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# Synthesis and Structural Characterization of Aluminum Iminophosphonamide Complexes

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Monoanionic iminophosphonamide ligands have a N−P−N linkage and undergo four-membered ring N,N-ligand formation when treated with aluminum compounds. The reaction of LLi (L = $[Ph_2P(NSiMe_3)_2]$) with equivalent amounts of $AlCl_3$ and $AlMeCl_2$ in toluene afforded $LAlCl_2$ (**3**) and LAlClMe (**4**), respectively. $L_2AlH$ (**5**), $LAlEt_2$ (**6**), and $LAl(NMe_2)_2$ (**7**) respectively were prepared by the reaction of LH with $AlH_3 \cdot NMe_3$, $AlEt_3$, and $Al(NMe_2)_3$ in *n*-hexane. Subsequently compounds **3**−**7** were characterized by elemental analysis, $^1H$, $^{13}C$, and $^{31}P$ NMR spectroscopy and X-ray crystallographic studies (for **3**, **4**, **5**, and **7**).

## Introduction

The importance of organoaluminum compounds is due to their use in a variety of applications, including organic syntheses and industrial catalytic processes. They have also been utilized as precursors in chemical vapor deposition (CVD) processes.[1] It has been observed that stable aluminum compounds involving nitrogen substituents or neutral nitrogen donors are useful in the preparation of aluminum nitride or AlN-containing materials. As a result, there is considerable interest in the structures, properties, and transformations of molecules containing Al−N bonds.[2] Particularly, there has been immense research interest in synthesizing aluminum chlorides and methyl derivatives which can act as precursors in the controlled hydrolysis with water or reactive oxygen containing species which leads to the preparation of alumoxanes.[3]

There are very few reports on structurally characterized four-membered aluminum rings bearing halide, methyl, and hydride substituents probably because of the steric and electronic properties. The interest in these ligands is currently growing as a result of their specific steric and electronic features, and these properties can efficiently control the geometry at the metal center. Herein we report the synthesis and structural characterization of aluminum complexes with chloride, hydride, methyl, amide, and diethyl substituents based on an iminophosphonamide ligand.

## Results and Discussion

**Synthesis of $LAlCl_2$ (3), LAlMeCl (4).** Compound $Ph_2P(NSiMe_3)_2H$ (**1**) was prepared by a previously reported method.[4,5] Treatment of iminophosphonamide with MeLi or *n*BuLi yielded the lithium salt of iminophosphonamide LLi (**2**) (L = $Ph_2P(NSiMe_3)_2$) in high yield.[6] Further reactions were carried out either by isolating **2** or by in situ reaction of **2** with the corresponding aluminum compounds. Synthesis of $LAlCl_2$ (**3**) (Scheme 1) was accomplished by reacting the lithiated precursor **2** with $AlCl_3$ under the elimination of LiCl in moderate yield. The solution of $AlCl_3$ in toluene was added drop by drop to the solution of **2** in a 1:1 stoichiometric ratio in toluene and stirred at 25 °C for 14 h to yield the colorless complex **3**. In a similar route, complex **4** was prepared by slow

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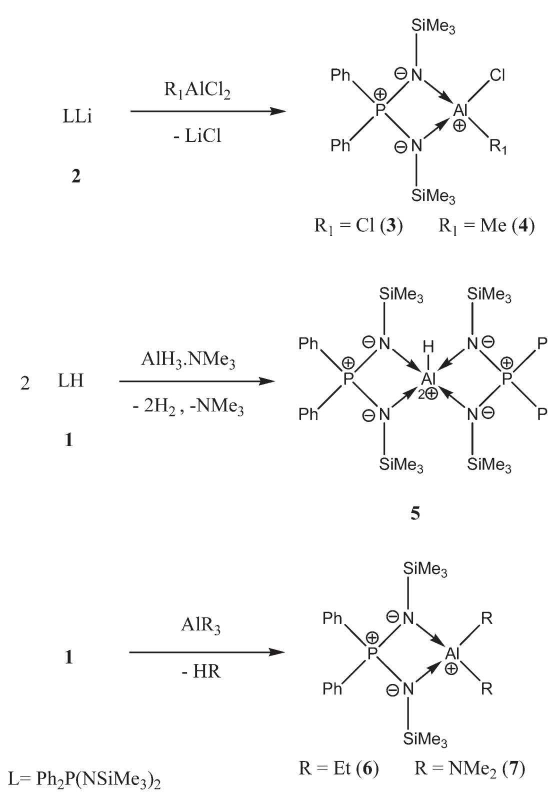
**Scheme 1.** Preparation of Aluminum Iminophosphonamide Complexes



