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(Phosphinomethyl)aluminum Compounds: The Role of Coligands and X-ray Structure Determinations of the Heterocycles (TMEDA)LiClAlMe$_2$C(SiMe$_3$)$_2$PMe$_2$ and (Me)(Cl)AlC(SiMe$_3$)$_2$PMe$_2$SiMe$_2$C(SiMe$_3$)PMe$_2$

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From the 1:1 reaction of R$_2$AlCl (**a**, R = Cl; **b**, R = Me) with {Li[C(SiMe$_3$)$_2$(PMe$_2$)]}$_2$, six-membered heterocycles [R$_2$AlC(SiMe$_3$)$_2$(PMe$_2$)]$_2$ (**1a,b**) are obtained. The 1:2 reaction for R = Cl involves a facile methyl migration from the silicon to aluminum and leads to the novel heterocycle (Me)(Cl)AlC(SiMe$_3$)$_2$PMe$_2$SiMe$_2$C(SiMe$_3$)PMe$_2$ (**2**), exhibiting a number of unusual structural features, as shown by the X-ray structure determination of **2**, which crystallizes from pentane (colorless crystals, triclinic, space group $P\bar{1}$, a = 9.161 (1), b = 15.280 (2), and c = 11.832 (1) Å, α = 109.62 (1), β = 74.57 (1), and γ = 98.39 (1)°, V = 1500.9 Å^3, Z = 2, R = 0.035 for 283 refined parameters and 4841 observables). A formal [3 + 2] cycloaddition is observed in the same 1:1 reaction in the presence of tetramethylethylenediamine (TMEDA) to give five-membered heterocycles (TMEDA)LiClAlR$_2$C(SiMe$_3$)$_2$PMe$_2$ (**3a,b**), incorporating five different elements within the ring. **3b** crystallizes from pentane (colorless crystals, monoclinic, space group $P2_1/n$, a = 8.915 (1), b = 18.887 (2), and c = 16.558 (2) Å, α = 90.0 (1), β = 92.52 (1), γ = 90.0 (1)°, V = 2785.3 Å^3, Z = 4, R = 0.064 for 268 refined parameters and 3830 observables). An X-ray structure determination shows the ambidentate phosphinomethanide ligand to be bound to the lithium atom via phosphorus and to the aluminum atom via carbon. **3b** thermally is converted to **1b** by loss of TMEDA, whereas **3a** is stable to thermolysis. In the presence of tetrahydrofuran (THF), the 1:1 reaction for R = Me gives rise to Me$_2$(THF)Al[C(SiMe$_3$)$_2$(PMe$_2$)] (**4**), which is also obtained from **3b** and THF. As a byproduct, due to some traces of HCl, in the 1:1 reaction (R = Cl) the ylide complex Cl$_3$AlC(SiMe$_3$)$_2$PMe$_2$H (**5**) is identified spectroscopically and eventually can be isolated. **5** either is converted by further addition of HCl to [HC(SiMe$_3$)$_2$PMe$_2$H][AlCl$_4$] (**6**) or rearranges to its tautomer Cl$_3$AlPMe$_2$C(SiMe$_3$)$_2$H (**7**), thus constituting a novel example for an ylide ⇌ phosphane diadic relationship. **7** is also obtained directly from AlCl$_3$ and HC(SiMe$_3$)$_2$(PMe$_2$).

Introduction

The diagonal relationship of phosphorus and carbon in the periodic system gives renewed significance to phosphorus chemistry, as it has emerged in the last decade that this relationship is not only a formal one but also represents a useful guideline to the understanding of such distinct species as polyphosphanes and unsaturated (low-coordinated) organophosphorus compounds (e.g., phosphaalkenes, -alkines, and -allenes, dihposphenes, and phospha heteroaromatics). It is particularly challenging to compare the reactivity of carbon and phosphorus in species where both elements are linked together directly. Ambidentate phosphinomethanides (I) are distinguished in having the same coordination number and the same total of valence electrons for both elements. Thus

$$\underset{\text{I}}{[R_2\bar{C}-\bar{P}R'_2]^{\ominus}} \qquad \underset{\text{II}}{Li\,[R_2\bar{C}-\bar{P}R'_2]}$$

phosphinomethanides are ideal candidates for a comparison of carbon and phosphorus reactivity[1] and in particular for comparison of the lone pair reactivity of a second- and a third-row element.

The nucleophilicity of carbon and phosphorus in I largely depends on the substitution pattern, i.e., on R and R′. Within a series of f, d, and s/p block element derivatives of I, it could be demonstrated, that various kinds of coordination to a metal center are possible and that fluxionality and flexibility in coordination numbers and oxidation states are frequently encountered in such compounds. Particularly, silyl substituents at carbon (R = SiMe$_3$) change the ligand properties of phosphinomethanides considerably: whereas for R = H, the C nucleophilicity clearly dominates over that of the P atom, with R = SiMe$_3$ the P nucleophilicity increases to such an extent that it becomes comparable to that of the C atom. In fact, not only steric but also electronic effects[2] contribute to a modification of ligand properties in transition-metal complexes with, e.g., Zr,[3] as well as in main-group complexes with, e.g., Pb[1,4,5] Sn,[1,4,5] Ge,[1,4] Al,[6] and Li[7] metal centers. In this latter case, also the coligands to lithium play an important role in determining the coordination mode. Since these lithium phosphinomethanides (II), either alone or in the presence of coligands like THF or TMEDA, usually are used to introduce the phosphinomethanide ligand into metal complexes, it was of interest to study the influence of these coligands on the course of the reactions. In the present work, aluminum chlorides are allowed to react with fully C-silyl-substituted lithium

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[1] Karsch, H. H.; Appelt, A.; Reisacher, H.-U.; Müller, G. *Phosphorus Sulfur* 1987, *30*, 417.

[2] Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* 1984, *106*, 6467.

[3] Karsch, H. H.; Deubelly, B.; Hofmann, J.; Müller, G. *J. Am. Chem. Soc.* 1988, *111*, 3654.

[4] (a) Karsch, H. H.; Appelt, A.; Hanika, G. *J. Organomet. Chem.* 1986, *C1*, 312. (b) Karsch, H. H.; Deubelly, B.; Hanika, G.; Riede, J.; Müller, G. *J. Organomet. Chem.* 1988, *344*, 153.

[5] Balch, A. L.; Oram, D. E. *Inorg. Chem.* 1987, *26*, 1906.

[6] (a) Karsch, H. H.; Zellner, K.; Lachmann, J.; Müller, G. *J. Organomet. Chem.* 1991, *409*, 109. (b) Karsch, H. H.; Appelt, A.; Köhler, F. H.; Müller, G. *Organometallics* 1985, *4*, 231.

[7] (a) Karsch, H. H.; Deubelly, B.; Müller, G. *J. Organomet. Chem.* 1988, *352*, 47. (b) Karsch, H. H.; Appelt, A.; Deubelly, B.; Zellner, K.; Riede, J.; Müller, G. *Z. Naturforsch.* 1988, *43b*, 1416. (c) Karsch, H. H.; Zellner, K.; Mikulcik, P.; Lachmann, J.; Müller, G. *Organometallics* 1990, *9*, 190.

