Phosphine Complexes of Main Group Elements. A Bis-phosphinomethyl Lithiate as an Anionic Diphosphine Ligand to Lithium: Synthesis and Structure of $\{[Me_2N(CH_2)_2NMe_2]Li[(Me_2P)C(SiMe_3)_2]_2Li\}$

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A novel type of Li complexation has been established by *X*-ray crystallography for the title compound revealing two distinctly different Li atoms, whereas the related complexes $\{(thf)Li[(Me_2P)_2CX]\}_2$ (X = $SiMe_3$, PMe_2; thf = tetrahydrofuran) feature equivalent environments for both lithium atoms.

During our investigations of phosphine complexes of main group elements, we showed that anionic phosphine ligands such as phosphinomethanides (**1**) and phosphinomethyl aluminates (**2**) are versatile ligands for the formation of a wide variety of neutral main group phosphine complexes, which are stable towards hard donor solvents (amines, ethers).[1] The anionic ligands are normally prepared as their lithium 'salts,' so their interaction with Li^+ in the solid state is particularly interesting. Moreover reports of alkali metal phosphine complexes are rare.

In initial studies we found that anions (**1a**, $n = 2$, R = $SiMe_3$; **b**, $n = 3$) act as chelating ligands to $[Li(thf)]^+$ (thf = tetrahydrofuran) with an additional π-heteroallyl type interaction completing the Li co-ordination sphere in the dimeric molecule (**3a**, X = $SiMe_3$; **b**, X = PMe_2).[1a,d] In (**4**),[1b] a six-membered ring is formed *via* phosphinomethyl bridges between an (anionic) aluminate and a (cationic) lithium co-ordination centre.

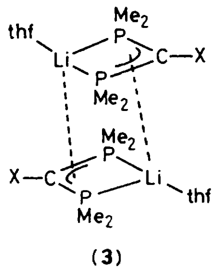
The unique P and C interaction of Li^+ in (**3**) prompted us to investigate systematically the co-ordination behaviour of differently substituted phosphinomethanides to Li, particularly in view of Eaborn's discovery that $[C(SiMe_3)_3]^-$ co-ordinated to Li^+ to form the lithiate anion $\{Li[C(SiMe_3)_3]_2\}^-$ (**5**).[2] A phosphinomethyl lithiate, if isolable, might behave as an anionic phosphine ligand towards Li^+ and thus might function as a link between the phosphinomethyl aluminate (**4**) and the lithiate (**5**).

$[R_{(3-n)}C(PMe_2)_n]^-$

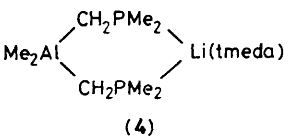
(**1**)

$[R_{(4-n)}Al(CH_2PMe_2)_n]^-$

(**2**)



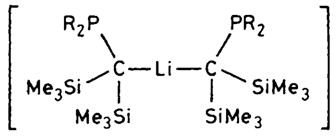
(**3**)



(**4**)

$[(thf)_4Li]^+\ [(Me_3Si)_3C\text{—}Li\text{—}C(SiMe_3)_3]^-$

(**5**)



(**8**)

$$\underset{(6)}{(Me_2P)(SiMe_3)_2CH} \xrightarrow{i} \underset{(7)}{\{Li[C(PMe_2)(SiMe_3)_2]\}_2(L)}$$

$$L = Me_2N(CH_2)_2NMe_2(tmeda)$$

Scheme 1. *Reagents:* i; Bu^{t}Li, pentane, tmeda.

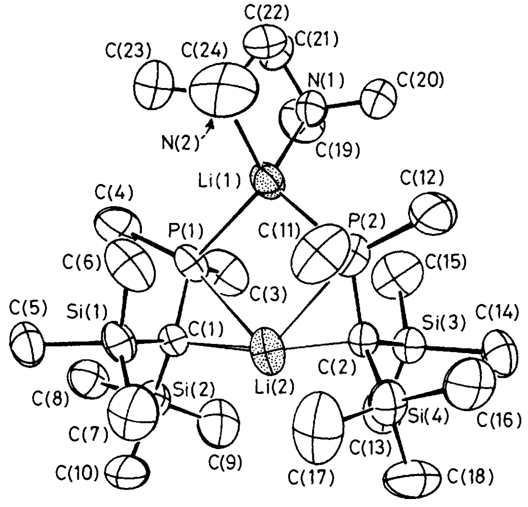


Figure 1. Molecular structure of (7) (ORTEP, thermal ellipsoids at the 50% probability level, without H-atoms). Principal distances (Å) and angles (°) are: Li(1)–P(1) 2.716(9), Li(1)–P(2) 2.72(1), Li(1)–N(1) 2.24(1), Li(1)–N(2) 2.20(1), Li(2)–P(1) 2.88(1), Li(2)–P(2) 2.92(1), Li(2)–C(1) 2.17(1), Li(2)–C(2) 2.16(1), Li(1)$\cdots$Li(2) 3.55(2), C(1)–P(1) 1.780(5), C(2)–P(2) 1.790(5), C(1)–Si(1) 1.848(6), C(1)–Si(2) 1.850(5), C(2)–Si(3) 1.853(6), C(2)–Si(4) 1.833(5); P(1)–Li(1)–P(2) 106.1(3), C(1)–Li(2)–C(2) 167.4(7), Li(1)–P(1)–C(1) 121.5(3), Li(1)–P(2)–C(2) 120.7(3), P(1)–C(1)–Li(2) 92.9(4), P(2)–C(2)–Li(2) 94.8(4).