addition of $AlMeCl_2$ (1.0 M in *n*-hexane) to the toluene solution of **2** and stirring at room temperature for 14 h. Compounds **3** and **4** are soluble in common organic solvents such as toluene, tetrahydrofuran (THF), and *n*-hexane, and they are stable in the solid state at room temperature for several months under an inert atmosphere. **3** is easily oxidized and hydrolyzed on exposure to air as indicated by a color change from colorless to a light yellow oily solid, and we were not able to measure the elemental analysis of **3** because of its sensitivity. The $^{31}P$ NMR spectra of **3** and **4** exhibit downfield shifts when compared with those of complex **2** (37.8 ppm for **3**, 33.2 ppm for **4**, 7.4 ppm for **2**). The $^{1}H$ NMR of **4** exhibits a single resonance (0.04 ppm) which can be assigned to Al-Me. The 18 protons of $SiMe_3$ resonate as a singlet at −0.03 ppm, and the aromatic protons of Ph are shown at 7.46−7.79 ppm.

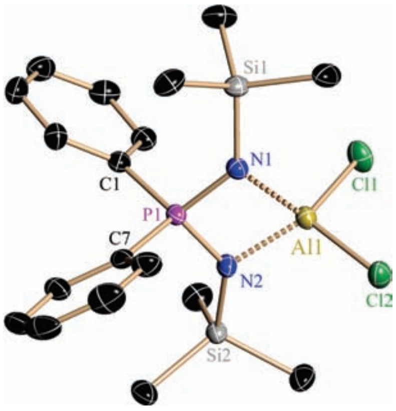


**Figure 1.** Molecular structure of **3**. Table 1 contains selected bond lengths [Å] and angles [deg]. Anisotropic displacement parameters are drawn at the 50% probability level. Only one of the two crystallographically independent molecules is shown. H atoms are omitted for clarity.

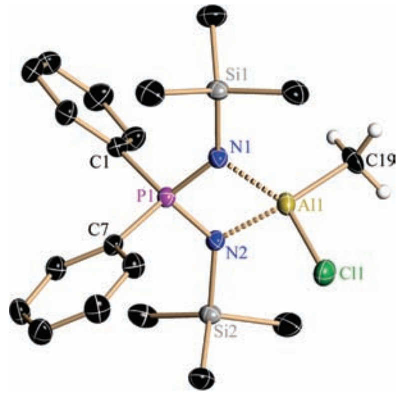


**Figure 2.** Molecular structure of **4**. Table 1 contains selected bond lengths [Å] and angles [deg]. Anisotropic displacement parameters are drawn at the 50% probability level. H atoms (except for those of C19) and half toluene solvent molecule are omitted for clarity.

**Crystal Structures of $LAlCl_2$ (3), LAlMeCl (4).** Complexes **3** and **4** were characterized further by X-ray crystallography, and the molecular structures are presented in Figures 1 and 2. Table 1 contains important bond parameters of compounds **3** and **4**, and crystallographic data for the structural analyses are listed in Table 2. Compound $[Ph_2P(NSiMe_3)_2AlCl_2]$ (**3**) crystallizes in the triclinic space group $P\bar{1}$ with two molecule in the asymmetric unit whereas $[Ph_2P(NSiMe_3)_2AlMeCl]$ (**4**) is monomeric in the solid state and crystallizes in the monoclinic space group $P2_1/c$. Colorless crystals of **3** and **4** suitable for X-ray structure analysis were grown from toluene and *n*-hexane at −78 °C, respectively. In both structures the aluminum atoms show a distorted tetrahedral environment, and the metrical parameters associated with the $PN_2$ ligand are quite similar.[7] All N atoms bearing $SiMe_3$ groups show a planar arrangement; the Si−N bonds are slightly shorter than the sum of the covalent radii of 1.87 Å,[8] and the P−N distances in the range of 1.614(12)−1.629(16) Å have been previously rationalized to range between single and double P−N bonds.[9] However, recent experimental charge density studies proved the shortening mainly to be caused by electrostatic contributions.[10] In addition to the P−N $\sigma$-bonds, there is Coulomb attraction between the positively charged phosphorus atoms and the negatively charged nitrogen atoms and, in return, repulsion between the competing N-atoms across the central P-atom. This "seesaw" effect is most prominent in the structures from the tetra(amino) phosphonium cation, $[P(NHPh)_4]^+$, to the tetra(imino) phosphate trianion, $[P(NPh)_4]^{3-}$: Despite the diversity of the P−N bond lengths, the average P−N bond length within the $PN_4$ tetrahedra is very

