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An NMR Study of the Reactions of Phosphorus(III) Halides with Halide Ion Acceptors. Two-Coordinate Phosphorus Cations with Bulky Ligands

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The cations $[(Me_2N)(t\text{-}Bu)P]^+$, $[(Me_2N)(t\text{-}BuMe_2Si)_2NP]^+$, $[(Me_2N)(Me_3Si)_2NP]^+$, $[((Me_3Si)_2N)_2P]^+$, and $[ClP(N\text{-}t\text{-}Bu)_2P]^+$ have been prepared by treatment of the respective precursor chlorides with the stoichiometric quantity of Al_2Cl_6 in CH_2Cl_2 solution. The cation $[(Me_2N)(t\text{-}Bu)P]^+$ is noteworthy in two respects. First, it features a P–C bond, and, second, the ^{31}P chemical shift (+513.2 ppm) is the largest such value ever reported. The stereochemistries of the new cations are discussed on the basis of variable-temperature NMR data. It was not possible to prepare the cation $[(t\text{-}Bu)(Me_3Si)_2NP]^+$ by treatment of $(t\text{-}Bu)(Me_3Si)_2NPCl$ with Al_2Cl_6, or by the reaction of $(t\text{-}Bu)(Me_3Si)_2NPF$ with PF_5. Both reactions resulted in P-bonded Lewis acid–base complexes. The reaction of $(t\text{-}Bu)Me_2NPF$ with PF_5 is sensitive to reactant stoichiometry and yields varying amounts of the acid–base complexes $(t\text{-}Bu)(Me_2N)(F)P{\rightarrow}PF_5$ and $[(t\text{-}Bu)(Me_2N)(F)P{\rightarrow}P(t\text{-}Bu)(NMe_2)]^+$.

Introduction

There is a steadily growing iterest in the synthesis[2] and coordination chemistry[3] of two-coordinate phosphorus cations (phosphenium ions). With the exception of $[(Me_2N)(Cl)P]^+$, all phosphenium ions reported to date feature substitution by two amido groups. Arguing on the basis of structural information,[4] dynamic NMR data,[2a,4] and molecular orbital orbital calculations,[2e,4] it is clear that the stabilization of these electron-deficient species stems from conjugation between the nitrogen lone pairs and a formally vacant P(3p) orbital at the cationic center. The principal objective of the present work was to explore the possibility of kinetic stabilization of phosphenium ions by using bulky substituents. This approach has resulted in the synthesis of the first persistent[5] phosphenium ion featuring a phosphorus–carbon bond.[6]

Results and Discussion

Preparation of Precursor Halides. The chlorides $(t\text{-}Bu)(Me_2N)PCl$,[7] $(t\text{-}Bu)(Me_3Si)_2NPCl$,[8] $(Me_2N)(Me_3Si)_2NPCl$,[9] and $ClP(N\text{-}t\text{-}Bu)_2PCl$[10] are known compounds. The silylamino compound $[(Me_3Si)_2N]_2PCl$[11] has also been synthesized previously; however, we present some new NMR data in the Experimental Section. The chloride $(Me_2N)(t\text{-}BuMe_2Si)_2NPCl$ is new and was prepared by the action of $(t\text{-}BuMe_2Si)_2NLi$ on Me_2NPCl_2. Like other silylamino-substituted phosphorus chlorides,[8,9,11] it undergoes facile elision of silyl chloride. The fluorides $(t\text{-}Bu)(Me_2N)PF$ and $(t\text{-}Bu)(Me_3Si)_2NPF$ are new compounds and were sufficiently stable to permit characterization by elemental analysis and NMR spectroscopy. The former fluoride was prepared by the action of SbF_3 on the corresponding chloride; however, this approach could not be employed for the synthesis of the latter fluoride because of the thermal instability of $(t\text{-}Bu)(Me_3Si)_2NPCl$. Accordingly, $(t\text{-}Bu)(Me_3Si)_2NPF$ was prepared by the action of $(Me_3Si)_2NLi$ on $t\text{-}BuPF_2$.

