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## THE SILYLATION OF THE PHOSPHAZENIUM SALT $[\text{H}_2\text{NPPh}_2\text{NPPh}_2\text{NH}_2]^+\text{Cl}^-$

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Various routes have been developed to synthesize mono-, di- and trisilylated derivatives of the phosphazanium salt  $[\text{H}_2\text{NPPh}_2\text{NPPh}_2\text{NH}_2]^+\text{Cl}^-$  (**1**) in moderate to good yields. The trisilylated phosphazene compound **6** has been characterized by X-ray structure determination.

**Key words:** Silylated phosphazenes; X-ray.

### INTRODUCTION

We previously have reported on the synthesis of various metallacyclopophosphazenes formed by the reaction of the phosphazanium salt  $[\text{H}_2\text{NPPh}_2\text{NPPh}_2\text{NH}_2]^+\text{Cl}^-$  (**1**) with metal halides and metal nitrido chlorides, respectively.<sup>1</sup> However, success of this reaction was limited to halogenated species only. Substitution of chlorine atoms in subsequent reactions could only be sparingly achieved.<sup>2</sup> With the preparation of silylated phosphazene precursors it is possible to enlarge the synthetic pool for cyclisation reactions.<sup>3</sup> Acyclic compounds are also accessible.<sup>4</sup>

### RESULTS AND DISCUSSION

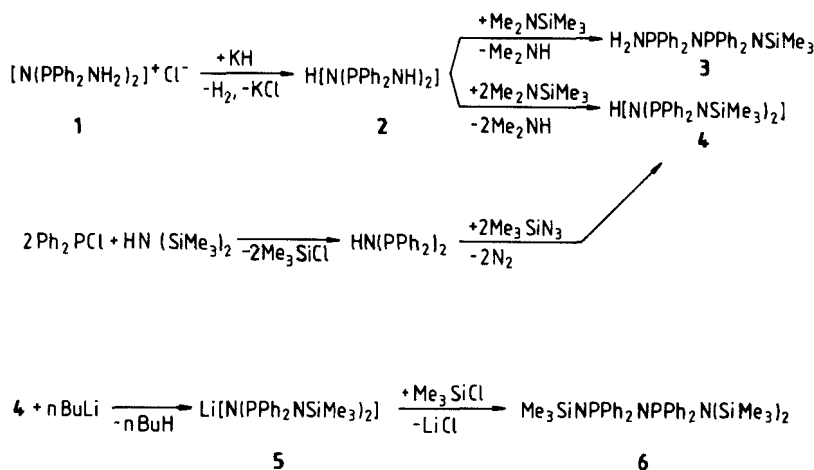
It was found that silyl groups can be transferred to **1** using  $\text{Me}_2\text{NSiMe}_3$ . The reaction of **1** with an excess of  $\text{Me}_2\text{NSiMe}_3$ , however leads to a mixture of products.<sup>2</sup>

In a first step **1** must be dehydrohalogenated yielding  $\text{H}[\text{N}(\text{PPh}_2\text{NH})_2]$  (**2**). In contrast to previous experiments which used  $\text{NaOMe}$ <sup>5</sup> to obtain **2** this product is also formed as an intermediate using  $\text{KH}$  or  $\text{NEt}_3$ .<sup>6</sup> Reacting **2** directly with  $\text{Me}_2\text{NSiMe}_3$  depending on the molar ratio,  $\text{H}_2\text{NPPh}_2\text{NPPh}_2\text{NSiMe}_3$  (**3**) and  $\text{H}[\text{N}(\text{PPh}_2\text{NSiMe}_3)_2]$  (**4**) are formed quantitatively. Even with an excess of  $\text{Me}_2\text{NSiMe}_3$  further silylation cannot be achieved.

