# Lithium, Sodium, and Copper(I) Supersilylphosphanediides $M_2PSi\mathit{t}Bu_3$: Compounds with Novel Spherical $(M_2P)_n$ Frameworks**

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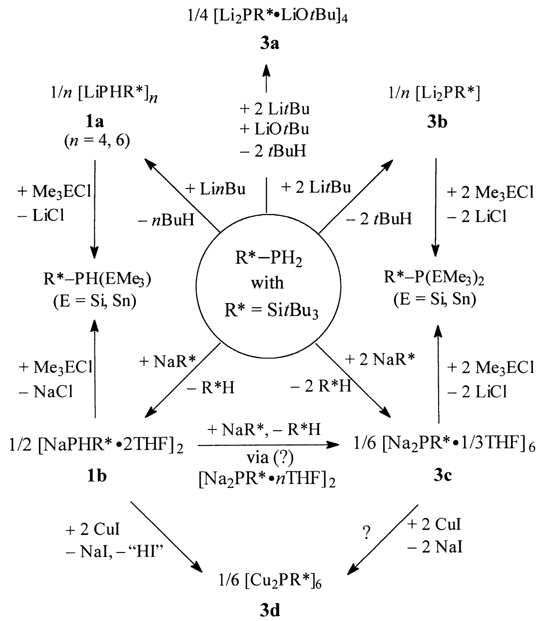
*Dedicated to Professor Gerd Becker
on the occasion of his 60th birthday*

Among the alkali metal phosphanides and phosphanediides **1**–**3**, suitable as phosphanide transfer agents,[1] hitherto only the—more soluble and more readily crystallizable—phosphanides **1** and **2** (ratio M:P = 1:1) have been structurally investigated in detail (see below). Herein we report on the synthesis, reactions, and structures of several phosphanediides **3** (ratio M:P = 2:1) with space-filling supersilyl groups R = R* = Si*t*Bu$_3$[2] (for structurally characterized alkali metal phosphides $M_3P$ (ratio M:P = 3:1) see ref. [3], for several supersilylphosphanides and -phosphanediides of the type **1** and **3** with the divalent metals $Mg^{2+}$, $Ba^{2+}$, and $Sn^{2+}$ see ref. [4]).

| MPHR | $MPR_2$ | $M_2PR$ |
|---|---|---|
| **1** | **2** | **3** |

(M = alkali metal; R = H, organyl, silyl)

*Syntheses:* Donor-containing and donor-free *supersilylphosphanides* **1** are readily accessible by the reaction of alkali metal organyl or silyl compounds with supersilylphosphane $R^*PH_2$ in alkanes, benzene, or ethers (Scheme 1). For instance, the air- and moisture-sensitive phosphanides **1a** and **1b** are formed at room temperature by reaction of equimolar amounts of $R^*PH_2$ and Li*n*Bu in *n*-pentane or NaR* in THF, respectively (NaR* is an ideal sodiating agent as result of its good solubility in organic media and its high basicity). Compound **1a**, which is soluble in hot benzene and toluene, crystallizes in the form of colorless parallelpipeds on cooling from the mentioned solvents. These contain—according to preliminary X-ray structure analyses[5]—molecules of $[LiPHR^*]_4$ (from $C_6H_6$) and $[LiPHR^*]_6$ (from $C_6H_5CH_3$). Compound **1b** crystallizes from THF at −25 °C as colorless needles with $[NaPHR^*\cdot 2THF]_2$ units (see Experimental Section).



Scheme 1. Preparation of lithium, sodium, and copper(I) supersilylphosphanediides (NaR* used as $\mathit{t}Bu_3SiNa(THF)_2$).

Among the *supersilylphosphanediides* **3** (Scheme 1), the air- and moisture-sensitive compound **3a** forms by reaction of $R^*PH_2$ in *n*-heptane with two molar equivalents of Li*t*Bu/*n*-pentane in the presence of LiO*t*Bu, and the air- and moisture-sensitive compound **3b** forms by reaction of $R^*PH_2$ in toluene with two molar equivalents of Li*n*Bu/*n*-hexane or Li*t*Bu/*n*-pentane. Both give colorless powders which are soluble in toluene at 100 °C. On slow cooling of the solutions **3a** crystallizes as colorless octahedra, which were suitable for X-ray structure analysis (see below), whereas **3b** precipitated again as a colorless powder. The reaction of **1b** with an equimolar amount of NaR* (as THF adduct) in benzene led at 60 °C (Scheme 1)—probably via dimeric $Na_2PR^*$ (see Experimental Section)—to the extremely air- and moisture-sensitive, pale yellow, donor-poor phosphanediide **3c.** The likewise air- and moisture-sensitive phosphanediide $K_2PR^*$ can be obtained particularly conveniently by reaction of $PCl_3$ with four- to fivefold molar amounts of KR* in benzene at room temperature. It crystallizes from benzene as orange-red parallelpipeds, which have to date proved unsuitable for X-ray structure analyses.

