

May C. Copsey and Tristram
Chivers*Department of Chemistry, University of Calgary,
2500 University Drive NW, Calgary, AB,
Canada T2N 1N4

Correspondence e-mail: chivers@ucalgary.ca

Key indicators

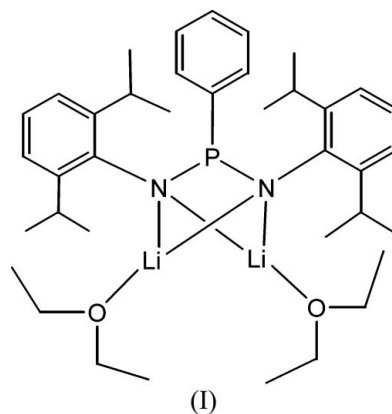
Single-crystal X-ray study
 $T = 173$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.050
 wR factor = 0.123
Data-to-parameter ratio = 16.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.A monomeric N,N' -dilithio-bis(amido)organo-
phosphane

The title compound [μ_2 -bis(2,6-diisopropylphenylamido)-phenylphosphane]bis(diethyl ether)dilithium(I), $[\text{Li}_2(\text{C}_{30}\text{H}_{39}\text{N}_2\text{P})(\text{C}_4\text{H}_{10}\text{O})_2]$ or $\text{Li}_2(\text{Et}_2\text{O})_2[\text{PhP}(\text{NDipp})_2]$ (Dipp = 2,6-diisopropylphenyl), has been structurally characterized. This is the first example of a monomeric N,N' -dilithio-bis(amido)organophosphane. The steric constraints of the bulky diisopropylphenyl substituents bonded to the N atom and the solvation of the lithium ions by a donor solvent prevent the formation of a higher oligomer.

Received 7 June 2006
Accepted 8 June 2006

Comment

Lithium derivatives of bis(amino)organophosphanes, $\text{Li}_2[\text{RP}(\text{NR}')_2]$, are versatile reagents in the synthesis of new $\text{N}-\text{P}-\text{N}$ heterocyclic or chain compounds. The bis(imido)phosphane can also act as a dianionic ligand itself, either by N,N -chelation or donation through the lone pair on phosphorus. Transition metal derivatives could be easily accessed by the reaction of these lithium reagents with metal halides.



Several examples have been synthesized, and the effect of the organic substituents R and R' on the observed solid-state structure has been investigated (Eichhorn *et al.*, 1999). It has been shown that the use of less sterically-hindered organic groups can lead to formation of larger oligomers; for example, in the case of $R = R' = \text{Ph}$, the structure is dimeric, whereas for smaller substituents $R = \text{Me}$, $R' = ^i\text{Pr}$, a tetramer is observed. The presence of donating solvents such as diethyl ether or thf can also be a factor, with solvation of the lithium centres preventing the formation of higher oligomers. A similar trend is seen for $\text{R}_2\text{PN}(\text{Li})\text{R}'$, with a monomeric structure observed for $R = 2,4,6$ -tri-*tert*-butylphenyl (Poetschke *et al.*, 1997). We report here the first monomeric structure of a dilithio-bis(amido)organophosphane $\text{Li}_2(\text{Et}_2\text{O})_2[\text{PhP}(\text{NDipp})_2]$ (Dipp = 2,6-diisopropylphenyl), (I).

