Multidentate Phosphinoalkoxides: Synthesis, Deprotonation, and Building Blocks in Polylithium Mixed-Anion Aggregates

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The bis((dimethylphosphino)methyl)-substituted alcohol $(Me_2PCH_2)_2CHOH$ (**1**) was prepared from the respective bis(3,5-dimethylbenzyl)phosphonium dichloride by reductive elimination of mesitylene with lithium alanate in 56% yield. Deprotonation with *n*-butyllithium or elemental sodium gave the respective alkali metal alcoholates $[(Me_2PCH_2)_2CHOM]_6$ (M = Li (**2**), Na (**3**)). Both compounds have a core consisting of two stacked M_3O_3 hexagons held together by short M−O bonds. In **2**, in addition to three oxygen atoms, each lithium atom is coordinated by one phosphino group of an adjacent ligand in a distorted tetrahedral geometry (Li−P = 2.60(1) Å). In **3** each sodium atom is coordinated by two phosphino groups from different ligands in addition to the oxygen atoms. The coordination geometry at the sodium atom is a distorted trigonal bipyramid (O_3P_2), the two phosphine donors being in axial and equatorial positions, respectively (Na−P = 3.083(2), 3.151(2) Å). The tris((dimethylphosphino)methyl)-substituted alcohol $(Me_2PCH_2)_3COH$ (**4**) was synthesized from 1-chloro-2,3-epoxy-2-(chloromethyl)propane by reaction with 3 equiv of $LiPMe_2$ in 69% yield. Its crystal structure contains a O−H···P hydrogen bond (O···P = 3.460(1) Å). Reaction of **4** with excess *n*-butyllithium in the absence of solvent gave the dimeric polylithium mixed-anion aggregate $[(Me_2PCH_2)_3COLi\cdot 2Li\text{-}n\text{-}Bu]_2$ (**5**), the core of which consists of two stacked LiOLiCLiC hexagons. Each $(Me_2PCH_2)_3CO^-$ anion is coordinated to three Li^+ cations via O−Li and P−Li bonds. The same reaction in toluene led to further deprotonation of the methylene groups in **4**, subsequent loss of Li_2O, and formation of the symmetrically tris(phosphino)-substituted trimethylenemethane dianion. It crystallizes as the mixed-anion aggregate $[(Me_2PCH_2)_3CO^-\cdot 3Li^+\cdot(Me_2PCH)_3C^{2-}]$ (**6**), consisting of an almost equilateral triangle of lithium atoms sandwiched between the two anions. Each lithium atom has a severly distorted tetrahedral coordination geometry consisting of two phosphino donors, one oxygen atom, and one methylene group.

Introduction

Phosphinoalkoxides[1,2] have received much attention as ligands to transition metals.[3] Much of the pertinent interest in these ligands undoubtedly stems from the fact that some of their complexes are effective catalyst precursors used in a variety of important substrate transformations also on an industrial scale.[4] The combination of hard (oxygen) and soft (phosphorus) donor sites (ambidentate ligands) and particularly their anionic nature make phosphino-substituted alcoholates ideal candidates for phosphine coordination to main-group elements.[5,6] In contrast to the plethora of transition metal complexes of phosphino alcoholates, structurally characterized main-group-element complexes are limited to a few cases.[3b−d,4c,7] The same applies to f elements.[8]

Despite their conceptual simplicity, the multidentate phosphino alcohols **I** and **II** have not been explored in

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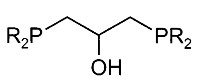
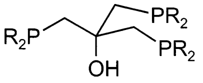
depth.[3c,9] Recent studies were mainly concerned with synthesis and transition metal complexes of a few perphenylated examples of **I** and **II**. To the best of our knowledge, the permethylated phosphino alcohols **I** and **II** (R = Me) have not been described previously at all. We have been interested in multidentate phosphino alcoholates as ligands to alkali and alkaline-earth metals because the additional phosphino groups might complex more metal cations than are required for charge neutrality, thereby leading to strongly Lewis acidic mixed-anion and potentially also mixed-metal aggregates, which have been the subject of much recent work. In particular, mixed alkyl/alkoxide aggregates of group 1 metals attracted considerable interest as models for superbases[10,11] and for the enantioselective addition of Li-*n*-Bu to aldehydes mediated by chiral alcoholates.[12] Mixed alkyl phenoxides were used as initiators for the ring-opening polymerization of L-lactides.[13]



I



II

We report here on efficient syntheses of **I** and **II** (R = Me) and their deprotonation with Li-*n*-Bu and elemental sodium (in the case of **I** only), resulting, inter alia, in polynuclear Li^+ and Na^+ salts and mixed-anion aggregates and in the unexpected formation of a tris(phosphino)-substituted trimethylenemethane dianion which is expected to have considerable potential in complex chemistry. A preliminary report has appeared.[14]

Experimental Section

All experiments were carried out with rigorous exclusion of air and moisture under purified dry argon in standard Schlenk tube glassware. Solvents were dried under argon over sodium or sodium−potassium alloy and were freshly distilled prior to use. Reagents: 1,3-dichloro-2-propanol (Aldrich); 1-chloro-2,3-epoxy-2-(chloromethyl)propane, from 3-chloro-2-(chloromethyl)-1-propene (95%, Acros) and 3-chloroperbenzoic acid (Fluka) at 0 °C in chloroform by standard procedures; $LiAlH_4$ (Merck); 2.5 M Li-*n*-Bu/hexane (Aldrich); sodium (Merck); (3,5-dimethylbenzyl)dimethylphosphine, from (3,5-dimethylbenzyl)dibromophosphine[15] and MeMgCl/THF in diethyl ether; $LiPMe_2$, from 100 mmol of $HPMe_2$[16] and 100 mmol of Li-*n*-Bu in 150 mL of THF at −78 °C.[17] NMR instruments: JEOL JMN-GX-400 (^1H, ^{13}C (101 MHz), ^{31}P (162 MHz), ^7Li (155 MHz)), Bruker AMX-600 (^1H, ^{13}C (152 MHz), ^{31}P (243 MHz)). Standards: $^1H/^{13}C$ NMR, internal toluene or external tetramethylsilane (TMS); ^7Li NMR, external 1 M LiBr in THF-d_8; ^{31}P NMR, external 85% H_3PO_4/H_2O. Chemical shifts are in ppm with negative signs referring to high field. ^1H and ^{13}C chemical shifts are reported relative to TMS, while those of ^7Li and ^{31}P are reported relative to the standards mentioned above. IR spectra: Perkin-Elmer 1760 X FT-IR. EI-MS: Varian MAT 112S (70 eV). FAB-MS: Finnigan MAT312/AMD 5000 (700 eV, 70 °C). The elemental analyses were performed by the microanalytical laboratory of the University of Konstanz on a Heraeus CHN-O-Rapid instrument. Melting points were determined in sealed capillaries in a Büchi 530 apparatus and are uncorrected.

$[\{(3,5\text{-}Me_2C_6H_3CH_2)Me_2PCH_2\}_2CHOH]^{2+}Cl^-{}_2$. A mixture of 28.8 g (160 mmol) of (3,5-dimethylbenzyl)dimethylphosphine, 10.3 g (80 mmol) of 1,3-dichloro-2-propanol, and 80 mL of ethanol was heated in a 250 mL steel autoclave under inert gas to 105 °C for 4 days. After all volatiles were pumped off in vacuo, a slowly crystallizing viscous residue remained, which was washed with 50 mL of diethyl ether and dried again in vacuo. Further purification may be done by recrystallization from ethanol/diethyl ether. Yield: 36.8 g of raw product (75.2 mmol, 94%). Mp: 243 °C. Anal. Calcd for $C_{25}H_{40}Cl_2OP_2$: C, 61.35; H, 8.24. Found: C, 60.28; H, 8.15. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.36 (d, $^3J_{HH} = 9$ Hz, 1 H, OH), 6.87−6.89 (br, 6 H, *o*-/*p*-H), 4.91 (br m, 1 H, CHO), 3.93 (d, $^2J_{HP} = 16$ Hz, 4 H, PCH_2Ar), 3.35 (m, PCH_2CO, 2 H), 3.01 (m, PCH_2CO, 2 H), 2.25 (s, 12 H, $ArCH_3$), 2.01 (d, $^2J_{HP} = 11.6$ Hz, 12 H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C): δ 139.1 (s, *m*-C), 130.1 (s, *p*-C), 127.8 (s, *o*-C), 126.8 (s, *ipso*-C), 61.5 (s, COH), 31.9 (d, $N = 68$ Hz, AXX′, PCH_2CO),[18] 30.1 (d, $^1J_{CP} = 49$ Hz, PCH_2Ar), 21.2 (s, $ArCH_3$), 7.4 (d, $^1J_{CP} = 36$ Hz, PCH_3), 6.9 (d, $^1J_{CP} = 36$ Hz, PCH_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ 27.9 (s). IR (KBr, cm^{-1}): 3406 s, 3348 s, 3200 br s, 2968 s, 2944 s, 2918 br s, 2082 w, 1608 s, 1469 m, 1425 m, 1394 m, 1375 m, 1334 m, 1314 s, 1297 s, 1262 m, 1237 s, 1208 m, 1171 m, 1156 m, 1071 s, 1036 m, 988 s, 974 s, 940 s, 909 m, 902 m, 872 m, 855 s, 802 m, 770 m, 734 w, 706 s, 658 m, 644 m, 532 m, 496 m, 474 m, 460 m. FAB-MS (*m*/*z*): 453 (9%) $(M - Cl)^+$, 417 (10%) $(M - 2Cl)^+$.