The reaction of a phosphinous halide R_2PCl with 1 equiv of $AlCl_3$ units could, in principle, proceed by any of four pathways: (i) simple adduct formation to $R_2(Cl)P{\rightarrow}AlCl_3$, (ii) formation of a phosphenium salt, $[R_2P]^+[AlCl_4]^-$, (iii) oxidation to a cation radical, $[R_2PCl]^{+\cdot}$,[12] and (iv) ligand exchange, $R_2PCl + {}^1/_2Al_2Cl_6 \rightarrow (1/n)(RAlCl_2)_n + RPCl_2$. None of the reactions described in the present paper resulted in paramagnetic products, thus eliminating pathway iii. Furthermore, pathway iv is eliminated by ^{31}P NMR monitoring of the reaction mixtures. In no instance did we find a ^{31}P NMR signal corresponding to $RPCl_2$ (or PCl_3). We are thus left to distinguish between $AlCl_3$ adduct and phosphenium ion formation. Elemental analytical data cannot be used for this purpose since the elemental analyses are the same for both products. Furthermore, we found that the products are very moisture sensitive and in some cases thermally unstable. Like other workers in this field,[2c,d] therefore, we have relied on ^{31}P NMR spectroscopy as the primary identification tool. Typically, P-bonded $AlCl_3$ adducts exhibit ^{31}P chemical shifts in the range +50 to +110 ppm,[13,14] while for phosphenium ions the ^{31}P chemical shifts are >+260 ppm.[2c-e] Strong support for the validity of the ^{31}P NMR criterion of phosphenium ion formation is provided by the X-ray crystal structure of $[(i\text{-}Pr_2N)_2P]^+[AlCl_4]^-$ (313 ppm).[4] Inspection of the NMR data in Table I reveals that phosphenium ions have been formed (**1**–**4**). The cation $[(Me_2N)(t\text{-}Bu)P]^+$ (**1**) is particularly noteworthy because it is the first phosphenium ion to feature a P–C bond. Interestingly, we have since been able to prepare $(ferrocenyl)_2P^+$, a phosphenium ion with two P–C bonds.[3e] As in the case of ferrocenyl-substituted carbocations,[15] the sta-

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(1) To whom correspondence should be addressed.

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(12) Elegant work by Bock and co-workers has shown that Al_2Cl_6 in CH_2Cl_2 solution can function as an oxidizing agent: (a) Bock, H.; Brähler, G.; Fritz, G.; Matern, E. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 699–700. (b) Bock, H.; Kaim, W. *J. Am. Chem. Soc.* **1980**, *102*, 4429–4438. (c) Bock, H.; Kaim, W.; Connolly, J. W. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 700–701. (d) Bock, H.; Kaim, W.; Nöth, H.; Semkow, A. *J. Am. Chem. Soc.* **1980**, *102*, 4421–4428. (e) Bock, H.; Kaim, W. *Chem. Ber.* **1978**, *111*, 3552–3572.

(13) For example: $(t\text{-}Bu)_3P{\rightarrow}AlCl_3$, +57.8 ppm; $(t\text{-}Bu)_2(Cl)P{\rightarrow}AlCl_3$, 108.6 ppm (duMont, W.-W.; Kroth, H.-J.; Schumann, H. *Chem. Ber.* **1976**, *109*, 3017–3024]; $F_3P{\rightarrow}AlCl_3$, +104.5 ppm (Alton, E. R.; Montemayor, R. G.; Parry, R. W. *Inorg. Chem.* **1974**, *13*, 2267–2270).

(14) A plus means downfield (deshielded) and a minus means upfield (shielded) with respect to external 85% H_3PO_4.

(15) (a) Cais, M. *Organomet. Chem. Rev.* **1976**, *1*, 435–454. (b) Watts, W. E. *J. Organomet. Chem. Lib.* **1979**, *7*, 399–459. (c) Hill, E. A.; Weisner, R. *J. Am. Chem. Soc.* **1969**, *91*, 509–510.

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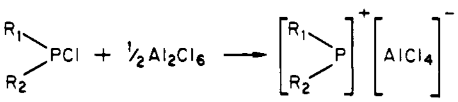
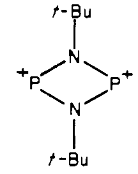


$$R_1R_2PCl + \tfrac{1}{2}Al_2Cl_6 \longrightarrow [R_1R_2P]^+[AlCl_4]^-$$

1, $R_1 = Me_2N$, R_2 = *t*-Bu
2, $R_1 = Me_2N$, R_2 = $(t\text{-}BuMe_2Si)_2N$
3, $R_1 = Me_2N$, $R_2 = (Me_3Si)_2N$
4, $R_1 = R_2 = (Me_3Si)_2N$

bilization of this species probably stems from the delocalization of the positive charge on to the ferrocenyl moieties. Cation **1** is also significant in that it exhibits the largest ^{31}P chemical shift reported thus far. One of the obvious reasons that **1** is >150 ppm more deshielded than previously reported phosphenium ions[2c–e] is that a π-donor dialkylamino group has been replaced by a nonconjugating *tert*-butyl group.

