

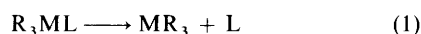
## Adducts of Trimethylaluminium with Phosphine Ligands; Electronic and Steric Effects

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Complexes of the type  $\text{Me}_3\text{AlPR}_2\text{R}'$  have been synthesised and studied by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  n.m.r. spectroscopy. The change in  $^{31}\text{P}$  chemical shift on co-ordination,  $\Delta(^{31}\text{P})$ , decreases, becoming more negative, with sterically bulkier phosphines and with increasing donor ability. The aluminium-methyl  $^{13}\text{C}$  resonance shifts downfield with increasing phosphine steric bulk, and with increased donor ability. Steric effects, however, are found to be the major factor contributing to the changes in both  $\Delta(^{31}\text{P})$  and methyl  $^{13}\text{C}$  chemical shifts.

Group 13 (Ölander numbering) trialkyls readily form adducts with donor molecules,<sup>1</sup> e.g. amines and phosphines. The stability of the adducts to dissociation (1) is an indication of



M = Al, Ga, or In

L =  $\text{OR}'_2$ ,  $\text{SR}'_2$ ,  $\text{NR}'_3$ , or  $\text{PR}'_3$

their chemical reactivity,<sup>2</sup> i.e. those that dissociate readily are more reactive towards nucleophiles. For a small number of these compounds gas-phase dissociation measurements or calorimetric determinations have provided information concerning their relative stabilities to dissociation.<sup>1</sup> These techniques, however, are inconvenient in the majority of cases, due to low volatility and/or a tendency of the compounds to undergo decomposition.

Previously reported n.m.r. studies<sup>3</sup> on trimethylgallium complexes with a variety of simple Group 15 and 16 ligands indicated a linear correlation between the  $^1\text{H}$  chemical shift of the  $\text{Ga-CH}_3$  protons and the experimentally determined heat of dissociation ( $\Delta H$ ) of the complex [equation (1)]. Furthermore, it was found that more stable adducts had a greater downfield shift of the methyl resonance when compared to that observed for unco-ordinated  $\text{GaMe}_3$ . More recently Bradley *et al.*<sup>4</sup> have reported that on co-ordination with amines the methyl proton resonance of  $\text{InMe}_3$  also shifts downfield. They found, however, that the more stable adducts had the greatest upfield shift, a result contrary to the  $\text{GaMe}_3$  study. In these and other studies<sup>5</sup> no systematic effort was made to separate electronic and steric effects.

Clearly the results of these early studies show that adduct stability alone cannot be the only factor influencing chemical shift. Therefore in order to gain a better understanding of what does influence the chemical shifts an extensive series of phosphine adducts of trimethylaluminium have been synthesised and studied by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  n.m.r. spectroscopy.

### Results and Discussion

A series of compounds  $\text{Me}_3\text{AlPR}_2\text{R}'$  (1)–(14), see Tables 1 and 2, have been prepared by reaction of the phosphine with  $\text{AlMe}_3$  [equation (2)]. Only  $\text{Me}_3\text{AlPMe}_3$  (1) and  $\text{Me}_3\text{AlPPh}_3$



(7) were reported previously.<sup>6,7</sup> The adducts are either white crystalline solids or viscous liquids at room temperature. All the

