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# PREPARATION AND IMINOCARBONYLATION REACTIONS OF ORGANO-ALUMINIUM CHELATE COMPOUNDS CONTAINING P<sup>V</sup>---NMe---Al BONDS

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# Summary

New organoaluminium compounds containing  $P^v$ —NMe—Al bonds, diethylaluminium dialkyl N-methylphosphoramidate, (RO)<sub>2</sub>P(O)NMeAlEt<sub>2</sub>, and tetraalkylphosphorodiamidic N-methylamide, (R<sub>2</sub>N)<sub>2</sub>P(O)NMeAlEt<sub>2</sub>, were prepared. Cryoscopic measurements showed these compounds to be dimeric by intermolecular coordination. The introduction of bulky substituents on the phosphorus atom decreased the degree of association. The coordination of oxygen atom of P=O bonds to organoaluminium moiety was indicated by spectroscopic evidence.

In the reactions of  $(RO)_2 P(O)$ —NMe—AlEt<sub>2</sub> with aromatic aldehydes or phenyl isocyanate, the corresponding imino compounds were obtained by an addition—elimination process.

#### Introduction

Some Group III organometallic chelate compounds of phosphinic acid derivatives have been studied [1-4]. In particular, organoaluminium, gallium and indium derivatives of alkyl (or aryl) phosphinic acids,  $R_2P(O)-O-MR'_2$ , were shown to exhibit strong intermolecular interaction between  $R'_2M$  (M = Al, Ga and In) moieties and the oxygen atom of phosphinyl group. However, little was known about the structural or chemical behavior of organoaluminium chelates of phosphoramidates  $X_2P(O)-NMe-AlEt_2$ .

It is well known that the specific affinity of phosphorus to oxygen atom is the driving force of Wittig type reactions. In this context, the dialkyl *N*-alkylphosphoramidate anion was recently reported to act as an iminocarbonylating agent [5, 6]. In pseudo-Wittig type reactions of organoaluminium compounds, a facile formation of stable Al—O bonds is considered to be the key step. For example, thiocarbonylation reactions with  $(Et_2Al)_2S$  [7] and iminocarbonylation with Me<sub>2</sub>Al—NMe—SiMe<sub>3</sub> [8] may be included in this category. Since both organoaluminium and organophosphorus groups show strong affinity to oxygen atoms, formation of a stable Al—O—P bond is expected in some addition—elimination reactions.

From the above point of view, we describe here the preparation of diethylaluminium derivatives of dialkyl N-methylphosphoramidates,  $(RO)_2P(O)$ —NMe-AlEt<sub>2</sub> (Ib—Vb), and tetraalkylphosphorodiamidic N-methylamides  $(R_2N)_2$ -P(O)—NMe-AlEt<sub>2</sub> (VIb, VIIb), together with the iminocarbonylation by means of diethylaluminium dialkyl N-methylphosphoramidates.

#### **Results and discussion**

Preparation of compounds  $X_2P(O)$ -NMe-AlEt<sub>2</sub> (X = RO and  $R_2N$ ) (Ib-VIIb)

Dialkyl N-methylphosphoramidates (Ia—Va), obtained by the reaction of dialkyl hydrogen phosphites with  $CCl_4$  and  $MeNH_2$  [9], reacted with triethylaluminium to give the corresponding diethylaluminium derivatives (Ib—Vb) in 60—80% yield based on  $Et_3$  Al used (eqn. 1).

$$(RO)_{2}P(O)NHMe + Et_{3}Al \xrightarrow{benzene}{80^{\circ}C} (RO)_{2}P(O)NMeAlEt_{2} + C_{2}H_{6}$$
(1)  
(Ia-Va) (Ib-Vb)

(I, R = Me; II, Et; III, i-Pr; IV, i-Bu; V, i-Am)

Tetraalkylphosphorodiamidic N-methylamide (VIa, VIIa) gave the corresponding aluminium compounds (VIb, VIIb) according to eqn. 2. Yields, b.p.'s and analyses of Ib-VIIb are summarized in Table 1.