Facile deprotonation of the parent phosphine (**6**)[3] with Bu^{t}Li yielded (**7**), which was isolated as colourless crystals from pentane (Scheme 1).† In dimeric (**7**),‡ one Li atom bridges the carbanion centres C(1) and C(2) of two anions, without carrying additional donor molecules (Figure 1). The Li–C bonding distances [2.17(1) and 2.16(1) Å] compare well with those in (**5**) [2.16(1) and 2.20(1) Å].[2] The bis(phosphinomethyl)lithiate thus formed acts as a chelating phosphine ligand to the second lithium atom, which completes its distorted tetrahedral co-ordination sphere with one molecule of tmeda. The entire dimer possesses approximate C_2 symmetry, the planes P(1), Li(1), Li(2), P(2) and C(1), Li(2), Li(1), C(2) being skewed by 16.2°. Thus the molecular structure of (**7**) combines features of both (**4**) (phosphine co-ordination to Li) and (**5**) (lithiate formation) within the same molecule and with different co-ordination modes of the two Li atoms. It should be noted that (**7**) is formed even with excess of tmeda, which distinguishes it from the related centrosymmetric dimer [(tmeda)LiCH$_2$(PMe$_2$)]$_2$, where both Li atoms bridge one C and one P donor in a head-to-tail fashion giving a six-membered ring, with *both* metal atoms also being co-ordinated by one molecule of tmeda.[4] The co-ordination mode observed in (**7**) has some distinct geometrical implications which deserve comment. (i) The angle at Li(2), formed by the two carbanionic C atoms, deviates from linearity [167.4(7)°] whereas in (**5**) strict linearity was observed. This nonlinearity must be caused by the geometrical requirements of the six-membered ring as formed by the Li–P co-ordination. (ii) The distances from Li(2) to the phosphine centres P(1) and P(2) are longer by only 0.2 Å than those from Li(1). In a sense, the equalization of the Li–P distances in (**7**) may be described as a novel bridging co-ordination mode of a tertiary phosphine centre between two metal atoms.§ In accordance with a more ionic description of the bonding in organolithium compounds[6] the observed overall geometry of (**7**) should be predominantly governed by the propensity to aggregation of Li$^+$ and anion, and the steric requirements of the substituents. The marked difference from (**3**) and (**5**) shows, however, that a delicate balance between these influences and the overall co-ordination mode at the lithium centre(s) is observed. In (**7**) the different Li–P interactions, which should be largely ion–dipole in character, are apparently optimized by the observed bond length equalization.

Finally the structure of (**7**) indicates, at least in principle, that phosphinomethyl lithiates (**8**) may act as anionic phosphine ligands to main group elements in a similar way to phosphinomethanides (**1**) or phosphinomethyl aluminates (**2**). In contrast with the only lithiate hitherto known, *i.e.* the salt-like compound (**5**), the additional P co-ordination to a cationic Li$^+$ in (**7**) gives rise to a neutral, cyclic molecule of the betaine type.

Received, 23rd January 1987; Com. 092

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† Satisfactory C, H, and Li microanalyses were obtained.

‡ *Crystal data* for (**7**): $C_{24}H_{64}Li_2N_2P_2Si_4$, $M = 568.96$, orthorhombic, space group $P2_12_12_1$, $a = 9.091(2)$, $b = 18.392(2)$, $c = 22.917(3)$ Å, $U = 3831.8$ Å^3, $D_c = 0.986$ g/cm^3, $Z = 4$, μ(Mo-K_α) = 2.5 cm^{-1}. 7434 Reflections were measured on an Enraf-Nonius CAD-4 diffractometer, Mo-K_α radiation, $\lambda = 0.71069$ Å, graphite monochromator, $T = 23$ °C, of which 6725 were unique and 3575 'observed' ($\Delta\omega = 0.95 + 0.35 \tan\theta$, $(\sin\theta/\lambda)_{max} = 0.594$, $+h$, $+k$, $\pm l$). Solution by direct methods (SHELXS-86). Refinement gave $R = 0.054$, $R_w = 0.039$, $w = 1/\sigma^2$ (F_o) for 307 refined parameters. Enantiopol refinement according to Flack[7] gave $x = 0.09(19)$. $\Delta\rho_{fin}$ (max/min) = +0.45/−0.42 e/Å^3. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ It is interesting to note that the P–C bond bridging by Li(2) as observed in (**7**) is very similar to that predicted theoretically for the LiCH$_2$PH$_2$ monomer.[5]