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Functionalization of Aminophosphanes: Synthesis and X-Ray Crystal Structure of Novel Dilithium and Trilithium Complexes Containing Silicon-Fused Heteronuclear SiN_2PLi Five-Membered Rings[†]

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A first structurally characterized primary aminophosphane (Ar_2PNH_2 (**2**); Ar = 2,4,6-*i*$Pr_3C_6H_2$) that is a stable solid at room temperature without decomposition by self-condensation is reported. Reactions of N-phosphanyllithium amide (*t*Bu_2PNHLi (**3**)) with Me_2SiCl_2 and $MeSiCl_3$ in Et_2O result in the formation of $Me_2Si(NHP\mathit{t}Bu_2)_2$ (**4**) and $MeSi(NHP\mathit{t}Bu_2)_3$ (**5**), respectively. Subsequent treatment of **4** and **5** with 2 and 3 equiv of *n*BuLi gave the dilithium (**6**) and trilithium (**7**) complexes, respectively. Further treatment of **5** with 3 equiv of $AlMe_3$ yielded the trialuminum complex $MeSi[N(AlMe_2)P\mathit{t}Bu_2]_3$ (**8**). These three complexes were investigated by microanalysis and multinuclear NMR spectroscopy. The dilithium complex $[Me_2Si(NLiP\mathit{t}Bu_2)_2 \cdot 3THF]$ (**6**) and the trilithium complex $[MeSi(NLiP\mathit{t}Bu_2)_3 \cdot 3Et_2O]$ (**7**) were further characterized by single-crystal X-ray structural analysis.

Introduction

Compounds with single or multiple P−N bonds are important in organometallic chemistry due to their versatility in terms of their bonding properties[1] and their utility in catalytic processes.[2] The polyphosphazenes are sometimes advantageous products compared with the omnipresent silicones, due to their biocompatible and biodegradable properties.[3] Primary phosphane amines are precursors in syntheses of N,P-organometalated phosphane imines[4,5] but are less stable because of self-condensation with the evolution of ammonia gas, which is a thermodynamically favorable pathway.

The problem of decomposition can easily be overcome by attaching bulky substituents to the phosphorus atom. Some phosphane amines are exhibiting tautomeric equilibria in solution due to hydrogen atom transfer from the N to the P atom.[6] Depending on the nature of the substituent and on the temperature, the equilibrium can be partially or totally shifted either to the aminophosphane or to the iminophosphorane species.[7]

Results and Discussion

In general, primary aminophosphanes of composition R_2PNH_2 (R = alkyl or aryl group) are easily prepared in good yields by the ammonolyses of chlorophosphanes in diethyl ether as a solvent at −50 °C. The formation of solid ammonium chloride indicates the progress of the reaction. Herein, we discuss two primary aminophosphanes R_2PNH_2 with R = *t*Bu (**1**) and 2,4,6-*i*$Pr_3C_6H_2$ (**2**). They are prepared analogously to previously reported literature procedures.[8] The NH_2 group of primary aminophosphanes is suitable for further functionalization. Complex **2** is a solid at room temperature and forms crystals from a concentrated diethyl

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[†] Dedicated to Professor Heinrich Nöth on the occasion of his 80th birthday.

