PHOSPHATRIAFULVENES – PHOSPHAALKENES WITH INVERSE ELECTRON DENSITY [1]

Eberhard P. O. Fuchs[a], Heinrich Heydt[a], Manfred Regitz[a,*], Wolfgang W. Schoeller[b], and Thilo Busch[b]

[a] Fachbereich Chemie, Universität Kaiserslautern, Erwin-Schrödinger-Str., D-6750 Kaiserslautern, FRG
[b] Fakultät für Chemie, Universität Bielefeld, Universitätsstr., D-4800 Bielefeld 1, FRG

Abstract: The phosphatriafulvenes **3a,b**, accessible from the cyclopropenone 1 and the lithium phosphides 2, possess inverse electron density as indicated by structure **B**; this can also be deduced from ab initio calculations. In accord with the electronic structure, methyllithium attacks at a carbon atom of the three–membered ring (to **4/5**), carboxylic acid chlorides effect P̲-acylation (to **6**), and dimethyl acetylenedicarboxylate inserts into the P/Si bond (to **8**).

Triafulvenes and the heteroanalogous cyclopropenones and iminocyclopropenes are of interest both in preparative and in theoretical chemistry[2]. Whereas "normal" phosphaalkenes possess electrophilic phosphorus and nucleophilic carbon atoms (as shown by **A**), just the opposite electron distribution (as shown by **B**) is to be expected for triafulvenes **3** with an exocyclic double bond because of the Hückel aromaticity of the three–membered ring unit[3,4].

$$\text{`P}=\text{C}\langle \longleftrightarrow \text{`}\overset{\oplus}{\underset{}{\text{P}}}-\overset{\ominus}{\text{C}}\langle \quad \mathbf{A}_{\text{(normal)}} \qquad\qquad \text{`P}=\text{C}\langle \longleftrightarrow \text{`}\overset{\ominus}{\underset{}{\text{P}}}-\overset{\oplus}{\text{C}}\langle \quad \mathbf{B}_{\text{(inverse)}}$$

We now report on the first synthesis, spectroscopic properties, reactions, and ab initio calculations of such compounds. In analogy to the proven phosphaalkene synthesis from carbonyl compounds and silylated phosphanes[5], reactions of di-tert-butylcyclopropenone[6] (1) with lithium trimethylsilylphosphides[7] **2a,b** give rise to the (2,3-di-tert-butylcyclopropenylidene)phosphanes **3a** (80%) and **b** (90%) in good yields. Formation of the P/C double bond is achieved by cleavage of trimethylsilanolate in the sense of a Peterson olefination; in order to facilitate its separation from **3**, the silanolate is converted to hexamethyldisiloxane and lithium chloride by treatment with chlorotrimethylsilane. Product **3a** is crystalline whereas **3b** is a yellow oil which can be purified by distillation [bulb-to-bulb; 110-120 °C (oven temp.)/5·10⁻⁵ torr]; both are sensitive to hydrolysis and oxidation.
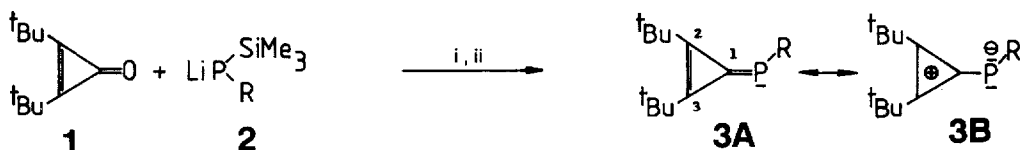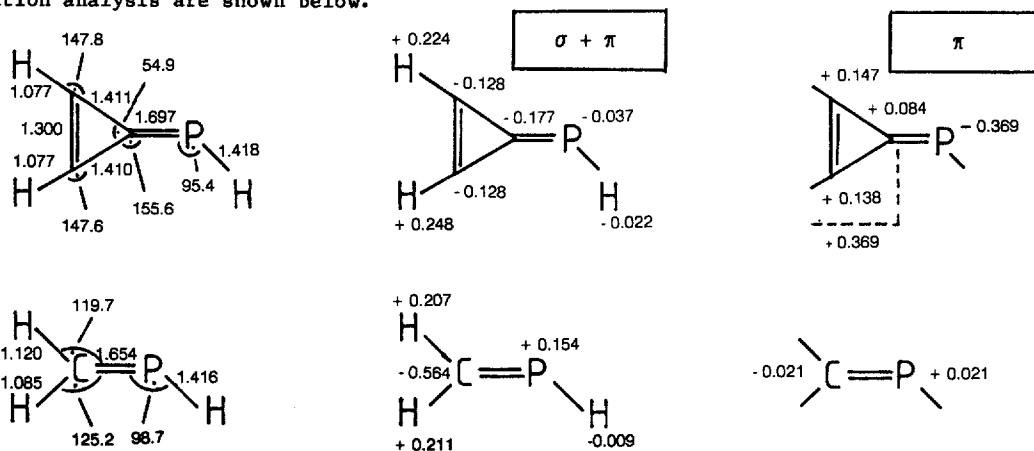