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[6] Anionic phosphines are conveniently subdivided into those having the anionic function directly attached to phosphorus, as is the case in phosphinomethanides and phosphinoamides, and those having the anionic function more remote from phosphorus. The negative charge directly adjacent to phosphorus in phosphinomethanides and phosphinoamides considerably enhances the electron density and donor capacity of their phosphino groups, while the second type of ligands resembles more closely neutral phosphines in its donor capacity. Phosphino alcoholates generally fall into this second class of anionic phosphines. It should be noted that organophosphides PR_2^- show a completely different metal complexation behavior due to the presence of two lone pairs and an even more increased charge at phosphorus. In addition to complexation of d elements, organophosphides have been shown to be excellent ligands also to s-, p-, and f-block elements.

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$(Me_2PCH_2)_2CHOH$ (1). A 500 mL round-bottom, three-necked flask fitted with a reflux condenser with gas outlet was charged with 36.4 g (74 mmol) of $[\{(3,5\text{-}Me_2C_6H_3CH_2)Me_2PCH_2\}_2CHOH]^{2+}Cl^{-}{}_2$ and 150 mL of THF. With stirring 8.5 g (224 mmol) of $LiAlH_4$ was carefully added. Stirring was continued until no apparent reaction took place any more, after which the mixture was refluxed. The reaction was finished after 8 h, as judged by the complete dissappearance of the solid phosphonium salt. The reaction mixture was hydrolyzed with 10% aqueous NH_4Cl solution followed by a 10% aqueous sodium potassium tartrate solution, which favored the phase separation. The aqueous phase was washed with three 50 mL portions of diethyl ether, and the combined organic phases were dried over $MgSO_4$. The solvents were distilled off at room temperature. Subsequent fractional distillation at 5 mbar yielded first mesitylene followed at 108 °C by **1**, which was initially contaminated with $3,5\text{-}Me_2C_6H_3CH_2PMe_2$. The colorless liquid distilling at 112 °C was pure **1**. Yield: 7.4 g (41 mmol, 56%). Bp: 112 °C/5 mbar. Anal. Calcd for $C_7H_{18}OP_2$: C, 46.67; H, 10.07. Found: C, 46.53; H, 10.01. ^1H NMR (400 MHz, benzene-d_6, 25 °C): δ 3.87 (quin, $^3J_{HH} = 6.7$ Hz, 1 H, CH), 1.98 (br, 1 H, OH), 1.53 (d, $^3J_{HH} = 6.7$ Hz, 4 H, CH_2), 0.88 (d, $^2J_{HP} = 2.2$ Hz, 6 H, PCH_3), 0.84 (d, $^2J_{HP} = 1.5$ Hz, 6 H, PCH_3). $^{13}C\{^1H\}$ NMR (101 MHz, benzene-d_6, 5 °C): δ 68.8 (t, $^2J_{CP} = 14$ Hz, CO), 43.3 (dd, $^1J_{CP} = 13$ Hz, $^3J_{CP} = 8$ Hz, CH_2), 14.7 (d, $^1J_{CP} = 14$ Hz, PCH_3), 14.6 (d, $^1J_{CP} = 15$ Hz, PCH_3). $^{31}P\{^1H\}$ NMR (162 MHz, benzene-d_6, 25 °C): δ −57.7 (s). IR (cm^{-1}): 3406 br s, 2953 s, 2922 s, 2895 s, 2814 m, 1711 m, 1607 w, 1429 s, 1343 m, 1292 s, 1288 m, 1171 w, 1119 w, 1061 m, 1020 s, 986 m, 940 s, 910 m, 707 s, 670 w.

$[(Me_2PCH_2)_2CHOLi]_6$ (2). A 1.0 g (5.6 mmol) portion of **1** was dissolved in 10 mL of hexane, and 2.4 mL of a 2.5 M solution of Li-*n*-Bu in hexane was added dropwise with stirring at −80 °C. Stirring was continued overnight. After the solution stood for several weeks at −30 °C, colorless single crystals formed which proved suitable for X-ray structure determination. These crystals were also used for analysis and spectroscopy. Anal. Calcd for $C_7H_{17}LiOP_2$: C, 45.18; H, 9.21. Found: C, 43.77; H, 8.80. ^1H NMR (400 MHz, benzene-d_6, 25 °C): δ 4.13 (br, 1 H, CH), 1.92 (d, $^2J_{HP} = 6.6$ Hz, 2 H, CH_2), 1.70−1.80 (br m, 2 H, CH_2), 1.07 (d, $^2J_{HP} = 3.4$ Hz, 6 H, PCH_3), 1.03 (d, $^2J_{HP} = 10.7$ Hz, 6 H, PCH_3). $^{13}C\{^1H\}$ NMR (101 MHz, benzene-d_6, 25 °C): δ 68.2/67.2 (br, 2:1, CH), 49.6/48.4 (br, 1:2, CH_2), 14.4 (br m, PCH_3). $^{31}P\{^1H\}$ NMR (162 MHz, benzene-d_6, 25 °C): δ −58.3/−58.0 (s, 2:1). $^7Li\{^1H\}$ NMR (155 MHz, toluene-d_8, 25 °C): δ 0.5 (br, $w_{1/2} = 40$ Hz), 0.3 (s). $^7Li\{^1H\}$ NMR (−50 °C): δ 0.5 (br, $w_{1/2} = 78$ Hz).

$[(Me_2PCH_2)_2CHONa]_6$ (3). A 1.0 g (5.6 mmol) portion of **1** was dissolved in 10 mL of toluene, and freshly cut sodium metal (ca. 250 mg) was added. Stirring of the solution at 80 °C was continued for several hours until H_2 evolution was no longer observable. The solvent was removed in vacuo, and the remaining solid was redissolved in toluene. Prolonged standing of the solution at −30 °C led to the formation of colorless single crystals suitable for X-ray structure determination. These crystals contained toluene (see crystal structure determination below). The substance used for analysis and spectroscopy was largely freed of toluene by pumping in vacuo. Anal. Calcd for $C_7H_{17}NaOP_2$: C, 41.59; H, 8.48. Found: C, 42.22; H, 9.65. ^1H NMR (400 MHz, benzene-d_6, 25 °C): δ 4.28 (br m, 1 H, CH), 1.70 (d, $^3J_{HH} = 6.8$ Hz, 4 H, CH_2), 1.05 (s, 6 H, PCH_3), 1.03 (s, 6 H, PCH_3). $^{13}C\{^1H\}$ NMR (101 MHz, benzene-d_6, 25 °C): δ 68.1 (t, $^2J_{CP} = 9$ Hz, CH), 51.6 (d, $^1J_{CP} = 2$ Hz, CH_2), 14.9 (d, $^1J_{CP} = 10$ Hz, PCH_3), 14.0 (d, $^1J_{CP} = 12$ Hz, PCH_3). $^{31}P\{^1H\}$ NMR (162 MHz, benzene-d_6, 25 °C): δ −58.7 (s).