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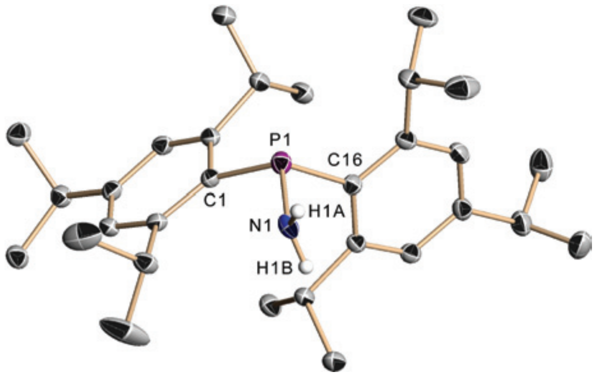
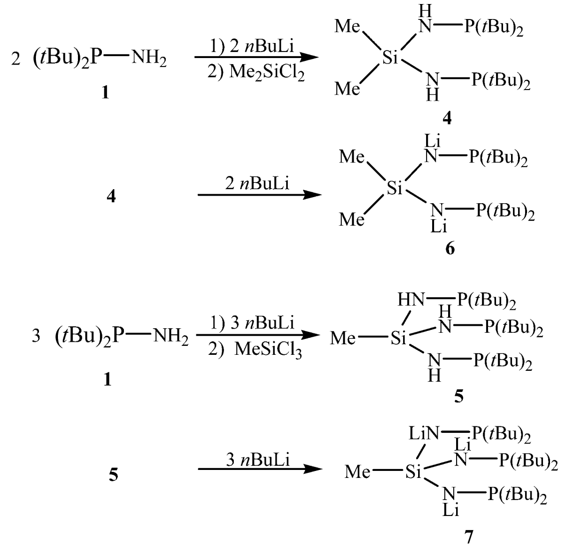


Figure 1. Molecular structure of **2**. Selected bond lengths [Å] and angles [deg]; anisotropic displacement parameters are depicted at the 50% probability level, and all restrained refined hydrogen atoms are omitted for clarity: P1−N1, 1.7998(15); P1−C1, 1.8684(16); P1−C16, 1.8590(17); N1−P1−C1, 111.52(7); N1−P1−C16, 99.67(7); C1−P1−C16, 101.79(7).

ether solution at 0 °C. Colorless compound **2** was characterized by mass spectrometry, elemental analysis, multinuclear NMR spectroscopy, and single crystal X-ray structural analysis. The molecular structure of **2** is shown in Figure 1. The P−N bond distance of 1.7998 Å is comparable with those of P−N single bonds.[9] The phosphorus atom shows a distorted tetrahedral geometry with a bond angle sum at the phosphorus atom of 312.98°, indicating a stereochemical, active lone pair. The structure of Ph_2PNH_2 is not known, although the phosphorus(V) derivatives $Ph_2P(O)NH_2$ and $Ph_2P(S)NH_2$ are structurally characterized. The P−N bond lengths are shorter (1.630 and 1.660 Å, respectively) compared to that of **2** due to the smaller radius of the phosphorus(V) atom in the latter compounds.[10]

The dilithium derivatives of bis(amino)silanes are used as building blocks for inorganic ring compounds.[11] The reaction of the N-phosphanyllithium amide $t\text{Bu}_2\text{PNHLi}$ (**3**) with Me_2SiCl_2 in diethyl ether results in the formation of the Si-bridged difunctional phosphane amine $Me_2Si(NHP\textit{t}Bu_2)_2$ (**4**) (Scheme 1). After removing the LiCl by filtration, the remaining solution was treated with 2 equiv of *n*BuLi, and crystallization from tetrahydrofuran (THF) gave the complex $[Me_2Si(NLiP\textit{t}Bu_2)_2 \cdot 3THF]$ (**6**). The lithiation reaction is essentially quantitative. Colorless compound **6** was characterized by mass spectrometry, elemental analysis, multinuclear NMR spectroscopy, and single-crystal X-ray structural analysis. The molecular structure is depicted in Figure 2 and reveals interesting features. The central backbone contains a SiN_2PLi five-membered ring. A structural motif of this composition has not been reported to date, which was confirmed by a search in the Cambridge structural database.[12]

Scheme 1. Syntheses of Dilithium **6** and Trilithium **7** Complexes



The P−N and Si−N bond lengths are comparable to those found in the literature.[13]

In **6**, two different phosphorus as well as lithium sites are established. Although each lithium atom is 3-fold coordinated, one is coordinated to two THF molecules and a single nitrogen atom and the other one is coordinated to only one THF molecule and chelated by one nitrogen and one phosphorus atom. Interestingly, in a solution of **6**, it is not possible to distinguish between the two phosphorus centers at room temperature because of the rapid exchange, and therefore only one resonance is observed in the ^{31}P NMR spectrum ($\delta = 85.65$ ppm). At 278 K, the ^{7}Li NMR spectrum shows one single resonance at 1.45 ppm.

