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Article

NMR, PGSE Diffusion, and X-ray Diffraction Studies of Lithium and Potassium Salts Derived from Diphenylphosphino(*o*-cyanophenyl)aniline and Their Crown Ether Complexes

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^{1}H, ^{31}P, and ^{7}Li pulsed-gradient spin-echo (PGSE) diffusion and variable-temperature NMR results for THF solutions of the lithium and potassium salts derived from diphenylphosphino(*o*-cyanophenyl)aniline are reported and compared to the solid-state results obtained via X-ray diffraction studies. The solution results favor mononuclear salts, sometimes strongly ion paired, whereas the solid-state data reveal dinuclear species. The structures of the products from reactions of these salts with crown ethers are determined via PGSE and ^{1}H Overhauser NMR methods.

Introduction

The chemistry of compounds containing P−N bonds continues to attract considerable attention, with applications in increasingly diverse fields.[1,2] Primary and secondary aminophosphines are especially interesting because the NH acidic hydrogen is easily removed, yielding anions, with a negative charge residing on the P−N unit.[3] The P−N bond in the anion is shorter than the normal P−N single bonds observed in aminophosphines but longer than the P=N double bond moieties found in phosphazenes,[4,7d] suggesting that the bond is intermediate between the two. The facile deprotonation of the N−H bond to afford the corresponding iminophosphoranide anion leads to questions with respect to the distribution of the negative charge.[5,6] Cleavage of iminophosphoranes can also provide phosphinoamides.[7]

A number of interesting "PN" salts have been studied (Chart 1). X-ray diffraction studies for the lithium salt $[\{Li(PPh_2NPh)(Et_2O)_2\}_2]$ (**1**)[8] reveal a dinuclear structure with the two N and two Li centers forming a four-membered ring. The phosphorus lone pair appears oriented toward the lithium ion, hinting at the presence of a P···Li bond, although this interaction is not observed in solution. Interestingly, the structure of the lithium salt $[Li(PPh_2NPPh_2)(THF)_3]$ (**2**) was found to be monomeric with the lithium cation interacting with both the P and N centers.[9] For $LiPPh_2$ (**3**), it has been suggested that polymeric chainlike structures exist in a THF solution.[10] However, using ^{7}Li pulsed-gradient spin-echo (PGSE) diffusion NMR spectroscopy, we have recently reported that the structure is monomeric with the Li cation solvated as $Li(THF)_4^+$.[11] The lithium salts **4**−**8** have been prepared by treatment of the corresponding aminophosphines with *n*-BuLi in diethyl ether or THF. Both $[\{LiPPh_2N$-

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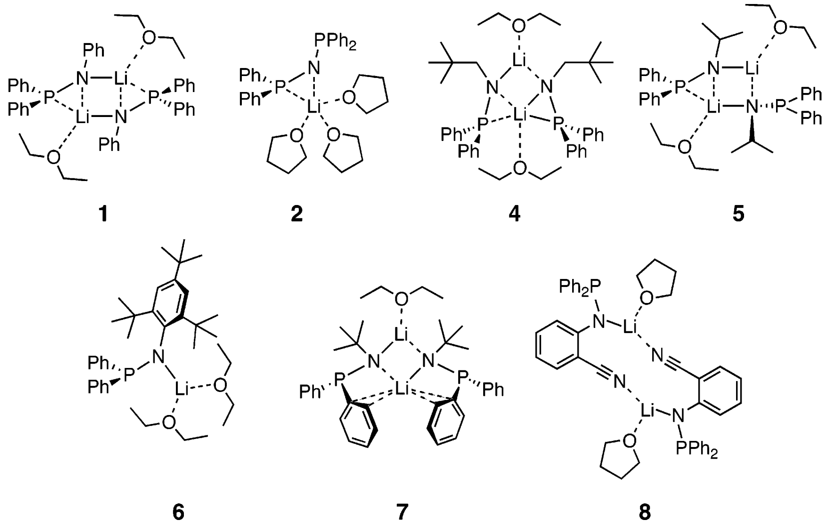
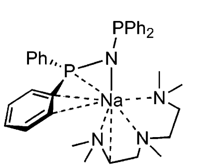
Chart 1. Structures of Known Lithium Salts



(neopentyl)(Et$_2$O)}$_2$] (**4**)[12] and [{LiPPh$_2$N(isopropyl)(Et$_2$O)}$_2$] (**5**)[12] have dinuclear structures in the solid state and are only marginally different from the anion **1**. Compound [LiPPh$_2$N(supermesityl)(Et$_2$O)$_2$] (**6**)[12] is monomeric with a relatively large P···Li separation in the solid state, presumably because of the steric bulk at the N center. The salt [{LiPPh$_2$N(*t*-Bu}$_2$(OEt$_2$)] (**7**)[13] has a dinuclear structure, with two different lithium cations. The nitrile salt [{LiPPh$_2$N(*o*-CN−C$_6$H$_4$)(THF)}$_2$] (**8**) represents the first example of a characterized functionalized phosphinoamide anion.[14] In the solid-state structure of **8**, both lithium ions are equivalent and contribute toward the formation of a 12-membered ring.

A few anions derived from phosphinoamines with sodium and potassium have been described, and their solid-state structures differ depending on the cation and the solvent.[15,16] Reaction of (PPh$_2$)$_2$NH and NaH in the presence of pentamethyldiethylenetriamine (PMDTA) gives the sodium complex **9**.[15] The structure of the iminophosphine anion in the sodium salt, **9**, in the solid state is similar to that observed for **2**; however, weak interactions between the sodium ion and carbon atoms from a phenyl ring and an aliphatic carbon atom from the PMDTA ligand are also present. We also note the interesting THF salt [NaPPh$_2$N(SiMe$_3$)(THF)$_2$].[7c] The reaction of (PPh$_2$)$_2$NH and *t*-BuOK in the presence of PMDTA affords the potassium complex **10**, which is structurally related to **9**, although in **10** there is no interaction between the potassium cation and the phosphorus centers.[16]



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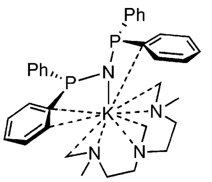

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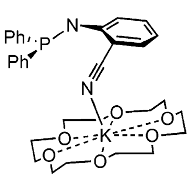

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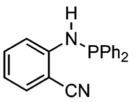
We know of only one report, for the potassium salt **11**, describing the use of a crown ether to trap a cation in this type of chemistry.[17] Interestingly, the nitrile group of the aminophosphine anion in salt **11**[17] seems to carry a substantial amount of negative charge, with the result that both the P and N atoms of the aminophosphine moiety are remote from the potassium ion.