*Reactions:* Among the reactions of the supersilylphosphanides and -phosphanediides, the silylations and stannylations of **1a**, **1b**, **3b**, and **3c** with $Me_3ECl$ (E = Si, Sn) are worthy of mention. These reactions lead smoothly (Scheme 1) at increased temperature ($Me_3SiCl$) or at room temperature ($Me_3SnCl$) to the compounds $R^*PH(EMe_3)$ and $R^*P(EMe_3)_2$, whose composition conversely allows conclusions about the number of alkali metal atoms in the used phosphanides and phosphanediides. A further reaction (Scheme 1) which demonstrates the suitability of the compounds obtained as phosphanide transfer agents[1] is that of CuI and **1b** (and probably also **3c**) with metal exchange to give the air- and moisture-stable dicopper phosphanediide **3d.** This compound, which crystallizes as yellow-green prisms, could not be characterized by NMR spectroscopy because of its insolubility

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[+] X-ray structure analyses

[**] Compounds of Silicon, Part 133; Supersilyl Compounds of Phosphorus, Part 6. This work was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie. Part 132: N. Wiberg, T. Passler, S. Wagner, *J. Organomet. Chem.* **2000**, *598/2*, 304; Part 5: N. Wiberg, A. Wörner, H.-W. Lerner, K. Karaghiosoff, H. Nöth, *Z. Naturforsch. B* **1998**, *53*, 1004.

in organic solvents such as THF or benzene; however, the crystals were suitable for an X-ray structure analysis (see below).

*Structures:* Previous structure investigations have shown that monolithium phosphanides MPHR **1** and $MPR_2$ **2** display -M-P-M-P- *chains* of linked MP groups[6, 7] (e.g. polymeric $LiPH_2 \cdot DME$, $LiPHMe \cdot DME$, $LiPPh_2 \cdot 2THF$; DME = $MeOCH_2CH_2OMe$; for more complex structures of lithium and sodium phosphanides see ref. [8]). As expected, the repulsive forces remain small between ions of equivalent charge in chains with alternate cationic and anionic members. The chains in question can combine to give double chains[6, 9] (ladder structures; e.g. hexameric $LiP(SiMe_3)_2$) or rings[6, 10–12] (e.g. $3LiP(Si\mathit{i}Pr_3)_2 \cdot LiPH(Si\mathit{i}Pr_3)$; see also **1a, 1b**); in addition, they exist in a separated form as monomers [6, 13] (e.g. $LiP(SiMe_3)_2 \cdot (Me_2NCH_2CH_2)_2NMe$). According to preliminary structure investigations by Driess et al.,[8, 14] the dilithium phosphanediides $M_2PR$ **3** display *spherical frameworks* from linked $M_2P$ groups. Evidently, the formation of such structures allows a minimization of the repulsive forces between ions of equivalent charge in dialkali metal phosphanediides. According to previous studies,[14] additional stabilization of the spherical phosphanediides **3** can be achieved by incorporation of an anion in the center of the framework (e.g. $[Li_2PSiR_3]_8 \cdot Li_2O$ and $[Li_2PSiR'_3]_{12} \cdot Li_2O$ with $SiR_3 = Si\mathit{i}Pr_2Mes$ and $SiR'_3 = SiMe_2(CMe_2\mathit{i}Pr)$) or by cation expulsion (e.g. $Li_{16}P_{10}(Si\mathit{i}Pr_3)_{10}$ with Li:P = 1.6:1). The phosphanediides presented herein show for the first time—probably as a result of the phosphane-bound space-filling supersilyl groups—structures of spherical $(M_2P)_n$ frameworks without anion centers.

Figure 1 shows the comparatively symmetrical structure of $[Li_2PR^* \cdot LiO\mathit{t}Bu]_4$ **3a** in the crystal (orthorhombic; molecular point group $S_4$) together with selected bond lengths and angles.[15] Apparently the compound is based on a spherical framework comprising P, O, and Li atoms. Each P atom is six- (Si + 5Li), each O atom five- (C + 4Li), and each Li atom three-coordinate (2P + O or P + 2O). The structure of **3a** can be described as follows: The twelve Li atoms occupy the corners of a polyhedron formed from annelated $Li_5$ and $Li_4$ rings (see Figure 2). In this polyhedron all $Li_5$ rings are each capped by a $PR^{*2-}$ group and all $Li_4$ rings are each capped by one of the less extended $O\mathit{t}Bu^-$ groups. Thus, the four P and the four O atoms occupy the corners of interpenetrating tetrahedra (Figure 1).

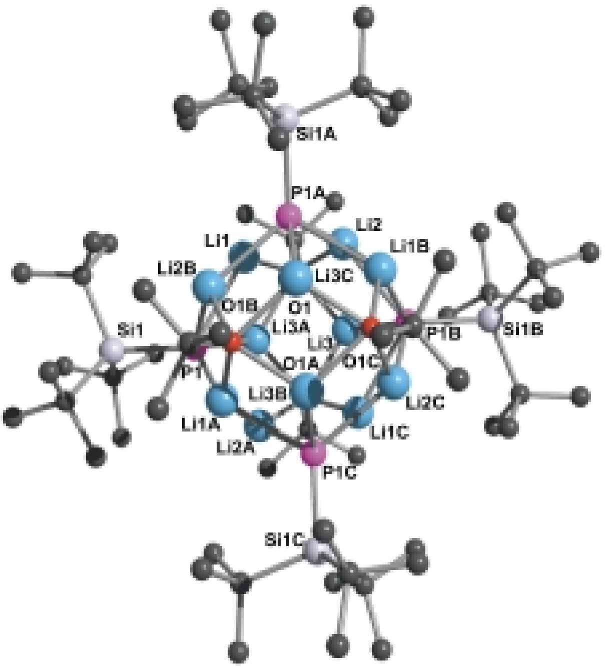

Figure 1. Structure of $[Li_2PSi\mathit{t}Bu_3 \cdot LiO\mathit{t}Bu]_4$ **3a** in the crystal (local symmetry $S_4$; SCHAKAL; hydrogen atoms are omitted for clarity). Selected bond lengths [Å]: P1-Si1 2.218(2), P1-Li1/Li1B/Li2A/Li2B/Li3A 2.54(1)/2.49(1)/2.54(1)/2.52(1)/2.48(1), P1A-Li2/Li3 2.54(1)/2.48(1), P1C-Li1/Li2 2.49(1)/2.52(1), O1-Li1/Li2/Li3/Li3A 2.06(1)/2.08(1)/2.00(1)/2.01(1), O1A-Li3 2.01(1), Si-C 1.96 (average).