Table 1. Selected n.m.r. data for trimethylaluminium-phosphine complexes

Compound	$^1\text{H}$	$^{13}\text{C}$	$^{31}\text{P}$	$\Delta^a$
(1) $\text{Me}_3\text{AlPMe}_3$ <sup>b</sup>	-0.41	-9.73	-47.5	+12.5
(2) $\text{Me}_3\text{AlPMe}_2\text{Ph}$	-0.35	-8.87	-36.9	+10.1
(3) $\text{Me}_3\text{AlPEt}_3$	-0.15	-7.55	-17.0	+4.0
(4) $\text{Me}_3\text{AlP}(\text{CH}_2\text{CH}_2\text{CN})_3$	-0.16	-7.80	-19.5	+3.5
(5) $\text{Me}_3\text{AlPMePh}_2$	-0.22	-8.28	-24.2	+3.9
(6) $\text{Me}_3\text{AlP}(\text{C}_6\text{H}_4\text{Me-}i>p)_3$	-0.02	-7.29	-9.5	-1.5
(7) $\text{Me}_3\text{AlPPh}_3$ <sup>c</sup>	-0.09	-7.39	-7.3	-1.4
(8) $\text{Me}_3\text{AlP}(\text{C}_6\text{H}_4\text{F-}i>p)_3$	-0.14	-7.46	-10.2	-1.2
(9) $\text{Me}_3\text{AlPPh}_2(\text{C}_6\text{H}_{11})$	-0.07	-6.50	-6.6	-2.2
(10) $\text{Me}_3\text{AlPPh}(\text{C}_6\text{H}_{11})_2$	-0.12	-6.25	-12.0	-9.5
(11) $\text{Me}_3\text{AlP}(\text{CH}_2\text{Ph})_3$	-0.28	-7.67	-15.5	-3.5
(12) $\text{Me}_3\text{AlP}(\text{C}_6\text{H}_{11})_3$	-0.19	-5.69	-3.7	-13.1
(13) $\text{Me}_3\text{AlPBu}^i_3$	-0.17	-3.25	41.4	-20.5
(14) $\text{Me}_3\text{AlP}(\text{C}_6\text{H}_4\text{Me-}i>o)_3$	-0.31	-6.68	-22.5	+7.7

<sup>a</sup>  $\Delta = \delta(^{31}\text{P})_{\text{complex}} - \delta(^{31}\text{P})_{\text{free phosphine}}$ . <sup>b</sup> See ref. 6. <sup>c</sup> See ref. 7.

compounds are soluble in organic solvents and are moisture-sensitive. The liquid compounds decompose rapidly in air, but under similar conditions the solid ones remain stable for several hours.

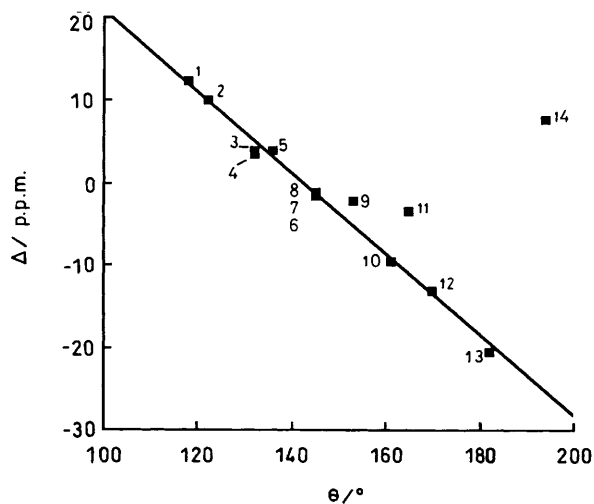
Tertiary phosphines have been well characterised in terms of their steric and electronic influence in transition-metal complexes,<sup>8</sup> although comparable studies have not been undertaken for main-group organometallics. In transition-metal complexes, phosphine steric factors have been calibrated in terms of the ligand cone angle,  $\theta$ .<sup>9</sup> A variety of electronic parameters<sup>10</sup> have been used as an indication of Lewis basicity. For instance, the frequency ( $\nu$ ) of the  $A_1$  carbonyl stretching mode in  $\text{Ni}(\text{CO})_3\text{L}$  has been used.<sup>10b</sup> Both  $\theta$  and  $\nu$  have been tabulated for a wide variety of phosphines by Tolman.<sup>8</sup> Because of the ready availability of the  $\theta$  and  $\nu$  values, and their successful use in the transition-metal systems, they were used in the present study as the steric ( $\theta$ ) and electronic ( $\nu$ ) parameters for the phosphine ligands.

