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1,2-Addition Reaction of a Protic Phosphonium Cation with a Phosphaalkyne

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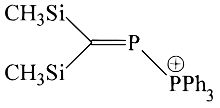
Structural simplicity and high reactivity have resulted in the use of phosphaalkynes **1** as versatile synthetic reagents in cycloaddition[2] and transition metal[2−4] chemistry.[5] The coordination chemistry of anions (primarily derivatives of cyclopentadiene) prepared from phosphaalkyne precursors has been reported;[6] however, cations derived from phosphaalkynes have largely been ignored.[7] Two recent reports have described the synthesis and structure of novel cations **2** and **3**, which contain formal phosphorus−element np$_\pi$−np$_\pi$ bonds.[8] Phosphorus cations have been shown to engage both σ[9,10] and π[11] donors, and these new species represent potentially strategic probes of this chemistry. The cations **2** and **3** were prepared *via* nucleophilic displacement of a suitable leaving group (**2** by chloride ion substitution with PPh_3 in the presence of $AlCl_3$,[12] and **3** by PPh_3 displacement of amine from an ammonium-substituted diphosphene[13]). Interestingly, base-free methylene phosphenium cations have recently been observed in the gas phase.[14] Compounds **2** and **3** may be considered as *P*-phosphoniophosphaalkenes and -diphosphenes (**4**), respectively. The reactivity of these π bonds has yet to be probed, but it may be assumed that they will demonstrate striking differences from the parent systems due to their modified electronic structures.

Our interest in main group element π systems has lead us to examine the synthesis and reactivity of the *P*-phosphonio-substituted phosphaalkene **5**. Here we report the synthesis and NMR characterization of **5**, which is prepared from the reaction of $C_{10}H_{15}C{\equiv}P$ with the protic phosphonium compound $[HPPh_3][CF_3SO_3]$. Regeneration of the phosphaalkyne is realized by the treatment of **5** with BuLi.

R−C≡P

1



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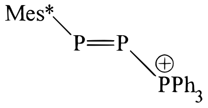

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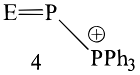
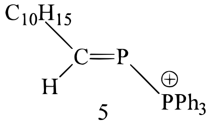


4

E = CR_2, PR



5

The reaction of the protic phosphonium cation $[HPPh_3][CF_3SO_3]$ with $C_{10}H_{15}C{\equiv}P$ produces a white powder identified as the *P*-phosphonio-substituted phosphaalkene **5**.[15,16] NMR spectra (^1H, ^{13}C, and ^{31}P) obtained on reaction mixtures indicate that the reaction is quantitative. The absence of starting material in these reaction mixtures indicates that the reactants do not adopt an equilibrium in CD_2Cl_2 solution at room temperature, and no intermediates were identified. The ionic nature of the product is supported by its insolubility in hydrocarbon solvents such as hexane. Infrared studies on the solid reaction product indicate the absence of the characteristic P−H stretch (2400 cm^{-1}) observed for $[HPPh_3][CF_3SO_3]$.

The AX splitting pattern observed in the $^{31}P\{^1H\}$ spectrum ($^1J_{PP}$ = 366 Hz) is consistent with the formation of a P−P bond. The deshielded $^{13}C\{^1H\}$ NMR resonance (δ = 225.5 ppm) for

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(3) See, for example: Nixon, J. F. *Chem. Ind.* **1993**, 404−407.

(4) Nixon, J. F. *Chem Rev.* **1988**, *88*, 1327−1362.

(5) For reviews, see: (a) Regitz, M.; Binger, P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1484−1508. (b) Regitz, M. *Chem. Rev.* **1990**, *90*, 191−213. (c) Regitz, M. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme: New York, 1990; pp 58−89. (d) Regitz, M. *Bull. Soc. Chim. Belg.* **1992**, *101*, 359−379.

(6) See, for example: Bartsch, R.; Hitchcock, P. B.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1987**, 1146−1148; **1988**, 819−820; **1989**, 1046−1048.

(7) To the authors' knowledge, the only report of the synthesis of a cation derived from a phosphaalkyne is the [2 + 3] cycloaddition reaction between *t*-BuC≡P and SNS^+. See Parsons, S.; Passmore, J.; Sun, X. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1994**, *93−94*, 435−436.

