Synthesis and Characterization of New Phosphanylium and Phosphanetriylammonium Salts. Molecular Structures of $[(Me_2N)PN(AlCl_3)R]$ and $[P(NPr^i_2)(NHR)]^+[CF_3SO_3]^-$ ($R = C_6H_2Bu^t_3$-2,4,6)†

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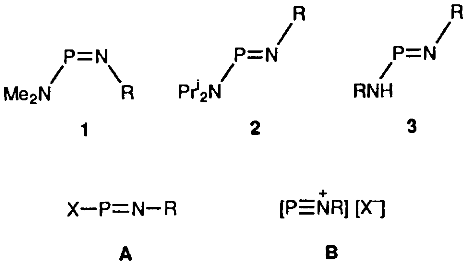
The new internal salts $[(R^1R^2N)PN(ECl_3)R]$ (E = Al or Ga; R = 2,4,6-$Bu^t_3C_6H_2$) and phosphanylium salts $[P(NR^1R^2)(NHR)]^+[CF_3SO_3]^-$ have been synthesized by treating aminoiminophosphanes $(R^1R^2N)P{=}NR$ with $AlCl_3$, $GaCl_3$ or CF_3SO_3H. Protonation of RHN–P=NR with trifluoromethanesulfonic acid led to the first stable phosphanylium salt $[P(NHR)_2]^+[CF_3SO_3]^-$ with two primary amino groups. In contrast, the reaction of $AlCl_3$ with the (aryloxy)iminophosphane $(R'O)P{=}NR$ (R' = 4-Me-2,6-$Bu^t_2C_6H_2$) led to the new aryl(phosphanetriyl)ammonium complex $[PNR]^+[(R'O)AlCl_3]^-$. All compounds were characterized by multinuclear NMR spectroscopy. The crystal structures of $[(Me_2N)PN(AlCl_3)R]$ and $[P(NPr^i_2)(NHR)]^+[CF_3SO_3]^-$ have been determined by single-crystal X-ray diffractometry.

In 1976 Niecke and Kroher[1] showed that electrophilic attack of $AlCl_3$ on the P=N double bond of the aminoiminophosphane R_2N–P=NR (R = Me_3Si) generates the internal salt R_2N–P^+–$N(AlCl_3^-)R$. Since that time the reactions of iminophosphanes with Lewis acids have been considered as a promising synthetic pathway to phosphanylium species.[2] Nevertheless, contrary to the synthesis of the phosphanylium cations $[P(NR_2)_2]^+$ *via* $AlCl_3$-promoted halide abstraction from chlorophosphine precursors, the literature contains very few examples of the reaction of iminophosphanes and Lewis acids.[3] Furthermore, it was recently reported[4] that reaction of the chloroiminophosphane $ClP{=}NC_6H_2Bu^t_3$-2,4,6 with $AlCl_3$ leads to the stable salt $[PNC_6H_2Bu^t_3\text{-}2,4,6]^+[AlCl_4]^-$ instead of the expected phosphanylium adduct, ClP^+–$N(AlCl_3^-)C_6H_2Bu^t_3$-2,4,6. Previously both we[5] and Niecke and co-workers[6] have shown that the structure and the reactivity of the iminophosphanes $XP{=}NC_6H_2Bu^t_3$-2,4,6 are considerably dependent on the substituent X bonded to the two-co-ordinated phosphorus. Thus, according to the size of the dialkylamino group in aminoiminophosphanes $(R_2N)P{=}NC_6H_2Bu^t_3$-2,4,6, *cis* (*Z*) **1** or *trans* (*E*) isomers **2**, **3** (R = $C_6H_2Bu^t_3$-2,4,6) are thermodynamically stable. In a *cis* configuration the s character of the phosphorus–nitrogen multiple bond is more pronounced than in the *trans* configuration.

The bonding situation within the central skeleton X–P=N is also strongly influenced by the electronic properties of the substituent X. In particular, we demonstrated[7] that the (aryloxy)iminophosphane $(R'O)P{=}NC_6H_2Bu^t_3$-2,4,6 (R' = 2,6-di-*tert*-butyl-4-methylphenyl) contains a very short phosphorus–nitrogen double bond (1.50 Å) and an almost linear configuration of the P–N–C unit (173.7°) which probably results from the considerable contribution of the canonical form $[R'O]^-[P{=}NC_6H_2Bu^t_3\text{-}2,4,6]^+$. The latter assumption was confirmed by the observations that an increase in the electronegativity of the R'O group in the compounds $(R'O)P{=}NC_6H_2Bu^t_3$-2,4,6 leads from structures with a covalent P–O bond to those where the $[R'O]^-$ anion is separated from the cationic fragment $[PNC_6H_2Bu^t_3\text{-}2,4,6]^+$.[8]



1 **2** **3**

A **B**

In the light of these findings it was of interest to study the influence of structural changes around the P=N double bond in aminoiminophosphanes $(R_2N)P{=}NC_6H_2Bu^t_3$-2,4,6 and (aryloxy)iminophosphanes $(R'O)P{=}NC_6H_2Bu^t_3$-2,4,6 on the reactivity of these species towards Lewis acids. It can be expected that, depending on the structural peculiarities, the above compounds react with electron-deficient molecules either in their 'classical' $(p\text{–}p)_\pi$ bond form **A** or as the highly polarized species **B** containing a formally triple phosphorus–nitrogen bond. This paper reports our results concerning the reactions of aminoiminophosphanes **1**–**3** and the (aryloxy)iminophosphane $(R'O)P{=}NC_6H_2Bu^t_3$-2,4,6 with $AlCl_3$ and $GaCl_3$. In addition we have studied the reaction of $(R'_2N)P{=}NC_6H_2Bu^t_3$-2,4,6 with trifluoromethanesulfonic acid leading to new stable phosphanylium derivatives.

