Phosphine Complexes of Main Group Elements: $\mathrm{Al[C(PMe_2)_2X]_3}$ ($\mathrm{X = PMe_2}$ or $\mathrm{SiMe_3}$), the First Examples of Six-co-ordinate Aluminium Phosphine Complexes

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Neutral, homoleptic phosphinomethyl aluminium compounds $\mathrm{Al[C(PMe_2)_2X]_3}$ ($\mathrm{X = PMe_2}$ or $\mathrm{SiMe_3}$) have been synthesized and characterized as octahedral aluminium phosphine complexes by means of n.m.r. spectroscopy (^{1}H, ^{13}C, ^{31}P, and ^{27}Al).

Phosphinomethyl substituted compounds (A) are of rapidly growing interest, both in transition and main group element chemistry.[1] With aluminium as the co-ordination centre E and the $\mathrm{(CH_2PMe_2)^-}$ ligand [(A), X = Me, Cl, or $\mathrm{CH_2PMe_2}$, $n = 2, x = 1$], neutral, phosphinomethyl bridged dimers are formed by both C and P co-ordination.[2] Increasing the number of the methyl group substituents in (A), *e.g.* in going from $x = 1$ to 2[3] and 3 increases the steric bulk and decreases the nucleophilicity of the (formal) carbanion. Particularly in the latter case ($x = 3$), co-ordination of the carbon atom to the metal centre should be less likely, thus favouring P co-ordination. This argument led to a new concept for the preparation of main group element phosphine complexes,[4] which proved to be successful for the preparation of homoleptic tin(II) phosphine complexes, such as $\mathrm{Sn[C(PR_2)_3]_2}$.[5] If this is a general route to main group element phosphine complexes, a similar successful procedure should give rise to homoleptic phosphine complexes of aluminium, which possibly might exhibit an octahedral phosphine environment at the aluminium centre for the first time.

$$\mathrm{X}_n\mathrm{E[CH_{(3-x)}\,(PMe_2)_x]} \qquad (x = 1\text{—}3)$$

(A)

This, indeed, is the case. From the reaction of a mixture of $\mathrm{AlCl_3}$ with $\mathrm{Li[C(PMe_2)_3]}$[6] or $\mathrm{Li[C(PMe_2)_2SiMe_3]}$[7] (3 equiv.) and after removal of the tetrahydrofuran (thf) solvent, compounds (**1a**) and (**1b**) were obtained as colourless solids by pentane extraction and subsequent sublimation of the extractants [(**1a**): sublimation temperature 180 °C at 10^{-3} Torr; (**1b**): 175 °C at 10^{-3} Torr].[†]

$$\mathrm{AlCl_3 + 3\,Li[C(PMe_2)_2X]} \xrightarrow[-3\mathrm{LiCl}]{\mathrm{thf}} \mathrm{Al[(PMe_2)_2CX]_3}$$

(**1**)

a; X = $\mathrm{PMe_2}$
b; X = $\mathrm{SiMe_3}$

The most straightforward confirmation of the proposed octahedral structure of (**1a**) and (**1b**) is provided by their ^{27}Al n.m.r. spectra.[‡] Whereas tetrahedral phosphinomethyl aluminium compounds show only very broad ^{27}Al resonances because of their low symmetry at 170—150 p.p.m.,[2] much sharper resonances of octahedral aluminium complexes with a symmetrical environment are expected at a lower frequency (50—0 p.p.m.).[8] The signals for (**1a**) and (**1b**) both fall in the expected range for octahedral aluminium [(**1a**): 27.64; (**1b**): 35.14 p.p.m.]. In both cases, septets are observed at +100 °C (Figure 1), thus clearly indicating the octahedral environment, constituted by the six equivalent phosphorus atoms and with a one-bond ^{27}Al–^{31}P coupling being observed for the first time [(**1a**): ^1J(AlP) 97.7; (**1b**): 91.6 Hz]. The ^{31}P n.m.r. spectra confirm these findings. At −80 °C, (**1b**) shows a sharp singlet (−1.26 p.p.m.), whereas (**1a**) shows two singlets [$\delta(\mathrm{P_A})$ 2.27,

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[†] Satisfactory elemental analysis values were obtained for (**1a**) and (**1b**).