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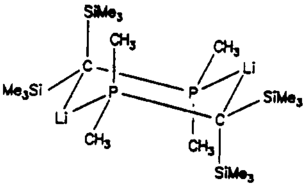
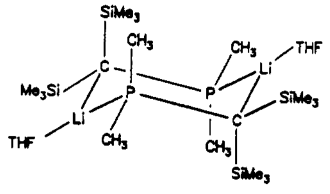
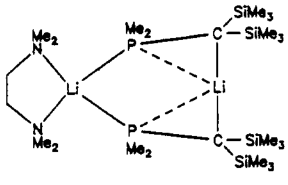
phosphinomethanides of solid-state structures III–V. Preliminary results have been reported.[8]



III[7c]



IV[9]



V[7b]

Experimental Section

A. Preparation and Characterization of Compounds. All compounds were prepared and handled in a dry nitrogen atmosphere by using conventional vacuum line techniques. Sodium/potassium alloys were employed for drying and storage of the solvents, which were redistilled immediately prior to their use. $AlCl_3$ was sublimed in vacuo (180 °C/10^{-2} mbar), $\{Li[C(SiMe_3)_2(PMe_2)]\}_2$,[7c] TMEDA·$\{Li[C(SiMe_3)_2(PMe_2)]\}_2$,[7b] $CH(SiMe_3)_2(PMe_2)$,[7b] $\{THF{\cdot}Li[C(SiMe_3)_2(PMe_2)]\}_2$,[9] and Me_2AlCl[10] (used as toluene solution) were prepared and purified according to the literature. NMR spectra were recorded on Jeol JNM GX400 (^{31}P, 161.7 MHz; ^{27}Al, 104.17 MHz) and Bruker WP100SY (^1H, 100 MHz; ^{13}C, 25.12 MHz) spectrometers at +20 °C in benzene-d_6 unless otherwise stated. Chemical shifts are reported in parts per million and refer to Me_4Si (^1H, ^{13}C), 85% H_3PO_4 (^{31}P), or $Al(H_2O)_6^{3+}$ (^{27}Al). Multiplets arising from $X_nAA'X_n'$ spin systems are denoted as "d" ("filled-in doublet") or "t" (deceptively simple triplet) with N = distance between outer lines. Melting points were measured in sealed capillaries and were uncorrected. Elemental analyses were performed by Mikroanalytisches Labor des Anorganisch-chemischen Instituts, Technische Universität München. In some cases satisfactory analytical values were not obtained, in line with earlier observations on similar compounds.[6b,11]

Preparation of 1a. $AlCl_3$ (0.33 g, 2.5 mmol) and $\{Li[C(SiMe_3)_2(PMe_2)]\}_2$ (III) (0.56 g, 1.25 mmol) were mixed in 50 mL of toluene at −78 °C. The suspension was allowed to warm to room temperature and stirred for 2 days. The reaction mixture was filtered and the solvent was removed in vacuo. A white solid (0.68 g, 1.1 mmol, 85.7%) was obtained, mp 95–96 °C. Anal. Calcd for $C_{18}H_{48}Cl_4Al_2P_2Si_4$ (634.34): C, 34.06; H, 7.62; Cl, 22.35. Found: C, 32.43; H, 7.23; Cl, 25.14. ^{31}P NMR δ −33.55 (s). ^{27}Al NMR δ 120.68 (s). ^1H NMR δ 1.43 ("d", N = 7.3 Hz, 6 H, PMe_2).

Preparation of 1b. To a stirred suspension of $\{Li[C(SiMe_3)_2(PMe_2)]\}_2$ (III) (0.79 g, 1.75 mmol) in 50 mL of pentane was added 3.18 mL (3.5 mmol) of a 1.1 M solution of Me_2AlCl in toluene at −78 °C. The mixture was allowed to warm to room temperature and stirred for 24 h. After filtration the solvent was removed and the colorless crystals obtained (0.81 g, 1.5 mmol, 83.7%) were dried in vacuo, mp 110–112 °C. Anal. Calcd for $C_{22}H_{60}Al_2P_2Si_4$ (552.96): C, 47.79; H, 10.93; Al, 9.75; Cl, 0. Found: C, 42.88; H, 10.70; Al, 11.50; Cl, 0. ^{31}P NMR δ −30.12 (s). ^{27}Al NMR δ 161.90 (s). ^{13}C NMR δ 15.53 ("t", N = 12.8 Hz, PMe_2), 8.15 (s, $SiMe_3$), −2.34 (s, $AlMe_2$). ^1H NMR δ 1.28 ("t", N = 4.9 Hz, 6 H, PMe_2), 0.32 (s, 18 H, $SiMe_3$) −0.25 ("t", N = 5.2 Hz, 6 H, $AlMe_2$).

Preparation of 2. $AlCl_3$ (0.13 g, 1.0 mmol) and $\{Li[C(SiMe_3)_2(PMe_2)]\}_2$ (III) (0.46 g, 1.0 mmol) were combined in 50 mL of pentane at −78 °C. The mixture was allowed to warm to room temperature and stirred for 12 h. The suspension was filtered from the solid residue, the solvent was evaporated, and colorless crystals (0.4 g, 0.8 mmol, 80%) were obtained, mp 73–75 °C. Anal. Calcd for $C_{18}H_{48}AlClP_2Si_4$ (501.3): C, 43.13; H, 9.65; Cl, 7.0. Found: C, 43.01; H, 9.91; Cl, 6.8. ^{31}P NMR (toluene-d_8) δ −19.58 (d, 28.0 Hz), −42.75 (s, br); −100 °C, δ −21.13 (d, 28.0 Hz), −42.39 (d, 28.0 Hz). ^{27}Al NMR δ 146.12 (s). ^{13}C NMR δ 21.86 (d, 26.6 Hz, PMe), 18.55 (d, 35.2 Hz, PMe), 14.70 (d, 35.2 Hz, PMe), 13.51 (d, 28.5 Hz, PMe), 7.16 (d, 3.3 Hz, SiMe), 6.74 (d d, 1.0/2.5 Hz, $SiMe_3$), 6.14 (d, 2.7 Hz, $SiMe_3$), 5.68 (d, 3.7 Hz, $SiMe_3$), 4.93 (d, 8.0 Hz, SiMe). ^1H NMR δ 1.55 (d, 6.3 Hz, 3 H, PMe), 1.46 (d, 5.7 Hz, PMe), 1.31 (d, 8.0 Hz, 3 H, PMe), 0.94 (d, 9.2 Hz, 3 H, PMe), 0.38 (s, 9 H, $SiMe_3$), 0.33 (s, 9 H, $SiMe_3$), 0.32 (s, 9 H, $SiMe_3$), 0.27 (s, 3 H, SiMe), 0.12 (s, 3 H, SiMe), −0.10 (d, 2.8 Hz, 3 H, AlMe). The heterocycle **2** was also obtained by using TMEDA·$\{Li[C(SiMe_3)_2(PMe_2)]\}_2$ (V) instead of $\{Li[C(SiMe_3)(PMe_2)]\}_2$ (III).

Preparation of 3a. At −78 °C, 0.3 mL of TMEDA (2.1 mmol) was added to a stirred suspension of $AlCl_3$ (0.56 g, 4.2 mmol) and TMEDA·$\{Li[C(SiMe_3)_2(PMe_2)]\}_2$ (V) (1.20 g, 2.1 mmol) in 50 mL of toluene. The reaction mixture was allowed to warm to room temperature and stirred for another 12 h. The mixture was filtered. Concentration of the filtrate to a small volume gave a colorless crystalline solid (1.52 g, 3.2 mmol, 76%), mp 150–152 °C. Anal. Calcd for $C_{15}H_{40}N_2AlCl_3LiPSi_2$ (475.92): C, 37.86; H, 8.47; N, 5.88; Cl, 22.35. Found: C, 38.33; H, 8.72; N, 5.30; Cl, 20.41. ^{31}P NMR (toluene-d_8) δ −33.07 (s); −60 °C, δ −34.28 (q, 74.5 Hz). ^{27}Al NMR δ 116.96 (s). ^7Li NMR δ 1.14 (s). ^{13}C NMR δ 57.24 (s, NCH_2), 45.94 (s, NCH_3), 16.63 (d, 15.6 Hz, PMe_2), 5.29 (d, 4.88 Hz, $SiMe_3$). ^1H NMR δ 1.89 (s, 4 H, NCH_2), 1.74 (s, 12 H, NCH_3), 1.55 (d, 1.83 Hz, 6 H, PMe_2), 0.64 (s, 18 H, $SiMe_3$). Without addition of TMEDA, a mixture of **3a** and **1a** was obtained, which was identified by NMR spectroscopy.