i) ether, -78°C → + 20°C , - LiCl
ii) Me₃SiCl , - (Me₃Si)₂O

2, 3 a: R = SiMe₃; b: R = (structure)

The spectroscopic data of the phosphatriafulvenes, in particular the extreme high-field shifts of the ^{31}P-NMR signals in comparison to those of other phosphaalkenes [C_6D_6; **3a**: $\delta = -74.1$; **3b**: $\delta = -23.2$; cf. mesityl(diphenylmethylidene)phosphane: $\delta = 233.1$; further data for **3a,b**, see Tab. 1] clearly show that the ylide limiting structure **3B** makes a significant contribution to the description of the electron distribution in these phosphaalkenes. Hence, the phosphatriafulvenes **3a,b** represent the first examples of phosphaalkenes bearing exclusively carbon substituents that exhibit inverse electron density.

For an unequivocal confirmation of the constitutions of these unusual phosphaalkenes, **3b** was reacted with W(CO)$_5\cdot$(THF) in tetrahydrofuran at 20 °C and the crystal structure of the resultant pentacarbonyltungsten complex (yellow crystals; m.p. 105 °C) was determined[8].

Ab initio calculations with a double – zeta basis and with inclusion of d functions for the elements P and C[9] for the unsubstituted phosphatriafulvene gave geometry parameters which were in good agreement with the experimental values of the metal complex of **3b**. The geometry-optimized structure as well as the total and π-charge distributions obtained by the Mullikan population analysis are shown below.

The inverse π-electron distribution in phosphatriafulvene is mainly a result of the cyclic conjugated system present, as is also the larger P/C double bond length. The highest occupied molecular orbitals 3a'' (π) and 15a' (σ) have ionization potentials of 7.57 and 9.96 eV, respectively. Comparable calculations on methylenephosphane furnish a reversed polarization of the π-bond (see above).

The inverse electron distribution of the phosphatriafulvenes can also be demonstrated convincingly by chemical means. For example, when **3a** is reacted with methyllithium, regiospecific addition to give the cyclopropenylphosphide **4** occurs (**3b** reacts similarly). After silylation with chlorotrimethylsilane, the cyclopropenylphosphane **5** (70%; colorless oil; purified by bulb-to-bulb distillation at 150 °C/5·10^{-3} torr; spectroscopic data, Tab. 1) is obtained. Reactions with phenyl- and tert-butyllithium also proceed analogously and provide no indication for the formation of products with reversed substitution patterns.

i) MeLi / ether, -78°C → + 20°C   ii) Me$_3$SiCl, - LiCl
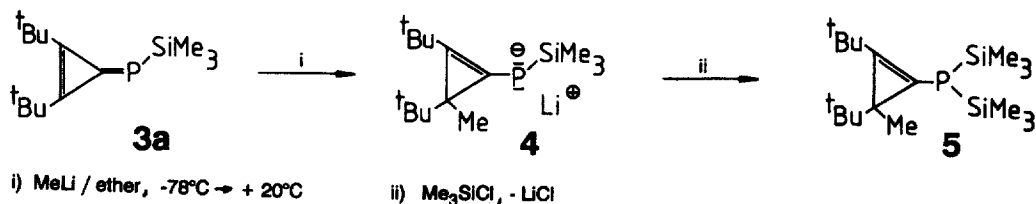
Table 1. Selected NMR Spectroscopic Data [δ (ppm), $\underline{J}$ (Hz)] for Products **3a,b**, **5**, **6a**, and **8**.