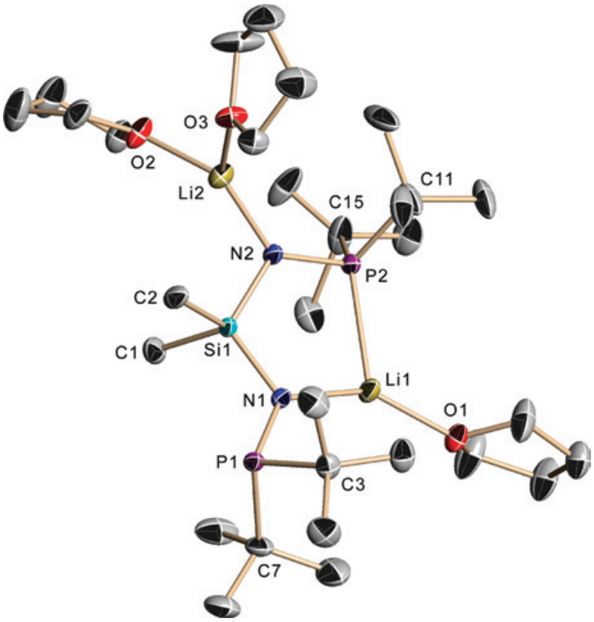


Figure 2. Molecular structure of **6**. Selected bond lengths [Å] and angles [deg]; anisotropic displacement parameters are depicted at the 50% probability level: Si1−N1, 1.7069(12); Si1−N2, 1.7184(12); Si1−C1, 1.8951(16); N1−P1, 1.6642(12); Li1−N1, 1.919(3); Li1−P2, 2.507(3); N2−P2, 1.6477(12); N2−Li2, 1.925(3); Li1−O1, 1.968(3); Li2−O2, 1.939(3); N1−Si1−N2, 113.54(6); Si1−N1−Li1, 111.74(10); Si1−N2−Li2, 104.37(10).

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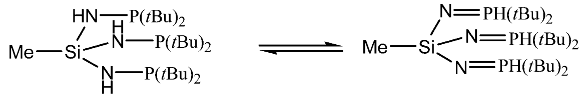
Scheme 2. Equilibrium between the Aminophosphane Form and the Iminophosphorane Form



5

The reaction of the N-phosphanyllithium amide ($t\mathrm{Bu_2PNHLi}$ (**3**)) with $\mathrm{MeSiCl_3}$ resulted in the Si-capped tripodal phosphane amine $\mathrm{MeSi(NHP}t\mathrm{Bu_2)_3}$ (**5**) (Scheme 1). Compound **5** is a colorless solid that melts at 81 °C without decomposition and is stable in a N_2 or Ar atmosphere. In a C_6D_6 solution of **5**, an equilibrium is observed between the tautomeric form $\mathrm{MeSi[N{=}P(H)}t\mathrm{Bu_2]_3}$ and the phosphane amine $\mathrm{MeSi(NHP}t\mathrm{Bu_2)_3}$ (**5**) (Scheme 2). Intermediates such as $\mathrm{MeSi[\{N{=}P(H)}t\mathrm{Bu_2\}_2(NHP}t\mathrm{Bu_2)]}$ were not observed. The IR spectrum of **5** shows a strong absorption at 3200 $\mathrm{cm^{-1}}$, while a P−H absorption was not observed in the IR spectrum. Obviously, in the solid state, the $\mathrm{MeSi(NHP}t\mathrm{Bu_2)_3}$ (**5**) isomer is the preferred form. In the NMR spectrum of **5**, the N−H proton exhibits a resonance at 1.88 ppm, and the P−H resonance of the tautomeric form is observed at 6.09 ppm in the ^{31}P decoupled spectrum, while in the ^{31}P−^{1}H coupled spectrum the P−H resonance is shown at 6.49 and 5.69 ppm. The P−H coupling constant of $J(^{31}\mathrm{P}-^{1}\mathrm{H}) = 403.0$ Hz is comparable with the previously reported values.[14]