We have occasionally observed that the solution and solid-state structures of group 1 salts may be different and are strongly dependent on the choice of solvent.[11,18,19] Consequently, we have studied the solution structures of the potassium and lithium species, **13** and **14** (derived from ligand **12**), via multinuclear NMR spectroscopy at variable temperatures together with ^{1}H, ^{7}Li, and ^{31}P PGSE NMR diffusion measurements. As a supplement to the X-ray



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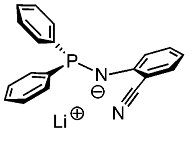

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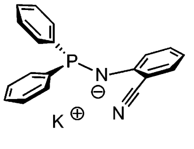

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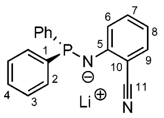
Table 1. ^{1}H and ^{13}C NMR Data for **13** and **14** (**12** in Parentheses) in THF at 299 K



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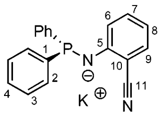
Site	^{1}H	^{13}C
1	-	145.2 (139.5)
2	7.46 (7.57-7.46)	127.9 (128.8)
3	7.26 (7.57-7.46)	132.2 (131.5)
4	7.21 (7.57-7.46)	127.4 (129.5)
5	-	166.4 (150.2)
6	6.97 (7.57-7.46)	118.5 (116.6)
7	6.91 (7.57-7.46)	132.7 (133.9)
8	6.13 (6.88)	110.6 (119.6)
9	7.10 (7.57-7.46)	131.5 (133.0)
10	-	98.6 (100.9)
11	-	125.1 (117.1)



14b

Site	^{1}H	^{13}C
1	-	147.3 (139.5)
2	7.53 (7.57-7.46)	127.9 (128.8)
3	7.27 (7.57-7.46)	131.5 (131.5)
4	7.19 (7.57-7.46)	127.0 (129.5)
5	-	161.6 (150.2)
6	6.72 (7.57-7.46)	118.5 (116.6)
7	6.81 (7.57-7.46)	132.2 (133.9)
8	5.97 (6.88)	108.7 (119.6)
9	7.03 (7.57-7.46)	132.1 (133.0)
10	-	[a] (100.9)
11	-	124.0 (117.1)

[a] Not observed.

structure for **8** (a dinuclear complex), we also report new solid-state results for a potassium analogue, with the composition [$KPPh_2N(o\text{-}CN-C_6H_4)$] (**14**). In the following discussion on measured diffusion constants, we will often refer to a hydrodynamic radius, r_H (which we derive from the Stokes−Einstein equation, where k is the Boltzmann constant, T the temperature, and η the viscosity of the solvent).

$$D = kT/6\eta\pi r_H$$

Although this radius is a solution parameter, it is often useful to compare these r_H values with those based on the literature X-ray data, cited above. For the dinuclear structures **1**, **4**, **5**, **7**, and **8**, one can estimate the radii to be ca. 6.2, 6.3, 6.1, 6.0, and 6.3 Å, respectively, and ca. 6.0 and 6.1 Å for the mononuclear derivatives **2** and **6**, respectively. The X-ray structure for the $Li(THF)_4^+$ cation is known[20a] and affords a radius of ca. 4.9 Å. From the solid-state structures of the PMDTA salts, **9** and **10**, we can estimate radii of 5.8 and 5.9 Å, respectively. The radius estimated for **11** is 6.6 Å. Interestingly, based on the structures for **1**−**11**, in the solid state, the differences in size from mononuclear to dinuclear salts are not always clearly evident. Generally, the r_H value from the PGSE measurement is in good agreement with that calculated from X-ray data.[20b]

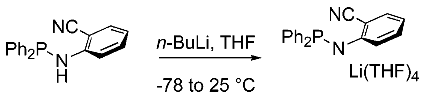
Results and Discussion

Lithium Phosphinoamide (13). The lithium salt of **12**, [$LiPPh_2N(o\text{-}CN-C_6H_4)$] (**13**), has been described previously.[14a] A sample of **13** for NMR studies was prepared by adding *n*-BuLi to the neutral compound $Ph_2PNH(o\text{-}CN-C_6H_4)$ in 1 mL of dry THF-d_8 at −78 °C and then transferring 0.5 mL of this solution to an oven-dried 5-mm NMR tube.

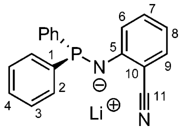
Table 2. D ($\times 10^{10}$ m^2 s^{-1}) and r_H (Å) Values[a] in THF for **12** and **13** at 299 and 209 K

	nucleus	D^b	$r_H{}^c$	r^d	$\delta(^7Li)$	$\Delta\upsilon_{1/2}$
		299 K				
$Li(NAr)PPh_2$	^7Li	9.87	4.8		0.41	5.2
	^{31}P	8.92	5.3			
	^1H	8.99	5.3			
$Li(NAr)PPh_2$	^7Li	9.39	5.0		0.50	11.0
120 mM	^1H	8.58	5.5			
$ArNHPPh_2$	^1H	10.6	4.5	5.1		
	^{31}P	10.6	4.5			
		209 K				
$Li(NAr)PPh_2$	^7Li	1.52	6.0		0.22	19.8
	^{31}P					
	^1H	1.46	6.3			
$ArNHPPh_2$	^1H	2.04	4.5	5.1		
	^{31}P	2.07	4.4			

[a] All at 60 mM. [b] Experimental error is ca. ±2%. [c] η(THF): 299 K = 0.461×10^{-3} kg s^{-1}; 209 K = 1.669×10^{-3} kg s^{-1} (Ar = o-CN−C_6H_4). [d] Estimated using ChemBats3D, by averaging the distances between the centroid and the outer hydrogen.