$(Me_2PCH_2)_3COH$ (4). $LiPMe_2$ (6.8 g, 100 mmol) was suspended in 20 mL of diethyl ether and cooled to −78 °C. 1-Chloro-2,3-epoxy-2-(chloromethyl)propane (3.5 g, 25 mmol) in 25 mL of diethyl ether was added dropwise with stirring. Stirring was continued overnight without cooling. Subsequent refluxing for 3 h resulted in a colorless precipitate and a yellow solution which was hydrolyzed with 20 mL of a 10% aqueous NH_4Cl solution. Diethyl ether and other volatile components (mostly phosphines) were removed in vacuo, and the remaining aqueous phase was extracted with three 30 mL portions of diethyl ether. The combined organic phases were dried over $MgSO_4$ and concentrated in vacuo. The oily raw product was distilled at 1.5 mbar. The main fraction distilled at 80−95 °C. It was further purified by condensation at 0.1 mbar into a cold trap. The colorless oil obtained in this way crystallized after a few minutes, and single crystals suitable for X-ray diffraction were selected from this crop. Yield: 4.4 g (17 mmol, 69% based on epoxide). Mp: 40 °C. Bp: 85 °C/1.5 mbar. Anal. Calcd for $C_{10}H_{25}OP_3$: C, 47.24; H, 9.91. Found: C, 47.33; H, 9.07. ^1H NMR (400 MHz, benzene-d_6, 25 °C): δ 2.29 (br, 1 H, OH), 1.94 (d, $^2J_{HP} = 3.0$ Hz, 6 H, CH_2), 0.96 (s, 18 H, PCH_3). $^{13}C\{^1H\}$ NMR (101 MHz, benzene-d_6, 25 °C): δ 75.9 (q, $^2J_{CP} = 12$ Hz, CO), 47.7 (m, CH_2), 15.7 (d, $^1J_{CP} = 10$ Hz, PCH_3). $^{31}P\{^1H\}$ NMR (162 MHz, benzene-d_6, 25 °C): δ −59.8 (s). IR (cm^{-1}): 3383 br s, 2951 s, 2893 s, 2814 m, 2342 m, 1633 w, 1602 w, 1430 s, 1343 m, 1292 s, 1276 m, 1226 w, 1175 s, 1101 w, 1073 m, 1008 s, 941 s, 916 s, 879 m, 857 m, 799 m, 747 m, 705 s, 671 m. EI-MS (*m/z*): 239 (88%) $(M - CH_3)^+$.

$[(Me_2PCH_2)_3COLi\cdot 2Li\text{-}n\text{-}Bu]_2$ (5). To 0.3 g (1.2 mmol) of **4** was added 2.0 mL (5.0 mmol) of a 2.5 M solution of Li-*n*-Bu in hexane at −78 °C. The reaction mixture was warmed to room temperature, whereupon a clear solution formed, from which small colorless crystals of **5** immediately precipitated that proved suitable for X-ray diffraction. 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 **5** (see the synthesis of **6**).

$[(Me_2PCH_2)_3CO^-\cdot 3Li^+\cdot (Me_2PCH)_3C^{2-}]$ (6). Toluene (0.75 mL) was added to 110 mg (1.7 mmol) of neat Li-*n*-Bu (prepared from a hexane solution by evaporation of the solvent in vacuo). Subsequently 140 mg (0.55 mmol) of **4** in 0.75 mL of toluene was added dropwise at room temperature; the solution was thoroughly mixed and left standing for 2 days. The yield of **6** in solution is about 70% (^{31}P NMR). Colorless needles formed which proved suitable for X-ray diffraction. They were isolated by decantation. Mp: 165 °C dec. Anal. Calcd for $C_{20}H_{45}Li_3OP_6$: C, 47.27; H, 8.92. Found: C, 47.02; H, 8.34. ^1H NMR (600 MHz, toluene-d_8, 25 °C): alkoxide, δ 1.37 (m, 3 H, $CH_2{}^A$), 1.23 (m, 3 H, $CH_2{}^B$), 0.85 (s, 9 H, $CH_3{}^A$), 0.81 (s, 9 H, $CH_3{}^B$); dianion, δ 3.23 (m, 3 H, CH), 1.34 (s, 9 H, $CH_3{}^A$), 1.30 (s, 9 H, $CH_3{}^B$). $^{13}C\{^1H\}$ NMR (151 MHz, toluene-d_8, 25 °C): alkoxide, δ 73.8 (q, $^2J_{CP} = 9$ Hz, CO), 51.1 (s, CH_2), 15.3 (d, $^1J_{CP} = 5$ Hz, $CH_3{}^B$), 14.0 (s, $CH_3{}^A$); dianion, δ 56.1 (br s, CH), 19.7 (d, $^1J_{CP} = 19$ Hz, $CH_3{}^B$), 17.0 (d, $^1J_{CP} = 13$ Hz, $CH_3{}^A$). $^{31}P\{^1H\}$ NMR (162 MHz, toluene-d_8, 25 °C): 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, $^1J_{PLi} = 58$ Hz, $^2J_{PP} = 19$ Hz); $T_C \approx -45$ °C. $^7Li\{^1H\}$ NMR (155 MHz, toluene-d_8, 25 °C): 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.

Structure Analyses. Single crystals of **2**, **3**, **5**, and **6** suitable for X-ray diffraction were obtained as described above. Those of **4** were obtained from the melt. They were mounted under nitrogen on glass fibers in an inert oil drop at 153(2) K.[19] The crystals were examined directly on a four-circle diffractometer (Enraf-Nonius CAD4) with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å). The crystal systems indicated by preliminary search and indexing procedures were checked for higher metrical symmetry by reduced-cell calculations (DELOS,[20] LePage[21]). Exact cell dimensions were determined by refinement of the Bragg angles of 25 selected high-

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Table 1. Crystal Structure Data for 2−6

	2	**3**	**4**	**5**	**6**
formula	$C_{42}H_{102}Li_6O_6P_{12}$	$C_{42}H_{102}Na_6O_6P_{12}$	$C_{10}H_{25}OP_3$	$C_{36}H_{84}Li_6O_2P_6$	$C_{20}H_{45}Li_3OP_6$
M_r	1116.52	1212.82	254.21	776.49	508.20
cryst size, mm	0.45 × 0.4 × 0.4	0.3 × 0.25 × 0.2	0.3 × 0.3 × 0.3	0.5 × 0.3 × 0.3	1.0 × 0.4 × 0.4
cryst syst	cubic	trigonal, hex axes	monoclinic	monoclinic	triclinic
space group	$Pa\bar{3}$	$R\bar{3}$	$P2_1/n$	$C2/c$	$P\bar{1}$
a, Å	19.067(2)	15.621(6)	10.261(2)	21.440(2)	9.087(2)
b, Å	19.067(2)	15.621(6)	10.657(2)	17.254(1)	11.851(2)
c, Å	19.067(2)	27.707(6)	13.723(1)	14.121(1)	15.175(3)
α, deg	90	90	90	90	81.323(7)
β, deg	90	90	91.21(2)	103.000(9)	89.812(7)
γ, deg	90	120	90	90	73.27(2)
V, Å^3	6932(1)	5855(3)	1900.3(4)	5089.8(8)	1545.7(5)
Z	4	3	4	4	2
D_{calcd}, g cm^{-3}	1.070	1.032	1.125	1.013	1.092
μ(Mo Kα), cm^{-1}	3.3	3.3	3.71	2.36	3.57
F(000), e	2400	1944	552	1696	544
hkl range	0 to +13	−18 to +14	−13 to 0	−25 to +24	−10 to 0
	−22 to 0	−18 to +18	−13 to 0	0 to +20	−14 to +13
	−22 to 0	−32 to +22	−17 to +17	0 to +16	−18 to +18
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.595	0.595	0.652	0.595	0.604
no. of rflns measd/unique	1928/1779	7184/2296	3547/3364	4698/4498	6105/5713
R_{int}	0.103	0.035	0.016	0.022	0.015
no. of params refined	100	150	227	236	295
$R(F)/R_w(F^2)^a$ (all reflns)	0.264/0.285	0.072/0.163	0.030/0.067	0.078/0.132	0.048/0.120
GOF$(F^2)^a$	0.993	1.08	1.06	1.04	1.036
$\Delta\rho_{fin}$ (min/max), e Å^{-3}	−0.32/0.64	−0.42/0.57	−0.18/0.31	−0.37/0.41	−0.47/0.64

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_c|$. $R_w(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. GOF$(F^2) = S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$. n is the number of reflections, p is the total number of parameters refined, $w = 1/[\sigma^2(F_o^2) + (XP)^2 + YP)]$, and $P = [\max(F_o^2, 0) + 2F_c^2]/3$. **2**: $X = 0.1351$, $Y = 0.0$. **3**: $X = 0.1043$, $Y = 1.4636$. **4**: $X = 0.0362$, $Y = 0.3090$. **5**: $X = 0.0773$, $Y = 3.2699$. **6**: $X = 0.0854$, $Y = 0.4894$.

angle reflections from various parts of reciprocal space carefully centered on the diffractometer. Lp and linear decay corrections were applied. Absorption was corrected for empirically on the basis of ψ scans around the diffraction vectors of nine reflections near $\chi = 90°$, which served to evaluate the transmission curves (**2**, $T_{min} = 0.74$, $T_{max} = 1.00$; **5**, $T_{min} = 0.81$, $T_{max} = 1.00$). Refinements were done on F^2 of all reflections with anisotropic displacement parameters for the non-H atoms. Programs used: SHELXS-/SHELXL-97 (structure solution and refinement),[22] PLATON (molecular geometry),[23] ORTEP-III (molecular drawings).[24] Crystal data and numbers pertinent to data collection and structure refinement are summarized in Table 1. Tables 2−5 contain selected distances and angles.

