Donor Stabilization, Transfer Reactions, and Bonding Properties of a Methylenediylphosphenium Ion

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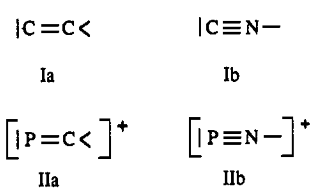
In contrast to isonitriles **Ib**, the methylenecarbenes **Ia** are well known to undergo facile rearrangement to the corresponding acetylenes, as a result of the electron deficiency at the terminal carbon atoms.[1] Correspondingly, the isoelectronic methylenediylphosphenium ions **IIa** are expected to be highly reactive with respect to the iminophosphenium ions **IIb**, which have been recently identified as stable species.[2]

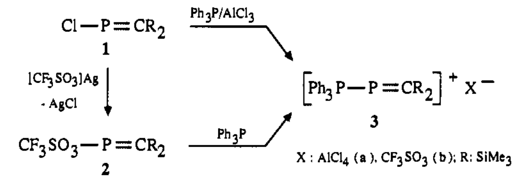


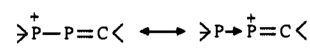
Here, we report on the donor stabilization of the methylenediylphosphenium cation, $[P{=}C(SiMe_3)_2]^+$. The preparation is analogous to that of $[PNAr][AlCl_4]$[2] or $[PNAr][CF_3SO_3]$[3] from $ClP{=}NAr$[2] and $AlCl_3$ or CF_3SO_3Ag but requires the presence of a phosphane donor (Ph_3P).

In a typical preparation, to a toluene solution of chloromethylenephosphane, $ClP{=}C(SiMe_3)_2$[4] (**1**) and Ph_3P (2 mmol) was added an equimolar quantity of $AlCl_3$. Stirring of the reaction mixture for 36 h resulted in the separation of two phases. Removal of the solvent phase gave a viscous oil, from which the product $[Ph_3PP{=}C(SiMe_3)_2][AlCl_4]$ (**3a**) crystallized as a pale yellow solid (yield 35%). The synthesis of $CF_3SO_3P{=}C(SiMe_3)_2$ (**2**) was performed from **1** and $[CF_3SO_3]Ag$ in ether at 25 °C. Precipitation of AgCl indicated the formation of the methylenephosphane **2**.[5] Removal of AgCl by filtration, evaporation of the solvent, and subsequent addition of an equimolar amount of Ph_3P to a cooled (0 °C) solution of **2** in toluene yields $[Ph_3PP{=}C(SiMe_3)_2][CF_3SO_3]$ (**3b**) which has been isolated by crystallization at -30 °C (85% yield).

The AX-type ^{31}P NMR spectrum of **3a**[**b**[6]] (δ 20.2, 300.5; J_{PP} = 450.5 Hz) indicates the linkage of two phosphorus atoms, while the sharp ^{27}Al NMR signal at δ 102 ($\Delta W_{1/2}$ = 2.5 Hz) is in accord with the formation of the ion pair. However, unequivocal

Scheme 1





A B

support for the constitution of **3a**[7][**b**[8]] comes from the X-ray structure analysis (Figure 1). The formation of an isolated anion of **3a** was proven by the ideal tetrahedral symmetry of the anion $[AlCl_4]^-$, as well as the shortest Cl(1)···P(1) contact (3.69 Å), which falls outside the sum of the van der Waals radii. The atoms P(2)–P(1)–C(1)–Si(1)–Si(2) are arranged nearly in one plane, indicating an effective electron transfer from P(1) to the π^*-orbital of the P/C double bond, as shown in resonance structure **A** (a phosphoniomethylenephosphane). However, the lengthening of the P(1)–P(2) bond (2.27 Å), as compared to phosphino-substituted methylenephosphanes,[9] and the relatively large valence angle at phosphorus (113°), as well as the short P(1)–C(1) bond (1.635 Å), provide evidence for some participation of resonance structure **B** (a phosphane–methylenediylphosphenium adduct) to the ground-state **A**. Isomeric *C*-phosphoniophosphaalkenes have been described in the literature.[10-12] The cation reveals the characteristic *E*/*Z* asymmetry of the P–C–Si angles.[13] The structural data of **3b**[8] correspond to those of **3a**.