The assignments of the ^{1}H and ^{13}C NMR signals for this THF solution of **13** are given in Table 1. The ^{1}H and ^{13}C spectra give rise to 7 and 11 individual resonances, respectively.



The ^{1}H NMR spectrum at 299 K exhibits a signal at δ = 6.13, assigned to H8, shifted by ca. 0.8 ppm to lower frequency, relative to the neutral precursor Ph_2PNAr (Ar = o-CN−C_6H_4), **12**, thereby suggesting charge delocalization via this ring. This is supported by the carbon spectrum in which C8 is found shifted 9 ppm to lower frequency. The *ipso* carbon C5 of the NAr fragment and the nitrile carbon are shifted 16.2 and 8.0 ppm to higher frequency, consistent with substantial changes in the aniline aryl moiety.

The ^{31}P NMR spectrum at room temperature of a 60 mM THF solution of **13** consists of a sharp singlet at δ = 40.0 ($\Delta\delta$ = 8.2 ppm), whereas in the ^{7}Li NMR spectrum, a single resonance with a line width of $\Delta\upsilon_{1/2}$ = 5.2 Hz at δ = 0.41 is found. For a 120 mM sample, the observed lithium resonance was broader, $\Delta\upsilon_{1/2}$ = 11.0 Hz, and shifted slightly (see Table 2).

^{1}H, ^{7}Li, and ^{31}P PGSE diffusion data for **13** for the two different concentration samples, 60 and 120 mM, at 299 K are given in Table 2. The agreement between the ^{1}H and ^{31}P PGSE data provides a check on the reliability of the results in that these nuclei reside within the same anion.[21] The ^{7}Li diffusion constant is significantly larger (and the r_H value smaller) than those from the ^{1}H and ^{31}P measurements. Our calculated r_H values of 4.8 Å for the cation and 5.3 Å for the anion in THF indicate a mononuclear rather than a

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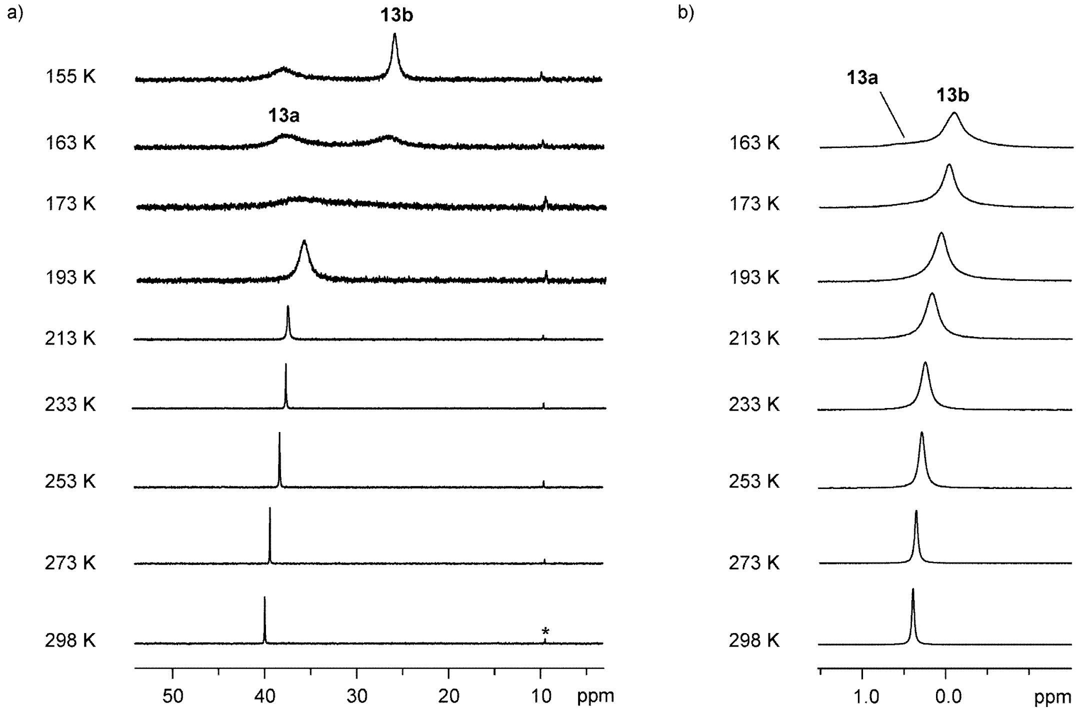

Figure 1. (a) ^{31}P NMR (161.92 MHz) and (b) ^{7}Li NMR (155.45 MHz) spectra of a 60 mM sample of **13** in THF as a function of temperature.

dinuclear species. These r_H values at room temperature suggest separation of the Li^+ and Ph_2PNAr anion and a Li cation probably surrounded by four THF molecules. This is in contrast to the reported X-ray study (i.e., for **8**).[14a]

The PGSE data from the 120 mM sample afford only slightly larger r_H values possibly because of aggregation (remember that the ^{7}Li line width is slightly broader, $\Delta\upsilon_{1/2} = 11.0$ Hz (Table 2), relative to that of the 60 mM sample, $\Delta\upsilon_{1/2} = 5.2$ Hz). We have previously noted that $\Delta\upsilon_{1/2}$ for $Li(THF)_4^+$ as a chloride salt is 2.2 Hz.[19]

A series of ^{1}H, ^{31}P, and ^{7}Li NMR spectra were measured at decreasing temperatures in steps of 20 °C. These ^{31}P and ^{7}Li spectra obtained are shown in Figure 1. There is no $^{31}P-{}^{7}Li$ coupling observed in the range 299−155 K, in keeping with separated ions in a THF solution. At 155 K, two broad ^{31}P signals separated by 12.1 ppm ($\delta = 37.8$ for **13a** and $\delta = 25.7$ for **13b**) in the ratio 1:0.8 are observed. A new sample at 10 mM was prepared and studied at low temperature together with the 120 mM sample. All three concentrations afford essentially the same result (Figure 2), so that we assign these to two isomeric structures rather than differing aggregation states, whose populations are expected to be concentration-dependent.