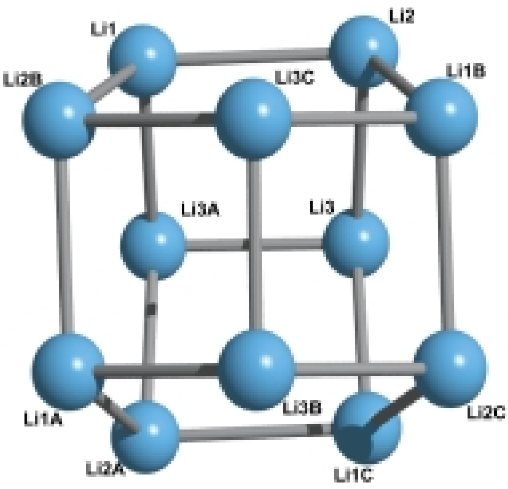

Figure 2. Positions of the Li atoms of **3a** (Figure 1) in the crystal (local symmetry $S_4$; the solid lines do not represent bonds, but only highlight the polyhedron whose corners are occupied by Li atoms).

The structure of $[Na_2PR^*]_6 \cdot 2THF$ **3c** in the crystal (monoclinic, molecular point group $C_s$) is illustrated in Figure 3 together with selected bond lengths and angles.[15] According to this Na and P form a „spherical“ atomic framework, which is dented on one side. The twelve Na atoms occupy (see Figure 4) the corners of six annelated five-membered rings (half-chair), which are each capped by a PR* group. The $Na_{12}$ polyhedron (Figure 4) can be derived from the $Li_{12}$ polyhedron (Figure 2) after replacement of Li for Na and the movement of the common atoms of a pair of annelated $M_4$ rings. This movement takes place in the middle of the common edges of both pairs of annelated $M_4$ rings (thus Li3/Li3A in Figure 2 correspond to Na1/Na6 in Figure 4). In this way the $M_4$ rings of the $Li_{12}$ polyhedron, which are evidently less suitable for $PR^{*2-}$ caps, are converted into the $M_5$ rings of the $Na_{12}$ polyhedron. Moreover, one of the displaced M atoms (Na6 in Figure 3) migrates towards the center of the polyhedron, where it can be additionally coordinated by two P atoms (Figure 3). The four Na atoms (Na7/Na7/Na8/Na8) in the $Na_5$ rings adjacent to this Na atom (Na6), which links the rings, are additionally coordinated to two THF molecules (Figure 3). The other displaced M atom (Na1 in Figure 3) forms contacts with one methyl group each of two adjacent supersilyl groups (C8/C8 in Figure 3). Thus the coordination number of the P atoms is six (Si + 5Na) or seven (Si + 6Na) and that of the Na atoms is three (3P or

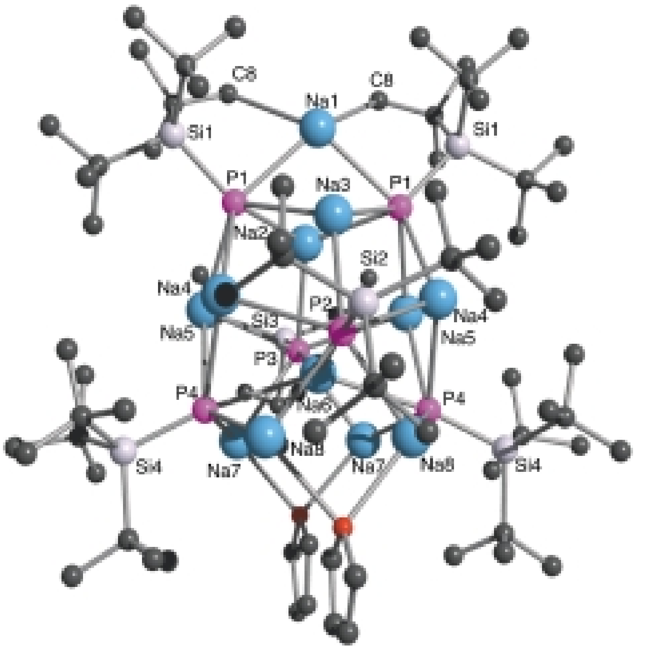

Figure 3. Structure of $[Na_2PSi\mathit{t}Bu_3]_6\cdot 2\,THF$ **3c** in the crystal (local symmetry $C_s$; SCHAKAL; hydrogen atoms are omitted for clarity). Selected bond lengths [Å]: P1-Na1/Na2/Na3 2.832(3)/2.898(5)/2.871(5), P2-Na3/Na4/Na6/Na8 2.839(6)/3.112(4)/3.006(7)/2.890(4), P3-Na2/Na5/Na6/Na7 2.876(5)/3.085(4)/3.021(7)/2.877(4), P4-Na4/Na5/Na6/Na7/Na8 2.942(4)/2.979(4)/2.959(2)/2.822(5)/2.820(5), P1-Si1/P2-Si2/P3-Si3/P4-Si4 2.210(3)/2.210(6)/2.223(6)/2.201(3), Na7-O1/Na8-O2 2.624(12)/2.548(9), Na1-C8 3.03(2).