In solution, **3a** remains unchanged at room temperature, while **3b** decomposes quantitatively to the phosphaalkyne $P{\equiv}CSiMe_3$[14] (**4**) by loss of Ph_3P and $CF_3SO_3SiMe_3$. The reaction conditions differ remarkably from the generally very drastic reaction conditions required in the synthesis of phosphaalkynes.[15] Treatment[16] of **3a** with bis(triphenylphosphane)cyclooctadienenickel(0) furnishes the salt $[(Ph_3P)_3Ni{=}P{=}C(SiMe_3)_2][AlCl_4]$ (**6**)

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(2) Niecke, E.; Nieger, M.; Reichert, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1715–1716.

(3) Detsch, R.; Niecke, E.; Nieger, M.; Reichert, F.; Schoeller, W. W. *Bull. Soc. Chim. Fr.* **1993**, *130*, 25–31.

(4) Appel, R.; Westerhaus, A. *Tetrahedron Lett.* **1981**, *22*, 2159–2160.

(5) Although **2** is stable in solution at 25 °C, removal of the solvent accelerated decomposition to polymeric products, which so far have prevented workup and isolation of pure **2**. However, characterization was possible by means of NMR spectroscopy: ^{31}P NMR δ 343 ($^4J_{PF}$ = 7 Hz); ^{13}C NMR δ 181.5 ($^1J_{CP}$ = 79 Hz), 119 ($^1J_{CF}$ = 320 Hz), 2.0 ($^3J_{CP}$ = 3.4 Hz), 1.2 ($^3J_{CP}$ = 14.5 Hz).

(6) ^{31}P NMR δ 20, 317 ($^1J_{PP}$ = 455 Hz). The instability of **3b** in solution so far prevented determination of the ^{13}C NMR data.

(7) Crystal data for **3a**: ($[C_{25}H_{33}P_2Si_2][AlCl_4]{\cdot}C_7H_8$): MW = 712.5; yellow crystals, dimensions 0.6 × 0.6 × 1.0 mm^3; orthorhombic, space group $P2_12_12_1$ (No. 19); a = 10.585(2), b = 18.665(5), and c = 19.945(5) Å, V = 3.940(2) nm^3, Z = 4, d_{calc} = 1.201 g cm^{-3}, μ(Mo Kα) = 0.485 mm^{-1}, F(000) = 1488. A total of 5175 symmetry-independent reflections ($2\theta_{max}$ = 45°, ω scans) were recorded on a Nicolet R3m diffractometer at T = 293 K. Of these, 3896 reflexions with $|F| > 4\sigma(F)$ were used for the structure solution (direct methods) and refinement (323 parameters) using the SHELXTL-Plus program system. Non-hydrogen atoms were refined anisotropically [full-matrix least-squares, toluene is isotropically with phenyl as a rigid group (r(CC) = 1.395 Å, $\angle$(CCC) = 120°)]. For the resolution of the H-atoms, the riding model was used. R = 0.052 (R_w = 0.054, $w^{-1} = \sigma^2(F) + 0.002F^2$). The absolute structure was determined by a η-refinement (η = 1.3(3)).

(8) Crystal data for **3b**: triclinic, space group $P\bar{1}$ (No. 2); a = 9.509(1), b = 10.987(2), and c = 18.871(5) Å, α = 98.25(2)°, β = 90.45(2)°, γ = 94.65(2)°, V = 1944(1) Å^3, Z = 2, μ (Cu Kα) = 2.51 mm^{-1}. According to the poor quality of the data (no absorption corrections), the disorder of the triflic anion (F and O) and of the solvent (1.5 equiv of toluene in the asymmetric unit), the R value converges to 0.180 (for $|F| > 4\sigma(F)$). Selected data: P(1)–P(2) 2.271(4) Å, P(1)–C(2) 165(1) Å, P(1)–P(2)–C(1) 113.9(4)°, P(1)···O-(SO$_2$CF$_3$) > 4.10 Å.

