

Unexpected Coordination of Aminoiminophosphoranate Ligands with Alkali Metals

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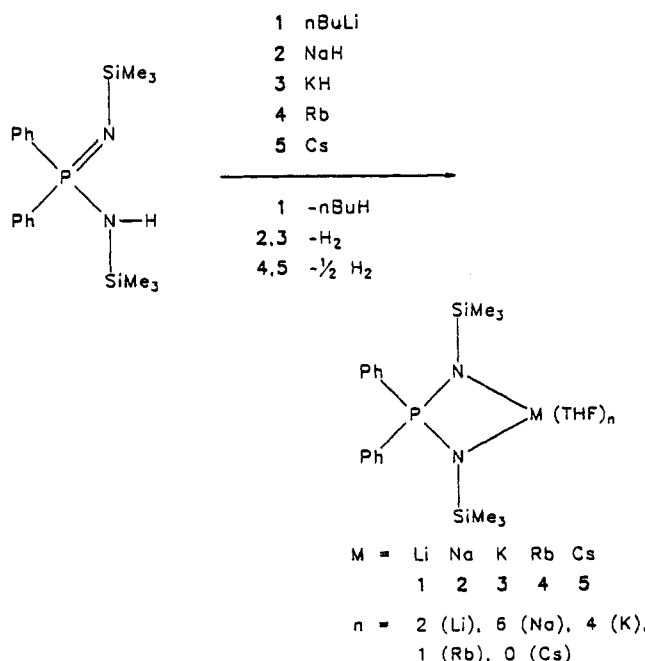
The crystal structures of the derivatives $[\text{Ph}_2\text{P}(\text{Me}_3\text{SiN})_2\text{Li}(\text{THF})_2]$,¹ $[\text{Na}(\text{THF})_6][\text{Na}\{\text{NSiMe}_3\}_2\text{PPh}_2]$, $[\text{Ph}_2\text{P}(\text{Me}_3\text{SiN})_2\text{K}(\text{THF})_4]$, $[\text{Ph}_2\text{P}(\text{Me}_3\text{SiN})_2\text{Rb}(\text{THF})_2]$, and $[\text{Ph}_2\text{P}(\text{Me}_3\text{SiN})_2\text{Cs}]_2$ have been determined by low-temperature X-ray structure analysis. The lithium and the potassium compounds form monomeric structures, whereas the sodium derivative forms a previously unheard of sodium–sodiumate structure, where one sodium is surrounded by two anions and the other by six THF molecules. The rubidium and the cesium derivatives adopt a stair-shaped dimeric structure. In the latter, a very close intramolecular metal– π system contact is observed. A long-range intermolecular metal– π system contact binds the dimers in an overall polymeric area, resulting in molecular rods.

Introduction

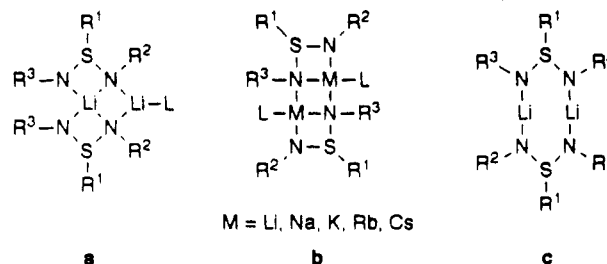
Chelating ligands are of basic interest in both heterocycle and coordination chemistry. One of the most fruitful systems has been the $[\text{R}-\text{N}-\text{E}-\text{N}-\text{R}]^-$ ligand coordinating with two nitrogen atoms. Substituents of frequent use are $[\text{R}-\text{N}-\text{C}(\text{R})-\text{N}-\text{R}]^-$,^{2–6} $[\text{R}-\text{N}-\text{Si}(\text{R})_2-\text{O}-\text{R}]^-$,^{7,8} and $[\text{R}-\text{N}-\text{S}(\text{R})-\text{N}-\text{R}]^-$.^{9,10} The preparation of compounds containing these chelates normally involves the lighter alkali metal precursors. The lithium and sodium aminoiminophosphoranates $[\text{R}-\text{N}-\text{P}(\text{R})_2-\text{N}-\text{R}]\text{M}$ ($\text{M} = \text{Li}, \text{Na}$) were prepared previously,^{11–13} but their structures have remained unknown. We synthesized all alkali metal derivatives to study the coordination of the aminoiminophosphoranate ligand. The low-temperature X-ray structures of $\text{Ph}_2\text{P}(\text{Me}_3\text{SiN})_2\text{M}$ where $\text{M} = \text{Li}$ (1), Na (2), K (3), Rb (4), and Cs (5) are presented.