Preparation of 3b. A suspension of TMEDA·$\{Li[C(SiMe_3)_2(PMe_2)]\}_2$ (V) (0.48 g, 0.85 mmol) in 50 mL of pentane was cooled to −78 °C. Me_2AlCl 1.59 mL (1.07 M in toluene, 1.7 mmol), and 0.13 mL of TMEDA (0.85 mmol) were added. After warming to room temperature the mixture was stirred for 3 h and filtered. Removal of the solvent from the filtrate left colorless crystals (0.62 g, 1.4 mmol, 83.8%), mp 98–100 °C. Anal. Calcd for $C_{17}H_{46}N_2AlClLiPSi_2$ (435.08): C, 46.93; H, 10.65; N, 6.43; Al, 6.2. Found: C, 45.13; H, 11.00; N, 6.12; Al, 5.8. ^{31}P NMR (toluene-d_8) δ −32.21 (s); −60 °C, δ −32.66 (q, 69.5 Hz). ^{27}Al NMR (toluene-d_8) δ 153.54 (s). ^7Li NMR (toluene-d_8) 1.28 (s). ^{13}C NMR δ 56.62 (s, NCH_2), 45.64 (s, NCH_3), 16.52 (d, 7.8 Hz, PMe_2), 6.13 (d, 3.7 Hz, $SiMe_3$), −0.46 (s, $AlMe_2$). ^1H NMR δ 1.86 (s, 4 H, NCH_2), 1.70 (s, 12 H, NCH_3), 1.34 (s, 6 H, PMe_2), 0.51 (s, 18 H, $SiMe_3$), −0.09 (s, 6 H, $AlMe_2$). Without addition of TMEDA, a mixture of **3b** and **1b** was obtained, which was identified by NMR spectroscopy. Heating of solid **3b** to 80 °C for 3 h in vacuo yielded solid **1b** (together with LiCl). Similarly, heating of a benzene solution of **3b** to 60 °C for 4 h, filtration, and removal of volatile constituents in vacuo yielded pure **1b** (NMR).

Preparation of 4. (a) Me_2AlCl, 1.4 mL (1.1 M in toluene, 1.5 mmol), was added to a suspension of $\{THF{\cdot}Li[C(SiMe_3)_2(PMe_2)]\}_2$ (IV) (0.45 g, 0.75 mmol) in 50 mL of pentane at −78 °C. The mixture was allowed to warm to room temperature, stirred for 12 h, and filtered. Evaporation of the filtrate gave a yellow oil (0.45 g, 1.3 mmol, 88.46%).

(b) **3b** (0.5 g, 1.2 mmol) was dissolved in 30 mL of THF and stirred for 3 h at 20 °C. The solvent was replaced by 20 mL of pentane, and after filtration, the pentane was removed in vacuo and a yellow oil (0.39 g, 1.1 mmol, 93.2%) was obtained.

(c) **1b** (0.45 g, 0.8 mmol) was dissolved in 30 mL of THF and stirred for 3 h. From the clear solution the solvent was removed in vacuo: yellow oil (0.53 g, 1.5 mmol, 96.4%). Anal. Calcd for

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[8] (a) Karsch, H. H.; Zellner, K.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1990**, 1621. (b) *Ibid.* **1991**, 466.

[9] Karsch, H. H.; Zellner, K.; Gamper, S.; Müller, G. *J. Organomet. Chem.*, in press.

[10] Marsel, C. L.; Kalil, E. O.; Reidinger, A.; Kramer, L. *Adv. Chem. Ser.* **1959**, *23*, 172.

[11] (a) Karsch, H. H.; Appelt, A.; Müller, G. *Organometallics* **1985**, *4*, 1624. (b) Karsch, H. H.; Appelt, A.; Riede, J.; Müller, G. *Organometallics* **1987**, *6*, 316. (c) Haaland, A.; Hougen, J.; Volden, H. V.; Hanika, G.; Karsch, H. H. *J. Organomet. Chem.* **1987**, *322*, C24.

Table I. Crystal Structure Data for 2 and 3b

	2	**3b**
formula	$C_{18}H_{48}AlClP_2Si_4$	$C_{17}H_{46}AlClLiN_2PSi_2$
M_r	501.309	435.09
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	9.161 (1)	8.915 (1)
b, Å	15.280 (2)	18.887 (2)
c, Å	11.832 (1)	16.558 (2)
α, deg	109.62 (1)	90.0
β, deg	74.57 (1)	92.52 (1)
γ, deg	98.39 (1)	90.0
V, Å^3	1500.9	2785.3
Z	2	4
D_{calcd}, g/cm^3	1.109	1.037
μ(Mo Kα), cm^{-1}	4.2	3.1
F(000), e	544	952
T, °C	−50	−35
diffractometer	Syntex-P2_1	Syntex-P2_1
radiation	Mo Kα, λ = 0.71069	Mo Kα, λ = 0.71069 Å
monochromator	graphite	graphite
scan	ω	ω
scan width (ω), deg	0.8	0.8
scan speed, °/min	0.7–29.3	0.8–29.3
$(\sin \vartheta/\lambda)_{max}$, Å^{-1}	0.595	0.595
hkl range	+10, ±18, ±14	+10, +22, ±19
standard rflns	200, 050, 004	200, 060, 004
rflns (measd/unique)	5286/5275	5400/4903
R_{int}	0.02	0.03
rflns obsd	4841 [$F_o \geq 2.0\sigma(F_o)$]	3830 [$F_o \geq 4.0\sigma(F_o)$]
params ref	283	268
R^a	0.035	0.064
$R_w{}^b$	0.044	0.061
(shift/error)$_{max}$	0.39	0.03
$\Delta_{\rho fin}$ (max/min), e/Å^3	0.33/−0.29	1.55/−0.43

$^a R = \sum(||F_o| - |F_c||)/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$; $w = 1/\sigma^2(F_o)$; function minimized, $\sum w(|F_o| - |F_c|)^2$.

$C_{15}H_{38}OAlPSi_2$ (348.59): C, 51.7; H, 10.9; Al, 7.7; Cl, 0. Found: C, 48.4; H, 10.5; Al, 9.9; Cl, 0. ^{31}P NMR δ 7.82 (s). ^{27}Al NMR δ 156.42 (s). ^{13}C NMR δ 62.92 (m, OCH_2), 33.65 (m, OCH_2), 18.71 (d, 56.6 Hz, PMe_2), 6.92 (d, 3.6 Hz, $SiMe_3$), −8.74 (s, $AlMe_2$). ^{1}H NMR δ 3.34 (s, 4 H, OCH_2), 1.22 (s, 4 H, OCH_2), 0.92 (s, 6 H, PMe_2), 0.33 (s, 18 H, $SiMe_3$), −0.48 (s, 6 H, $AlMe_2$).

