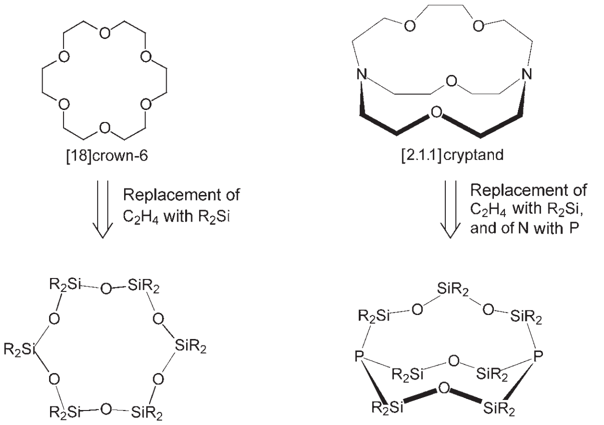
Cage Compounds

DOI: 10.1002/anie.200604673

Stepwise Synthesis and Coordination Compound of an Inorganic Cryptand[**]

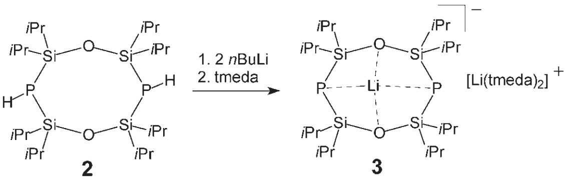
Carsten von Hänisch, Oliver Hampe, Florian Weigend, and Sven Stahl*

Crown ethers and cryptands are very useful ligands in the stabilization of unusual saltlike compounds.[1] They are currently the most widely used ligands in the preparation of crystalline materials containing Zintl anions.[2] Formal substitution of the C_2H_4 groups in crown ethers by SiR_2 groups yields cyclosiloxanes. These inorganic crown ethers have been shown recently to act also as ligands.[3] Herein we report the synthesis and characterization of an inorganic cryptand. The molecular structure of this compound can be deduced from an organic cryptand by replacing the C_2H_4 groups with SiR_2, and the nitrogen atoms with phosphorus atoms (Scheme 1).



Scheme 1. Comparison of organic and inorganic ligands with six donor atoms.

As reported recently, the reaction of the dichlorosiloxane $O(SiiPr_2Cl)_2$ with $[Li(dme)PH_2]$ (dme = 1,2-dimethoxyethane) yields the diphosphanylsiloxane $O(SiiPr_2PH_2)_2$ (**1**).[4] Moreover the cyclic compound $[O(SiiPr_2)_2PH]_2$ (**2**) was obtained with a yield of 25%.[5] The reaction of **2** with two equivalents *n*BuLi after recrystallization from an *n*-pentane/THF/tmeda mixture, yields the ionic compound $[\{O(SiiPr_2)_2P\}_2Li]^-$ $[Li(tmeda)_2]^+$ (**3**; tmeda = *N*,*N*,*N*′,*N*′-tetramethylethlyenediamine).

 (1)

Compound **3** crystallizes in the monoclinic space group $P2_1/n$.[6] In **3**, one of the Li^+ ions (Li2) is bound to two tmeda ligands, whereas the second Li^+ ion (Li1) is coordinated by the dianionic ring $[\{O(SiiPr_2)_2P\}_2]^{2-}$ (Figure 1). Li1 is not only coordinated by the two phosphorus atoms but also by the two oxygen atoms of the siloxane groups. The eight-membered ring is bent slightly into a boat conformation with the lithium cation being located virtually on the P–P axis, but above the two oxygen atoms (P-Li-P angle: 167.2°, O-Li-O angle: 113.9°). The average Li–P bond length is 257.6 pm, similar to a typical bond length observed in other lithium phosphanides. The Li–O bonds in **3** (204.1 pm on average) are slightly

