Novel Heterocycles: An Unexpected Facile Methylation of Aluminium by a Methyl-silane Functionality and Formation of a Novel Ylidic Heterocycle

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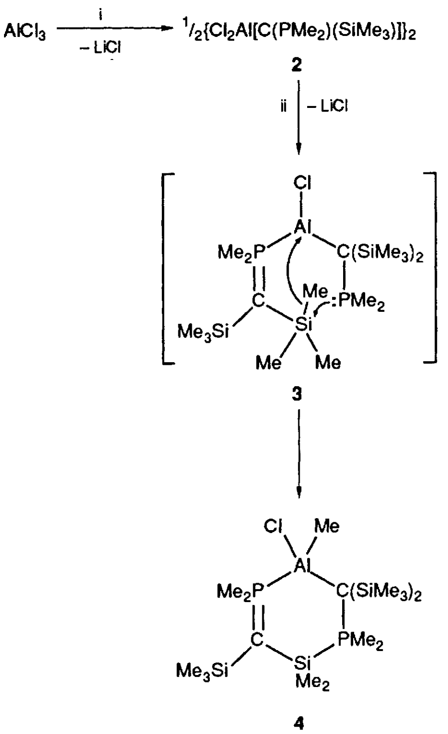
From $AlCl_3$ and $Li[C(PMe_2)(SiMe_3)_2]$ in a 1 : 2 stoichiometric ratio a novel heterocycle $(Me)(Cl)\overline{Al{-}C(SiMe_3)_2{-}PMe_2{-}SiMe_2{-}C(SiMe_3){-}P}Me_2$ **4**, exhibiting a number of unusual features, is obtained by methyl migration from silicon to aluminium.

Whereas the Me–Cl exchange between aluminium halides and methyl-silanes at elevated temperature is known,[1a] information concerning facile alkylation reactions under ambient conditions is lacking.[1b,c]

In the course of our investigations on the synthesis of novel heterocycles by the reaction of phosphinomethanides $[R_2PCR_2']^-$ with main group element halides,[2] we observed the formation of a methyl–aluminium bond during the reaction even at 20 °C. This Me–Al functionality is obviously derived from a trimethylsilyl group of the phosphinomethanide.

When $\{Li[C(PMe_2)(SiMe_3)_2]\}_2$ **1**[3] is allowed to react with $AlCl_3$ at 20 °C in toluene in a 1 : 1 stoichiometric ratio, colourless crystals of **4**[†] in 80% yield may be obtained *via* an intermediate **2**. Compound **2** is isolable when a 1 : 2 ratio is used (Scheme 1).

[†] **2** Colourless oil; **4** colourless crystals, m.p. 73–75 °C; *selected NMR data* [ppm referred to internal $SiMe_4$, external 85% H_3PO_4 and 10% $Al(NO_3)_3$ aqueous solution; C_6D_6, 20 °C]; **2**: δ PCH_3 1.03 (d; 6H, $X_6AA'X_6'$ spin system $N = 3.4$ Hz), δ $SiCH_3$ 0.05 (s, 18H), δ *P* −34.4 (s), δ *Al* 115 (s, br); **4**: δ PCH_3 0.94 (d, 9H, *J* 9.2 Hz), 1.31 (d, 3H, *J* 8.0 Hz), 1.46 (d, 3H, *J* 5.7 Hz), 1.55 (d, 3H, *J* 6.3 Hz); δ $SiCH_3$ 0.22 (s, 3H), 0.27 (s, 3H), 0.32 (s, 9H), 0.33 (s, 9H), 0.38 (s, 9H); δ $AlCH_3$ −0.10 (d, 3H, *J* 2.8 Hz), δ *P* −18.58 (d, *J* 28 Hz), −42.7 (s, br), δ *Al* 146 (s, br).



Scheme 1 Reaction of $AlCl_3$ with $\{Li[C(PMe_2)(SiMe_3)_2]\}_2$ **1**. i, **1** (0.5 equiv.), toluene, 20 °C, 1 h; ii, **1** (0.5 equiv.), pentane or toluene, 20 °C, 6 h)

Whereas the constitution of **2** has not yet been determined unambiguously, the structure of **4** as a novel heterocycle was established by X-ray crystallography (Fig. 1).‡

