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A multidentate phosphinoalkoxide ligand as a building block in mixed polylithium aggregates

Alexander Feustel and Gerhard Müller*

Fachbereich Chemie, Universität Konstanz, Universitätsstr. 10, 78464 Konstanz, Germany. E-mail: gerhard.mueller@chemie.uni-konstanz.de

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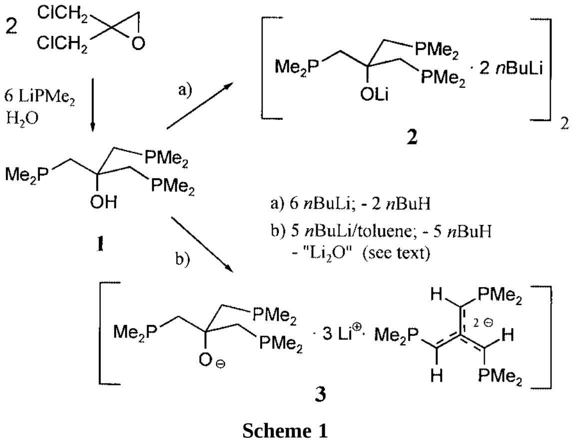
The tris(dimethylphosphinomethyl)-substituted lithium alkoxide [$LiOC(CH_2PMe_2)_3$] acts as a building block in mixed polylithium aggregates, effectively capping triangular Li_3 polyhedral faces; it further reacts with lithium organyls to yield the Y-conjugated, symmetrically tris(dimethylphosphino)-substituted trimethylenemethane dianion.

Chelating phosphinoalkoxides[1] have been used extensively as ligands to transition metals where much of the pertinent interest stems from the fact that many such complexes are effective catalyst precursors in a variety of industrially useful processes.[2,3] In contrast to this, only a few main group metal complexes of phosphinoalkoxides have been described.[3b–d,f,4] The same applies to lanthanide complexes.[5] We are interested in multidentate phosphinoalkoxides which we expect to effectively complex more lithium cations than required for charge neutrality (lithium trap) thereby resulting in mixed multinuclear lithium aggregates which also incorporate additional anions.

The tris(phosphinomethyl)-substituted alcohol **1** was found to be particularly useful in this respect. It was prepared from 1-chloro-2,3-epoxy-2-chloromethylpropane by reaction with 3 equivalents of $LiPMe_2$ (Scheme 1)[6] following the synthesis of the corresponding perphenyl compound.[3c] Compound **1** reacts with excess *n*BuLi (2.5 M solution in hexane)[3c] at −78 °C without additional solvent to form the lithium alkoxide which crystallizes with two equivalents of *n*BuLi as a hexalithium dimer† with crystallographic inversion symmetry (compound **2**; Scheme 1).‡ In the mixed *n*-butyllithium/lithium alkoxide aggregate **2** the six lithium atoms are arranged at the corners of a slightly distorted octahedron (Fig. 1). Two opposite triangular Li_3 faces of the octahedron are capped each by the μ_3-oxygen atoms of one alkoxide ligand. In addition, each of the lithium atoms of these Li_3 faces is coordinated by one of the phosphino groups of the same ligand. Thereby three lithium atoms are held closely together by one of the deprotonated monoanionic ligands **1** in a very compact and effective way. Particular indications of this are the short Li–O bonds and the Li–P bond distances (see Fig. 1).[7] Charge neutrality in dimeric **2** is achieved by four additional *n*-butyl anions which bridge four of the remaining triangular faces of the octahedron. As is often the case for hexameric octahedral compounds with a 1 : 1 stoichiometry of cation to anion, the two unbridged faces of the octahedron are on opposite sides of the polyhedron. It should be noted that solid *n*BuLi itself is an octahedral hexamer.[8] To our knowledge, in addition to [*n*BuLi· LiO*t*Bu]$_4$[9] only one other mixed organolithium/lithium alkoxide aggregate has been structurally characterized to date.[10]



Scheme 1

Formation and structural details of **2** strongly suggest that [$LiOC(CH_2PMe_2)_3$], formed initially by deprotonation of **1**, has further lithium binding capacity trapping two additional lithium cations. The fragment [$Li_3OC(CH_2PMe_2)_3$]$^{2+}$ itself seems to be an ideal building block for mixed oligomeric lithium aggregates, in which the lithium atoms are at the vertices of trigonal polyhedral faces.