Results and Discussion

Reactions of Aminoiminophosphanes **1**–**3** *with Lewis Acids* ($AlCl_3$, $GaCl_3$).—Reaction of the *cis*-aminoiminophosphane **1** with 1 equivalent of $AlCl_3$ in toluene at 0 °C leads to a colourless solid, which shows a low-field phosphorus chemical shift [$\delta(^{31}P)$ 268] compared with that of the starting compound [$\delta(^{31}P)$ 203]. This solid is stable and was readily isolated in high

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

yield. Its complete characterization as the phosphanylium salt **4a** was achieved by elemental analysis, NMR spectroscopy and single-crystal X-ray diffraction studies. Similarly, aminoiminophosphane **1** on treatment with $GaCl_3$ gives the 1:1 adduct **4b** (Scheme 1).

In contrast with **1**, the reaction between *trans*-aminoiminophosphanes **2** and **3** with $AlCl_3$ in dichloromethane or toluene affords the unstable adducts **5a** and **6a** which decompose readily in solution at room temperature (Scheme 2); therefore it was only possible to obtain their spectral characteristics (without purification) 2 h after mixing the reagents in $CDCl_3$ at 0 °C (Table 1). All attempts to isolate the compounds from the reaction mixture failed. However, the major products of the decomposition of **5a** and **6a** were respectively identified as **5c** and **6c** especially from the ^{31}P and ^{13}C NMR data. We have noticed that the use of dichloromethane instead of toluene as solvent favoured side reactions. This result could be explained in terms of a one-electron-transfer reaction since it is known that dichloromethane solutions of $AlCl_3$ act as rather strong one-electron oxidizing agents.[9] So, it is likely that the interaction of sterically crowded aminoiminophosphane involves the generation of a radical cation and its subsequent reaction with the solvent.

In the case of $GaCl_3$, which possesses less pronounced oxidizing properties than those of $AlCl_3$, the interaction with aminoiminophosphane **2** led quantitatively to the expected phosphanylium salt $Pr^i_2N\text{-}P^+\text{-}N(GaCl_3{}^-)C_6H_2Bu^t_3$-2,4,6 **5b** (*cf.* ref. 10).

Reaction of Aminoiminophosphanes **1–3** *with Trifluoromethanesulfonic Acid* (CF_3SO_3H).—Direct formation of the salts **4d–6d** containing a primary amino substituent was observed upon protonation of the two-co-ordinated nitrogen atom of the iminophosphanes **1–3** with CF_3SO_3H in CH_2Cl_2 solution at −70 °C (Scheme 3). The cations **4d–6d** proved to be stable and were isolated in a pure state as colourless crystals. The assigned structures were confirmed by NMR spectroscopy (Table 1) and the crystal structure of $[P(NPr^i_2)\{NH(C_6H_2Bu^t_3\text{-}2,4,6)\}]^+[CF_3SO_3]^-$ **5d** was determined by X-ray diffraction (see below).

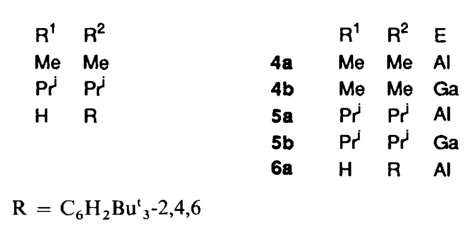
Reaction of an (Aryloxy)iminophosphane with $AlCl_3$.—This reaction proceeded more slowly than those of aminoiminophosphanes **1–3** and yielded a 1:1 adduct which could be isolated as a reasonably stable, orange-yellow solid. In contrast with **1** and **2**, no reaction was observed when $(R'O)P{=}NC_6H_2Bu^t_3$-2,4,6 **7** ($R' = C_6H_2Bu^t_2$-2,6-Me-4) was treated with $GaCl_3$ in toluene or dichloromethane solution at room temperature. The NMR spectra of the adduct **7**·$AlCl_3$ differ greatly from those of **1–3** with $AlCl_3$; in particular, the ^{31}P resonance is shifted to higher field [$\Delta\delta(^{31}P)$ −61] as compared to that of the starting reagent [$\delta(^{31}P)$ 138]. Comparison with the $\delta(^{31}P)$ of salt-like complexes $[P{\equiv}NC_6H_2Bu^t_3\text{-}2,4,6]^+[A]^-$ [A = $AlCl_4$, $\delta(^{31}P)$ 79.3;[4] A = CF_3CO_2, $\delta(^{31}P)$ 78.7; A = CF_3SO_3, $\delta(^{31}P)$ 55.4[8]] shows that the phosphorus chemical shift of our adduct **7**·$AlCl_3$ [$\delta(^{31}P)$ 77] lies among the typical values for aryl(phosphanetriyl)ammonium derivatives. In view of these considerations we assigned to the **7**·$AlCl_3$ adduct the structure $[P{\equiv}NC_6H_2Bu^t_3\text{-}2,4,6)]^+[(R'O)AlCl_3]^-$ **8**.

This structure is further supported by the fact that the reactivities of the compounds **4a–6a** and **8** towards triphenylphosphine differ widely. While the reaction of the former gave instantaneously the aminoiminophosphine, in toluene at −30 °C the latter resulted in generation of compound **9** the ^{31}P NMR parameters (δ 84 and 21, J_{PP} = 338 Hz) for which were close to those of the compound obtained from reaction of $[P{\equiv}NC_6H_2Bu^t_3\text{-}2,4,6]^+[AlCl_4]^-$ with PPh_3.[11] At elevated temperatures, **9** undergoes a slow transformation into the starting (aryloxy)iminophosphane (Scheme 4).