Preparation of 5. Not rigorously dried $AlCl_3$ (0.4 g, 3 mmol) and $\{Li[C(SiMe_3)_2(PMe_2)]\}_2$ (III) (0.68 g, 1.5 mmol) were combined in 50 mL of toluene. The mixture was allowed to warm to room temperature and stirred for 12 h. After filtration the solvent was removed and the colorless oil (1.0 g, 2.8 mmol, 94.2%) dried in vacuo. Anal. Calcd for $C_9H_{25}Cl_3AlPSi_2$ (353.78): C, 30.55; H, 7.12, Cl, 30.06. Found: C, 28.93; H, 7.01; Cl, 29.12. $\{^1H\}^{31}P$ NMR δ −1.19 (s). ^{31}P NMR δ −1.19 (d, 457.8 Hz). ^{27}Al NMR δ 112.95 (s). ^{13}C NMR δ 11.71 (d, 54.9 Hz, PMe_2), 3.54 (d, 3.7 Hz, $SiMe_3$). ^{1}H NMR δ 5.17 (d sept, 458.4/5.3 Hz, 1 H, PH), 1.40 (d d, 13.3/5.3 Hz, 6 H, PMe_2), 0.34 (s, 18 H, $SiMe_3$).

The same result was obtained, when in the above-described procedure for the preparation of **1a** some contact to air occurred accidently after the combination of the reactants. Varying amounts of **5** are identified spectroscopically in all similar reactions, even if solvents and reagents were dried very thoroughly.

Preparation of 7. $CH(SiMe_3)_2(PMe_2)$ (0.5 g, 2.3 mmol) was added to $AlCl_3$ (0.3 g, 2.3 mmol) in 30 mL of pentane at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. After the solvent was removed, the white solid (0.8 g, 2.26 mmol, 98.2%) was dried in vacuo, mp 53–55 °C. Anal. Calcd for $C_9H_{25}Cl_3AlPSi_2$ (353.78): C, 30.55; H, 7.12; Cl, 30.06. Found: C, 29.73; H, 7.10; Cl, 29.47. ^{31}P NMR δ −33.19 (s). ^{27}Al NMR δ 115.68 (s). ^{13}C NMR δ 13.23 (d, 20.8 Hz, PMe_2), 2.73 (d, 3.7 Hz, $SiMe_3$). ^{1}H NMR δ 1.03 (d, 3.7 Hz, 6 H, PMe_2), 0.05 (s, 18 H, $SiMe_3$), −0.10 (d, 1.1 Hz, 1 H, CH). **7** was also obtained by keeping a soluton of **5** in C_6D_6 at room temperature for 14 days and identified by NMR spectroscopy (after 7 days, the transformation was not complete: **5**:**7** = 1:1)

Preparation of 6. **5** or **7** (0.5 g, 1.4 mmol) were dissolved in HCl (conc) at room temperature and stirred some minutes. The suspension was concentrated and the colorless oil was dried in vacuo (0.52 g, 1.3 mmol, 95%). Anal. Calcd for $C_9H_{26}Cl_4AlPSi_2$ (390.24): C, 27.70; H, 6.72; Cl, 36.33. Found: C, 26.93; H, 6.59; Cl, 35.71. $\{^1H\}^{31}P$ NMR δ 0.78 (s). ^{31}P NMR δ 0.78 (d, 483.9 Hz). ^{13}C NMR δ 8.96 (d, 52.7 Hz, PMe_2), 1.94 (d, 2.9 Hz, $SiMe_3$). ^{1}H NMR δ 4.44 (d sept, 471.0/5.4 Hz, 1 H, PH), 1.21 ("d", 9.7 Hz, 6 H, PMe_2), 0.25 (s, 18 H, $SiMe_3$).

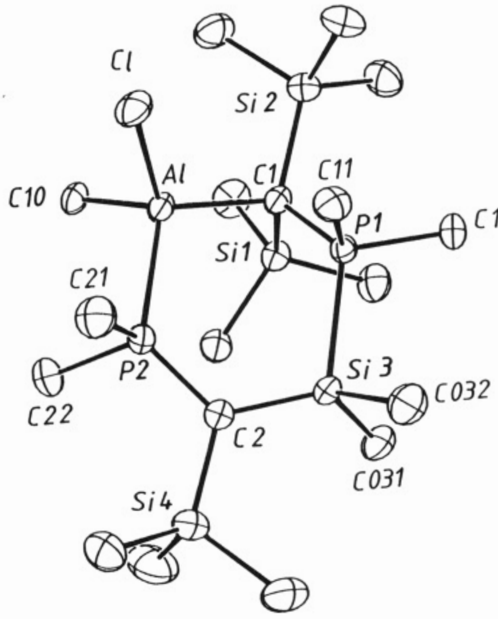

Figure 1. Molecular structure of **2** in the crystal and atomic numbering scheme adopted (ORTEP, displacement ellipsoids at the 50% level; H atoms omitted for clarity).

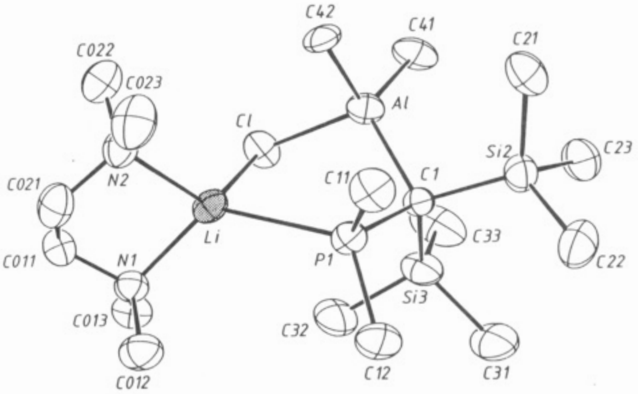

Figure 2. Molecular structure of **3b** without H atoms.

B. X-ray Structure Determination of 2 and 3b. Crystal data and a summary of data pertinent to data collection and structure refinement are collected in Table I. Exact cell dimensions were obtained by least-squares refinement on the Bragg angles of 15 selected reflections centered on the diffractometer. Reduced cell calculations did not reveal symmetry higher than triclinic (**2**) or monoclinic (**3b**). Three standard reflections, measured after every 50 reflections showed only random intensity fluctuations. Therefore a correction for crystal decay was not considered necessary, neither was one for absorption. Both structures were solved with direct methods (**2**, SHELXS-86; **3b**, MULTAN-87) and completed with Fourier techniques. After preliminary anisotropic refinement of the non-H atoms, for **2** all H atoms could be located in difference maps, whereas only 38 were found for **3b**. The remainder was calculated at idealized geometrical positions. Final refinement was done with anisotropic displacement parameters. For both compounds the methyl groups were treated as rigid groups (H atoms with U_{iso} fixed at 0.08/0.05 Å^2 respectively for **2** and **3b**).

The atomic form factors used in the refinement were of the usual source.[12] Corrections for anomalous scattering were applied to all atoms except hydrogen.[13] The programs used included

