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Strong P=P π Bonds: The First Synthesis of a Stable Phosphanyl Phosphenium Ion**

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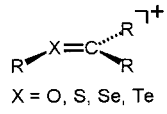
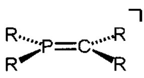
Hansjörg Grützmacher*

Dedicated to Professor Hans Bock
on the occasion of his 71st birthday

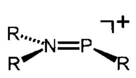
α-Heteroatom-substituted carbenium ions **A** (X = S, Se, Te),[1] methylene phosphonium ions **B**,[2] and amino phosphenium ions **C**[3] can be formally described as donor–acceptor π-bond systems. In context with our investigations on these quite polar bond systems (i.e., $(X,P)^{\delta+},C^{\delta-}$ in **A**, **B**; $N^{\delta-},P^{\delta+}$ in **C**), we became interested in an ion analogous to **C** in which only third-row elements are involved in π bonding. The plan for the synthesis appeared simple: Protonation or alkylation of a diphosphene, R–P=P–R, should give a phosphanyl phosphenium ion, $[R_2P{=}PR]^+$, in which a phosphanyl group, R_2P, serves as π-electron donor towards an electron-deficient phosphenium unit, PR^+.[4] Others have attempted this approach in condensed phase; however, these ions have never been detected.[5] In the gas phase these species are observed as fragmentation products of $[R_2P{-}PR_2]^{\cdot+}$ radical cations.[6] Calculations show the planar $[H_2P{=}PH]^+$ ion to be the global minimum on the $[H_3,P_2]^+$ singlet potential energy surfaces.[7] Our own efforts to obtain $[\text{Mes*MeP}{=}\text{PMes*}]^+$ (**3**; Mes* = 2,4,6-tBu$_3$C$_6$H$_2$) were initially frustrating since no reaction occurred when diphosphene **1**[8] was treated with stoichiometric amounts of methyl trifluoromethanesulfonate (methyl triflate, **2**) in CH_2Cl_2. However, in the presence of a 35-fold excess of **2**, the methylated cation **3** was formed quantitatively (Scheme 1).



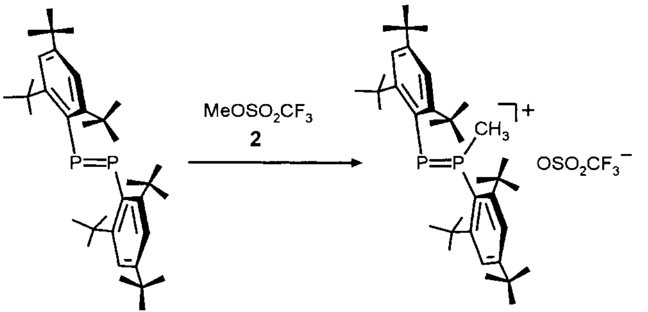
A



B



C



1 **3**

Scheme 1. Synthesis of phosphanyl phosphenium ion **3**.

Only two doublets at $\delta = 237$ (Mes*MeP) and 332.2 (Mes*P; $^1J_{PP} = 633$ Hz) were observed in the ^{31}P NMR spectrum. Note that the creation of a positive charge causes a considerable low-frequency shift of both ^{31}P NMR resonances ($\Delta\delta(P1) = 258$; $\Delta\delta(P2) = 163$) when compared to neutral **1** ($\delta(^{31}P) = 495$). The n → π* ($\lambda = 364$ nm) and π → π* transitions ($\lambda = 249$ nm) of the P=P chromophore are shifted to shorter wavelengths by 98 and 92 nm, respectively.

