Generation of the First Persistent Phosphirenylium Cation

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First synthesized by Breslow in the late 1950s,[4] the cyclopropenium cation, **1**, has occupied a central position in carbocation chemistry as the lowest energy form of $C_3H_3^+$ [5] and the smallest (2π) Hückel aromatic cation.[6] NMR studies,[7,8] theory,[5] mass spectrometric studies,[9] and X-ray analysis[10] have underscored the importance of the mesomeric **1B** form of the cation (Scheme 1).

Whereas a number of cyclopropenium cations have been prepared and characterized as stable salts including the parent cation,[6,8] the corresponding phosphirenylium cations, the phosphorus analogues of cyclopropenium ions, have remained hitherto elusive. Thus the relative importance of mesomeric forms **2A** and **2B** and the potential aromaticity of the system (form **2C**) remained open questions (Scheme 1).

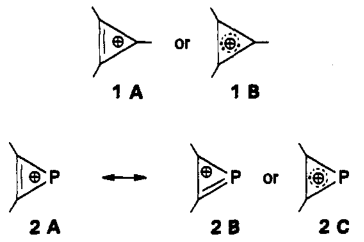
Parent **2** is the lowest energy $C_2H_2P^+$ isomer at the HF/6-31G* level.[11] Its C-substituted derivatives had been observed in the EI mass spectra of **7** and **12** (Scheme 4) and other phosphaalkyne cyclooligomers,[12] as well as by collisional decomposition of phosphonium ions derived from tetra-*tert*-butyltetraphosphacubane and 1,2,5,6-tetraphosphatricyclo-[4.2.0.0^{2,5}]octadiene.[13]

In principle, ionization of **7** under suitable conditions could provide access to **2**. The synthesis of **7** was achieved by Regitz et al. according to Scheme 2.[14]

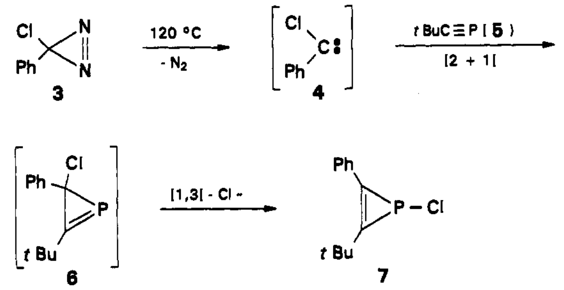
Low-temperature reaction of **7** with $AgPF_6$ gave the fluorophosphirene **9**,[15] and the room temperature reaction of **7** with sodium tetraphenylborate (Scheme 3) gave **11**.[16,17]

In an attempt to prevent nucleophile transfer and quenching, ionization of **7** with silver triflate was tried (Scheme 4); instead of **13**, the covalent 1-trifloxy-1*H*-phosphirene **12** was isolated (NMR data in Table 1).

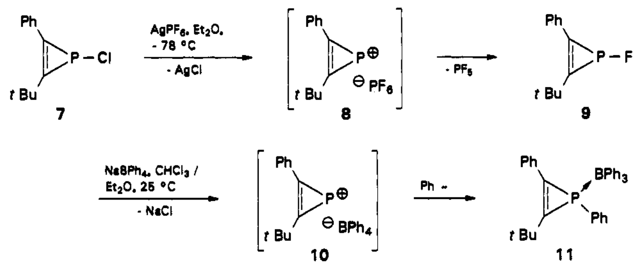
Scheme 1



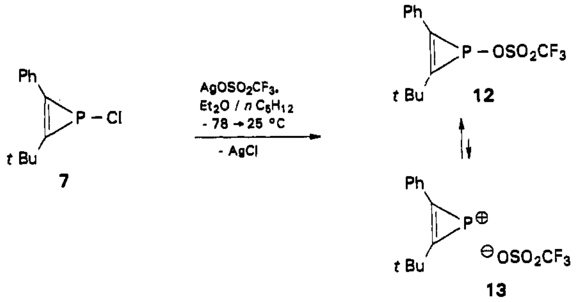
Scheme 2



Scheme 3



Scheme 4



There is a consistent trend of deshielding at phosphorus in the Cl → F → OTf sequence, pointing to increased ionic character of the P–X bond (the ^{31}P NMR resonance for **7** is at −73.4 ppm;[14] those for **9** and **12** are at −38.2 and −8.9 ppm, respectively[18]). ^{31}P NMR studies on **12** as a function of solvent polarity[19] suggested partial positive charge development at phosphorus and involvement of phosphirenylium cation.[19] Triflate **12** was trapped with *N*,*N*-dimethylaniline.[12] The ambient ^{17}O NMR spectrum of **12** gives just one resonance at 159.2 ppm for the triflate group (no $^1J_{OP}$ coupling), implying dynamic averaging by dissociation/recombination.[19]

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(3) (a) University of Kaiserslautern. (b) Organophosphorus Compounds. 90. Part 89: Slany, M.; Regitz, M. *Synthesis*, in the press.

