

Understanding Structure Does Not Always Explain Reactivity: A Phosphinoamide Anion Reacts as an Iminophosphide Anion

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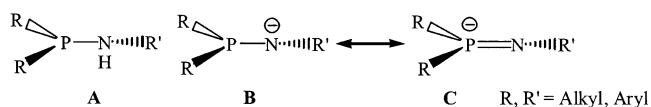
The aminophosphine $C_6H_4(o-CN)NHPPH_2$, **1**, containing an electron-withdrawing nitrile group, was prepared from the lithiation of 2-aminobenzonitrile followed by addition of Ph_2PCl . Lithiation of **1** using $tBuLi$ affords the anion $[Ph_2PN(Li)C_6H_4(o-CN)(thf)]_2$, **2**. Compound **2** reacts with Ph_2PCl or Mel to afford $C_6H_4(o-CN)N=PPh_2-PPh_2$, **3**, and $[C_6H_4(o-CN)N=PPh_2(CH_3)(Li)(C_2H_5O)]_2$, **4**, respectively. In these products new P–P and P–C bonds have been formed rather than N–P and N–C bonds. The structures of **1–4** have been determined by single-crystal X-ray diffraction analysis, and the synthetic results are discussed in terms of the structural data and NMR spectroscopic studies.

Introduction

The chemistry of aminophosphines has been intensively explored over the years,¹ and very recently they have been the subject of a review.² Functionalized aminophosphines have proven to be, for example, particularly interesting ligands in coordination chemistry, with the functional group often exerting a significant influence on the outcome of the reaction.³ Apart from their coordination chemistry, aminophosphines of general formula R_2P-NHR' (**A**) are readily reduced to anions. For example, they can be deprotonated by lithium reagents to give anions of the type $[R_2PNR]^-$ (**B** or **C**) illustrated in Chart 1.

Although anions of type **B** have been known for many years, almost as long as their parent aminophosphines of type **A**,⁴ detailed studies on these species have attracted less attention. As long ago as 1982, Cowley presented spectro-

Chart 1. Aminophosphine and Its Anions

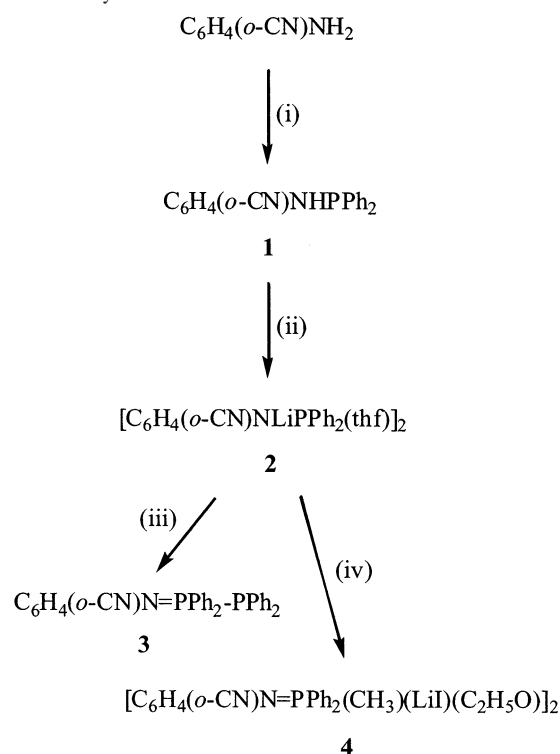


scopic and synthetic evidence concerning a $R_2N-PH-NHR$ ($R = Me_3Si$) system which indicates that an anion similar to type **C** was preferred over type **B**.⁵ However, as far as we are aware, the first known X-ray structure of an aminophosphine anion was not reported until 1992.⁶ The anion in question, $[Ph_2PNPh]^-$, exhibits a dimeric structure and also contains diethyl ether, and is best described as $[Ph_2PN(Li)Ph(OC_2H_5)]_2$. Because there are both P–Li and N–Li interactions in the solid state, this anion was viewed as a resonance hybrid iminophosphide–phosphinoamide (**C–B**) ion. Since then several papers have been published describing the structure of some related anions and dianions in which the lithium ion is not always associated exclusively with the nitrogen.^{7–9} In all the examples where a P–Li interaction is observed in the solid state, no P–Li interaction could be observed in solution using ^{31}P or 7Li NMR spectroscopy. Complexation of these anions gives interesting heterometallic complexes in which both the N- and P-centers are involved

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(1) For example, see: (a) Hartley, F. R. *The Chemistry of Organophosphorus Compounds*; John Wiley & Sons: Manchester, U.K., 1990; Vol. 1. (b) Scherer, O. J. *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Georg Thieme Verlag: Stuttgart, Germany, 1990.
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(4) (a) Scherer, O.; Janssen, W. M. *J. Organomet. Chem.* **1969**, *20*, 111. (b) Schmidpeter, A.; Burget, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 580.