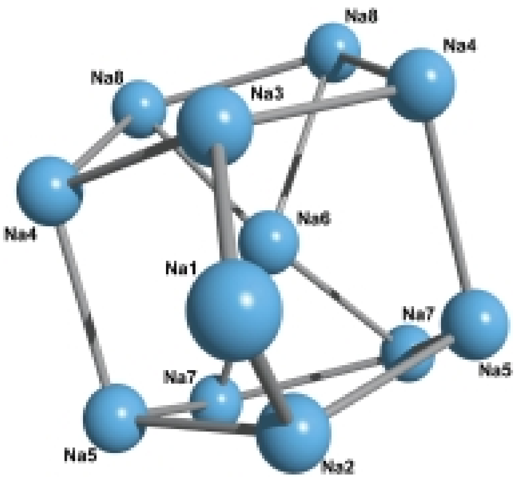

Figure 4. Positions of the Na atoms of **3c** (Figure 3) in the crystal (local symmetry $C_s$; the solid lines do not represent bonds, but only highlight the polyhedron whose corners are occupied by Na atoms).

2 P + O) or four (4 P or 2 P + 2 $CH_3$). The P atoms occupy the corners of a distorted octahedron (Figure 3).

Figure 5 displays the highly symmetrical structure of $[Cu_2PR^*]_6$ **3d** in the crystal (trigonal; molecular point group $S_6$) together with selected bond lengths and angles.[15] In this case, the Cu and P atoms form a spherical atomic framework, in which each P atom is five- (Si + 4 Cu) and each Cu atom six-coordinate (2 P + 4 Cu). The twelve Cu atoms occupy the corners of a regular cuboctahedron; only the six $Cu_4$ rings of which bear PR* caps. It follows that, whereas in the above-mentioned polyhedra from alkali metal cations each face of the polyhedron is capped (to achieve a good charge balance), polyhedra from copper cations, whose ionic bonds to phosphorus are probably significantly polarized, do not require all faces to be capped. In addition, $M_4$ rings are capped instead of $M_5$ rings. The structure of **3d** resembles the structure of the cluster $[Cu_2PPh\cdot PPh_3]_6$, recently synthesized from $PhP(SiMe_3)_2$ and CuCl in the presence of $PPh_3$ and THF, in which the twelve Cu atoms occupy the corners of a compressed cuboctahedron and the six PPh groups cap the $Cu_4$ rings of the $Cu_{12}$ polyhedron.[16] However, the six Ph groups are not sufficient to completely surround the $Cu_{12}$ framework, which as a result of this adds an additional six $PPh_3$ groups—for the stabilization of the $Cu_{12}$ polyhedron—with the formation of $CuPPh_3$ building blocks. The only other neutral dicopper phosphanediide without additional donor ligands, $[Cu_2PR^*]_{12}$ with R = $SiMe_2(CMe_2\mathit{i}Pr)$, was synthesized by Driess and co-workers.[17]

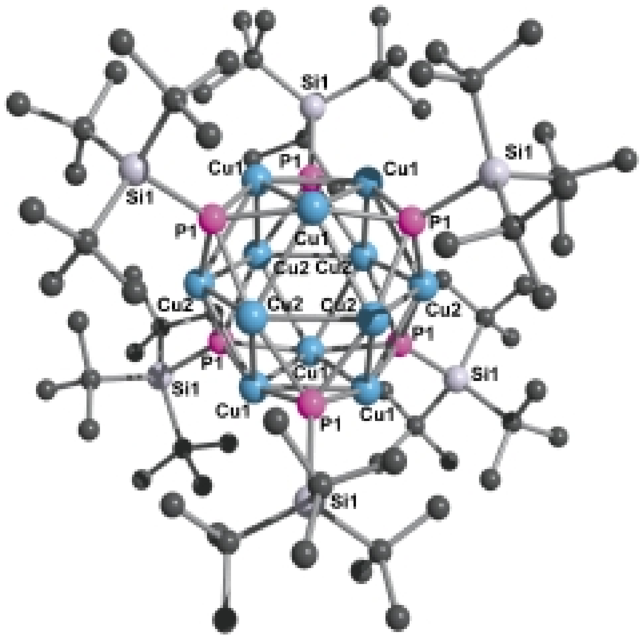

Figure 5. Structure of $[\mathit{t}Bu_3SiPCu_2]_6$ **3d** in the crystal (local symmetry $S_6$; SCHAKAL; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Cu1-Cu2 2.611(1), Cu2-P1 2.239(2), P1-Si1 2.241(3), Si-C 1.95 (average); P1-Cu2-Cu1 113.90(7), Cu2-P1-Si1 125.9(1), C-Si-C 112.2 (average).