The metalation of **4** with  $n\text{BuLi}$  or  $\text{LiNH}_2$  produces the chelating-complex  $\text{Li}[\text{N}(\text{PPh}_2\text{NSiMe}_3)_2]$  (**5**). NMR investigations indicate a symmetrical structure (see Table I). Compound **5** reacts with  $\text{Me}_3\text{SiCl}$  under salt elimination to give the trisilylated linear phosphazene  $\text{Me}_3\text{SiNPPh}_2\text{NPPh}_2\text{N}(\text{SiMe}_3)_2$  (**6**).

In addition to spectroscopic investigations we carried out an X-ray structural determination. Suitable crystals were obtained from  $\text{Et}_2\text{O}/n\text{-hexane}$ . Figure 1 shows a molecule with one amidic and one imidic terminal nitrogen atom. Within ex-

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SCHEME I Synthetic pathways to 3, 4, 5, and 6

perimental error the environment at N(5) is planar due to the known influence of silyl groups.<sup>7</sup> Bond lengths and angles are given in Tables II and III.

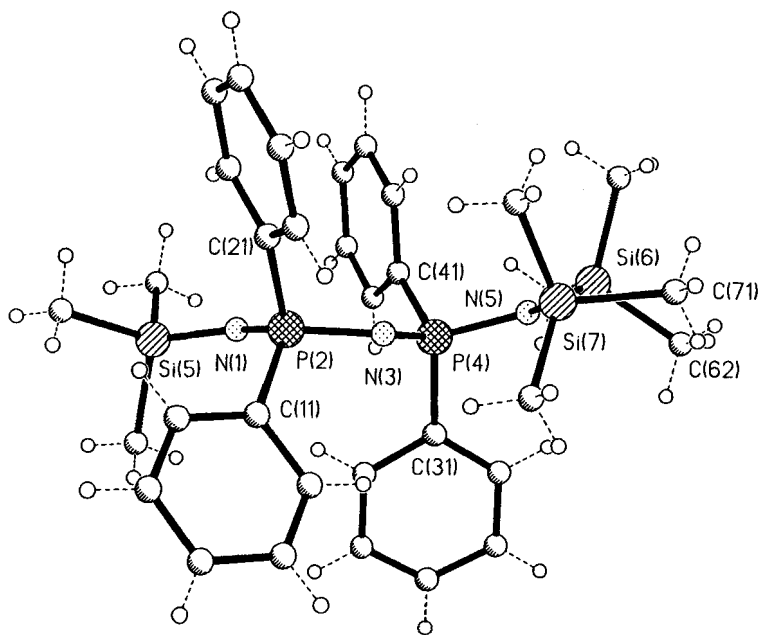
Migration of silyl groups is not observed. The four mentioned reaction steps from 1 over 2, 4 and 5 to 6 can be carried out in a "one pot"-synthesis (yields: 40–60%).

Having the experience of this method we could also use another synthetic approach to form 4. Recently Oakley *et al.* reported on the synthesis of 4 by oxidation of HN(PPh<sub>2</sub>)<sub>2</sub> with Me<sub>3</sub>SiN<sub>3</sub>.<sup>8</sup> Repeating this reaction we obtained only a viscous

TABLE I  
Compilation of NMR data

	$\delta$ <sup>1</sup> H-NMR <sup>a</sup>	$\delta$ <sup>29</sup> Si-NMR <sup>b</sup>	$\delta$ <sup>31</sup> P-NMR <sup>c</sup>
<u>3</u>	+ 0.2 (s, -SiMe <sub>3</sub> ) + 2.9 (s, -NH <sub>2</sub> ) + 8.3 - 6.9 (m, -Ph)	-16.3 d <sup>d</sup>	+ 0.9 d <sup>f</sup> + 17.6 d
<u>4</u>	- 0.2 (s, -SiMe <sub>3</sub> ) + 8.1 - 7.1 (m, -Ph)	- 4.6 m	+ 11.3 s + 11.1 s (C <sub>6</sub> D <sub>6</sub> )
<u>5</u>	- 0.3 (s, -SiMe <sub>3</sub> ) + 8.1 - 6.9 (m, -Ph)	- 10.5 m	+ 10.9 s + 11.3 s (C <sub>6</sub> D <sub>6</sub> ) + 4.2 s (TMEDA)
<u>6</u>	- 0.2 (s, -SiMe <sub>3</sub> ) + 0.1 (s, -2SiMe <sub>3</sub> ) + 8.0 - 7.1 (m, -Ph)	+ 8.7 s - 18.9 d <sup>e</sup>	- 8.8 d <sup>g</sup> + 17.5 d