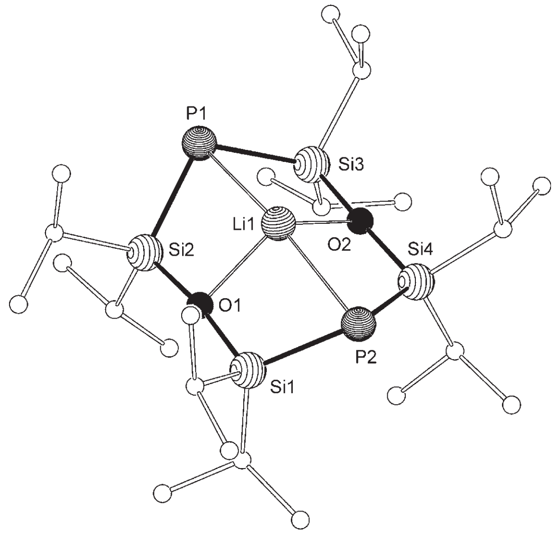


Figure 1. Structure of the anion in **3** (hydrogen atoms are omitted for clarity). Selected bond lengths [pm] and bond angles [°]: Li1-P1 257.8(5), Li1-P2 257.4(4), Li1-O1 204.3(5), Li1-O2 203.8(5), P1-Si2 220.74(10), P1-Si3 220.79(11), P2-Si1 221.38(12), P2-Si4 220.74(10), Si1-O1 167.79(18), Si2-O1 167.33(18), Si3-O2 167.88(18), Si4-O2 167.81(18); P1-Li1-P2 167.20(18), O1-Li1-O2 113.9(2), Si2-P1-Si3 107.83(4), Si1-P2-Si4 108.79(4), Si1-O1-Si2 170.69(11), Si3-O2-Si4 170.23(11).

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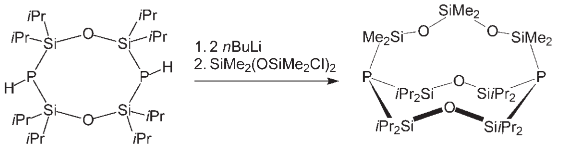
[*] PD Dr. C. von Hänisch, PD Dr. O. Hampe, Dr. F. Weigend, S. Stahl
Institut für Nanotechnologie
Forschungszentrum Karlsruhe
Postfach 3640, 76021 Karlsruhe (Germany)
Fax: (+49) 7247-82-6368
E-mail: carsten.vonhaenisch@int.fzk.de

[**] This work was financially supported by the Deutsche Forschungsgemeinschaft. The authors are grateful to Dr. E. Matern (University of Karlsruhe) for his help with the NMR experiments and Prof. Dr. I. Krossing (University of Freiburg) for providing the salt $Li[Al(OR_F)_4]$ and for offering helpful suggestions about the structure analysis of compound **5**.

longer than typical Li–O bonds in complexes with organic ethers.[7]

The compound $[P_2\{O(SiiPr_2)_2\}_2\{SiMe_2(OSiMe_2)_2\}]$ (**4**) can be synthesized by lithiation of **2** and subsequent reaction with the dichlorotrisiloxane $SiMe_2(OSiMe_2Cl)_2$.



2 **4** (2)

Compound **4** crystallizes in the triclinic space group $P\bar{1}$. Two phosphorus atoms are linked by two disiloxane bridges and one trisiloxane bridge (Figure 2). The disiloxane bridges in **4** are almost linear, with Si-O-Si angles of 172.9 and 171.8°. The two Si-O-Si units of the trisiloxane entity have angles of 142.5° and 144.7° with one oxygen atom (O4) pointing into and one (O3) pointing out of the cage.

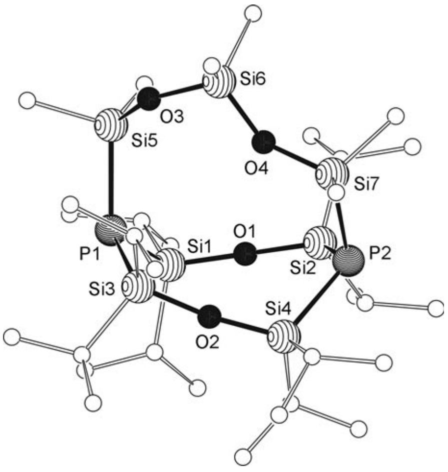


Figure 2. Molecular structure of **4** (hydrogen atoms are omitted for clarity). Selected bond lengths [pm] and angles [°]: P1-Si1 223.98(10), P1-Si3 224.66(10), P1-Si5 224.35(8), P2-Si2 226.10(10), P2-Si4 225.21(10), P2-Si7 223.27(8), Si1-O1 163.61(14), Si2-O1 163.25(14), Si3-O2 163.32(13), Si4-O2 163.18(13), Si5-O3 163.68(5), Si6-O3 162.42(14), Si6-O4 161.87(13), Si7-O4 163.37(4); Si1-O1-Si2 172.86(9), Si3-O2-Si4 171.84(3), Si5-O3-Si6 142.53(9), Si6-O4-Si7 144.67(9).

