Lithio(diphenylphosphino)methane−Tetramethylethylenediamine: It's a Dimer!

Steffen Blaurock, Olaf Kühl, and Evamarie Hey-Hawkins*

Institut für Anorganische Chemie der Universität Leipzig, Talstrasse 35, D-04103 Leipzig, Germany

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Summary: The crystal structure determination of the tetramethylethylenediamine (TMEDA) adduct of lithio(diphenylphosphino)methane has shown this compound to be dimeric in the solid state rather than monomeric as reported previously.

The tetramethylethylenediamine (TMEDA) adduct of lithio(diphenylphosphino)methane (**1**) was previously reported to be monomeric in the solid state,[1] whereas the corresponding TMEDA adducts of lithio(dimethylphosphino)methane and lithio(methylphenylphosphino)methane are dimeric.[2] This unusual finding was rationalized by variable-temperature NMR studies, comparison with the results of ab initio calculations on monomeric $CH_2PH_2^-$,[3] and MNDO calculations by the authors.[1]

We have by chance redetermined the crystal structure of **1** and found that, while the crystallographic data (unit cell parameters and atomic coordinates) reported previously[1] are consistent with our findings,[4] the interpretation of the crystallographic data was erroneous. Thus, the triclinic unit cell of **1** does not contain two monomeric molecules of **1**; instead, **1** is *dimeric* in the solid state with the C and P atoms of CH_2PPh_2 moieties bridging two lithium centers to form a six-membered heterocyclic ring, which, as in dimeric Li(TMEDA)CH_2PMe_2,[2] adopts the chair conformation (Figures 1 and 2).

The overall structure of **1** is comparable to those of $[Li(TMEDA)CH_2PMe_2]_2$ and $[Li(TMEDA)CH_2PMePh]_2$.[2]

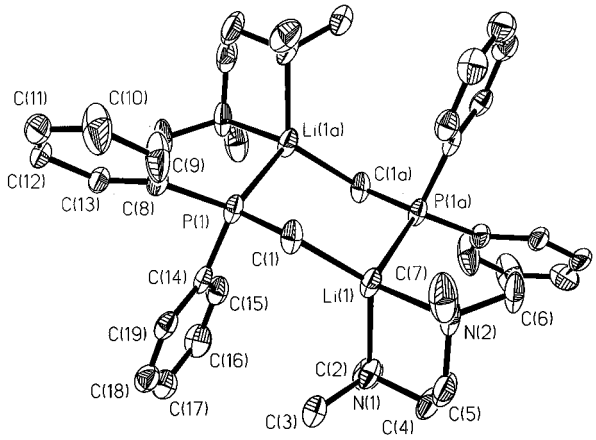

Figure 1. Molecular structure of dimeric Li(TMEDA)CH_2PPh_2 (**1**) (ORTEP plot, SHELXTL PLUS; XP).[5] Selected bond lengths and angles are given in Table 1. Hydrogen atoms are omitted for clarity.

Selected bond lengths and bond angles are given in Table 1.

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(1) Fraenkel, G.; Winchester, W. R.; Williard, P. G. *Organometallics* **1989**, *8*, 2308.
(2) Byrne, L. T.; Engelhardt, L. M.; Jacobsen, G. E.; Leung, W.-P.; Papasergio, R. I.; Raston, C. L.; Skelton, B. W.; Twiss, P.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1989**, 105.
(3) Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rhode, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467.

(4) The unit cell parameters and the atomic coordinates reported previously are in agreement with our determination. Crystal data for $[Li(TMEDA)CH_2PPh_2]_2$ (**1**): $C_{38}H_{56}Li_2N_4P_2$, M_r = 322.34 g, crystals grown from toluene/hexane at −20 °C, space group *P*1, (No. 2), a = 10.1723(12) Å, b = 10.9213(13) Å, c = 11.3514(13) Å, α = 61.258(2)°, β = 65.620(2)°, γ = 68.748(2)°, V = 985.7(2) Å^3, Z = 1, d_{calcd} = 1.086 g cm^{-3}, μ(Mo Kα) = 0.139 mm^{-1}. Data (Mo Kα = 0.710 73 Å) were collected with a Siemens CCD at 200(2) K; 93 reflections (2Θ range 4−47°) were used for determination of the unit cell parameters. The structure was solved by direct methods (SHELXS-86)[5] and subsequent difference Fourier syntheses and refined by least-squares techniques (SHELXL-93)[5]. Final R1 = 0.0549 and wR2 = 0.1300 (for reflections with $I > 2\sigma(I)$); R1 = 0.0865, and wR2 = 0.1473 (all data).