The reaction of **5** with 3 equiv of *n*BuLi in $\mathrm{Et_2O}$ gave the trilithium salt $[\mathrm{MeSi(NLi\ P}t\mathrm{Bu_2)_3\cdot 3Et_2O}]$ (**7**) (Scheme 1). The trilithio compound **7** crystallizes from the reaction solution upon cooling. The lithiation reaction is essentially quantitative. Surprisingly, the reactivity of the NH function did not decrease with proceeding metalation. In order to gain more insight into the polymetalation reaction, we monitored the lithiation by ^{29}Si NMR spectroscopy. The appearance of a single resonance at −20.45 ppm was observed when 3 equiv of *n*BuLi were added to the solution of **5**. There was no indication of nonreacted *n*BuLi or nonreacted phosphane amine $\mathrm{MeSi(NHP}t\mathrm{Bu_2)_3}$ (**5**), and on the assumption that the resonances do not coincide due to mono-, di-, and trisubstituted products, we conclude that the lithiation is not random and the formation of **7** is favored.[15]

This result is consistent with a previous polymetalation reaction of compound $\mathrm{MeSi(NHSiMe_3)_3}$.[16] The colorless compound **7** has been characterized by mass spectrometry, elemental analysis, multinuclear NMR spectroscopy, and single-crystal X-ray structural analysis. The molecular structure of **7** is shown in Figures 3 and 4.

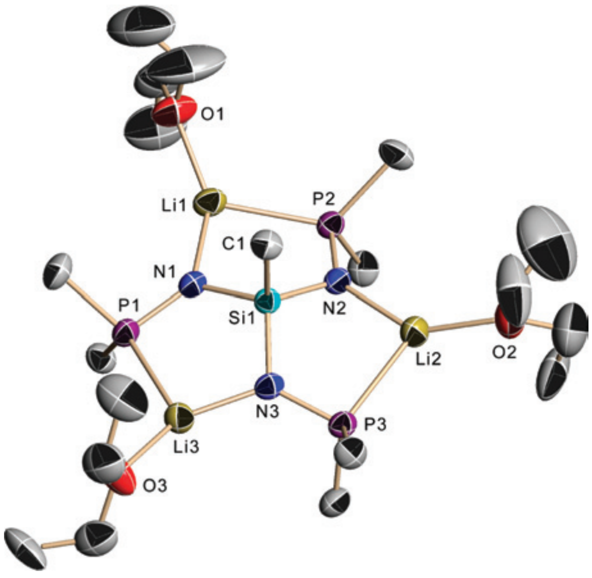


Figure 3. Molecular structure of **7**. For reasons of clarity, the Me groups of the *t*-Bu substituents are omitted, and only one occupation site of the disordered N, P, and C atoms is depicted in each case. Selected bond lengths [Å] and angles [deg]; anisotropic displacement parameters are depicted at the 50% probability level: Si1−N1, 1.755(3); N1−P1, 1.635(4); N1−Li1, 1.974(6); Li1−O1, 1.962(5); N1Si1−N2, 110.92(16); Si1−N1−P1, 121.4(2); N1−Li1−P2, 93.80(18).

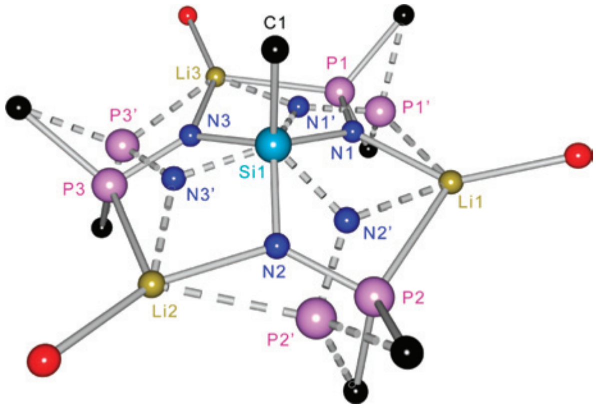


Figure 4. Molecular structure of **7** showing all disordered N and P atoms (site occupation factors: 0.57/0.43). The carbon atoms of the diethyl ether molecules are omitted for clarity; bonds to atoms of different occupation sites are drawn as dashed lines.