Five atoms [Al, P(2), C(2), Si(3), P(1)] of the six-membered ring lie roughly within a plane [max. deviation of an atom from the best plane: P(2) −0.24 Å], whereas the tetrahedral C(1) atom deviates by 0.75 Å from this plane. In contrast, C(2) is planar as expected for a *C*-silyl substituted phosphorus ylide and the P(2)–C(2) and C(2)–Si(3) bonds are significantly shortened. Consequently, **4** may be regarded as a first *P*-organoaluminium substituted phosphorus ylide. The P(2)–Al distance lies well within the normal single bond values.[4] Most noteworthy is the presence of a methyl group [C(10)] at the aluminium atom, which together with one chlorine atom and P(2) and C(1) constitutes the distorted tetrahedral environment of aluminium. The relative orientation of C(10) and Cl atoms with respect to the silyl groups at C(1) may be the outcome of steric requirements. The resultant inequivalence of the methyl and trimethylsilyl groups at P(1), P(2), Si(3) and C(1) respectively is also observed in the ^1H and ^{13}C NMR spectra at room temperature in solution. The Me–Al functionality is possibly formed *via* an intermediate **3** (Scheme 1) with subsequent methyl migration under the assistance of a neighbouring PMe_2 group. Both a pentacoordinate silicon and a tricoordinate aluminium centre in close proximity would thus be responsible for this unexpected facile methyl transfer from silicon to aluminium. As a consequence of this methyl group transfer, a slightly elongated P(1)–Si(3) bond is formed, representing a rare case of a silyl phosphonium moiety. In the light of the relatively short bond of Si(3) to the sp^2-C(2) atom it is tempting to interpret heterocycle **4** as a cyclic analogue of donor stabilized silenes, *e.g.* $Me_2Si{=}C(SiMe_3)(SiMeBu^t{}_2)\cdot(thf)$ (thf = tetrahydrofuran).[5] The angle between planes P(2)–C(2)–Si(4) and C(031)–Si(3)–C(032) is noticeably different from the corresponding one in the above mentioned donor stabilized silene, but this is obviously due to the ring constraints. Furthermore, it is consistent with an ylide formalism of the type $R^{1\pm}SiR_2{-}\overset{=}{\ddot{C}}X_2$,[5] or (better) $R_2R'\overset{+}{P}{-}\overset{=}{\ddot{C}}X{-}SiR_2{}^{\pm}R'$.

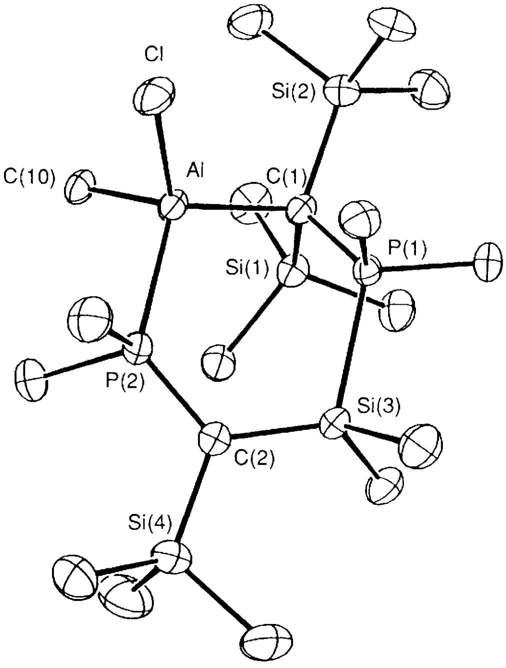


Fig. 1 Molecular structure of $(Me)(Cl)\overline{Al{-}C(SiMe_3)_2{-}PMe_2{-}SiMe_2{-}C(SiMe_3){-}P}Me_2$, **4**. Important bond distances (Å) and angles (°): Al–Cl 2.195(1), Al–C(10) 1.970(2), Al–C(1) 2.046(2), Al–P(2) 2.452(1), P(2)–C(2) 1.732(2), C(2)–Si(3) 1.791(2), C(2)–Si(4) 1.842(2), Si(3)–P(1) 2.329(1), P(1)–C(1) 1.795(2), C(1)–Al–P(2) 109.6(1), Al–P(2)–C(2) 122.2(1), P(2)–C(2)–Si(3) 122.3(1), C(2)–Si(3)–P(1) 110.3(1), Si(3)–P(1)–C(1) 120.8(1), P(1)–C(1)–Al 105.7(1).

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4 *Cf.* for instance: H. H. Karsch, A. Appelt, F. H. Köhler and G. Müller, *Organometallics*, 1985, **4**, 231; H. H. Karsch, A. Appelt and G. Müller, *Organometallics*, 1985, **4**, 1624.

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‡ *Crystal structure data*: $C_{18}H_{48}AlClP_2Si_4$, M_r = 501.309, triclinic, space group $P\bar{1}$ (No. 2), a = 9.161(1), b = 15.280(2), c = 11.832(1) Å, α = 109.62(1), β = 74.57(1), γ = 98.39(1)°, V = 1500.9 Å^3, Z = 2, D_c = 1.109 g cm^{-3}, μ(Mo-Kα) = 4.2 cm^{-1}, T = −50 °C. The structure was solved by direct methods and refined on 4841 unique observables with $F_o > 2.0\sigma(F)_o)$ to $R(wR)$ = 0.035 (0.044) [$w = 1/\sigma^2(F_o)$; anisotropic, Me as rigid groups, 283 refined parameters]. The residual electron density was featureless ($\Delta\rho_{fin}$ = +33/−0.29 e Å^{-3}). Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.