Since **3** proved to be particularly unstable in nonpolar organic solvents, crystals suitable for an X-ray analysis were grown within five minutes by diffusion of diethyl ether into a solution of **3** in CH_2Cl_2 under a microscope. A rapidly formed small yellow platelet was selected and mounted on the diffractometer, and the resulting stucture of **3** is shown in Figure 1.[9]

The phosphorus center P1 in **3** is trigonal-planar coordinated. The O2 center of the triflate anion is in line with the P=P vector and has a long contact with the two-coordinate phosphorus atom P2 (P2–O2 3.148(3) Å; P1-P2-O2 175.6°), without causing a structural perturbation. There is no twist around the P=P bond; the central skeleton of the cation is

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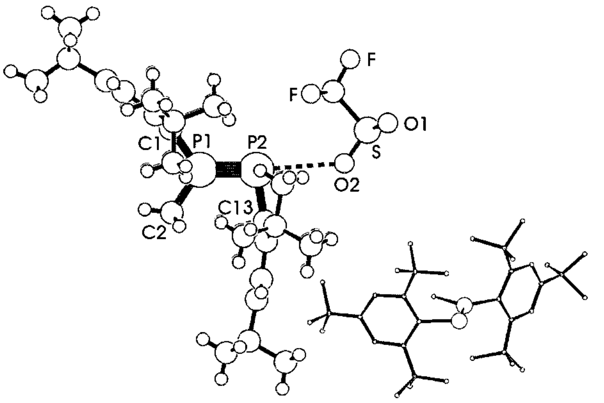
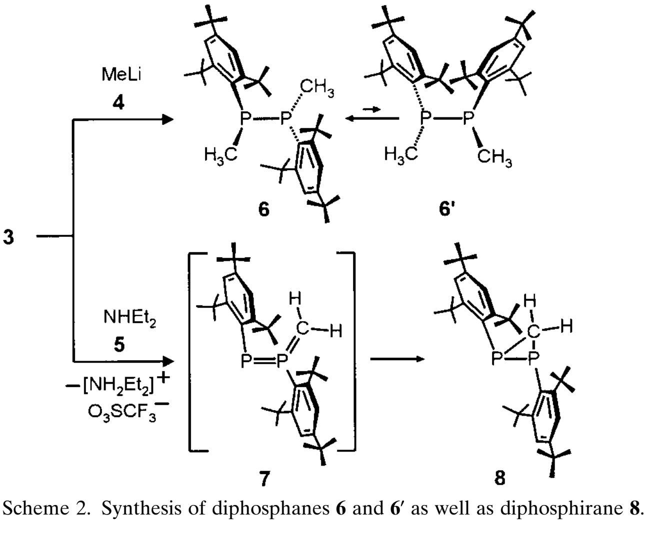


Figure 1. Two different views of the molecular structure of **3**. Left: The mirror plane running through S, O2, P2, P1, C13, C2, C1 coincides with the plane of the page; right: view showing the planar arrangement of the central skeleton. Selected bond lengths [Å] and angles [°]: P1−P2 2.024(2), P1−C1 1.817(5), P1−C2 1.799(4), P2−C13 1.866(4); C1-P1-C2 111.7(3), C1-P1-P2 123.1(2), C2-P1-P2 125.2(2), C13-P2-P1 99.4(2).

perfectly planar (τ(C1-P1-P2-C13) = 0°). The P1=P2 bond (2.024(2) Å) is not significantly shorter than that in diphosphene **1** (2.034(2) Å). The only notable structural difference between the diphosphene **1** and **3** concerns the C_{ispo}-P-P angle, which opens from 102.8° in **1** to 123.1(2)° in **3**.

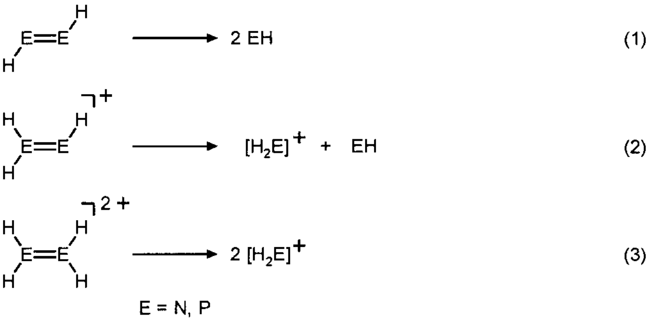
The $[Mes^*P{=}P(Mes^*){-}CH_3]^+$ cation in **3** can be regarded as a λ^5,σ^3-analogue of a λ^5,σ^4-methylphosphonium ion, $[R_3P{-}CH_3]^+$. Since these salts are deprotonated by strong bases to give Wittig ylides, $R_3P{=}CH_2$, **3** was treated with MeLi (**4**) at low temperatures. However, the products are the diastereomeric diphosphanes **6** and **6'**, which arise from addition of the methanide ion (Scheme 2).[10]



Scheme 2. Synthesis of diphosphanes **6** and **6'** as well as diphosphirane **8**.