The lithium atoms are 3-fold coordinated by N, P, and O atoms in an almost trigonal-planar geometry. The central backbone consists of three fused five-membered $\mathrm{SiN_2PLi}$ rings that share the central silicon atom. The average Li−N and Li−P bond distances are 1.952 and 2.453 Å. For both distances, this is almost identical to the mean values in the Cambridge Crystallographic Data Center (CCDC; Li−N reaching from 1.45 to 2.80 Å with a mean of 2.07 Å and Li−P reaching from 1.72 to 3.18 Å with a mean of 2.57 Å).[12] The average P−N bond distance in **7** of 1.641 Å is in accord with an electrostatically shortened P−N single bond.[17] The lithium salt is quite different from the precursor $\mathrm{MeSi(NHP}t\mathrm{Bu_2)_3}$ (**5**) with respect to the multinuclear NMR results. The ^{29}Si NMR spectrum for $\mathrm{MeSi(NHP}t\mathrm{Bu_2)_3}$ exhibits two resonances (−17.97 and −33.20 ppm); each signal shows a quartet due to the coupling of three ^{31}P nuclei with the Si atom, with a coupling constant of $^{2}J(^{29}\mathrm{Si}-^{31}\mathrm{P})$

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Table 1. Crystallographic Data for the Structural Analyses of Compounds **2**, **6**, and **7**

	2	**6**	**7**
empirical formula	$C_{30}H_{48}NP$	$C_{30}H_{66}Li_2N_2O_3P_2Si$	$C_{37}H_{87}Li_3N_3O_3P_3Si$
CCDC No.	679028	679029	668449
T [K]	100(2)	100(2)	100(2)
cryst syst	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$
a [Å]	9.631(3)	11.7583(6)	11.1371(7)
b [Å]	10.779(3)	18.0055(9)	17.0011(10)
c [Å]	14.484(5)	19.3288(10)	25.8204(16)
α [deg]	106.199(3)	87.7880(10)	90
β [deg]	95.848(4)	72.9230(10)	90
γ [deg]	98.495(3)	73.4670(10)	90
V [Å^3]	1411.9(8)	3745.5(3)	4888.9(5)
Z	2	4	4
D_{calcd} [g cm^{-3}]	1.067	1.076	1.038
μ [mm^{-1}]	0.114	0.177	0.179
F(000)	500	1336	1688
θ range [deg]	1.48−26.07	1.66−27.92	1.43−26.02
reflns collected	28805	59281	46209
independent reflns	5572	16997	9632
data/restraints/parameters	5572/4/318	16997/6/818	9632/44/662
$R1$, $wR2$ [$I > 2\sigma(I)$]^a	0.0466, 0.1232	0.0426, 0.1127	0.0492, 0.1382
$R1$, $wR2$ (all data)^a	0.0515, 0.1281	0.0554, 0.1197	0.0621, 0.1573
GOF	1.025	1.058	1.088
$\Delta\rho$(max), $\Delta\rho$(min) [e Å^{-3}]	0.593, −0.476	0.716, −0.374	0.503, −0.607

[a] $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$.

= 28.81 Hz. In contrast, the ^{29}Si NMR spectrum of **7** only one quartet resonance (−20.45 ppm) with a coupling constant of $^2J(^{29}Si-^{31}P) = 30.79$ Hz.