Further Considerations for 2. All H atoms were placed at idealized geometrical positions and included as fixed-atom contributions into structure factor calculations (U(iso) = 0.05 Å^2). Due to poor crystal quality and a truncated data set, the structure could only be refined to $R(F) = 0.264$ (all reflections). For comparison, $R(F) = 0.089$ for 697 reflections with $I > 2.0\sigma(I)$.

Further Considerations for 3. The three hexamers pack in the crystal with cocrystallized disordered toluene molecules with crystallographic inversion symmetry. As all attempts to describe it with a split-atom model failed, its electron density was removed with the routine SQUEEZE[25] in PLATON, and the resulting data set was used for the final refinement cycles. As the exact amount of toluene per hexamer could not be determined by refinement (three molecules of toluene per hexamer given full occupancy), the numerical values sensitive to the cell content (F(000), absorption coefficient, density) were calculated without it. With the exception of the oxygen atom and one PMe_2 group (P1), all other ligand atoms were found to be disordered. The disorder was described with a split-atom (68:32) model, and the respective atoms were refined with anisotropic displacement parameters, with the exception of the alternative C11 position, which was refined isotropically. In the tables the split atoms are labeled a and b, respectively. All H atoms were placed at idealized geometrical positions and included as fixed-atom contributions into structure factor calculations.

Further Considerations for 4. All H atoms could be located in difference Fourier syntheses. They were refined freely with isotropic displacement parameters. The positional and isotropic displacement parameters of the hydroxyl H atom also were refined, but the O−H bond length was restrained to 0.85(1) Å to avoid an unrealistically short O−H bond.

Further Considerations for 5. The methyl hydrogen atoms were placed at idealized geometrical positions; all others could be located in difference Fourier syntheses. All H atoms were included as fixed-atom contributions into structure factor calculations.

Further Considerations for 6. The methyl hydrogen atoms were placed at idealized geometrical positions; all others could be located in difference Fourier syntheses. The CH atoms were refined freely with isotropic displacement parameters; all others were included as fixed-atom contributions into structure factor calculations.

Results and Discussion

Preparation of $(Me_2PCH_2)_2CHOH$ (1). The synthesis of **1** via a bis(benzylphosphonium) salt and reductive elimination of mesitylene with $LiAlH_4$ (Scheme 1) was undertaken in an effort to find an efficient synthesis which avoids the use of $LiPMe_2$. The latter, and especially so its educt $HPMe_2$, is notoriously difficult to handle and requires a multistep synthesis.[16,17] Although our synthesis allows the straightforward preparation of **1** in acceptable yields of 50% over both steps

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[23] Spek, A. L. PLATON, A Multipurpose Crystallographic Tool; Utrecht University, Utrecht, The Netherlands, 2000. See also: Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C34.

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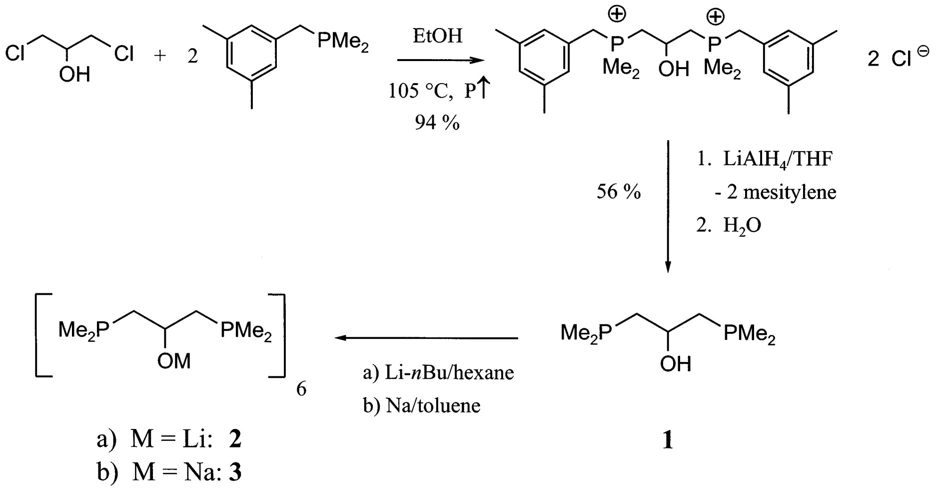
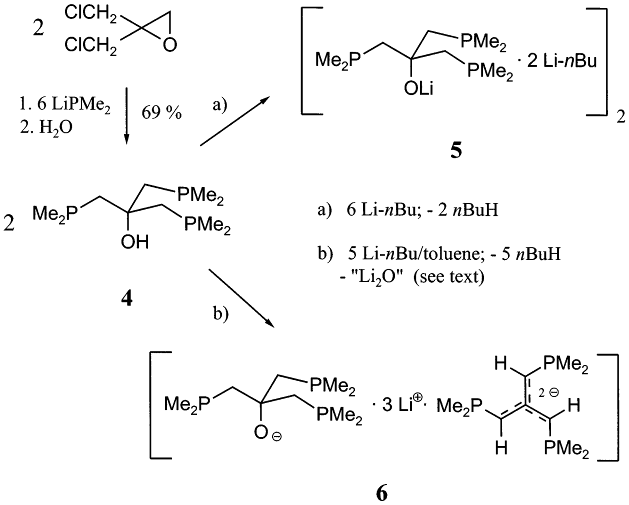
[25] Van der Sluis, P.; Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, 194.

Scheme 1



Scheme 2



(see Scheme 1), the synthesis by direct reaction of 1,3-dichloro-2-propanol or (chloromethyl)oxirane (epichlorohydrine)[3c,9] with LiPMe$_2$ might be preferable, however.[26] This is also born out by the synthesis of **4** from an oxirane with LiPMe$_2$ (Scheme 2) which was found to be particularly convenient and efficient once the necessary LiPMe$_2$ had been prepared.

The bis((dimethylphosphino)methyl)-substituted alcohol **1** is a colorless air-sensitive liquid (bp 112 °C/5 mbar) with a characteristic odor. It is easily characterized by NMR and IR spectroscopy (see Experimental Section), although diastereotopic CH$_3$ proton and carbon atoms with concomitant ^{31}P coupling result in two sets of signals. The diastereotopic CH$_2$ protons seem to be isochronous, while the ^{13}CH$_2$ signals show clearly discernible $^1J_{CP}$ and $^3J_{CP}$ coupling constants with both phosphorus atoms.

Lithium and Sodium Complexes of (Me$_2$PCH$_2$)$_2$CHOH (1). Metal complexes of **1** were synthesized in the form of lithium (**2**) and sodium (**3**) salts of its alcoholate (Scheme 1). Complex **2** was prepared by reaction of **1** with Li-*n*-Bu, while **3** formed by contact of **1** with elemental sodium. Their NMR spectra (Experimental Section) are not grossly different from that of the parent **1**. Particularly noteworthy is the appearance of two signals in the room-temperature ^{31}P and ^{7}Li spectra of **2**. In the ^{31}P spectrum they are in a ratio of 2:1, while this information is more difficult to extract from the ^{7}Li spectrum due to line broadening. Upon cooling, the lines coalesce in both cases. The lack of discernible ^{31}P−^{7}Li coupling at any temperature does not allow immediate clues with regard to rapid exchange of free and coordinated phosphino groups, but the solid-state structure of **2** (below), showing lithium-coordinated and uncoordinated phosphino groups, makes such solution equilibria highly probable. In addition, equilibria between oligomers of different size in solution cannot be excluded. The presence of different oligomers has been proven for lithium phenolate in dioxolane solution.[27] In the solid state complexes **2** and **3** are hexameric, as was shown by crystal structure determination.