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Scheme 1. Synthesis of **1** and **2**^a

^a Reagents and conditions: (i) ⁿBuLi (1.6 M in hexane), Ph₂PCl, -20 °C; (ii) ⁿBuLi (1.6 M in hexane), -78 °C; (iii) Ph₂PCl, -78 °C; (iv) CH₃I, -78 °C.

in coordination to the metal centers.^{10–12} In addition to the experimental work, ab initio calculations have been carried out that focus on the short P–N bond to delineate the distribution of negative charge and pinpoint the location of the negative charge.¹³ The theoretical investigation suggests that most simple alkyl/aryl derivatives are best described as phosphinoamide anions with the negative charge essentially located on nitrogen. However, examples of products derived from the anions characterized by X-ray crystallography are unknown.

In this paper, we describe a new aminophosphine and its lithiated anion which provide clear structural evidence, in solution and the solid state, for the type **B** structure. To probe the location of the negative charge further, we carried out some reactions with the lithiated aminophosphine which result, in all cases, in oxidative addition at the phosphorus center. The results from these studies are described herein.

Results and Discussion

The reactions described in this paper are summarized in Scheme 1. The new aminophosphine C₆H₄(*o*-CN)NHPPH₂, **1**, was prepared as a colorless solid in high yield by the lithiation of 2-aminobenzonitrile followed by addition of Ph₂PCl in diethyl ether. The ³¹P NMR spectrum contains a

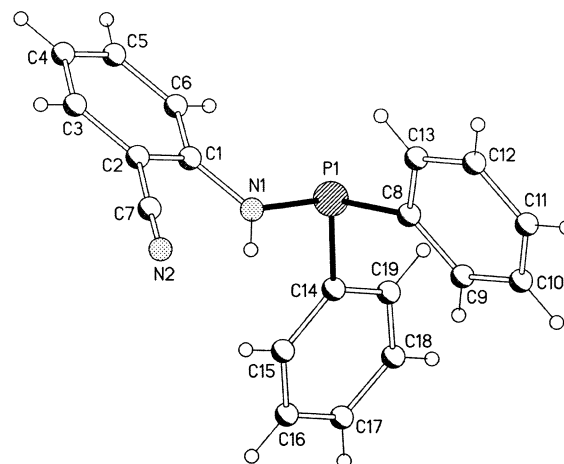


Figure 1. Molecular structure of **1** in the solid state. Key bond lengths (Å) and angles (deg): P1–N1, 1.7155(14); N1–C1, 1.393(2); N2–C7, 1.152(2); N1–P1–C14, 103.99(7); N1–P1–C8, 99.36(7); C14–P1–C8, 102.02(8); C1–N1–P1, 123.68(12).

singlet resonance at 28.5 ppm comparable with those of other aminophosphines.¹⁴ The CN group appears to have a negligible effect on the chemical shift; the chemical shift of the related compound Ph₂PNHPh in the same solvent has the same value.¹⁵ Definitive characterization of **1** was provided by X-ray diffraction analysis which was carried out on a crystal grown from diethyl ether solution at -22 °C.

The solid-state structure of **1** is shown in Figure 1, and key bond parameters are given in the caption. Structural details for compounds **1–4** are listed in Table 1. The P–N distance of 1.7155(14) Å is slightly longer than usually found in aminophosphines with similar structures,¹⁶ and could be due to the electron-withdrawing effect of the nitrile group. The geometry around N1 and P1 shows no particular deviations, and no pyramidalization has been observed for N1. The torsion angle P1–N1–C1–C6 of 17.7(2)° indicates a slight rotation of the phenyl ring with respect to the P1–N1–C1 plane, which could be due to a relatively strong hydrogen bond (Figure 2) linking NH with CN moieties of neighboring molecules related by an inversion center [N–H, 0.88 Å; H···N, 2.25 Å; N···N, 3.086(2) Å; N–H···N, 159.6°].