The variable-temperature ^{7}Li NMR spectra (Figure 1b) reveal two broad partially overlapped signals at 163 K[22] (labeled with **13a**[22] and **13b**[22]). The ^{7}Li line width of 19.8 Hz at 213 K is larger than that observed at ambient temperature, $\Delta\upsilon_{1/2} = 5.2$ Hz. There was no detectable $^{13}C-{}^{7}Li$ coupling constant over the whole range of temperatures, in the ^{13}C NMR spectra.

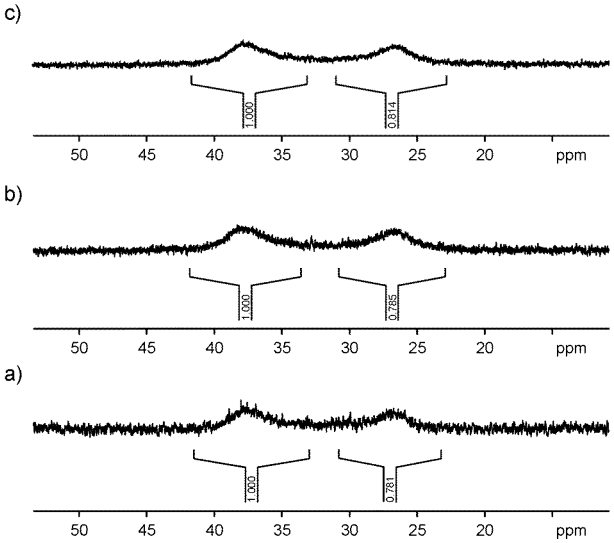

Figure 2. ^{31}P NMR spectra of **13a** and **13b** at 163 K as a function of concentration: (a) 10 mM, (b) 60 mM, and (c) 120 mM (THF, 161.92 MHz).

The ^{1}H and ^{7}Li PGSE data for **13** at 209 K[23] are shown in Table 2. The calculated r_H values of 6.0 and 6.3 Å for cation and anion, respectively, are larger than those found at 299 K, suggesting relatively strong ion pairing and/or aggregation at low temperature. However, on the basis of the variable-concentration study, we suggest that at 209 K, in a THF

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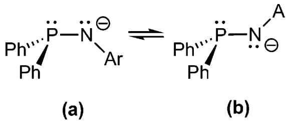
(22) It has been suggested that there is sufficient hyperconjugative bonding in anionic phosphinamides to enforce cis and trans ground-state conformations:



See: Trinquier G.; Ashby, M. T. *Inorg. Chem.* **1994**, *33*, 1306−1313. We presume that the placement of the lithium atom is such that these two afford different Li relaxation time values in **a** and **b**. However, we cannot completely exclude a mixture of dinuclear and mononuclear salts.

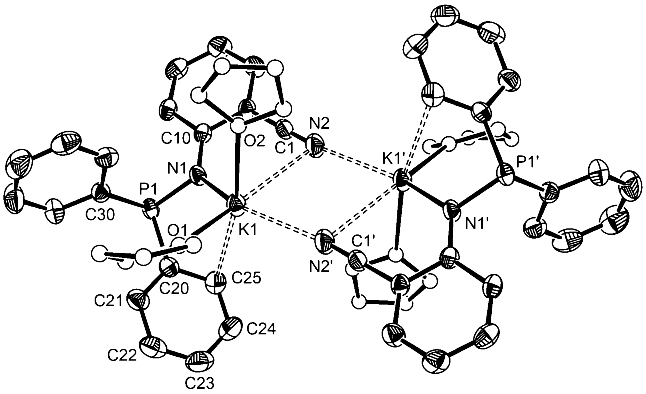
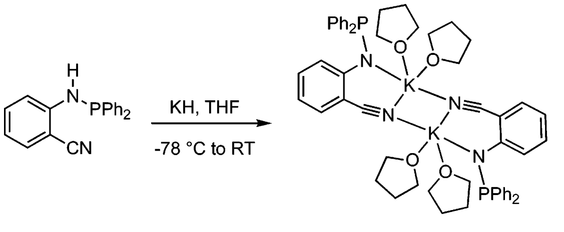


Figure 3. Molecular structure and numbering scheme for salt **14a**. Thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms are omitted for clarity; the atoms of the coordinated THF molecules are drawn with arbitrary radii. Selected bond lengths [Å] and angles [deg]: P1−N1, 1.679(2); C1−N2, 1.145(4); K1−O1, 2.703(3); K1−O2, 2.638(4); K1−N1, 2.783(2); K1−N2′, 2.799(3); K1−N2, 3.125(3); K1−C1, 3.323(3); K1−C20, 3.337(3); K1−C25, 3.346(4); P1−N1−C10, 117.5(2); N1−K1−O1, 123.84(8); N1−K1−O2, 108.9(1); N1−K1−N2, 71.21(7); N2−K1−N2′, 80.45(9); N2−K1−O2, 83.7(1); N2′−K1−O1, 88.74(9); N2′−K1−O2, 88.2(1); O1−K1−C25, 102.1(1); N2−K1−C25, 95.2(1); N2′−K1−C25, 104.75(9); N1−P1−C20, 99.6(1); N1−P1−C30, 105.6(1) (equivalent atoms generated by $-x + 1$, $-y + 1$, $-z + 1$).

solution, the ions of salt **13** are strongly ion paired, explaining the smaller *D* values and larger size.[23]

Potassium Phosphinoamide 14a,b. Reaction of Ph_2PNHAr (**12**) with KH in a THF solution at −78 °C for 10 min gave a bright yellow solution that was filtered. Addition of *n*-pentane, followed by storage overnight at room temperature, afforded yellow crystals of [$\{Ph_2PN(o\text{-}CN{-}C_6H_4)K(THF)_2\}_2$] (**14a**), suitable for X-ray diffraction, as an air-sensitive solid (see eq 1). Compound **14a** is quite stable for several weeks in the absence of air or moisture.



