

[*P,P*-Di-*tert*-butyl-*N*-trimethylsilyl-*P*-(trimethylsilylamino)phosphine imidato- κ^2 N,N']bis(pyridine- κ N)-lithium(I)

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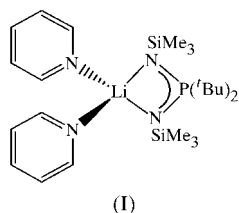
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In the title compound, $[\text{Li}(\text{C}_{14}\text{H}_{36}\text{N}_2\text{PSi}_2)(\text{C}_5\text{H}_5\text{N})_2]$, the bulky chelating monoanionic *P,P*-di-*tert*-butyl-*N*-trimethylsilyl-*P*-(trimethylsilylamino)phosphine imidate ligand and two pyridine ligands bind to Li in a pseudo-tetrahedral arrangement with twofold symmetry. The Li–N_{phosphine} distance is 2.048 (5) Å, while the Li···P distance is 2.520 (6) Å.

Comment

In the course of research involving *P,P*-di-*tert*-butyl-*N*-trimethylsilyl-*P*-(trimethylsilylamino)phosphine imidate (Scherer & Schieder, 1968) as a chelating monoanionic ligand to transition metals (Straub *et al.*, 1999, 2000*a,b*; Straub & Hofmann, 2001), the lithium complex of this ligand was crystallized from a reaction mixture containing $\text{NiCl}_2(\text{py})_4$ (py is pyridine), with two molecules of pyridine also coordinated, *i.e.* $\text{Li}[\text{tBu}_2\text{P}(\text{NSiMe}_3)_2](\text{py})_2$, (I). This is similar to the reported synthesis of the related species bearing phenyl groups on the P centre, $\text{Li}[\text{Ph}_2\text{P}(\text{NSiMe}_3)_2](\text{py})_2$ (Müller *et al.*, 1996). The lithium complex of that phosphanamide has also been structurally characterized with coordinated tetrahydrofuran (THF), $\text{Li}[\text{Ph}_2\text{P}(\text{NSiMe}_3)_2](\text{THF})_2$ (Steiner & Stalke, 1993).



The Li atom of (I) has a pseudo-tetrahedral coordination environment and lies, together with the P atom, on a twofold special position, so that the asymmetric unit consists of half a molecule. The distance from Li to the N atoms of the aminophosphine imidate ligand is 2.048 (5) Å, while to the N atoms of the pyridine ligands, the distance is 2.114 (5) Å. The corresponding distances in the phenyl-substituted analogue,

which has a very similar structure, are Li–N_{ligand} 2.123 (4) and 2.052 (4) Å, and Li–N_{py} 2.043 (4) and 2.079 (3) Å (Müller *et al.*, 1996). Similarly, in $\text{Li}[\text{Ph}_2\text{P}(\text{NSiMe}_3)_2](\text{THF})_2$, the Li–N distances are 2.08 (1) and 2.044 (9) Å (Steiner & Stalke, 1993). Thus, both the distorted tetrahedral coordination environment and the bond distances about Li are typical for these compounds.

While there are several other recently reported examples of compounds containing an N–P–N anionic chelate bound to Li, most of these involve P^{III} rather than P^V, and many have been characterized as dimers or clusters (Lawson *et al.*, 2000; Brask *et al.*, 1999; Schranz *et al.*, 1998; Raithby *et al.*, 1997; Van der Maelen Uria *et al.*, 1994; Detsch *et al.*, 1992). Distorted tetrahedral geometry is found about the Li atom in all of these structures, although the bond distances vary with the coordination environment.

The only reported crystal structures involving the amino-phosphine imidate used in this study contain it as a chelating ligand to Cu (Straub *et al.*, 1999, 2000*a,b*). These structures exhibit similar ligand geometries to that found for (I). The influence of the more electropositive Li centre on the ligand backbone can, however, be observed in the bond lengths and angles when they are compared with those in the Cu structures.