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(12) Cromer, D. T.; Wabner, J. T. *Acta Crytallogr.* **1965**, *18*, 104. Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 2 ($U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i\mathbf{a}_j$)

atom	x/a	y/b	z/c	U(eq), Å^2
Cl	−0.19878 (6)	0.67338 (4)	0.08335 (6)	0.041
P(1)	0.25711 (6)	0.69339 (4)	0.07180 (5)	0.025
P(2)	0.10331 (6)	0.71334 (4)	−0.16778 (5)	0.029
Si(1)	0.25331 (7)	0.90678 (4)	0.15788 (6)	0.030
Si(2)	0.03398 (8)	0.79128 (5)	0.31860 (6)	0.036
Si(3)	0.40566 (7)	0.67895 (4)	−0.12596 (6)	0.029
Si(4)	0.39319 (8)	0.69197 (6)	−0.37957 (6)	0.045
Al	−0.01486 (7)	0.77822 (5)	0.05225 (6)	0.027
C(1)	0.1401 (2)	0.7901 (2)	0.1540 (2)	0.026
C(2)	0.2950 (3)	0.6946 (2)	−0.2210 (2)	0.032
C(10)	−0.1132 (3)	0.8912 (2)	0.0747 (2)	0.031
C(11)	0.1434 (3)	0.5835 (2)	0.0430 (2)	0.037
C(12)	0.3791 (3)	0.6785 (2)	0.1622 (2)	0.039
C(21)	−0.0159 (3)	0.6111 (2)	−0.2321 (3)	0.047
C(22)	0.0533 (3)	0.7961 (2)	−0.2314 (3)	0.047
C(011)	0.4388 (3)	0.9158 (2)	0.2019 (3)	0.045
C(012)	0.2955 (3)	0.9287 (2)	0.0058 (2)	0.037
C(013)	0.1457 (3)	1.0084 (2)	0.2707 (3)	0.048
C(021)	0.1532 (3)	0.8478 (2)	0.4343 (2)	0.052
C(022)	−0.0296 (3)	0.6738 (2)	0.3392 (3)	0.051
C(023)	−0.1429 (3)	0.8553 (2)	0.3699 (3)	0.052
C(031)	0.5822 (3)	0.7571 (2)	−0.1103 (3)	0.045
C(032)	0.4723 (3)	0.5590 (2)	−0.1641 (3)	0.052
C(041)	0.2828 (4)	0.6266 (2)	−0.4992 (3)	0.057
C(042)	0.4450 (4)	0.8119 (3)	−0.3937 (3)	0.073
C(043)	0.5762 (4)	0.6326 (3)	−0.4343 (3)	0.078

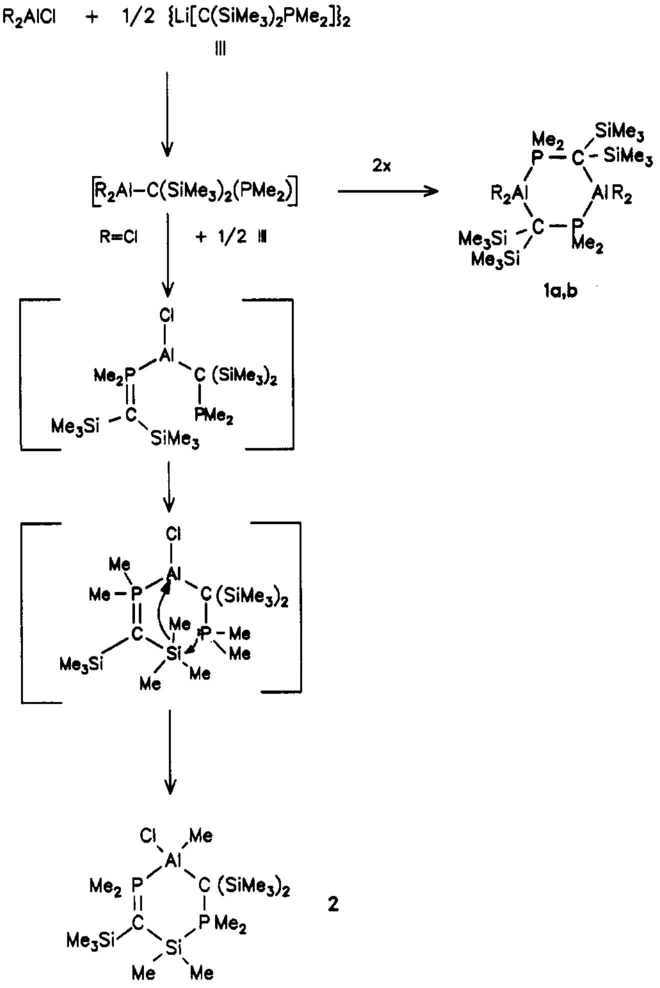
Table III. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 3b

atom	x/a	y/b	z/c	U(eq), Å^2
Cl	0.4599 (1)	0.09802 (6)	0.50597 (6)	0.046
P(1)	0.5514 (1)	0.23943 (6)	0.65275 (6)	0.036
Si(2)	0.3627 (2)	0.36044 (6)	0.55880 (8)	0.043
Si(3)	0.6247 (2)	0.27848 (8)	0.48115 (8)	0.052
Al	0.3194 (1)	0.19695 (7)	0.52396 (7)	0.038
N(1)	0.7705 (4)	0.0432 (2)	0.6545 (2)	0.039
N(2)	0.4791 (4)	0.0318 (2)	0.7285 (2)	0.043
C(1)	0.4700 (4)	0.2747 (2)	0.5567 (2)	0.029
C(11)	0.4297 (6)	0.2684 (3)	0.7340 (2)	0.048
C(12)	0.7199 (6)	0.2930 (3)	0.6826 (3)	0.055
C(21)	0.1702 (5)	0.3508 (3)	0.6001 (3)	0.055
C(22)	0.4566 (7)	0.4331 (3)	0.6190 (4)	0.067
C(23)	0.3235 (6)	0.3976 (3)	0.4542 (3)	0.061
C(31)	0.7311 (6)	0.3639 (3)	0.4835 (4)	0.077
C(32)	0.7721 (6)	0.2082 (3)	0.4976 (4)	0.067
C(33)	0.5535 (7)	0.2637 (4)	0.3728 (3)	0.082
C(41)	0.1939 (5)	0.2109 (3)	0.4256 (3)	0.053
C(42)	0.1937 (5)	0.1637 (2)	0.6132 (3)	0.039
C(011)	0.7198 (5)	−0.0224 (2)	0.6937 (3)	0.047
C(012)	0.8692 (6)	0.0850 (3)	0.7103 (3)	0.054
C(013)	0.8536 (6)	0.0241 (3)	0.5832 (3)	0.051
C(021)	0.6138 (6)	−0.0082 (3)	0.7586 (3)	0.053
C(022)	0.3709 (6)	−0.0149 (3)	0.6875 (3)	0.058
C(023)	0.4077 (7)	0.0650 (3)	0.7967 (3)	0.063
Li	0.5695 (8)	0.0990 (4)	0.6389 (4)	0.038

Table IV. Important Bond Distances (Å) and Angles (deg) in the Structure of 2 with Esd's in Units of the Last Significant Digit in Parentheses

Al–P(2)	2.452 (1)	Al–C(1)	2.046 (2)
Al–Cl	2.195 (1)	Al–C(10)	1.970 (2)
P(1)–Si(3)	2.329 (1)	P(1)–C(1)	1.795 (2)
P(1)–C(11)	1.821 (2)	P(1)–C(12)	1.822 (2)
C(1)–Si(1)	1.921 (2)	C(1)–Si(2)	1.926 (2)
C(2)–P(2)	1.732 (2)	C(2)–Si(3)	1.791 (2)
C(2)–Si(4)	1.842 (2)	P(2)–C(21)	1.832 (3)
P(2)–C(22)	1.835 (2)		
Al–C(1)–P(1)	105.7 (1)	Si(1)–C(1)–Si(2)	110.2 (1)
Al–C(1)–Si(1)	105.9 (1)	Al–C(1)–Si(2)	109.1 (1)
P(1)–C(1)–Si(1)	111.7 (1)	P(1)–C(1)–Si(2)	113.8 (1)
C(1)–Al–P(2)	109.6 (1)	Cl–Al–C(10)	106.3 (1)
C(1)–P(1)–Si(3)	120.8 (1)	C(11)–P(1)–C(12)	102.7 (1)
Al–P(2)–C(2)	122.2 (1)	C(21)–P(2)–C(22)	99.7 (1)
P(1)–Si(3)–C(2)	110.3 (1)	C(031)–Si(3)–C(032)	103.5 (1)
P(2)–C(2)–Si(3)	122.3 (1)	P(2)–C(2)–Si(4)	120.2 (1)
Si(3)–C(2)–Si(4)	117.5 (1)		

Scheme I. Proposed Reaction Pathway for the Formation of 1a,b and 2 (a, R = Cl; b, R = Me)



SHELXS-86 and MULTAN-87 (structure solution), SHELX-76 (refinement), and ORTEP (molecular drawings), as well as locally written routines.[14]

Tables II and III contain the atomic coordinates and Tables IV and V important distances and angles. Figures 1 and 2 show the molecular structures. See the note at the end of the paper for supplementary material available.

