Novel Heterocycles: A Five Membered Ring Incorporating Five Different Elements, Formally Derived from an Inorganic [3+2] Cycloaddition

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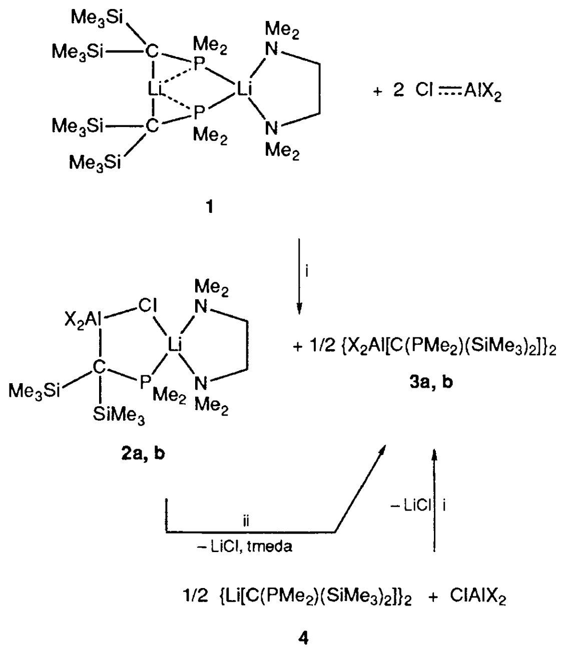
The novel five-membered heterocycles $(\text{tmeda})\overline{\text{Li-Cl-Al(X)}_2\text{-C(SiMe}_3)_2\text{-P}}\text{Me}_2$ (**2a**: X = Me, **2b**: X = Cl; tmeda = tetramethylethylenediamine), incorporating lithium chloride as a ring forming entity, are obtained from a formal 1,3 dipolar addition of $(\text{tmeda})\text{Li}[(\text{Me}_2\text{P})\text{C}(\text{SiMe}_3)_2]$ to an Al–Cl bond of $X_2\text{AlCl}$, as shown by an X-ray structure determination of **2a**.

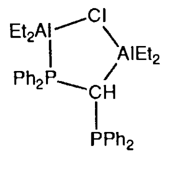
Ring formation by cycloaddition of unsaturated compounds is a common strategy in organic synthesis. In contrast examples in inorganic chemistry are much less frequent. The formation of rings with all ring members being different is even less frequently encountered, the incorporation of lithium chloride in organometallic heterocycles having not yet been described.

In substitution reactions of (organo)metal halides with ambidentate phosphinomethanides[1] as their lithium salts in ethereal solvents, yields of pure products occasionally are diminished owing to difficulties in removing the lithium salts from the product. However, well defined salt adducts could not be obtained either. We now report on such a substitution reaction, where an intact LiCl moiety is incorporated into a well defined heterocycle.

The reaction of $X_2\text{AlCl}$ (X = Me, Cl) with $\text{tmeda}\cdot\{\text{Li}[\text{C}(\text{PMe}_2)(\text{SiMe}_3)_2]\}_2$, **1**[2] results in the formation of two products



Scheme 1 Reaction of **1** and **4** with $ClAlX_2$ (**a**: X = Me; **b**: X = Cl): i, pentane, +25 °C; ii, X = Me, benzene, 60 °C



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2a,b and **3a,b**[3] respectively, according to Scheme 1.† Compound **2a** can be transformed to **3a** by heating, thus completing the substitution reaction, whereas **2b** is stable to salt elimination. Compounds **3a** and **b** are obtained in pure form starting from tmeda-free $\{Li[C(PMe_2)(SiMe_3)_2]\}_2$, **4**.[4] It appears therefore, that the completion of the Li coordination-sphere is essential for the stabilization of the heterocycles **2a,b**. The formation of **2a,b** also indicates that reactions of this kind do not follow simple substitution pathways, but rather may be regarded as an addition/elimination process. In this specific case, a 1,3 dipolar addition of the fragment (tmeda)Li-$[C(PMe_2)(SiMe_3)_2]$, generated from **1** by dissociation in solution to the unsaturated Cl–Al functionality as the 'en' component, seems to occur, as depicted in Scheme 1. The remainder, *i.e.* $Li[C(PMe_2)(SiMe_3)_2]$, is thought to react with X_2AlCl presumably in a similar manner, but the intermediate heterocycle formed is not stable and decomposes to **3a,b** by salt elimination in just the same way as is observed in the reaction of **4** with X_2AlCl. To our knowledge **2a,b** are the first examples where an alkali salt with an intact halogen–alkali metal bond is incorporated into a cyclic, isolable reaction intermediate which could be characterized structurally by X-ray diffraction, as in the case of **2a**‡ (Fig. 1). Quantitatively, and hence free of **3a,b**, the heterocycles **2a,b** are obtained by addition of the appropriate amount of tmeda to the mixtures in reaction (i) (Scheme 1).