According to Scheme 1, the cagelike molecular structure of **4** can be regarded as an inorganic analogue of the organic ligand [2.1.1]cryptand. Using **4** as a ligand for alkali-metal cations is thus an obvious idea. Since siloxanes are known as remarkably weak ligands,[8] we investigated the reaction of **4** with the lithium salt of the weakly coordinating anion $[Al(OR_F)_4]^-$ ($R_F = C(CF_3)_3$)[9] in different solvent mixtures. The $^7Li\{^1H\}$ NMR spectrum of such a solution in $C_6H_5CF_3$/C_6D_6 exhibits a triplet at $\delta = 0.0$ ppm. This triplet arises from the coupling between the ^{7}Li nucleus and the two equivalent ^{31}P nuclei ($^1J_{P,Li} = 1.38$ Hz), which clearly suggests that the Li^+ ion resides symmetrically between the P atoms in the cage.

Electrospray mass spectrometry was employed as another independent analytical method to characterize the ionic species present in solution.[10] Figure 3 shows mass spectra obtained when spraying a $C_6H_5CF_3$ solution from a 1:1 mixture of **4** and $Li[Al(OR_F)_4]$. In the positive-ion channel, the mass spectrum is dominated by a strong signal at m/z 763.37, clearly attributable to the $[Li@\mathbf{4}]^+$ ion. At the same time a single negative-ion peak is recorded at m/z 966.94, which is attributed to $[Al(OR_F)_4]^-$ (see upper left inset in Figure 3). Observation of the $[Li@\mathbf{4}]^+$ ion in the gas phase is proof of the complexation of Li^+ by the cage molecule **4** in solution. However, the exact position of the Li^+ ion within the complex cannot be specified.

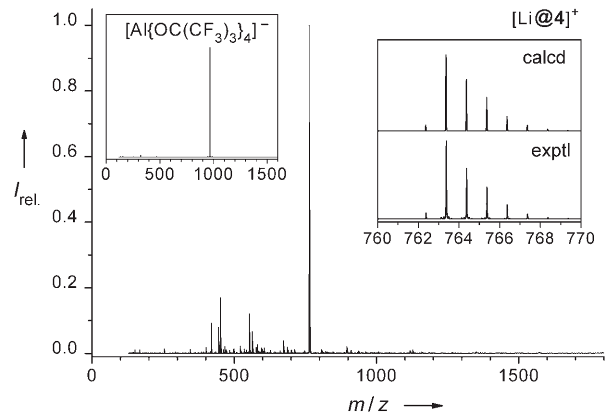


Figure 3. ESI-FT mass spectra (cation mode) from a solution of **4** and $Li[Al(OR_F)_4]$. The upper right inset shows the calculated isotopomer distribution of $[Li@\mathbf{4}]^+$ (composition: $[(SiiPr_2)_4(SiMe_2)_3O_4P_2Li]^+$) and the experimental observation. The left inset shows the mass spectrum in anion mode.