Lithiation of **1** using ⁿBuLi in thf affords the anion [Ph₂PN(Li)C₆H₄(*o*-CN)(thf)]₂, **2**, in near quantitative yield. Compound **2** exhibits a singlet resonance in the ³¹P NMR spectrum at 39 ppm and a singlet resonance at 0.2 ppm in the ⁷Li NMR spectrum; no evidence for a P–Li interaction is present in solution. Crystallization of **2** from thf and diethyl ether provides a structure that is consistent with the NMR data, and yet initially surprising, since it is dimeric despite the presence of the nitrile group. However, the dimeric

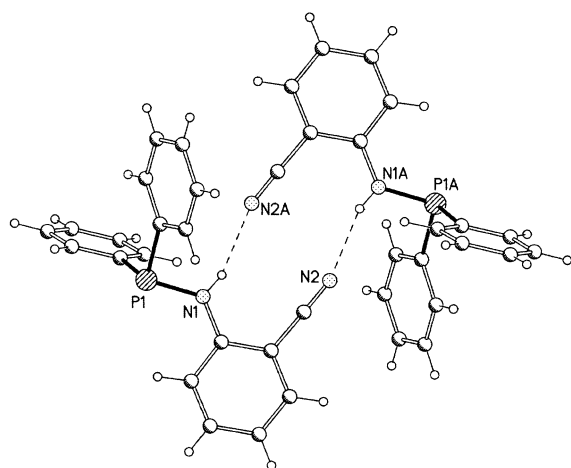
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 (16) For example see, (a) Nöth, H.; Kluck, E. *Z. Naturforsch., Teil B* **1984**, 39, 744. (b) Aucott, S. M.; Slawin, A. M. Z.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **2000**, 2559. (The P–N distance in Ph₂PNHPh is 1.696 Å,¹¹ in PhP(NHPh)₂ 1.695 Å,⁷ in Ph₂PNHPPH₂ 1.692 Å,^{16a} and in Ph₂PNHPy (Py = pyridyl) 1.705 Å.^{16b})

Table 1. Crystal Data and Details of the Structure Determination for 1–4

	1	2	3	4
empirical formula	C ₁₉ H ₁₅ N ₂ P	C ₄₆ H ₄₄ Li ₂ N ₄ O ₂ P ₂	C ₃₁ H ₂₄ N ₂ P ₂	C ₄₈ H ₅₄ I ₂ Li ₂ N ₄ O ₂ P ₂
fw	302.30	760.67	486.46	1048.57
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	P1	P2 ₁ /n	C2/c	P2 ₁ /c
a (Å)	8.5332(8)	8.9580(6)	16.144(6)	20.056(6)
b (Å)	9.5074(9)	21.8518(15)	12.158(7)	13.951(4)
c (Å)	11.2744(14)	10.5675(6)	25.886(11)	18.284(6)
α (deg)	94.107(12)	90	90	90
β (deg)	111.894(9)	96.175(5)	93.72(3)	103.50(3)
γ (deg)	107.422(8)	90	90	90
vol (Å ³)	792.23(14)	2056.6(2)	5070(4)	4974(3)
Z	2	2	8	4
D _{calcd} (g cm ⁻³)	1.267	1.228	1.275	1.400
F(000)	316	800	2032	2112
μ (mm ⁻¹)	0.171	0.148	0.194	1.368
temp (K)	140	140	293	293
wavelength (Å)	0.71073	0.71073	0.71070	0.71070
no. of measured reflns	4686	11807	14205	28584
no. of unique reflns	2453	3545	4456	8776
no. of unique reflns [I > 2σ(I)]	2200	2762	1380	3407
no. of data/params	2453/200	3545/328	4456/317	8776/542
R1 ^a [I > 2σ(I)]	0.0350	0.0359	0.0567	0.0548
wR2 ^a (all data)	0.1086	0.0928	0.1823	0.1821
GOF ^b	1.108	1.064	0.812	0.890

^a R1 = $\sum||F_o| - |F_c||/\sum|F_o|$, wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. ^b GOF = $\{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of data and p is the number of parameters refined.