*Effects on Phosphorus.*—The electronegativity of the substituents, R, on phosphorus and the angle between them, R–P–R, are the two most important contributions in determining the  $^{31}\text{P}$  chemical shift ( $\delta$ ).<sup>11</sup> For complexes the co-ordination chemical shift,<sup>12</sup>  $\Delta = \delta_{\text{complex}} - \delta_{\text{free}}$ , will depend on the metal moiety, in this case  $\text{AlMe}_3$ , a constant, and on the change in R–P–R angles on co-ordination. In transition-metal complexes, angle opening correlates with a downfield shift

**Table 2.** Analytical data for all new compounds

Compound	M.p. <sup>a</sup> °C	B.p. <sup>b</sup> °C	Analysis (%) <sup>c</sup>	
			C	H
(2) Me <sub>3</sub> AlPMe <sub>2</sub> Ph		84	62.8 (62.9)	9.5 (9.5)
(3) Me <sub>3</sub> AlPEt <sub>3</sub>		68	57.0 (56.8)	12.5 (12.6)
(4) Me <sub>3</sub> AlP(CH <sub>2</sub> CH <sub>2</sub> CN) <sub>3</sub>		73	54.3 (54.3)	8.0 (7.9)
(5) Me <sub>3</sub> AlPMePh <sub>2</sub>		123	70.7 (70.6)	8.0 (8.1)
(6) Me <sub>3</sub> AlP(C <sub>6</sub> H <sub>4</sub> Me- <i>p</i> ) <sub>3</sub>	110		76.5 (76.6)	8.0 (8.0)
(8) Me <sub>3</sub> AlP(C <sub>6</sub> H <sub>4</sub> F- <i>p</i> ) <sub>3</sub>	100–103		71.8 (72.0)	6.0 (6.0)
(9) Me <sub>3</sub> AlPPh <sub>2</sub> (C <sub>6</sub> H <sub>11</sub> )		181	(74.1)	(8.8)
(10) Me <sub>3</sub> AlPPh(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub>		193	72.9 (72.8)	10.3 (10.4)
(11) Me <sub>3</sub> AlP(CH <sub>2</sub> Ph) <sub>3</sub>	92–93		76.3 (76.6)	7.9 (8.0)
(12) Me <sub>3</sub> AlP(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub>	104		72.3 (72.2)	12.0 (12.0)
(13) Me <sub>3</sub> AlPBu <sub>3</sub>	148–151		65.9 (65.7)	13.0 (13.1)
(14) Me <sub>3</sub> AlP(C <sub>6</sub> H <sub>4</sub> Me- <i>o</i> ) <sub>3</sub>	118		76.3 (76.6)	8.0 (8.0)

<sup>a</sup> Melting with decomposition. <sup>b</sup> At 0.04 mmHg. <sup>c</sup> Required values in parentheses.

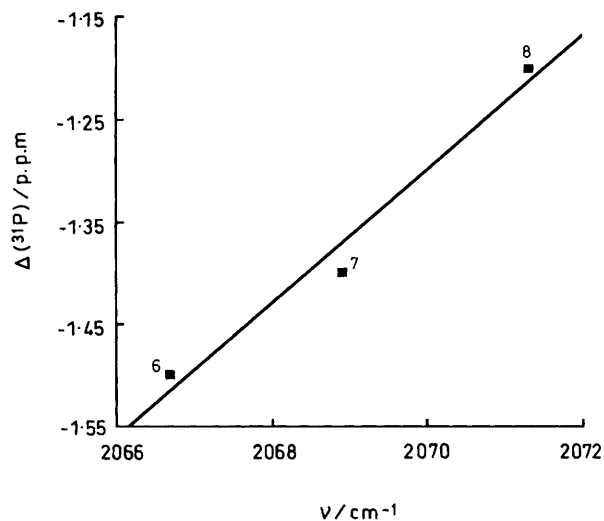


**Figure 1.** Phosphorus-31 co-ordinate chemical shift ( $\Delta$ ) as a function of phosphine cone angle ( $\theta$ ):  $\Delta = 69.84 - 0.49\theta$ ,  $R = 0.99$

(positive  $\Delta$ ); therefore, it is assumed that downfield shifts will correlate with larger R–P–R angles in these aluminium complexes.

The variation of  $\Delta(^{31}\text{P})$  (the difference in shift between the free phosphine and its  $\text{AlMe}_3$  complex) with cone angle ( $\theta$ ) for  $\text{Me}_3\text{AlPR}_2\text{R}'$  is linear (Figure 1).<sup>\*</sup> For those ligands with a cone angle  $\theta < 142^\circ$ ,  $\Delta$  is negative, and therefore R–P–R must be opened with respect to the free phosphine. By the same reasoning, the plot shows that those phosphines with  $\theta > 142^\circ$

<sup>\*</sup> The numbering of the points in all the figures corresponds to that in Table 1.