Cation **4** is of interest because it is related to the persistent[5] phosphinyl radical $[(Me_3Si)_2N]_2P\cdot$ by one-electron reduction.[16] Great interest was associated with the dication **5** because,



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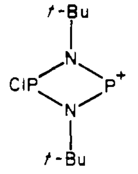

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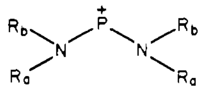
neglecting the phosphorus lone pairs (which are orthogonal to the π framework), this species possesses the same number of π electrons as cyclobutadiene. Unfortunately, however, it is only possible to remove one chloride ion from the precursor diazadiphosphetidine $ClP(N\text{-}t\text{-}Bu)_2PCl$ even when excess quantities of Al_2Cl_6 are employed. The ^{31}P AX pattern associated with the monocation **6** collapses to a singlet as the temperature is raised from −40 to +70°C (Figure 1). This averaging of the ^{31}P environments can be ascribed to either (a) rapid intramolecular transfer of Cl^- across the ring or (b) a rapid intermolecular process of the type

$$>P^+ + AlCl_4^- \rightleftarrows >P\text{–}Cl + AlCl_3$$

at both phosphorus centers. Attempts to generate **5** by treatment of $FP(N\text{-}t\text{-}Bu)_2PF$ with fluoride ion acceptors were not successful.[17] As will be discussed later, such reactions are less convenient than aluminum chloride-promoted chloride ion abstractions because they are often complicated by side reactions.

Stereochemical Considerations. Single-crystal X-ray diffraction of $[(i\text{-}Pr_2N)_2P]^+[AlCl_4]^-$ revealed that this cation possesses a near planar skeletal structure with approximately trigonal-planar geometries at the nitrogen and phosphorus centers.[4] Such an arrangement is understandable on the basis of optimization of the conjugation between the nitrogen lone pairs and a formally vacant phosphorus 3p orbital. Dynamic NMR studies[2d,3,4] have shown that many phosphenium ions are stereochemically nonrigid. For a typical cation, distinct R_a and R_b resonances are detectable at lower temperatures, averaging of the R_a and R_b environments in **7** occurring at



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higher temperatures when N–P bond rotation becomes rapid on the NMR time scale. Typically, torsional barriers are in the range 45–60 kJ/mol.

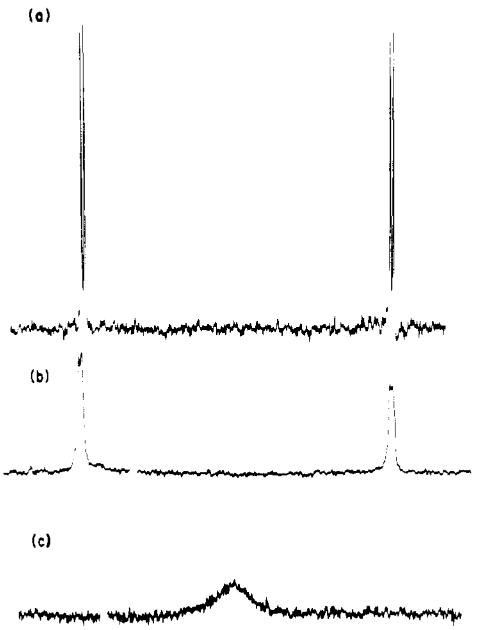

Figure 1. 36.43-MHz $^{31}P\{^1H\}$ NMR spectra of equimolar quantities of $ClP(N\text{-}t\text{-}Bu)_2PCl$ and $AlCl_3$ units in CH_2Cl_2 at various temperatures: (a) −40 °C; (b) 30 °C; (c) 70 °C.

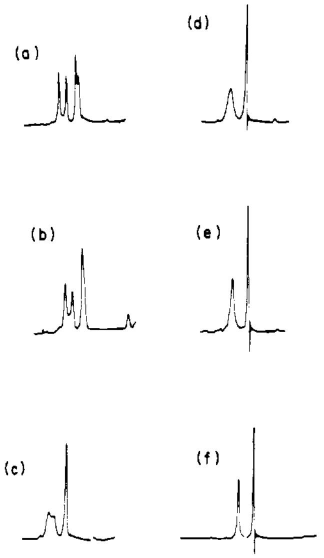

Figure 2. 100-MHz ^1H NMR spectra of $[(Me_2N)(Me_3Si)_2NP]^+$-$[AlCl_4]^-$ in CH_2Cl_2 solution at various temperatures: (a) 30 °C; (b) 35 °C; (c) 40 °C; (d) 46 °C; (e) 51.5 °C; (f) 60 °C.