## *Experimental Section*

**1a**: Over the course of three days **1a** precipitated as a colorless, fine powder from a solution of $R^*PH_2$ (0.770 g, 3.31 mmol)[18] in *n*-pentane (5 mL) and Li*n*Bu (3.42 mmol) in *n*-hexane (2 mL). (With regard to the reaction in $Et_2O$ see **1b.**) According to NMR spectroscopy the resulting solution contained no starting materials but small amounts of **1a**. Compound **1a** was dissolved by heating for 5 h in benzene or toluene (3 mL). On slow cooling of the solutions, colorless cubic, air- and moisture-sensitive crystals were formed (yield ca. 60%), which according to preliminary X-ray structure analytical studies contained tetramers (from benzene) and hexamers (from toluene), respectively, of lithium supersilylphosphanide **1a**. $^1H$ NMR ($C_6D_6$, TMS internal): $\delta = 1.31$ (br.; Si*t*$Bu_3$); $^{13}C\{^1H\}$ NMR ($C_6D_6$, TMS internal): $\delta = 24.25/32.30$ (br./br.; 3 $\mathit{C}Me_3$/3 $C\mathit{Me}_3$); $^{29}Si\{^1H\}$ NMR ($C_6D_6$, TMS external): $\delta = 34.15$ (d, br., $^1J_{Si,P} = 54.83$; Si*t*$Bu_3$); $^{31}P\{^1H\}$ NMR ($C_6D_6$, TMS internal): $\delta = -335.4$ ($h_{1/2} = 90.0$ Hz; LiHPR*); $^7Li$ NMR ($C_6D_6$, LiCl in $D_2O$ external): $\delta = 3.75$ ($h_{1/2} = 35.7$ Hz; LiHPR*). Notes: 1) LiHPR* (0.225 g, 0.950 mmol) and $Me_3SiCl$ (4.0 mmol) were heated to 60 °C for 24 h in $C_6D_6$ (1 mL). According to NMR spectroscopy complete conversion to supersilyltrimethylsilane $R^*PHSiMe_3$ had taken place, which, after removal of soluble components and volatile components, remained as a colorless, air- and moisture-sensitive solid. $^1H$ NMR ($C_6D_6$, TMS internal): $\delta = 0.297$ (d, $^3J_{H,P} = 4.42$ Hz; $SiMe_3$), 1.186 (s; $SitBu_3$); $^{13}C\{^1H\}$ NMR ($C_6D_6$, TMS internal): $\delta = 7.55$ (d, $^2J_{C,P} = 11.6$ Hz; $SiMe_3$), 24.5/31.9 (d, $^2J_{C,P} = 9.1$ Hz/br.; $3\,CMe_3/3\,CMe_3$); $^{29}Si\{^1H\}$ NMR ($C_6D_6$, TMS external): $\delta = 28.0$ (d, $^1J_{Si,P} = 45.8$ Hz; $SitBu_3$); $^{31}P$ NMR ($C_6D_6$, 85 % $H_3PO_4$ external): $\delta = -245.58$ (d, $^1J_{H,P} = 194.8$ Hz; $R^*PHSiMe_3$). 2) After treatment of LiHPR* (0.225 g, 0.950 mmol) in $C_6D_6$ (1 mL) with $Me_3SnCl$ (2.0 mmol), a colorless precipitate (LiCl) formed immediately. According to NMR spectroscopy complete conversion to supersilyltrimethylstannane $R^*PHSnMe_3$ had taken place, which, after removal of insoluble components and volatile components, remained as a colorless, air- and moisture-sensitive solid. $^1H$ NMR ($C_6D_6$, TMS internal): $\delta = 0.046$ (d, $^3J_{H,P} = 2.36$ Hz, Sn coupling constants 46.66, 43.02 Hz; $SnMe_3$), 1.160 (s; $SitBu_3$); $^{13}C\{^1H\}$ NMR ($C_6D_6$, TMS internal): $\delta = -1.31$ (d, $^2J_{C,P} = 7.08$ Hz, Sn coupling constants 308.88, 277.99 Hz; $SnMe_3$), 24.30/31.18 (d/d, $^2J_{C,P} = 7.8$, $^3J_{C,P} = 2.68$ Hz; $3\,CMe_3/3\,CMe_3$); $^{29}Si\{^1H\}$ NMR ($C_6D_6$, TMS external): $\delta = 28.1$ (d, $^1J_{Si,P} = 56.08$ Hz; $SitBu_3$); $^{31}P$ NMR ($C_6D_6$, 85 % $H_3PO_4$ external): $\delta = -275.30$ (d, $^1J_{H,P} = 187.9$ Hz, Sn coupling constants 723.9, 694.9 Hz; $R^*PHSnMe_3$); $^{119}Sn\{^1H\}$ NMR: $\delta = 15.26$ (d, $^1J_{^{119}Sn,P} = 723.9$ Hz). 3) LiHPR* reacted with $tBu_2HSiF$ and $tBu_2SiF_2$ to give $R^*PHSiHtBu_2$ and $R^*PHSiFtBu_2$, respectively.[18]