**Figure 2.**  $\Delta(^{31}\text{P})$  as a function of the electronic parameter ( $\nu$ ) for the complexes  $\text{Me}_3\text{AlP}(\text{C}_6\text{H}_4\text{X-}i>p)_3$ , where X = Me, H, or F:  $\Delta = -136.9 + 0.066\nu$ ,  $R = 0.99$

must have a more acute R–P–R angle on co-ordination. This is presumably due to steric repulsion involving the aluminium methyl groups. The  $\Delta$  values are much smaller than those generally found for transition-metal fragments.

The complexes  $\text{Me}_3\text{AlP}(\text{CH}_2\text{Ph})_3$  (11) and  $\text{Me}_3\text{AlP}(\text{C}_6\text{H}_4\text{-Me-}i>o)_3$  (14) do not fit the trend closely. These exceptions are discussed in a separate section (see below).

A trend consistent with increasing steric interaction, and therefore greater change in R–P–R angle (more negative  $\Delta$ ), with increased donor ability (smaller  $\nu$ ) is observed for the sterically equivalent phosphines  $\text{P}(\text{C}_6\text{H}_4\text{X-}i>p)_3$ , X = Me (6), H (7), F (8) (Figure 2). This suggests that the stronger donors produce shorter P–Al bond lengths, thereby increasing steric repulsion between the substituents on phosphorus and the methyl groups on aluminium. It should be noted, however, that the variation of  $\Delta$  with  $\nu$  is small compared to that observed where there are large differences in steric repulsion.

*Effects on the Trimethylaluminium.*—Although it would be desirable to use the  $^{27}\text{Al}$  n.m.r. chemical shifts of the adducts as a probe to their structure, the insensitivity of such shifts to substitution<sup>13</sup> and the large linewidths observed (1 000–3 000 Hz)<sup>14</sup> make meaningful comparisons exceptionally difficult.

In previous studies<sup>3</sup> the  $^1\text{H}$  n.m.r. shift of the Group 13 metal methyl group has been used as an indication of bond strength. As shown in the previous section the major contribution to  $\Delta(^{31}\text{P})$  is steric. Presumably steric effects will dominate the methyl  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts as well. Indeed, an increase in phosphine cone angle is concurrent with a downfield shift in the  $\text{Al-CH}_3$   $^1\text{H}$  n.m.r. resonance, Figure 3. This trend breaks down for phosphine cone angles  $> 150^\circ$  where an upfield trend is observed. This latter trend can be explained by taking into account shielding of the aluminium methyl groups by the most bulky ligands. Such shielding, however, should not affect the methyl  $^{13}\text{C}$  shifts. This is evident from Figure 4, where  $\theta$  is plotted versus methyl  $^{13}\text{C}$  chemical shift.

As shown in Figure 4, a linear correlation is found between  $\theta$  and the  $^{13}\text{C}$  chemical shift of the aluminium-methyl carbons. The larger the cone angle the more downfield is the shift, with complexes of  $\text{P}(\text{CH}_2\text{Ph})_3$  and  $\text{P}(\text{C}_6\text{H}_4\text{-Me-}i>o)_3$  again being the exceptions to the trend. As with  $\Delta(^{31}\text{P})$ , an indication of the extent of electronic effects on the  $\text{Al-CH}_3$  groups can be probed

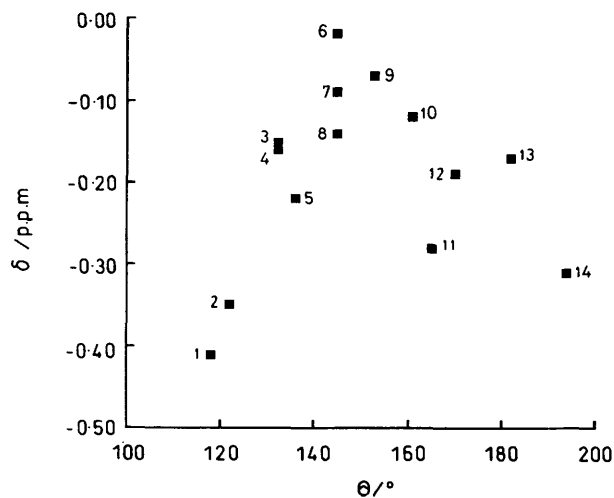


Figure 3. Aluminium methyl  $^1\text{H}$  n.m.r. shift ( $\delta$ ) as a function of phosphine cone angle ( $\theta$ ) for a series of compounds  $\text{Me}_3\text{AlPR}'_2$