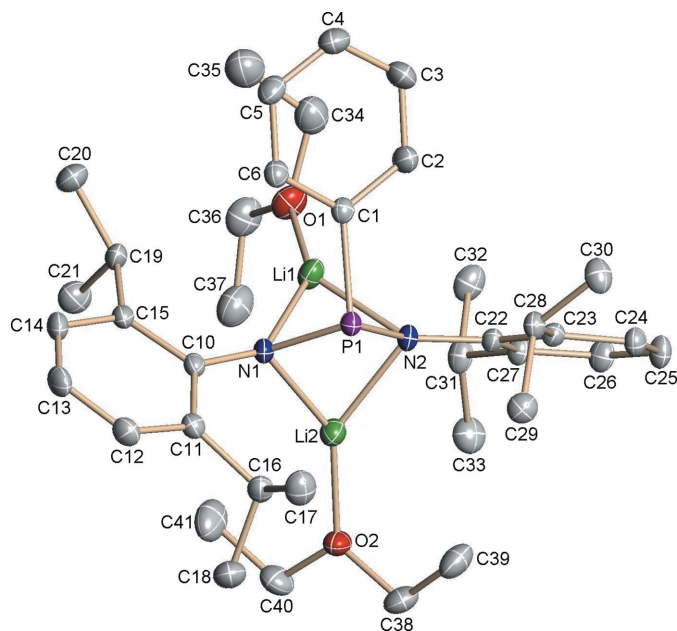


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

Complex (I) contains a pyramidal phosphorus centre, bonded to one phenyl group and two imido nitrogen centres. The P–N bond lengths (Table 1) are slightly different and can be considered as single bonds, falling at the upper end of the observed range for compounds of the type $\text{Li}_2[\text{RP}(\text{NR}')_2]$ [1.656 (5)–1.715 (2) Å; Eichhorn *et al.*, 1999]. The N atoms are each coordinated to two lithium centres with a total of four N–Li bonds. Each lithium centre is three-coordinate with distorted trigonal-planar geometry, solvated by a molecule of diethyl ether. The tendency of species of this type to form higher oligomers in the solid state has been prevented in this case by a combination of the sterically demanding groups on nitrogen and the presence of diethyl ether to solvate the lithium centres.

Experimental

The title compound, $\text{PhP}(\text{Cl})\text{NHDipp}$, was prepared according to the literature method of Chivers *et al.* (2005). $n\text{-BuLi}$ (4 ml, 2.5 M in hexanes, 10 mmol) was added dropwise to a solution of DippNH_2 (1.77 g, 10 mmol) in diethyl ether (20 ml) at 233 K. The reaction solution was warmed slowly to room temperature and stirred for 1 h. A solution of $\text{PhP}(\text{Cl})\text{NHDipp}$ (3.20 g, 10 mmol) in diethyl ether (20 ml) was added slowly at 233 K to the stirred reaction solution. The solution was warmed slowly to room temperature and stirred for 2 h to give a cloudy reaction mixture. The white precipitate was removed by filtration giving a colourless solution. A solution of $n\text{-BuLi}$ (8 ml, 2.5 M in hexanes, 20 mmol) was added dropwise, resulting in a yellow solution. Reduction in volume under vacuum (10 ml) and storage at 255 K yielded yellow blocks after several hours.

Crystal data

$[\text{Li}_2(\text{C}_{30}\text{H}_{39}\text{N}_2\text{P})(\text{C}_4\text{H}_{10}\text{O})_2]$
 $M_r = 620.72$
 Monoclinic, $P2_1/n$
 $a = 15.679$ (3) Å
 $b = 15.381$ (3) Å
 $c = 16.734$ (3) Å
 $\beta = 109.78$ (3)°
 $V = 3797.7$ (13) Å³

$Z = 4$
 $D_x = 1.086$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.11$ mm⁻¹
 $T = 173$ (2) K
 Block, yellow
 $0.30 \times 0.20 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor 1997)
 $T_{\min} = 0.969$, $T_{\max} = 0.990$

12831 measured reflections
 6675 independent reflections
 4532 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$
 $\theta_{\text{max}} = 25.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.123$
 $S = 1.02$
 6675 reflections
 418 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 1.8002P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.45$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.26$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

P1–N2	1.7049 (18)	N1–Li1	2.042 (4)
P1–N1	1.7185 (17)	N2–Li2	2.021 (4)
N1–Li2	2.011 (4)	N2–Li1	2.081 (4)
N2–P1–N1	91.02 (9)	O1–Li1–N2	139.2 (2)
N2–P1–C1	101.50 (9)	N1–Li1–N2	72.64 (14)
N1–P1–C1	102.32 (9)	O2–Li2–N1	142.9 (2)
O1–Li1–N1	146.9 (2)	O2–Li2–N2	140.4 (2)

All H atoms were placed in geometrically idealized positions (0.95–0.99 Å) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{parent atom})$.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We thank the University of Calgary and the Natural Science and Engineering Research Council (Canada) for funding.

References

- Bruker (2000). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
 Chivers, T., Copesey, M. C., Fedorchuk, C., Parvez, M. & Stubbs, M. (2005). *Organometallics*, **24**, 1919–1928.
 Eichhorn, B., Nöth, H. & Seifert, T. (1999). *Eur. J. Inorg. Chem.* pp. 2355–2368.
 Hooft, R. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
 Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
 Poetschke, N., Kiefer, M., Khan, M. A., Niecke, E. & Ashby, M. T. (1997). *Inorg. Chem.* **36**, 4087–4093.