3a ^{1}H-NMR (C$_6$D$_6$): 0.60 (d, 9H, $^3\underline{J}_{H,P}$ = 3.7, Me$_3$Si), 1.25 (s, 18H, 2/3-$\underline{t}$Bu), ^{31}P-NMR (C$_6$D$_6$): -74.1; ^{13}C-NMR (C$_6$D$_6$): 2.6 [d, $^2\underline{J}_{C,P}$ = 10.0, (H$_3\underline{C}$)$_3$Si], 27.4, 28.3 [each s, (H$_3\underline{C}$)$_3$C], 33.2, 33.5 [each s, (H$_3$C)$_3\underline{C}$], 158.7 (d, $^2\underline{J}_{C,P}$ = 33.5, C3), 165.1 (d, $^2\underline{J}_{C,P}$ = 11.5, C2), 174.6 (d, $^1\underline{J}_{C,P}$ = 102.5, C1).

3b ^{1}H-NMR (C$_6$H$_6$): 0.83 (s, 9H, $\underline{t}$Bu), 1.10 (s, 9H, $\underline{t}$Bu), 2.18 (s, 3H, $\underline{p}$-Me), 2.66 (s, 6H, $\underline{o}$-Me), 6.90 (d, 2H, $^4\underline{J}_{H,P}$ = 0.68, aromatic H); ^{31}P-NMR (C$_6$H$_6$): -23.2; ^{13}C-NMR (C$_6$D$_6$): 21.0 (s, p-CH$_3$), 23.9 (d, $^3\underline{J}_{C,P}$ = 9.7, $\underline{o}$-CH$_3$), 27.5, 27.9 [each s, (H$_3\underline{C}$)$_3$C], 32.2, 32.6 [each s, (H$_3$C)$_3\underline{C}$], 128-142 (aromatic C), 153.4 (d, $^2\underline{J}_{C,P}$ = 11.9, C2), 156.9 (d, $^2\underline{J}_{C,P}$ = 26.6, C3), 163.7 (d, $^1\underline{J}_{C,P}$ = 85.6, C1).

5 ^{1}H-NMR (C$_6$H$_6$): 0.40 (d, 18H, $^3\underline{J}_{H,P}$ = 4.8, Me$_3$Si), 1.20, 1.35 (each s, 9H, 2/3-$\underline{t}$Bu), 1.38 (s, 3H, Me); ^{31}P-NMR (C$_6$H$_6$): -174.8; ^{13}C-NMR (C$_6$H$_6$): 1.7 [d, $^2\underline{J}_{C,P}$ = 10.9, (H$_3\underline{C}$)$_3$Si], 22.5 (s, CH$_3$), 29.3, 30.0 [each s, (H$_3\underline{C}$)$_3$C], 29.6 [s, (H$_3$C)$_3\underline{C}$], 33.2 [d, $^3\underline{J}_{C,P}$ = 12.8, (H$_3$C)$_3\underline{C}$], 36.3 (s, C3), 109.1 (d, $^1\underline{J}_{C,P}$ = 50.0, C1), 146.7 (d, $^2\underline{J}_{C,P}$ = 18.5, C2).

6a ^{1}H-NMR (C$_6$H$_6$): 1.05 (s, 9H, CO-$\underline{t}$Bu), 1.45 (s, 18H, 2/3-$\underline{t}$Bu); ^{31}P-NMR (C$_6$D$_6$): 9.7; ^{13}C-NMR (C$_6$D$_6$): 27.4 [s, (H$_3\underline{C}$)C]; 27.5 [d, $^3\underline{J}_{C,P}$ = 7.8, (H$_3\underline{C}$)$_3$C-CO], 28.3 [s, C($\underline{C}$H$_3$)$_3$], 32.7 [d, $^3\underline{J}_{C,P}$ = 2.3, (H$_3\underline{C}$)$_3$C], 34.0 [s, (H$_3$C)$_3\underline{C}$], 47.4 [d, $^2\underline{J}_{C,P}$ = 35.8, (H$_3$C)$_3\underline{C}$-CO], 161.4 (d, $^2\underline{J}_{C,P}$ = 11.3, C2), 164.4 (d, $^2\underline{J}_{C,P}$ = 24.6, C3), 174.7 (d, $^1\underline{J}_{C,P}$ = 89.2, C1), 230.6 (d, $^1\underline{J}_{C,P}$ = 88.5, CO).