Results and Discussion

Preparation of 1–5. Diphenyl((trimethylsilyl)amino)-((trimethylsilyl)imino)phosphorane reacts in THF with butyllithium (1), sodium hydride (2), potassium hydride (3), rubidium metal (4) and cesium metal (5) to give the alkali metal derivatives in quantitative yields. Filtration and recrystallization from THF



at -35°C give colorless low-melting crystals. The sodium and potassium compounds (2, 3) lose their coordinated THF molecules in vacuum completely, whereas in the lithium (1) and rubidium (4) derivative this coordination is stable. The cesium metal in 5 is not coordinated by THF at all, even though the synthesis and crystallization were carried out in this solvent. The structures and chemistry of the sulfinamidinato alkali metal compounds $\text{PhS}(\text{Me}_3\text{SiN})_2\text{M}$ ($\text{M} = \text{alkali metal}$) were probed by us recently, and these studies have revealed three classes of structures a–c.^{9,10}



In a, two SN_2Li four-membered rings are placed on adjacent sides of the central Li_2N_2 four-membered ring, which results in a twisted tricyclic structure with C_2 symmetry. In b, the two SN_2Li four-membered rings are fused on opposite sides of the central M_2N_2 four-membered ring. Both, the stair-shaped tricyclic structure in b and the eight-membered ring in c adopt C_1 symmetry. Furthermore, we isolated and identified the "ate" type derivative $[\text{Li}(12\text{-crown-4})][\text{Li}\{\text{NSiMe}_3\}_2\text{SPh}_2]$ by X-ray structure analysis and ^7Li solid state NMR.¹⁴

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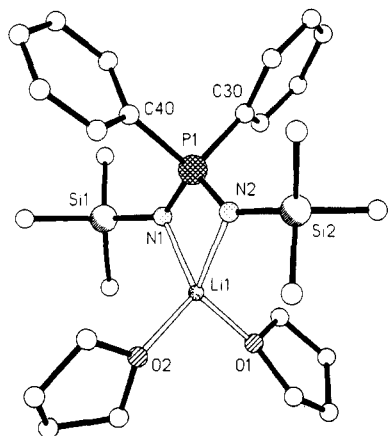


Figure 1. Structure of **1** in the solid state.

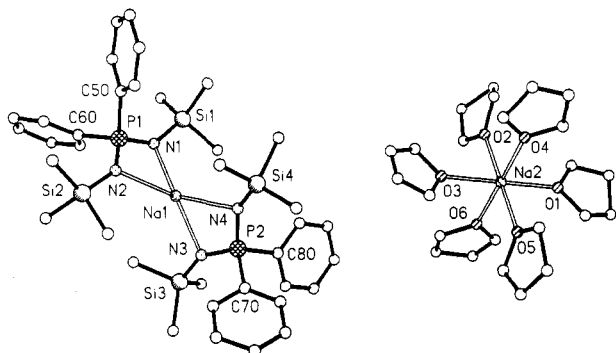


Figure 2. Structure of **2** in the solid state. Two uncoordinated THF molecules have been omitted for clarity.

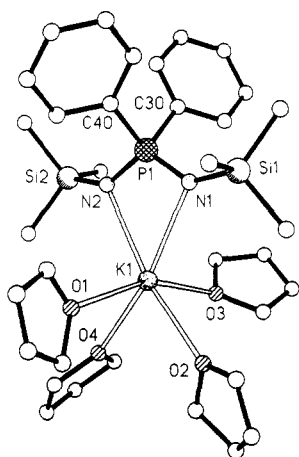


Figure 3. Structure of **3** in the solid state.

The experiments reported in this paper have been carried out to investigate whether or not the results for the $\text{PhS}(\text{Me}_3\text{SiN})_2\text{M}$ system are directly transferable to the $\text{Ph}_2\text{P}(\text{Me}_3\text{SiN})_2\text{M}$ ($\text{M} =$ alkali metal) system. Our investigations show that they are not. The derivatives $[\text{Ph}_2\text{P}(\text{Me}_3\text{SiN})_2\text{Li}(\text{THF})_2]$ (**1**) and $[\text{Ph}_2\text{P}(\text{Me}_3\text{SiN})_2\text{K}(\text{THF})_4]$ (**3**) are monomers in the solid state (Figures 1 and 3). The sodium derivative $[\text{Na}(\text{THF})_6][\text{N}(\text{NSiMe}_3)_2\text{PPh}_2]_2$ (**2**) is, to our knowledge, the first sodium-sodiumate structure (Figure 2). Only two other structures with a $\text{Na}(\text{THF})_6^+$ cation are known.^{15,16} In the structure of the cryptobase-stabilized sodium electride Na^- is the counterion.¹⁷ The two heavier derivatives $[\text{Ph}_2\text{P}(\text{Me}_3\text{SiN})_2\text{Rb}(\text{THF})_2]$ (**4**) (Figure 4) and $[\text{Ph}_2\text{P}(\text{Me}_3\text{SiN})_2\text{Cs}]_2$ (**5**) (Figure 5), however,

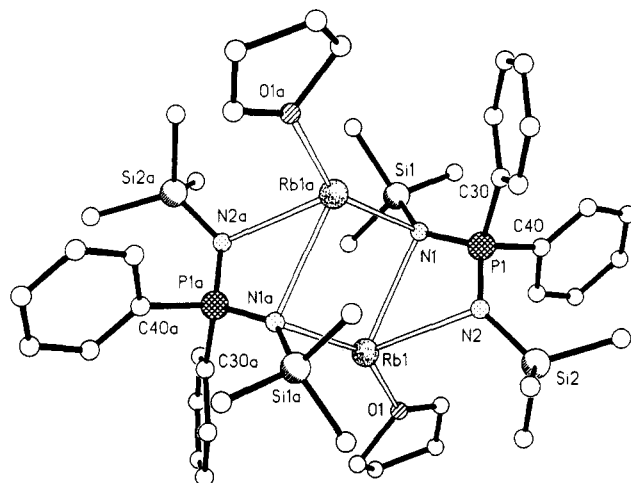


Figure 4. Structure of **4** in the solid state.