At 30 °C, the $[(Me_2N)(Me_3Si)_2NP]^+$ cation exhibits a four-line ^1H and ^{13}C spectra in the Me_2N region and doublets in the Me_3Si region (Table I). The ^1H Me_2N resonance collapses as the temperature is raised, emerging as a doublet above 60 °C (Figure 2). Throughout the temperature range studied, both the ^1H and ^{13}C spectra exhibit *equivalent* Me_3Si groups. This observation contrasts with our earlier work[4] on $[(Me_2N)(i\text{-}Pr)_2NP]^+$ in which we observed anisochronous Me *and i*-Pr groups. In the case of **3**, our explanation for the equivalence of the Me_3Si groups is that they are rotated out of the N–P–N plane to a sufficient degree that anisochrony is not detectable. We note that a similar explanation has been offered by Neilson and Wells[18] to explain the equivalence of Me_3Si goups in $(Me_3Si)_2N$-substituted boranes. If the fore-

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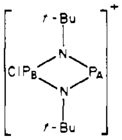
[16] (a) Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P.; Goldwhite, H. *J. Chem. Soc., Chem. Commun.* **1976**, *623*–624. (b) Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P.; Goldwhite, H. J. Chem. *Soc., Dalton Trans.* **1980**, 2428–2433.

[17] Cowley, A. H.; Lattman, M., unpublished observations.

[18] Neilson, R. H.; Wells, R. L. *Inorg. Chem.* **1977**, *16*, 7–11.

Table I. Summary of NMR Data for Phosphenium Ions

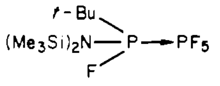
cation	chemical shifts, ppm[a,b]			coupling constants, Hz
	^{31}P	^{13}C	^{1}H	
$[(Me_2N)(t\text{-Bu})P]^+$ (1)	+513.2	45.40 (NMe_a), 45.04 (NMe_b), 26.47 (Me_3C)	3.2 (NMe_2), 1.5 (Me_3C)	$J_{PNC_a} = 3.4$, $J_{PNC_b} = 3.0$
$[(Me_2N)((t\text{-Bu})Me_2Si)_2NP]^+$ (2)	+370.1	43.86 (NMe_a), 41.20 (NMe_b), 27.33 (Me_3C), 0.13 (Me_2Si)	3.58 (NMe_a), 3.43 (NMe_b), 1.01 (Me_3C), 0.48 (Me_2Si)	$J_{PNC_a} = 33.5$, $J_{PNC_b} = 13.3$ $J_{PNCC} = 3.8$, $J_{PNSiC} = 5.4$, $J_{PNCH_a} = 12.3$, $J_{PNCH_b} = 4.2$, $J_{PNSiCH} = 1.1$
$[(Me_2N)(Me_3Si)_2NP]^+$ (3)	+354.3	43.82 (NMe_a), 41.32 (NMe_b), 3.54 (Me_2Si)	3.54 (NMe_a), 3.35 (NMe_b), 0.49 (Me_3Si)	$J_{PNC_a} = 35.3$, $J_{PNC_b} = 14.0$, $J_{PNSiC} = 5.5$, $J_{PNCH_a} = 5.3$, $J_{PNCH_b} = 1.6$, $J_{PNSiCH} = 0.9$
$[((Me_3Si)_2N)_2P]^+$ (4)	+450.3	3.54	0.55	$J_{PNSiC} = 5.0$, $J_{PNSiCH} = 1.2$
 (6)	+365.7 (P_A), +176.6 (P_B)			$J_{P_AP_B} = 73.2$

[a] See Experimental Section for statement of references used. [b] See ref 14 for chemical shift convention.

going explanation is accepted, the changes in the ^1H spectra of **3** may be ascribed to restricted rotation around the $P-NMe_2$ bond. A barrier of 68.6 kJ/mol was determined for this process by using standard NMR line-shape methods. The NMe_2 groups of $[(Me_2N)(t\text{-Bu})P]^+$ (**1**) and $[(Me_2N)(t\text{-}BuMe_2Si)_2NP]^+$ (**2**) are also nonequivalent at ambient temperature (Table I), hence similar arguments apply to the ground-state geometries of these cations.

