of Me_3SiNMe_2 to $PhPCl_2$ in ether at 0 °C. The (silylamino)phosphines $(Me_3Si)_2NP(R)Me$ (R = Ph, Me)[14] and $(Me_3Si)_2NP{=}ESiMe_3$ (E = CH,[5a] N[15]) were prepared and purified according to the published procedures. The azidoborane $(Me_3Si)_2NB(^tBu)N_3$ (**1**) was prepared by the reaction of Me_3SiN_3 with the chloroborane $(Me_3Si)_2NB(^tBu)Cl$ as previously reported.[10] After removal of the excess silyl azide, undistilled **1** was checked for purity by ^{1}H and ^{13}C NMR spectroscopy and then dissolved in dry hexane to give a 2.0 M stock solution of **1** for use in subsequent reactions. Proton, $^{13}C\{^1H\}$, and $^{11}B\{^1H\}$ NMR spectra were recorded on a Varian XL-300 spectrometer; $^{31}P\{^1H\}$ NMR spectra were obtained on a JEOL FX-60 instrument. Mass spectra were obtained on a Finnigan GC-MS instrument. 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 following procedures are representative of those used for the synthesis of the new compounds prepared in this study.

Preparation of $(Me_3Si)_2NP(Ph)(Me){=}NB(^tBu)N(SiMe_3)_2$ (2). The aminophosphine $(Me_3Si)_2NP(Ph)Me$ (11.3 g, 40 mmol) was added via syringe to a stirred solution of the azidoborane **1** (20 mL, 2.0 M, 40 mmol) in hexane. The mixture was then refluxed (at ca. 65 °C) overnight. The mixture was cooled to room temperature, and the solvent was removed under reduced pressure, leaving **2** as a white solid that was purified by recrystallization from hexane or CH_2Cl_2 (Tables I and II).

Preparation of $(Me_3Si)_2NPMe_2{=}NB(^tBu)N(SiMe_3)_2$ (3). In a similar manner, **1** (18 mL, 2.0 M, 36 mmol) was treated with $(Me_3Si)_2NPMe_2$ (8.0 g, 36 mmol) in hexane and the mixture was heated at 50 °C for 3 h. After solvent removal, the viscous liquid residue was identified by NMR spectroscopy as **3** with only minor impurities being noted. Fractional distillation resulted in partial thermal decomposition (to $(Me_3Si)_2NPMe_2{=}NSiMe_3$[4] and other unidentified products), but a pure fraction (3.4 g) of **3** was isolated.

Preparation of $(Me_2N)_2P(Ph){=}NB(^tBu)N(SiMe_3)_2$ (4). Similarly, the aminophosphine $(Me_2N)_2PPh$ (3.9 g, 20 mmol) was added to a hexane solution of **1** (10 mL, 2.0 M, 20 mmol) and the mixture was refluxed for 4 h. Solvent removal followed by distillation gave **4** (6.2 g) as a colorless liquid that crystallized on standing at room temperature.

Preparation of $(Me_3Si)_2NP({=}CHSiMe_3){=}NB(^tBu)N(SiMe_3)_2$ (5). Similarly, the methylene phosphine $(Me_3Si)_2NP{=}CHSiMe_3$ (9.7 g, 35 mmol) was added to a hexane solution of **1** (36 mmol) and the mixture was stirred at room temperature for 3 days. Solvent removal, followed by distillation, afforded **5** (18.2 g) as a colorless liquid.

Preparation of $(Me_3Si)_2NP({=}NSiMe_3){=}NB(^tBu)N(SiMe_3)_2$ (6). The iminophosphine $(Me_3Si)_2NP{=}NSiMe_3$ (15.5 g, 56 mmol) was added to a neat sample of **1** (15.1 g) (preliminary experiments showed that this reaction was very slow in hexane solution), and the mixture was heated overnight at ca. 95 °C. At this point, the mixture had turned to a white solid, from which pure **6** (20.9 g) was obtained by recrystallization from CH_2Cl_2.

Acknowledgment. We thank the Office of Naval Research, the Robert A. Welch Foundation, and the TCU Research Fund for generous financial support of this work.

Registry No. **1**, 118318-90-4; **2**, 118318-91-5; **3**, 118318-92-6; **4**, 118318-93-7; **5**, 118334-36-4; **6**, 118318-94-8; $(Me_3Si)_2NP(Ph)Me$, 68437-87-6; $(Me_3Si)_2NPMe_2$, 63744-11-6; $(Me_2N)_2PPh$, 6143-71-1; $(Me_3Si)_2NP{=}CHSiMe_3$, 76173-65-4; $(Me_3Si)_2NP{=}NSiMe_3$, 50732-21-3; $(Me_3Si)_2NPMe_2{=}NSiMe_3$, 21385-93-3.

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