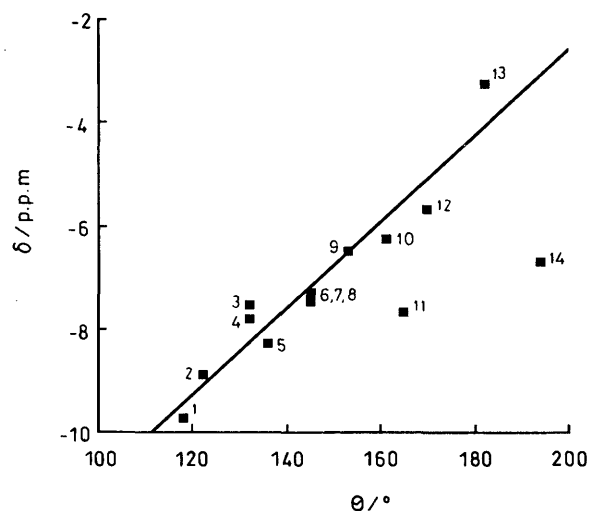


Figure 4. Aluminium methyl  $^{13}\text{C}$  n.m.r. shift ( $\delta$ ) as a function of phosphine cone angle ( $\theta$ ):  $\delta = -19.29 + 0.084\theta$ ,  $R = 0.96$

by choosing phosphines with equivalent cone angles, *i.e.* the *para*-substituted triarylphosphine complexes (6)–(8). The linear correlation observed in Figure 5 indicates a downfield shift for the better donor ligands. This is in agreement with the results found for  $\text{Me}_3\text{Ga}\cdot\text{L}$  complexes ( $\text{L} = \text{OMe}_2$ ,  $\text{SMe}_2$ ,  $\text{NMe}_3$ , or  $\text{PMe}_3$ ).<sup>3</sup>

*The Exceptions: P(CH<sub>2</sub>Ph)<sub>3</sub> and P(C<sub>6</sub>H<sub>4</sub>Me-*o*)<sub>3</sub>.*—Complexes of  $\text{P}(\text{CH}_2\text{Ph})_3$  and  $\text{P}(\text{C}_6\text{H}_4\text{Me-}o)_3$  are exceptions to the trends found for  $\Delta(^{31}\text{P})$ , and the  $^{13}\text{C}$  shift of the Al-CH<sub>3</sub> groups, Figures 1 and 4 respectively. From the  $\Delta(^{31}\text{P})$  shift it would appear that the R-P-R angles in  $\text{P}(\text{CH}_2\text{Ph})_3$  are closed far less on co-ordination than its calculated cone angle (165°)<sup>15</sup> would suggest that it should be. Indeed an effective cone angle of *ca.* 142° can be estimated from Figure 4. Tolman *et al.*<sup>16</sup> have shown that under steric strain the cone angle of phosphines and phosphites with large internal degrees of freedom can decrease. Thus, the apparent reduction in cone angle for  $\text{P}(\text{CH}_2\text{Ph})_3$  in (11) can be explained as being a consequence of the benzyl groups adopting a conformation that limits the steric repulsion with the aluminium methyl groups.