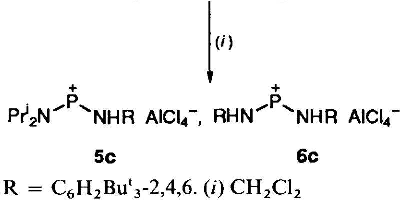
We conclude that, independently of the configuration of the aminoiminophosphane $(R'_2N)P{=}NC_6H_2Bu^t_3$-2,4,6, addition of $AlCl_3$ or $GaCl_3$ to these compounds leads to the corresponding derivatives $P(NR'_2)N(ECl_3)C_6H_2Bu^t_3$-2,4,6. Reaction of the (aryloxy)iminophosphane **7** with $AlCl_3$ involves electrophilic attack of the Lewis acid on the oxygen centre giving the salt **8**.

NMR Spectra.—Formulation of the compounds **4a–6a**, **4b**, **5b** and **4d–6d** as two-co-ordinated phosphorus cations is clearly confirmed by their ^{31}P NMR spectra which display signals in the range typical for $N\text{-}P^+\text{-}N$ ions[3] (δ 261–311, Table 1). For all of these derivatives the ^{31}P resonances occur to low field compared with those of the starting aminoiminophosphanes [$\delta(^{31}P)$ 203 **1**, 268 **2** and 272 **3**]. Note that according to the literature data[4] the formation of the monoco-ordinated phosphorus cation $[P{\equiv}NC_6H_2Bu^t_3\text{-}2,4,6]^+[AlCl_4]^-$ from $ClP{=}NC_6H_2Bu^t_3$-2,4,6 is accompanied by a high-field shift of the ^{31}P resonance [$\Delta\delta(^{31}P) \approx -60$].

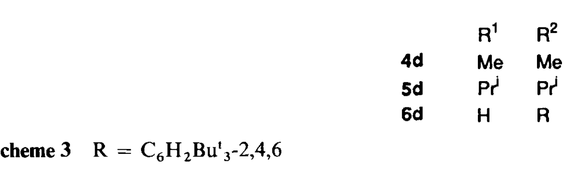
Comparison of the ^{31}P NMR chemical shifts of $[P(NMe_2)_2]^+$ [$\delta(^{31}P)$ 264][3] and $[P(NMe_2)\{NH(C_6H_2Bu^t_3\text{-}2,4,6)\}]^+$ **4d** [$\delta(^{31}P)$ 261] shows that the influence of the 2,4,6-$Bu^t_3C_6H_2NH$ substituent is similar to that of Me_2N. On the other hand, the large difference between the ^{31}P chemical shift of **4d** and that of



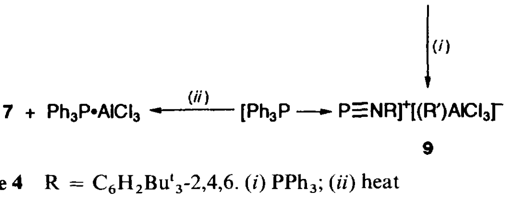
Scheme 1 $R = C_6H_2Bu^t_3$-2,4,6



Scheme 2 $R = C_6H_2Bu^t_3$-2,4,6. (*i*) CH_2Cl_2



Scheme 3 $R = C_6H_2Bu^t_3$-2,4,6



Scheme 4 $R = C_6H_2Bu^t_3$-2,4,6. (*i*) PPh_3; (*ii*) heat

Table 1 Proton, ^{19}F, ^{27}Al and ^{31}P NMR data[a]

	^{1}H (J_{PH}/Hz)							
Compound	*o*-Bu^t	*p*-Bu^t	H_3CCN	H_nCN	H_{arom}	NH	^{27}Al($\Delta\nu_{\frac{1}{2}}$/Hz) or ^{19}F	^{31}P-{^{1}H}
4a[b]	1.59	1.28		2.90 (3.8) 3.27 (14.2)	7.45		103 (49)	282.9
4b	1.57	1.28		2.88 (3.7) 3.27 (14.3)	7.45			277.2
5a′	1.70	1.20	0.62[c] 1.06[c]	3.18[d] 4.28[d]	7.52		102 (1500)	300.3
5a″	1.63	1.25	1.03[c] 1.15[c]	3.35[d] 5.50[d]	7.58		98 (1500)	304.8
5b′	1.51	1.18	0.99[c] 1.21[c]	3.70[d] 4.27[d]	7.34			295.7
5b″	1.46	1.20	1.27[c] 1.47[c]	3.80[d] 4.25[d]	7.39			299.5
6a	1.56[e]	1.32			7.47	10.2 (br)	98 (270)	311.3
4d	1.46	1.31		3.50 (br)	7.44	10.4 (br)	−78.8	261.4
5d	1.47	1.32	1.49[f] 1.59[f]	4.09[d] 5.30[d]	7.46	10.6 (14)	−79.8	274.8
6d	1.59	1.32			7.50	11.6 (13.2)	−79.7	279.7
8	1.56[g]	1.29			7.39		83.0 (650)	77.3

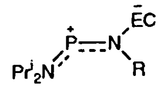
[a] In $CDCl_3$ solution. [b] ^{15}N NMR spectrum: δ −208 (br, $NC_6H_2Bu^t_3$-2,4,6) and −234 (d, $^{1}J_{PN}$ 100 Hz, NMe_2). [c] d, $^{3}J_{HH}$ 6.6 Hz. [d] Complex pattern arising from H–H and P–P coupling. [e] Signals for 2,4,6-$Bu^t_3C_6H_2NH$: δ 1.33 (*p*-Bu^t), 1.65 (*o*-Bu^t), 7.53 (H_{arom}) and 10.25 (br s, NH). [f] d, $^{3}J_{HH}$ 7.0 Hz. [g] Signals for 4-Me-2,6-$Bu^t_2C_6H_2$: δ 1.46 (*o*-Bu^t), 2.38 (*p*-Me) and 7.33 (H_{arom}).

