Phosphine Complexes of Main Group Elements: Crystal Structure of {Li[C(PMe₂)₃]-(tetrahydrofuran)}₂

Hans H. Karsch and Gerhard Müller

Anorganisch-Chemisches Institut, Technische Universität München, Lichtenbergstr. 4, D-8046 Garching, West Germany

The X-ray structure determination of the title compound, obtained by recrystallisation of LiC(PMe₂)₃ from pentane–tetrahydrofuran (thf) as colourless crystals, reveals it to be dimeric with two nearly planar (Me₂P)₃C-moieties linked by (thf)Li fragments *via* chelating and additional π-type interactions.

The nature of heteroelement substituent carbanions, *e.g.* [X–C$\langle$]⁻ (X = heteroelement fragment) has been a subject of continuing controversy. With adjacent onium centres, *i.e.* in the case of ylides, the sp²-nature of the carbanion is well documented[1] and only a few exceptions are known.[2] In contrast to this, it was shown recently, that in {Li[C-(SiMe₃)₃]·2thf}₂ (thf = tetrahydrofuran)[3] and {Li[C-(SiMe₂Ph)₃]·thf},[4] the anionic carbon atoms adopt a pyramidal configuration upon complexation to Li. A related group of compounds, the phosphinomethanides, have not so far been structurally characterized. From reactivity patterns, there is some evidence for a mesomeric charge delocalisation involving the heteroelement atom.[5] In order to evaluate the extent of planarity *vs.* pyramidality of the carbanion in phosphinomethanides, an X-ray determination of LiC(PMe₂)₃·thf was undertaken.

Colourless crystals were obtained by dissolving LiC(PMe₂)₃[5] in pentane containing thf (2 equiv.) and subsequently slowly evaporating off the solvent.

Crystal data: $C_{11}H_{26}LiOP_3$, $M = 274.2$, monoclinic, $P2_1/n$, $a = 9.285(2)$, $b = 12.508(3)$, $c = 14.079(3)$ Å, $\beta = 100.07(1)°$, $U = 1609.9$ Å³, $D_c = 1.13$ g cm⁻³ for $Z = 4$, $\mu(Mo-K_\alpha) = 3.5$ cm⁻¹. 2524 Unique reflections (ω-scans, $1 \leqslant \theta \leqslant 24°$) were collected on a Syntex P2₁ automated four-circle diffractometer equipped with a graphite monochromator (temp. −40 °C, Mo-K_α radiation, $\lambda = 0.71069$ Å). After Lorentz–polarization corrections, 2160 reflections were deemed significant [$I \geqslant 1.96\sigma(I)$] and used for all further calculations. The structure was solved by Patterson methods and completed by Fourier syntheses. Full matrix least-squares refinement (non-hydrogen atoms anisotropic, H-atoms isotropic, Syntex-XTL) led to a final $R = 0.029$, $R_w = 0.030$, $w = 1/\sigma^2(F_o)$ for 249 parameters. A final difference map was qualitatively featureless, $\Delta\rho_{max} = 0.3$ e Å⁻³.†
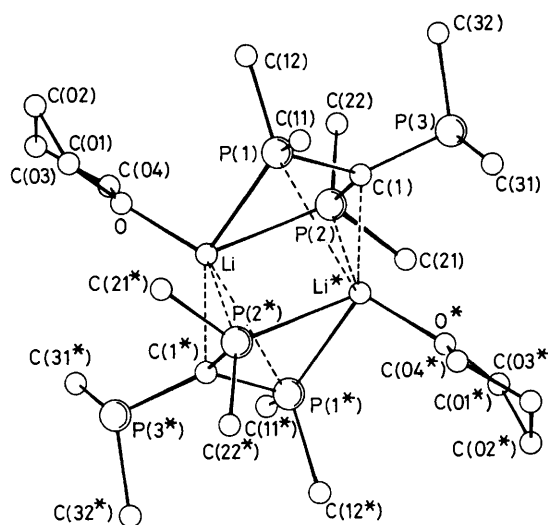
Figure 1. Molecular structure of {Li[C(PMe₂)₃]·thf}₂. Hydrogen atoms are omitted for clarity. Principal bond lengths (Å) and angles (°) are: P(1)–C(1) 1.795(2), P(2)–C(1) 1.796(2), P(3)–C(1) 1.812(2), Li–P(1) 2.588(3), Li–P(2) 2.684(3), Li–C(1*) 2.290(4), Li–O 1.923(3), Li–P(1*) 2.945(3), Li–P(2*) 2.998(3); P(1)–C(1)–P(2) 104.8(1), P(1)–C(1)–P(3) 129.5(1), P(2)–C(1)–P(3) 116.5(1), P(1)–Li–P(2) 65.3(1). The starred atoms are related to the unstarred atoms by a centre of inversion.