To study the behavior of **5** in metal coordination, the compound was reacted with $AlMe_3$ in a 1:3 ratio to yield the trialuminum complex $MeSi[N(AlMe_2)PtBu_2]_3$ (**8**). In the course of the reaction, there is an evolution of methane gas. Compound **8** shows no IR absorption in the region of the N−H stretching frequency. Colorless **8** has been characterized by mass spectrometry, elemental analysis, and multinuclear NMR spectroscopy. In the ^{1}H NMR spectrum, the Al−C*H*$_3$ resonance is observed at −0.26 ppm. The ratio of the integration of the three different types of protons (Si−C*H*$_3$, Al−C*H*$_3$, and P−C(C*H*$_3$)$_3$) of compound **8** is 1:6:18, which directly indicates the formation of compound $MeSi[N(AlMe_2)PtBu_2]_3$ (**8**). The ^{29}Si NMR spectrum of **8** shows only one resonance (−17.64 ppm) with a coupling constant of $^2J(^{29}Si-^{31}P) = 17.79$ Hz. We were not yet able to grow single crystals of **8** suitable for X-ray structural analysis. Table 1 gives crystallographic data for the structural analyses of compounds **2**, **6**, and **7**.

Conclusion

Starting from the primary aminophosphane R_2PNH_2 (R = *t*Bu (**1**)), we synthesized the N,P-dipodal lithium complex [$Me_2Si(NLiPtBu_2)_2 \cdot 3THF$] (**6**) and the tripodal c_3-symmetrical [$MeSi(NLiPtBu_2)_3 \cdot 3Et_2O$] (**7**) compound. Both contain the SiN_2PLi five-membered heterocycle. Obviously, the phosphane amine $MeSi(NHPtBu_2)_3$ (**5**) is a versatile ligand for metal coordination. The tautomerism of $MeSi(NHPtBu_2)_3$ versus $MeSi[N{=}P(H)tBu_2]_3$ is studied by spectroscopical means and reveals that the NH tautomer is favored in the solid state, while the PH tautomer is also present in solution. However, there is no evidence for a mixed NH−PH species, such as $MeSi[\{N{=}P(H)tBu_2\}_2(NHPtBu_2)]$.

Experimental Section

All the manipulations were performed under a dry and oxygen-free atmosphere (N_2) using standard Schlenk techniques or inside an MBraun MB 150-GI glovebox. All solvents were distilled from Na/benzophenone prior to use. The starting materials Ar_2PCl[18] and tBu_2PNH_2[4] were prepared using literature procedures. Other chemicals were purchased commercially and used as received. ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra were recorded on a Bruker Avance DRX 500 MHz instrument and referenced to the deuterated solvent in the cases of the ^{1}H and ^{13}C NMR spectra. ^{29}Si NMR spectra were referenced to $SiMe_4$ and those of ^{31}P NMR to 85% H_3PO_4. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Infrared spectral data were recorded on a Perkin-Elmer PE-1430 instrument. Electron impact mass spectrometry (EI-MS) was measured on a Finnigan Mat 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes with a Büchi melting point B 540 instrument and are not corrected.

Synthesis of ($2,4,6$-*i*$Pr_3C_6H_2)_2PNH_2$ (2). A solution of Ar_2PCl (2.40 g, 5.07 mmol) in diethyl ether (40 mL) was cooled to −50 °C, and dry ammonia gas was added in excess to this solution. Subsequently, the mixture was slowly warmed to room temperature. The precipitated ammonium chloride was filtered off, and the volatiles from the filtrate were removed *in vacuo* to give **2**. Yield: 2.70 g (85%); mp, 106 °C (decomp). ^{1}H NMR (500 MHz, C_6D_6): δ 7.16−7.27 (m, 4 H, Ar *H*), 4.20 (sep, 4 H, ortho C*H*(CH$_3$)$_2$), 2.95 (sep, 2 H, para C*H*(CH$_3$)$_2$), 1.92 (d, J = 18.25 Hz, 2 H, N−*H*), 1.35 (d, J = 8.0 Hz, 12H, para CH(C*H*$_3$)$_2$), 1.27 (d, J = 8.0 Hz, 24H, ortho CH(C*H*$_3$)$_2$). ^{29}Si NMR (99.35 MHz, C_6D_6): δ −17.97 and −33.20 (q, J = 28.81 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, C_6D_6): δ 22.75. IR (Nujol mull, cm^{-1}): 3439 cm^{-1}. EI-MS: *m/z* (%) 410 (100) [M^+-*i*Pr)]. Anal. calcd for $C_{30}H_{48}NP$ (453.35): C, 79.42; H, 10.66; N, 3.09. Found C, 78.73; H, 10.34; N, 2.46.