Reactions Not Resulting in Phosphenium Ions. The ^{31}P chemical shift of the product of the reaction of equimolar quantities of $(t\text{-Bu})(Me_3Si)_2NPCl$ and $AlCl_3$ units (70.4 ppm, see Experimental Section) indicates that a P-bonded $AlCl_3$ complex, $(t\text{-Bu})(Cl)(Me_3Si)_2NP{\rightarrow}AlCl_3$, has been formed.[13] Since the $[(t\text{-Bu}(Me_2N)P]^+$ cation is relatively stable and, moreover, since the kinetic stabilization afforded by a $(Me_3Si)_2N$ group is greater than that by a Me_2N group, this implied instability of the $[(t\text{-Bu})(Me_3Si)_2NP]^+$ cation seems best ascribed to (a) the smaller π-bonding ability of the $(Me_3Si)_2N$ group and (b) to the rotation of the Me_3Si moieties out of the N–P–N plane (vide supra).

Rather similar results were obtained when the corresponding fluoride, $(t\text{-Bu})(Me_3Si)_2NPF$, was treated with PF_5. The ^{31}P and ^{19}F NMR data (Experimental Section) of the product are consistent with the phosphine–PF_5 complex **8**. This complex



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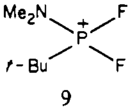
is analogous to the methylated series $Me_nH_{3-n}P{\rightarrow}PF_5$ (n = 1–3) reported by Schultz and Rudolph.[19]

The reaction of $(Me_2N)(t\text{-Bu})PF$ with AsF_5 produces the difluorophosphonium cation **9**. We have observed this type



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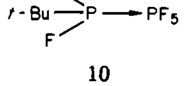
of reactions previously;[20,21] for instance, $(Me_2N)_2PF$ reacts with AsF_5 to yield $[(Me_2N)_2PF_2]^+$ and the reaction of $O_2S(t\text{-}BuN)_2PF$ with SbF_5 produces $[O_2S(t\text{-}BuN)_2PF_2]^+$. In each case, the net transfer of F^+ presumably involves a two-step reaction sequence: (i) oxidative fluorination of R_2PF to the corresponding trifluorophosphorane, R_2PF_3, aand (ii) fluoride ion abstraction from the latter to produce $[R_2PF_2]^+$.

When PF_5, a pentafluoride of lower oxidative fluorination capability, is employed the reaction takes a different course. In 1:1 molar stoichiometry, the reaction of $(Me_2N)(t\text{-Bu})PF$ with PF_5 produces an approximately 1:1 mixture of **10** and **11**. We have found that the relative amounts of **10** and **11**



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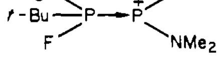

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produced depend on the reactant stoichiometry. If a 2:1 $(Me_2N)(t\text{-Bu})PF/PF_5$ stoichiometry is employed, the reaction mixture comprises mostly **11** and only traces of **10**. A 1:2 reactant stoichiometry produces the opposite result. The production of the phosphine–phosphenium complex **11** is not surprising. Parry and co-workers[2d] have noted previously that $[(Me_2N)_2P]^+$ reacts with tertiary phosphines to produce complexes analogous to **11**.[22] In the case of the $[(Me_2N)(t\text{-Bu})P]^+$ cation, the Lewis acidity is obviously quite high as evidenced by the substantially deshielded ^{31}P chemical shift of this species.

Experimental Section

Materials and General Procedures. The compounds $(t\text{-Bu})(Me_2N)PCl$,[7] $(t\text{-Bu})(Me_3Si)_2NPCl$,[8] $(Me_2N)(Me_3Si)_2NPCl$,[9] $ClP(N\text{-}t\text{-Bu})_2PCl$,[10] $(t\text{-}BuMe_2Si)_2NH$,[23] $t\text{-}BuPF_2$,[24] and Me_2NPCl_2[25] were synthesized and purified according to literature methods. Hexamethyldisilazane, PF_5, AsF_5, and SbF_3 were procured commercially and used without subsequent purification. Commercial Al_2Cl_6 was purified by sublimation in vacuo, and all solvents were dried and distilled prior to use.

Virtually all the materials desribed herein are moisture sensitive. Accordingly, it was necessary to perform all operations in vacuo or under an inert atmosphere.

Elemental analyses were carried out by Canadian Microanaytical Service, Ltd., Vancouver, B.C., Canada.

Spectroscopic Measurements. The ^1H and ^{19}F NMR spectra were recorded on Varian A-60 and EM-390 instruments operating at spectrometer frequencies of 60 and 84.96 MHz, respectively. The

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(19) Schultz, C. W.; Rudolph, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 1898–1903.

(20) Pagel, D. M.A. Thesis, The University of Texas at Austin, 1981. 36.43-MHz $^{31}P\{^1H\}$ NMR data for $[(Me_2N)_2PF_2]^+$: t, +20.8 ppm, J_{PF} = 1055.9 Hz.