the only so far known phosphanylium salt with an RNH group, $[P(NHBu^t)(C_5Me_5)]^+$ [δ(^{31}P) 106.7],[12] indicates a larger positive charge delocalization on the latter derivative due to multihapto bonding between the P^+ centre and the cyclopentadienyl ligand. In all of our cations **4a**–**6a**, **4b**, **5b** and **4d**–**6d** the stability results from both contributions: thermodynamic stabilization by means of $N\rightarrow P^+$ π bonding and kinetic stabilization due to the bulky 'supermesityl' substituent ($C_6H_2Bu^t_3$-2,4,6). It is noticeable that according to ^{31}P and ^{19}F NMR data **4d**–**6d** exist exclusively as ionic species, while $[P(NHBu^t)(C_5Me_5)]^+[CF_3SO_3]^-$ reveals in solution an equilibrium between a two-co-ordinated cation and a three-co-ordinated covalent compound.[12]

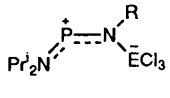
The ^{1}H NMR spectrum of compound **4a** is typical of this type of phosphanylium derivative. The most important feature is the non-equivalence of the methyls of the Me_2N group at room temperature; their signals appear as two doublets (δ 2.90, $^{3}J_{PH}$ = 3.8; δ 3.27, $^{3}J_{PH}$ = 14.2 Hz) due to the restricted rotation around the P–N bond.

In each case, the complexation of compound **2** with $AlCl_3$ and $GaCl_3$ results in the formation of two isomeric compounds with similar ^{31}P chemical shifts. Analysis of the complete sets of NMR data showed these compounds to be conformers, **5a′** and **5a″** (molar ratio 1.6:1) or **5b′** and **5b″** (molar ratio 2.4:1), with the various ligand arrangements at the partially double P–$NC_6H_2Bu^t_3$-2,4,6 bond. The assignments of the relative configurations of the Pr^i_2N–P–$NC_6H_2Bu^t_3$-2,4,6 fragment in **5a′**, **5a″** and **5b′**, **5b″** were based on a comparison of their ^{13}C NMR data (Table 2) with those of *cis*-**4a** and *trans*-**5d** (Table 2), the structures of which have been elucidated by X-ray crystallography. Especially indicative are the ^{13}C parameters (δ and J_{PC}) of the C^{ortho} (R), and of the *o-tert*-butyl group C^{13}(H_3CC and H_3CC) signals which are quite similar for **4a** and **5a′**, **5b′**. The same arguments allow the assumption that **6a** similar to **5a″** and **5b″** is of *trans* configuration in the RNH–P–N–R fragment. The range of ^{27}Al resonances for **4a**–**6a** [98 < δ(^{27}Al) < 102] is typical for a tetrahedrally co-ordinated aluminium atom.[13]

Molecular and Crystal Structures of Compounds **4a** *and* **5d**.—Selected bond lengths and angles for compounds **4a** and **5d** are listed in Tables 3 and 4; Figs. 1 and 2 show the cation geometry. The C(1)–N(1)(A1)–P–N(2) central bond system in **4a** is planar within an average deviation of 0.011(3) Å. The amino group C(19)N(2)C(20) is almost coplanar, whereas the C(1)–C(6) benzene ring is orthogonal to the central plane [dihedral angles 4.7(2.1) and 88.4(1)°] due to the steric repulsions between bulky substituents. The bond configuration for atoms N(1) and N(2) is trigonal planar and that for the Al atom is tetrahedral. It is worth noting that the conformation of molecule **4a** is the same as that in the initial molecule **1**.[7] The N(1)–P–N(2) angle in these two molecules is also practically the same [114.65(9) in **4a** and 115.9(3)° in **1**]. In contrast the P–N(1)–C(1) angle is decreased from 140.7(4) in **1** to 126.4(1)° in **4a** due to the change in the co-ordination number of N(1) from two to three. On going from **1** to **4a** the P–N(1) bond is elongated from 1.539(3) to 1.610(2) Å, whereas P–N(2) is shortened from 1.651(3) to 1.615(2) Å; as a result, P–N(1) and P–N(2) in **4a** are almost equal and coincide within experimental error limits with the corresponding values of 1.587(12), 1.601(12)[10] and 1.611(4), 1.615(4) Å observed in the cation $[P(NPr^i_2)_2]^+$.[14]



5a′ E = Al
5b′ E = Ga



5a″ E = Al
5b″ E = Ga

R = $C_6H_2Bu^t_3$-2, 4, 6

Therefore, the P–N bond-length distribution in compound **4a** is evidence for a more significant contribution of the zwitterionic form **C** relative to **D**. Nevertheless, the above-mentioned trend in bond lengths on going from **1** to **4a** may be partly attributed to weakening of the $n_{N(1)}$–$\sigma^*_{P-N(2)}$ interaction as well as to rehybridization of the N(1) atom due to the increasing P–N(1)–C(1) bond angle.

The Al–Cl bond lengths in compound **4a** (2.119–2.122, average 2.120 Å) as well as the length of Al–N(1) 1.935(2) Å are unexceptional and virtually coincide with the corresponding

Table 2 ^{13}C NMR data,[a] δ (J_{CP}/Hz)