Synthesis of $MeSi(NHPtBu_2)_3$ (5). *n*BuLi (11.7 mL, 1.6 M in hexane, 18.6 mmol) was added at a constant rate to a solution of tBu_2PNH_2 (3.00 g, 18.6 mmol) in diethyl ether (120 mL) at −78

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°C. The reaction mixture was stirred at this temperature for 1 h and then brought to ambient temperature and stirred overnight. It was then treated with a solution of $MeSiCl_3$ (0.728 mL, 6.2 mmol) in diethyl ether (80 mL) at −78 °C and allowed to rise to room temperature and stirred overnight. The precipitated LiCl was filtered off, and the volatiles from the filtrate were removed *in vacuo* to give **5**. Yield: 2.70 g (85%); mp 81 °C (decomp). ^1H NMR (500 MHz, C_6D_6): δ 0.65 (s, 3 H, $SiCH_3$), 1.14 (d, J = 10.2 Hz, 54 H, $C(CH_3)_3$), 1.87 (d, J = 5.02 Hz, N−H), 6.09 (d, J = 403.0 Hz, P−H). ^{13}C NMR (125.76 MHz, C_6D_6): δ 33.68, 28.42, 20.40. ^{29}Si NMR (99.35 MHz, C_6D_6): δ −17.97 and −33.20 (q, J = 28.81 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, C_6D_6): δ 64.17 and 31.85. IR (Nujol mull, cm^{-1}): 3200 cm^{-1}. EI-MS: m/z (%) 466 (100) [M^+-tBu)]. Anal. calcd for $C_{25}H_{60}N_3P_3Si$ (523.38): C, 57.33; H, 11.55; N, 8.02. Found C, 55.41; H, 11.18; N, 7.39.

Synthesis of [$Me_2Si(NLi\ PtBu_2)_2 \cdot 3THF$] (6). nBuLi (11.7 mL, 1.6 M in hexane, 18.6 mmol) was added at a constant rate to a solution of tBu_2PNH_2 (3.00 g, 18.6 mmol) in diethyl ether (120 mL) at −78 °C. The reaction mixture was stirred at this temperature for 1 h and then warmed to ambient temperature and stirred overnight. It was then treated with a solution of Me_2SiCl_2 (1.1 mL, 9.3 mmol) in diethyl ether (80 mL) at −78 °C and allowed to rise to room temperature and stirred overnight. The precipitated LiCl was filtered off, and the filtrate was reacted further with nBuLi (11.7 mL, 1.6 M in hexane, 18.6 mmol) at −78 °C. The reaction mixture was stirred at this temperature for 1 h and then warmed to ambient temperature and stirred overnight. All the volatiles were removed *in vacuo*. Recrystallization from THF solution at −30 °C gave crystals which were suitable for X-ray diffraction. Yield: 3.86 g (72%); mp 112 °C (decomp). ^1H NMR (200 MHz, C_6D_6): δ 0.59 (s, 6 H, $SiCH_3$), 1.12 (m, 12 H, THF), 1.33 (d, J = 10.0 Hz, 36 H, $C(CH_3)_3$), 3.51 (m, 12 H, THF). ^{13}C NMR (125.76 MHz, C_6D_6): δ 68.38, 34.11, 29.91, 28.58, 25.44. ^{29}Si NMR (99.35 MHz, C_6D_6): δ −20.45 (t, J = 30.79 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, C_6D_6): δ 85.65. EI-MS: m/z (%) 359 (100) [M^+-tBu, 3THF, Li)]. Anal. calcd for $C_{30}H_{66}N_2O_3P_2Si$ (606.46): C, 59.38; H, 10.96; N, 4.62. Found C, 57.89; H, 11.23; N, 4.69.