Results and Discussion

I. Reactions without Coligands. Both $AlCl_3$ and Me_2AlCl easily react with $\{Li[C(SiMe_3)_2(PMe_2)]\}_2$ (III) in toluene to give colorless solids **1a,b**, respectively (Scheme I). The proton NMR spectrum of **1a** shows a filled-in doublet ($X_6AA'X_6'$ spin systems) for the PCH_3 groups and thus indicates a dimeric nature, in line with the findings with **1b**.[6a] A monomeric intermediate is not detectable in

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(13) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV (Present distributor: Kluwer Academic Publishers, Dordrecht).

(14) SHELXS-86: Sheldrick, G. M. In *Crytallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: Oxford, 1985, p 175. MULTAN-87: Debaerdemaeker, T.; Germain, G.; Main, P.; Tate, C.; Woolfson, M. M. *Computer Programs for the automatic Solution of Crystal Structures from X-ray Diffraction Data*; University of York: York, England, Ulm, Germany, and Louvain, Belgium, 1987. SHELX-76: Sheldrick, G. M. *Program for Crystal Structure Determination*: University of Cambridge: Cambridge, England, 1976. ORTEP-II: Johnson, C. K. Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

Table V. Important Bond Distances (Å) and Angles (deg) in the Structure of 3b

Li–P(1)	2.669 (7)	Li–Cl	2.369 (6)
Li–N(1)	2.084 (8)	Li–N(2)	2.137 (7)
Al–Cl	2.276 (2)	Al–C(1)	2.047 (4)
Al–C(41)	1.953 (4)	Al–C(42)	1.994 (4)
C(1)–P(1)	1.843 (4)	C(1)–Si(2)	1.882 (4)
C(1)–Si(3)	1.904 (4)	P(1)–C(11)	1.847 (4)
P(1)–C(12)	1.859 (5)		
Cl–Li–P(1)	93.6 (2)	N(1)–Li–N(2)	87.9 (3)
Cl–Li–N(1)	115.4 (3)	Cl–Li–N(2)	119.2 (3)
P(1)–Li–N(1)	123.1 (3)	P(1)–Li–N(2)	120.3 (3)
Li–Cl–Al	94.5 (2)	Cl–Al–C(1)	105.4 (1)
C(41)–Al–C(42)	109.9 (2)		
Li–P(1)–C(1)	108.0 (2)	C(11)–P(1)–C(12)	98.0 (2)
Al–C(1)–P(1)	101.4 (2)	Si(2)–C(1)–Si(3)	111.3 (2)
Al–C(1)–Si(2)	107.1 (2)	Al–C(1)–Si(3)	109.8 (2)
P(1)–C(1)–Si(2)	118.5 (2)	P(1)–C(1)–Si(3)	108.1 (2)

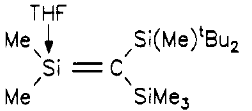
these reactions. (Thus, in contrast to Scheme I, also the dimeric **1a,b** in principle could form the monomeric bis-substitution intermediate with III. On the other hand, indirect evidence for the presence of a monomeric mono-substitution intermediate is given by the formation of **5**, vide supra). Further reaction with excess phosphinomethanide, either via such a monomer or with **1a** under concomitant monomerization, obviously cannot involve species with both phosphinomethanides being linked to the aluminum atom via carbon for steric reasons, and, therefore, one P–Al and one C–Al linkage should arise. The unsaturated aluminum and the electron-rich Si–CH_3 bonds (Si adjacent to a carbanionic functionality) together with the nucleophilic phosphine functionality in a favorable position to silicon thus generated allow for the easy transfer of one methyl group of a $SiMe_3$ functionality to the Al atom via a pentacoordinate silicon transition state to form **2** as the isolated product as depicted in Scheme I.[15] None of the proposed intermediates in Scheme I could be detected; however, the methyl transfer obviously is a fast process even under very mild conditions. If $AlCl_3$ and $\{Li[C(SiMe_3)_2(PMe_2)]\}_2$ are combined at −78 °C in toluene-d_8 and the reaction is monitored by ^{31}P NMR, a broad signal for **1a** appears at −40 °C (δ_P = −33.19) besides that of III. It should be noted at this point that all ^{31}P NMR signals of P nuclei directly attached to aluminum appear as broadened lines, which may serve as a diagnostic tool for the Al–P linkage.

At higher temperature (0 °C), the signals of **2** emerge at the expense of that of **1a**. No other signals are found (with the exception of those due to HCl impurities, see below). Even an excess of phosphinomethanide does not alter the reaction course nor is a further reaction observed with **2**, but it reduces the amount of impurities due to HCl.

The ^{31}P NMR spectrum of the heterocycle **2**, which is isolated from pentane as colorless crystals, confirms a novel coupling reaction of two phosphinomethanides at a metal center[16] by the appearance of an AB-type spectrum. The low-field doublet (δ = −19.58 (28 Hz)) is well-resolved and thus attributable to P1, while the high-field signal (δ = −42.75) is an unresolved broad signal at +20 °C and thus indicates P2 with an Al–P bond (at −100 °C a weak doublet splitting is observed also at the P2 signal). The latter shift value is quite remarkable for tetravalent phosphorus but corresponds to the respective shifts in other six-membered rings, e.g., **1a,b**. ^{1}H and ^{13}C NMR data are in full accord with the structure given in Scheme I, but the $AlCH_3$ moiety is only evident from the ^{1}H NMR spectrum, since, due to the quadrupolar Al nucleus, the respective ^{13}C resonance signal could not be detected.

The structure of **2** has been unambiguously established by X-ray crystallography (Figure 1). The molecule contains a six-membered heterocycle, where five atoms [Al, P(2), C(2), Si(3), and P(1)] lie roughly within a plane with a maximum deviation from the best plane through these atoms at P(2) (−0.24 Å), whereas the tetrahedral C(1) atom deviates by 0.75 Å from this plane. The main features of the ring are (i) an aluminum-complexed phosphorus ylide moiety consisting of tetrahedral Al and P(2) atoms and a planar C(2) atom with an Al–P bond in the normal range (2.452 (1) Å)[6,11] and with a short P(2)–C(2) bond (1.732 (2) Å) typical for phosphorus ylides and (ii) a rare case of a silyl phosphonium moiety [Si(3)–P(1) = 2.329 (1) Å], which obviously is due to the transfer of a methyl group from Si(3) to the Al atom. The presence of this exocyclic methyl group [Al–C(10) = 1.970 (2) Å], which together with one chlorine atom and atoms C(1) and P(2) makes up the tetrahedral coordination geometry at Al, is the most striking feature of the structure. The relative orientation of C(10) and Cl with respect to the silyl groups at C(1) obviously is a consequence of steric congestion. Three angles within the ring (at Al, C(1), and Si(3)) deviate only slightly from the tetrahedral value, whereas the other three (at P(1), P(2), and C(2)) amount to approximately 120°. Bond angles that are large for tetracoordinated P atoms within six-membered rings are not unusual[6] and occur even within more puckered rings. Also within normal range lies the terminal Al–Cl bond (2.195 (1) Å), which may be compared to the terminal Al–Cl bond in $[ClAl(CH_2PMe_2)_2]_2$[6b] (2.176 (1) Å).