Solid State Structures of 2 and 3. The lithium alcoholate **2** crystallizes in the space group $Pa\bar{3}$ (No. 205) with four hexamers in the cubic unit cell (Figure 1, Table 2). Each hexamer has crystallographic S_6 ($\bar{3}$) symmetry and consists of two Li$_3$O$_3$ hexagons stacked together such that each lithium atom comes to sit over an oxygen atom and vice versa. Alternatively, and more conventionally, the structure may be considered as a octahedron of lithium atoms with six of the eight triangular faces being capped by an oxygen atom while two triangular faces on opposite sides of the octahedron remain uncapped.[28] This octahedron is also indicated in Figure 1, but it should be remembered that the lines connecting the lithium atoms do not represent lithium−lithium bonds. The three different lithium−oxygen bonds in **2** (Table 2) are comparable in length to those in hexameric lithium alkoxides or siloxides or other related Li$_6$O$_6$ cages.[13,27,29] Noteworthy is the fact that within the Li$_3$O$_3$ hexagons the Li−O−Li angles (Li−O−Li^1 = 112.3(6)°) are much smaller than the O−Li−O angles (O−Li−O^3 = 126.3(8)°). One of the phosphino groups of each ligand is coordinated to an adjacent lithium atom with formation of a five-membered ring and completes the coordination sphere of

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(26) Compare the synthesis of similar bis((diphenylphosphino)-methyl)-substituted alcohols and of bis(dimethylphosphino)propane with lithium and sodium phosphides. See refs 3c and 9 and: Cloyd, J. C., Jr.; Meek, D. W. *Inorg. Chim. Acta* **1972**, *6*, 480.

(27) Jackman, L. M.; Cizmeciyan, D.: Williard, P. G.; Nichols, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 6262.

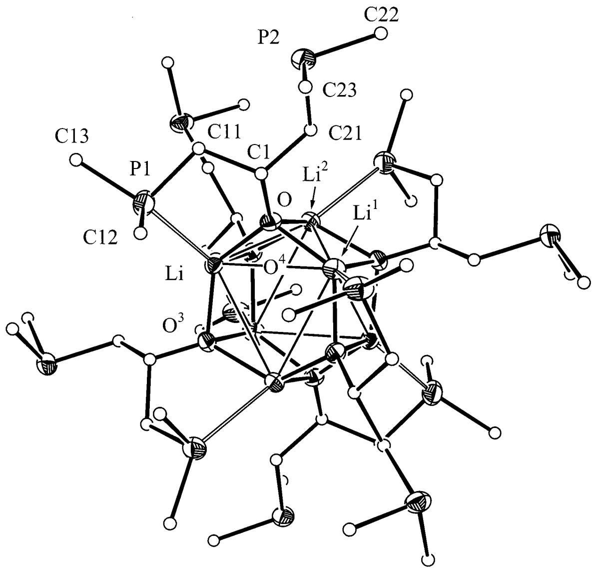

Figure 1. Hexameric molecular structure of **2** in the crystal state and crystallographic numbering scheme used (ORTEP-III; displacement ellipsoids at the 30% level; C atoms as spheres with arbitrary radii; H atoms omitted for clarity). The octahedral array of Li atoms is indicated by thin lines, while the Li–P bonds are shown as open bonds. Superscripts denote the following symmetry codes: (1) $0.5 + z, 0.5 - x, -y$; (2) $0.5 + y, z, 0.5 - x$; (3) $0.5 - y, -z, x - 0.5$; (4) $0.5 - z, x - 0.5, y$.

lithium to a distorted tetrahedron. The second phosphino group is uncoordinated and oriented to the outside of the complex. The Li–P bond length (Li1–P1 = 2.60(1) Å) is typical for lithium coordination by (anionic) organophosphines[30] but noticeably longer than in lithium phosphides $LiPR_2$.[31]

The sodium alcoholate **3** crystallizes in the trigonal space group $R\bar{3}$ (No. 148) with three hexamers in the unit cell (Figure 2, Table 2). As in the lithium compound **2**, each hexamer has crystallographic S_6 ($\bar{3}$) symmetry and consists of two Na_3O_3 hexagons stacked together such that each sodium atom of an hexagon comes to sit over an oxygen atom of the other. Similar Na_6O_6 cages have been the subject of much recent interest,[32] although the number of crystallographically characterized examples is still small.[33] It should be noted that in Na_6O_6 cages an alternative geometry has been observed, where the sodium and oxygen atoms are located at alternating corners of two face-fused cubes.[28,34] We are not aware of similar crystallographically characterized Li_6O_6 cages.[35] Not unexpectedly, the Na–O bonds in **3** are noticeably longer than the Li–O bonds in **2**. As a consequence, there is much more space around each sodium center, leading to a second phosphine coordination and an expansion of the sodium coordination sphere from 4 to 5. The two coordinated phosphino groups at

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 2 and 3 with Estimated Standard Deviations in Units of the Last Significant Figure in Parentheses[a]

2		3	
		(a) Distances	
Li–O	1.94(1)	Na–O	2.268(2)
Li–O^3	1.89(2)	Na–O^2	2.283(3)
Li–O^4	1.98(2)	Na–O^4	2.307(2)
Li$\cdots$Li^1	3.17(2)	Na$\cdots$Na^1	3.810(1)
Li$\cdots$Li^2	2.58(2)	Na$\cdots$Na^5	3.133(1)
Li–P1	2.60(1)	Na–P1	3.083(2)
		Na–P2a/b^4	3.151(2)/3.173(4)
		(b) Angles	
O–Li–O^3	126.3(8)	O–Na–O^2	126.1(1)
O–Li–O^4	95.7(6)	O–Na–O^4	93.59(9)
O^3-Li–O^4	97.3(6)	O^2-Na–O^4	93.18(9)
Li–O–Li^1	112.3(6)	Na–O–Na^1	113.7(1)
Li–O–Li^2	82.4(6)	Na–O–Na^5	86.46(7)
Li^1-O–Li^2	83.7(6)	Na^1-O–Na^5	86.10(9)
C1–O–Li	127.7(6)	C1a/b–O–Na	114.1(2)/129.3(4)
C1–O–Li^1	112.4(6)	C1a/b–O–Na^1	124.6(2)/97.6(4)
C1–O–Li^2	128.2(6)	C1a/b–O–Na^5	123.0(2)/136.5(4)
P1–Li–O	80.3(5)	P1–Na–O	71.55(6)
P1–Li–O^3	120.0(6)	P1–Na–O^2	114.66(7)
P1–Li–O^4	136.6(7)	P1–Na–O^4	152.13(8)
		P2a/b^4-Na–O	103.42(8)/108.8(1)
		P2a/b^4-Na–O^2	128.97(8)/122.9(1)
		P2a/b^4-Na–O^4	70.19(8)/66.7(1)
		P1–Na–P2a/b^4	89.98(7)/95.17(9)

[a] For the symmetry codes, see Figures 1 and 2.

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(28) The structure description of **2** (and that of **3** below) as two stacked M_3O_3 hexagons actually bridges the gap to the ladder structures frequently observed in alkali metal organoamides. These often consist of ladders obtained through "ring-laddering" of M–N–M–N four-membered rings. Following this description, the structures of **2** and **3** would be cyclic ladders consisting of three M–O–M–O rings and six M–O rungs (M = Li, Na). Cyclic ladders have also precedent in metal organoamide structures. As an alternative, "ring-stacking" of four-membered rings leads to structures consisting of face-fused heterocubane units. The simplest case, a single cube consisting of alternating metal and nonmetal corners, is nothing but the classical tetrahedron of metal atoms with the nonmetals bridging the trigonal faces, the best known example of which is probably the tetrameric structure of solid $[LiMe]_4$. For comprehensive discussions with many examples see: Mulvey, R. E. *Chem. Soc. Rev.* **1998**, *27*, 339. Snaith, R.; Wright, D. S. In *Lithium Chemistry: A Theoretical and Experimental Overview*; Sapse, A.-M., Schleyer, P. v. R., Eds.; Wiley: New York, 1995; p 227. Pauer, F.; Power, P. P. In *Lithium Chemistry: A Theoretical and Experimental Overview*; Sapse, A.-M., Schleyer, P. v. R., Eds.; Wiley: New York, 1995; p 295. Gregory, K.; Schleyer, P. v. R.; Snaith, R. *Adv. Inorg. Chem.* **1991**, *37*, 47. Mulvey, R. E. *Chem. Soc. Rev.* **1991**, *20*, 167.