Compound	o-H_3CC	p-H_3CC	o-H_3CC	p-H_3CC	H_nCN	H_3CCN	Aromatic C *ipso*	*o*	*m*	*p*
4a	34.2 (1.6)	31.2	37.9	34.5	42.0 (13.6) 42.7 (41.0)		133.1 (12.7)	143.0 (3.6)	126.2	148.4 (1.6)
4b	34.2	31.2	38.0	34.6	41.9 (12.7) 42.3 (40.3)		133.5 (15.2)	143.1 (4.1)	126.0	148.6 (1.3)
5a′	34.8 (1.3)	31.3	38.4	34.7	50.45 (22.3) 53.4 (12.1)	27.6 (15.4) 19.9	135.85 (13.9)	143.2 (3.9)	126.3	148.5 (0.8)
5a″	36.8 (6.1)	31.3	39.2 (1.6)	34.7	49.8 (24.0) 55.4 (12.7)	27.4 (15.6) 21.1 (1.8)	136.1 (18.7)	147.8 (8.6)	127.1 (3.7)	149.5 (4.6)
5b′	34.4 (1.8)	31.1	38.0	34.6	50.5 (22.3) 53.3 (11.4)	28.0 (15.4) 20.2 (1.3)	135.2 (15.8)	142.7 (4.0)	126.2 (0.6)	148.3 (1.2)
5b″	36.5 (6.0)	33.0	38.8 (2.0)	36.7	49.5 (24.5) 54.5 (11.4)	27.7 (15.1) 21.4 (1.4)	135.4 (18.7)	147.0 (8.4)	126.5 (3.7)	149.3 (4.3)
6a[b]	36.6	31.2	39.0	34.6			132.9 (15)	147.0	126.7	148.9
4d	33.8	31.2	36.7	35.1	42.3		127.1	148.8	124.1	151.5
5d	33.8 (1.3)	31.2	36.8	35.1	50.0 (22.2) 55.4 (10.9)	28.1 (13.7) 21.0	128.2 (19.3)	148.7 (5.2)	124.1 (5.2)	151.5 (2.5)
6d	33.7 (6.1)	31.1	36.9	35.0			128.3 (15.2)	148.3 (4.7)	124.1	151.3 (1.2)
8[c]	31.4	31.0	36.0	35.7			130.1 (39.4)	149.8 (4.6)	122.7	161.0

[a] In $CDCl_3$ solution. [b] Signals for 2,4,6-$Bu^t_3C_6H_2NH$: δ 31.1 (p-H_3CC), 33.9 (o-H_3CC), 34.8 (p-H_3CC), 36.9 (o-H_3CC), 124.2 (m-C_{ar}), 128.1 ($^2J_{PC}$ 16 Hz; *ipso*-C_{ar}), 149.0 (o-C_{ar}) and 150.3 (p-C_{ar}). [c] Signals for 4-Me-2,6-$Bu^t_2C_6H_2$: δ 20.7 (p-Me), 29.9 (o-H_3CC), 36.0 (o-H_3CC), 130.5 (m-C_{ar}), 131.0 (p-C_{ar}), 152.6 (o-C_{ar}) and 153.7 ($^2J_{PC}$ 6.7 Hz, *ipso*-C_{ar}).

Table 3 Selected bond distances (Å) and angles (°) for $(Me_2N)PN(AlCl_3)C_6H_2Bu^t_3$-2,4,6 **4a**

P–N(1)	1.610(2)	N(1)–C(1)	1.465(3)
P–N(2)	1.615(2)	N(2)–C(19)	1.491(3)
Al–N(1)	1.935(2)	N(2)–C(20)	1.489(3)
N(1)–P–N(2)	114.65(9)	P–N(2)–C(19)	135.0(2)
P–N(1)–Al	108.52(9)	P–N(2)–C(20)	114.2(2)
P–N(1)–C(1)	126.4(1)	C(19)–N(2)–C(20)	110.8(2)
Al–N(1)–C(1)	125.1(1)		

Table 4 Selected bond distances (Å) and angles (°) for $[P(NPr^i_2)\{NH(C_6H_2Bu^t_3\text{-}2,4,6)\}]^+[CF_3SO_3]^-$ **5d**

P–N(1)	1.602(1)	N(1)–H	0.81(2)
P–N(2)	1.602(1)	N(1)–C(1)	1.453(2)
N(2)–C(22)	1.518(2)	N(2)–C(19)	1.496(2)
N(1)–P–N(2)	107.79(7)	C(19)–N(2)–C(22)	116.3(1)
P–N(1)–C(1)	120.6(2)	P–N(2)–C(19)	124.3(2.0)
P–N(2)–C(19)	128.5(1)	C(1)–N(1)–H	115.0
P–N(2)–C(22)	115.3(1)		

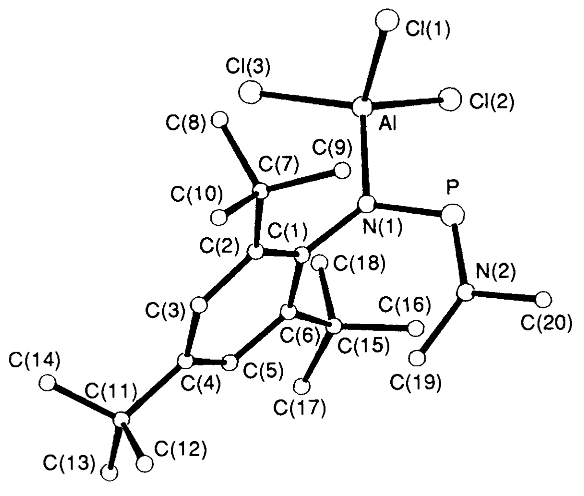
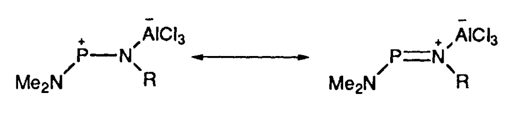


Fig. 1 Molecular structure of $(Me_2N)PN(AlCl_3)C_6H_2Bu^t_3$-2,4,6 **4a**



C D

values for $Cl_3Al{\cdot}NH_2(Bu^t)$ [Al–Cl 2.104–2.120, average 2.112(2); Al–N 1.936(4) Å].[15]