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similar ($\sum(d_{\mathrm{P-N}})\}/4 = 1.62(1)$ Å).[11] On this basis we state that there is no P=N double bonding and hence no hypervalent phosphorus present in the iminophosphonamide ligands presented in this paper.[12]

The Al−Cl bond lengths in compound **3** are shorter than those of compound **4**, while the ligand bite (N1−Al1−N2) in **3** (av 81.09°) is slightly bigger than that in **4** (80.04(5)°). The Al−Cl distances in **3** (av 2.129 Å) are quite similar to those observed in the mono 1-aza-allyl complex $[N(SiMe_3)C(Ph)C(SiMe_3)_2]AlCl_2$ (av 2.071 Å), but the core angle is significantly different because of non equivalent chelating backbone.[13]

**Synthesis of $L_2AlH$ (5), $LAlEt_2$ (6), and $LAl(NMe_2)_2$ (7).** Reaction of iminophosphonamide **1** with $AlH_3 \cdot NMe_3$ in 2:1 stoichiometric ratio in *n*-hexane/THF at −78 °C afforded the iminophosphonamide aluminum complex $[Ph_2P(NSiMe_3)_2]_2AlH$ (**5**) in moderate yield. The $^1H$ NMR spectrum of **5** exhibits a broad singlet at 5.1 ppm assigned to the AlH and two singlets at −0.22 and −0.13 ppm, which can be assigned to the 36 protons of the $SiMe_3$ units. The presence of two non equivalent $SiMe_3$ groups indicates a restricted fluctionality of these groups at room temperature. In the IR spectrum one weak absorption for the AlH stretching frequency is observed at 1853 $cm^{-1}$. Compound **6** was prepared as a white crystalline solid from the reaction of iminophosphonamide **1** with $AlEt_3$ in *n*-hexane at −78 °C. Reaction of **1** with $Al(NMe_2)_3$ in *n*-hexane at reflux temperature for 6 h afforded the aluminum amide complex **7**. Both compounds are soluble in common organic solvents such as *n*-hexane, toluene, and THF. **5** and **7** are stable in the solid state under an inert atmosphere and are slowly oxidized and hydrolyzed on exposure to air whereas **6** is not stable and very sensitive to air. Therefore we were not able to determine the elemental analysis. $^{31}P$ NMR spectra of **6** and **7** exhibit single resonances at 30.3 and 28.6 ppm, respectively. In both compounds the $^1H$ NMR and $^{29}Si$ NMR spectra exhibit only one singlet for the $SiMe_3$ groups. In compound **7** the 12 protons correspond to two $NMe_2$ and resonate at 3.06 ppm while the aromatic protons appear between 7.03 and 7.83 ppm.

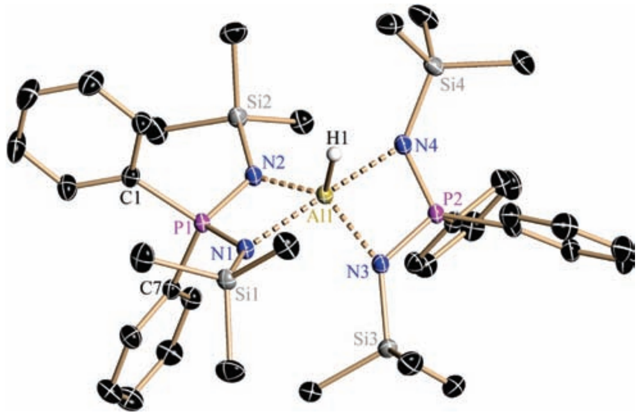

**Figure 3.** Molecular structure of **5**. Table 1 contains selected bond lengths [Å] and angles [deg]. Anisotropic displacement parameters are drawn at the 50% probability level. H atoms (except for those of Al1) and one THF solvent molecule are omitted for clarity.

