The First "Naked" Primary Phosphanide Anion $[ArPH]^{-}$[**]

Valentyn L. Rudzevich, Heinz Gornitzka,
Karinne Miqueu, Jean-Marc Sotiropoulos,
Geneviève Pfister-Guillouzo, Vadim D. Romanenko,
and Guy Bertrand*

Alkali metal phosphanides are key transfer agents in both main group and transition metal chemistry.[1] Although these species are normally represented simply as R_2PM or RPHM, they are usually strongly associated in solution and form aggregates in the solid state through the phosphorus centers bridging two or more metal centers.[2] The structural topology of alkali metal phosphanides is mainly determined by the donor base or coordinating solvent, the radius and polarizability of the metal, and the spatial requirement of the substituents.[3] Although several conceptual approaches have been developed to prevent intermolecular interactions,[4] only a few monomeric alkali metal diorganophosphanides are known, and compounds without a metal–phosphorus bond within a contact ion pair remain extremely scarce.[5] Moreover, despite extensive studies of the alkali metal salts of primary phosphanes, no monomeric structures and no naked monoorganylphosphanides have been described.[4d,f, 6] Here we report on the use of the bulky electron-withdrawing 2,6-bis(trifluoromethyl)phenyl (Ar_f) substituent[7] for the preparation of a naked primary phosphanide anion.

A commonly used synthetic strategy for the preparation of lithium phosphanides involves the treatment of primary or secondary phosphanes with *n*-butyllithium.[1] However, the reaction of organolithium reagents (MeLi and *n*BuLi) with Ar_fPH_2 (**1**) in diethyl ether proceeds in an entirely different manner. A C–P bond is broken, and $MePH_2$ and $nBuPH_2$ are formed as the only phosphorus-containing products after work-up.[8] It is likely that the reaction proceeds through a phosphoranide intermediate,[9] $[Ar_fPH_2(R)]^{-}Li^{+}$, which subsequently undergoes a P–C bond cleavage. Ab initio calculations[10] showed the σ^{*}_{PC} orbital of **1** to be 0.3 eV below that of $PhPH_2$, which readily explains the anomalous reactivity observed.

In contrast, the reaction of the phosphane **1** with one equivalent of KH in THF at −15 °C results in the immediate elimination of H_2 and the formation of a deep red colored solution of potassium phosphanide **2**. The chemical shift of the P atom in **2** ($\delta_P = -91$, $^1J_{P,H} = 173$ Hz, $^4J_{P,F} = 32$ Hz) is significantly deshielded relative to the phosphane precursor **1** ($\delta_P = -140$, $^1J_{P,H} = 216$ Hz, $^4J_{P,F} = 28$ Hz). A further deshielding of the ^{31}P NMR signal ($\delta_P = -73$, $^1J_{P,H} = 163$ Hz, $^4J_{P,F} = 32$ Hz) was observed by addition of one equivalent of [18]crown-6 to a solution of **2** in THF. This result is in sharp contrast to the results observed in the case of the lithium and potassium salts of $MesPH_2$ (Mes = 2,4,6-trimethylphenyl) for which no difference in the ^{31}P chemical shift was observed on addition of crown ethers.[6b] Red/orange crystals suitable for an X-ray crystallographic study were isolated from a mixture of toluene and THF (4:1) at −10 °C. The salt crystallizes as discrete units of formula $[K([18]crown\text{-}6)(Ar_fPH)]$ **3**, with no close intermolecular contacts (Figure 1).[11] The phosphorus atom is three-coordinate and adopts a distinctly trigonal-pyramidal configuration (sum of angles around the phosphorus atom: 345.8°). The P–K distance (329.3 pm) is comparable to those found in structurally characterized oligomeric potassium phosphanides.[6c,d] The potassium cation, in addition to being associated with the P1 atom, is encapsulated by six oxygen atoms of the crown ether, and probably interacts with one fluorine atom (K–F: 311.0 pm).[12] A significant participation of the Ar_f substituent in the delocalization of the negative charge is indicated by the relatively short P1–C1 bond (179.5 pm).

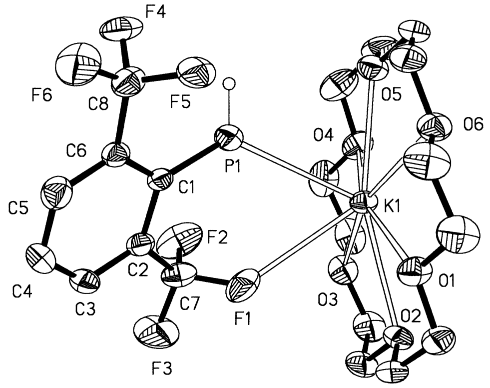

Figure 1. Molecular structure of $[K([18]crown\text{-}6)(Ar_fPH)]$ (**3**). Selected bond lengths [pm] and angles [°]: P1-C1 179.4(9), C1-C2 145.2(7), C2-C3 139.3(7), C3-C4 139.1(6), C4-C5 138.9(7), C5-C6 139.8(7), P1-K1 329.3(2), F1-K1 311.0(1); P1-C1-C2 120.1(2), P1-C1-C6 127.0(3), C2-C1-C6 112.9(3), C3-C4-C5 118.3(3).