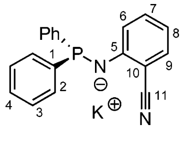
12 **14a** (1)

Figure 3 shows an ORTEP view of the salt **14a**. Details concerning the data collection and refinement are given in Table 3 and the Experimental Section. Clearly, as with **8**, the potassium salt prefers a dinuclear structure in the solid state. Half of the molecule is independent; the other half is generated via a symmetry operation. The observed P1−N1 bond separation of 1.679(2) Å is similar to that found for **1**. The P atom is not involved in bonding to potassium (K1−P1, 3.7252(9) Å) and the two K cations are well separated (K1−K1′, 4.527(1) Å). The local potassium coordination sphere can be regarded as that of a strongly distorted octahedron with four relatively short interactions stemming from the two THF oxygen atoms (K1−O1, 2.703(3) Å; K1−O2, 2.638(4) Å), the phosphinoamide nitrogen atom (K1−N1, 2.783(2) Å), and the donor bond from the remote (second) nitrile nitrogen atom (K1−N2′, 2.799(3) Å). In view of the rather short contacts from the potassium cations to several of the aromatic carbon atoms (K1−C20, 3.337(3) Å; K1−C25, 3.346(4) Å), further weak *π*-arene interactions are conceivable. The pseudo-octahedral environment around K1 is completed via a weak *π* interaction from the immediate nitrile function (3.125(3) Å for K1−N2 and 3.323(3) Å for K1−C1); however, because the C−N nitrile bond length of 1.145(4) Å is consistent with a routine triple bond, this *π* interaction is quite modest. Because of steric interactions between the phosphinoamide moiety and the THF donor molecules, markedly different bond angles around the potassium atom are observed. While the angles involving the phosphinoamide nitrogen atom and the oxygen atoms, 108.9(1)° for N1−K1−O2 and 123.84(8)° for N1−K1−O1, are relatively large, the remaining angles around K1 are fairly small (see the figure caption for more details). Owing to the *π*-arene interactions with the P−phenyl rings, the 12-membered heterocycle adopts a double “bent” arrangement. Assuming weak *π* interactions with the nitrile function, the central structural motif can alternatively be regarded as that of a ladder-type structure comprising two fused six-membered rings and one central K_2N_2 four-membered ring.

Table 3. Crystallographic Parameters for **14a**

formula	$C_{54}H_{60}K_2N_4O_4P_2$
M	969.20
crystal system	triclinic
space group	$P\bar{1}$ and $P\bar{1}$
a/Å	9.882(1)
b/Å	10.759(1)
c/Å	12.719(1)
α/deg	93.098(2)
β/deg	96.393(2)
γ/deg	100.469(2)
V/Å^3	1317.7(2)
Z	1
d/(mg m^{-3})	1.221
T/K	200
2θ range/deg	$3.86 \leq 2\theta \leq 56.56$
index ranges	$-13 \leq h \leq 13$ $-14 \leq k \leq 14$ $-16 \leq l \leq 16$
μ/mm^{-1}	0.287
cryst dimens/mm	0.61 × 0.24 × 0.16
radiation	Mo Kα; graphite monochromator
reflns measured	13 810
unique reflns	6495 ($R_{int} = 0.0242$)
no. of params/restraints	298/24
R1 (reflns $I > 2\sigma(I)$)	0.0783
wR2 (all data)	0.2155
max/min residual electron density [e Å^{-3}]	0.958/−0.553

The solution for the NMR study on this potassium salt, **14b**, was prepared as described above. The ^1H and ^{13}C NMR data for **14b** are similar to those found in **13**; see Table 1. Apart from the broadening of the signal for C10, one finds similar changes in C5 and C11.



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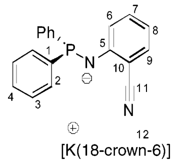
[23] PGSE measurements on very broad signals are not usually productive because the signal intensity is not readily monitored. The ^7Li T_1 at 209 K is 27 ms, but at lower temperatures, the T_1’s are <20 ms. Consequently, the diffusion studies were done at 209 K.

Table 4. D ($\times 10^{10}$ m^2 s^{-1}) and r_H (Å) Values[a] for **14** and **12** in THF at 299 K

	nucleus	D^b	$r_H{}^c$	r^d
K(NAr)PPh$_2$	^{31}P	8.56	5.5	
	^{1}H	8.60	5.5	
ArNHPPh$_2$	^{31}P	10.6	4.5	5.1
	^{1}H	10.6	4.5	

[a] All at 60 mM. [b] Experimental error is ca. ±2%. [c] η(THF): 299 K = 0.461 × 10^{-3} kg s^{-1}. [d] Estimated using ChemBats3D, by averaging the distances between the centroid and the outer hydrogen (Ar = o-CN−C$_6$H$_4$).