The crystalline compound $[Li@\mathbf{4}][Al(OR_F)_4]$ (**5**) can be obtained by mixing an *o*-xylene solution of **4** and a CH_2Cl_2 solution of $Li[Al(OR_F)_4]$ and subsequent evaporation of CH_2Cl_2 in a vacuum. As a result, an oily phase is separated, from which colorless crystals are precipitated within five days. Complex **5** crystallizes in the monoclinic space group *Pc*, and comprises two independent formula units in the asymmetric unit.[11] The $[Li@\mathbf{4}]^+$ ions can be refined without any problems, but description of the anions is hampered by the disorder in the CF_3 groups, requiring them to be described in split positions. The crystal structure reveals that the Li^+ ion is located in the cage and coordinates to three of the four oxygen atoms present (see Figure 4). The interatomic distances between Li and the two oxygen atoms of the disiloxane groups (O1 and O2) are 206.5 and 209.1 pm, whereas the Li1–O4 bond length is significantly shorter (197.9 pm), comparing favorably with the Li–O bond length in lithium–ether complexes of Li coordination number four.[7] This fact is reflected in the Si6-O4-Si7 angle of 135.5°, which is relatively small compared to the other Si-O-Si angles in **5**, which are between 149.4° and 166.2°. The Li1–P1 bond in **5** is 264.6 pm long, which is at the upper limit of the range usually observed for Li–P bonds in lithium phosphanides.[12] The Li1–P2 separation is 274.1 pm and, therefore, can only be considered

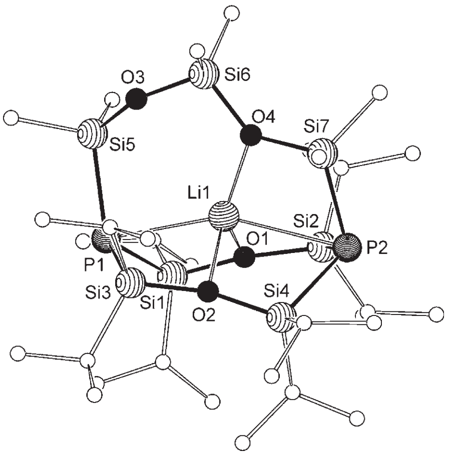


Figure 4. Structure of the cation in **5** (hydrogen atoms are omitted for clarity). Selected bond lengths [pm] and bond angles [°]: Li1-P1 264.6(10), Li1-P2 274.1(11), Li1-O1 209.1(11), Li1-O2 206.5(12), Li1-O4 197.9(11), P1-Si1 225.8(2), P1-Si3 226.5(2), P1-Si5 225.8(3), P2-Si2 226.5(2), P2-Si4 226.5(2), P2-Si7 224.2(2), Si1-O1 164.3(4), Si2-O1 167.5(4), Si3-O2 165.0(4), Si4-O2 166.9(5), Si5-O3 163.1(5), Si6-O3 160.1(5), Si6-O4 164.7(5), Si7-O4 166.8(4); P1-Li1-P2 155.0(5), O1-Li1-O2 104.7(5), O1-Li1-O4 130.0(6), O2-Li1-O4 119.6(5), Si1-O1-Si2 166.2(3), Si3-O2-Si4 165.3(3), Si5-O3-Si6 149.5(4), Si6-O4-Si7 135.5(3).

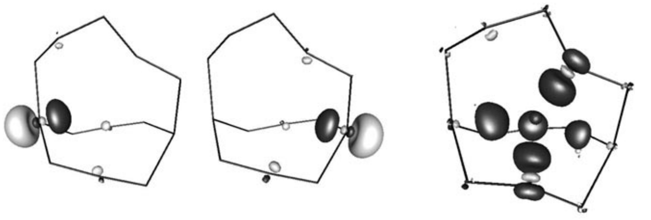


Figure 5. Left: Contour plot of the HOMO and HOMO−1 of **4**. Right: difference in total electron densities of the entire compound ([Li@**4**]$^+$) and the fragments Li$^+$ and **4**. Dark (light) shading indicates higher (lower) electron density for [Li@**4**]$^+$ than for Li$^+$ + **4**, isosurfaces are drawn for 0.005 electrons per Bohr^3. For labeling of atoms, see Figure 4.

as a weak interaction. At P1, the sum of the Si-P-Si angles amounts to 340.4°, corresponding to a strong p-orbital character of the lone pair, which presumably enables a better coordination of the Li$^+$ ion in the cage (see below). At P2, the sum of the bond angles is 320.8°.