To effect complete separation of the metal cation and phosphanide anion, two equivalents of [15]crown-5, which is known to form sandwich complexes with potassium cations, were added to a solution of Ar_fPHK in THF that was generated in situ from Ar_fPH_2 and KH. Recrystallization of the resulting precipitate from THF at −20 °C afforded extremely air and moisture sensitive deep red crystals of $[K([15]crown\text{-}5)_2][Ar_fPH]$ **4**. Analysis by X-ray diffraction reveals that complexation of the potassium cation by two molecules of [15]crown-5 indeed occurs, thus leaving the

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[*] Prof. G. Bertrand, Dr. V. D. Romanenko
UCR-CNRS Joint Research Chemistry Laboratory, UMR 2282
Department of Chemistry, University of California
Riverside, CA 92521-0403 (USA)
Fax: (+1) 909-787-2725
E-mail: gbertran@mail.ucr.edu

Dr. V. L. Rudzevich, Dr. H. Gornitzka
Laboratoire d'Hétérochimie Fondamentale et Appliquée, UMR 5069,
Université Paul Sabatier
118, route de Narbonne, 31062 Toulouse cedex O4 (France)

Dr. K. Miqueu, Dr. J.-M. Sotiropoulos, Dr. G. Pfister-Guillouzo
Laboratoire de Physico-Chimie Moléculaire, UMR 5624
Université de Pau & des Pays de l'Adour
Avenue de l'université, 64000 Pau (France)

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phosphorus atom dicoordinate (Figure 2).[11] Note, that the H atom bonded to the phosphorus atom has been located experimentally, and the observed planar structure was calculated to be around 17 kcal mol^{-1} lower in energy than the structure containing the P–H bond orthogonal to the benzene ring. The P1–C1 bond (179.3 pm) in **4** is half way between that observed for the P–C single bond in the diphosphanomethane **5** (186.9 pm)[13] and the P=C bond in the phosphaquinone **6** (170.5 pm).[14] The benzene ring in **4** exhibits an even stronger distortion than in **3**: the C1–C2 (143.9 pm) and C1–C6 (143.2 pm) bonds are significantly longer than the other C–C bonds in the benzene ring (137.6 – 139.5 pm). These data clearly indicate a delocalization of the negative charge over the ring (**4A**), as confirmed by calculations that found only a small negative charge (–0.32) at the phosphorus atom.[15]

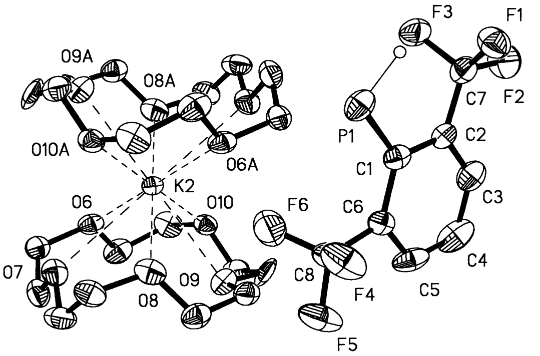
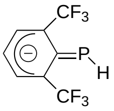
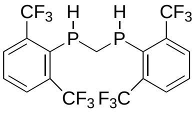


Figure 2. Molecular structure of [K([15]crown-5)$_2$][Ar$_f$PH] (**4**). There are two half molecules of the cationic part in the asymmetric unit, but for clarity only one cation is shown in its full environment. Selected bond lengths [pm] and angles [°]: P1-C1 179.3(6), C1-C6 143.2(7), C1-C2 143.9(7), C2-C3 139.5(8), C3-C4 137.6(8), C4-C5 137.8(8), C5-C6 139.0(8); P1-C1-C2 123.8(4), P1-C1-C6 122.8(4), C2-C1-C6 113.3(5), C1-C2-C3 121.8(5),C3-C4-C5 118.4(6), C4-C5-C6 120.9(6), C5-C6-C1 123.4(6).