**1b**: NaR* (2.15 mmol)[19] in THF (5 mL) was added to $R^*PH_2$ (0.500 g, 2.15 mmol)[18] in THF (3 mL). After 1 h the resulting deep red solution—which according to NMR spectroscopy contained exclusively **1b** and R*H[2]—was concentrated to 4 mL. Dark red needles of dimeric sodium supersilylphosphanide tetrahydrofuran (1/2) (**1b**) precipitated from this solution in the course of five days at −25 °C after addition of *n*-pentane (1 mL) (conversion to $R^*PHSiMe_3$ and $R^*PHSnMe_3$ is possible by reaction with $Me_3SiCl$ and $Me_3SnCl$, see **1a**). $^1H$ NMR ($C_6D_6$, TMS internal): $\delta = 1.40$ ($2\,SitBu_3$), 1.42/3.40 (m/m; $CH_2CH_2O/CH_2CH_2O$ from 4 THF); $^{13}C\{^1H\}$ NMR ($C_6D_6$, TMS internal): $\delta = 23.95/32.12$ ($6\,CMe_3/6\,CMe_3$), 25.67/67.78 ($CH_2CH_2O/CH_2CH_2O$ from 4 THF); $^{29}Si\{^1H\}$ NMR ($C_6D_6$, TMS external): $\delta = 33.74$ (d, $^1J_{P,Si} = 56.4$ Hz; $2\,SitBu_3$); $^{31}P$ NMR ($C_6D_6$, 85 % $H_3PO_4$ external): $\delta = -327.72$ (d, $^1J_{P,H} = 164.1$ Hz; NaHPR*). According to X-ray structure analysis[2] **1b** contains a planar NaPNaP four-membered ring (Na–P 2.840(4) Å, Na-P-Na/P-Na-P 85.7(1)/94.3(1)°) with distorted tetrahedrally coordinated P (2 Na + H + R*) and Na atoms (2 P + 2 THF) as well as *trans*-oriented R* groups (P–Si 2.197(3), Na–O 2.281(7), Na–O 2.330(8) Å; O-Na-O 91.5(3)°). Note: According to NMR spectroscopy, analogue **1b** is the dimeric lithium supersilylphosphanide diethyl ether (1/1) $LiHPR^* \cdot Et_2O$,[18] which is accessible from $R^*PH_2$ in $Et_2O$ and Li*n*Bu in *n*-hexane; **1b** only has one space-filling donor per Li atom.

**3a**: Li*Ot*Bu-containing Li*t*Bu (8.00 mmol) in *n*-pentane (8 mL) was added dropwise to a solution of $R^*PH_2$ (0.851 g, 3.66 mmol)[18] in *n*-heptane (10 mL). In the course of five days colorless **3b** formed from this mixture as an insoluble powder (see below) that was separated by decanting off the solution, which according to NMR spectroscopy contained some **3b** and a similar amount of Li*Ot*Bu. After removal of all volatile components from the decanted solution, the residue was taken up in benzene (1 mL). The suspension formed was heated to 100 °C for 5 h and the resulting solution was slowly allowed to cool to room temperature over two days during which tetrameric dilithium supersilylphosphanediide – lithium-*tert*-butylate (1/1) (**3a**) crystallized as colorless octahedra (yield not calculable since the concentrations of Li*Ot*Bu and **3b** unknown). The composition of **3a** was confirmed by X-ray structure analysis (see Figure 1). According to NMR spectra **3a** decomposes in solution into the components **3b** (see below) and Li*Ot*Bu [$^1H$ NMR ($C_6D_6$, TMS internal): $\delta = 1.22$ (s; *Ot*Bu); $^{13}C\{^1H\}$ NMR ($C_6D_6$, TMS internal): $\delta = 69.9/32.0$ ($OCMe_3/OCMe_3$)].