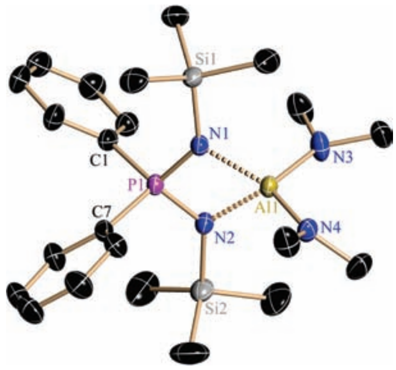

**Figure 4.** Molecular structure of **7**. Table 1 contains selected bond lengths [Å] and angles [deg]. Anisotropic displacement parameters are drawn at the 50% probability level. H atoms are omitted for clarity.

**Crystal Structures of $L_2AlH$ (5) and $LAl(NMe_2)_2$ (7).** Complexes **5** and **7** were characterized further by X-ray crystallography, and the molecular structures are presented in Figures 3 and 4. Table 1 contains important bond parameters of compounds **5** and **7**, and crystallographic data for the structural analyses are listed in Table 2. The X-ray structure reveals that in **5** the aluminum is five coordinate and in a distorted trigonal bipyramidal geometry with N1 and N4 in axial positions and N2, N3, and H in the equatorial plane. The N1−Al1−N4 axis is almost linear [N1−Al1−N4 175.80(5)°] in which the Al−N bond lengths of 2.08(13) Å for Al−N1 and 2.100(13) Å for Al1−N4 are almost the same. The equatorial Al1−N1 and Al1−N3 having almost the same bond lengths. [Al1−N2 1.94(13) Å, Al1−N3 1.93(13) Å]. The deviation from the ideal trigonal-bipyramidal geometry can be described by an angle of 73.94(26)° between the least-squares plane of N1, Al, N4, H and the equatorial plane. Clearly, the deviation from ideal trigonal-bypyramidal geometry arises from the steric requirements of the two chelating ligands. The axial Al−N bond lengths are in good agreement with those which are observed in similar five coordinate aluminum complexes[14] where Al−N bond lengths are found in the range from 2.051(18) Å to 2.179(7) Å. Colorless compound **7** crystallizes in the monoclinic space group $P2_1/n$, with one monomer in the asymmetric unit from *n*-hexane at −78 °C. The coordination polyhedron around the aluminum atom features a distorted tetrahedral environment and the metrical parameters associated with the $PN_2$ ligand are quite similar to those of **2** and **3**. The Al−N3 and Al−N4 bond distances are comparable to those reported in structurally characterized Al-bound terminal $NMe_2$ groups.[15] The Al−N1 and Al−N2 bond lengths (1.937(12)−1.950(12) Å) are longer than the Al−N3 and

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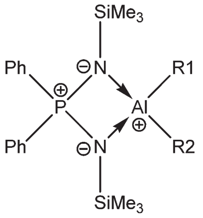
**Table 1.** Selected Bond Lengths [Å] and Angles [deg] of **3**[a], **4**, **5**, and **7**