Proof for this comes from a second, unexpected reaction of **1** with *n*BuLi. In contrast to the synthesis of **2**, which was performed in the absence of solvent (other than the hexane contained in the 2.5 M solution of *n*BuLi), **1** reacts with excess *n*BuLi in toluene alone at room temperature to form the Y-conjugated, symmetrically tris(dimethylphosphino)-substituted trimethylenemethane dianion which, to our knowledge, has not been described before.[11] It crystallizes with the beforementioned fragment [$Li_3OC(CH_2PMe_2)_3$]$^{2+}$ as counter ion (compound **3**; Scheme 1).† At the center of the molecular structure of **3** (Fig. 2)‡ is an equilateral triangle of lithium atoms which is capped on one side by the deprotonated alcohol **1** in much the same way as in the structure of **2**. The other side of the

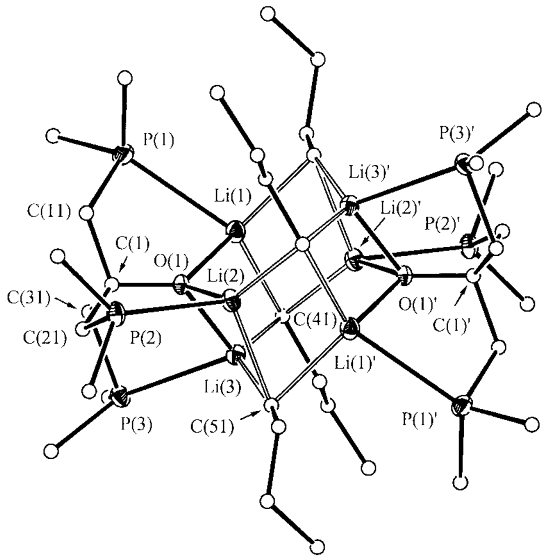


Fig. 1 Molecular structure of **2** in the crystal (ORTEP-III; displacement ellipsoids at the 30% probablility level. For clarity, C atoms are drawn as spheres with arbitray radii, and all H atoms have been omitted. Open bonds serve to highlight the Li–C bonds. Primed atoms are related to those without a prime by a center of inversion). Distances (Å): Li(1)–O(1) 1.904(4), Li(2)–O(1) 1.897(4), Li(3)–O(1) 1.916(4), Li(1)–P(1) 2.755(4), Li(2)–P(2) 2.613(4), Li(3)–P(3) 2.736(4).

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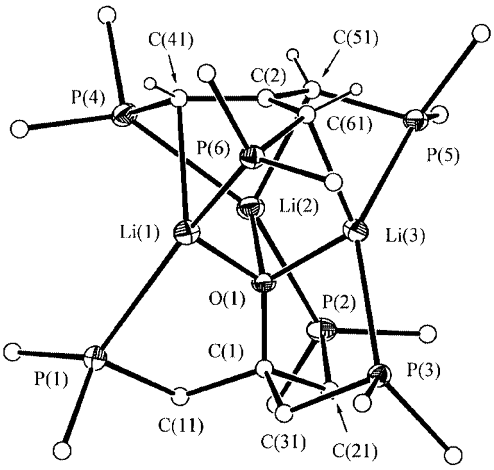

Fig. 2 Molecular structure of **3** in the crystal (ORTEP-III; displacement ellipsoids at the 30% level. For clarity, C atoms are drawn as spheres with arbitray radii; H atoms omitted except those at the methylene C atoms). Distances (Å): Li(1)–O(1) 1.888(4), Li(2)–O(1) 1.877(3), Li(3)–O(1) 1.885(4), Li(1)–P(1) 2.665(4), Li(2)–P(2) 2.696(4), Li(3)–P(3) 2.638(4), Li(1)–P(6) 2.550(3), Li(2)–P(4) 2.592(4), Li(3)–P(5) 2.562(4).

Li_3 triangle is coordinated by the tris(phosphino)-substituted trimethylenemethane dianion. Thereby each lithium atom is coordinated to one of the phosphino groups and a methylene carbanionoid carbon atom of an adjacent arm of the dianion. Each of the lithium atoms are four-coordinate, being bonded to one oxygen, two phosphorus, and one carbon atom. It should be noted that in the only other dilithium trimethylenemethane derivative structurally characterized so far,[12] the lithium atoms are disposed on opposite sides of the trimethylenemethane dianion while in **3** the fragment $[Li_3OC(CH_2PMe_2)_3]^{2+}$ forces the lithium atoms to be located on only one side, in accord with our assumption that $[Li_3OC(CH_2PMe_2)_3]^{2+}$ should be an ideal building block for trigonal polyhedral lithium faces. Both the structural data (Fig. 2) as well as the ^{31}P and particularly the ^{7}Li NMR spectra indicate that the Li atoms in **3** are more tightly bound to the trimethylene dianion rather than to the alkoxide. This follows clearly from the shorter Li–P bonds and the additional Li–C bonds to the dianion while the NMR data indicate that at room temperature the alkoxide is freely rotating around the central C–O axis with respect to the Li_3 triangle (with the dianion being held firmly in place).†