(21) Cowley, A. H.; Mehrotra, S. K.; Roesky, H. W. *Inrog. Chem.* **1981**, *20*, 712–716. 36.43 MHz $^{31}P\{^1H\}$ NMR data for $[O_2S(t\text{-}BuN)_2PF_2]^+$: t, +32.0 ppm, J_{PF} = 1187.4 Hz.

(22) Traces of the corresponding chloro complex $[(t\text{-Bu})(Me_2N)(Cl)P_A{\rightarrow}P_B(t\text{-Bu})(NMe_2)]^+$ are also observed in the reaction of $(t\text{-Bu})(Me_2N)PCl$ with Al_2Cl_6. The 36.43 MHz $^{31}P\{^1H\}$ NMR spectrum of this species consists of an AB pattern with δ_A +76.4, δ_B +221.1, and J_{AB} = 537.1 Hz.

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(24) Fild, M.; Schmutzler, R. *J. Chem. Soc. A* **1970**, 2359–2364.

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variable-temperature ^{1}H NMR experiments were conducted on a Varian HA 100 spectrometer. The ^{1}H and ^{19}F chemical shifts were measured with respect to internal CH_2Cl_2 (5.28 ppm relative to Me_4Si) and external CCl_3F, respectively. The ^{13}C (20 MHz) and ^{31}P (36.43 MHz) NMR spectra were measured in the FT mode on Varian FT80 and Bruker WH-90 instruments, respectively. Dichloromethane (54.2 ppm relative to Me_4Si) was employed as the internal reference for the ^{13}C spectra, and 85% H_3PO_4 was used as the external reference for the ^{31}P spectra.[14] The NMR data for the phosphenium ions are summarized in Table I.

Preparation of $[(Me_3Si)_2N]_2PCl$. This compound was prepared by the method of Scherer the Kuhn,[11] recrystallized from CH_2Cl_2 at low temperature, and stored at −78 °C until used to avoid elimination of Me_3SiCl. New NMR data for this compound: $^{13}C\{^{1}H\}$ (CH_2Cl_2), 5.23 ppm (d, J_{PNSiC} = 8.4 Hz); $^{31}P\{^{1}H\}$, +186.0 ppm (s).

Preparation of $(Me_2N)(t\text{-}BuMe_2Si)_2NPCl$. A 17.5-mL sample of a 2.42 M solution of *n*-BuLi in hexane was added dropwise to a solution of 10.0 g (40.7 mmol) of $(t\text{-}BuMe_2Si)_2NH$ in 30 mL of hexane at ambient temperature. A slow, exothermic reaction ensued, and the reaction mixture assumed an off-white color. After the reaction mixture was stirred for 2.0 h at ambient temperature, the solvent and other volatiles were removed by evacuation, leaving $(t\text{-}BuMe_2Si)_2NLi$ as a white paste. The lithium amide was redissolved in 40 mL of Et_2O, and the resulting solution was cooled to 0 °C. Dropwise addition of 5.6 mL (40.9 mmol) of Me_2NPCl_2 to the vigorously stirred solution of $(t\text{-}BuMe_2Si)_2NLi$ resulted in an immediate reaction as evidenced by the formation of a whitish yellow precipitate. The reaction mixture was stirred for approximately 2 h at 0 °C, after which time the precipitate was filtered off rapidly. Stripping of the solvent from the filtrate at 0 °C afforded orange solid $(Me_2N)(t\text{-}BuMe_2Si)_2NPCl$ which was stored at −78 °C. Since the product is thermally unstable it was not possible to obtain analytical data. However, the following NMR data were obtained: ^{1}H (90 MHz), NMe (d, 2.64 ppm, J_{PNCH} = 13.2 Hz), Me_3C (s, 1.00 ppm), MeSi (d, 0.48 ppm, J_{PSiCH} = 2.6 Hz), Me'Si (s, 0.37 ppm); $^{13}C\{^{1}H\}$ (Me_4Si), Me_2N (d, 38.22 ppm, J_{PNC} = 14.2 Hz), Me_3C (d, 29.27 ppm, J_{PNSiCC} = 3.2 Hz), MeSi (d, 3,53 J_{PNSiC} = 6.7 Hz), Me'Si (d, 3.01 ppm, $J_{PNSiC'}$ = 3.6 Hz).