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(10) See, for example: (a) Reed, R.; Reau, R.; Dahan, F.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 399−401. (b) Burford, N.; Losier, P.; Sereda, S. V.; Cameron, T. S.; Wu, G. *J. Am. Chem. Soc.* **1994**, *116*, 6474−6475.

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(14) Laali, K. K.; Wesdemiotis, C.; Polce, M.; Beranova, S. *Inorg. Chem.* **1995**, 1191−1195.

(15) The experimental procedures and instrumentation have been described previously [Bridson, J. N.; Schriver, M. J.; Zhu, S. *Can. J. Chem.* **1995**, *73*, 212−222] with the exception of the glassware [Burford, N.; Muller, J.; Parks, T. M. *J. Chem. Educ.* **1994**, *71*, 807−809]. $C_{10}H_{15}CP$ [Allspach, T.; Regitz, M.; Becker, G.; Becker, W. *Synthesis* **1986**, 31−36], $[HPPh_3][CF_3SO_3]$ [van den Akker, M.; Jellinek *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 275−288], and diazofluorene [Schonberg, A.; Awad, W. I.; Latif, N. *J. Chem. Soc.* **1951**, 1368−1369] were prepared following the literature procedures. The NMR spectra are reported in ppm with respect to external standards Cl_3CF [^{19}F], TMS [^1H, ^{13}C], and 85% H_3PO_4 [^{31}P]. The ^1H and ^{13}C NMR spectra were calibrated to the internal solvent signal.

(16) Ad-C≡P (0.24 g, 1.30 mmol) in 20 mL of CH_2Cl_2 was added over 5 min to a stirred solution of $[HPPh_3][CF_3SO_3]$ (0.55 g, 1.33 mmol) in 20 mL of the same solvent. The reaction mixture was stirred for 5 h at which time the solvent was removed *in vacuo* leaving a clear colorless oil. Exhaustive evacuation of the vessel containing this oil for an additional 30 min resulted in the formation of a white fluffy powder. This powder was washed with hexane, dried under vacuum, and characterized by NMR spectroscopy as **5** (0.33 g, 45%, mp 79−81 °C dec.). Attempts to recrystallize this material from solution (CH_2Cl_2/hexane or toluene) were unsuccessful. NMR data follow. $^{31}P\{^1H\}$: two doublets, 172 and 27 ppm ($^1J_{PP}$ = 366 Hz). $^{31}P-^1H$ coupling observed in the ^{31}P ^1H coupled spectra: $^2J_{PH}$ = 18 Hz, $^3J_{PH}$ = 33 Hz, respectively. ^1H: 9.24 (d of d $^2J_{PH}$ = 20 Hz, $^3J_{PH}$ = 33 Hz), 7.90−7.59 (aromatic, 15 H), 2.06−1.63 (adamantyl, 15 H). ^{13}C: 225.5 (d of d, $^1J_{PC}$ 61 Hz, $^2J_{PC}$ 8 Hz), 135.5 (s), 134.4 (d, J_{PC} = 11 Hz), 130.0 (d, J_{PC} = 8 Hz), 119.1 (d, J_{PC} = 71 Hz), 46.9 (overlapping d of d, $^2J_{PC}$ = $^3J_{PC}$ = 13 Hz), 41.8 (d, J_{PC} = 13 Hz, 36.0 (s), 28.2 (s). ^{19}F: −77.7 (sharp). Multiplicity analysis (^{13}C) confirms that the peak at 225.5 ppm is a C-H group, $^1J_{CH}$ = 151 Hz. IR (cm^{-1}): 1564 w, 1309 sh, 1271 sb, 1221 m, 1150 s, 1101 m, 1029 m, 995 w, 975 w, 891 w, 830 w, 689 s, 635 s, 570 s, 547 m, 509 m, 501 m. ^{31}P NMR studies on reaction mixtures obtained within minutes of sample preparation indicate the presence of only starting materials and **5**. ^1H NMR spectra of reaction mixtures remain unchanged after 2 months in CD_2Cl_2 solution.