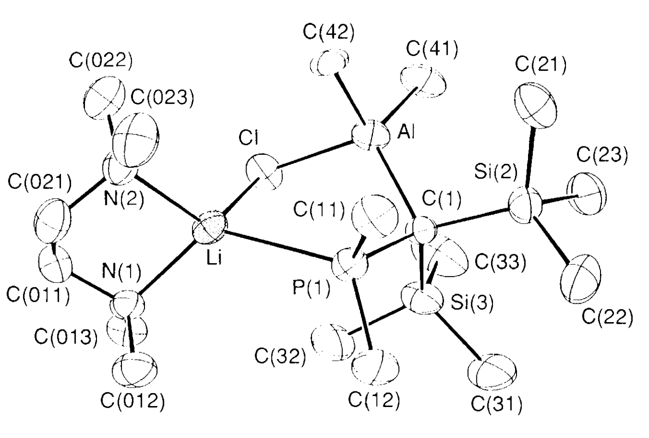

Fig. 1 Molecular structure of $\{tmeda\cdot\overline{Li\text{-}Cl\text{-}Al(Me)_2\text{-}C(SiMe_3)_2\text{-}P}\text{-}Me_2\}$, **2a** ORTEP (displacement ellipsoids at the 50% probability level; hydrogen atoms omitted); important bond distances (Å) and angles (°): Li–Cl 2.369(6), Al–Cl 2.276(2), Al–C(1) 2.047(4), P(1)–C(1) 1.843(4), Li–P(1) 2.669(7); Li–Cl–Al 94.5(1), Cl–Al–C(1) 105.4(1), Al–C(1)–P(1) 101.4(2), C(1)–P(1)–Li 108.0(2), P(1)–Li–Cl 93.6(2)

The lithium cation in **2a** acts as a spiro centre to the chelating moieties tmeda and $\{Cl(Me)_2Al[C(PMe_2)(SiMe_3)_2]\}^-$, thus forming two five-membered rings. Alternatively, the fragment $\{(Me)_2Al[C(PMe_2)(SiMe_3)_2]\}$ may be regarded as a chelating ligand to (tmeda)LiCl. The non-planar five membered ring $\overline{LiClAlCP}$§ with all ring members being different is comparable to the heterocycle **5**.[5] Since the LiN_2 fragment obeys an isovalence electronic relationship to the AlC_2 fragment, both **2a** and **5** should be comparable.

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† **2a**: Colourless crystals (from pentane), m.p. 98–100 °C; **2b**: colourless crystals (from toluene), m.p. 150–152 °C; **3a**: colourless crystals (from pentane), m.p. 110–112 °C. NMR data (ppm referred to internal $SiMe_4$, external 85% H_3PO_4 and 10% $Al(NO_3)_3$ aqueous solution; C_6D_6 or $C_6D_5CD_3$, +20 °C); **2a**: δ(P) −32.21 s(br) {−60 °C: −32.66 [q, ^1J(LiP) 69.5]}, δ(Al) 153.54s(br), δ(^{7}Li) +1.28s; δ(N*C*H_2) 56.62s, δN*C*H_3 45.64s, δ(P*C*H_3) 16.52 (d, *J* 7.8 Hz), δ(Si*C*H_3) 6.13 (d, *J* 3.7 Hz), δ(Al*C*H_3) − 0.46 s(br), δ(NC*H*$_2$) 1.86 (s, 4H), δ(NC*H*$_3$) 1.70 (s, 12H), δ(PC*H*$_3$) 1.34 (s, 6H), δ(SiC*H*$_3$) 0.51 (s, 18H), δ(AlC*H*$_3$) −0.09 (s, 6H); **2b**: δ(P) 33.07 s {−60 °C: −34.28 [q, ^1J(LiP) 74.5 Hz]}, δ(Al) 116.96s(br), δ(^{7}Li) +1.14s, δ(N*C*H_2) 57.24s, δ(N*C*H_3) 45.94s, δ(P*C*H_3) 16.63 (d, *J* 15.6 Hz), δ(Si*C*H_3) 5.29 (d, *J* 4.9 Hz), δ(NC*H*$_2$) 1.89 (s, 4H), δ(NC*H*$_3$) 1.74(s, 12H), δPC*H*$_3$ 1.55(d, 6H, *J* 1.8 Hz), δ(SiC*H*$_3$) 0.64 (s, 18H); **3a**: δ(P) −30.12s; δ(Al) 161.90s(br), δ(P*C*H_3) 15.53 (t, *N* 12.8 Hz), δ(Si*C*H_3) 8.15 s, δ(Al*C*H_3) −2.34s (br), δ(PC*H*$_3$) 1.28 (t, 6H, *N* 4.9 Hz), δ(SiC*H*$_3$) 0.32 (s, 18H), δ(AlC*H*$_3$) −0.25 (t, 6H, *N* 5.2 Hz).