8 ^{1}H-NMR (C$_6$D$_6$): 0.60 (d, 9H, $^5\underline{J}_{H,P}$ = 0.7, Me$_3$Si), 1.10, 1.40 (each s, 9H, $\underline{t}$Bu), 3.60, 3.70 (each s, 3H, COOMe); ^{31}P-NMR (C$_6$D$_6$): -10.9; ^{13}C-NMR (C$_6$D$_6$): 0.10 [d, $^4\underline{J}_{C,P}$ = 6.3, (H$_3\underline{C}$)$_3$Si], 27.2, 28.2 [each s, (H$_3\underline{C}$)$_3$C], 32.6, 32.7 [each s, (H$_3$C)$_3\underline{C}$], 51.0, 51.4 (each s, COO$\underline{C}$H$_3$), 149.7 (d, $^2\underline{J}_{C,P}$ = 23.1, ethenyl C2), 155.0 (d, $^1\underline{J}_{C,P}$ = 65.9, ethenyl C1), 156.1 (d, $^2\underline{J}_{C,P}$ = 14.3, ring C2), 157.8 (d, $^2\underline{J}_{C,P}$ = 27.5, ring C3), 165.9 (d, $^1\underline{J}_{C,P}$ = 88.4, ring C1), 169.9 (s, 2-$\underline{C}$OOMe), 171.1 (d, $^3\underline{J}_{C,P}$ = 10.3, 1-COOMe).

Electrophiles such as carboxylic acid chlorides or dimethyl acetylenedicarboxylate attack phosphatriafulvenes according to 3B at phosphorus and thus open up new possibilities for phosphaalkene chemistry in which the P/C double bond is not attacked. Thus, reactions of **3a**
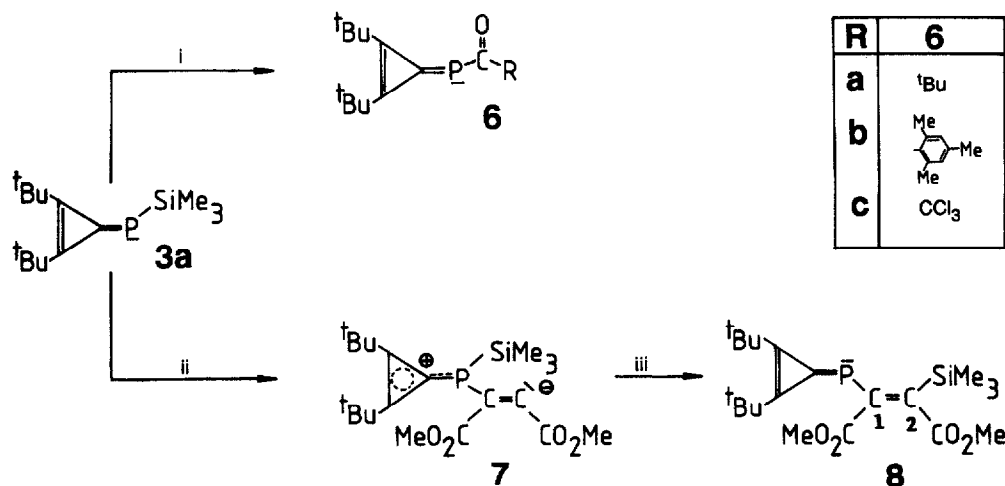
i) R-CO-Cl, ether -78°C → + 20°C, - Me$_3$SiCl

ii) MeO$_2$C-C≡C-CO$_2$Me, ether, 0°C   iii) 1,3 - SiMe$_3$ ∿

with carboxylic acid chlorides proceed via chlorotrimethylsilane elimination to furnish the acylphosphatriafulvenes **6a–c** in yields of about 50%. These products can be isolated as pale yellow crystals after several recrystallizations from pentane (m.p.'s: **6a**, 69 °C; **6b**, 153 °C; **6c**, 85 °C). The ^{31}P-NMR signals at δ = 9.7 (**6a**), 22.3 (**6b**), and 0.0 (**6c**) – i.e. still at very high field – are indicative of an electron distribution comparable to that shown by 3B (further NMR data of **6a**, see Tab. 1).

Dimethyl acetylenedicarboxylate undergoes spontaneous insertion into the P/Si bond of **3a** to form the vinylphosphatriafulvene **8** (90%, red crystals which melt at room temperature)[10]. The high-field ^{31}P-NMR signal at -10.9 (further NMR data, see Tab. 1) again reflects the unusual electronic structure of this class of compounds. It must be assumed that the reaction sequence begins with nucleophilic attack of phosphorus at the alkyne (to **7**)[11] and is concluded by subsequent 1,3-silyl shift (to **8**); the two ester groups are probably in a <u>cis</u>-orientation to each other[10].

References and Notes

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