The binding affinity (E_B) of **4** to Li$^+$ was compared to that of the five- and six-membered cyclic siloxane ligands, $(Me_2SiO)_5$ (**D5**) and $(Me_2SiO)_6$ (**D6**), used by Passmore and co-workers,[3] by considering the exchange reactions (3) and (4).

$$[\text{Li@}\mathbf{D5}]^+ + \mathbf{4} \rightarrow \mathbf{D5} + [\text{Li@}\mathbf{4}]^+ \quad (3)$$

$$[\text{Li@}\mathbf{D6}]^+ + \mathbf{4} \rightarrow \mathbf{D6} + [\text{Li@}\mathbf{4}]^+ \quad (4)$$

Fully optimized structural parameters were calculated at the DFT level,[13] and the reaction energies amount to $-24\,\text{kJ mol}^{-1}$ for reaction (3) and $+15\,\text{kJ mol}^{-1}$ for reaction (4). The differences in binding affinities of **4** versus **D6** and **D5** thus are significantly smaller than the difference of **D6** versus [18]crown-6, which was calculated to be about $100\,\text{kJ mol}^{-1}$ in reference [3]. Collecting the results, we roughly get: $E_B(\text{[18]crown-6}) \approx E_B(\mathbf{D6}) + 100\,\text{kJ mol}^{-1} \approx E_B(\mathbf{4}) + 115\,\text{kJ mol}^{-1} \approx E_B(\mathbf{D5}) + 140\,\text{kJ mol}^{-1}$.

In the left-hand part of Figure 5 contour plots of the HOMO and HOMO−1 of compound **4** are shown. They are predominantly formed by the lone pairs of the two P atoms. Electrons in these two orbitals together with those of the lone pairs at O1, O2, and O4 yield a significantly nuclear-attractive electrostatic potential in the molecular center (ca. 1.3 V), which means that already the charge distribution in the bare cage leads to an energy of 1.3 eV for the binding of a cation with a + 1 charge. Moreover, the presence of a positive charge (the Li$^+$ ion in this case) leads to a polarization of the lone electron pairs and thus to a higher electrostatic potential and finally to a higher binding affinity. The right-hand part of Figure 5 shows the difference in total electron densities of the entire compound ([Li@**4**]$^+$) and the fragments Li$^+$ and **4** (with unchanged structural parameters). A significant increase in electron density is observed for the portions of the p orbitals at O1, O2, and O4, and at P1 and P2 that are oriented toward the center of the cage.

The calculated influence of the presence/absence of the Li$^+$ ion on the structural parameters of **4** is similar to the influence on the cyclic siloxane **D6**.[3] Typically, smaller Si-O-Si and O-Si-O angles (by 8–15°) are observed for the Li$^+$-containing species than for the "empty" one, while the Si-P-Si angles are nearly unchanged.

In conclusion, the inorganic cryptand **4** was synthesized in a stepwise lithiation/silylation process starting from $O(Si\textit{i}Pr_2Cl)_2$, $[Li(dme)PH_2]$, and $Me_2Si(OSiMe_2Cl)_2$. A first coordination compound with this ligand was obtained from the reaction of **4** with $Li[Al(OR_F)_4]$. The existence of [Li@**4**]$^+$ was confirmed in the gas phase and in solution (ESI-MS and NMR spectroscopy) as well as in the solid state by single-crystal X-ray diffraction. The bond energy of the Li$^+$ ion to **4** is calculated to be similar to that for cyclic siloxanes. DFT calculations show that the bonding results mainly from Coulomb interaction of Li$^+$ with the lone electron pairs at three O and the two P atoms, which are moreover polarized by the presence of the cation. Ongoing studies are devoted to the synthesis and the coordination properties of other inorganic cage compounds.

Experimental Section

3: *n*BuLi (1.6 M solution in hexane; 0.45 mL, 0.72 mmol) was added to a solution of **2** (0.2 g, 0.36 mmol) in *n*-pentane (5 mL). After one hour of stirring, tmeda (1.5 mL) was added, and subsequently all volatile components were removed in a vacuum. Recrystallization from an *n*-pentane/THF mixture yielded **3** as colorless crystals. Yield: 0.18 g (62 %). Elemental analysis (%) calcd for $C_{36}H_{88}Li_2N_4O_2P_2Si_4$ (797.3): C 54.23, H 11.13, N 7.03; found: C 54.06, H 10.93, N 6.84. ^{1}H NMR (C_6D_6/THF): $\delta = 1.41$ (s, *i*Pr, 56 H), 2.00 (s, $N(CH_3)_2$, 24 H), 2.075 ppm (s, $C_2H_4(N(CH_3)_2)_2$, 8 H); ^{7}Li{^{1}H} NMR (C_6D_6/THF): $\delta = 2.00$ ppm (s); ^{29}Si{^{1}H} NMR (C_6D_6/THF): $\delta = 20.4$ ppm (d, $^1J_{P,Si} = 73$ Hz); ^{31}P NMR (C_6D_6/THF): $\delta = -324$ ppm (s, ^{29}Si satellites, $^1J_{P,Si} = 73$ Hz).

