Synthesis and Structural Elucidation of a "Free" Phosphinoamide Anion

Zhaofu Fei,[a] Rosario Scopelliti,[a] and Paul J. Dyson*[a]

Keywords: N,P ligands / Potassium / Crown ether / X-ray structure

The reaction of the aminophosphane C_6H_4(*o*-CN)$NHPPh_2$ with elemental potassium in the presence of 18-crown-6 affords the phosphinoamide-containing complex [C_6H_4(*o*-CN)N-PPh_2(THF)(18-Crown-6)K] which has been fully characterised in solution and the solid state. The potassium cation interacts with the nitrile substituent group and crown, but does not interact with the P–N bond. The anion appears to be considerably more reactive than related anions in which the cation interacts with the P-N unit, as demonstrated by the reaction with O_2/H_2O which affords [Ph_2P(:O)OK(18-Crown-6)] and C_6H_4(*o*-CN)NH_2. A co-crystal containing these two products was obtained and the structure has been elucidated by single-crystal X-ray diffraction analysis.

Introduction

The chemistry of aminophosphanes and their anionic derivatives (phosphinoamide anions) has been intensively explored over the years.[1] Phosphinoamide anions are frequently used as precursors in synthesis, including, for example, for the synthesis of compounds containing P−P bonds.[2] Detailed structural studies on these anions were first reported by Ashby in 1992,[3] and there are now numerous papers describing the synthesis, structure[4] and reactivity[5] of phosphinoamide anions. Much effort has been directed towards rationalising the nature of the P−N bond in these anions and various theoretical studies have been made.[6] The short P−N distance implies that the bond has mostly double-bond character with the negative charge located on the nitrogen centre; however, their reactivity often leads to different conclusions. For example, in [$Ph_2PNLiPh\cdot(Et_2O)]_2$, while there are both P−Li and N−Li interactions, reaction with Ph_2PCl quantitatively gives $(Ph_2P)_2NPh$. In contrast, the anion of the functionalised aminophosphane [$Ph_2PNLiC_6H_4$(*o*-CN)·(THF)]$_2$, which shows only a N−Li interaction in the solid state, reacts with Ph_2PCl to afford Ph_2P-PPh_2=NC_6H_4(*o*-CN) as the only product.[7]

As far as we are aware, there are no examples of phosphinoamide anions in which the P−N bond does not interact in some way with the cation. Free anions of other types of compounds have been isolated by incorporation of a crown ether during their synthesis which serves to separate the cation from the anion.[8] This strategy has also been used with phosphinoamide-type anions, but weak interactions with the P- and N-centres and the cation remain.[9] However, we proposed that it might be possible to isolate a free anion by combining the crown ether strategy with the use of an appropriate functional group attached to the aminophosphane precursor and we report on our findings in this communication.

Results and Discussion

The reaction of the aminophosphane C_6H_4(*o*-CN)-$NHPPh_2$ (**1**) with elemental potassium in the presence of 18-crown-6 gave the anion **2**. The reaction proceeds smoothly in toluene under ambient conditions. Tetrahydrofuran or diethyl ether can also be used in place of toluene, but the yield of **2** is somewhat lower, with side-products being formed in significant quantities. The ^{31}P NMR spectrum of the reaction mixture in THF exhibits a singlet at δ = 26.5 ppm as the main signal. A signal at δ = −19.1 ppm with low relative intensity (less than 5%) is also observed. Although many phosphinoamide anions have been reported in the last years, supporting ^{31}P and ^{7}Li NMR spectroscopic data are rare. In our experience, under inert conditions, these anions give sharp signals in THF. However, traces of moisture may cause the signals to broaden, sometimes to an extent that the signal is so broad it cannot be observed. The signal at δ = 26.5 ppm in the ^{31}P NMR spectrum of **2** is at slightly lower frequency than that of the parent aminophosphane **1** (δ = 28.5 ppm). In general, phosphinoamide anions give rise to signals at higher frequency than their precursor aminophosphanes.[4,7]

Compound **2** is stable in the solid state or in dry solution under an inert atmosphere and can be stored for weeks without any appreciable decomposition. Crystallisation of **2** from a solution of THF and diethyl ether yielded crystals that were analysed by single-crystal X-ray diffraction. The