<sup>a</sup>CDCl<sub>3</sub>, TMS ext., 80.13 MHz; <sup>b</sup>CDCl<sub>3</sub>, TMS ext. 49.694 MHz; <sup>c</sup>CDCl<sub>3</sub>, 85% H<sub>3</sub>PO<sub>4</sub> ext., 101.256 MHz; <sup>d</sup><sup>2</sup>J<sub>PSi</sub> = 22.0 Hz; <sup>e</sup><sup>2</sup>J<sub>PSi</sub> = 28.0 Hz; <sup>f</sup>P=NSiMe<sub>3</sub> <sup>2</sup>J<sub>PP</sub> = 3.8 Hz; <sup>g</sup>P=NSiMe<sub>3</sub> <sup>2</sup>J<sub>PP</sub> = 8.1 Hz.

FIGURE 1 Molecular structure of **6**TABLE II  
Bond lengths for **6** [pm]

N(1)-P(2)	154.1 (6)	N(1)-Si(5)	166.3 (7)
P(2)-N(3)	162.5 (8)	P(2)-C(11)	180.3 (9)
P(2)-C(21)	181.2 (10)	N(3)-P(4)	156.3 (7)
P(4)-N(5)	166.0 (7)	P(4)-C(31)	180.7 (10)
P(4)-C(41)	180.7 (8)	N(5)-Si(6)	179.9 (8)
N(5)-Si(7)	179.1 (6)	C(11)-C(12)	138.7 (15)
C(11)-C(16)	140.3 (15)	C(12)-C(13)	135.7 (15)
C(13)-C(14)	136.9 (18)	C(14)-C(15)	137.7 (18)
C(15)-C(16)	135.7 (15)	C(21)-C(22)	139.6 (13)
C(21)-C(26)	139.9 (11)	C(22)-C(23)	138.1 (18)
C(23)-C(24)	139.4 (16)	C(24)-C(25)	135.6 (18)
C(25)-C(26)	138.0 (16)	C(31)-C(32)	137.0 (16)
C(31)-C(36)	140.6 (14)	C(32)-C(33)	138.3 (17)
C(33)-C(34)	135.8 (19)	C(34)-C(35)	135.9 (21)
C(35)-C(36)	138.2 (16)	C(41)-C(42)	138.4 (14)
C(41)-C(46)	139.2 (11)	C(42)-C(43)	137.4 (14)
C(43)-C(44)	135.0 (15)	C(44)-C(45)	138.6 (18)
C(45)-C(46)	138.6 (14)	Si(5)-C(51)	186.9 (12)
Si(5)-C(52)	188.2 (12)	Si(5)-C(53)	185.7 (11)
Si(6)-C(61)	184.7 (9)	Si(6)-C(62)	186.2 (13)
Si(6)-C(63)	185.7 (10)	Si(7)-C(71)	185.7 (11)
Si(7)-C(72)	184.6 (10)	Si(7)-C(73)	184.8 (11)

TABLE III  
 Bond angles for **6** [°]