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(14) Appel, R.; Westerhaus, A. *Tetrahedron Lett.* **1981**, *22*, 2159–2160.

(15) The synthesis of alkynes by elimination reactions has been performed in general at high temperatures. See: Regitz, M. Phosphaalkynes. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme Verlag: Stuttgart, 1991; pp 58–89.

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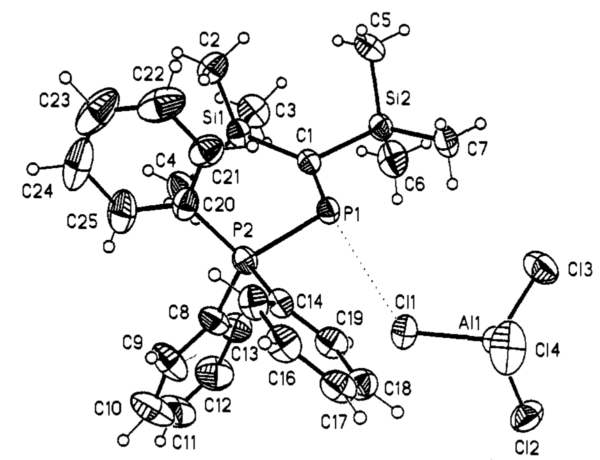

Figure 1. Crystal structure of **3a**. Selected bond lengths (pm) and angles (deg) (30% probability level): P(1)–P(2) 226.7(2), P(1)–C(1) 163.5(6), C(1)–Si(1) 190.2(6), C(1)–Si(2) 192.8(6); P(2)–P(1)–C(1) 112.7(2), P(1)–C(1)–Si(1) 137.0(3), P(1)–C(1)–Si(2) 106.6(3); Cl(1)···P(1) 368.6(3).

by elimination of the labile cyclooctadienyl (cod) ligand. The complex **5** seems to be a reasonable intermediate for the primary reaction step. A comparable reaction mechanism has been proven for the synthesis of metallophosphaallenes by a Cp*-shift from phosphorus to the metal.[17]

Elucidation of the constitution of **6**, which is isoelectronic with a methylidenecarbene complex, was possible on the basis of spectroscopic data. The unchanged sharp resonance in the ^{27}Al NMR at δ 102 proves **6** to be a salt. In the ^{31}P NMR spectrum, AX_3 patterns and a deshielding of the double coordinated P-atom (δ 504.0 (q), 28.8 (d), $^2J_{PP}$ = 77.5 Hz) is observed. However, the relative shielding of this P-atom with respect to the corresponding neutral species, Cp*(Ph_3P)NiP=C($SiMe_3$)$_2$[17c] (δ 722.5, 39.2, $^2J_{PP}$ = 35.0 Hz), as well as the relative large PP coupling constant, indicates an efficient electron transfer from the metal into the π^*-orbital of the PC double bond. Hence, the bonding situation at the phosphorus may be comparable with that found in metallaphosphaallenes, [(CO)$_3$(η^5-C_5H_5)M=P=C($SiMe_3$)$_2$.[18]

In accord with these findings, energy-optimized *ab initio* calculations [MP4SDTQ//6-31+g(d,p)][19] suggest for the parent system **IIa**, PCH_2^+ (r(PC) = 1.612 Å), a larger hydrid affinity

(16) Experimental procedure: in a typical preparation, a toluene suspension of **3a** (1.37 mmol) was added to a solution of an equimolar quantity of (Ph_3P)$_2$-Ni(COD) at 0 °C. After the solution was warmed to room temperature, the color changed frm red to green with formation of two phases. Separation of the solvent phase and cooling of the remaining oily residue to 0 °C afforded crystalline, dark green **6** in 45% yield (dec 65 °C): MS (m/e) 1203.747 ($C_{61}H_{63}AlCl_4NiP_4Si_2$).