As can be seen in Figure 1, the structure consists of dimers with a crystallographically imposed centre of inversion. Each monomer consists of an almost planar CP₃-moiety [deviation of C(1) from the P(1), P(2), P(3) plane 0.313(2) Å], which chelates the (thf)Li fragment *via* interactions with P(1) and P(2), *viz.* 2.588(3) and 2.684(3) Å, whereas P(3) is not involved [P(3)–Li* 3.421(3) Å]. From the pyramidal conformation about P(3) it may be inferred that its lone pair lies approximately in the plane containing all the P atoms. The resulting right angle of this lone pair with the p_z orbital of the approximately sp² C(1) carbon has also been observed in

related phosphorus ylides.[1,6] The C(1)–P distances are significantly shorter than the corresponding P–C distances in the neutral trisphosphine $(Me_2P)_3CH$ [average 1.856(7) Å].[7] However, they are somewhat longer than those in the ylidic dication $[(Me_3P)_3C]^{2+}$ (average 1.75 Å).[1] The relatively small P(1)–C(1)–P(2) angle of 104.8(1)° is obviously due to the chelating interaction between these P atoms and Li. The rather large difference between the other two P–C(1)–P angles may be attributed to the conformation of the PMe_2 groups. The reason for the deviation from planarity of C(1) [sum of P–C(1)–P angles 350.8°] is obviously due to its close contact with Li*, which with the corresponding C(1*)–Li contact forms the link between the two centrosymmetrically related monomers. This distance is unexpectedly long, compared to, e.g. $\{Li[C(SiMe_2Ph)_3] \cdot thf\}$[4] [Li–C 2.12(2) Å] and approaches the average value (2.33 Å) for the Li–C distances in $[(Me_3Si)_3C_5H_2]Li$(tetramethylethylenediamine) where the Li atom is positioned above the plane of an aromatic π-system.[8]

On closer scrutiny, it becomes evident that all bonding distances to Li, [except Li–O 1.923(3) Å], are rather long. The bonding situation between Li and C(1*) might therefore best be interpreted as an ion pair interaction of Li^+ with the anionic π-system of the phosphinomethanide. The Li–P(1*) and Li–P(2*) distances support this theory and one co-ordination site of Li can thus be considered as pointing towards the centre of gravity of the P(1*)C(1*)P(2*) skeleton. Together with the chelating interactions with P(1) and P(2), and the interaction with O, the Li cation adopts tetrahedral geometry. Thus, the interactions of Li with P(1*)C(1*)P(2*) result in a geometric situation for Li resembling that in π-allyl type complexes. This type of bonding has been suggested for diphosphinomethanide ligands in transition metal complexes.[9] There might be

similarities in the bonding of alkaline metals with anionic P-ylides, e.g. $M[CH_2PR_2=C(PR_2)_2]$ and $M[CH(PR_2)-PR_2=C(PR_2)_2]$, but these complexes have not so far been structurally characterized.[9,10]

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