[a] Institut de Chimie Moléculaire et Biologique, Ecole Polytechnique Fédérale de Lausanne, EPFL − BCH
1015 Lausanne, Switzerland
Fax: (internat.) + 41-21/6939885
E-mail: paul.dyson@epfl.ch

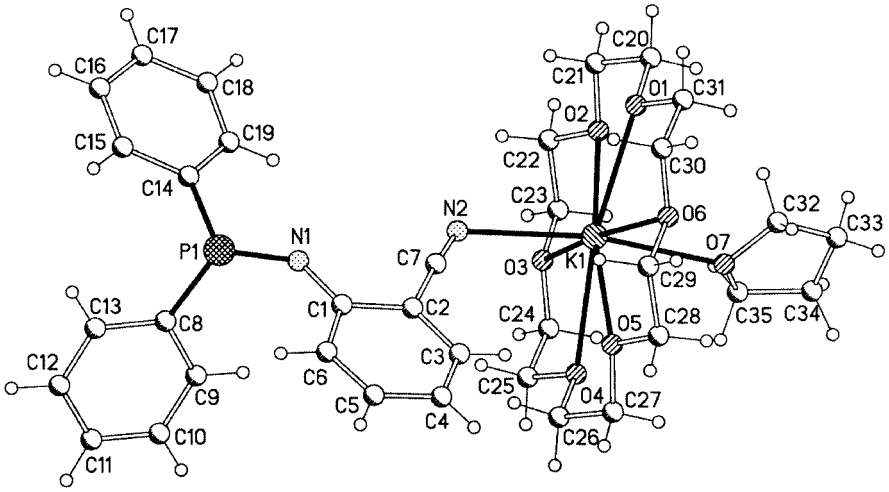

Figure 1. The molecular structure of **2** in the solid state (external THF has been omitted for clarity); key bond lengths (Å) and angles (°) include: P1−N1 1.675(5), N1−C1 1.353(7), N2−C7 1.145(7), K1−N2 2.862(5), N1−P1−C14 100.7(3), N1−P1−C8 106.0(3), C14−P1−C8 101.7(2), C1−N1−P1 118.3(4), C7−N2−K1 126.1(5)

molecular structure of **2** is shown in Figure 1 and key bond parameters are given in the caption. Compound **2** is monomeric, with both the crown ether and the nitrile functional group involved in coordinating to the potassium cation, leaving the P−N unit free. The P−N bond length is 1.675(5) Å, which is somewhat shorter than in the precursor C_6H_4(*o*-CN)NHPPh_2 **1** [1.7155(14) Å]; the N1−C1 bond is considerably shorter [1.353(7) vs. 1.393(2) Å].[7] The bond lengths associated with the P, N and the aromatic ring substituent show delocalization of the negative charge along the ring and, to some extent, towards the P centre.

In keeping with the distinct structural data in both solution and the solid state, the chemical behaviours of **2** differs from that of other phosphinoamide anions. Reaction of **2** with oxygen and water does not lead to the formation of the parent aminophosphane **1**, but results in cleavage of the P−N bond with the formation of [Ph_2P(:O)OK(18-crown-6)] (**3**) and C_6H_4(*o*-CN)NH_2.[10] Previously, re-protonation of phosphinoamide anions has been used to help establish their structure;[2c,2d] reformation of the aminophosphane takes place such that the P−N bond remains intact. For example, [Ph_2PNLiPh·(Et_2O)]$_2$ and [C_6H_4(*o*-CN)PNLiPh·(THF)]$_2$[7] react with O_2/H_2O to give the neutral aminophosphanes, as evidenced by ^{31}P NMR spectroscopy.[11]

The reaction of **2** with O_2/H_2O immediately gave two signals in the ^{31}P NMR spectrum at δ = 82.5 and 12.3 ppm, in approximately equal intensity, corresponding to Ph_2P−O−K[12] and **3**, respectively. After 48 hours, the signal at δ = 82.5 ppm disappears completely, and only the signal at δ = 12.3 ppm remains. There is no evidence for the formation of the original aminophosphane **1** or its oxide. The identity of **3** was confirmed by single-crystal X-ray diffraction analysis. The molecular structure of **3** is shown in Figure 2 and key bond parameters are given in the caption. The structure shows a heptacoordinate potassium cation coordinated to the crown ether and the Ph_2P(:O)O anion, similar structures to this latter unit are known.[13] The C_6H_4(*o*-CN)NH_2 by-product co-crystallises with **3** and interacts via hydrogen bonds with both O atoms of the anion [N1···O1, 3.072(10) Å; N1···O2, 3.270(11) Å] and with one oxygen of the crown ether [N1···O7, 3.195(13) Å].