4: *n*BuLi (1.6 M solution in hexane; 0.45 mL, 0.72 mmol) was added to a solution of **2** (0.2 g, 0.36 mmol) in diethyl ether (5 mL).

After one hour of stirring, $Me_2Si(OSiMe_2Cl)_2$ (0.1 g, 0.36 mmol) was added to this solution. The reaction mixture was stirred for another hour, and then all volatile components were removed in a vacuum. The residue was dissolved in *n*-heptane (5 mL). After filtration, the solution was cooled down to −30 °C. Compound **4** was obtained as colorless crystals within three days. Yield: 0.16 g (60 %). Elemental analysis (%) calcd for $C_{30}H_{74}O_4P_2Si_7$ (757.5): C 47.57, H 9.85; found: C 47.39, H 9.97. Crystals suitable for X-ray diffraction were obtained from benzene. ^1H NMR (C_6D_6): $\delta = 0.10$ (s, $OSi(CH_3)_2O$, 6 H), 0.59 (d, $^3J_{P,H} = 5.6$ Hz, $PSi(CH_3)_2O$, 12 H), 1.32 (d, $^3J_{H,H} = 7.6$ Hz, $CH(C\mathit{H}_3)_2$, 12 H), 1.35–1.45 (m, superposition of the CH and CH_3 groups of the isopropyl substituent, 40 H), 1.64 ppm (sept, $^3J_{H,H} = 7.6$ Hz, $C\mathit{H}(CH_3)_2$, 4 H); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 1.7$ (s, $OSi(CH_3)_2O$), 8.1 (d, $^2J_{P,C} = 21.8$ Hz, $PSi(CH_3)_2O$), 18.9 (d, $^3J_{P,C} = 5.1$ Hz, $CH\mathit{C}H_3$), 19.5 (d, $^3J_{P,C} = 2.8$ Hz, $CH\mathit{C}H_3$), 20.1 (d, $^2J_{P,C} = 7.5$ Hz, $\mathit{C}HCH_3$), 20.3 (d, $^3J_{P,C} = 5.4$ Hz, $CH\mathit{C}H_3$), 20.5 (s, $CH\mathit{C}H_3$), 21.4 ppm (d, $^2J_{P,C} = 22.4$ Hz, $\mathit{C}HCH_3$); $^{29}Si\{^1H\}$ NMR (C_6D_6): $\delta = -20.6$ (s, $OSi(CH_3)_2O$), 7.8 (d, $^1J_{P,Si} = 20.4$ Hz, $PSi(CH_3)_2O$), 11.5 ppm (d, $^1J_{P,Si} = 30.0$ Hz, $PSi(\mathit{i}Pr)_2O$); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = -242$ ppm (s); IR (KBr): $\tilde{\nu} =$ 2947 (vs), 2895 (s), 2867 (vs), 2725 (w), 2324 (m), 1464 (s), 1419(m), 1385 (m), 1371 (w), 1231 (w), 1214 (w), 1189 (m), 1161 (w), 1071 (m), 1043 (vs), 992 (s), 959 (m), 932 (w), 920 (w), 882 (s), 815(m), 694 (w), 655 (s), 610 (w), 568 (s), 538 (m), 498 (w), 460 cm^{-1} (m); MS (EI, 70 eV): *m*/*z* (%): 757 (100) $[M^+]$, 714 (46.3) $[M^+-C_3H_6]$, 671 (6.6) $[M^+-C_3H_6-\mathit{i}Pr]$, 550 (6.4) $[M^+-Si_3Me_6O_2]$, 512 (19.0) $[M^+-Si_2\mathit{i}Pr_4O]$, 481 (5.5) $[M^+-PSi_2\mathit{i}Pr_4O]$, 207 (25.9) $[Si_3Me_6O_2^+]$.