Addition of diethylamine (**5**) to **3** leads to clean deprotonation and subsequent electrocyclic ring closure to afford **8**. This compound can be obtained as yellow crystals. As previously suggested,[11] the methylenephosphenyl phosphorane **7** is assumed as intermediate. No 1,2-addition products are formed; futhermore, *t*BuOH does not react with **3**.

It is interesting to ask whether the P=P bond is stengthened or weakened upon protonation or alkylation.[12] To this end, we have calculated the bond dissociation energies for HP=PH (**9**), $[H_2P{=}PH]^+$ (**10**), and $[H_2P{=}PH_2]^{2+}$ (**11**; Scheme 3 and Table 1).[13]. For comparison, the corresponding energies for the analogous nitrogen compounds diazene, HN=NH (**12**), diazenium, $[H_2N{=}NH]^+$ (**13**), and $[H_2N{=}NH_2]^{2+}$ (**14**) were calculated as well (Table 1).



Scheme 3. Dissociation reactions of E_2H_2, $[E_2H_3]^+$, and $[E_2H_4]^{2+}$ (E = N, P).

Table 1. Calculated dissociation energies ΔE_{Diss} [kcal mol^{-1}] of **9**–**14** and singlet–triplet excitation energies $\Delta E_{(S\rightarrow T)}$ [kcal mol^{-1}] of EH and $[H_2E]^+$ fragments (E = N, P).[a]

E	ΔE_{Diss} [Eq. (1)]	ΔE_{Diss} [Eq. (2)]	ΔE_{Diss} [Eq. (3)]	$\Delta E_{(S\rightarrow T)}$(EH)	$\Delta E_{(S\rightarrow T)}([H_2E]^+)$
N	+109.7	+146.3	+7.2	−46.6	−31.5
P	+69.1	+87.3	−47.8	−30.3	+16.5

[a] Calculated at the CCSD(T)/6-311G(2d,2p)//MP2/6-31G(d,p) level.

As is the case for the N=N bond, the P=P bond becomes stronger upon protonation. This finding is supported by the observation of an absorption at 638 cm^{-1} in the IR spectrum of **3**, which is assigned to the P=P stretching vibration ($\tilde{\nu}_{calcd}([H_2P{=}PH]^+) = 714$,[7a] 636 cm^{-1} at the MP2/6-31G(d,p) level). This vibration appears at lower wavenumbers in the resonance Raman spectrum of **1** ($\tilde{\nu}_{exp}([Mes^*P{=}PMes^*]) = 610$ cm^{-1}, $\tilde{\nu}_{calcd}([HP{=}PH]) = 614$ cm^{-1} at the MP2/6-31G(d,p) level).[14] The slightly smaller increase of the E=E dissociation energy upon protonation (E = P: 26%; E = N: 33%) is (at least in part) due to the different electronic ground states of the product fragments $[H_2P]^+$ (singlet) and $[H_2N]^+$ (triplet; Table 1). The double bond energy in $[H_2P{=}PH]^+$ (**10**) is diminished by the excitation energy $\Delta E_{(S\rightarrow T)}$ of the $[H_2P]^+$ fragment. However, the sum of the singlet–triplet excitation energies ($\Sigma\Delta E_{(S\rightarrow T)} = -13.8$ kcal mol^{-1} for $[H_2P]^+$ and HP) is still negative. Thus the inequality $\Sigma\Delta E_{(S\rightarrow T)} < \frac{1}{2}E(\sigma+\pi)$ is fulfilled, and the "classical" planar structures seen in **3** or **10** are expected according to the Carter–Goddard–Malrieu–Trinquier (CGMT) model.[15] In this respect, although only third row elements are involved in double bonding, phosphanyl phosphenium ions **3** have a higher double bond quality than methylene phosphonium ions **B**, for which the difference between $\Sigma\Delta E_{(S\rightarrow T)}$ and $\frac{1}{2}E(\sigma+\pi)$ is smaller. However, the data in Table 1 also show that double protonation of diphosphene **9** leads to the unstable dication $[H_2P{=}PH_2]^{2+}$ (**11**),[16a] which suffers from Coulombic explosion, while the analogous nitrogen dications (**14**) are stable and derivatives have been detected by cyclic voltammetry.[16b]