‡ *Crystal structure data* for **2a**: Syntex $P2_1$ diffractometer, Mo-Kα radiation, $\lambda = 0.71069$ Å; graphite monochromator, $T = -35$ °C. $C_{17}H_{46}AlClLiN_2PSi_2$, $M = 435.09$, monoclinic space group $P2_1/n$ (No. 14) with $a = 8.915(1)$, $b = 18.887(2)$, $c = 16.558(2)$ Å, $\beta = 92.52(1)°$, $U = 2785.3$ Å^3, $D_c = 1.037$ g cm^{-3}, μ(Mo-Kα) = 3.1 cm^{-1}, $Z = 4$, $F(000) = 952$. 5400 Reflections were measured, 4903 of which were unique, and 3830 with $F_o \geqslant 4.0\,\sigma(F_o)$ 'observed' ($R_{int} = 0.026$) $(\sin\theta/\lambda)_{max} = 0.595$ Å^{-1}, *hkl*-range +10, +22, ±19, ω scans, Δω = 0.8°. Lorentz-polarisation corrections were applied, corrections for crystal decay (only statistical fluctuations in the net intensity of three periodically measured monitor reflections) and for absorption were not considered necessary. The structure was solved by direct methods (MULTAN87). The positions of 38 hydrogen atoms could be located in difference Fourier maps, the remainder were calculated at idealized geometrical positions. Refinement converged at $R(R_w) = 0.064$ (0.061), $w = 1/\sigma^2(F_o)$ for 268 refined parameters (anistropic, Me as rigid groups, other hydrogen atoms constant) (SHELX76). The residual electron density was +1.55/−0.43 e Å^{-3} with the maxima close to the heaviest atoms. Atomic coordinates, bond lengths and angles, thermal parameters, have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ The five-membered ring in **2a** shows an almost ideal envelope conformation, the envelope planes being Cl, Li, P(1), C(1) (torsions angle −1.5°) and Cl, Al, C(1). The respective dihedral angle is 119.3°.

In fact, this similarity holds for *d*[Al–C(1)] [in **5**: 2.047(4) Å], which is longer than *d*[Al–C(41)/(42)] [1.953(4)/2.994(4) Å] and, less convincing, for *d*(Al–Cl) [in **5**: 2.392(2) Å] and *d*[P(1)–C(1)] [in **5**: 1.811(4) Å]. This long P(1)–C(1) distance is at variance to the short P–C distances in lithium phosphinomethanides, *e.g.* **1**,[2] thus indicating, that no residual 'ylidic character' in this bond is preserved. In contrast to **5** [Al–Cl–Al: 106.8(1)°], the angle at the chlorine atom [94.5(2)°] approaches the 'p-only' value, which cannot be attributed merely to geometric constraints, since all the other interesting angles do not seem to be heavily distorted. In line with Pearson's concept[6] and with earlier findings in lithium phosphinomethyl aluminates[7] is the specific orientation of the phosphinomethanide moiety to the different metal centres in **2a:** it binds to Li *via* phosphorus and to Al *via* carbon. The Li–P distance [2.669(7) Å] is within the range encountered in lithium phosphinomethanide structures, as *e.g.*, in **1**.

The reactions of Scheme 1 underline the important role of coligands in lithium phosphinomethanide chemistry not only in their structural features,[8] but also in their reactivity. Furthermore, the formation, decomposition and structure of **2a** offer a rare case of a 'frozen' intermediate in substitution reactions and thus allow an insight into organometallic reactivity and pathways.

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References

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