**Figure 2.** Intermolecular hydrogen bond of 1 in the solid state.

structure is worth comparing to the intermolecular dimer formed by 1 in the solid state. Both form a 12-membered ring, compound 1 involving a dimeric structure based on intermolecular H-bonding (Figure 2), whereas in 2 the dimeric structure is connected via Li–N interactions. The structure of 2 is depicted in Figure 3, and key bond parameters are provided in the caption. Interestingly, the lithium atom is three-coordinated with an almost trigonal-planar geometry, the sum of bond angles around it being 359.9(2)° with an out-of-plane distance of 0.041 Å. There are numerous examples of three-coordinated lithium in the literature that arise because of steric hindrance¹⁷ or by the presence of weak Li–π interactions. In this case, the nitrile is not a very bulky group, and the Li–phenyl ring distances

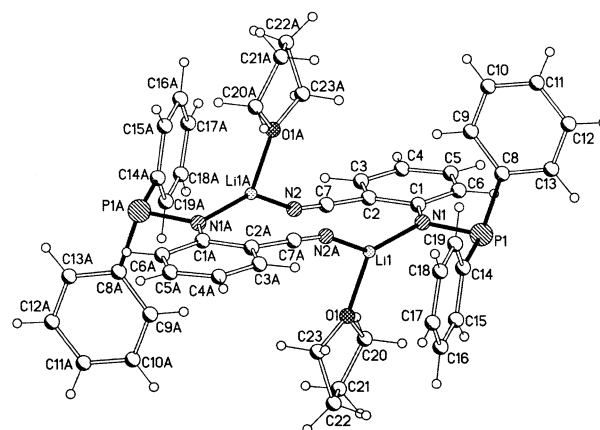
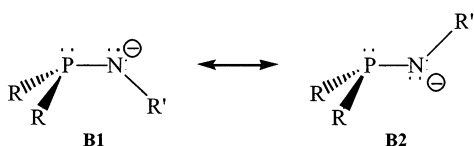


Figure 3. Molecular structure of 2 in the solid state. Key bond lengths (Å) and angles (deg): P1–N1, 1.6996(14); O1–Li1, 1.917(3); N1–C1, 1.359(2); N1–Li1, 1.979(3); N2–C7, 1.150(2); N2–Li1A, 2.010(3); N1–P1–C8, 104.01(7); N1–P1–C14, 98.21(7); C8–P1–C14, 100.44(8); C1–N1–P1, 118.07(11); C1–N1–Li1, 128.51(15); P1–N1–Li1, 111.79(12); C7–N2–Li1A, 158.29(18); O1–Li1–N1, 111.17(15); O1–Li1–N2A, 106.74(15); N1–Li1–N2A, 141.95(18). The letter “A” indicates the following symmetry transformation: $-x, -y, -z$.

are too long to be considered as interacting. The distance between Li and the CN triple bond is 2.618(4) Å, and to the phenyl ring or the closest C-atom the distances are 3.186(4) and 2.699(4) Å, respectively. It therefore seems that both factors contribute to the three-coordinate lithium. The Li–P distance of 3.050(3) Å is also long, showing that there is no interaction in the solid state. The P–N bond length of 1.6996(14) Å is shorter than in the parent compound 1b [1.7155(15) Å], but significantly longer than in [Ph₂PNLiPh(Et₂O)]₂ [1.672(2) Å], and is close to the P–N single bond in neutral aminophosphines, indicating that 2 is best represented as a B-type anion in Chart 1. The P–N bond lengths of aminophosphines with related structures are between 1.690 and 1.710 Å.¹⁶ It is also worth comparing the structure of 2

(17) For example, see: (a) MacDonnell, F. M.; Fackler, N. L. P.; Stern, C.; O'Halloran, T. V. *J. Am. Chem. Soc.* **1994**, *116*, 7431. (b) Veith, M.; Jarczyk, M.; Huch, V. *Angew. Chem., Int. Ed.* **1998**, *37*, 105. (c) Scholz, J.; Görls, H.; Schumann, H.; Weimann, R. *Organometallics* **2001**, *20*, 4394.

Chart 2



with that of **1**. In both structures the nitrile CN bond lengths are the same within experimental error, despite the interaction of the CN group with lithium in **2**.

Calculations on type **B** anions indicate that there is sufficient hyperconjugative bonding to enforce two ground-state configurations, *cis* (**B1**) and *trans* (**B2**); see Chart 2.¹⁸ The *cis* conformation tends to dominate the structures known, although structures with the *trans* conformation are not unprecedented. Compound **2** represents a further example of a *trans* (**B2**) anion.