Experimental Section

3: Methyl triflate (**2**, 5 g, 30.5 mmol) was added to a saturated solution of **1** (485 mg, 0.88 mmol) in CH_2Cl_2. Evaporation of solvent and excess **2** led to a yellow residue, which was dissolved in CH_2Cl_2. After addition of hexane, **3** precipitated as an analytically pure, microcrystalline powder, which was isolated by filtration and dried under vacuum (442 mg, 0.62 mmol, yield: 70%). Crystals suitable for an X-ray structure analysis could be obtained by layering a saturated solution of **3** in CH_2Cl_2 with diethyl ether. After 5 min sufficiently large platelets appeared, which had to be removed at once from the mother liquor to avoid decomposition. M.p. 118 °C (decomp.); UV/Vis: $\lambda = 249.4$ ($\pi \rightarrow \pi^*$, P=P), 283.7 ($\pi \rightarrow \pi^*$, aryl), 364.2 ($n \rightarrow \pi^*$, P=P); ^{31}P NMR (CD_2Cl_2): $\delta = 237.0$ (d, $ArCH_3P$), 332.2 (d, $^1J_{PP} = 633$ Hz, ArP); ^1H NMR (CD_2Cl_2): $\delta = 1.38$ (s, 9H, *p-t*Bu), 1.40 (s, 9H, *p-t*Bu), 1.55 (d, $^5J_{PH} = 2.44$ Hz, 18H, *o-t*Bu), 1.60 (s, 18H, *o-t*Bu), 1.86 (dd, $^2J_{PH} = 19.80$, $^3J_{PH} = 4.87$ Hz, 3H, CH_3), 7.66 (dd, $^4J_{PH} = 1.83$, $^5J_{PH} = 1.83$ Hz, 2H, aryl-H), 7.70 (d, $^4J_{PH} = 5.18$ Hz, 2H, aryl-H).

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[10] **6**: At room temperature, only an exchanged-broadened ^{31}P NMR signal is observed; the *meso* form **6** is the dominant diastereomer at low temperatures. M.p. 186 °C; ^{31}P NMR ($CDCl_3$, −60 °C): **6**: $\delta = -32.4$ (s); **6'**: $\delta = -35.8$ (s). The *meso* isomer **6** was also characterized by X-ray structure analysis, and showed no special features (P–P: 2.216(1) Å; $\Sigma°(P) = 315.9$): monoclinic, space group $P2_1/c$; $a = 11.0304(4)$, $b = 19.3032(10)$, $c = 18.2587(8)$ Å, $\beta = 102.003(2)°$; $V = 3802.7(3)$ Å^3; $Z = 4$. Further details can be obtained from the authors.

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Polyoxometalates as Reduction Catalysts: Deoxygenation and Hydrogenation of Carbonyl Compounds[**]

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Ronny Neumann[*]

Investigations concerning the use of polyoxometalates as catalysts in both liquid and gas-phase reactions have intensified significantly over the last decade. These catalytic applications in acid catalysis[1] and oxidation[2] have taken advantage of the strong Brønsted acidity of heteropoly acids and the inherent stability of the polyoxometalate framework to oxidative degradation in the presence of strong oxidants and at high temperatures. Although a few examples of

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