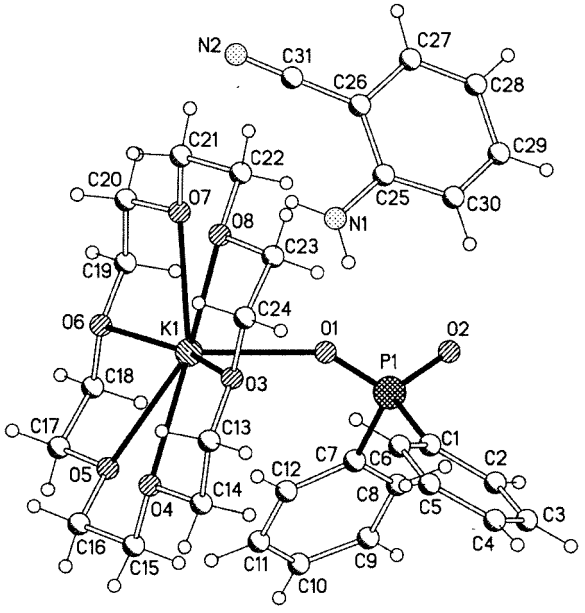

Figure 2. The molecular structure of **3**·C_6H_4(*o*-CN)NH_2 in the solid state; key bond lengths (Å) and angles (°) include: K1−O1 2.578(6), P1−O1 1.504(6), P1−O2 1.495(6), N1−C25 1.39(2), N2−C31 1.11(4), O2−P1−O1 119.7(4), P1−O1−K1, 148.2(3)

In conclusion, we have provided the first experimental example of a "free" phosphinoamide anion. The reactivity of the anion is also markedly different from that of lithium-coordinated anions, being considerably more reactive, although one cannot assume that the solution structure is the same as that observed in the solid state. However, this methodology, in which a crown ether and functional group are utilised in the synthesis of such anions, could lead to new phosphinoamide anion chemistry.

Experimental Section

The compound C_6H_4(*o*-CN)NHPPh_2 (**1**) was prepared by the literature method[7] and all other reagents were purchased from Aldrich and used as received. Solvents were dried using the appropriate reagents and distilled prior to use. NMR spectra were obtained at 20 °C on a Bruker DMX 200 instrument using $SiMe_4$ (for ^1H) and 85% H_3PO_4 (for ^{31}P) as external standards. ESI-MS spectra were recorded on a ThermoFinnigan LCQ Deca XP Plus quadrupole ion trap instrument using literature methods[14] with samples infused directly into the source at 5 μL min^{-1} using a syringe pump. Elemental analysis was carried out by the Institute of Molecular and Biological Chemistry (EPFL).

Synthesis of 2: Elemental potassium (0.078 g, 2.0 mmol) and dry toluene (10 mL) were heated to 100 °C for 5 min with stirring until the potassium was distributed as a fine suspension. After cooling to room temp. the suspension was transferred to a solution of **1** (0.604 g, 2.0 mmol) and 18-crown-6 (0.530 g, 2.0 mmol) in toluene (5 mL). After 5 h stirring at room temp. (heating should be avoided) the evolution of hydrogen gas was complete and all the potassium had disappeared completely. The solvent was removed under vacuum and the resulting solid was recrystallised from THF and diethyl ether. Yield: 1.150 g (81%). ^1H NMR ([D_8]THF): δ = 6.70−8.40 (m, aromatic H), 3.62 (m, OCH_2 of THF), 3.60 (s, OCH_2 of the crown), 1.75 (m, CH_2 of THF) ppm. ^{31}P NMR ([D_8]THF): δ = 26.5 (s) ppm. Positive ion ESI-MS: *m*/*z* = 303 $[C_{12}H_{24}O_6K]^+$. Negative ion ESI-MS: *m*/*z* = 301 $[(C_6H_5)_2PNC_6H_4(o\text{-}CN)]^-$.