P(2)-N(1)-Si(5)	149.7(5)	N(1)-P(2)-N(3)	117.5(4)
N(1)-P(2)-C(11)	112.4(4)	N(3)-P(2)-C(11)	105.7(4)
N(1)-P(2)-C(21)	112.6(4)	N(3)-P(2)-C(21)	105.1(4)
C(11)-P(2)-C(21)	102.1(4)	P(2)-N(3)-P(4)	131.7(4)
N(3)-P(4)-N(5)	108.5(3)	N(3)-P(4)-C(31)	111.5(4)
N(5)-P(4)-C(31)	107.7(4)	N(3)-P(4)-C(41)	111.3(4)
N(5)-P(4)-C(41)	108.9(4)	C(31)-P(4)-C(41)	108.7(4)
P(4)-N(5)-Si(6)	123.6(3)	P(4)-N(5)-Si(7)	116.4(4)
Si(6)-N(5)-Si(7)	119.3(4)	P(2)-C(11)-C(12)	121.0(8)
P(2)-C(11)-C(16)	122.8(8)	C(12)-C(11)-C(16)	116.2(9)
C(11)-C(12)-C(13)	122.3(10)	C(12)-C(13)-C(14)	121.0(12)
C(13)-C(14)-C(15)	117.8(10)	C(14)-C(15)-C(16)	121.9(11)
C(11)-C(16)-C(15)	120.8(10)	P(2)-C(21)-C(22)	120.3(6)
P(2)-C(21)-C(26)	122.1(7)	C(22)-C(21)-C(26)	117.5(9)
C(21)-C(22)-C(23)	121.1(8)	C(22)-C(23)-C(24)	120.4(10)
C(23)-C(24)-C(25)	118.6(12)	C(24)-C(25)-C(26)	122.0(9)
C(21)-C(26)-C(25)	120.4(9)	P(4)-C(31)-C(32)	124.6(8)
P(4)-C(31)-C(36)	118.1(8)	C(32)-C(31)-C(36)	117.1(9)
C(31)-C(32)-C(33)	122.4(11)	C(32)-C(33)-C(34)	118.3(13)
C(33)-C(34)-C(35)	122.4(12)	C(34)-C(35)-C(36)	118.8(11)
C(31)-C(36)-C(35)	121.0(11)	P(4)-C(41)-C(42)	117.4(6)
P(4)-C(41)-C(46)	123.5(7)	C(42)-C(41)-C(46)	118.9(8)
C(41)-C(42)-C(43)	121.1(8)	C(42)-C(43)-C(44)	120.6(11)
C(43)-C(44)-C(45)	119.3(10)	C(44)-C(45)-C(46)	121.3(9)
C(41)-C(46)-C(45)	118.8(9)	N(1)-Si(5)-C(51)	114.5(4)
N(1)-Si(5)-C(52)	111.2(5)	C(51)-Si(5)-C(52)	105.0(6)
N(1)-Si(5)-C(53)	110.4(4)	C(51)-Si(5)-C(53)	107.8(5)
C(52)-Si(5)-C(53)	107.5(5)	N(5)-Si(6)-C(61)	114.5(4)
N(5)-Si(6)-C(62)	109.8(5)	C(61)-Si(6)-C(62)	105.0(5)
N(5)-Si(6)-C(63)	110.1(5)	C(61)-Si(6)-C(63)	105.5(5)
C(62)-Si(6)-C(63)	111.8(5)	N(5)-Si(7)-C(71)	110.1(4)
N(5)-Si(7)-C(72)	111.9(4)	C(71)-Si(7)-C(72)	104.7(5)
N(5)-Si(7)-C(73)	111.2(4)	C(71)-Si(7)-C(73)	105.9(5)
C(72)-Si(7)-C(73)	112.7(5)		

oil, containing a high amount (> 90%) of **4**. Despite the impossibility of purifying it, **4** can be used to convert it to **5** and further silylation yields **6** as described. By preparing HN(PPh<sub>2</sub>)<sub>2</sub> after the method of Wang *et al.* a 70% yield of **6** in a straight forward synthesis is possible.<sup>8</sup>

## EXPERIMENTAL

All experiments were carried out in solvents using a dry nitrogen atmosphere. The solvents were dried by standard methods prior to use. IR spectra were recorded as nujol mulls on a Bio-Rad FTS-7 spectrometer in the range of 4000–400 cm<sup>-1</sup> using KBr cells. For NMR spectra a Bruker WP 80 SY and an AM-250 spectrometer were used. Mass spectra were obtained from a Finnigan Mat 8230. Elemental analysis was carried out by the Mikroanalytisches Laboratorium Beller (Göttingen) and the Analytisches Labor des Instituts für Anorganische Chemie.