Another important point in the molecular structure of **2** deserves comment: the structural moiety P(1)–Si(3)–C(2) with an sp^2 C atom may be regarded as a first example of a silene that is internally stabilized by a phosphine donor, thus resulting in a cyclic structure. Since the only known example of donor-stabilized silenes, i.e., VI,[17] is noncyclic, the different mutual orientation of the Si and C substituents in **2** and VI are easily attributed to the constraints of the ring.



VI[17]

In accordance with this description are the slightly elongated bond P(1)–Si(3) (vide supra) and the rather short Si(3)–C(2) (1.791 (2) Å), the latter being the shortest Si–C bond in the molecule, which is only by ca. 0.04 Å longer than Si–C in VI (1.747 (5) Å). This slight elongation might be due to the better (ylidic) charge delocalization in **2** compared to VI, as exemplified by the canonical formulas **2**-Y and VI-Y.

The above-mentioned byproducts in the formation of **2** also diserve some comment. The aluminum chloride–phosphorus ylide complex **5** is formed in modest yield according to Scheme II, if the $AlCl_3$ used is not purified rigorously. The formation of **5** (and **6**) may be rationalized by the assumption that the monomeric precursor of **1a** (see Scheme I) is trapped with hydrogen chloride (see Scheme II) and thus an indirect confirmation of the presence of

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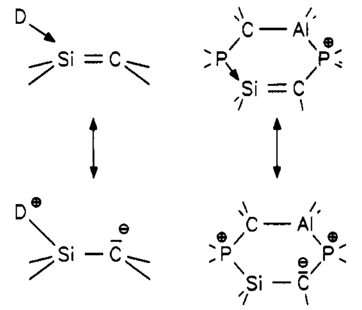
[15] In (silylmethyl)aluminum compounds (without the presence of a phosphine functionality) a similar facile methyl transfer has not yet been observed.

[16] Karsch, H. H.; Deubelly, B.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1988**, 517.

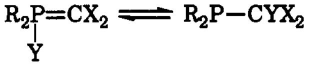
[17] Wiberg, N.; Wagner, G.; Müller, G.; Riede, J. *J. Organomet. Chem.* **1984**, *271*, 381. Wiberg, N.; Wagner, G.; Reber, G.; Riede, J.; Müller, G. *Organometallics* **1987**, *6*, 35.



VI–Y 2–Y

this precursor is at hand: in an NMR tube experiment in toluene-d_8, the signal of **5** together with that of **6** is the first to appear even at −60 °C. Both signals disappear at higher temperatures, provided an excess of lithium phosphinomethanide is present. Thus it appears, that **5** and **6** are deprotonated by lithium phosphinomethanide under formation of **1a** and $HC(SiMe_3)_2PMe_2$, the latter indeed also being detected in the reaction mixture. Both **5** and **6** are identified spectroscopically. Whereas **5** could also be isolated in a pure state from the reaction mixture, **6** was isolated as a pure compound by addition of HCl to **5** (see under Experimental Section). The most prominent features of **5** and **6** are the PH functionalities, which are identified by a doublet splitting in the ^{31}P NMR spectrum of 458 and 484 Hz for **5** and **6**, respectively. In accord with these findings, proton NMR signals of the PH functionalities are found at $\delta = 5.17$ for **5** and $\delta = 4.44$ for **6**, both showing a doublet–septet multiplicity. The P phosphonium character in **5** and **6** is also evident from the {^{1}H}^{13}C NMR signals of the PMe_2 groups, which exhibit a doublet splitting of 55 and 53 Hz, respectively.

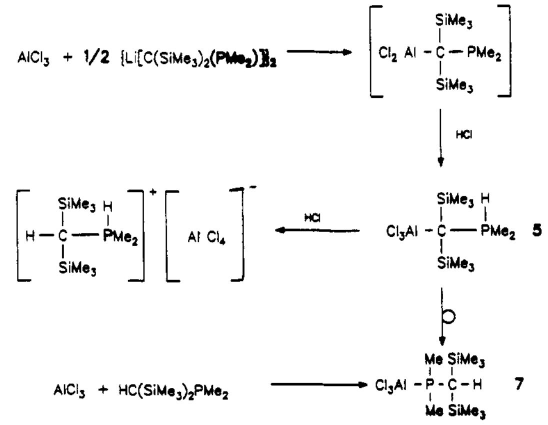
To our knowledge, PH-functionalized ylide complexes were not known prior to this work. In fact, also **5** is not indefinitely stable: within several days, it rearranges irreversibly in solution at room temperature to the tautomeric aluminum chloride phosphine complex **7**. Though without precedence, this rearrangement is formally related to other well-known diadic rearrangements of the type shown in eq 1.[18] The relative stability of **5** obviously is



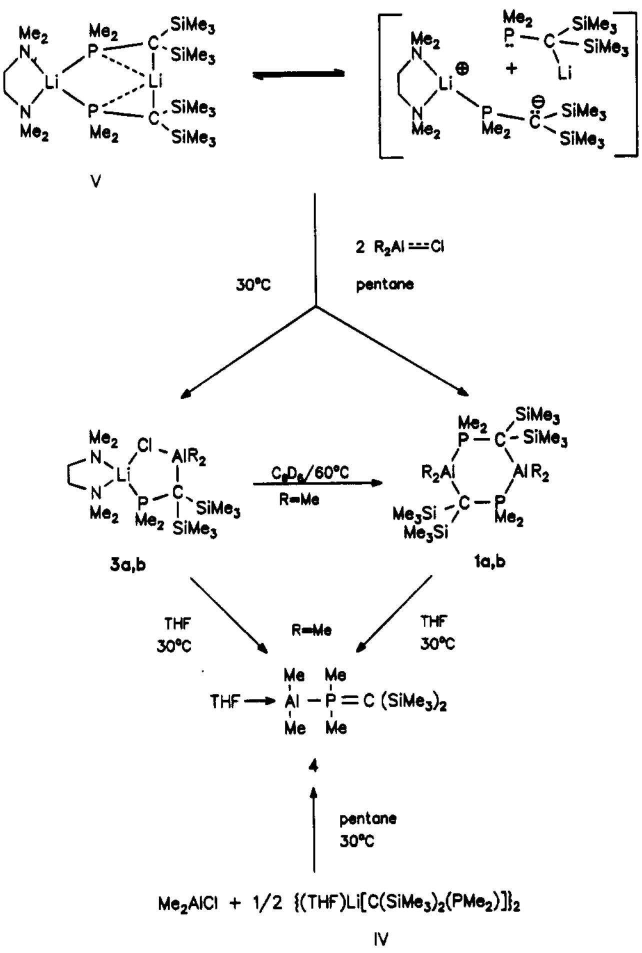
$$\underset{\displaystyle Y}{\overset{}{R_2\underset{|}{P}}}=CX_2 \rightleftharpoons R_2P-CYX_2 \qquad (1)$$

due to the two $SiMe_3$ groups, which effectively reduce the negative charge at the "carbanionic" C atom. Complex **7** is isolated in pure state from $AlCl_3$ and $HC(SiMe_3)_2(PMe_2)$ (Scheme II). Since the ^{31}P NMR signal of **7** appears at −33.19 as a broad single line, it hardly can be distinguished from the signal due to **1a**. Also the very broad ^{27}Al NMR resonances of **1a**, **5**, and **7** are not very diagnostic, and, therefore, ^{1}H and ^{13}C NMR spectra are indispensable for the identification and characterization of the compounds (see under Experimental Section).