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(19) All *ab initio* calculations were performed with the GAUSSIAN 90 program: Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachri, K.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A.; *GAUSSIAN 90*; Gaussian, Inc.: Pittsburgh, PA, 1990.

Scheme 2

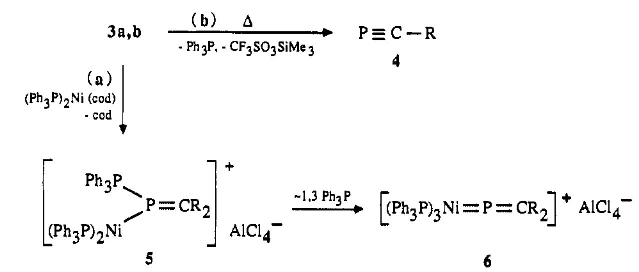

Table 1. Stabilization Enthalpies (in kcal/mol) for P=C(H)R$^+$ [a]

substituent R	conformation: cation	conformation: phosphaalkene[b]	relative energy
H			0.0
CH_3	staggered	staggered[c]	–6.5
SiH_3	staggered	staggered[c]	–20.9
C_6H_5	bridged	planar	–36.4
PH_2	bridged	stagered,[c] cis[c]	–41.2
NH_2	bridged	planar	–29.8
NH_2	planar	planar	–11.0
F			20.6
Cl			11.1

[a] Enthalpy of the reaction HP=C(H)R + P=CH_2 → HP=CH_2 + P=C(H)R$^+$. [b] Substituent R in trans position with respect to H(P). [c] With respect to H(C).

(–47.2 kcal/mol) compared to that of parent **IIb**, PNH^+ (r(PN) = 1.432 Å), as a result of corresponding group-transfer reactions.[20] Furthermore, the stabilization enthalpy and the structure of the cation of the type PC(H)R$^+$ depends strongly on the substituents R[21] (Table 1). Except for R = F, Cl, all substituents exert a sizable stabilization on the parent cation PCH_2^+, most strongly pronounced for R = PH_2 and C_6H_5. Furthermore, these cations adopt a bridged geometry,[21] as has been verified in a recent structural investigation on the diphosphirenium cation.[22] A borderline case is R = NH_2, which exists in a bridged as well as an open geometry.[23,24]

Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, and isotropic and anisotropic displacement coefficients for **3a** (5 pages). 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 the ACS; see any current masthead page for ordering information.

(20) According to PCH_2^+ + *trans*-HPNH → $HPCH_2$ + PNH^+ + E_1, negative values [MP4SDTQ//6-31+g(d,p)] for E_1 refer to an exothermic reaction balance.

(21) A similar geometry trend has been predicted for the P_2R^+ cation: Busch, T.; Schoeller, W. W. *Chem. Phys. Lett.* **1992**, *200*, 26–34. Busch, T.; Schoeller, W. W.; Niecke, E.; Nieger, M.; Westermann, H. *Inorg. Chem.* **1989**, *28*, 4334–4340.

(22) Castan, F.; Baceiredo, A.; Fischer, J.; De Cian, C.; Commenges, C.; Bertrand, G. *J. Am. Chem. Soc.* **1991**, *113*, 8160–8161.

(23) Finally, in contrast to methylenecarbene, the calculations [MP4SDTQ//6-31g(d,p) plus zero-point vibrational energy corrections] result PCH_2^+ being 88.7 kcal/mol more stable than its structural isomer CPH_2^+ (C_s symmetry, r(PC = 1.75 Å) and 38.5 kcal/mol more stable than its corresponding acetylenic isomer $HPCH^+$ (r(PC) = 1.47 Å, $C_{\infty v}$ (symmetry). The former species is separated by a minor enthalpy barrier (0.5 kcal/mol) from rearrangement to the most stable PCH_2^+.

(24) Schoeller, W. W.; Strutwolf, J. *J. Mol. Struct.* (*THEOCHEM*), in press.