5: A solution of **4** (0.10 g, 0.13 mmol) in *o*-xylene (5 mL) was added to a suspension of finely ground $Li[Al(OR_F)_4]$[9] (0.13 g, 0.13 mmol) in CH_2Cl_2 (10 mL). The mixture was heated to 40 °C, and the volume was then reduced to approximately 2 mL, which gave rise to a colorless oil. Colorless crystals of **5** grew from this oil within a few days at 6 °C. Yield: 0.20 g (87 %). ^1H NMR ($C_6D_6/C_6H_5CF_3$): $\delta = 0.10$ (s, $OSi(CH_3)_2O$, 6 H), 0.45 (d, $^3J_{P,H} = 4.8$ Hz, $PSi(CH_3)_2O$, 12 H), 1.09 (d, $^3J_{H,H} = 7.6$ Hz, $CH(CH_3)_2$, 12 H), 1.11–1.25 (m, superposition of the CH and CH_3 groups of the isopropyl substituent, 40 H), 1.35 ppm (sept, $^3J_{H,H} = 7.6$ Hz, $C\mathit{H}(CH_3)_2$, 4 H); $^7Li\{^1H\}$ NMR ($C_6D_6/C_6H_5CF_3$): $\delta = 0.00$ ppm (t, $^1J_{P,Li} = 1.38$ Hz); $^{13}C\{^1H\}$ NMR ($C_6D_6/C_6H_5CF_3$): $\delta =$ 0.8 (s, $OSi(CH_3)_2O$), 6.5 (d, $^2J_{P,C} = 18.3$ Hz, $PSi(CH_3)_2O$), 17.9 (d, $^3J_{P,C} = 4.5$ Hz, $CH\mathit{C}H_3$), 18.5 (d, $^3J_{P,C} = 2.7$ Hz, $CH\mathit{C}H_3$), 19.7 (d, $^3J_{P,C} =$ 5.4 Hz, $CH\mathit{C}H_3$), 20.0 (d, $^3J_{P,C} = 8.8$ Hz, $CH\mathit{C}H_3$), 20.8 (d, $^2J_{P,C} =$ 8.9 Hz, $\mathit{C}HCH_3$), 21.5 ppm (d, $^2J_{P,C} = 18.4$ Hz, $\mathit{C}HCH_3$); ^{19}F NMR ($C_6D_6/C_6H_5CF_3$): $\delta = 75.3$ ppm (s); $^{29}Si\{^1H\}$ NMR ($C_6D_6/C_6H_5CF_3$): $\delta = -7.2$ (s, $OSi(CH_3)_2O$), 17.5 (d, $^1J_{P,Si} = 30.0$ Hz, $PSi(CH_3)_2O$), 25.7 ppm (d, $^1J_{P,Si} = 37.9$ Hz, $PSi(\mathit{i}Pr)_2O$); $^{31}P\{^1H\}$ NMR ($C_6D_6/C_6H_5CF_3$): $\delta = -252$ ppm (s, full width at half maximum: 7.0 Hz).

Electrospray mass spectra were taken on a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (Bruker Daltonics, APEX II) equipped with a 7-T magnet and an elecrospray ionization source (Analytica of Branford). The *m*/*z* values given in the text correspond to the most abundant peak of a given isotopomer distribution.

Received: November 16, 2006
Revised: January 17, 2007

Keywords: cage compounds · cryptands · phosphorus · silicon · weakly coordinating anions

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[5] Compound **2** can also be obtained by lithiation of **1** and subsequent reaction with $O(Si\mathit{i}Pr_2Cl)_2$.