Table 5. ^{1}H and ^{13}C NMR Data for **15** (**14** in Parentheses) in THF at 299 K

	Site	^{1}H	^{13}C
 **15**	1	-	149.4 (147.3)
	2	7.69 (7.53)	127.2 (127.9)
	3	7.16 (7.27)	131.2 (131.5)
	4	7.06 (7.19)	126.1 (127.0)
	5	-	164.2 (161.6)
	6	6.56 (6.72)	118.5 (118.5)
	7	6.71 (6.81)	132.7 (132.2)
	8	5.82 (5.97)	106.8 (108.7)
	9	6.97 (7.03)	132.4 (132.1)
	10	-	[a]
	11	-	124.4 (124.0)
	12	3.52	70.47

[a] Not observed.

The 299 K ^{31}P NMR spectrum consists of a sharp singlet at $\delta = 37.6$, ca. 2.4 ppm to lower frequency relative to the lithium analogue **13**, $\delta = 40.0$.

^{1}H and ^{31}P PGSE diffusion data for a 60 mM sample at 299 K are given in Table 4. The calculated radius of 5.5 Å for the anionic fragment is rather similar to, but slightly larger than, those obtained for **13** and *much* smaller than that estimated from the data from the X-ray structure for the dinuclear structure, **14a**, 6.8 Å. The low-temperature ^{31}P NMR spectra (see the Supporting Information) showed only a single resonance down to 155 K. Once again, it appears that the solution structure in THF is different from that for **14a**; i.e., the solution structure, **14b**, is a solvated mononuclear salt rather than a dinuclear, bridged species.

Complexation with Crown Ethers. Treatment of the potassium salt generated in a THF solution at room temperature with a stoichiometric amount of 18-crown-6 ether, followed by stirring for 30 min, afforded the new salt, **15**. The 299 K ^{31}P NMR spectrum consists of a sharp singlet at $\delta = 32.3$, shifted 5.3 ppm from the solution value for **14b**, $\delta = 37.6$. The low-temperature ^{31}P NMR sequence for **15**, in the presence of crown ether (see the Supporting Information), shows only a single sharp signal down to 155 K. The ^{1}H and ^{13}C spectra reveal a single new species, whose NMR characteristics do not differ markedly from those found in **14b** (Table 5).

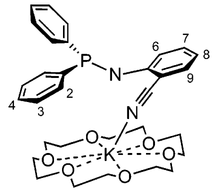
^{1}H and ^{31}P PGSE diffusion data for a 60 mM sample of the potassium salt **15** at 299 K are given in Table 6, along with the D value for 18-crown-6. The anionic fragment and the crown ether are moving at almost the same rate; i.e, there is an interaction between these two moieties, leading to r_H values (6.6−6.9 Å) that are much larger than those of either of the two separate components. Our r_H values are in agreement with the radius of 6.6 Å found in the solid state for the crown ether salt, **11**.[17]

Table 6. D ($\times 10^{10}$ m^2 s^{-1}) and r_H (Å) Values[a] for the Crown Ether Complexes in THF at 299 K

	nucleus	D^b	$r_H{}^c$	r^d	$\delta(^7$Li)	$\Delta\nu_{1/2}$
K(NAr)PPh$_2$ (**14b**) + 18-crown-6 (1 equiv)	^{31}P	6.86	6.9			
	^{1}H	6.83	6.9			
	^{1}H(crown)	7.18	6.6			
	^{1}H(THF)	25.5	1.8	1.7		
Li(NAr)PPh$_2$ (**13**) + 18-crown-6 (1 equiv)	^{7}Li	9.83	4.8		0.37	5.5
	^{31}P	8.80	5.4			
	^{1}H	8.76	5.4			
	^{1}H(crown)	12.1	3.9			
Li(NAr)PPh$_2$ (**13**) + 12-crown-4 (1 equiv)	^{7}Li	9.46	5.0		0.46	6.2
	^{31}P	8.43	5.6			
	^{1}H	8.50	5.6			
	^{1}H(crown)	14.6	3.3			
Li(NAr)PPh$_2$ (**13**) + 18-crown-6 (6 equiv)	^{7}Li	8.23	5.8		0.21	5.8
	^{31}P	7.48	6.3			
	^{1}H	7.52	6.3			
	^{1}H(crown)	10.5	4.5			
18-crown-6	^{1}H	12.5	3.8	4.3		
12-crown-4	^{1}H	14.7	3.2	4.0		

[a] All at 60 mM (Ar = o-CN−C$_6$H$_4$). [b] Experimental error is ca. ±2%. [c] η(THF, 299 K) = 0.461 × 10^{-3} kg s^{-1}. [d] Estimated using ChemBats3D, by averaging the distances between the centroid and the outer hydrogen.

The ^{1}H−^{1}H NOESY spectrum of **15** (Figure 4) reveals strong selective contacts from the crown ether methylene protons (vertical axis) to the two ortho and meta protons of the aryl phosphine plus a weak interaction with the p-phenyl protons of the same rings and a specific contact to H9 of the nitrile moiety. Consequently, in a THF solution, we favor an ion-paired structure in which the Ph$_2$PNAr anion approaches the complexed potassium cation via the nitrile nitrogen atom as shown above. This structure brings H9 close to the crown ether. The two equivalent P−phenyl groups can approach the macrocyclic ether via rotations around the N−C5 and P−N bonds.



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Treatment of the lithium phosphinoamide, **13**, with stoichiometric amounts of 18-crown-6 and then, separately, with 12-crown-4 ethers gave no apparent change in their NMR spectra. The ^{1}H, ^{7}Li, and ^{31}P diffusion results reveal no effect on the translation of the ions (see Table 6); i.e., neither of the crown ethers trap the lithium cation. Interestingly, a pronounced change in the ^{1}H and ^{13}C chemical shifts is observed when a 6-fold excess of the 18-crown-6 ether is employed. The ^{31}P NMR chemical shift for this solution appears at $\delta = 39.0$, and the ^{7}Li NMR spectrum at 299 K reveals a singlet at $\delta = 0.21$ with a line width of 5.8 Hz.