(4) Breslow, R. *J. Am. Chem. Soc.* **1957**, *79*, 5318. Breslow, R.; Yuan, C. *J. Am. Chem. Soc.* **1958**, *80*, 5991.

(5) Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 10.

(6) Garratt, P. J. *Aromaticity*; Wiley: New York, 1986; pp 137–141.

(7) Breslow, R.; Groves, J. T.; Ryan, G. *J. Am. Chem. Soc.* **1967**, *89*, 5048.

(8) Ciabattoni, J.; Nathan, E. C., III. *J. Am. Chem. Soc.* **1969**, *91*, 4766.

(9) Lossing, F. P. *Can. J. Chem.* **1972**, *50*, 3973.

(10) Sunderlingham, M.; Jensen, L. H. *J. Am. Chem. Soc.* **1966**, *88*, 198.

(11) Maclagen, G. A. R. *Chem. Phys. Lett.* **1989**, *163*, 349.

(12) Regitz, M.; Wagner, O. Unpublished results.

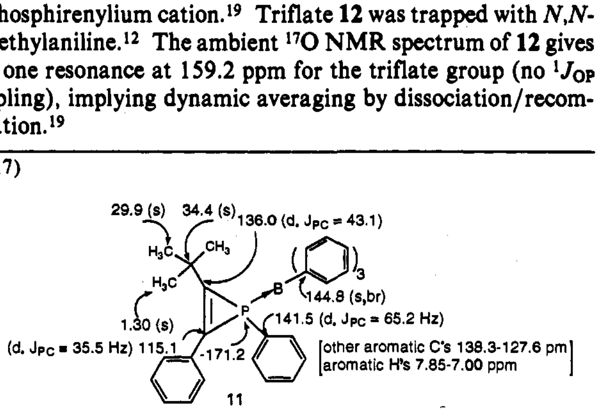
(13) Laali, K. K.; Geissler, B.; Regitz, M.; Wesdemiotis, C.; Polce, M.; Beranova, S. *J. Org. Chem.*, to be submitted.

(14) Wagner, O.; Ehle, M.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 225.

(15) Wagner, O.; Ehle, M.; Birkel, M.; Hoffmann, J.; Regitz, M. *Chem. Ber.* **1991**, *124*, 1207.

(16) Hoffmann, J. Ph.D. Dissertation, University of Kaiserslautern, 1990.

(17)



(18) Wagner, O. Ph.D. Dissertation, University of Kaiserslautern, 1989.

(19) Memmesheimer, H.; Regitz, M. *Rev. On. Heteroatom Chem.* **1994**, *10*, 61.

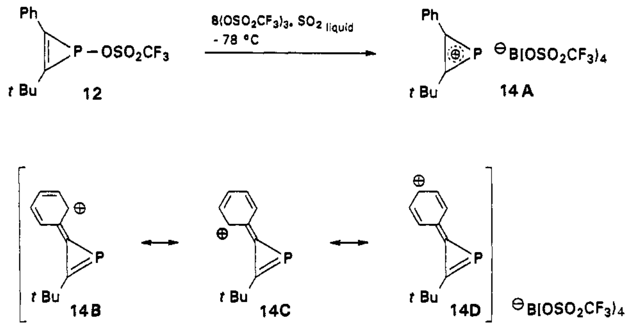
0002-7863/94/1516-9407$04.50/0

Table 1. Multinuclear NMR Data on **12** and **14**

compd	solvent/temp	^{31}P NMR	^{11}B NMR	^{13}C NMR	^{1}H NMR
12	$CDCl_3$/rt[a]	–3.02[b]		155.4 (d, $^{1}J_{PC}$ = 70.5 Hz; *C*–tBu) 142.1 (d, $^{1}J_{PC}$ = 66 Hz; *C*–Ph) 132.2 (s; Ph); 132.1 (s; Ph); 129.7 (s; Ph) 125.9 [d, $^{2}J_{PC}$ = 5.2 Hz; Ph (ipso C)] 119.0 (q, $^{1}J_{PF}$ = 318 Hz; CF_3) 34.3 (d, $^{2}J_{PC}$ = 3.9; *C*Me$_3$); 29.3 (s; C*Me*$_3$)	7.6 (m, 5H; Ph) 1.22 (s, 9H; CMe_3)
14	SO_2/–73 °C	309.7 (s) [Δδ = 313]	–3.49 (s) [Δδ = –7.6]	215.4 (d, $^{1}J_{PC}$ = 94.9 Hz; *C*–tBu); Δδ = 60.0 197.0 (d, $^{1}J_{PC}$ = 83.3 Hz; *C*–Ph); Δδ = 54.9 139.0 [s; Ph (para C)] 136.0 [s; Ph (meta C)] 130.7 [s; Ph (ortho C)] 124.9 [s; Ph (ipso C)] 117.8 (q, J_{CF} = 315 Hz; CF_3) 40.1 (s; *C*Me$_3$) 27.4 (s; C*Me*$_3$)	8.28 (d, 2H; ortho) 7.86 (t, 1H; para) 7.73 (t, 2H; meta) 1.60 (s, 9H; CMe_3)