**3b**: Li*n*Bu (6.68 mmol) in *n*-hexane (4 mL) or Li*t*Bu (6.72 mmol) in *n*-pentane (4 mL) was added dropwise to $tBu_2SiPH_2$ (0.770 g, 3.31 mmol)[18] in toluene (8 mL) and the clear, pale yellow solutions were concentrated to 2 mL, which led to the precipitation of colorless **3b** as a fine powder in 90 % yield. According to NMR spectroscopy (exchange of the solvent by $C_6D_6$), the two solutions contained the same supersilyl-group-containing compound (**3b**) and were free of starting material. Colorless, microcrystalline, air- and moisture-sensitive, oligomeric dilithium supersilylphosphanediide **3b**, which is insoluble in pentane and sparingly soluble in benzene and toluene, also precipitated as microcrystals on cooling of toluene solutions; however, these crystals were not suitable for X-ray structure analysis. $^1H$ NMR ($C_6D_6$, TMS internal): $\delta = 1.41$ (v br.); $^{13}C\{^1H\}$ NMR ($C_6D_6$, TMS internal): $\delta = 24.2/33.1$ (v br./v br.; $CMe_3/CMe_3$); $^{29}Si\{^1H\}$ NMR ($C_6D_6$, TMS external): very broad signal ($h_{1/2} = 136$ Hz) with four sharp lines at $\delta = 39.59$, 38.98, 38.44, 37.91; $^{31}P\{^1H\}$ NMR ($C_6D_6$, 85 %.$H_3PO_4$ external): very broad signal ($h_{1/2} = 1243$ Hz) with five maxima at $\delta = -395.5$, −397.0, −400.0, −404.5, −406.5; $^7Li$ NMR ($C_6D_6$, LiCl in $D_2O$ external): $\delta = 6.6$ ($h_{1/2} = 130$ Hz; $Li_2PR^*$). Notes: 1) According to NMR spectroscopy ($C_6D_6$), after $Li_2PR^*$ (0.230 g, 0.94 mmol) and $Me_3SiCl$ (4.0 mmol) in $C_6D_6$ (1 mL) had been heated to 100 °C for three days, complete conversion had occurred to supersilylbis(trimethylsilyl)phosphane $R^*P(SiMe_3)_2$, which, after removal of insoluble components and volatile components, remained as a colorless, air- and moisture-sensitive solid. $^1H$ NMR ($C_6D_6$, TMS internal): $\delta = 0.463$ (d, $^3J_{H,P} = 4.21$ Hz; $2\,SiMe_3$), 1.230 (s; $SitBu_3$); $^{13}C\{^1H\}$ NMR ($C_6D_6$, TMS internal): $\delta = 25.0$ (d, $^2J_{C,P} = 8.83$ Hz; $3\,CMe_3$), 32.2 (br.; $3\,CMe_3$), 4.23 (d, $^2J_{C,P} = 10.45$ Hz; $2\,SiMe_3$); $^{29}Si\{^1H\}$ NMR ($C_6D_6$, TMS external): $\delta = 35.3$ (d, $^1J_{Si,P} = 50.85$; $SitBu_3$). 2) $Li_2PR^*$ (0.230 g, 0.94 mmol) in $C_6D_6$ (1 mL) was combined with $Me_3SnCl$ (3.0 mmol). According to NMR spectroscopy ($C_6D_6$) this reaction led to the complete conversion to supersilylbis(trimethylstannyl)phosphane $R^*P(SnMe_3)_2$, which, after removal of insoluble components and volatile components, remained as a colorless, air- and moisture-sensitive solid. $^1H$ NMR ($C_6D_6$, TMS internal): $\delta = 1.201$ (s; $SitBu_3$), 0.398 (d, $^3J_{H,P} = 2.25$ Hz; Sn coupling constants 51.24, 47.49 Hz; $2\,SnMe_3$); $^{13}C\{^1H\}$ NMR ($C_6D_6$, TMS internal): $\delta = -1.21$ (d, $^2J_{C,P} = 7.07$ Hz; Sn coupling constants 302.68, 291.53 and 7.83 Hz; $2\,SnMe_3$), 24.57 (d, $^2J_{C,P} = 7.63$ Hz; Sn coupling constants 7.72 Hz; $3\,CMe_3$), 31.86 (d, $^3J_{C,P} = 3.06$ Hz; $3\,CMe_3$); $^{29}Si$ NMR: $\delta = 32.68$ (d, $^1J_{Si,P} = 78.24$ Hz; Sn coupling constants 37.4 Hz; $^{31}P\{^1H\}$ NMR ($C_6D_6$, 85 % $H_3PO_4$ external): $\delta = -293.10$ (s; Sn coupling constants $SitBu_3$ 839.3, 799.2 Hz; $R^*P(SnMe_3)_2$); $^{119}Sn\{^1H\}$ NMR: 25.42 (d, $^1J_{^{119}SnP} = 839.3$, $^2J_{^{119}Sn^{117}Sn} = 236.5$ Hz; $2\,SnMe_3$).

**3c**: A solution of NaR* (3.10 mmol)[19] in THF (3.5 mL) was added dropwise to $R^*PH_2$ (0.359 g, 1.55 mmol),[18] which led to the formation of **1b** together with R*H (see above). After this all volatile components were removed under vacuum, the remaining $R^*PHNa \cdot 2\,THF$ and $NaR^* \cdot 2\,THF$ (each 1.55 mmol) were dissolved in benzene (1.5 mL), and the solution was heated to 60 °C for 18 h, after which it was free from starting material (quantitative formation of the phosphanediide, which formed only very slowly from **1b** at room temperature; see note 1). After 24 h all volatile components ($C_6H_6$, THF, R*H) were removed under vacuum at room temperature and the residue was dissolved in benzene (1 mL). Hexameric disodium supersilylphosphanediide precipitated slowly from this solution as THF-adduct **3c** in the form of yellow crystals (yield ca. 50 %). $^1H$ NMR ($C_6D_6$, TMS internal): $\delta = 1.40$ (br.; $6\,SitBu_3$), 1.42/3.40 (m/m; 2 THF); $^{13}C\{^1H\}$ NMR ($C_6D_6$, TMS internal): $\delta = 24.3/33.0$ (br./br.; $18\,CMe_3/18\,CMe_3$); $^{29}Si$ NMR ($C_6D_6$, TMS external): $\delta = 39.2$ (br., $h_{1/2} = 130$ Hz; $6\,SitBu_3$); $^{31}P\{^1H\}$ NMR ($C_6D_6$, 85 % $H_3PO_4$ external): $\delta = -398.0/-405.5/-409.0$ (very broad; $h_{1/2} = 350/404/404$ Hz; 6 PR*); X-ray structure analysis: see Figure 3. Notes: 1) According to the NMR spectrum, the solution formed by the reaction of the THF-adduct **1b** in benzene with $NaR^* \cdot 2\,THF$ at 60 °C for 18 h initially contained $Na_2PR^*$ as a THF adduct (not isolated; transformation into $R^*P(SiMe_3)_2$ and $R^*P(SnMe_3)_2$ possible by reaction with $Me_3SiCl$ and $Me_3SnCl$; cf. **3b**). Owing to its good solubility, the diphosphanediide could be at most a dimer and according to NMR spectroscopy it is symmetric [$^{29}Si\{^1H\}$ NMR ($C_6D_6$, TMS external): $\delta = 40.0$ (d, $^1J_{Si,P} = 84.0$ Hz; $SitBu_3$); $^{31}P\{^1H\}$ NMR ($C_6D_6$, 85 % $H_3PO_4$ external): $\delta = -405.0$ (s; $h_{1/2} = 40$ Hz; $Na_2PSitBu_3$)]. Possibly, the compound is based on a framework of four Na atoms, which are coordinated to THF, localized at the corners of a square; the $Na_4$ rings in this case would be capped on both sides by PR* groups. 2) $[K_2PR^*]_x$ (together with H.-W. Lerner): KR* (0.131 g, 0.550 mmol)[19] and $PCl_3$ (0.021 g, 0.15 mmol) were left in $C_6D_6$ (0.6 mL) for four weeks at room temperature. According to NMR spectroscopy the initially green solution contained R*KP–PKR* ($\delta(^{31}P) = -255.2$). In the course of the formation of $K_2PR^*$ the solution became red (after addition of $Me_3SiCl$ or $Me_3SnCl$ one obtained $R^*P(SiMe_3)_2$ or $R^*P(SnMe_3)_2$, repectively; cf. **3b**). Orange-red cubes, which were not suitable for an X-ray structure analysis, were formed from the reaction solution in the course of a few months. $^1H$ NMR ($C_6D_6$, TMS internal): $\delta = 1.387$ (br.; $SitBu_3$); $^{29}Si\{^1H\}$ NMR ($C_6D_6$, TMS external): as in the cases of other potassium salts of supersilyloligophosphanes[2] no $^{29}Si$ NMR signals were observed; $^{31}P\{^1H\}$ NMR ($C_6D_6$, 85% $H_3PO_4$ external): $\delta = -319.4$ ($K_2PR^*$). The reaction of $KR^*$ and $PCl_3$ in the molar ratio 2:1 gave quantitative amounts of $R^*ClP{-}PClR^*$ ($\delta(^{31}P) = 188$).[2]