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(35) For crystallographically characterized K_6O_6 cages, see ref 32. To our knowledge, there are no structurally characterized M_6O_6 cages (M = Rb, Cs).

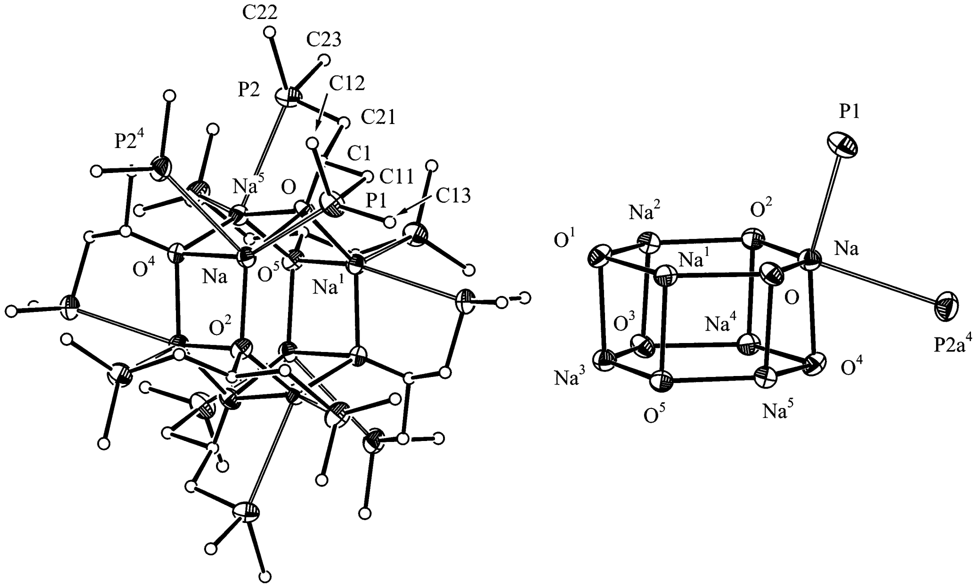

Figure 2. Molecular structure of **3** in the crystal and crystallographic numbering scheme used (ORTEP-III; displacement ellipsoids at the 30% level; C atoms as spheres with arbitrary radii; H atoms omitted for clarity): (left) entire hexameric aggregate; (right) Na_6O_6 molecular core with phosphorus coordination to one sodium atom. Of the 2-fold positional disorder of most of the ligand atoms only the majority component is shown. Superscripts denote the following symmetry codes: (1) $-y, x - y, z$; (2) $-x + y, -x, z$; (3) $-x, -y, 2 - z$; (4) $y, -x + y, 2 - z$; (5) $x - y, x, 2 - z$.

each sodium come from two different ligands, or, in other words, each ligand binds to two different sodium atoms through its two phosphino groups. Probably also as a consequence of the increased space around the Na_6O_6 core, most of the ligand atoms are disordered. As described in the Experimental Section, this disorder could be well resolved. For clarity, only one ligand position is shown in Figure 2.

The coordination geometry at sodium is a severely distorted trigonal bipyramid, as is shown on the right-hand side of Figure 2. The Na−P bonds are exceedingly long (Na−P1 = 3.083(2) Å, Na−P2a/b^4 = 3.151(2)/3.173(4) Å) even when compared with Li−PR_3 bonds, which average around 2.6 Å. Crystallographically characterized sodium−phosphorus bonds of the type Na−PR_3 are now well documented, though still rare.[3d,4c,30,36] They usually range between 2.85 and 3.25 Å. Apart from distance criteria, an attractive Na−P interaction in **3** may also be inferred from the presumed orientation of the lone pairs at the phosphorus atoms, which clearly point toward the sodium atoms.

Preparation and Structure of $(Me_2PCH_2)_3COH$ (4). The tris(phosphino) alcohol **4** was prepared from the geminal bis(chloromethyl)oxirane by substitution and nucleophilic ring-opening reaction with 3 equiv of lithium dimethylphosphide in 69% yield in diethyl ether (Scheme 2). This synthesis is essentially the same as that of the corresponding perphenyl compound.[3c] Pure **4** is crystalline at room temperature but melts at 40 °C. It can be distilled at 85 °C/1.5 mbar. It is easily characterized by its NMR spectra. As expected, ^{31}P coupling is very small in the ^1H NMR spectra but more pronounced in the ^{13}C spectra.

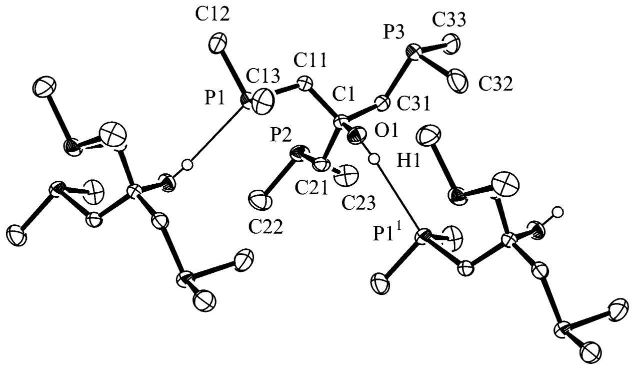

Figure 3. Chainlike arrangement of **4** in the crystal (ORTEP-III; displacement ellipsoids at the 50% level; C atoms as spheres with arbitrary radii; H atoms omitted for clarity). Individual molecules are connected by O−H···P hydrogen bonds (thin lines). The superscript denotes the following symmetry code: (1) $0.5 - x, 0.5 + y, 1.5 - z$.

Crystals of **4** are monoclinic, space group $P2_1/n$, with four molecules in the unit cell (Figure 3, Table 3). The most noteworthy feature of the crystal structure is the formation of infinite strands through O−H···P hydrogen bonds, as depicted in Figure 3. Especially the directionality of the hydrogen bond (O1−H1···P1^1 = 176(1)°) leaves little doubt about the very existence of an attractive interaction between the slightly acidic proton and the slightly basic phosphine phosphorus.[37] As is evident from Figure 3, the directionality is also manifested in the orientation of the lone pair at phosphorus, presumed to be at the fourth tetrahedral site, which as a hydrogen bond acceptor points toward the hydroxyl group. The hydrogen bond distances (O1···P1^1 = 3.458(1), H1···P1^1 = 2.64(1) Å) may be compared with phenolic O−H···PR_3 hydrogen bonds as reported by

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Table 3. Selected Interatomic Distances (Å) and Angles (deg) for 4[a]

(a) Distances			
C1−O1	1.438(1)	P2−C21	1.853(1)
C1−C11	1.531(2)	P2−C22	1.834(2)
C1−C21	1.537(2)	P2−C23	1.835(2)
C1−C31	1.538(2)	P3−C31	1.849(1)
P1−C11	1.845(1)	P3−C32	1.834(2)
P1−C12	1.830(2)	P3−C33	1.836(2)
P1−C13	1.825(2)		
(b) Angles			
C11−P1−C12	98.72(6)	C31−P3−C32	100.74(7)
C11−P1−C13	102.70(6)	C31−P3−C33	97.15(6)
C12−P1−C13	99.76(8)	C32−P3−C33	98.74(8)
C21−P2−C22	99.48(6)	C1−C11−P1	116.83(7)
C21−P1−C23	100.77(6)	C1−C21−P2	115.15(7)
C22−P2−C23	98.92(8)	C1−C31−P3	117.51(8)

(c) Hydrogen Bond

O1−H1	H1···P1^1	O1···P1^1	O1−H1···P1^1
0.82(1)[b]	2.64(1)[b]	3.458(1)	176(1)

[a] For the symmetry code, see Figure 3. [b] O−H restrained to 0.85(1) Å during refinement.