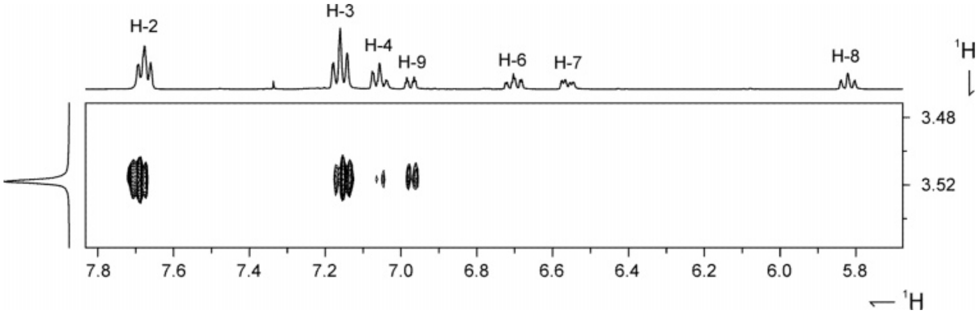

Figure 4. ^{1}H−^{1}H NOESY spectrum of **15** revealing the selective contacts from the crown ether methylene protons to H9, plus the ortho, meta, and para phosphine phenyl protons (THF, 400 MHz).

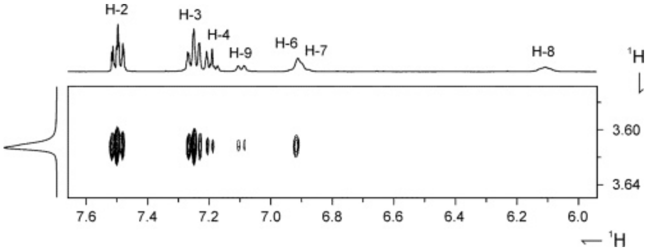

Figure 5. ^{1}H−^{1}H NOESY spectrum of **13** revealing the selective contacts from the crown ether methylene protons to the ortho, meta, and para phosphine phenyl protons plus selective contacts to H6(7) and now a weak contact to H9 (THF, 400 MHz).

^{1}H, ^{7}Li, and ^{31}P PGSE diffusion data reveal considerably larger r_H (and smaller D) values for the lithium cation, 5.8 Å, the phosphinoamide anion, 6.3 Å, and the 18-crown-6 ether, 4.5 Å (see Table 6). The coordination of the lithium to the larger 18-crown-6 ether at the expense of THF slows the translation of the lithium cation and produces a decrease in the ^{7}Li D value. The 6-fold excess of crown ether serves to shift the equilibrium in favor of the metal complex with a consequent slowing of the *average* movement of the crown ether.

In the presence of the excess crown ether, the ^{1}H−^{1}H NOESY spectrum (Figure 5) now reveals close interactions between the methylene protons of the ether and the anionic P−N moiety. Selective cross-peaks to the three P−phenyl protons are observed. Further, one finds a modest contact to H6 (or H7) and only a weak interaction to H9. The presence of a stronger contact to H6 (or H7) suggests that the solution structure of this Li salt may be different from that of the potassium analogue, **15**,[24] but still involves the aniline moiety. Interestingly, low-temperature NMR measurements on the solution containing 6 equiv of the crown ether sample and **13** now reveal only one of the two presumed isomers (Figure 6).

Conclusions. It is clear that, in general, the solution structures of salts, in THF, do not always correspond to the solid-state structures. For **13** and **14b**, we favor mononuclear salts in solution, whereas in the solid state, dinuclear species are observed. Specifically, the low-temperature NMR results at 155 K for lithium salt **13** suggest that two isomeric salts exist in approximately equal amounts. For the solutions containing crown ethers,[25] we find some differences between **13** and **14** based on the NOE results. Whereas the potassium salt seems to have the nitrile bound structure, found via X-ray diffraction, the smaller lithium cation prefers a different position. The NMR methods presented are not always unambiguous; however, it is clear that the NOE/PGSE approach to the solution structure is increasingly valuable.

Experimental Section

NMR. All multinuclear PGSE experiments were carried out using standard sequences.[26] As is known, there is a linear dependence of log I (I = resonance intensity) on G^2 (G = gradient field strength). The slope of the log I vs G^2 plot is proportional to the self-diffusion coefficient of the diffusing molecule (D), which is related to its hydrodynamic radius by the Stokes−Einstein equation. The measurements were performed on a 400-MHz Bruker AVANCE spectrometer equipped with a microprocessor-controlled gradient unit and an inverse multinuclear probe, with an actively shielded z-axis gradient coil. The shape of the gradient pulse was rectangular, and its strength varied automatically in the course of the experiments. The measurements were carried out without spinning. The ^{1}H spectra at 400 MHz were referenced to TMS as an external standard. ^{7}Li and ^{31}P chemical shifts were referenced to external LiCl (155.4 MHz) for ^{7}Li and 85% H_3PO_4 (161.92 MHz) for ^{31}P. The sample temperature was calibrated, before the PGSE measurements, by introducing a thermocouple inside the bore of the magnet. The calibration of the gradients was carried out via a diffusion measurement of HDO in D_2O, which afforded a slope of 2.022×10^{-4}. We estimate the experimental error in the D values at ±2%. All of the data leading to the reported D values afforded lines whose correlation coefficients were >0.999, and 8−12 points have been used for regression analysis. To check reproducibility, three different measurements with different diffusion parameters (δ and/or Δ) were always carried out. The gradient strength was incremented in 8% steps from 10% to 98%. A measurement of ^{1}H, ^{7}Li, and ^{31}P T_1 was carried out before each diffusion experiment, and the recovery delay was set to $5T_1$.

^{1}H PGSE diffusion measurements: 299 K, $\Delta = 68-118$ ms, $\delta = 2$ ms; 209 K, $\Delta = 71-96$ ms, $\delta = 5-6$ ms. The number of

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(24) Perhaps the P−N moiety is now directly involved in the Li complexation.