The unexpected formation of the tris(dimethylphosphino)-substituted trimethylenemethane dianion in **3** upon reaction of **1** with excess *n*BuLi involves the formal loss of Li_2O. At present we do not know whether Li_2O is actually formed in the reaction sequence, or whether the O^{2-} anion is part of a larger mixed aggregate.[13] We believe that expulsion of O^{2-} occurs after multiple deprotonation of **1** not only at oxygen but also at one or more of the methylene carbon atoms. The formation of the trimethylenemethane dianion from **1** is then believed to be driven by the reduction of negative charge on the anion by loss of O^{2-} and by the formation of a Y-conjugated π-system.[14]

Notes and references

† *Syntheses*: **2**: to 0.3 g (1.2 mmol) of **1** 2.0 ml (5.0 mmol) of a 2.5 M solution of *n*BuLi in hexane was added at −78 °C. The reaction mixture was warmed to room temperature whereupon a clear solution formed from which immediately small colorless crystals of **2** precipitated. After 30 min the crystals rapidly decomposed to an amorphous solid. The recording of NMR spectra is hampered by the necessity to avoid solvents in the synthesis of **2** (see synthesis of **3**).

3: Toluene (0.75 ml) was added to 110 mg (1.7 mmol) of neat *n*BuLi. Subsequently 140 mg (0.55 mmol) of **1** was added dropwise at room temperature, throughly mixed, and left standing for 2 d. The yield of **3** in solution is *ca.* 70% (^{31}P NMR). Colorless needles formed which proved suitable for X-ray diffraction. Mp 165 °C (decomp.); Anal. $C_{20}H_{45}Li_3OP_6$; calc: C, 47.27; H, 8.92; found: C, 47.02; H, 8.34%. $^{31}P\{^1H\}$ NMR (162 MHz, toluene-d$_8$, 25 °C, ext. 85% H_3PO_4): alkoxide: δ −59.5 [br s]; dianion: −64.2 [q (1 : 1 : 1 : 1), $^1J_{PLi}$ 58 Hz]; $^{31}P\{^1H\}$ NMR (toluene-d$_8$, −80 °C): alkoxide: δ −63.3 [m]; dianion: −64.2 [qd, $^1J_{PLi}$ 58, $^2J_{PP}$ 19 Hz], $T_C \approx -45$ °C; $^7Li\{^1H\}$ NMR (155 MHz, toluene-d$_8$, 25 °C, ext. 1 M LiBr in THF-d$_8$): δ 0.35 [dq, $^1J_{LiP}$ 14 Hz, with 3 alkoxide P, $^1J_{LiP}$ 58 Hz, with 1 dianion P]; $^7Li\{^1H\}$ NMR (toluene-d$_8$, −80 °C): δ 0.35 [dd, $^1J_{LiP}$ 42 Hz, with 1 alkoxide P, $^1J_{LiP}$ 58 Hz, with 1 dianion P], $T_C \approx -20$ °C.

‡ *Crystallography*: single crystals of **2**, grown as described above, were transferred immediately to the diffractometer (Enraf-Nonius CAD4) and examined at −78 °C under strict exclusion of air and moisture in a frozen oil drop (Mo-Kα radiation, λ = 0.71069 Å). *Crystal data* for **2**: $C_{36}H_{84}Li_6O_2P_6$, M = 776.49, monoclinic, space group $C2/c$, a = 21.440(2), b = 17.254(1), c = 14.121(1) Å, β = 103.000(9)°, V = 5089.8(8) Å^3, Z = 4, D_c = 1.013 g cm^{-3}, μ(Mo-Kα) = 2.4 cm^{-1}. 4498 unique reflexions (*hkl* range: ±25, +20, +16) up to $((\sin\theta)/\lambda)_{max.}$ = 0.595 Å^{-1}, $R/wR/S$ = 0.047/0.132/1.04 for 236 refined parameters and all data (non-H atoms anisotropic, H atoms fixed). $\Delta\rho_{fin}$(max./min.) = 0.41/−0.37 e Å^{-3} (SHELXS-97, SHELXL-97).

Single crystals of **3**, grown as described above, were examined at −78 °C in a frozen oil drop. *Crystal data* for **3**: $C_{20}H_{45}Li_3OP_6$, M = 508.20, triclinic, space group $P\bar{1}$, a = 9.087(2), b = 11.851(2), c = 15.175(3) Å, α = 81.323(7), β = 89.812(7), γ = 73.27(2)°, V = 1545.7(5) Å^3, Z = 2, D_c = 1.092 g cm^{-3}, μ(Mo-Kα) = 3.6 cm^{-1}. 5713 unique reflexions (*hkl* range: −10, ±14, ±18) up to $((\sin\theta)/\lambda)_{max.}$ = 0.604 Å^{-1}, $R/wR/S$ = 0.040/0.120/1.04 for 295 refined parameters and all data (non-H atoms anisotropic, methylene H atoms refined freely with isotropic displacement parameters, all others fixed). $\Delta\rho_{fin}$(max./min.) = 0.64/−0.47 e Å^{-3}.

CCDC 155751 and 155752. See http://www.rsc.org/suppdata/cc/b0/b010115j/ for crystallographic data in .cif or other electronic format.

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