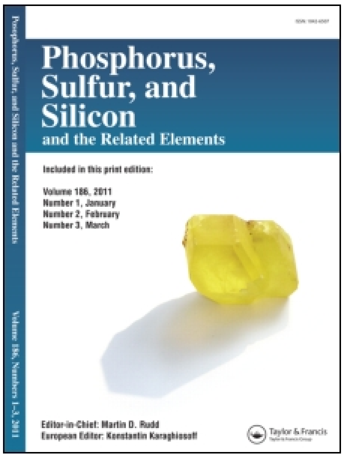

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FORMATION AND STRUCTURAL CHARACTERIZATION OF $Ph_2P(NSiMe_3)_2Li(py)_2$ (py = PYRIDINE)

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FORMATION AND STRUCTURAL CHARACTERIZATION OF $Ph_2P(NSiMe_3)_2Li(py)_2$ (py = PYRIDINE)

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$Ph_2P(NSiMe_3)_2Li(py)_2$ (**4**) has been obtained as a by-product from the reaction of $Ti(=N^tBu)Cl_2(py)_2$ (**1**) with $Li[Ph_2P(NSiMe_3)_2]$ (**2**) or in a more straightforward fashion by treatment of **2** with two equivalents of pyridine. The molecular structure of **4** has been determined by X-ray diffraction.

Keywords: Phosphorus; nitrogen; silicon; lithium; diiminophosphinates

1. INTRODUCTION

Bulky diiminophosphinate anions such as $[Ph_2P(NSiMe_3)_2]^-$ have been demonstrated to be versatile building blocks in main group chemistry as well as in the coordination chemistry of various transition metals.[1] They have also been frequently used as starting materials for the synthesis of heterocycles containing NPN units.[2–4] The structural chemistry of alkali metal derivatives of the $[Ph_2P(NSiMe_3)_2]^-$ anion has been investigated by Stalke et al. However, in all cases THF has been used as a stabilizing Lewis base for the coordinative saturation of the alkali metals.[5] We describe here the formation and structural characterization of the hitherto unknown pyridine-stabilized lithium salt $Ph_2P(NSiMe_3)_2Li(py)_2$ (**4**).

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2. RESULTS AND DISCUSSION

2.1 Preparative Results

As part of our ongoing investigation of metal complexes containing bulky heteroallylic ligands we studied the reaction of the imidotitanium(IV) precursor $Ti(=N^tBu)Cl_2(py)_2$ (**1**) with various lithium salts of heteroallylic ligands, including $Li[Ph_2P(NSiMe_3)_2]$ (**2**).[6] The titanium complex **1** reacts with **2** in a molar ratio of 1:2 to afford the disubstitution product $[Ph_2P(NSiMe_3)_2]_2Ti(=N^tBu)$ (3) according to Equation 1:

$$\underset{\mathbf{1}}{Ti(=N^tBu)Cl_2(py)_2} + 2\,\underset{\mathbf{2}}{Li[Ph_2P(NSiMe_3)_2]} \xrightarrow[-2\,py]{THF} \underset{\mathbf{3}}{[Ph_2P(NSiMe_3)_2]_2Ti(=N^tBu)} + 2\,LiCl \qquad (1)$$

During recrystallization of the red product **3** from hexane the presence of a less soluble by-product was noted, which could be isolated in the form of pale yellow crystals. This crystalline material did not contain titanium and analyzed as $Ph_2P(NSiMe_3)_2Li(py)_2$ (**4**). In addition to the elemental analysis the presence of two pyridine ligands was confirmed by gas-chromatography after hydrolysis. The formation of **4** is easily rationalized as pyridine is liberated during the reaction. Due to severe steric crowding no additional pyridine ligand is coordinated in the imido complex **3**.[6]

Good yields of pure, white bis(pyridine) adduct **4** can be obtained in a straightforward manner by reacting $Li[Ph_2P(NSiMe_3)_2]$ (**2**) directly with two equivalents of pyridine in hexane solution (Eq. 2). In this case **4** crystallizes directly from the reaction mixture. The ^{31}P NMR spectrum shows a singlet at 7.4 ppm.

$$\underset{\mathbf{2}}{Li[Ph_2P(NSiMe_3)_2]} + 2\,C_5H_5N \rightarrow \underset{\mathbf{4}}{Ph_2P(NSiMe_3)_2Li(py)_2} \qquad (2)$$

2.2 Crystal and Molecular Structure of 4

Compound **4** crystallizes in the monoclinic space group $P2_1/n$ (Fig. 1, Tables I and II). Like the THF-solvated species $Ph_2P(NSiMe_3)_2Li(THF)_2$ (**5**)[7] the bis(pyridine) derivative consists of monomeric molecules in the solid state. Together