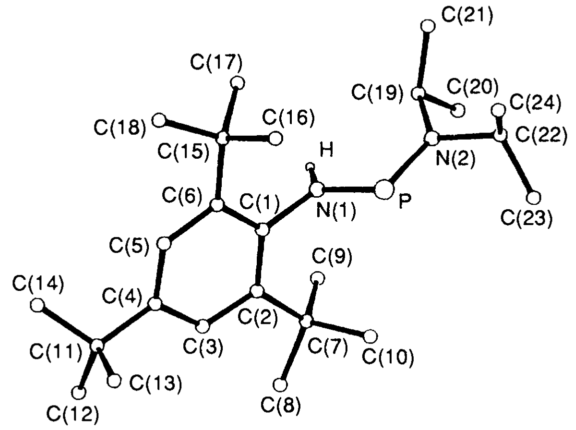


Fig. 2 Molecular structure of $[P(NPr^i)_2\{NH(C_6H_2Bu^t_3\text{-}2,4,6)\}]^+$-$[CF_3SO_3]^-$ **5d**

Molecules **4a** are kept within the crystal by means of normal van der Waals interactions. No shortened intermolecular contacts are observed. The shortest Cl···Cl and Cl···C distances are 3.627(8) and 3.567(5) Å, respectively (the corresponding sums of van der Waals radii are 3.60 and 3.50 Å).[16]

As in molecule **4a**, the C(1)–N(1)–P–N(2) central bond system in cation **5d** is practically planar [deviations from least-squares plane do not exceed 0.010 15(2) Å]. The amino group

Table 5 Crystal data, structure analysis and refinement[a]

	4a	**5d**
Formula	$C_{20}H_{35}AlCl_3N_2P{\cdot}CH_2Cl_2$	$[C_{24}H_{44}N_2P]^+[CF_3SO_3]^-{\cdot}CH_2Cl_2$
M	552.8	625.6
Crystal size/mm	0.14 × 0.20 × 0.36	0.22 × 0.25 × 0.34
a/Å	9.140(5)	9.194(5)
b/Å	9.415(4)	13.256(5)
c/Å	19.074(9)	14.889(5)
α/°	96.90(4)	82.72(3)
β/°	90.40(4)	74.38(4)
γ/°	117.04(4)	72.24(4)
U/Å^3	1447.8	1662.2
D_c/g cm^{-3}	1.27	1.25
μ/cm^{-1}	55.9	32.1
F(000)	580	664.0
T/°C	−85	−100
θ_{max}/° for data	54	52
No. of reflections:		
total	3245	4014
unique	2964	3719
in refinement	2552 [$I > 5\sigma(I)$]	3447 [$I > 3\sigma(I)$]
No. variables	289	347
Observations/variables	8.8	9.9
R	0.062	0.047
R'	0.098	0.079
Goodness of fit[b]	4.43	3.55
Largest shift/e.s.d.	0.36	0.92
Maximum peak in final difference map/e Å^{-3}	1.01	0.25

[a] Details in common: triclinic, space group $P\bar{1}$; $Z = 2$; $R = \Sigma(|F_o - F_c|)/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. [b] A small number of ill fitting reflections were elucidated at the final stages of refinement of both structures. Relatively high values of the goodness of fit are probably connected with the crystal decay (only a linear decay correction was applied). Disorder of the solvent molecule CH_2Cl_2 in **4a** may also be a factor.

C(19)N(2)C(22) is almost coplanar, whereas the C(1)–C(6) benzene ring [dihedral angles being 4.0(4) and 89.0(1)°] is orthogonal to the central plane due to the steric repulsions. The P–N(1) and P–N(2) bond lengths coincide within experimental errors, slightly shorter than the corresponding values in **4a**. In **5d** the cation and the anion are connected by a N(1)–H(N1) ··· O(2) hydrogen bond: N(1) ··· O(2) 2.809(2), N(1)–H(N1) 0.81(2), H(N1) ··· O(2) 2.05(2) Å, N(1)–H(N1)–O(2) 156.1(2.8)° (the average statistical value, typical for hydrogen bridges of this type, is 2.89 Å).[17]

Experimental

General Comments.—All syntheses were carried out using standard inert-atmosphere techniques and the solvents were dried and distilled under dry argon. Dichloromethane was shaken with concentrated H_2SO_4, rinsed twice with water, washed with 5% aqueous $NaHCO_3$, then with water and dried overnight over $CaCl_2$. After decantation, the solvent was stirred with CaH_2 overnight at reflux and then distilled. Toluene was distilled from sodium–benzophenone and then transferred under vacuum prior to use. Deuteriochloroform was dried over molecular sieves.

Iminophosphanes **1**–**3**[18] and **7**[19] were synthesized as reported previously. Proton, ^{13}C and ^{27}Al NMR spectra were recorded on a Varian VXR-300 instrument, and chemical shifts are reported relative to internal $SiMe_4$ (^1H, ^{13}C) and external $Al_2(SO_4)_3$ (^{27}Al). The ^{31}P NMR spectra were recorded on a Bruker WP-200 spectrometer using 85% H_3PO_4 as the external reference.

For all phosphanylium salts **4a**–**6a**, **4b**, **5b** and **4d**–**6d** and the salt **8** the NMR data are given in Tables 1 and 2.

Crystal Structure Determinations of $(Me_2N)PN(AlCl_3)C_6H_2Bu^t_3$-2,4,6 **4a** *and* $[P(NPr^i_2)\{NH(C_6H_2Bu^t_3\text{-}2,4,6)\}]^+[CF_3SO_3]^-$ **5d**.—Crystal data and details of the data collection and processing are given in Table 5. Fractional atomic coordinates are listed in Tables 6 and 7. The X-ray structural studies of compounds **4a** and **5d** were performed on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Cu-Kα radiation ($\lambda = 1.541\,84$ Å, ω–2θ scan mode, ratio scanning rates ω:θ = 1.2:1).