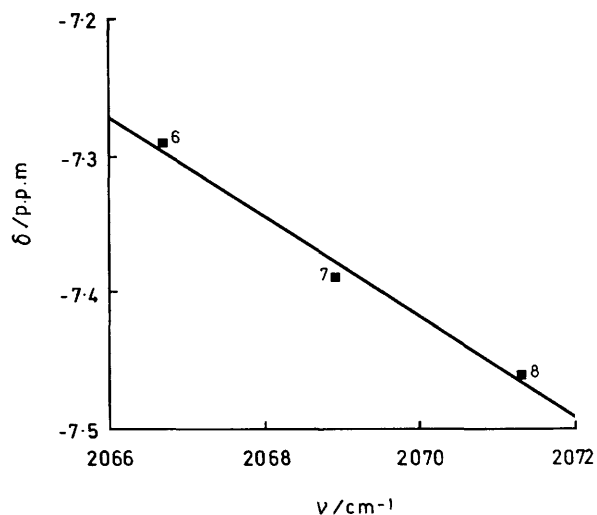


Figure 5. Aluminium methyl  $^{13}\text{C}$  n.m.r. shift ( $\delta$ ) as a function of phosphine electronic parameter ( $\nu$ ) for the complexes  $\text{Me}_3\text{AlP}(\text{C}_6\text{H}_4\text{X-}p)_3$ , where X = Me, H, or F:  $\delta = 68.83 - 0.037\nu$ ,  $R = 0.99$

The  $\Delta(^{31}\text{P})$  value for  $\text{Me}_3\text{AlP}(\text{C}_6\text{H}_4\text{Me-}o)_3$  indicates a larger R-P-R angle on co-ordination than in free phosphine. A possible explanation for the larger (more positive) than expected  $\Delta$  value for  $\text{P}(\text{C}_6\text{H}_4\text{Me-}o)_3$  is as follows: in calculating the cone angle for  $\text{P}(\text{C}_6\text{H}_4\text{Me-}o)_3$  (194°)<sup>8</sup> it was assumed that the methyl groups would point away from each other, *i.e.* *out*. Such a conformation would result in a larger steric interaction on co-ordination to  $\text{AlMe}_3$ , and consequently a decrease in the R-P-R angle. In the solid state the phenyl rings of  $\text{Me}_3\text{AlPPh}_3$ <sup>17</sup> are staggered with respect to the aluminium methyl groups. In order for the tolyl rings to pack in a similar way, and to relieve steric strain, it is probable that one or more of the tolyl-methyl groups point towards the tolyl rings, *i.e.* *in*. These conformations would require the R-P-R angle to increase in comparison to the free (*out*) value due to the steric interaction between the rings and the *o*-methyl groups. Unfortunately crystals of compound (14) were twinned and were not suitable for X-ray crystallographic study.

*Steric versus Electronic Effects.*—For transition-metal phosphine complexes, Tolman<sup>8</sup> has proposed a method to summarise data that depends on both electronic and steric factors. A parameter  $Z$ , which is dependent on both electronic,  $\nu$ , and steric factors,  $\theta$ , can be described by a plane according to equation (3). Applying this equation for the shift of the methyl

$$Z = a\nu + b\theta + c \quad (3)$$

carbons, Figures 3 and 5, values for  $a$ ,  $b$ , and  $c$  can be determined, equation (4):\* these values for  $a$ ,  $b$ , and  $c$  give good

$$Z(\delta^{13}\text{C}) = 0.037\nu + 0.084\theta - 96.24 \quad (4)$$

agreement between predicted and experimental  $\delta$  values. In addition, by use of equation (5), it is possible to estimate the percentage of steric character involved in determining the shifts of the Al-CH<sub>3</sub> carbons as approximately 70%.<sup>8</sup>

$$\% \text{ Steric character} = 100[a/(a + b)] \quad (5)$$

\* The straight lines drawn in Figures 1 and 4 do not include compounds (11) and (14).

Considering only electronic factors, one would predict that strong Lewis bases should give strong Al-P interactions. This would result in large downfield shifts due to an increase in  $p$  character in the Al-C bond in going from planar  $sp^2$  to tetrahedral  $sp^3$ , i.e. the stronger the Al-P bond the more tetrahedral the aluminium centre will become. A similar argument can be used for the change in  $^1\text{H}$  n.m.r. shifts.

Because of steric repulsion, one would expect the largest ligands to have the weakest Al-P interactions and therefore the smallest changes in the methyl  $^{13}\text{C}$  shifts. In this study the opposite has found to be true. In order to explain this it must be assumed that the bulkier phosphines force the aluminium to become more distorted from planarity, due to steric repulsion. The Al-CH<sub>3</sub> carbon resonance would then be moved downfield because of increased  $p$  character in the Al-C bond.