Preparation of $(t\text{-}Bu)(Me_2N)PF$. A 3.05-g (17.1 mmol) sample of SbF_3 was added to a stirred solution of 4.29 g (25.8 mmol) of $(t\text{-}Bu)(Me_2N)PCl$ in 10 mL of hexane at ambient temperature. Monitoring of the reaction mixture by ^{1}H NMR spectroscopy revealed that no reaction had taken place after stirring 15 h at ambient temperature. After 2 h of refluxing, however, the reaction was virtually complete. Vacuum fractionation with U traps held at −23, −45, and −196 °C afforded 2.29 g (15.1 mmol, 58.8% yield) of pure $(t\text{-}Bu)(Me_2N)PF$ in the −45 °C trap. Anal. Calcd. for $C_6H_{15}FNP$: C, 47.7; H, 10.00; N, 9.27. Found: C, 46.15; H, 11.22; N, 9.08. NMR: ^{1}H (60 MHz), Me_2N (d of d, 2.42 ppm, J_{PNCH} = 8.5 Hz, J_{FPNCH} = 4.5 Hz), Me_3C (d of d, 0.67 ppm, J_{PCCH} = 13.0 Hz, J_{FPCCH} = 1.4 Hz); $^{13}C\{^{1}H\}$ (Me_4Si), Me_2N (d of d, 39.48 ppm, J_{PNC} = 19.3 Hz, J_{FPNC} = 1.6 Hz), Me_3C (d of d, 35.06 ppm, J_{PC} = 25.1 Hz, J_{FPC} = 14.0 Hz), Me_3C (d of d, 24.79 ppm, J_{PCC} = 19.9 Hz, J_{FPCC} = 2.5 Hz); $^{31}P\{^{1}H\}$, d, +179.1 ppm, J_{PF} = 952.2 Hz.

Prepartion of $(t\text{-}Bu)(Me_3Si)_2NPF$. A 3.36-g (26.6 mmol) sample of $t\text{-}BuPF_2$ was added to a solution of 4.25 g (25.8 mmol) of $(Me_3Si)_2NLi$[26] in 30 mL of Et_2O at 0 °C. Following the addition, stirring was continued for 0.5 h at 0 °C, for a further 1.5 h at ambient temperature, and finally for 2.0 h at reflux. The solvent was stripped from the reaction mixture, and the residue was distilled using a short path column to afford 3.3 g (12.3 mmol, 47.8% yield) of clear colorless $(t\text{-}Bu)(Me_3Si)_2NPF$ (bp 39 °C (10^{-2} torr)): NMR ^{1}H (100 MHz), Me_3C (d of d, 1.03 ppm, J_{PCCH} = 12.6 Hz, J_{FPCCH} = 1.5 Hz), Me_3Si (d of d, 0.29 ppm, J_{PNSiCH} = 1.3 Hz, $J_{FPNSiCH}$ = 1.1 Hz); $^{13}C\{^{1}H\}$-(Me_4Si), Me_3C (d of d, 25.90 ppm, J_{PCC} = 19.6 Hz, J_{FPCC} = 3.5 Hz), Me_3Si (d of d, 5.29 ppm, J_{PNSiC} = 7.8 Hz, J_{FPNSiC} = 2.3 Hz); $^{31}P\{^{1}H\}$, d, +201.8 ppm, J_{PF} = 982.7 Hz. Anal. Calcd for $C_9H_{27}FNP$: C, 44.90; H, 10.17. Found: C, 45.1; H, 10.0.

Reaction of Phosphorus(III) Chlorides with Aluminum Chloride. These reactions were performed in 8-mm NMR tubes attached via a modified Claisen head to a vacuum system. Typically, a frozen mixture of equimolar quantities of the phosphorus(III) chloride and $AlCl_3$ units (ca. 3 mmol of each) in 1.5 mL of CH_2Cl_2 was sealed in vacuo at −196 °C. The tube was allowed to warm slowly to room temperature, and the contents were shaken until NMR measurements were made (Table I). In most instances, the Al_2Cl_6 was added to a frozen solution of the phosphorus chlorde in CH_2Cl_2; however, in the case of $(t\text{-}Bu)(Me_2N)PCl$, the inverse addition was employed. In the case of $ClP(t\text{-}BuN)_2PCl$, 1:2 and 1:4 chlorophosphine/$AlCl_3$ ratios were also used. However, the NMR spectra for these experiments were identical with those recorded for 1:1 stoichiometries.