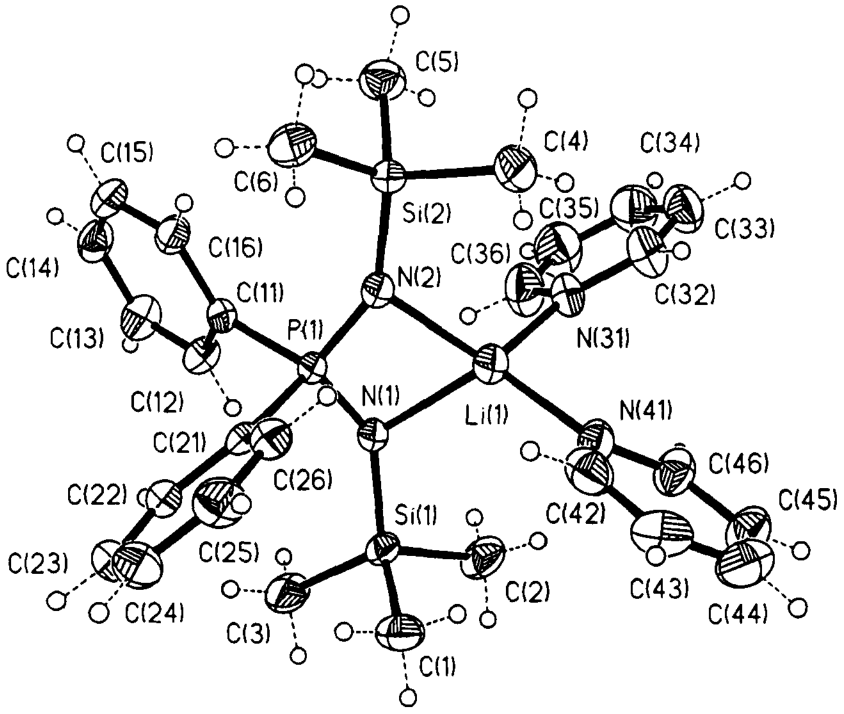

FIGURE 1 Molecular structure of $Ph_2P(NSiMe_3)_2Li(py)_2$ (**4**).

with the lithium atom the NPN unit forms a planar, four-membered, kite-shaped metallaphosphazene ring. A formal coordination number of 4 at lithium is a attained by coordination of two pyridine ligands. The coordination geometry around lithium can be described as distorted tetrahedral. With 157.2(2) and 158.1(2) the P-N distances within the ring are equal, as are the N-Si bond lengths (167.7(2) and 168.8(2) pm). These values are in good agreement with the corresponding bond lengths in **5**. A structural difference as compared to the bis(THF) adduct **5** is found for the Li-N distances which are significantly different in the titel compound (Li(1)-N(1) 212.4(4), Li(1)-N(2) 205.2(4) pm). The corresponding values for **5** are 207.7(9) and 204.4(9), respectively.

EXPERIMENTAL

The reaction was carried out under purified nitrogen. Solvents were carefully dried over sodium/benzophenone and freshly distilled under nitrogen prior to

TABLE I Atomic coordinates (× 10^4) and equivalent isotropic displacement coefficients ($\mathrm{pm}^2 \times 10^{-1}$) for **4**. *U*(eq) is defined as one-third of the orthogonalized U_{ij} tensor

	x	*y*	*z*	*U(eq)*
P(1)	1840(1)	2956(1)	9361(1)	23(1)
Si(1)	3362(1)	3781(1)	8102(1)	28(1)
Si(2)	906(1)	1369(1)	9714(1)	24(1)
N(1)	2932(1)	3138(1)	8824(1)	26(1)
N(2)	1548(1)	2108(1)	9293(1)	27(1)
Li(1)	2784(3)	2023(2)	8386(2)	36(1)
C(1)	2268(2)	3902(1)	7085(2)	42(1)
C(2)	4769(2)	3454(1)	7691(2)	45(1)
C(3)	3675(2)	4716(1)	8617(2)	48(1)
C(4)	828(2)	630(1)	8829(2)	42(1)
C(5)	1787(2)	1002(1)	10751(1)	40(1)
C(6)	−641(2)	1530(1)	9993(1)	36(1)
C(11)	2139(2)	3281(1)	10533(1)	24(1)
C(12)	3021(2)	3795(1)	10759(1)	32(1)
C(13)	3277(2)	4037(1)	11647(1)	39(1)
C(14)	2645(2)	3766(1)	12321(1)	36(1)
C(15)	1756(2)	3266(1)	12107(1)	36(1)
C(16)	1503(2)	3023(1)	11222(1)	32(1)
C(21)	534(2)	3489(1)	8937(1)	25(1)
C(22)	441(2)	4248(1)	9085(1)	31(1)
C(23)	−530(2)	4637(1)	8702(1)	39(1)
C(24)	−1415(2)	4280(1)	8168(2)	45(1)
C(25)	−1339(2)	3532(1)	8022(2)	42(1)
C(26)	−374(2)	3140(1)	8404(1)	33(1)
N(31)	4226(2)	1380(1)	8747(1)	35(1)
C(32)	4445(2)	687(1)	8510(2)	46(1)
C(33)	5453(2)	317(1)	8846(2)	47(1)
C(34)	6219(2)	676(2)	9472(2)	56(1)
C(35)	5994(3)	1368(2)	9714(2)	64(1)
C(36)	5000(2)	1694(2)	9363(2)	53(1)
N(41)	2409(2)	1778(1)	7016(1)	36(1)
C(42)	1322(2)	1820(1)	6579(2)	43(1)
C(43)	1083(2)	1693(1)	5663(2)	50(1)
C(44)	1983(2)	1525(2)	5166(2)	53(1)
C(45)	3096(2)	1478(1)	5588(2)	47(1)
C(46)	3277(2)	1603(1)	6500(2)	39(1)