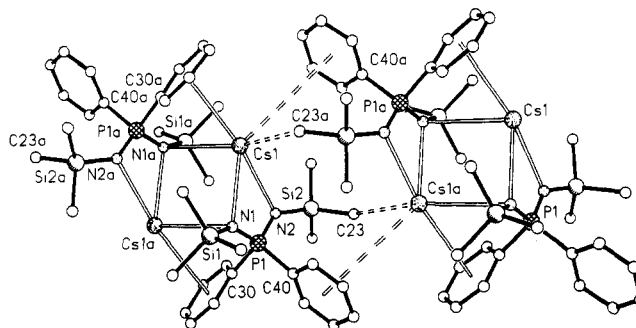


Figure 5. Structure of **5** in the solid state. Two dimers have been depicted to elucidate the polymerization.

are closely related to the structural class **b**, mentioned earlier. The cesium cation in **5** forms a remarkably close intramolecular and a weak intermolecular contact to a phenyl ligand, resulting in infinite molecular rods.

Crystal Structures of 1–5. The structures of the lithium aminoiminophosphoranate **1** and the potassium aminoiminophosphoranate **3** are monomeric in the solid state. The anion is chelating both metals, resulting in four-membered kite-shaped PN_2Li (Figure 1) and PN_2K (Figure 3) rings. The two P–N bonds (average 158 pm in **1** and 157 pm in **3**) and two metal–N bonds (average 206 pm in **1** and 281 pm in **3**) are of the same length (Table I), which means that the metal is located on the bisection of the N–P–N angle. The lithium atom in **1** is in the plane of the anion, while the potassium in **3** is 1.2 pm out of the plane, possibly because of steric hindrance. In addition, the lithium atom in **1** is coordinated by two THF molecules whereas the potassium atom in **3** is coordinated by four THF molecules. This results in a much lower melting point of **3**, although the structures of **1** and **3** are very similar. **1** melts at 165 °C whereas **3** decomposes at temperatures higher than –20 °C. It is worthy to note that a close contact between the π -electron system of the phenyl ligand at the phosphorus and the potassium metal could not be observed in this molecule as in the potassium sufinamidinate.⁹

The most surprising structure in this series is the sodium sodiumate **2**. In the sodium aminoiminophosphoranate, one sodium atom is coordinated by two anions and the cation is formed by the second sodium surrounded by six THF molecules. Obviously this arrangement is favorable to the $[\text{Ph}_2\text{P}(\text{Me}_3\text{SiN})_2\text{Na}(\text{THF})_3]$ monomeric molecule one might expect regarding the structures of **1** and **3**. Thus **2** is related to the lithium (sulfonamidinato)lithiate.¹⁴ As in the latter, the $\text{P}(1)\cdots\text{Na}(1)$ and $\text{P}(2)\cdots\text{Na}(1)$ vectors intersect at an angle of 174.2°, indicating that the anions try to maximize their distance. The $\text{P}(1)\text{N}(1)\text{N}(2)\text{Na}(1)$ and the $\text{P}(2)\text{N}(3)\text{N}(4)\text{Na}(1)$ planes are only twisted by 2.9° from being perpendicular to each other.

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Table I. Selected Bond Lengths (pm) and Angles (deg) for 1–5

	1 (M = Li ¹)	2 (M = Na)	3 (M = K)	4 (M = Rb)	5 (M = Cs)
P(1)–N(1)	157.9(4)	156.7(5)	156.7(6)	158.5(3)	157.5(1)
P(1)–N(2)	158.0(4)	157.5(7)	157.1(5)	156.7(4)	157.6(1)
P(2)–N(3)		157.3(7)			
P(2)–N(4)		157.6(6)			
M···P(1)	252.0(9)	290.5(3)	333.6(4)	348.0(1)	363.8(1)
M···P(2)		291.4(3)			
M–N(1)	207.7(11)	242.4(7)	280.3(6)	291.7(4)	314.1(2)
M–N(2)	204.4(9)	242.1(6)	281.9(6)	298.9(2)	301.0(2)
M–N(3)		238.9(6)			
M–N(4)		242.2(6)			
M–N(1a)				299.2(3)	360.5(2)
M–O(av)	192.9	236.6	273.5	287.1	
M···ring center (C30a)				397.1	338.5
M···ring center (C40)					480.8
N(1)–P(1)–N(2)	109.4(2)	112.8(3)	114.1(3)	113.7(2)	113.7(1)
N(3)–P(2)–N(4)		111.2(3)			
P(1)–N(1)–Si(1)	139.3(3)	140.3(4)	137.7(4)	139.2(2)	144.9(1)
P(1)–N(2)–Si(2)	142.8(3)	141.1(4)	138.1(4)	135.5(2)	137.5(1)
P(2)–N(3)–Si(3)		146.2(4)			
P(2)–N(4)–Si(4)		141.9(4)			