[‡] The n.m.r. spectra were recorded in the temperature range −90 to +100 °C; +ve δ values (p.p.m.) refer to low field, *J* values are in Hz: ^{1}H (60 MHz, $\mathrm{C_6D_5CD_3}$, +30 °C, $\mathrm{SiMe_4}$ ext.): (**1a**): $\delta(\mathrm{P_AMe})$ 1.40 (br. s) and 1.90 (br. s); δ $(\mathrm{P_BMe})$ 1.54 (d, $^2J_{\mathrm{PCH}}$ 3.2); (**1b**): δ(PMe) 1.45 (br. s) and 1.69 (br. s); δ (SiMe) 0.57 (s); ^{13}C (50.35 MHz, $\mathrm{C_6D_6}$, +30 °C, $\mathrm{SiMe_4}$ ext.): (**1a**): δ $(\mathrm{P_AMe})$ 20.51 (unsymmetrical m); $\delta(\mathrm{P_BMe})$ 18.26 (dt, $^1J_{\mathrm{PC}}$ 14.0, $^3J_{\mathrm{PCPC}}$ 1.7); $\delta(\mathrm{P_3C})$ 13.3 [td, $^1J(\mathrm{P_AC})$ 8.8, $^1J(\mathrm{P_BC})$ 1.5]; (**1b**): δ(PMe) 21.41 (br. s); $\delta(\mathrm{P_2CSi})$ 16.74 (t, $^1J_{\mathrm{PC}}$ 17.8) at −80 °C; δ(SiMe) 5.04 (s); ^{31}P (36.44 MHz, $\mathrm{C_6D_5CD_3}$, 85% $\mathrm{H_3PO_4}$ ext.): see text; ^{27}Al [52.115 MHz, $\mathrm{C_6D_5CD_3}$, $\mathrm{Al(NO_3)_3}$–$\mathrm{D_2O}$ ext.]: see text.

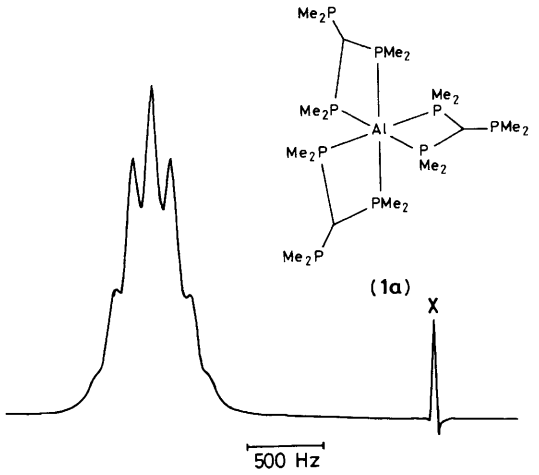

Figure 1. ^{27}Al N.m.r. spectrum of (**1a**); X is the reference signal.‡

$\delta(P_B)$ −45.31 p.p.m.] in a 2:1 ratio. On warming, the low-field signals, which are attributed to the co-ordinated phosphorus nuclei, broaden and finally, a complex, unresolved multiplet is observed in the temperature range −20 to +90 °C, due to coupling with ^{27}Al. In addition, the ^{1}H and ^{13}C n.m.r. data clearly indicate the anisochronic nature of the respective MeP nuclei due to the chelating function of the ligands in an octahedral co-ordination sphere.

From these and our previous[5] findings it emerges that anionic phosphine ligands are suitable for the preparation of homoleptic phosphine complexes in a general sense and that phosphinomethanides are the ligands of choice for the generation of high phosphine co-ordination numbers.

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