Heinicke et al., which are notably shorter (H···P = 2.30−2.41 Å).[38] They also have to be compared with the shortest nonbonding intramolecular C−H···P contacts in **4**, which feature only slightly longer H···P distances but slightly shorter C···P distances.[39] However, as stated above, it is especially the directionality which gives the most decisive evidence for an attractive hydrogen bond interaction.[37]

Reaction of $(Me_2PCH_2)_3COH$ (4) with Li-*n*-Bu. Compound **4** reacts with excess Li-*n*-Bu (2.5 M solution in hexane) at −78 °C without additional solvent to form the lithium alkoxide, which crystallizes with 2 equiv of Li-*n*-Bu (compound **5**; Scheme 2). When the mixture was warmed to room temperature, single crystals precipitated from the reaction mixture, which served to determine the solid-state structure. Due to the necessity to avoid solvents in the synthesis of **5**, no NMR characterization could be undertaken. It should be noted that in their investigation of perphenyl bis- and tris(phosphino) alcohols derived from **I** and **II** (R = Ph), van der Heijden et al. observed the formation of "impure alkoxides" when reacting $(Ph_2PCH_2)_2C(Me)OH$ with Li-*n*-Bu and attributed the impurities to the formation of mixed alkyl/alkoxide aggregates which were not investigated further, however.[3c] No mixed-aggregate formation was observed when **II** (R = Ph) was reacted with Li-*n*-Bu.[3c] As described below, further reaction of **4** with Li-*n*-Bu in toluene as solvent leads to the tris(dimethylphosphino)-substituted trimethylenemethane dianion.

Solid-State Structure of $[(Me_2PCH_2)_3COLi\cdot 2Li$-*n*-Bu$]_2$ (5). According to the crystal structure, **5** is a mixed alkyl alkoxide consisting of 1 equiv of lithium alkoxide and 2 equiv of *n*-butyllithium, the entire aggregate crystallizing as a dimer with crystallographic inversion symmetry (Figure 4). The molecular structure of **5** consists of two LiOLiCLiC hexagons stacked together by Li−O and Li−C bonds (Table 4). Each $(Me_2PCH_2)_3CO^-$ anion is coordinated to a triangle of three Li^+ cations via O−Li and P−Li bonds. Alternatively, **5** may be viewed as six lithium atoms at the corners of a slightly distorted octahedron. Two opposite triangular Li_3 faces of the octahedron are each capped 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 **4** in a very compact and effective way. Particular indications of this are the short Li−O bonds (Li1−O1 = 1.904(4) Å, Li2−O1 = 1.897(4) Å, Li3−O1 = 1.916(4) Å) and the Li−P bond distances. The latter are 2.755(4), 2.613(4), and 2.736(4) Å and thus are close to

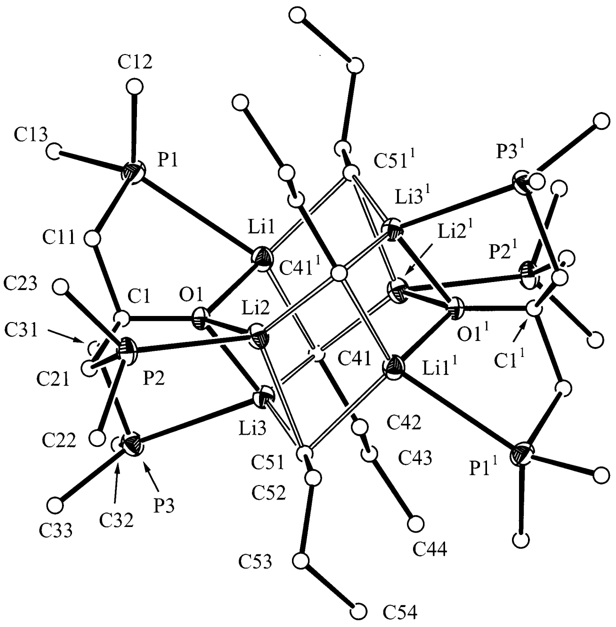

Figure 4. Molecular structure of **5** in the crystal and crystallographic numbering scheme used (ORTEP-III, displacement ellipsoids at the 30% level; C atoms as spheres with arbitrary radii; H atoms omitted for clarity). Open bonds serve to highlight the Li−C bonds. Superscripts denote the following symmetry code: (1) 1.5 − *x*, 1.5 − *y*, 1 − *z*.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for 5[a]

(a) Distances			
Li1−O1	1.904(4)	Li2−C51	2.297(5)
Li2−O1	1.897(4)	Li3−C41	2.186(4)
Li3−O1	1.916(4)	Li3−C51	2.198(5)
Li1−P1	2.755(4)	Li1···Li2	3.043(5)
Li2−P2	2.613(4)	Li2···Li3	2.494(5)
Li3−P3	2.736(4)	Li1···Li3	2.517(6)
Li1−C41	2.363(5)	Li1···Li2^1	2.487(6)
Li1−C51^1	2.215(5)	Li2···Li3^1	3.146(5)
Li2−C41^1	2.144(5)	Li1···Li3^1	3.101(6)
(b) Angles			
O1−Li1−C51^1	138.5(2)	P1−Li1−O1	80.1(1)
O1−Li2−C41^1	134.2(2)	P1−Li1−C41	138.2(2)
C41−Li3−C51	134.7(2)	P1−Li1−C51^1	101.5(2)
Li1−O1−Li2	106.4(2)	P2−Li2−O1	85.2(2)
Li3−C41−Li2^1	93.2(2)	P2−Li2−C41^1	115.2(2)
Li3−C51−Li1^1	89.3(2)	P2−Li2−C51	107.9(2)
C1−O1−Li1	123.4(2)	P3−Li3−O1	82.9(2)
C1−O1−Li2	124.7(2)	P3−Li3−C41	97.3(2)
C1−O1−Li3	124.3(2)	P3−Li3−C51	119.5(2)

[a] For the symmetry code, see Figure 4.

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[38] Heinicke, J.; Kadyrov, R., Kindermann, M. K.; Kösling, M.; Jones, P. G. *Chem. Ber.* **1996**, *129*, 1547.

[39] C21−H211···P1: H···P = 2.78(1) Å, C···P = 3.242(1) Å, C−H···P = 110(1)°. C31−H311···P2: H···P = 2.82(1), C···P = 3.247(1) Å, C−H···P = 108(1)°. Also, the shortest intramolecular P···O distances P1···O1 (3.223(1) Å) and P3···O1 (3.244(1) Å) are shorter than the hydrogen bond P···O distance.

reference values for typical Li$-$PR$_3$ bonds, which are centered around 2.65 Å.[30] Charge neutrality in dimeric **5** is achieved by four additional *n*-butyl anions. If **5** again is viewed as an octahedron of lithium atoms, the *n*-butyl anions 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 Li-*n*-Bu itself is an octahedral hexamer.[40] In **5** there are six short (average 2.499 Å) and six long Li$\cdots$Li distances (average 3.097 Å), the long distances belonging to the unbridged faces. This parallels exactly the situation in [Li-*n*-Bu]$_6$, where Li$\cdots$Li distances centered around 2.429 and 2.939 Å were found.[40] To our knowledge, in addition to [Li-*n*-Bu·LiO-*t*-Bu]$_4$[10] only a few other mixed organolithium/lithium alkoxide aggregates have been structurally characterized to date.[12,13]

Preparation of [(Me$_2$PCH$_2$)$_3$CO$^-$·3Li$^+$·(Me$_2$PCH)$_3$C^{2-}] (6). Formation and structural details of **5** strongly suggest that [LiOC(CH$_2$PMe$_2$)$_3$], formed initially by deprotonation of **4**, has further lithium binding capacity, trapping two additional lithium cations. The fragment [Li$_3$OC(CH$_2$PMe$_2$)$_3$]$^{2+}$ 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 **4** with Li-*n*-Bu. In contrast to the synthesis of **5**, which was done in the absence of solvent (other than the hexane contained in the 2.5 M solution of Li-*n*Bu), **4** reacts with excess Li-*n*-Bu 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.[41] It crystallizes with the previously mentioned fragment [Li$_3$OC(CH$_2$PMe$_2$)$_3$]$^{2+}$ as counterion, as was revealed by X-ray structure determination (compound **6**; Scheme 2).