[6] STOE-IPDS2, $Mo_{K\alpha}$ radiation, graphite monochromator, $\lambda =$ 0.71073 Å. The structures were solved by direct methods and refined by full-matrix least-squares techniques against F^2 (SHELX-97 program package, G. Sheldrick, Universität Göttingen, Germany **1997**). Molecular diagrams were prepared using the SCHAKAL-97 program (SCHAKAL-97, E. Keller, Universität Freiburg, Germany **1997**). **3**: $C_{36}H_{88}Li_2N_4O_2P_2Si_4$, $M_r = 797.3\ g\,mol^{-1}$, $2.0 \times 0.2 \times 0.2\ mm^3$, $a = 1915.9(4)$, $b =$ 1317.4(3), $c = 2017.4.5(3)$ pm, $\beta = 106.11(3)°$, $V = 5065.5(17) \times 10^6\ pm^3$, monoclinic, space group $P2_1/n$, $Z = 4$, $\rho_{calcd} =$ 1.045 $g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 0.211\ mm^{-1}$, $T = 190$ K, $2\Theta_{max} = 52°$; 25575 reflections measured, 9247 independent reflections, ($R_{int} = 0.0284$), 7267 independent reflections with $F_o > 4\sigma(F_o)$, 451 parameters (P, Si, O, N, C, Li refined anisotropically, H atoms were calculated in ideal positions); $R1 = 0.0528$, $wR2 =$ 0.1533 (all data), residual electron density: 1.150 e $Å^{-3}$. **4**·$^1/_2C_6H_6$: $C_{30}H_{74}O_4P_2Si_7\cdot{}^1/_2C_6H_6$, $M_r = 796.5\ g\,mol^{-1}$, $0.4 \times 0.4 \times$ 0.3 mm^3, $a = 1166.9(2)$, $b = 1185.7(2)$, $c = 1897.9(4)$ pm, $\alpha =$ 86.18(3), $\beta = 83.99(3)$, $\gamma = 66.06(3)°$, $V = 2386.0(8) \times 10^6\ pm^3$, triclinic, space group $P\bar{1}$, $Z = 2$, $\rho_{calcd} = 1.109\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) =$ 0.297 mm^{-1}, $T = 170$ K, $2\Theta_{max} = 52°$; 16608 reflections measured, 8429 independent reflections, ($R_{int} = 0.0405$), 7323 independent reflections with $F_o > 4\sigma(F_o)$, 417 parameters (P, Si, O, C refined anisotropically, H atoms were calculated in ideal positions); $R1 = 0.0348$, $wR2 = 0.0955$ (all data), residual electron density: 0.270 e $Å^{-3}$. **5**: $C_{46}H_{74}AlF_{36}LiO_8P_2Si_7$,$M_r = 1731.5\ g\,mol^{-1}$, $0.4 \times$ $0.2 \times 0.2\ mm^3$, $a = 1232.5(3)$, $b = 1290.7(3)$, $c = 4726.7(10)$ pm, $\beta = 91.39(3)°$, $V = 7516(3) \times 10^6\ pm^3$, monoclinic, space group Pc, $Z = 4$, refined as inversion twin, Flack parameter = 0.24(11), $\rho_{calcd} = 1.530\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 0.315\ mm^{-1}$, $T = 170$ K, $2\Theta_{max} =$ 48°; 29007 reflections measured, 17357 independent reflections, ($R_{int} = 0.0379$), 15062 independent reflections with $F_o > 4\sigma(F_o)$, 1755 parameters (P, Si, Al, F, O, C, Li refined anisotropically, some of the CF_3 groups are disordered and were refined in split positions, H atoms were calculated in ideal positions); $R1 =$ 0.0904, $wR2 = 0.2479$ (all data), residual electron density: 0.894 e $Å^{-3}$. CCDC-627532 (**3**), -627533 (**4**), and -627534 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[11] An inversion center can be excluded because of the non-centrosymmetric molecular structures of the anions and the

cations, and because of the almost parallel orientation of the two $[Al(OR_F)_4]^-$ anions with one tetrahedron corner along the crystallographic *c* axis.

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[13] All calculations were carried out with the TURBOMOLE program system (a); DFT calculations were performed with the B-P86 functional (b, c) within the RI-J approximation (d), using def2-TZVP basis sets (e) and appropriate RI-J auxiliary basis sets (f). a) TURBOMOLE, Version 5–8, Universität Karlsruhe, **2005**; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; c) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822; d) K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283–290; e) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305; f) F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065.