**3d**: A solution of **1b** (0.199 g, 0.500 mmol) in THF (2 mL) was added to CuI (0.160 g, 0.840 mmol), and after 1 h the insoluble components were removed by centrifugation. Hexameric dicopper supersilylphosphanediide (**3d**) crystallized in the form of yellow-green prisms (yield ca. 50%) from the remaining solution in the course of five days. The compound **3d**, which was insoluble in organic media, was characterized by X-ray structure analysis (Figure 5).

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[15] Crystal structure analyses: **3a**: orthorhombic, space group $P4(2)/n$, $a = 17.9170(2)$, $c = 13.0721(2)$ Å, $Z = 9$, $V = 4196.39(9)$ Å$^3$, 2439 independent reflections ($I > 2\sigma$(I)). All non-hydrogen atoms were refined anisotropically and the H atoms were included in calculated positions. $R1 = 0.0904$ (observed reflections), $wR2 = 0.1984$ (all data). **3c**: monoclinic, space group $P2(1)/m$, $a = 16.320(2)$, $b = 22.210(4)$, $c = 18.410$ (4) Å, $\beta = 108.46(2)^\circ$, $Z = 4$, $V = 6329.5(1)$ Å$^3$, 10419 independent reflections ($I > 2\sigma(I)$). All non-hydrogen atoms were refined anisotropically and the H atoms were included in calculated positions. $R1 = 0.099$ (observed reflections), $wR2 = 0.265$ (all data). The cell contained twelve solvent molecules ($C_6H_6$). The $R1$ value could not be improved further as a result of the poor quality of the crystal and a disorder of the *t*Bu groups bound to Si as well as the cocrystallizing benzene molecules. **3d**: trigonal, space group $R\bar{3}$ (no. 148), $a = 14.742(3)$, $c = 39.586(7)$ Å, $Z = 3$, $V = 7451(2)$ Å$^3$, 2488 independent reflections ($I > 2\sigma(I)$). All non-hydrogen atoms were refined anisotropically and the H atoms were included in calculated positions. $R1 = 0.0541$ (observed reflections), $wR2 = 0.1334$ (all data). The intensities were measured with a Siemens-P4 apparatus with a CCD area detector (**3a**), a Stoe imaging plate (**3c**), and a Nonius Mach-3 appratus (**3d**) ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, respectively, $\omega$ scan, **3c**: $\phi = 0-120^\circ$; $\Delta\phi = 0.3^\circ$; 10 min irradiation time), $T = 173(2)$, 193(2), and 293(2) K), respectively. The structures were solved by direct methods (SHELXS-97, SHELXL-93) and refined with full matrix against $F^2$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-138960 (**3a**), CCDC-139064 (**3c**), and CCDC-138956 (**3d**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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# Confinement of $[(H_2O)_2 \cap ([18]\text{Crown-6})]$ in a Disc-Shaped Cavity Lined with Six Nickel(II) Macrocycle Dimers Acting as Divergent Receptor Molecules**

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The nickel(II) complex [Ni(tmtaa)] (Equation (1)) and its analogue with two methyl groups on each of the phenyl rings of the ligand, [Ni(omtaa)], are versatile receptors for a range of globular molecules.[1–4] A 1:1 complex between [Ni(tmtaa)] and fullerene is known, in which the macrocycle acts as a divergent receptor for $C_{60}$. A fullerene perches in each macrocycle cavity in an infinite zigzag array.[1] A similar structure is found for $C_{70}$ with [Ni(omtaa)].[3] For smaller globular molecules, including 1,2-dicarba-*closo*-dodecaborane(12), tetraphosphorus trisulfide, tetraphosphorus triselenide, and *cyclo*-octasulfur, the [Ni(tmtaa)] complex self associates through aromatic faces into dimers and these dimers then act as divergent homotopic receptors with a 1:2 ratio of guest:host

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