Table II. Crystal Data for 15

	1 ¹	2	3	4	5
formula	C ₂₆ H ₄₄ LiN ₂ O ₂ PSi ₂	C ₆₄ H ₁₁₂ N ₄ Na ₂ O ₇ P ₂ Si ₄	C ₃₄ H ₆₀ KN ₂ O ₃ PSi ₂	C ₄₄ H ₇₂ N ₄ O ₂ P ₂ Rb ₂ Si ₄	C ₃₆ H ₅₆ Cs ₂ N ₂ P ₂ Si ₄
fw	510.7	1269.9	687.1	1034.3	985.0
crystal size (mm)	0.3 × 0.3 × 0.2	0.4 × 0.4 × 0.1	0.8 × 0.5 × 0.5	0.3 × 0.4 × 0.5	0.4 × 0.3 × 0.3
space group	<i>Pn</i>	<i>P2₁</i>	<i>C2/c</i>	<i>P1</i>	<i>P2₁/n</i>
<i>a</i> (pm)	1080.2(2)	1347.3(2)	3659(3)	1118.3(3)	1019.7(2)
<i>b</i> (pm)	1035.7(2)	1727.3(2)	1095.7(4)	1164.4(3)	1215.6(2)
<i>c</i> (pm)	1375.7(2)	1818.8(2)	2055.2(11)	1297.7(3)	1824.5(4)
α (deg)	90	90	90	66.584(8)	90
β (deg)	94.78(2)	105.39(2)	94.54(5)	88.618(12)	98.06(2)
γ (deg)	90	90	90	69.791(14)	90
<i>V</i> (nm ³)	1.533	4.0809	8.214	1.377	2.240
<i>Z</i>	2	2	8	1	2
ρ_c (Mgm ⁻³)	1.106	1.033	1.111	1.256	1.461
μ (mm ⁻¹)	0.185	0.167	0.261	1.971	1.835
<i>F</i> (000)	552	1367	2976	540	922
2 θ range (deg)	8–50	8–50	8–48	8–48	8–60
no. of measd reflns	4036	14 001	9581	4361	7138
no. of unique reflns	3806	13 511	6481	4273	6511
no. of obsd reflns	2865	10 376	4408	3589	5987
<i>p</i> for <i>F</i> > <i>p</i> σ (<i>F</i>)	4	3	3	3	3
<i>R</i>	0.057	0.093	0.107	0.042	0.023
<i>R_w</i>	0.055	0.103	0.128	0.048	0.030
goodness of fit	1.28	2.04	2.51	1.70	1.69
weighting factor <i>g</i>	0.0005	0.001	0.001	0.0003	0.0001
refined parameters	308	752	397	253	233
highest difference peak (e nm ⁻³)	320	1230	1370	570	430
η	1.3(5)	1.1(3)			

The trimethylsilyl groups slot into each other like in a “molecular gear-wheel”, leaving the central Na⁺ covered with a hydrocarbon surface. As the sodium cation is covered with THF molecules, the whole material is quite soluble, even in nonpolar hydrocarbons.

We tried to confirm the two different sodium sites in solution and in the solid state by NMR techniques. We have detected only one, albeit broad, ²³Na NMR signal in solution, even at –80 °C, probably as a result of a fluxional process. In the solid state, we found a split ²³Na MAS NMR signal, but we could not exclude the fact that this was an effect of quadrupolar splitting. Furthermore, **2** has a very low decomposition point and the vapor pressure of the coordinated THF as well as the uncoordinated lattice THF is very low, so we cannot guarantee that the material in the solid-state rotor has the same modification as in the single crystal.

The two derivatives [Ph₂P(Me₃SiN)₂Rb(THF)]₂ (**4**) and [Ph₂P(Me₃SiN)₂Cs]₂ (**5**) are dimers in the solid state. **4** consists of three four-membered rings fused to a stair-shaped structure. The normal of the central Rb₂N₂ ring intersects the normal of the RbN₂P ring at an angle of 92.9°. Each rubidium of the dimer is coordinated by one additional THF molecule. The Rb–

phenyl ring center distance is 397 pm, hence 27 pm longer than in [PhS(Me₃SiN)₂Rb(THF)]₂⁹ and even 78.2 pm longer than in Ph₂CPhRb(PMDETA);¹⁸ PMDETA = (Me₂NCH₂CH₂)₂NMe. Therefore, the interaction between the π system of the ligand and the metal in **4** is very weak. The opposite is the case in **5** (Figure 5). The distance between the ring center and the cesium metal is 338.5 pm, hence 16.6 pm shorter than in [PhS(Me₃SiN)₂Cs(THF)]₂⁹ and only 5 pm longer than in Ph₂CPhCs(PMDETA).¹⁸ This seems remarkable because in the Ph₂P(NSiMe₃)₂⁻ ion the negative charge is almost entirely located at the nitrogen atoms whereas in the Ph₃C⁻ ion it is almost entirely located in the coordinated phenyl ring. Nevertheless, the phenyl group in **5** is surprisingly attractive for the soft and easy to polarize cesium metal. The normal of the central Cs₂N₂ ring intersects the normal of the CsN₂P ring at an angle of 96.6°. Relatively weak interactions with a second phenyl group (480.8 pm) and with a methyl group of another dimeric molecule lead to an overall