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the methylene carbon center of **5** exhibits the anticipated doublet of doublets. Multiplicity analysis confirms the resonance as a C−H center, and the magnitude of $^1J_{CH}$ (151 Hz) is typical of a sp^2 hybridized carbon.[17] Also notable is the doublet of doublets ($\delta = 9.24$ ppm; $^2J_{PH} = 20$ Hz, $^3J_{PH} = 33$ Hz) which is observed in the ^{1}H NMR spectra for the unique proton. NMR (^{1}H, ^{13}C, and ^{31}P) data have recently been reported for *tert*-butyl−C(H)=POSO$_2$CF$_3$ and the low field chemical shift that was observed [^{1}H; δ(unique H) = 8.93 ppm] is consistent with the values observed for **5**.[18] The ^{13}C resonance for the methylene carbon center in **2** was not identified due to its instability in solution; however, preparation of a hydrogen-substituted derivative, **5**, allows for observation of this NMR signal due to an efficient relaxation mechanism.[19]

It has not yet been possible to prepare a crystalline sample of **5** on which to perform a crystallographic study; however, it is anticipated that the *E* isomer is formed in preference to the *Z* isomer for steric considerations, as observed in the molecular structures of **3**.[13]

The P−C bond in both phosphaalkynes and phosphaalkenes is polar;[5] however, the *P*-phosphonio-substituent will undoubtedly change the reactivity of the phosphorus−carbon π bond in **5**. The strong electron-withdrawing inductive effect of the *P*-phosphonio group reduces the basicity of the carbon center and increases the acidity of the phosphorus center relative to RC≡P and other phosphaalkenes. The net effect of this electronic modification of the P−C double bond may make this species less likely to engage in cycloaddition reactions, and this has been confirmed by the reaction of **5** with diazofluorene.[20] Phosphaalkynes and phosphaalkenes have been observed to undergo cycloaddition reactions with diazoalkanes.[5] In contrast, **5** does not undergo analogous reactions with diazofluorene; rather, mixtures of diazofluorene and **5** gives unreacted **5** and bifluorenylidene quantitatively as indicated by ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy. Conversion of diazofluorene to bifluorenylidene has previously been observed in TiCl$_3$/LiAlH$_4$ or TiCl$_3$/Na mixtures[21] or catalytically with copper(II) salts.[22]

The phosphaalkyne C$_{10}$H$_{15}$C≡P can be regenerated by reaction of **5** with BuLi in THF.[23] ^{31}P NMR spectra of the reaction mixtures indicate the presence of PPh$_3$, C$_{10}$H$_{15}$C≡P, and a minor unknown impurity at 412 ppm.

In conclusion, significant reversible modification of RC≡P reactivity can be achieved with [HPPH$_3$][CF$_3$SO$_3$].

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Supporting Information Available: NMR spectra [^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H}] of **5** (4 pages). Ordering information is given on any current masthead page.

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(20) Reaction of **5** with diazofluorene in a 1:1 stoichiometry in CD$_2$Cl$_2$ results in the formation of a dark brick red solution which after 3 h turns clear orange. NMR studies (^{31}P, ^{13}C, ^{1}H) indicate the presence of **5** and bifluorenylidene in solution. Bifluorenylidene was isolated by treatment of a reaction mixture with ethanol and hexane (50/50) followed by purification by elution with hexane through a silica column. Solvent was removed and the red residue recrystallized from ethanol. Mp: 176−179 °C (lit. mp 184−185 °C). Mass spectrum: M$^+$ 328 (100%). An NMR study on the reaction of diazofluorene (0.15 g, 0.78 mmol) with *ca.* 3 mg (0.005 mmol) of **5** in 6 mL of CH$_2$Cl$_2$ results in quantitative formation (3 h) of bifluorenylidene (^{1}H NMR). Attempts to spectroscopically identify intermediates were inconclusive. C$_{10}$H$_{15}$C≡P reacts with diazofluorene to give a single phosphorus-containing species (^{31}P 22 ppm).

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(23) Deprotonation of **5**: **5** (0.04 g, 0.068 mmol) was dissolved in THF, *ca.* 5 mL, in an NMR tube under a positive pressure of nitrogen, and the sample was cooled to pentane slush temperature. BuLi (0.05 mL, 1.6 M) was added dropwise from a syringe. The solution was slowly warmed to room temperature with shaking, during which time the solution went from clear yellow to clear colorless. The solution was concentrated *in vacuo* to *ca.* 1.5 mL, and ^{31}P NMR of the reaction mixture indicated the presence of two phosphorus-containing species: −5 (PPh$_3$) and −69 (C$_{10}$H$_{15}$C≡P). A small signal (<10%) was observed at 412 ppm (unknown).