Reaction of $(t\text{-}Bu)(Me_3Si)_2NPF$ with PF_5. In a typical reaction, a mixture of 0.411 g (2.72 mmol) of $(t\text{-}Bu)(Me_3Si)_2NPF$, 2.72 mmol of PF_5, and 2 mL of CH_2Cl_2 was sealed in vacuo in an 8-mm NMR tube. The tube was warmed to −78 °C and skaken occasionally before measuring the NMR spectra. NMR of $(t\text{-}Bu)(F')(Me_3Si)_2NP_A \rightarrow P_BF_5$ (**8**): $^{31}P\{^{1}H\}$ P_A (d of d of quintets (16-line pattern), +131.3 ppm, $J_{P_AF'}$ = 1013.2 Hz, $J_{P_AP_B}$ = 787.4 Hz, $J_{P_AP_BF}$ = 225.8 Hz), P_B (complex m, −141.7 ppm, $J_{PF_{eq}}$ = 836.2, $J_{PF_{ax}}$ = 781.2, $J_{F'P_AP_B}$ = 97.7 Hz).

Reaction of $(t\text{-}Bu)(Me_2N)PF$ with AsF_5. The reaction was carried out as described in the previous section by using 0.43 g (2.84 mmol) of $(t\text{-}Bu)(Me_2N)PF$ and 0.48 g (2.84 mmol) of AsF_5 in CH_2Cl_2 solution. NMR data for $[(t\text{-}Bu)(Me_2N)PF_2]^+$ (**9**): ^{1}H (60 MHz), Me_2N (d of t, 3.08 ppm, J_{PNCH} = 10.4 Hz, J_{FPNCH} = 3.5 Hz), Me_3C (d of t, 1.53 ppm, J_{PCCH} = 22.5 Hz, J_{FPCCH} = 1.1 Hz); $^{13}C\{^{1}H\}$ (Me_4Si), Me_2N (d, 37.70 ppm, J_{FPNC} = 3.9 Hz), Me_3C (s, 23.03 ppm); $^{31}P\{^{1}H\}$, t, +69.4 ppm, J_{PF} = 1211.5 Hz.

Reaction of $(t\text{-}Bu)(Me_2N)PF$ with PF_5. The reactions were carried out as described above by using 1:1, 2:1, and 1:2 mole ratios of $(t\text{-}Bu)(Me_2N)PF$ and PF_5 in CH_2Cl_2 solution. As noted in the Results and Discussion, this led to varying amounts of $(t\text{-}Bu)(F)(Me_2N)P \rightarrow PF_5$ (**10**) and $[(t\text{-}Bu)(F)(Me_2N)P \rightarrow P(NMe_2)(t\text{-}Bu)]^+$ (**11**). NMR data for $(t\text{-}Bu)(F')(Me_2N)P_A \rightarrow PF_5$ (**10**): $^{31}P\{^{1}H\}$, P_A (d of d of quintets, +114.5 ppm, $J_{PF'}$ = 1101.7 Hz, $J_{P_AP_B}$ = 799.5 Hz, $J_{P_AP_BF_{eq}}$ = 225.9 Hz), P_B (complex m, −139.5 ppm, $J_{PF_{eq}}$ = 869.3 Hz, $J_{PF_{ax}}$ = 791.6 Hz, $J_{F'P_AP_B}$ = 74.0 Hz). For $[(t\text{-}Bu)(F)(Me_2N)P_A \rightarrow P_B(NMe_2)(t\text{-}Bu)]^+$ (**11**): $^{31}P\{^{1}H\}$ P_A (d of d, +131.5 ppm, J_{P_AF} = 1147.5 Hz, $J_{P_AP_B}$ = 506.5 Hz), P_B (d of d, +67.9 ppm, $J_{P_BP_AF}$ = 48.9 Hz).

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Registry No. **1**, 74900-32-6; **2**, 78108-53-9; **3**, 74900-29-1; **4**, 74900-31-5; **6**, 78108-54-0; **8**, 78108-56-2; **9**, 78108-57-3; **10**, 78108-58-4; **11**, 78108-59-5; $[(Me_2N)(Me_3Si)_2NP]^+[AlCl_4]^-$, 78109-43-0; $[(Me_3Si)_2N]_2PCl$, 53327-45-0; $(Me_2N)(t\text{-}BuMe_2Si)_2NPCl$, 78108-60-8; $(t\text{-}Bu)(Me_2N)PF$, 53099-02-8; $(t\text{-}Bu(Me_3Si)_2NPF$, 78108-55-1; Al_2Cl_6, 13845-12-0; $(t\text{-}BuMe_2Si)_2NH$, 41879-38-3; Me_2NPCl_2, 683-85-2; $(t\text{-}Bu)(Me_2N)PCl$, 53899-06-2; $t\text{-}BuPF_2$, 29149-32-4; $(Me_3Si)_2NLi$, 4039-32-1.

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