(5) SHELXTL PLUS, Siemens Analytical X-ray Instruments, Inc., 1990: XS, Program for Crystal Structure Solution; XL, Program for Crystal Structure Determination; XP, Interactive Molecular Graphics.

Table 1. Comparison of Selected Bond Lengths (Å) and Bond Angles (deg) in $[Li(TMEDA)CH_2PMe_2]_2$,[2] $[Li(TMEDA)CH_2PMePh]_2$,[2] and $[Li(TMEDA)CH_2PPh_2]_2$ (1)

	$[Li(TMEDA)CH_2PMe_2]_2$[a]	$[Li(TMEDA)CH_2PMePh]_2$[a]	$[Li(TMEDA)CH_2PPh_2]_2$ (**1**)
Li−P	2.593(7), 2.615(6)	2.67(1), 2.61(1)	2.686(5)
Li−C(1)	2.150(8), 2.141(6)	2.15(1), 2.12(1)	2.174(6)
Li−N	2.218(5), 2.169(8), 2.177(8), 2.216(7)	2.17(1), 2.17(2), 2.14(2), 2.17(1)	2.105(7) (N1), 2.170(5) (N2)
P−C(1)	1.751(3), 1.754(5)	1.730(8), 1.755(7)	1.752(3)
P−C(14)			1.836(3)
P−C(8)			1.872(3)
P−Li−C(1)	110.7(2), 108.2(3)	112.9(5), 115.2(5)	113.2(2)
P−Li−N	110.0(3), 109.7(3), 109.7(3), 109.5(2)	113.1(5), 116.6(6), 106.3(6), 106.1(5)	107.6(2), 108.8(2)
Li−P−C(1)	114.4(2), 112.7(2)	101.8(4), 102.6(3)	109.4(2)
P−C(1)−Li	113.2(3), 111.8(3)	108.6(5), 109.1(5)	114.0(2)

[a] Two independent molecules are observed in the asymmetric unit.

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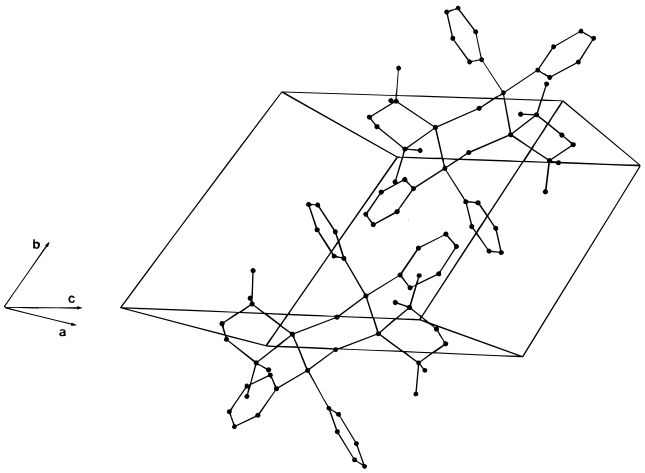

Figure 2. Unit cell of dimeric **1** (SHELXTL PLUS; XP).[5]

Conclusion

In the series $[Li(TMEDA)CH_2PMe_2]_2$,[2] $[Li(TMEDA)CH_2PMePh]_2$,[2] and $[Li(TMEDA)CH_2PPh_2]_2$ (**1**) all compounds are *dimeric* in the solid state, with $[Li(TMEDA)CH_2PMe_2]_2$ and $[Li(TMEDA)CH_2PPh_2]_2$ having a chair conformation and $[Li(TMEDA)CH_2PMePh]_2$ a boat conformation.

Supporting Information Available: Tables of crystal data and details of intensity collection, positional parameters, anisotropic thermal parameters, and bond lengths and angles (5 pages). Ordering information is given on any current masthead page.

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