| | **3**[a](R1 = R2 = Cl) | **3**[b](R1 = R2 = Cl) | **4** (R1 = Cl, R2 = Me) | **5** (R1 = N3, R2 = N4) | **7** (R1 = N3, R2 = N4) |
|---|---|---|---|---|---|
| Al1−N1 | 1.880(17) | 1.890(18) | 1.899(13) | 2.080(13) | 1.937(12) |
| Al1−N2 | 1.885(17) | 1.874(18) | 1.909(13) | 1.947(13) | 1.950(12) |
| Si1−N1 | 1.739(16) | 1.744(18) | 1.736(12) | 1.7252(13)[c] | 1.727(12) |
| Si2−N2 | 1.747(17) | 1.742(18) | 1.733(12) | 1.7381(13)[c] | 1.728(12) |
| P1−N1 | 1.629(16) | 1.625(17) | 1.614(12) | 1.5923(13)[c] | 1.614(11) |
| P1−N2 | 1.623(16) | 1.628(17) | 1.617(12) | 1.6162(12)[c] | 1.606(12) |
| Al1−R1 | 2.132(8) | 2.122(8) | 2.155(6) | 1.939(13) | 1.795(12) |
| Al1−R2 | 2.130(8) | 2.131(8) | 1.947(15) | 2.100(13) | 1.790(13) |
| R1−Al1−R2 | 109.51(3) | 108.95(3) | 111.89(6) | 75.66 (5) | 111.61(6) |
| Al1−N1−P1 | 90.59(8) | 90.44(8) | 90.89(6) | 89.23(6)[c] | 91.38(6) |
| Al1−N2−P1 | 90.57(8) | 90.90(8) | 90.41(6) | 93.90(6)[c] | 91.14(6) |
| N1−P1−N2 | 97.65(8) | 97.50(9) | 98.56(6) | 101.10(6)[c] | 99.15(6) |
| N1−Al1−N2 | 81.11(7) | 81.07(7) | 80.04(5) | 75.75(5) | 78.21(5) |
| C1−P1−C7 | 107.16(9) | 106.72(9) | 106.846(7) | 106.58(7)[c] | 104.23(7) |
| Si1−N1−Al1 | 132.34(9) | 128.49(10) | 131.52(7) | 133.46(7)[c] | 131.04(6) |
| Si1−N1−P1 | 132.44(10) | 135.25(11) | 136.69(8) | 133.13(8)[c] | 133.52(7) |
| Si2−N2−Al1 | 132.11(9) | 132.31(10) | 128.83(7) | 135.69(7)[c] | 130.33(6) |
| Si2−N2−P1 | 137.02(10) | 134.97(10) | 134.17(8) | 128.08(8)[c] | 133.57(7) |
| R1−Al1−N1 | 114.04(6) | 112.37(6) | 110.81(4) | 102.38(5) | 113.12(6) |
| R2−Al1−N1 | 116.42(6) | 119.22(6) | 120.92(7) | 175.80(5) | 118.87(6) |
| R1−Al1−N2 | 115.83(6) | 116.73(6) | 109.69(4) | 110.34(6) | 119.33(6) |
| R2−Al1−N2 | 117.67(6) | 116.49(6) | 119.69(6) | 101.33(5) | 112.27(6) |

[a] a and b are the two independent molecules. [c] Averaged values, esds are extremes.

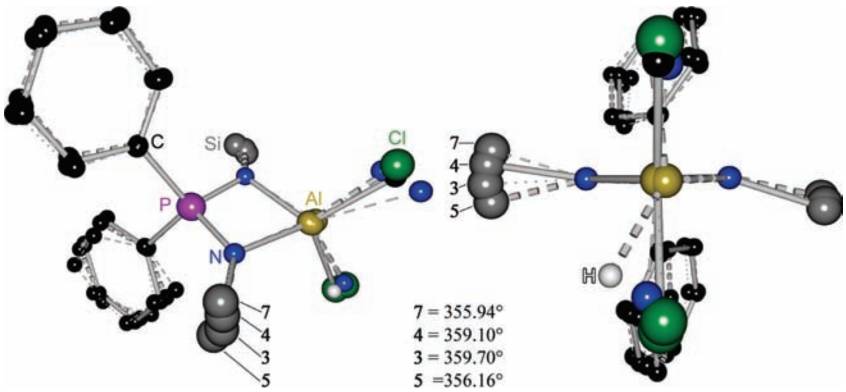


**Figure 5.** Superposition of **3**, **4**, **5**, and **7**, depicting the response of the trimethylsilyl group at N1 to the bulk of the two other substituents at the aluminum atom.

Al−N4 distances (1.790(13)−1.795(12) Å), because of the electronically delocalized $PN_2$ ligand.

**Structural Comparison of $LAlCl_2$ (3), LAlMeCl (4), $L_2AlH$ (5), and $LAl(NMe_2)_2$ (7).** The superposition of the $PN_2Al$ four-membered rings in the four structures in Figure 5 reveals that not only does this motif remains widely unchanged but even the phenyl groups adopt the same orientation. Also the remaining substituents at aluminum stay almost in place. Remarkably, only one of the two $Me_3Si$ groups responds to the various steric requirements of those two exocyclic substituents. Switching one of the chlorine substituents in **2** to a methyl group in **4** leaves the angle sum at the nitrogen atom virtually unchanged (359.7 vs 359.1°), and the silyl atom almost shares the plane with the $PN_2Al$ four-membered ring. Only the second iminophosphonamide ligand in **5** and the two dimethylamino groups in **7** remove that silyl group from the plane, indicated by an angle sum of only 356.16 and 355.94°, respectively.