On the basis of the solid structure of **2**, which indicates that the negative charge is located at the N center, reaction with Ph₂PCl might be expected to give a product with a second P–N bond. However, electrophilic attack takes place at the P center, and the only product formed is the iminobiphosphine C₆H₄(*o*-CN)N=PPh₂–PPh₂, **3**. Although iminobiphosphines such as **3** have been reported before,^{4a,19} X-ray structures are rare.²⁰ In fact, compound **3** is the first structure of a compound generated from a fully lithiated P–N ligand (also of known structure). The ³¹P NMR spectrum of the reaction mixture displays an AB system at 7.5 and –16.0 ppm (¹J(PP) value of 262 Hz). No evidence of a P–N–P product was observed.

Compound **3** is a colorless air-stable solid and can be purified by washing with water. Although it decomposes slowly in halogenated solvents, X-ray suitable crystals can still be obtained within 15 min at –22 °C in dichloromethane/diethyl ether. The structure of **3** is depicted in Figure 4, and key bond parameters are provided in the caption. The most noteworthy features of this structure are the short P=N bond length of 1.569(4) Å and a length of 2.230(3) Å for the P–P bond. The geometry shows no particular deviation for P2, while for P1 the angles are larger [N1–P1–P2, 120.5(2)°], due to steric hindrance. A similar effect is observed for N1, which bears an angle of 132.9(4)° due to the P=N.

It is worth comparing the reaction of **2** with Ph₂PCl with that of [Ph₂PN(Li)Ph(OC₂H₅)₂]₂, in which there is a P–Li interaction in addition to the N–Li interaction [the Li–P distance is 2.684(3) Å].⁶ The reaction of [Ph₂PN(Li)Ph(OC₂H₅)₂]₂ with Ph₂PCl in diethyl ether gives only PhN(PPh₂)₂ in near quantitative yield as indicated by a singlet in the ³¹P NMR spectrum at 67.7 ppm.²¹ No product with a P–P bond was observed. Therefore, the electron-withdrawing CN group and steric effect in the anion **2** would appear to be the determining factors in stabilization of the N=P–P system.

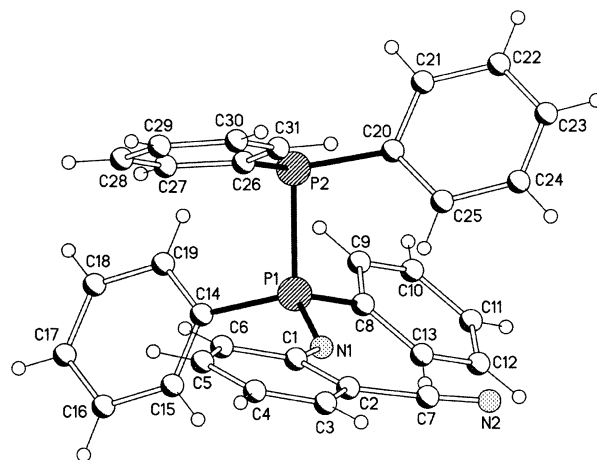


Figure 4. Molecular structure of **3** in the solid state. Key bond lengths (Å) and angles (deg): P1–N1, 1.569(4); P1–P2, 2.230(3); N1–C1, 1.361(6); N2–C7, 1.114(8); N1–P1–C8, 106.3(3); N1–P1–C14, 116.1(3); N1–P1–P2, 120.5(2); C8–P1–P2, 101.5(2); C14–P1–P2, 103.9(2); C20–P2–P1, 101.1(2); C26–P2–P1, 99.84(19); C1–N1–P1, 132.9(4).

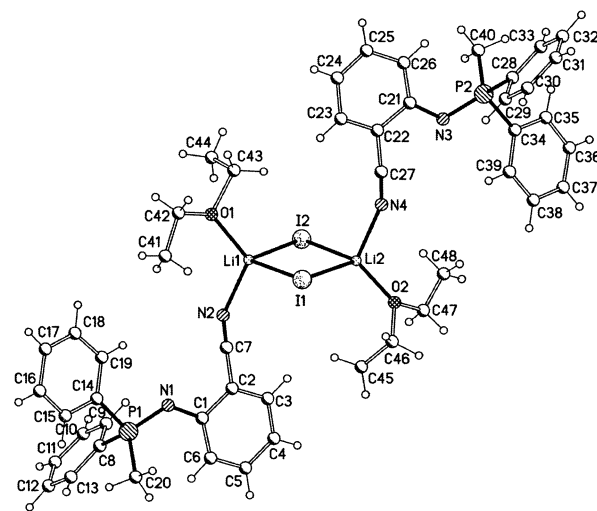


Figure 5. Molecular structure of **4** in the solid state. Key bond lengths (Å) and angles (deg): P1–N1, 1.573(7); P1–C20, 1.771(9); P2–N3, 1.579(7); P2–C40, 1.770(9); N1–C1, 1.370(10); N3–C21, 1.379(10); Li1–I1, 2.805(16); Li1–I2, 2.785(16); Li1–N2, 2.068(19); Li2–I1, 2.767(16); Li2–I2, 2.867(16); Li2–N4, 2.056(18); N1–P1–C20, 117.4(4); N3–P2–C40, 117.2(4); C1–N1–P1, 126.7(6); C21–N3–P2, 124.1(6).