Scheme II. Proposed Reaction Pathway for the Formation of 5–7



Scheme III. Reactions of R_2AlCl with {Li[C(SiMe$_3$)$_2$(PMe$_2$)]}$_2$ in the Presence of TMEDA and/or THF (a, R = Cl; b, R = Me)



II. Reaction in the Presence of Coligands. If $AlCl_3$ or Me_2AlCl in pentane are allowed to react with V instead of III, i.e., if $^1/_2$TMEDA for one aluminum chloride is present in the reaction mixture, the reaction takes a different course (Scheme III): besides **1a,b**, which also are found as in the coligand-free case (Scheme I), the novel five-membered heterocycles **3a,b** are obtained in high yields. Obviously, V dissociates in solution in a TMEDA-free lithium phosphinomethanide, the latter being responsible for the formation of **1a,b** as in Scheme I. The remainder may be regarded as a 1,3-dipole, which under cycloaddition to the unsaturated Al–Cl functionality forms the heterocycles **3a,b**. This kind of a formal [3 + 2] cycloaddition is thought to be a prototypal case for many inorganic substitution reactions, which rather should be regarded as addition/elimination processes. Indeed, **3b** easily is converted to the formal substitution product **1b** by gentle heating its solution under elimination of TMEDA·LiCl. **3a** is stable under these conditions, however, and decomposes only about ca. 140 °C to unidentified products. Both **3a** and **3b** are obtained quantitatively (without formation of **1a,b**), if a 1:1 mixture of V and TMEDA is used in the reaction with R_2AlCl (eq 2). With a 1:1 ratio of $AlCl_3$

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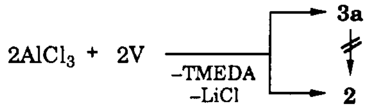
(18) Mastryukova, T. A.; Kabachnik, M. I. *Russ. Chem. Rev.* **1983**, *52*, 1012.

and V (instead of 2:1), **2** is obtained along with **3a** (eq 3) just as it is the case in the absence of TMEDA (Scheme I), whereas **3a** does *not* react with further V or (III) (eq 3). Since the **2**/**3** ratio (10:1) observed is much higher than

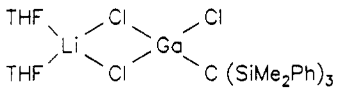
$$2R_2AlCl + V + TMEDA \longrightarrow 2\,\mathbf{3a,b} \qquad (2)$$



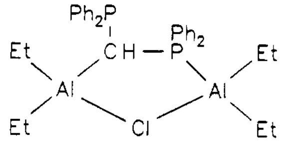
(3)

1:1 and keeping in mind that **1a** *does* react with further lithium phosphinomethanides to give **2** (Scheme I), we conclude that the reaction of the TMEDA-free Li[C$(SiMe_3)_2(PMe_2)$] monomer with $AlCl_3$ to give **1a** (or its monomeric analogue) is faster than that of the TMEDA-containing counterpart to give **3a**.

An X-ray structure determination of **3b** (Figure 2) confirms it to contain a spirocyclic lithium atom with chelating TMEDA and $\{Cl(Me)_2Al[C(SiMe_3)_2(PMe_2)]\}^-$ ligands, thus forming a five-membered ring. Alternatively, the fragment $Me_2Al[C(SiMe_3)_2(PMe_2)]$ may be regarded as a chelating ligand to TMEDA·LiCl. As is the case in lithium phosphinomethyl aluminates,[11a] aluminum binds to carbon and lithium to phosphorus. This can also be derived from the $\{^1H\}^{13}P$ NMR spectra of **3a**/**3b**, where a ^7Li–P coupling (**3a**, 74.5 Hz; **3b**, 69.5 Hz) is observed as a nonbinominal quartet splitting of the signals at low temperature (−60 °C). The five-membered heterocycle LiClAlCP with five different ring atoms adopts an envelope conformation in the solid state with the plane Cl, Al, C(1) forming a dihedral angle of 119.3° with the best plane through Cl, Li, P, and C(1). Surprisingly small angles are found at Li (93.6 (2)°) and, more strikingly, at Cl (94.5 (1)°). All other endocyclic angles are within expectations. The endocyclic bond distances, however, seem to be slightly elongated and approach the upper end of commonly accepted single-bond values. This follows also immediately from a comparison of the exocyclic and endocyclic Al–C and P–C bond lengths, as well as from the rather long Li–P distance (2.669 (7) Å), which exceeds most respective values in lithium phosphinomethanides. Particularly interesting is also the long P(1)–C(1) bond (1.843 (4) Å). It is this bond that in other phosphinomethanide complexes[3,4,6,7] still reflects some ylidic character by a significant shortening with respect to P–C single bonds. In the present case it is in the same range as P(1)–C(11)/C(12), however. The Li–Cl bond (2.369 (6) Å) is slightly shorter than Li–Cl in the comparable structure VII[19] (2.43 (3) Å), while Al–Cl (2.276 (2) Å) is longer than the terminal Al–Cl bond in **2** (2.195 (1) Å). The overall atom rearrangement also is closely related to that in VIII,[20] because the fragment $(R_3N)_2Li$ is an isovalence electronic counterpart of the fragment $(R_3C)_2Al$.[11a] In VIII, Al–Cl's are 2.273 (2) and 2.392 (2) Å, whereas the angle Al–Cl–Al (106.8(1)°) is expanded compared to Li–Cl–Al (94.5 (2)°) in **3b**.



VII[19]



VIII[20]

All other structural features of **3b** are within the range of expectation, which also holds for the (TMEDA)Li pentacycle.

The easy formation of **1b** from **3b** obviously is initiated by the loss of TMEDA·LiCl with subsequent dimerization of the $R_2AlC(SiMe_3)_2PMe_2$ monomer. This monomeric entity is stabilized in the presence of THF by its coordination to aluminum. The resulting compound **4**, obtained as a yellow oil, may be compared to **2** as it represents again an aluminum substituted P ylide. **4** is obtained not only by dissolving **3b** in THF but also from **1b** and THF and more directly by reacting IV with Me_2AlCl (Scheme III). Obviously, THF is a better donor to aluminum than TMEDA; whereas with lithium, the order is reversed. The constitution of **4** is evident from the NMR data, which are in accord with the expectations. Particularly diagnostic is the ^1J(PC) coupling constant of the PMe_2 groups (56.0 Hz; for uncoordinated PMe_2 groups, the coupling is much smaller).

In conclusion, novel heterocycles with a number of unusual features are obtained from lithium phosphinomethanides and R_2AlCl. These reactions demonstrate that addition/elimination reactions may dominate over simple substitution pathways and underline the determining role of coligands (or solvents) in these reactions. Furthermore, it is shown that the chemoselective combination of two electron-rich ligands at an electron-deficient metal center may promote otherwise unfavored reaction pathways and, once again, that the isovalence electronic count for $(R_3N)_2Li$ and $(R_3C)_2Al$ fragments results in comparable structures. Nevertheless, lithium and aluminum metal centers are distinguished by their different tendency to coordinate hard and soft donors, which decisively contributes to the reaction course and structures of the products. Finally, we believe that the above-mentioned findings may have some model character in organolithium reactivity in a quite general sense.

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Supplementary Material Available: Tables of additional crystal structure data, displacement parameters, and H atom coordinates (10 pages); tables of observed and calculated structure factor amplitudes (48 pages). Ordering information is given on any current masthead page.

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(19) Atwood, J. L.; Bott, S. G.; Hitchcock, P. B.; Eaborn, C.; Shariffudin, R. S.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Dalton Trans.* **1987**, 747.

(20) Schmidbaur, H.; Lauteschläger, S.; Müller, G. *J. Organomet. Chem.* **1985**, *281*, 23.