## Experimental Section

**General Procedures.** All experimental manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. The samples for spectral measurements

**Table 2.** Crystal Data and Structure Refinement for Compounds **3**, **4**, **5**, and **7**

| | **3** | **4** 0.5 $C_7H_8$ | **5** 1 THF | **7** |
|---|---|---|---|---|
| empirical formula | $C_{18}H_{28}AlCl_2N_2PSi_2$ | $C_{22.5}H_{35}AlClN_2PSi_2$ | $C_{40}H_{65}AlN_4OP_2Si_4$ | $C_{22}H_{40}AlN_4PSi_2$ |
| formula weight | 457.45 | 483.11 | 819.24 | 474.71 |
| $T$ [K] | 100(2) | 100(2) | 100(2) | 100(2) |
| crystal system | triclinic | monoclinic | monoclinic | monoclinic |
| space group | $P\bar{1}$ | $P2_1/c$ | $P2_1/n$ | $P2_1/n$ |
| $a$, Å | 9.8445(7) | 10.8667(10) | 12.7603(12) | 11.2941(8) |
| $b$, Å | 10.1246(7) | 10.8034(10) | 19.0226(18) | 17.1485(12) |
| $c$, Å | 28.090(2) | 23.915(2) | 19.412(2) | 14.4640(10) |
| α, deg | 81.2820(10) | 90 | 90 | 90 |
| $\beta$, deg | 89.0870(10) | 102.5070(10) | 96.103(2) | 91.8650(10) |
| $\gamma$, deg | 61.8080(10) | 90 | 90 | 90 |
| $V$, Å$^3$ | 2434.2(3) | 2740.9(4) | 4685.3(8) | 2799.9(3) |
| $Z$ | 4 | 4 | 4 | 4 |
| $\rho_{calcd}$, Mg m$^{-3}$ | 1.248 | 1.171 | 1.161 | 1.126 |
| $\mu$, mm$^{-1}$ | 0.473 | 0.329 | 0.248 | 0.231 |
| $F$(000) | 960 | 1028 | 1760 | 1024 |
| $\theta$ range for data collcn [deg] | 2.68−26.36 | 1.74−26.05 | 1.50−26.74 | 1.84−27.51 |
| no. of reflections collected | 53683 | 52109 | 41456 | 72209 |
| no. of indept reflections | 9866 | 5405 | 9929 | 6427 |
| data/restraints/parameters | 9866/0/481 | 5405/0/288 | 9929/0/484 | 6427/0/292 |
| GoF | 1.057 | 1.068 | 1.047 | 1.077 |
| $R1$, $wR2[I > 2\sigma(I)]$[a] | 0.0341, 0.0722 | 0.0298, 0.0799 | 0.0318, 0.0809 | 0.0361, 0.0943 |
| $R1$, $wR2$ (all data) | 0.0465, 0.0771 | 0.0329, 0.0818 | 0.0394, 0.0842 | 0.0448, 0.0989 |
| largest diff peak, hole ($e$ Å$^{-3}$) | 0.66/−0.326 | 0.409/−0.364 | 0.441/−0.254 | 0.342/−0.280 |

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

were prepared in a glovebox. The solvents were purified according to conventional procedures and were freshly distilled prior to use. $AlEt_3$, $MeAlCl_2$, and $AlCl_3$ were purchased from Aldrich, and $AlH_3{\cdot}NMe_3$ was prepared by published methods.[16] NMR spectra were recorded either on a Bruker Avance 200 or on 500 NMR spectrometers and referenced to the deuterated solvent in the case of the $^1H$ and $^{13}C$ NMR spectra. $^{29}Si$ NMR spectra were referenced to $SiMe_4$ and those of $^{31}P$ NMR to 85% $H_3PO_4$. All NMR measurements were carried out at room temperature. Melting points were measured in sealed glass tubes on a Büchi B-540 melting point apparatus and are uncorrected. Elemental analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry at Göttingen. *N*,*N*′-Bis(trimethylsilyl)diphenyliminophosphonamide[4] and $[Al(NMe_2)_3]_2$[17] were prepared according to literature procedure.