To ascertain whether attack at the P center is sterically controlled, **2** was reacted with the less sterically demanding CH₃I. A suspension of **2** in diethyl ether was treated with equal molar quantities of CH₃I to afford [C₆H₄(*o*-CN)N=PPh₂(CH₃)(LiI)(C₂H₅O)₂]₂, **4**, in near quantitative yield. Compound **4** is insoluble in diethyl ether solution and crystallizes from solution after the reaction is complete. The ³¹P NMR spectrum of **4** shows one singlet at 12.9 ppm in CD₂Cl₂. In the ¹H NMR spectrum, the CH₃ group displays a doublet at 2.26 ppm with a ²J(PH) value of 12.8 Hz.

Crystals of **4** suitable for X-ray analysis were obtained from a solution of dichloromethane and diethyl ether at 5 °C. The structure of **4** is shown in Figure 5, and key bond parameters are provided in the caption. Geometrical parameters dealing with the two P centers and P=N unit are similar to those observed in compound **3**. It is interesting, anyway, to note the presence of LiI, which links two ligands, related

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(21) Seidel, W.; Alexiev, M. Z. *Anorg. Allg. Chem.* **1978**, *438*, 68.

by a *pseudo*-2-fold axis, by their CN moieties. It would appear that the CN group traps the LiI byproduct before it precipitates from the reaction.

Attempts to prepare **3** without going via the anion **2** were made. Direct reaction of **1** with Ph₂PCl in the presence of triethylamine in thf affords **3**, but since the reaction with **1** is considerably slower than the corresponding reaction with the anion **2**, the reaction can be monitored by ³¹P NMR spectroscopy. At the start of the reaction, the reaction mixture shows the same pattern characteristic of **3**, and a peak corresponding to the unreacted aminophosphine **1** at 28.5 ppm, together with a peak at 81 ppm corresponding to the Ph₂PCl starting material. After 4 days of stirring at room temperature, the signals corresponding to **1** and Ph₂PCl disappear completely and only the signals for **3** remain. There is no evidence of the formation of a P–N–P compound in thf, even at low temperature (–20 °C). Under analogous conditions, reaction of Ph₂PNHPh with Ph₂PCl gave only the P–N–P product as indicated by a singlet at 67.7 ppm in the ³¹P NMR spectrum. It is well-known that aminophosphines R₂PNHR may be involved in prototropism, which can lead to imidophosphoranes, viz., R₂PH=NR'.²² It is possible that the presence of the electron-withdrawing CN group may determine that the iminophosphorane R₂PH=NR' is dominant in the reaction of Ph₂PCl.

Concluding Remarks

The structural data and reactivity observed for **2** lead to very different inferences concerning the location of the negative charge. The structural data firmly place the negative charge on the N center, whereas the reactivity toward Ph₂PCl and CH₃I clearly suggests that the anion **2** should be treated as an iminophosphide anion. Of course, it is also possible that initial attack occurs at the N center and then the incoming group is transferred to the P center, but we have no evidence to support such a hypothesis. Many structures of such anions have been published in the past few years; however, functionalized aminophosphine anions may prove more interesting, especially in relation to their reactivities. The reaction of anions such as **2** with Ph₂PCl provides a facile route to iminobiphosphine systems with a N=P–P backbone, which we are currently investigating with a wide variety of reagents. Compound **3**, which contains a P–P single bond, is also highly novel, with no similar compounds obtained by similar reactions having been structurally characterized. The P–P bond is long, which would suggest it is weak. In keeping with this conclusion, all the reactions with **3** that we have carried out thus far result in cleavage of the P–P bond, and we intend to report on these reactions in due course.