Synthesis of 3: A solution of **2** (0.709 g, 1.0 mmol) in THF (10 mL) was exposed to moisture at room temp. for 48 h. The solvent was removed under vacuum and the resulting solid was crystallised from THF and diethyl ether to give the product as colourless crystals. Yield: 0.562 g; 88%. M.p: 101 °C. ^1H NMR ([D_8]THF): δ = 6.60−8.20 (m, aromatic H), 5.95 (broad signal, NH_2), 3.60 (s, OCH_2 of crown) ppm. ^{31}P NMR ([D_8]THF): 12.3 (s) ppm. Positive ion ESI-MS: *m*/*z* = 303 $[C_{12}H_{24}O_6K]^+$. Negative ion ESI-MS: *m*/*z* = 217 $[(C_6H_5)_2P(O)O]^-$. $C_{31}H_{40}KN_2O_8P$ (638.7): C 58.29, H 6.31, N 4.39; found C 58.43, H 6.46, N 4.33.

Crystal Data for 2: $C_{39}H_{54}KN_2O_8P$, *M* = 748.91, monoclinic, space group $P2_1/c$, *a* = 9.5723(6), *b* = 14.3422(12), *c* = 28.928(3) Å, β = 95.072(6)°, *V* = 3955.9(5) $Å^3$, *T* = 140(2) K, *Z* = 4, μ = 0.227 mm^{-1}, λ = 0.71073 Å, 22845 measured reflections, 6367 independent reflections, R_{int} = 0.0771, R_1 [$I > 2\sigma(I)$] = 0.0627, wR_2 (all data) = 0.1771.

Crystal Data for 3: C_6H_4(*o*-CN)NH_2: $C_{31}H_{40}KN_2O_8P$, *M* = 638.72, monoclinic, space group $P2_1/n$, *a* = 9.7036(13), *b* = 14.6000(19), *c* = 23.287(3) Å, β = 93.277(11)°, *V* = 3293.8(7) $Å^3$, *T* = 140(2) K, *Z* = 4, μ = 0.260 mm^{-1}, λ = 0.71073 Å, 19252 measured reflections, 5506 independent reflections, R_{int} = 0.1238, R_1 [$I > 2\sigma(I)$] = 0.0806, wR_2 (all data) = 0.2041.

CCDC-203628 (**2**) and -203629 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We thank the EPFL and Swiss National Science Foundation for financial support.

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[10] In order to assess the influence of the CN group and the crown moiety, two more reactions were carried out: (1) The reaction of the unfunctionalised aminophosphane Ph_2PNHPh with elemental potassium in the presence of 18-crown-6 in a 1:1:1 ratio in THF under the same conditions gave an orange powder that was highly soluble in THF. Recrystallisation from THF and diethyl ether gave orange crystals, but not of sufficient quality for X-ray diffraction analysis. The ^{31}P NMR spectrum ([D_8]THF) of the orange compound displays a singlet at δ = 32.8 ppm. The ESI-MS (positive ion mode) exhibits a peak at *m*/*z* = 303 indicative of $[C_{12}H_{24}O_6K]^+$ (18-crown-6-K)$^+$, indicating that the potassium ion is coordinated to the crown moiety. The ESI-MS (negative ion mode) gives a low intensity peak corresponding to the anion at 276, with the main peak at 292, which is the oxidised product. Based on these data, we are not sure if the potassium is coordinated to the N. Reprotonation of this compound gave signals at δ = 81.3 (Ph_2P-O-K), 27 ($Ph_2P-NHPh$), −71 and −77 ppm (Ph_2P-K?) as the main signals. (2) The reaction of C_6H_4(*o*-CN)NHPPh_2 (**1**) and elemental potassium in a 1:1 ratio without 18-crown-6 gave a yellow powder with a chemical shift of δ = 32.7 ppm in the ^{31}P NMR spectrum. Re-protonation of this compound gave **1** in quantitative yield as indicated by a singlet at δ = 30.7 ppm in the ^{31}P NMR spectrum and a broad signal centred at δ = 5.5 ppm in the ^1H NMR spectrum.

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Received May 1, 2003
Early View Article
Published Online September 12, 2003