*Bis[imino(P-diphenyl)phosphoranyl]amine (2)*: A mixture of 9.0 g (20.0 mmol) **1** and 0.8 g (20.0 mmol) KH is suspended in 80 ml of toluene and refluxed for 3–4 h (end of H<sub>2</sub> evolution). Having small solubility of **2** in cold toluene makes it advisable to remove the KCl by filtration after the reaction with Me<sub>2</sub>NSiMe<sub>3</sub>.

*N'* [*N''*-trimethylsilyl]imino-(*P*-diphenyl)phosphoranyl]imino-(*P*-diphenyl)phosphoranylamine (**3**): 2.3 g (20 mmol)  $\text{Me}_2\text{NSiMe}_3$  are added via syringe to a warm (ca. 70°C) suspension of **2** prepared in the manner described above. The mixture is then heated to reflux for 3–4 h (end of  $\text{Me}_2\text{NH}$  evolution). After cooling to r.t. the clear, slightly yellowish solution is separated from KCl using a glass filter frit. After removal of the solvent in vacuo **3** remains quantitatively as a colourless powder. mp. 115°C. — IR: 3310 w, 1438 s, 1257 s, 1240 s, 1202 vs, 1170 s, 1113 s, 982 s, 825 s, 742 s, 715 s, 696 s, 550 s. — MS(EI):  $m/z$  (%) = 487 (26)  $[\text{M}^+]$ , 472 (100)  $[\text{M}^+ - \text{Me}]$ . — Anal. Calcd. for  $\text{C}_{27}\text{H}_{31}\text{N}_3\text{P}_2\text{Si}$  (487.6): C, 66.5; H, 6.4; N, 8.6. Found: C, 66.2; H, 6.5; N, 8.8.

TABLE IV  
Crystal structure solution and refinement data

Crystal system :	Monoclinic
Space group :	$\text{P } 2_1/c$
Cell constants (pm, °)	
$a =$	1824.2(4)
$b =$	970.3(2)
$c =$	2179.0(5)
$\beta =$	108.89
Volume (nm <sup>3</sup> ) :	3.6494(14)
Formula/cell Z :	4
Calculated density $\rho$ (Mg m <sup>-3</sup> ) :	1.15
Absorption coefficient $\mu_{\text{Mo-K}\alpha}$ (mm <sup>-1</sup> ) :	0.237
STOE four circle diffractometer $\text{Mo-K}\alpha$ , T = 20°C, $2\theta, \omega$ scans	
Crystal size (mm <sup>3</sup> ) :	0.3 * 0.5 * 0.8
Reflections up to $2\theta_{\text{max}}$ (°) :	45
Measured :	4102
Unique :	3385
$R_{\text{int}}$ :	0.047
With $ F_o  > p \sigma( F_o )$ ; $p$ :	3
observed reflections $m$ :	2402
Refined parameters $n$ :	370
Goodness of fit	
$[\sum w( F_o  -  F_c )^2 / (m - n)]^{1/2}$ :	1.74
$R = \sum  F_o  -  F_c  / \sum  F_o $ :	0.077
$wR = R_g = [\sum w( F_o  -  F_c )^2 / \sum w F_o ^2]^{1/2}$ :	0.085
Weighting scheme	
$w^{-1} = [\sigma^2( F_o ) + g F_o ^2]$ ; $g$ :	0.001
Residual electron density (10 <sup>6</sup> e pm <sup>-3</sup> )	
Max./min.	0.38/-0.56
Program:	SHELXTL

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein Leopoldshafen 2 (FRG), on quoting the deposit number CSD 50 60 98, the name of the authors, and the journal citation.