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Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{pm}^2 \times 10^{-1}$) for **2**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Na(1)	-1084(2)	7559	-2257(2)	46(1)	C(84)	-5012(8)	5756(6)	-3629(6)	72(4)
P(1)	1064(1)	7561(2)	-2277(1)	35(1)	C(85)	-4212(6)	6123(5)	-3099(4)	52(3)
N(1)	188(4)	7165(4)	-2907(3)	40(2)	Na(2)	-7112(2)	2430(2)	-2787(2)	41(1)
Si(1)	-13(2)	6388(2)	-3476(1)	51(1)	O(1)	-8519(4)	1591(3)	-3203(3)	55(2)
C(11)	708(8)	6448(7)	-4225(6)	87(5)	C(16)	-9440(8)	1617(7)	-2946(6)	83(4)
C(12)	-1421(7)	6321(7)	-3979(6)	90(5)	C(17)	-10217(7)	1132(6)	-3502(7)	89(5)
C(13)	346(7)	5466(5)	-2954(6)	71(4)	C(18)	-9519(7)	529(6)	-3713(6)	77(4)
N(2)	645(4)	8012(4)	-1670(4)	42(2)	C(19)	-8601(7)	974(6)	-3713(6)	79(4)
Si(2)	949(2)	8747(2)	-1050(1)	50(1)	O(2)	-6247(4)	1877(3)	-3649(3)	55(2)
C(21)	-141(9)	8875(6)	-600(7)	100(5)	C(26)	-5628(9)	1183(7)	-3549(7)	96(5)
C(22)	1060(7)	9692(5)	-1516(6)	74(4)	C(27)	-5778(22)	929(10)	-4393(12)	90(9)
C(23)	2202(8)	8622(6)	-309(6)	88(5)	C(27')	-4980(34)	1324(36)	-4154(18)	112(23)
C(50)	2014(5)	6839(4)	-1811(4)	39(2)	C(28)	-5733(10)	1723(9)	-4788(8)	114(7)
C(51)	2727(5)	6522(5)	-2158(5)	50(3)	C(29)	-6249(9)	2232(7)	-4352(6)	86(5)
C(52)	3373(5)	5912(5)	-1820(5)	51(3)	O(3)	-5698(4)	3285(3)	-2398(3)	53(2)
C(53)	3335(7)	5626(5)	-1145(5)	62(4)	C(36)	-5587(9)	3774(8)	-1791(7)	108(6)
C(54)	2627(7)	5931(6)	-796(5)	66(4)	C(37)	-4574(12)	4019(11)	-1520(10)	145(6)
C(55)	1984(6)	6525(5)	-1107(4)	51(3)	C(38)	-4094(16)	3717(13)	-1916(11)	189(8)
C(60)	1828(5)	8175(4)	-2744(5)	42(3)	C(39)	-4758(9)	3270(8)	-2605(8)	105(6)
C(61)	2802(5)	8447(5)	-2327(5)	55(3)	O(4)	-6261(4)	1543(3)	-1842(3)	57(2)
C(62)	3386(7)	8901(5)	-2677(7)	65(4)	C(46)	-6664(10)	852(8)	-1642(10)	127(7)
C(63)	3002(9)	9078(5)	-3437(8)	82(5)	C(47)	-5920(11)	442(8)	-1081(8)	117(6)
C(64)	2034(9)	8824(6)	-3860(7)	84(5)	C(48)	-5075(14)	875(10)	-947(12)	167(7)
C(65)	1469(6)	8376(5)	-3492(5)	60(3)	C(49)	-5278(11)	1642(8)	-1316(9)	144(7)
P(2)	-3224(1)	7387(2)	-2226(1)	37(1)	O(5)	-7949(5)	2992(4)	-1928(3)	64(2)
N(3)	-2793(4)	8070(3)	-2623(3)	41(2)	C(56)	-7890(10)	2685(9)	-1194(7)	120(7)
Si(3)	-3079(1)	8854(2)	-3178(1)	44(1)	C(57)	-8631(16)	3183(13)	-893(14)	210(9)
C(31)	-3783(9)	9612(6)	-2773(7)	89(5)	C(58)	-8879(15)	3849(11)	-1396(9)	157(6)
C(32)	-1834(7)	9279(6)	-3257(6)	73(4)	C(59)	-8471(12)	3742(8)	-2044(9)	139(8)
C(33)	-3863(9)	8668(8)	-4155(6)	104(5)	O(6)	-7918(4)	3362(4)	-3711(3)	65(2)
N(4)	-2350(4)	6789(3)	-1856(3)	38(2)	C(66)	-7505(9)	4112(6)	-3861(7)	100(5)
Si(4)	-2021(2)	6130(2)	-1159(2)	52(1)	C(67)	-8089(9)	4403(8)	-4592(7)	101(5)
C(41)	-1673(12)	5182(7)	-1547(8)	131(7)	C(68)	-9007(10)	3859(8)	-4783(8)	138(6)
C(42)	-814(13)	6369(10)	-473(9)	218(10)	C(69)	-8888(9)	3271(7)	-4292(9)	121(6)
C(43)	-2987(11)	5897(8)	-644(9)	134(7)	O(7)	-1504(14)	3145(16)	-3758(16)	93(10)
C(70)	-3831(5)	7783(4)	-1521(4)	42(3)	C(76)	-2244(27)	2851(13)	-4171(16)	122(15)
C(71)	-4669(5)	7435(6)	-1340(5)	59(3)	C(77)	-3193(14)	3338(18)	-4347(14)	104(11)
C(72)	-5087(6)	7738(7)	-782(5)	65(4)	C(78)	-2799(23)	4051(14)	-3981(16)	112(13)
C(73)	-4714(7)	8376(8)	-418(5)	75(4)	C(79)	-1786(23)	3824(22)	-3620(20)	164(19)
C(74)	-3860(8)	8755(6)	-576(5)	77(4)	O(7')	-1786(19)	1001(14)	-1129(12)	217(12)
C(75)	-3446(6)	8444(6)	-1124(5)	62(3)	C(76')	-1218(14)	1205(13)	-1646(14)	116(8)
C(80)	-4299(5)	6892(4)	-2892(4)	39(2)	C(77')	-1943(21)	1541(16)	-2362(11)	187(15)
C(81)	-5206(5)	7280(5)	-3211(4)	48(3)	C(78')	-2811(16)	1853(14)	-2059(15)	125(9)
C(82)	-6026(6)	6906(6)	-3745(5)	60(3)	C(79')	-2441(19)	1646(17)	-1218(13)	175(14)
C(83)	-5922(7)	6167(6)	-3930(5)	65(4)					