4A



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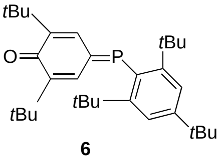

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The ^{31}P NMR signal for complex **4** in THF at room temperature is only slightly deshielded ($\delta_P = -67$) compared to that for **3** and appeared as a doublet of septets ($^1J_{PH} = 163$ Hz, $^4J_{PF} = 32$ Hz), which indicates the magnetic equivalence of the CF_3 groups. However, the ^{19}F NMR signal ($\delta_F = +10$) is broad, which suggests a dynamic phenomenon. The CF_3 groups become magnetically nonequivalent, as evident by the observation of two broad ^{19}F signals at –20 °C. Decreasing the temperature to –50 °C gave well-resolved multinuclear NMR spectra, which clearly supports structure **4A**.[16] For example, the $^{31}P\{^1H\}$ NMR signal obtained at –50 °C is a quartet of quartets ($J_{P,F} = 72$ and 9 Hz), and the six ring carbon atoms are different: the *para* carbon atom is at very high field ($\delta_C = 105.9$) and the *ipso* carbon atom at very low field ($\delta_C = 170.3$), which is in the range expected for phosphaalkenes.

The existence of the naked phosphanide **4**, both in the solid state and in solution, is in line with the calculated high gas-phase acidity of Ar$_f$PH$_2$ (1410 kJ mol^{-1}), compared to those of $PhPH_2$ (1475 kJ mol^{-1}) and PH_3 (calcd: 1524, expt.: 1549 kJ mol^{-1})[17]). In fact, the gas-phase acidity of Ar$_f$PH$_2$ is comparable to that of HCO_2H (calcd: 1401, expt.: 1442 kJ mol^{-1}).[17]

Experimental Section

All reactions and manipulations were carried out in an atmosphere of dry argon by using standard Schlenk procedures or a glove box. Solvents were distilled over Na/K alloy. 2,6-Bis(trifluoromethyl)phenyldichlorophosphane was prepared according to a known procedure.[18]

1: A solution of Ar$_f$PCl$_2$ (13.1 g, 41.5 mmol) in diethyl ether (25 mL) was added dropwise at –60 °C to a stirred suspension of $LiAlH_4$ (3.1g, 82.9 mmol) in diethyl ether (55 mL). After the addition was complete, stirring was continued for 1 h at –60 °C, for 2 h at –30 °C, and for 10 h at room temperature. The solution was then cooled to –30 °C and a 20% aqueous solution of NH_4Cl (20 mL) slowly added. The organic layer was separated, the aqueous phase then treated with 40 mL of a 30% aqueous solution of NaOH and extracted immediately with diethyl ether (100 mL). The combined organic phases were dried with sodium sulfate and **1** purified by distillation: b.p. 31 – 32 °C/0.5 torr (63% yield).

3: A solution of **1** (337 mg, 1.37 mmol) in THF (1 mL) was added to a suspension of KH (55 mg, 1.37 mmol) in THF (3 mL) at –15 °C. The orange solution was stirred for 30 min and then treated with [18]crown-6 (362 mg, 1.37 mmol). After evaporation of the solvent, **3** was recrystallized from a mixture of toluene and THF (4:1; 75% yield).

4: Potassium phosphanide was treated with two equivalents of [15]crown-5 in a similar procedure as for **3**. After recrystallization from THF, **4** was isolated as deep red crystals (83% yield).

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[8] Formally this reaction represents a rare example of the nucleophilic substitution of an organyl group in primary phosphanes. Similar behavior was reported for Cp^*PH_2 (Cp^* = pentamethylcyclopentadienyl): P. Jutzi, G. Reumann, *J. Chem. Soc. Dalton Trans.* **2000**, 2237.

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[10] Ab initio calculations were performed with the Gaussian 98 program.[19, 20] The density functional method[21] used was the hybrid exchange functional B3LYP.[22] This functional includes a linear combination of a small amount (20%) of exact exchange[22a] with the Becke 88 gradient-corrected exchange and with the correlation energy functional LYP.[22c] The basis set retained for all calculations is the 6-31G+(d,p) set, since the inclusion of polarization and diffuse functions is necessary for the obtention of accurate energies. The optimized structure were confirmed as minima on the potential energy surface by second-derivative calculations. All energies were corrected for zero-point energy (ZPE) and temperature using unscaled density functional frequencies. Gas-phase acidities of HA (or proton affinities of A^-) were calculated by $E_{\text{anion}} - E_{\text{neutral}}$.