*Bis[(N-trimethylsilyl)imino-(P-diphenyl)phosphoranyl]amine (4)*: a) The preparation is in analogy to **3**. 40–45 mmol  $\text{Me}_2\text{NSiMe}_3$  are taken; b) If  $\text{NEt}_3$  is used as a base instead of  $\text{KH}$ , this amine is added simultaneously with  $\text{Me}_2\text{NSiMe}_3$  to a suspension of **1** in toluene. The total refluxing period is reduced to 3–4 h. The volatile components and  $\text{NEt}_3\cdot\text{HCl}$  are removed from the warm solution under reduced pressure. This method is especially suitable for small amounts (5 mmol). **4** is obtained as a sticky colourless solid in quantitative yields. mp.  $112^\circ\text{C}$ . —IR: 3010 m, 1435 vs, 1310 s, 1255 vs, 1235 vs, 1195 vs, 1170 vs, 1115 vs, 970 s, 845 vs, 825 vs, 540 vs. —MS(EI) :  $m/z$  (%) = 559 [ $\text{M}^+$ ] (30), 544 [ $\text{M}^+ - \text{Me}$ ] (100). —Anal. Calcd. for  $\text{C}_{30}\text{H}_{39}\text{N}_3\text{P}_2\text{Si}_2$  (559.8) : C, 64.4; H, 7.0; N, 7.5. Found: C, 65.0; H, 6.9; N, 7.5.

TABLE V  
Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement  
coefficients ( $\text{pm}^2 \times 10^{-1}$ ) for **6**

	x	y	z	U(eq)
N(1)	2668(3)	1136(7)	4803(3)	50(3)
P(2)	1952(1)	1223(3)	4187(1)	44(1)
N(3)	2052(3)	712(7)	3509(3)	44(3)
P(4)	2762(1)	105(2)	3348(1)	42(1)
N(5)	2442(3)	-666(7)	2630(3)	46(3)
C(11)	1563(4)	2944(9)	4037(4)	47(4)
C(12)	1220(5)	3560(10)	4450(5)	60(5)
C(13)	957(6)	4878(12)	4367(6)	72(5)
C(14)	1027(5)	5671(11)	3870(6)	67(5)
C(15)	1348(6)	5072(11)	3444(5)	67(5)
C(16)	1615(5)	3756(11)	3520(5)	59(5)
C(21)	1136(5)	255(9)	4261(4)	41(4)
C(22)	1244(6)	-730(10)	4750(5)	61(5)
C(23)	631(8)	-1500(10)	4803(5)	71(6)
C(24)	-111(7)	-1324(12)	4361(7)	72(6)
C(25)	-217(6)	-369(13)	3885(6)	77(5)
C(26)	388(5)	406(10)	3820(5)	61(5)
C(31)	3430(5)	1442(10)	3297(5)	55(4)
C(32)	3700(5)	1620(12)	2785(5)	68(5)
C(33)	4169(7)	2717(14)	2748(7)	87(6)
C(34)	4374(6)	3633(13)	3246(7)	89(6)
C(35)	4116(6)	3532(12)	3763(5)	73(5)
C(36)	3640(5)	2442(11)	3791(5)	62(5)
C(41)	3278(5)	-1139(9)	3950(4)	42(4)
C(42)	2862(5)	-2248(11)	4062(5)	62(4)
C(43)	3205(7)	-3216(11)	4526(6)	80(5)
C(44)	3954(7)	-3089(12)	4896(5)	80(6)
C(45)	4379(6)	-1972(13)	4802(5)	71(5)
C(46)	4050(5)	-986(10)	4333(5)	55(4)
Si(5)	3113(1)	1561(3)	5573(1)	52(1)
C(51)	2449(6)	1894(13)	6054(5)	86(5)
C(52)	3687(7)	3197(11)	5637(5)	95(6)
C(53)	3800(6)	183(12)	5992(5)	89(5)
Si(6)	2995(2)	-1915(3)	2355(1)	64(1)
C(61)	4005(5)	-2126(12)	2892(5)	85(5)
C(62)	3075(7)	-1367(13)	1560(5)	98(6)
C(63)	2546(6)	-3647(10)	2307(5)	80(5)
Si(7)	1442(1)	-408(3)	2173(1)	54(1)
C(71)	1238(6)	-1059(14)	1333(5)	96(6)
C(72)	1188(5)	1438(10)	2076(5)	71(5)
C(73)	805(5)	-1401(10)	2520(5)	66(4)