^a *U*(eq) is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

polymeric structure. Although synthesis and crystallization were carried out in THF, no donor molecule is present in the solid state.

Conclusion

Compared to the series of alkali metal sufinamidates, the series of alkali metal aminoiminophosphoranates presented here does structurally not seem to be so homogeneous as the first. Surprisingly, the sodium derivative forms a sodium-sodiumate structure, whereas the cesium derivative forms a polymer with a remarkably close intramolecular metal- π electron contact. This distance is as close as the one to the π system of the Ph₃C⁻ anion exclusively containing carbon atoms.

Experimental Section

All manipulations were performed under an inert atmosphere of dry argon gas with Schlenk techniques or in an argon glovebox. The *n*-hexane, diethyl ether, and THF solvents were dried over Na/K alloy and distilled prior to use.

NMR spectra were obtained with a Bruker MSL 400 or AM 250 instrument. All NMR spectra were recorded in toluene-*d*₈ or benzene-*d*₆ with SiMe₄, H₃PO₄, LiCl, NaCl, or CsCl as external standard.

[Ph₂P(Me₃SiN)₂Li(THF)₂] (**1**).^{2,11-13} A solution of 10 mL of *n*-butyllithium in hexane (1.6 M; 16 mmol) was added to 5.8 g of diphenyl((trimethylsilyl)amino)((trimethylsilyl)imino)phosphorane (16 mmol) in 30 mL of diethyl ether over a period of 1/2 h at room temperature. The mixture was refluxed for 1 h and the ether removed under reduced pressure. A 20-mL portion of THF was added, and the mixture was again refluxed for 1 h. After a few days at -22 °C, colorless crystals were

obtained. Mp: 165 °C. NMR: ¹H (C₆D₆) δ 0.153 (Me₃Si), 1.389, 3.633 (THF), 7.0-8.0 (Ph); ⁷Li (C₆D₆) δ 0.560; ³¹P (C₆D₆) δ 7.444.

[Na(THF)₆][Na{(NSiMe₃)₂PPh₂}] (**2**). To a suspension of 0.6 g of NaH (25 mmol) in 20 mL of dry THF was added 7.5 g of diphenyl-((trimethylsilyl)amino)((trimethylsilyl)imino)phosphorane (20 mmol) in 20 mL of THF over a period of 1/2 h. The reaction mixture was refluxed for 1 h. The remaining NaH was filtered off from the cold mixture and the volume reduced to the half. Colorless crystals were obtained at -35 °C after several days. Mp: \leq -20 °C dec. NMR: ¹H (C₇D₈) δ 0.078 (Me₃Si), 1.392, 3.439 (THF), 6.8-7.9 (Ph); ²³Na (C₇D₈) δ 13.1 (broad signal); ³¹P (C₇D₈) δ 8.650.

[Ph₂P(Me₃SiN)₂K(THF)₄] (**3**). To a suspension of 1 g of potassium hydride (25 mmol) in 20 mL of THF was added 7.5 g of diphenyl-((trimethylsilyl)amino)((trimethylsilyl)imino)phosphorane (20 mmol) in 20 mL THF over a period of 1/2 h. The reaction mixture was refluxed for 1 h. The remaining KH was filtered off from the cold mixture and the volume reduced to the half. After several days at -35 °C colorless crystals were obtained. Mp: \leq -20 °C dec. NMR: ¹H (C₇D₈) δ 0.03 (Me₃Si), 1.435, 3.50 (THF), 7.1-7.8 (Ph); ³¹P (C₇D₈) δ 4.08.