The  $\Delta(^{31}\text{P})$  value can be related to the steric and electronic factors of the phosphine in the same way that the Al-CH<sub>3</sub>  $^{13}\text{C}$  shifts have been treated. By use of the data from Figures 1 and 2, equation (6) can be written.

$$\Delta(^{31}\text{P}) = 0.066v - 0.4900 - 42.18 \quad (6)$$

The percentage of steric character involved in determining the change in shift on co-ordination for a given phosphine is approximately 90%. With increased cone angle, a greater steric repulsion would be expected between the Al-CH<sub>3</sub> groups and the substituent (R) on phosphorus. Such an increase would force the R-P-R angle to decrease resulting in a more negative  $\Delta$ . This trend is indeed observed.

## Conclusions

It has been shown that the dominant factor influencing chemical shifts in  $\text{Me}_3\text{AlPR}_2\text{R}'$  complexes is steric repulsion between the aluminium-methyl groups and the phosphine substituents. Indeed, even for the sterically equivalent phosphines,  $\text{P}(\text{C}_6\text{H}_4\text{X}-p)_3$  (X = F, H, or Me), adduct chemical shifts correlated with a secondary steric effect. It is only when steric factors and donor ability coincide that chemical shifts and adduct stability correlate, therefore chemical shifts should *not* be used as an indication of adduct stability or reactivity.

The changes in  $^{13}\text{C}$  chemical shift of the Al-CH<sub>3</sub> groups may be used, however, as a good indication of the distortion from planarity of aluminium.\* Crystallographic evidence in support of this is at present sparse, although Bradley *et al.*<sup>4</sup> have demonstrated that increasing the steric bulk of amines bound to trimethylindium results not only in an increased In-N bond distance, and a concomitant reduction in bond strength, but also a greater distortion from planarity for indium, as compared to sterically less hindering amines.

The change in  $^{31}\text{P}$  chemical shift of phosphines on co-ordination to  $\text{AlMe}_3$  correlates closely to the steric bulk of the phosphine. From the n.m.r. results, presented above, a significant increase in R-P-R angle would be predicted for  $\text{PMe}_3$  on co-ordination to  $\text{AlMe}_3$ . An increase of *ca.* 5° is indeed observed by gas-phase electron diffraction.<sup>18</sup> A comparison of the X-ray crystallographically determined geometry around phosphorus for  $\text{Me}_3\text{AlPPh}_3$ <sup>17</sup> and  $\text{PPh}_3$ <sup>19</sup> shows only minimum variation in R-P-R angles, again consistent with solution n.m.r. results. No structures of bulkier phosphines complexes have yet been reported.

## Experimental

All operations were performed under an atmosphere of purified nitrogen using Schlenk-style apparatus and a glove-box. Solvents were distilled and degassed before use. The compounds  $\text{AlMe}_3$  (in hexane),  $\text{PPh}_3$ , and  $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$  were obtained from commercial sources; all other phosphines,<sup>20</sup>  $\text{Me}_3\text{AlPMe}_3$ ,<sup>6</sup> and  $\text{Me}_3\text{AlPPh}_3$ <sup>7</sup> were prepared by literature methods. Microanalyses were by Multichem Laboratories (MA). Melting points were determined in sealed capillaries and are uncorrected.

Physical and analytical data are given in Table 2.

N.m.r. spectra (in  $\text{C}_6\text{D}_6$ ) were recorded on a Bruker AM-250 ( $^1\text{H}$  and  $^{13}\text{C}$ ) or WM-300 ( $^{31}\text{P}$ ) spectrometer;  $\delta$  in p.p.m. relative to  $\text{SiMe}_4$  ( $^1\text{H}$  and  $^{13}\text{C}$ ) or external 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ). N.m.r. shifts given are the average for three or more samples of various concentrations. Selected n.m.r. data are given in Table 1.

All phosphine adducts were prepared by the addition of a hexane solution of trimethylaluminium (5 cm<sup>3</sup>, 10 mmol) to benzene solutions (25 cm<sup>3</sup>) of the appropriate phosphine (10 mmol). After stirring for 6 h the solvent was removed and the resulting compound purified by distillation under vacuum [0.04 mmHg, *ca.* 5.32 Pa; compounds (2)–(5), (9), and (10)] or recrystallisation from pentane [–20 °C; compounds (1), (6)–(8), and (11)–(14)].

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\* It should be noted that trimethylaluminium is dimeric in solution therefore the data presented here are relative to each other and not to trigonal planar trimethylaluminium, which is only present in the gas phase.