Solid State and Solution Structure of 6. At the center of the solid-state molecular structure of **6** (Figure 5; Table 5) is an equilateral triangle of lithium atoms which is capped on one side by the deprotonated alcohol **4**, in much the same way as in the structure of **5**. The other side of the 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 individual lithium atoms is four-coordinate, being bonded to one oxygen atom, two phosphorus atoms, and one carbon atom. It should be noted that in the only other dilithium trimethylenemethane derivative structurally characterized as yet,[42] the lithium atoms are disposed on opposite sides of the trimethylenemethane dianion, while in **6** the fragment [Li$_3$OC(CH$_2$PMe$_2$)$_3$]$^{2+}$ forces the lithium atoms to be located on only one side, in accord with our assumption that [Li$_3$OC(CH$_2$PMe$_2$)$_3$]$^{2+}$ should be an ideal building block for trigonal polyhedral lithium faces. Both the structural data and the ^{31}P and particularly the ^{7}Li NMR spectra indicate that the Li atoms in **6** are more tightly bound to the trimethylene dianion than to the alkoxide. This follows clearly from the shorter Li$-$P bonds and the additional Li$-$C bonds to the dianion (Table 5), 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 while the dianion still is held firmly in place. This fascinating fluxional behavior is clearly evident from the ^{31}P and ^{7}Li spectra. At room temperature the alkoxide ^{31}P resonance is a broad singlet, while that of the trimethylenemethane dianion is a sharp 1:1:1:1 quartet resulting from coupling to one ^{7}Li nucleus (I =

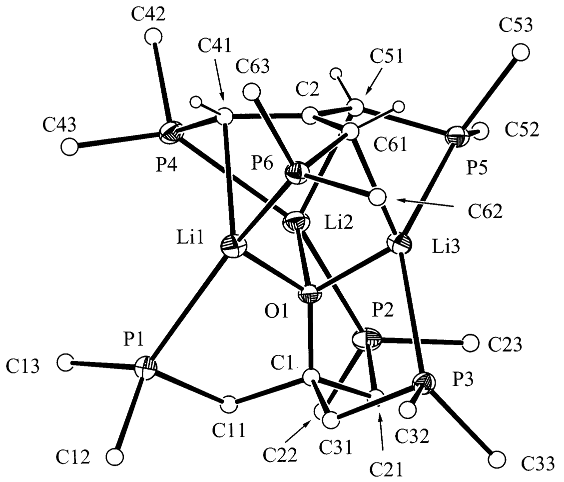

Figure 5. Molecular structure of **6** in the crystal and crystallographic numbering scheme used (ORTEP-III; displacement ellipsoids at the 30% level; C atoms as spheres with arbitrary radii; H atoms omitted for clarity except those at the methylene C atoms).

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for 6

(a) Distances			
Li1$-$P1	2.665(4)	Li1$-$P6	2.550(3)
Li2$-$P2	2.696(4)	Li2$-$P4	2.592(4)
Li3$-$P3	2.638(4)	Li3$-$P5	2.562(4)
Li1$-$O1	1.888(4)	Li1$-$C41	2.290(4)
Li2$-$O1	1.877(3)	Li2$-$C51	2.272(4)
Li3$-$O1	1.885(4)	Li3$-$C61	2.267(4)
C2$-$C41	1.433(3)	P4$-$C41	1.771(2)
C2$-$C51	1.432(3)	P5$-$C51	1.776(2)
C2$-$C61	1.437(3)	P6$-$C61	1.774(2)
Li1$\cdots$Li2	2.790(5)	Li2$\cdots$Li3	2.800(4)
Li1$\cdots$Li3	2.792(5)		
(b) Angles			
C1$-$O1$-$Li1	121.7(2)	O1$-$Li2$-$P4	111.7(2)
C1$-$O1$-$Li2	121.6(2)	O1$-$Li2$-$C51	105.3(2)
C1$-$O1$-$Li3	120.0(2)	P4$-$Li2$-$C51	79.4(1)
Li1$-$O1$-$Li2	95.6(2)	P3$-$Li3$-$O1	83.7(1)
Li1$-$O1$-$Li3	95.4(2)	P3$-$Li3$-$P5	145.4(2)
Li2$-$O1$-$Li3	96.2(2)	P3$-$Li3$-$C61	127.9(1)
P1$-$Li1$-$O1	81.8(1)	O1$-$Li3$-$P5	112.1(1)
P1$-$Li1$-$P6	147.6(1)	O1$-$Li3$-$C61	105.4(2)
P1$-$Li1$-$C41	126.9(1)	P5$-$Li3$-$C61	79.2(1)
O1$-$Li1$-$P6	113.1(2)	C41$-$C2$-$C51	119.9(2)
O1$-$Li1$-$C41	105.5(2)	C41$-$C2$-$C61	119.5(2)
P6$-$Li1$-$C41	78.5(1)	C51$-$C2$-$C61	120.3(2)
P2$-$Li2$-$O1	82.4(1)	C2$-$C41$-$P4	121.9(2)
P2$-$Li2$-$P4	147.9(1)	C2$-$C51$-$P5	120.4(2)
P2$-$Li2$-$C51	126.2(2)	C2$-$C61$-$P6	120.3(2)

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[40] Kottke, T.; Stalke, D. *Angew. Chem.*, **1993**, *105*, 619; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 580.

[41] Van Doorn, J. A.; van der Heijden, H. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 302.

[42] Wilhelm, D.; Dietrich, H.; Clark, T.; Mahdi, W.; Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 7279. Wilhelm, D.; Clark, T.; Schleyer, P. v. R.; Buckl, K.; Boche, G. *Chem. Ber.* **1983**, *116*, 1669.

$^3/_2$). At −80 °C ($T_c \approx -45$ °C) the alkoxide ^{31}P resonance is a broad multiplet, while the dianion P nuclei show a 1:1:1:1 quartet of doublets due to additional coupling to one alkoxide phosphino group. The ^{7}Li room temperature resonance is a doublet of 1:2:2:1 quartets due to coupling to three equivalent alkoxide P atoms and one dianion P, while at −80 °C ($T_c \approx -20$ °C) a doublet of doublets pattern results from coupling to one P atom each from alkoxide and dianion. The respective coupling constants (see Experimental Section) firmly back this assignment.

One other aspect in the molecular structure of the trimethylenemethane dianion in **6** should be commented on here. To a very good approximation, the trimethylenemethane dianion obeys noncrystallographic 3-fold symmetry, as does the entire molecule (with the atoms C1, O1, and C2 forming the pseudo-3-fold axis). This is certainly a consequence of the symmetrical disposition of the lithium atoms and nicely reflects the Y-conjugated π system.[43] As a consequence of the Y conjugation, the dianion is strictly planar at the central carbon atom (sum of the angles at C2: 359.7 °), while only the phosphino substituents are slightly tilted toward the central Li_3 triangle. The Y-conjugation is also clearly seen in the shortened C−C bond lengths (Table 5) and even extends into the P−CH bonds, which are close to the values found for ylidic P−C bonds. Here the lithium coordination of the phosphino substituents of the trimethylenemethane dianion is certainly helpful, as the partial onium character of phosphorus also serves to reduce the P−CH bond lengths by polar attraction.

The unexpected formation of the tris(dimethylphosphino)-substituted trimethylenemethane dianion in **6** upon reaction of **4** with excess Li-*n*-Bu 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[44] unidentified as yet. It should be noted that the total amount of **6** formed in our preparation results only in the formation of minute amounts of Li_2O, which should not be visible in the reaction flask even when precipitating as a solid. We believe that expulsion of O^{2-} occurs after multiple deprotonation of **4**, not only at oxygen but also at one or more of the methylene carbon atoms. The formation of the trimethylenemethane dianion from **4** is then believed to be driven by the reduction of negative charge of the anion by loss of O^{2-} and by the formation of a Y-conjugated π system.[43]

In summary, we have shown that the multidentate phosphine alkoxide ligand derived from **4** is capable of forming mixed-anion aggregates, so far with lithium as exclusive counterion. After multiple deprotonation and loss of Li_2O it reacts to the phosphine-substituted trimethylenemethane dianion. In contrast to covalent metal complexes especially of the transition metals, where different ligands are all too common, the alkali-metal cations have a strong tendency to crystallize with just one counteranion. Also, mixed-metal compounds of the alkali metals are rare. This is most probably due to the predominantly ionic nature of group 1 metal salts, which also holds for lithium organyls. Crystallization of monovalent cations with more than one counteranion would be strongly favored, then, by the formation of a solid solution (mixed crystals) which is increasingly more improbable with increasing complexity of the anion. Also, the well-known structural diversity of homologous alkali metal salts of more complex anions is prohibitive for the formation of solid solutions. Despite the recent burst in activity in the field of mixed-anion and mixed-metal compounds, especially of the alkali metals (and magnesium), the number of mixed organyl/alkoxide[10,12] or organyl/phenoxide[11f,13] compounds of group 1 metals is still very small. It seems particularly worthwhile, therefore, to find more precise criteria which favor such aggregates.

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Supporting Information Available: Tables of crystal data, atomic coordinates, anisotropic displacement parameters, hydrogen atom coordinates, and bond lengths and angles for **2**−**6**; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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