**Synthesis of LLi (2).** To a solution of **1**[5] (3.0 g, 8.33 mmol) in toluene (80 mL) at −78 °C was added *n*BuLi (2.5 M, 3.4 mL, 8.5 mmol). The mixture was warmed to room temperature and stirred overnight. Toluene was removed under reduced pressure, and the product was recrystallized from a mixture of toluene and *n*-hexane. $[LiPh_2P(NSiMe_3)_2]$ formed colorless crystals. Yield (0.84 g, 83%), whose spectral data agreed with those reported in literature.[6] $^1H$ NMR (200 MHz, $C_6D_6$, 298 K): $\delta$ 0.12 (s, 18H, Si-Me), 7.61−7.80 (m, 4H, o-Ar), 6.98−7.07 (m, 6H, p-/m-Ar). $^{31}P$ NMR (121.50 MHz, $C_6D_6$, 298 K): $\delta$ 7.4.

**Synthesis of $LAlCl_2$ (3).** A toluene solution of freshly prepared **2** (1.0 g, 2.73 mmol) was added drop by drop to a cold suspension of freshly sublimed $AlCl_3$ (0.36 g, 2.73 mmol) in toluene at −78 °C. The temperature was raised to 0 °C and stirred for 1 h, and stirring was continued for 3 h. The solution was allowed to attain room temperature, and stirring was continued for 12 h. Then the mixture was filtered, and the concentrated solution was stored in a freezer at −30 °C to obtain colorless crystals. Yield (0.76 g 61%); mp 135 °C (dec); $^1H$ NMR (200 MHz, $C_6D_6$, 298 K): $\delta$ −0.2 (s, 18H, Si−Me), 7.65−7.81 (m, 4H, o-Ar), 6.95−7.07 (m, 6H, p-/m-Ar). $^{13}C$ NMR (125.76 MHz, $C_6D_6$, 298 K): $\delta$ 1.91, 1.93, 132.3−127.4. $^{31}P$ NMR (121.50 MHz, $C_6D_6$): $\delta$ 37.8.

**Synthesis of LAlMeCl (4).** $AlMeCl_2$ (1.0 M in *n*-hexane, 1.4 mL, 1.4 mmol) was added drop by drop to the solution of freshly prepared **2** (0.5 g, 1.36 mmol) in toluene (70 mL) at −78 °C. The mixture was stirred at −78 °C for 1 h, and then the temperature was slowly raised to 0 °C and stirring was continued for 3 h. After that the solution was allowed to attain room temperature, and stirring was continued for 12 h. Then the mixture was extracted with *n*-hexane (70 mL), and the concentrated solution was stored in a freezer at −30 °C to obtain colorless crystals. Yield (0.41 g 68%); mp 135 °C; $^1H$ NMR (200 MHz, $C_6D_6$, 298 K): $\delta$ −0.03 (s, 18H, Si-Me), 0.04 (s, 3H, Al-Me), 7.65−7.85 (m, 4H, o-Ar), 6.92−7.07 (m, 6H, p-/m-Ar). $^{13}C$ NMR (125.76 MHz, $C_6D_6$, 298 K): $\delta$ −0.69, 1.71, 1.66, 131.6−129.2. $^{31}P$ NMR (121.50 MHz, $C_6D_6$, 298 K): $\delta$ 33.2. $^{29}Si$ NMR (59.6 MHz, $C_6D_6$, 298 K): $\delta$ −0.31, −0.34. Anal. Calcd for $C_{19}H_{31}AlClN_2PSi_2$: C, 52.22; H, 7.15; N, 6.41. Found C, 52.54; H, 7.15; N, 6.21.

**Synthesis of $L_2AlH$ (5).** The *n*-hexane solution (30 mL) of **1** (1.0 g, 2.7 mmol) was added drop by drop to a cold suspension of freshly sublimed $AlH_3{\cdot}NMe_3$ in THF (30 mL), (0.12 g, 1.39 mmol) at −78 °C. The mixture was stirred at −30 °C for 1 h and then the temperature was slowly raised to 0 °C and the stirring was continued for 3 h. Then the solution was allowed to attain room temperature under stirring for 12 h. Then the mixture was concentrated and stored in a freezer at −30 °C to obtain colorless crystals. Yield: (0.64 g 61%); mp 107 °C (dec); $^1H$ NMR (200 MHz, $CDCl_3$, 298 K): $\delta$ −0.22 (s, 18H, Si-Me), −0.13 (s, 18H, Si-Me), 5.1 (very br, 1H, Al−H), 7.78−7.92 (m, 4H, *o*-Ar), 7.45−7.59 (m, 6H, p-/m-Ar). $^{13}C$ NMR (125.76 MHz, $C_6D_6$, 298 K): $\delta$ 1.52, 1.56, 3.75, 3.80, 133.1−131.2. $^{31}P$ NMR (121.50 MHz, $C_6D_6$, 298 K): $\delta$ 29.2, 34.6. $^{29}Si$ NMR (59.6 MHz, $C_6D_6$, 298 K): $\delta$ −4.15, −4.22. IR (cm$^{-1}$): $\tilde{\nu}$ (AlH) 1853. Anal. Calcd for $C_{37}H_{60}AlN_4P_2Si_4$: C, 58.31; H, 7.93; N, 7.35. Found C, 57.94; H, 7.83; N, 7.21.