Experimental Section

All manipulations were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried using the appropriate reagents and distilled prior to use. NMR

spectra were obtained with a Bruker DMX 200 instrument using SiMe₄ for ¹H, 85% H₃PO₄ for ³¹P, and LiCl for ⁷Li as external standards. ESI-MS spectra were recorded on a ThermoFinnigan LCQ Deca XP Plus quadrupole ion trap instrument. Samples were infused directly into the source at 5 μL min^{–1} using a syringe pump. The spray voltage was set at 5 kV and the capillary temperature at 50 °C. The MS detector was tuned automatically on the base peak, which optimized the remaining parameters. IR spectra were recorded on a Perkin-Elmer 2000 FT IR system. Elemental analysis was carried out by the Institut de Chimie Moléculaire et Biologique, Ecole Polytechnique Fédérale de Lausanne.

X-ray Characterization. Details concerning the crystals and their structure refinement are listed in Table 1, whereas relevant geometrical parameters, including bond lengths and angles, are included into the figure captions. Data collections were performed at 140 K on a four-circle κ goniometer equipped with an Oxford Diffraction KM4 Sapphire CCD for compounds **1** and **2**. Diffraction data for **3** and **4** were measured at room temperature on a marresearch mar345 IPDS. Data reduction was carried out with CrysAlis RED, release 1.6.9 β.²³ Absorption correction was applied to data sets belonging to **2–4**. For **2** a semiempirical method²⁴ has been employed, whereas for **3** and **4** an empirical method²⁵ has been used. Structure solution and refinement as well as molecular graphics and geometrical calculations were performed for all structures with the SHELXTL software package, release 5.1.²⁶ The structures were refined using the full-matrix least-squares method on *F*² with all non-H atoms anisotropically defined. H atoms were placed in calculated positions using the “riding model”. Some disorder problems have been encountered during the refinement of **2** and **4**. In the case of **2** C21 and C22 of a THF ring system have been treated using the splitting method with 0.7 and 0.3 as occupancy factors for sites A and B, respectively. In compound **4** some geometrical restraints have been applied to the Et₂O directly linked to lithium atoms.

Synthesis of C₆H₄(*o*-CN)NHPPPh₂, **1.** The reagent ⁿBuLi (12.5 mL, 1.6 M in hexane, 20.0 mmol) was slowly added to (C₆H₄-*o*-CN)NH₂ (2.36 g, 20 mmol) in 50 mL of dry diethyl ether at –78 °C. The resulting suspension was allowed to warm to –20 °C over 30 min, and Ph₂PCl (4.41 g, 20.0 mmol) was added. The reaction was stirred at room temperature for 30 min and then filtered. From the filtrate large crystals were obtained on cooling at –22 °C. Yield: 4.89 g, 81%. Mp: 88 °C.

¹H NMR (CDCl₃): 5.5 (br signal, 1H, NH), 8.0–6.6 (m, 14H, aromatic H) ppm. ³¹P NMR (CDCl₃): 28.5(s) ppm. IR (cm^{–1}): 3068, 2222, 1599, 1573, 1487, 1455, 1285, 1163, 1092, 896. ESI-MS⁺: *m/z* 303 [M + H]⁺. Anal. Calcd for C₁₉H₁₅N₂P: H, 5.00; C, 75.49; N, 9.27. Found: H, 5.29; C, 75.63; N, 9.18.

Synthesis of [C₆H₄(*o*-CN)NLiPPh₂(thf)]₂, **2.** The reagent ⁿBuLi (1.25 mL, 1.6 M in hexane, 2.0 mmol) was slowly added to compound **1** (0.60 g, 2.0 mmol) in 10 mL of dry thf at –78 °C. The reaction mixture was then stirred for 10 min at room temperature, and the solution was concentrated to about 1 mL. Diethyl ether (10 mL) was added. Crystals were obtained after the solution was cooled at –22 °C overnight. Yield: 0.75 g, 98%.

¹H NMR (thf-*d*₈): 1.75 (m, 8H, CH₂), 3.55 (m, 8H, OCH₂), 6.6–8.1 (m, 28H, aromatic H) ppm. ³¹P NMR (thf-*d*₈): 39.0(s) ppm. ⁷Li NMR (thf-*d*₈): 0.20 (s) ppm.