[a] Room temperature. [b] Slightly concentration dependent (previously found at –8.9 ppm).[18]

Scheme 5



Scheme 6

We report here the first successful generation of **14** in solution (Scheme 5). Our strategy exploits the superior Lewis acidity of $B(OTf)_3$ (compared to BCl_3 and BBr_3)[20] and the high affinity of BX_3 (X = halogen or triflate) to coordinate triflate ligands, a protocol previously utilized in attempted ionization of R_3SiOTf with BX_3 to make silicenium ions.[21]

A solution of $B(OTf)_3$ (prepared via BCl_3 and 3TfOH) in SO_2 was carefully added to frozen **12** at dry ice/acetone temperature under argon. Efficient vortex mixing led to a smooth reaction with a distinct brown-red color developing.

The ^{31}P NMR spectrum of the resulting solution (Table 1) exhibited a single phosphorus resonance at 309.7 ppm, deshielded by 313 ppm from the precursor.[22] The ^{13}C NMR spectrum shows two diagnostic ring carbons at 215.4 (*C*–tBu) and 197.0 ppm (*C*–Ph) deshielded by 60.0 and 54.9 ppm, respectively (relative to **12**). The $^{1}J_{PC}$ values for the ring carbons change from 70.5 and 66.0 Hz in **12** to 94.9 and 83.3 in **14**, clearly showing increased P–C bond order. The ^{11}B NMR spectrum exhibits a single resonance at –3.49 ppm ($W_{1/2}$ = 17.8 Hz) shielded by 7.6 ppm relative to $B(OTf)_3$ in SO_2, also showing much narrowing [$W_{1/2}$ [$B(OTf)_3/SO_2$ = 93 Hz].[23]

The deshielded positions of tBu and Ph substituents are also noteworthy. The $\delta_{^1H}$ (tBu) at 1.60 ppm is nearly identical to a tBu attached to cyclopropenium ion.[8] The similarity of the ^{1}J P–C coupling constants in **14** suggests that **14A** is the major contributing structure,[24] although the phenyl deshielding trend argues that some contribution by forms **14B**, **14C**, and **14D** must exist (Scheme 5).

The aromatic character of **2** is corroborated by ab initio calculations[25] at the HF/6-31+G* level. All bond distances and bond orders (bo) resulting from NBO analysis clearly show that 1-fluoro-1*H*-phosphirene has typical single and double bonds (P/C, 1.7732 Å, bo = 0.972; C/C, 1.3012 Å; bo = 1.943), whereas the bonds in **2** are clearly delocalized (P/C, 1.7032 Å, bo = 0.980; C/C, 1.3406 Å, bo = 1.776).

We calculated the relative reaction energies for P–X bond heterolysis (Scheme 6 and Table 2) (supplementary material). The P–F bond is about 54 kcal/mol more stable than the P–Cl bond.[26] Methyl substitution lowers the energy by 15 kcal/mol. Complexation of the leaving group with BX_3 lowers the reaction energy further (ca. 97 kcal/mol) for the dimethyl derivative, which is still highly endothermic. In preliminary studies at minimal basis sets we find that when gegenion complexation with SO_2 is taken into account, reaction energies decrease further. Clearly, the role of solvent in stabilizing the gegenion in solution is important; endothermicity of the ionization process in the gas phase further suggests that there is a driving force in the system which reduces this energy.

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Supplementary Material Available: Table 2 of relative reaction energies (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.

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(20) Olah, G. A.; Laali, K.; Farooq, O. *J. Org. Chem.* **1984**, *49*, 5491.

(21) Olah, G. A.; Laali, K.; Farooq, O. *Organometallics* **1984**, *3*, 1337.

(22) The $\Delta\delta_{^{31}P}$ in Cowley's phosphenium ions $[(R_2N)_2P]^+$ are typically ca. 100 ppm (see: Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367).

(23) Cation **14** was stable even at –40 °C (^{31}P NMR). Attempts to convert it back to **12** by treating the cold reaction mixture with AgOTf or TMSOTf followed by evaporation of SO_2 gave in both cases complex mixtures of products whose ^{31}P NMR resonances showed them to be singlets in the range for phosphirenes. Thus the triflate was not obtained selectively by these experiments.

(24) The $^{1}J_{PC}$ in (1-Ad)CH=P ~ OSO_2F is 57.2 Hz (Laali, K. K.; Geissler, B.; Regitz, M. *J. Org. Chem.*, in preparation.

(25) All calculations were performed with the program package Gaussian 92, Revision E.3: Pople, J. A., et al., Gaussian, Inc., Pittsburgh, PA, 1992.

(26) Nguyen, M. T.; Vansweevelt, H.; Vanquickenboren, L. A. *Chem. Ber.* **1992**, 125, 923.