**Synthesis of $LAlEt_2$ (6).** $AlEt_3$ (2.2 mL, 2.2 mmol) was added to a *n*-hexane (50 mL) solution of **1** (0.8 g, 2.2 mmol) at −78 °C. The mixture was stirred for 1 h at this temperature and then was allowed to attain room temperature, and stirring was continued for 12 h. The mixture was concentrated and stored in a freezer at −30 °C to give white microcrystalline solid. Yield: (0.86 g, 88%); $^1H$ NMR

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(500 MHz, $C_6D_6$, 298 K): $\delta$ −0.05 (s, 18H, Si-Me), 0.45 (q, 4H, $CH_2$), 1.52 (t, 6H, $CH_3$), 7.71−7.81 (m, 4H, *o*-Ar), 6.97−7.11 (m, 6H, p-/m-Ar). $^{13}C$ NMR (125.8 MHz, $C_6D_6$, 298 K): $\delta$ 1.99, 2.04, 10.4, 134.5−131.9. $^{31}P$ NMR (121.50 MHz, $C_6D_6$, 298 K): $\delta$ 30.3. $^{29}Si$ NMR (59.6 MHz, $C_6D_6$, 298 K): $\delta$ −2.61, −2.54.

**Synthesis of LAl($NMe_2$)$_2$ (7).** *n*-Hexane (30 mL) solution of **1** (0.9 g, 2.5 mmol) was added to $[Al(NMe_2)_3]_2$ (0.4 g, 1.25 mmol) in *n*-hexane (20 mL), and then heated under reflux for 6 h. The mixture was cooled to room temperature, concentrated, and stored in a freezer at −30 °C to obtain a colorless microcrystalline solid. Yield: (0.69 g, 58%); mp 156 °C; $^{1}H$ NMR (500 MHz, $C_6D_6$, 298 K): $\delta$ 0.024 (s, 18H, Si-Me), 3.06 (s, 12H, $CH_3$), 7.73−7.83 (m, 4H, *o*-Ar), 7.03−7.08 (m, 6H, p-/m-Ar). $^{13}C$ NMR (125.8 MHz, $C_6D_6$, 298 K): $\delta$ 1.86, 1.92, 41.8, 134.3−132.0. $^{31}P$ NMR (121.50 MHz, $C_6D_6$, 298 K): $\delta$ 28.6. $^{29}Si$ NMR (59.6 MHz, $C_6D_6$, 298 K): $\delta$ −2.67, −2.72. Anal. Calcd for $C_{22}H_{40}AlN_4PSi_2$: C, 55.66; H, 8.49; N, 11.80. Found C, 55.11; H, 8.63; N, 11.94.

**X-ray Structure Determination of 3, 4, 5, and 7.** All data were collected from shock-cooled crystals on Bruker SMART-APEX II diffractometers with D8 goniometers at 100 K[18] (Mo K$\alpha$ radiation, $\lambda$ = 71.073 pm; **3**: graphite-monochromated; **4** and **5**: INCOATEC Helios mirror optics; **7** INCOATEC Quazar mirror optics). The data were integrated with SAINT,[19] and an empirical absorption correction (SADABS) was applied.[20] The structures were solved by direct methods (SHELXS)[21] and refined on $F^2$ using the full-matrix least-squares methods of SHELXL.[22] All non-hydrogen atoms were refined with anisotropic displacement parameters. With the exception of H1 (**5**), 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 position of the Al-bonded hydrogen atom H1 (**5**) was taken from the difference map and refined freely (Table 2).

**Supporting Information Available:** X-ray data for **3**, **4**, **5**, and **7** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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