(25) A reviewer asked about "triple ions" because these are well documented: (a) Romersberg, F. E.; Bernstein, M. P.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* **1993**, *115*, 3475−3483. (b) Hay, B. P.; Rustad, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 6316−6326. (c) Reich, H. J.; Holladay, J. E.; Mason, J. D.; Sikorski, W. H. *J. Am. Chem. Soc.* **1995**, *117*, 12137−12150. (d) Lucht, B. L.; Bernstein, M. P.; Remenar, J. F.; Collum, D. B. *J. Am. Chem. Soc.* **1996**, *118*, 10707−10718. We believe that our experimental D values exclude significant quantities of these species; however, we cannot exclude a few percent because our D values represent an average and would not be sensitive to the presence of small quantities of such salts.

(26) (a) Stilbs, P. *Prog. NMR Spectrosc.* **1987**, *19*, 1−45. (b) Price, W. S. *Annu. Rep. NMR Spectrosc.* **1996**, *32*, 51−142.

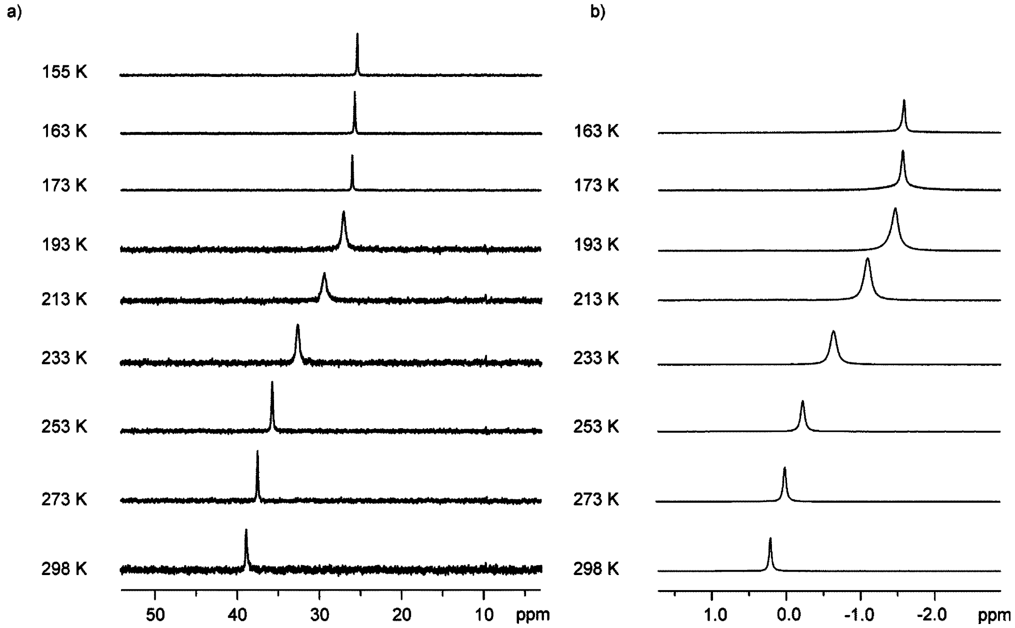

Figure 6. (a) ^{31}P NMR (161.92 MHz) and (b) ^{7}Li NMR (155.45 MHz) spectra as a function of temperature for a 60 mM sample of **13**, in THF, with 6 equiv of 18-crown-6 ether.

scans varied between 16 and 32 scans per increment. Typical experimental times were 1−2 h.

^{7}Li PGSE diffusion measurements: 299 K, $\Delta = 31-42$ ms, $\delta = 5-6$ ms; 209 K, $\Delta = 14-15$ ms, $\delta = 25-26$ ms. The number of scans varied between 256 and 512 scans per increment. Typical experimental times were 2−10 h.

^{31}P PGSE diffusion measurements: 299 K, $\Delta = 19-26$ ms, $\delta = 8-9$ ms; 209 K, $\Delta = 35-45$ ms, $\delta = 18$ ms. The number of scans varied between 256 and 1024 scans per increment. Typical experimental times were 2−10 h.

To avoid convection, the PGSE diffusion measurements at 209 K were carried out using a commercial coaxial insert (i.d. = 1.96 mm; o.d. = 2.97 mm) inserted into a standard 5-mm NMR tube and held in a concentric manner with a spacer.[27]

X-ray. Single crystals of **14a** were mounted in perfluoroether oil on the top of a glass fiber and then immediately brought into the cold nitrogen stream of a low-temperature device (200 K) so that the oil solidified. The X-ray structure was solved by direct methods and successive interpretation of the difference Fourier maps, followed by full matrix least-squares refinement (against F^2) with SHELXTL (version 6.12) and SHELXL-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in idealized positions and included as riding atoms. Upon convergence, the final Fourier difference map showed no significant peaks. Additionally, an empirical absorption correction SADABS (version 2.03) was applied. Because of partial disorder, the atoms of one THF molecule had to be restricted using the ISOR restraint. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-271429. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax (+44) 1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

Preparation of **13** was made by adding *n*-BuLi (41 μL, 1.6 M in hexane, 0.066 mmol) to the neutral compound **12** (18.2 mg, 0.061 mmol) in 1 mL of dry THF-d_8 at −78 °C. The reaction mixture was then stirred for 10 min and warmed to room temperature. The potassium amide **14** was synthesized by treating **12** with 2 equiv of KH in 1 mL of dry THF-d_8 at 0 °C. The reaction mixture was then stirred for 10 min, warmed to room temperature, and filtered. In both cases, 0.5 mL was taken by using a syringe and added to oven-dried 5-mm NMR tubes. The metalated phosphinoamides were stable at room temperature for several days. The preparation of **15** was carried out in the same way as **14b** by adding 1.0 equiv of 18-crown-6 ether after metalation.

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Supporting Information Available: Figure showing two low-temperature ^{31}P results, plus the CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) Martinez-Viviente, E.; Pregosin, P. S. *Helv. Chim. Acta* **2003**, *86*, 2364−2378.