\*U(eq) defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

*Lithium-bis[(N-trimethylsilyl)imino-(P-diphenyl)phosphoranyl]amide (5)*: 8.5 ml of a 2.36 M nBuLi solution in n-hexane are added dropwise to an ice cooled solution of 11.2 g (20 mmol) **4** in 80 ml toluene. The solution is heated to reflux for 2–3 h (end of n-butane evolution). The volatile components are removed in vacuum. The residue is recrystallized from 150 ml n-hexane. 6.6 g (58%) **5** is isolated as long, colourless needles which contain n-hexane if not dried carefully. mp. 245°C. —IR: 1437 s, 1254 s, 1240 s, 1186 vs, 1146 vs, 1112 s, 1102 s, 854 vs, 830 vs, 747 s, 710 s, 697 s, 543 s, 530 vs, 511 s. —MS (EI) : m/z (%) = 565 [M<sup>+</sup>] (26), 559 [M<sup>+</sup>—Li] (52), 550 [M<sup>+</sup>—Me] (65), 544 [M<sup>+</sup>—Me—Li] (100). —<sup>7</sup>Li NMR (toluene/C<sub>6</sub>D<sub>6</sub>, 97.211 MHz) : δ = 1.88 (s). —Anal. Calcd. for C<sub>30</sub>H<sub>38</sub>LiN<sub>3</sub>P<sub>2</sub>Si<sub>2</sub> (565.7) : C, 63.7; H, 6.8; N, 7.4. Found: C, 63.5; H, 6.9; N, 7.5.

*N-Bis(trimethylsilyl)-N'[(N''-trimethylsilyl)imino-(P-diphenyl)-phosphoranyl]imino-(P-diphenyl)phosphoranylamin (6)*: 2 ml Me<sub>3</sub>SiCl (excess) are added to 8.0 g (14.1 mmol) **4** in 80 ml toluene and the solution is heated to approximately 70°C for 16 h.

The precipitate of LiCl is filtered and washed with a small amount of toluene. The volatile components are removed in vacuo and the residue is recrystallized from Et<sub>2</sub>O/n-hexane (1:2). The yield of the colourless crystals is 5.6 g (63%). mp. 120°C. —IR: 1438 vs, 1297 s, 1254 s, 1219 s, 1113 s, 986 vs, 857 vs, 825 s, 746 s, 722 vs, 693 s, 536 s. —MS (FI) : m/z (%) = 559 [M<sup>+</sup>—SiMe<sub>3</sub>] (100). —Anal. Calcd. for C<sub>33</sub>H<sub>47</sub>N<sub>3</sub>P<sub>2</sub>Si<sub>3</sub> (631.9) : C, 62.7; H, 7.5; N, 6.7. Found C, 63.0; H, 7.5; N 6.7.

When **6** is prepared in a “one pot”-synthesis using **4** as an intermediate a slightly yellow material is formed. This could be obtained colourless by washing with n-hexane. A yield of 70% over all steps is achieved. This reaction can be carried out on a scale of at least 135 mmol Ph<sub>2</sub>PCL.

The data for crystal structure solution and refinement are listed in Table IV and V.

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