[Ph₂P(Me₃SiN)₂Rb(THF)₂] (**4**). A 1-g sample of elemental rubidium (11.8 mmol) was suspended in 20 mL of THF. To this suspension was added 4.3 g of diphenyl((trimethylsilyl)amino)((trimethylsilyl)imino)phosphorane (11.8 mmol) in 20 mL hexane over a period of 1/2 h at 50 °C. After being stirred for 1 h at this temperature, the cold solution was filtered off. Colorless crystals were obtained at -35 °C after several days. Mp: 95 °C. NMR: ¹H (C₆D₆) δ 0.855 (Me₃Si), 1.404, 3.515 (THF), 7.0-8.0 (Ph); ³¹P (C₆D₆) δ 3.194.

[Ph₂P(Me₃SiN)₂Cs]₂ (**5**). A 1-g sample of elemental cesium (7.5 mmol) was suspended in 20 mL of THF. To this suspension was added 2.7 g

Table IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{pm}^2 \times 10^{-1}$) for **3**

	x	y	z	$U(\text{eq})^a$
K(1)	3767(1)	3104(2)	2075(1)	57(1)
P(1)	3765(1)	1418(2)	723(1)	41(1)
N(1)	3475(1)	1268(5)	1239(3)	50(2)
Si(1)	3162(1)	234(3)	1429(1)	67(1)
C(11)	2868(2)	-384(10)	734(4)	89(4)
C(12)	2842(3)	964(15)	1963(5)	151(7)
C(13)	3376(3)	-1086(12)	1861(7)	145(6)
N(2)	4050(1)	2469(5)	884(3)	44(2)
Si(2)	4346(1)	3303(2)	492(1)	46(1)
C(21)	4643(2)	4159(8)	1106(4)	73(3)
C(22)	4656(2)	2420(8)	-16(4)	74(3)
C(23)	4114(2)	4435(7)	-73(4)	67(3)
C(30)	3530(2)	1657(6)	-83(3)	48(2)
C(31)	3678(2)	1381(9)	-656(3)	74(3)
C(32)	3488(3)	1664(11)	-1258(4)	98(5)
C(33)	3156(3)	2188(10)	-1297(4)	90(4)
C(34)	3005(3)	2485(9)	-734(5)	88(4)
C(35)	3186(2)	2224(7)	-122(4)	63(3)
C(40)	4004(2)	-39(6)	630(3)	45(2)
C(41)	3844(2)	-1030(7)	321(4)	67(3)
C(42)	4022(2)	-2131(7)	303(5)	69(3)
C(43)	4367(2)	-2267(7)	583(4)	65(3)
C(44)	4538(2)	-1301(7)	873(4)	72(3)
C(45)	4364(2)	-179(6)	900(4)	56(3)
O(1)	4282(3)	1946(9)	2882(4)	166(5)
C(51)	4438(9)	1001(28)	2684(11)	317(17)
C(52)	4598(7)	324(19)	3248(12)	271(14)
C(53)	4529(4)	839(17)	3806(9)	151(8)
C(54)	4334(7)	1968(15)	3609(7)	205(10)
O(2)	3403(2)	3112(8)	3194(3)	110(3)
C(61)	3201(5)	2393(16)	3579(6)	191(9)
C(62)	3106(2)	2924(13)	4153(5)	112(5)
C(63)	3184(3)	4220(12)	4025(6)	110(5)
C(64)	3446(3)	4232(11)	3520(5)	108(5)
O(3)	3259(2)	4824(5)	1663(3)	81(2)
C(71)	3242(3)	5240(11)	1002(4)	95(4)
C(72)	2859(3)	5404(18)	810(6)	151(8)
C(73)	2671(3)	5321(19)	1362(8)	173(9)
C(74)	2915(4)	4892(18)	1873(7)	176(9)
O(4)	4131(2)	5144(5)	2540(3)	78(2)
C(81)	4449(2)	5251(9)	2998(5)	84(4)
C(82)	4524(4)	6526(12)	3055(7)	149(7)
C(83)	4326(5)	7136(11)	2549(9)	163(8)
C(84)	4023(3)	6311(9)	2320(6)	109(5)

^a $U(\text{eq})$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

of diphenyl((trimethylsilyl)amino)((trimethylsilyl)amino)phosphorane (7.5 mmol) in 20 mL of *n*-hexane over $1/2$ h. The reaction mixture was refluxed for 1 h, and overnight a crop of colorless crystals was obtained. Mp: 203 °C dec. NMR: ^1H (C_7D_8) δ 0.065 (Me₃Si, $^4J(\text{H},\text{P}) = 0.34$ Hz), 7.1–7.9 (Ph); ^{29}Si (C_7D_8) δ -18.75 ($^2J(\text{Si},\text{P}) = 22.8$ Hz); ^{31}P (C_7D_8) δ 1.53; ^{133}Cs (C_7D_8) δ 101.7.