Synthesis of $MeSi(NLiPtBu_2)_3 \cdot 3Et_2O$ (7). nBuLi (17.34 mL, 1.6 M in hexane, 27.75 mmol) was added at a constant rate to a solution of $MeSi(NHPtBu_2)_3$ (4.845 g, 9.25 mmol) in diethyl ether (100 mL) at −78 °C. The reaction mixture was stirred at this temperature for 1 h and then warmed to ambient temperature and stirred overnight. All the volatiles were removed *in vacuo* to yield **7**. Recrystallization from a diethyl ether solution gave crystals which were suitable for X-ray diffraction. Yield: 5.08 g (72%); mp, 112 °C (decomp). ^1H NMR (500 MHz, C_6D_6): δ 0.53 (s, 3 H, $SiCH_3$), 1.13 (d, J 11.2 Hz, 54 H, $C(CH_3)_3$). ^{13}C NMR (125.76 MHz, C_6D_6): δ 68.30, 65.80, 30.32, 25.25, 15.00. ^{29}Si NMR (99.35 MHz, C_6D_6): δ −20.45 (q, J = 30.79 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, C_6D_6): δ 81.25. EI-MS: m/z (%) 466.3 (100) [M^+-tBuLi$_3$)]. Anal. calcd for $C_{37}H_{87}Li_3N_3O_3P_3Si$ (763.62): C, 58.17; H, 11.48; 9.63, N, 5.50. Found C, 53.48; H, 9.63; N, 5.54.

Synthesis of $MeSi[N(AlMe_2)PtBu_2]_3$ (8). $AlMe_3$ (4.8 mL, 2.0 M in hexane, 9.60 mmol) was added at a constant rate to a solution of **5** (1.650 g, 3.15 mmol) in toluene (40 mL) at −78 °C. The reaction mixture was stirred at this temperature for 1 h and then raised to ambient temperature and stirred overnight. All the volatiles were removed *in vacuo* to give **8**. Yield: 1.43 g (66%); mp, 127 °C (decomp). ^1H NMR (500 MHz, C_6D_6): δ −0.26 (s, 18 H, $Al(CH_3)_2$), 0.82 (s, 3 H, $SiCH_3$), 1.15 (d, J = 12.2 Hz, 54 H, $C(CH_3)_3$). ^{13}C NMR (125.76 MHz, C_6D_6): δ 34.76, 28.42, 4.21, −4.89. ^{29}Si NMR (99.35 MHz, C_6D_6): δ −17.64 (q, J = 17.79 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, C_6D_6): δ 58.32. EI-MS: m/z (%) 466.3 (100) [M^+-tBuAl$_3$Me$_6$)]. Anal. calcd for $C_{31}H_{75}Al_3N_3P_3Si$ (691.4): C, 53.81; H, 10.93; N, 6.07. Found: C, 53.67; H, 10.66; N, 6.22.

Crystallographic Details for Compounds 2, 6, and 7. All data were collected from shock-cooled crystals on a Bruker SMART-APEX II diffractometer with a D8 goniometer at 100 K[19] (graphite monochromated Mo Kα radiation, λ = 0.71073 Å). The data were integrated with SAINT,[20] and an empirical absorption correction (SADABS) was applied.[21] The structures were solved by direct methods (SHELXS)[22] and refined on F^2 using the full-matrix least-squares methods of SHELXL.[23] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms bonded to sp^2 (sp^3) carbon atoms were assigned ideal positions and refined using a riding model with U_{iso} constrained to 1.2 (1.5) times the U_{eq} value of the parent carbon atom. The absolute structure of **7** was determined unambiguously by refining the *Flack x* parameter[24] to 0.01(10).

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Supporting Information Available: X-ray data for **2**, **6**, and **7** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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