In particular, the P–N and N–Si distances in (I) [1.579 (2) and 1.672 (2) Å, respectively] are somewhat shorter than in the Cu^I structure [P–N 1.601 (2) and N–Si 1.706 (2) Å; Straub *et al.*, 1999] and significantly shorter than in the Cu^{III} complex [P–N 1.606 (5) and N–Si 1.725 (5) Å; Straub *et al.*, 2000*a*]. That is, more electropositive metal centres lead to shorter P–N and N–Si bonds in the aminophosphine imidate ligand. This can be rationalized by a higher bond order of the N–P and N–Si bonds when the metal centre is more electropositive, as electron density is transferred from the metal to appropriate N–P and N–Si π -bonding orbitals.

As a consequence of the smaller PN₂Si core in the ligand when bound to Li, the N–P–N [108.5 (2)°] and P–N–Si [153.6 (2)°] angles in (I) are slightly increased relative to their

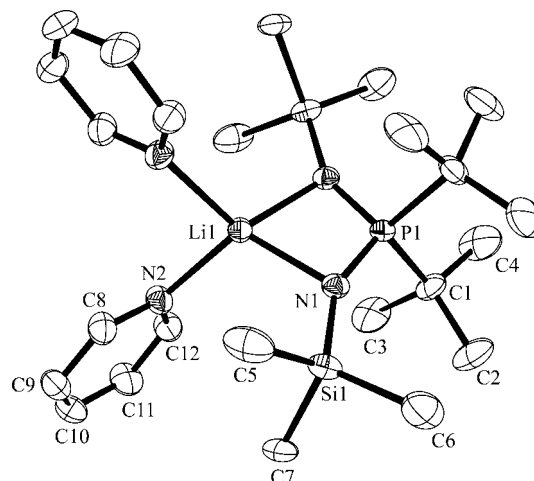


Figure 1

The molecular structure of (I) showing 30% probability displacement ellipsoids. H atoms have been omitted.

values in the Cu^I-ethylene complex [N—P—N 104.3 (1) and P—N—Si 151.4 (1)°; Straub *et al.*, 1999] and significantly larger than in the Cu^{III} complex [N—P—N 100.7 (2) and P—N—Si 148.1 (4)°; Straub *et al.*, 2000a]. This change in the geometry around the N atom leads to lower steric repulsion between the bulky ^tBu and SiMe₃ substituents.

Experimental

The protonated ligand ^tBu₂P(NSiMe₃)NHSiMe₃ (0.5 g, 1.56 mmol; Scherer & Schieder, 1968) was weighed into a Schlenk flask and dissolved in heptane (5 ml). *n*-Butyllithium (1.26 ml, 1.6 M, 2 mmol) was added and the solution was heated to reflux for 2 min. The resulting colourless solution was transferred to a flask containing a suspension of NiCl₂(py)₄ in hexane (10 ml). The reaction mixture was stirred and heated to reflux and then filtered, which resulted in a pale-green-blue solution from which colourless crystals of (I) precipitated. Attempts to cut the long thin needle-like crystals resulted in shattering. Therefore, a crystal was used which was longer than the beam width. Correction for this by *SADABS* (Sheldrick, 1996) may be the cause of the low *T*_{min}. The long crystals did not diffract at higher angles.

Crystal data

[Li(C₁₄H₃₆N₂PSi₂)(C₅H₅N)₂]
*M*_r = 484.74
 Monoclinic, *C*2/*c*
a = 8.8980 (2) Å
b = 19.3848 (5) Å
c = 17.5894 (3) Å
 β = 92.302 (1)°
V = 3031.48 (12) Å³
Z = 4

*D*_x = 1.062 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 3164 reflections
 θ = 2.1–24.1°
 μ = 0.19 mm⁻¹
T = 200 (2) K
 Needle, colourless
 0.83 × 0.29 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
*T*_{min} = 0.56, *T*_{max} = 0.97
 11 861 measured reflections

2410 independent reflections
 1674 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.075
 θ _{max} = 24.1°
h = -10 → 10
k = -22 → 22
l = -20 → 20

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.053
wR (*F*²) = 0.144
S = 1.05
 2410 reflections
 152 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0764P)^2 + 1.4419P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.029$
 $\Delta\rho_{\max} = 0.42 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.34 \text{ e } \text{Å}^{-3}$

All H atoms were treated as riding, with C—H = 0.95–0.98 Å and *U*_{iso}(H) = 1.2–1.5*U*_{eq}(C).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1011). Services for accessing these data are described at the back of the journal.

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