X-ray Measurements of 1–5

The intensities for all structures were collected on a Stoe-Siemens AED with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 71.073$ pm). Data were collected from oil-coated rapidly-cooled crystals at -120 °C with a profile-fitted method.¹⁹ The structures were solved by direct methods or Patterson methods with SHELXS-90.²⁰ All structures were refined by full-matrix least-squares procedures using SHELXTL-Plus, PC version.²¹ A riding model was employed to refine the hydrogen atom positions. The data for **2**, **4**, and **5** were corrected for absorption by a semiempirical method. The structures of **2–4** contain disordered THF molecules. In **2** and **4**, most of the disordered atom positions could be refined. Selected bond lengths and angles are shown in Table I, relevant crystallographic data for structures **2–5** in Table II, and fractional coordinates of **2** in Table III, of **3** in Table IV, of **4** in Table V, and of **5** in Table VI.

Acknowledgment. We wish to thank the Deutsche For-

Table V. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{pm}^2 \times 10^{-1}$) for **4**

	x	y	z	$U(\text{eq})^a$
Rb(1)	1518(1)	21(1)	4177(1)	41(1)
P(1)	-1848(1)	2046(1)	2780(1)	30(1)
Si(1)	-1039(1)	-1032(1)	3298(1)	37(1)
Si(2)	-991(1)	4283(1)	2378(1)	47(1)
N(1)	-1113(3)	369(3)	3443(2)	33(1)
N(2)	-1056(3)	2744(3)	3055(3)	35(1)
C(11)	-1836(5)	-642(4)	1868(4)	54(2)
C(12)	778(4)	-2394(4)	3590(4)	57(2)
C(13)	-1875(4)	-1896(4)	4388(4)	50(2)
C(21)	702(5)	3934(6)	1962(5)	85(4)
C(22)	-2309(5)	5646(4)	1044(4)	63(3)
C(23)	-1221(6)	5188(5)	3333(4)	71(3)
C(30)	-3535(4)	2721(4)	3164(3)	35(2)
C(31)	-3988(4)	3782(4)	3531(3)	43(2)
C(32)	-5240(4)	4228(5)	3885(4)	57(2)
C(33)	-6024(5)	3610(5)	3882(4)	65(3)
C(34)	-5592(4)	2545(5)	3532(5)	66(3)
C(35)	-4357(4)	2098(4)	3176(4)	53(2)
C(40)	-2173(4)	2571(4)	1252(3)	38(2)
C(41)	-3426(4)	3290(4)	560(3)	48(2)
C(42)	-3542(5)	3638(5)	-612(4)	69(3)
C(43)	-2399(6)	3250(5)	-1077(4)	74(3)
C(45)	-1016(4)	2206(4)	745(3)	50(2)
C(44)	-1133(5)	2525(5)	-404(4)	67(3)
O(1)	3065(7)	-378(8)	2500(6)	72(2)
O(1')	3629(9)	-91(9)	2770(7)	89(2)
C(51)	2844(13)	-51(14)	1309(11)	86(3)
C(51')	3314(15)	723(16)	1589(14)	110(4)
C(52)	3925(15)	-366(16)	1014(13)	212(5)
C(53)	5164(16)	-1512(16)	2045(13)	102(4)
C(53')	4508(20)	-1739(20)	1923(17)	129(6)
C(54)	4662(15)	-1126(17)	2974(13)	96(4)
C(54')	4448(16)	-1667(17)	2966(14)	104(5)

^a $U(\text{eq})$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VI. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{pm}^2 \times 10^{-1}$) for **5**

	x	y	z	$U(\text{eq})^a$
Cs(1)	6702(1)	-982(1)	-327(1)	29(1)
P(1)	7195(1)	1787(1)	417(1)	18(1)
N(1)	6817(1)	814(1)	918(1)	23(1)
Si(1)	6760(1)	402(1)	1794(1)	24(1)
C(11)	5570(3)	1182(2)	2300(2)	53(1)
C(12)	8369(2)	433(2)	2435(1)	53(1)
C(13)	6179(3)	-1056(2)	1771(1)	47(1)
N(2)	7394(1)	1420(1)	-388(1)	22(1)
Si(2)	8253(1)	1848(1)	-1055(1)	24(1)
C(21)	7695(2)	3210(2)	-1476(1)	39(1)
C(22)	8027(2)	802(2)	-1822(1)	38(1)
C(23)	10087(2)	1940(2)	-745(1)	46(1)
C(30)	5871(1)	2816(1)	363(1)	20(1)
C(31)	5091(2)	3059(1)	-309(1)	24(1)
C(32)	3954(2)	3705(2)	-330(1)	30(1)
C(33)	3605(2)	4131(2)	314(1)	32(1)
C(34)	4404(2)	3942(1)	985(1)	31(1)
C(35)	5525(2)	3290(1)	1008(1)	26(1)
C(40)	8640(2)	2567(1)	840(1)	21(1)
C(41)	9745(2)	2019(2)	1208(1)	29(1)
C(42)	10890(2)	2603(2)	1480(1)	37(1)
C(43)	10950(2)	3726(2)	1375(1)	36(1)
C(44)	9867(2)	4282(2)	1008(1)	35(1)
C(45)	8720(2)	3697(2)	746(1)	28(1)

^a $U(\text{eq})$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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Supplementary Material Available: Tables of crystal and diffractometer data, bond lengths, bond angles, anisotropic displacement parameters, and H atom coordinates and isotropic displacement parameters (28 pages). Ordering information is given on any current masthead page.

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