Both structures were solved by direct methods and refined by full-matrix least-squares techniques in the anisotropic approximation. The weighting scheme $w = (\sigma^2F + 0.00\,16F^2)^{-1}$ was used. Only part (about 60%) of the hydrogen atoms in compound **4a** were located in the Fourier-difference maps; the positions of the remainder were calculated. In **5d** all hydrogen atoms of the cation were located in the Fourier-difference maps and only the positions of two hydrogen atoms of the solvent molecule CH_2Cl_2 were calculated. All hydrogen atoms in both structures were included in the final refinement with fixed positional and thermal parameters ($B_{iso} = 5$ Å^2 for **4a** and 4 Å^2 for **5d**); only atom H(N) in **5d** was refined isotropically. Corrections for Lorentz and polarization effects but not for absorption were applied. All structural calculations were carried out on a PDP-11/23+ computer using the SDP-PLUS program package.[20] Neutral atom scattering factors were taken from the usual source.[21]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Preparations.—$(Me_2N)PN(AlCl_3)C_6H_2Bu^t_3$-2,4,6 **4a**. A solution of (dimethylamino)iminophosphane **1** (5.17 g, 15.5 mmol) in toluene (30 cm^3) was added quickly to a suspension of $AlCl_3$ (2.16 g, 16 mmol) in toluene (20 cm^3) at 0 °C. The mixture was stirred vigorously during 3 h, then the light yellow solution was reduced in volume at ambient temperature and the solvent removed *in vacuo*. The residue recrystallized from CH_2Cl_2 afforded colourless solid compound **4a** (4.61 g, 63%), m.p. 136–141 °C (Found: C, 51.55; H, 7.50; Cl, 22.75. Calc. for $C_{20}H_{35}AlCl_3N_2P$: C, 51.35; H, 7.55; Cl, 22.75%).

$(Me_2N)PN(GaCl_3)C_6H_2Bu^t_3$-2,4,6 **4b**. A solution of the

Table 6 Atomic coordinates with estimated standard deviations (e.s.d.s) in parentheses for $(Me_2N)PN(AlCl_3)C_6H_2Bu^t_3\text{-}2,4,6{\cdot}CH_2Cl_2$ **4a**

Atom	*x*	*y*	*z*
Cl(1)	0.335 3(1)	0.116 9(1)	0.968 15(5)
Cl(2)	0.029 4(2)	−0.221 8(1)	0.880 48(9)
Cl(3)	0.379 7(2)	0.010 3(1)	0.791 85(7)
Cl(4A)*	0.351 6(4)	0.074 1(3)	0.541 0(2)
Cl(4B)*	0.447 7(8)	0.123 7(5)	0.564 9(2)
Cl(5A)*	0.648 0(5)	0.270 4(6)	0.629 7(3)
Cl(5B)*	0.695 3(4)	0.391 2(5)	0.656 6(2)
P	−0.024 6(1)	0.134 4(1)	0.894 19(5)
Al	0.210 6(1)	0.012 6(1)	0.866 85(6)
N(1)	0.107 7(3)	0.138 3(3)	0.838 1(2)
N(2)	−0.120 1(3)	0.236 5(3)	0.878 1(2)
C(1)	0.148 2(4)	0.225 2(4)	0.776 6(2)
C(2)	0.268 5(4)	0.390 8(4)	0.784 8(2)
C(3)	0.292 5(5)	0.471 6(5)	0.726 6(2)
C(4)	0.205 6(5)	0.400 4(5)	0.661 9(2)
C(5)	0.092 7(5)	0.240 3(5)	0.654 7(2)
C(6)	0.059 1(5)	0.147 8(4)	0.710 3(2)
C(7)	0.381 4(5)	0.492 3(4)	0.853 2(2)
C(8)	0.523 9(5)	0.450 0(5)	0.858 4(3)
C(9)	0.296 3(5)	0.472 6(5)	0.923 2(2)
C(10)	0.456 9(7)	0.672 4(5)	0.848 5(3)
C(11)	0.237 5(6)	0.500 7(6)	0.599 3(2)
C(12)	0.184(1)	0.625 6(6)	0.618 5(3)
C(13)	0.145 7(9)	0.400 0(7)	0.531 2(3)
C(14)	0.414(1)	0.577(1)	0.586 9(4)
C(15)	−0.078 7(6)	−0.028 6(5)	0.691 9(2)
C(16)	−0.208(1)	−0.081 5(9)	0.738 9(5)
C(17)	−0.139(1)	−0.072 7(9)	0.616 7(3)
C(18)	−0.004(1)	−0.138 8(8)	0.695 5(8)
C(19)	−0.120 1(5)	0.331 6(4)	0.821 1(2)
C(20)	−0.231 6(6)	0.243 5(6)	0.933 5(3)
C(21)	0.469 3(9)	0.196(1)	0.639 0(4)

* The atoms Cl(4) and Cl(5) of the solvent molecule CH_2Cl_2 are disordered over two positions with equal occupancy.

Table 7 Atomic coordinates with e.s.d.s in parentheses for $[P(NPr^i_2)\{NH(C_6H_2Bu^t_3\text{-}2,4,6)\}]^+[CF_3SO_3]^-{\cdot}CH_2Cl_2$ **5d**