use. NMR spectra were recorded using a Bruker AM 250 spectrometer. X-ray crystallography: Intensities were collected at −120°C on a Stoe-Siemens AED with graphite-monochromated Mo Kα radiation (λ = 71.073 pm). The structure was solved by the Patterson method with SHELXS-90[8] and refined by full-matrix least-squares procedures using SHELXTL-Plus, PC version.[9] A riding model was employed to refine the hydrogen atom positions. The starting material $\mathrm{Li[Ph_2P(NSiMe_3)_2]}$ (**2**) was prepared according to the literature procedure.[2,4]

TABLE II Selected bond lengths [pm] and angles [°] for **4**

P(1)-N(1)	158.1(2)	N(1)-P(1)-N(2)	110.2(1)
P(1)-N(2)	157.2(2)	N(1)-Li(1)-N(2)	76.5(1)
N(1)-Si(1)	168.8(2)	P(1)-N(1)-Li(1)	85.0(1)
N(2)-Si(2)	167.7(2)	P(1)-N(2)-Li(1)	87.7(1)
Li(1)-N(1)	212.4(4)	N(31)-Li(1)-N(41)	102.4(2)
Li(1)-N(2)	205.2(4)	P(1)-N(1)-Si(1)	139.4(1)
Li(1)-N(31)	204.2(4)	P(1)-N(2)-Si(2)	148.6(1)
Li(1)-N(41)	207.9(4)	Li(1)-N(1)-Si(1)	118.8(1)
P(1)-C(11)	183.2(2)	Li(1)-N(2)-Si(2)	122.7(1)
P(1)-C(21)	183.2(2)	C(11)-P(1)-C(21)	102.8(1)

Bis(pyridine)lithium-P,P-diphenyl-N,N′-bis(trimethylsilylimino)phosphinate (4)

1.83 g (5.0 mmol) **2** were dissolved in 60 ml of hexane at ambient temperature and filtered to remove small amounts of insoluble particles. 0.85 ml (0.84 g, 10.6 mmol) of pyridine were added with stirring to the clear filtrate. An initially formed precipitate redissolves upon gentle warming. Slow cooling of the resulting solution to −20 °C during 24 h afforded the product as white crystals which were isolated by filtration and dried *in vacuo*. Yield: 2.11 g (80%), m.p. 143–145; °C. ^{1}H NMR (C_6D_6): δ 8.60 (m, 4 H, *o*-C_5H_5N), 8.01 (m, 4 H, *o*-C_6H_5), 7.19 (m, 6 H, *m,p*-C_6H_5), 6.91 (m, 2 H, *p*-C_5H_5N), 6.64 (m, 4 H, *m*-C_5H_5N), 0.14 (s, 18 H, $SiMe_3$) ppm. ^{31}P NMR (C_6D_6): δ 7.4 (s) ppm.

$C_{28}H_{38}LiN_4PSi_2$ (524.71) calc. C 64.09 H 7.30 Li 1.32 N 10.68
found C 63.71 H 7.22 Li 1.34 N 10.31

Crystal structure determination of 4

$C_{28}H_{38}LiN_4PSi_2$ (524.71), monoclinic, space group $P2_1/n$, a = 1141.6(1), b = 1811.5(2), c = 1481.9(2) pm, β = 95.88(1)°, V = 3.0485(6) nm^3, Z = 4, d = 1.143 Mg/m^3, μ = 0.191 mm-1, F(000) = 1120, crystal dimensions: 0.70 × 0.70 × 0.30 mm, 2θ range: 8–45°, number of measured reflexions: 11135 (3994 unique and 3992 observed), refined parameters: 331, goodness of fit: 1.032, R = 0.0317, $wR2$ = 0.0794, min./max electron density: 235/−228 e nm^{-3}. Further details of the crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-, the names of the authors, and the journal citation.

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