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Synthesis of $C_6H_4(o-CN)N=PPh_2-PPh_2$, **3. Method A.** To a solution of **2** freshly prepared from **1** (0.60 g, 2.0 mmol) and $nBuLi$ (1.25 mL, 1.6 M in hexane, 2.0 mmol) in dry thf (10 mL) was added Ph_2PCl (0.44 g, 2.0 mmol) at $-78\text{ }^\circ\text{C}$. The reaction mixture was stirred at this temperature for 30 min and then warmed to room temperature. The solvent was removed in a vacuum, and the resulting solid was washed with degassed water ($2 \times 5\text{ mL}$). The colorless solid was then washed with diethyl ether ($2 \times 5\text{ mL}$) and dried under vacuum to give the product **3**.

Method B. To a solution of **1** (0.60 g, 2.0 mmol) and triethylamine (0.21 g, 2.05 mmol) in dry thf (20 mL) was added Ph_2PCl (0.44 g, 2.0 mmol) at $0\text{ }^\circ\text{C}$. The reaction mixture was stirred at room temperature for 4 days and then filtered. The white solid was washed with thf ($3 \times 20\text{ mL}$), and the filtrate was collected. After removal of the solvent the resulting white solid was washed with diethyl ether (10 mL) to give the product. Yield: 0.92 g, 95%. Mp: $158\text{ }^\circ\text{C}$ dec.

1H NMR (thf- d_8): 6.6–8.1 (m, aromatic H) ppm. ^{31}P NMR (thf- d_8): 7.5, -16.0 ($^1J(PP) = 262\text{ Hz}$) ppm. IR (cm^{-1}): 3056, 2215, 1588, 1474, 1446, 1432, 1357, 1285, 1093. ESI-MS $^+$: m/z 487 $[M + H]^+$. Anal. Calcd for $C_{31}H_{24}N_2P_2$: H, 4.97; C, 76.54; N, 5.76. Found: H, 5.16; C, 76.63; N, 5.59.

Synthesis of $C_6H_5N(PPh_2)_2$. To a suspension of $[Ph_2PN(Li)Ph(OC_2H_5)]_2$ in 20 mL of diethyl ether freshly prepared from 0.277 g of Ph_2PNHPh and 0.625 mL of 1.6 M $nBuLi$ ether using a literature method was added 0.221 g of Ph_2PCl at $0\text{ }^\circ\text{C}$. The reaction mixture was stirred at room temperature for 15 min, and then the solvent was removed in a vacuum. The resulting solid was washed with degassed water to give the product. Yield: 0.45 g, 98%. The spectroscopic data were in excellent agreement with those reported in ref 21.

Synthesis of $[C_6H_4(o-CN)N=PPh_2(CH_3)(Li)(C_2H_5O)]_2$, **4.** To a solution of **2**, freshly prepared from **1** (0.60 g, 2.0 mmol), and 1.25 mL of $nBuLi$ (1.6 M in hexane, 2.0 mmol) in dry thf (10 mL) was added CH_3I (0.28 g, 2.0 mmol) at $-78\text{ }^\circ\text{C}$. The reaction mixture was stirred at this temperature for 30 min and then warmed to room temperature. After being stirred for 2 h, the reaction mixture was placed in a freezer at $5\text{ }^\circ\text{C}$ for 24 h. The resulting solid was collected by filtration. Yield: 1.04 g, 99%. X-ray suitable crystals were obtained by cooling a dichloromethane and diethyl ether mixture at $5\text{ }^\circ\text{C}$. Mp: $78\text{ }^\circ\text{C}$.

1H NMR (CD_2Cl_2 , ppm): 6.50–7.90 (m, 28H, aromatic H), 3.50 (q, 8H, $^3J(HH) = 7.0\text{ Hz}$, CH_2 of ether), 2.26 (d, 6H, $^2J(PH) = 12.80\text{ Hz}$, PCH_3), 1.26 (t, 12H, $^3J(HH) = 7.0\text{ Hz}$, CH_3 of ether). ^{31}P NMR (CD_2Cl_2): 12.9 (s) ppm. IR (cm^{-1}): 3053, 2229, 1589, 1471, 1435, 1344, 1284, 1044. ESI-MS $^+$: m/z 316 $[(C_6H_5)_2(CH_3)P=NC_6H_4(o-CN)]^+$; 323 $[(C_6H_5)_2(CH_3)P=NC_6H_4(o-CN)+Li]^+$. Anal. Calcd for $C_{48}H_{54}I_2Li_2N_4O_2P_2$: H, 5.19; C, 54.98; N, 5.34. Found: H, 5.21; C, 55.03; N, 5.29.

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Supporting Information Available: Complete X-ray crystallographic data for **1–4** (CIF format). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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