Atom	*x*	*y*	*z*
Cl(1)	0.218 53(9)	0.542 37(7)	0.252 82(6)
Cl(2)	0.188 2(1)	0.628 40(8)	0.430 07(7)
S	0.215 54(7)	0.102 40(5)	0.738 50(5)
P	0.755 19(7)	−0.202 00(5)	0.739 88(5)
F(1)	0.054 7(3)	0.243 3(2)	0.862 3(2)
F(2)	0.248 7(3)	0.126 8(2)	0.902 4(1)
F(3)	0.040 9(3)	0.085 0(2)	0.906 3(2)
O(1)	0.078 8(2)	0.121 3(2)	0.703 9(2)
O(2)	0.297 7(2)	−0.008 6(1)	0.748 4(1)
O(3)	0.314 7(2)	0.168 8(2)	0.700 0(1)
N(1)	0.571 1(2)	−0.177 9(2)	0.746 2(1)
N(2)	0.794 2(2)	−0.090 7(2)	0.729 1(1)
C(1)	0.501 3(2)	−0.264 1(2)	0.753 3(2)
C(2)	0.436 8(3)	−0.304 1(2)	0.842 4(2)
C(3)	0.362 4(3)	−0.381 3(2)	0.845 7(2)
C(4)	0.348 2(3)	−0.418 9(2)	0.767 1(2)
C(5)	0.417 5(3)	−0.378 9(2)	0.680 9(2)
C(6)	0.493 9(3)	−0.300 9(2)	0.670 4(2)
C(7)	0.442 3(3)	−0.265 9(2)	0.935 7(2)
C(8)	0.342 6(4)	−0.314 9(3)	1.020 2(2)
C(9)	0.373 4(5)	−0.145 2(3)	0.942 8(2)
C(10)	0.609 9(4)	−0.302 0(3)	0.948 7(2)
C(11)	0.268 3(3)	−0.507 0(2)	0.774 4(2)
C(12)	0.142 2(4)	−0.504 3(2)	0.865 6(3)
C(13)	0.394 6(4)	−0.613 8(2)	0.769 0(3)
C(14)	0.189 9(3)	−0.497 1(2)	0.694 5(2)
C(15)	0.567 6(3)	−0.263 0(2)	0.570 6(2)
C(16)	0.747 7(3)	−0.308 8(3)	0.546 0(2)
C(17)	0.524 9(3)	−0.141 7(2)	0.554 3(2)
C(18)	0.510 0(3)	−0.302 8(2)	0.497 3(2)
C(19)	0.687 0(3)	0.018 3(2)	0.719 0(2)
C(20)	0.660 9(4)	0.080 0(3)	0.803 2(2)
C(21)	0.751 4(4)	0.073 5(3)	0.627 9(2)
C(22)	0.962 7(3)	−0.097 6(2)	0.727 7(2)
C(23)	1.003 5(4)	−0.149 9(3)	0.816 5(3)
C(24)	1.073 9(4)	−0.151 3(3)	0.642 3(3)
C(25)	0.135 3(4)	0.141 2(2)	0.857 4(3)
C(26)	0.121 2(5)	0.637 5(4)	0.332 3(4)

phosphane **1** (1.0 g, 3 mmol) in dichloromethane (4 cm^3) was added to a stirred ice-cooled suspension of $GaCl_3$ (0.530 g, 3 mmol) in CH_2Cl_2 (3 cm^3). After stirring for 1 h the solution was concentrated *in vacuo* to a final volume of 3 cm^3. Addition of hexane produced a colourless precipitate, which was filtered off, washed with pentane and dried *in vacuo* (1.45 g, 95%), m.p. 84–91 °C (Found: C, 46.80; H, 6.70; Cl, 20.55. Calc. for $C_{20}H_{35}Cl_3GaN_2P$: C, 47.05; H, 6.90; Cl, 20.85%).

$(Pr^i_2N)PN(GaCl_3)C_6H_2Bu^t_3\text{-}2,4,6$ **5b**. The procedure described above was used to synthesize compound **5b** starting from $(Pr^i_2N)P{=}NC_6H_2Bu^t_3\text{-}2,4,6$ **2** (1.20 g, 3 mmol) and $GaCl_3$ (0.53 g, 3 mmol); a white powder was obtained (1.60 g, 93%), m.p. 72 °C (Found: C, 50.95; H, 7.60; Cl, 18.50. Calc. for $C_{24}H_{43}Cl_3GaN_2P$: C, 50.85; H, 7.65; Cl, 18.55%).

Reaction of phosphanes **1**–**3** *with trifluoromethanesulfonic acid: salts* **4d**–**6d**. Trifluromethanesulfonic acid (15.7 mg, 10 mmol) was added dropwise by a microsyringe to a solution of the phosphane **1** (3.34 g, 10 mmol), **2** (3.90 g, 10 mmol) or **3** (5.50 g, 10 mmol) in CH_2Cl_2 (20 cm^3) at −78 °C. After the addition was complete the solution was warmed to room temperature and concentrated *in vacuo* to *ca.* 6 cm^3; addition of pentane resulted in slow precipitation of colourless and hygroscopic solids: **4d** (3.12 g, 93%), m.p. 110 °C (decomp.) (Found: C, 51.85; H, 7.70; F, 11.55. Calc. for $C_{21}H_{36}F_3N_2O_3PS$: C, 52.05; H, 7.50; F, 11.75%); **5d** (3.56 g, 91%), m.p. 100 °C (decomp.) (Found: C, 55.55; H, 8.30; F, 10.45. Calc. for $C_{25}H_{44}F_3N_2O_3PS$: C, 55.55; H, 8.20; F, 10.55%); **6d** (4.03 g, 73%), m.p. 186–193 °C (Found: C, 63.35; H, 8.75; F, 8.05. Calc. for $C_{37}H_{60}F_3N_2O_3PS$: C, 63.40; H, 8.65; F, 8.15%).

$[P{\equiv}NC_6H_2Bu^t_3\text{-}2,4,6]^+[(R'O)AlCl_3]^-$ **8** ($R' = C_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4$). The (aryloxy)iminophosphane **7** (3.12 g, 6.2 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and this solution was added to a stirred, ice-cooled suspension of $AlCl_3$ (8.66 g, 6.4 mmol) in CH_2Cl_2 (10 cm^3). The deep orange solution was stirred during 6 h at room temperature, then the solvent was evaporated *in vacuo* yielding an orange microcrystalline solid compound **8** (3.98 g, 95%). This was recrystallized from $CHCl_3$–hexane (1 : 1) at −30 °C, m.p. 125 °C (with decomposition) (Found: C, 61.30; H, 8.15; Cl, 16.90. Calc. for $C_{33}H_{52}AlCl_3NOP$: C, 61.60; H, 8.15; Cl, 16.55%).

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