[11] Crystal data for **3** and **4**: **3**: $C_{20}H_{28}F_6KO_6P$, $M_r = 548.49$, monoclinic, space group $P2_1/n$, $a = 10.44(6)$, $b = 17.38(8)$, $c = 14.53(13)$ Å, $\beta = 94.4(3)^\circ$, $V = 2629(30)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.386$ Mg m^{-3}, $F(000) = 1136$, $\lambda = 0.71073$ Å, $T = 193(2)$ K, $\mu(\text{Mo}_{K\alpha}) = 0.337$ mm^{-1}, crystal size $0.1 \times 0.4 \times 0.7$ mm^3, $1.83 \leq \theta \leq 26.37^\circ$, 15730 reflections (5367 independent, $R_{\text{int}} = 0.0358$), $T_{\min} = 0.825186$, $T_{\max} = 1.0$, 311 parameters, $R1$ $[I > 2\sigma(I)] = 0.0424$, $wR2$ (all data) = 0.0985, max. residual electron density: 0.423 e Å^{-3}. **4**: $C_{28}H_{44}F_6KO_{10}P$, $M_r = 724.70$, monoclinic, space group $P2_1/c$, $a = 11.964(2)$, $b = 12.251(2)$, $c = 23.154(3)$ Å, $\beta = 96.195(3)^\circ$, $V = 3374.0(8)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.427$ Mg m^{-3}, $F(000) = 1520$, $\lambda = 0.71073$ Å, $T = 173(2)$ K, $\mu(\text{Mo}_{K\alpha}) = 0.290$ mm^{-1}, crystal size $0.01 \times 0.5 \times 0.6$ mm^3, $1.71 \leq \theta \leq 21.97^\circ$, 13038 reflections (4108 independent, $R_{\text{int}} = 0.0798$), $T_{\min} = 0.749166$, $T_{\max} = 1.000000$, 4108 parameters, 440 restraints, $R1$ $[I > 2\sigma(I)] = 0.0599$, $wR2$ (all data) = 0.1424, max. residual electron density: 0.529 e Å^{-3}. Data for both structures were collected at low temperature using oil-coated shock-cooled crystals on a Bruker-AXS CCD 1000 diffractometer. Semi-empirical absorption corrections were employed.[23] The structures were solved by direct methods (SHELXS-97)[24] and refined using the least-squares method on F^2.[25] CCDC-166948 (**3**) and -166949 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[15] For comparaison, calculations have shown that the phosphorus atom of the phenylphosphanide bears a charge of −0.43.

[16] Selected NMR data for **4** ($[D_8]$THF, −50 °C): ^{1}H NMR: $\delta = 3.02$ (dqq, 1H, J(P,H) = 161 Hz, J(H,F) = 10 Hz and 4 Hz, PH), 5.69 (pseudo-t, 1H, J(H,H) = 7.5 Hz, p-H$_{\text{arom}}$), 6.80 and 6.81 (m, 1H, m-H$_{\text{arom}}$); ^{19}F NMR: $\delta = 8.4$ (dd, 3F, J(F,P) = 72 Hz, J(F,H) = 10 Hz, CF_3), 10.2 (dd, 3F, J(F,P) = 9 Hz, J(F,H) = 4 Hz, CF_3); ^{31}P NMR: $\delta = -70$ (dqq, J(P,H) = 161 Hz, J(P,F) = 72, 9 Hz); ^{13}C{^{1}H} NMR: 105.9 (d, J(C,P) = 6 Hz, p-C$_{\text{arom}}$), 125.2 and 125.3 (m, o-C$_{\text{arom}}$), 126.8 and 127.1 (q, J(F,C) = 273 Hz, CF_3), 127.6 and 128.1 (s, m-C$_{\text{arom}}$), 170.3 (d, J(C,P) = 87 Hz, i-C$_{\text{arom}}$).

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Cation-Promoted Hierarchical Formation of Supramolecular Assemblies of Self-Organized Helical Molecular Components**

Anne Petitjean, Louis A. Cuccia, Jean-Marie Lehn,*
Hélène Nierengarten, and Marc Schmutz

Helical conformations of organic and inorganic entities have received much attention as a result of their occurence in many biological systems. Maintained by multiple hydrogen bonds and electrostatic interactions, α-helices are involved in

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[*] Prof. Dr. J.-M. Lehn, A. Petitjean, Dr. L. A. Cuccia
Laboratoire de Chimie Supramoléculaire, ISIS-ULP
4 rue Blaise Pascal, 67000 Strasbourg (France)
Fax: (+33) 390-24-11-17
E-mail: lehn@chimie.u-strasbg.fr

Dr. H. Nierengarten
Laboratoire de Spectrométrie
de Masse Bio-Organique, ECPM
25 rue Becquerel, 67000 Strasbourg (France)

Dr. M. Schmutz
Institut de Génétique et de Biologie Moléculaire et Cellulaire, CNRS/INSERM/ULP
BP 163, 67404 Illkirch (France)

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