 $(R_2N)_2P(O)NHMe + Et_3Al \xrightarrow{benzene} (R_2N)_2P(O)NMeAlEt_2 + C_2H_6$ (2) (VIa, VIIa) (VIb, VIIb)

(VI, R = Me; VII, Et)

These compounds (especially Ib-Vb) were thermally stable (up to ca.  $200^{\circ}$ ) and distillable under reduced pressure. Cryoscopic molecular weight determinations showed that these compounds were dimeric in benzene by intermolecular coordination in the case of less bulky substituents (RO = MeO, EtO or Me<sub>2</sub>N).



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	PHYSICAL	AND ANAL	YTICAL D/	ATA OF THE COM	POUNDS X <sub>2</sub> P(0)	NMeAlEt2				
(w)         ( Untur)         C         H         Al         an anomaticative parameterative parametera	Compound	×	Yield	B.p.	Analysis	found (calcd.) (%)		M.W. (caled.	Degree of	Concentration
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			(%)	( ctmm)	o	Н	Al	tamonom su	ntsociation	(ar. 1M)
IID         EtO         78 $140-146$ (0.01) $37.67$ (0.11) $6.55$ (10.20) $381$ (2.32) $177$ (2.65 $2.76$ IID $1+PtO$ 71 $160-166$ (0.25) $47.13$ (0.97) $9.23$ (0.74) $466$ (281) $1.62$ 2.76           IVD $1-BuO$ 70 $146-165$ (0.25) $47.13$ (0.01) $9.67$ (0.07) $1.27$ 2.96           VD $1-AmO$ 60 $156-166$ (0.5) $63.30$ (0.017) $8.75$ (0.07) $1.27$ 2.96           VD $1-AmO$ 60 $110-120$ (0.3) $63.37$ (0.017) $8.76$ (365) $1.27$ 2.96           VD $Me_2N$ 60 $110-120$ (0.3) $47.3$ (363) $1.27$ 2.96           VID $Me_2N$ 84 $110-120$ (0.3) $43.37$ (0.011) $474$ (249) $1.91$ $3.16$ VID $E_2N$ 84 $10.05$ $10.01$ $10.20$ $10.54$ $3.13$ VID $E_2N$ $10.011$ $10.26$ $11.27$ 2.96 $2.87$ VID $Me_2N$ $84$ $10.011$ $10.20$	ą	MeO	72	135-142 (0.2)	8) 37.35	8.67	11.92	466 (223)	2.05	3.70
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	411	014	10	1 40 -1 46 40 01	(37.67)	(8.58)	(12.10)	381 (223) ADE (221)	1.71	2.66 2.76
		013	0	0'0) 05 T-05T	(13.03.03)	12.0	10.74	(107) 004	70.1	
	quii	I-PrO	11	160-165 (0.2	5) 47.13	9.58	9.53	405 (279)	1.45	2.76
	. '				(47.31)	( 9.74)	( 9.67)			•
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	٩VI	I-BuO	70	145-152 (0.1	3) 50.97 /50.90)	9.92	8,65 / 070)	390 (301)	1.27	2.96
VID         Me <sub>2</sub> N         60         110-120 (0.3)         (53.72) (10.52) (10.52) (10.61)         11.26 (1.91) (1.91)         11.26 (1.91) (1.91)         11.26 (1.91) (1.91)         11.26 (1.91) (1.91)         11.26 (1.91) (1.91)         3.61 (1.91) (1.91) (1.91)           TABLE 2         DIFFERENCES IN $v(P=O)$ of $v(P=O$	٨b	i-AmO	60	166-165 (0.5	) 53.90	10.33	8.75	465 (335)	1,39	2.87
VIb         Me <sub>2</sub> N         60         110-120 (0.3)         43.53         10.01         11.26         474 (249)         1.91         3.61           VIIb         Et <sub>2</sub> N         84         Iquid         (3.37)         (10.11)         (10.64)         1.64         3.13           VIIb         Et <sub>2</sub> N         84         Iquid         (43.37)         (10.11)         (10.64)         4.70 (305)         1.54         3.13           TABLE 2         TABLE 2         (10.11)         (10.86)         (8.64)         4.70 (305)         1.54         3.13           TABLE 2         VR         (10.11)         (10.89)         (10.86)         (8.64)         3.13           TABLE 2         VR         9.34         470 (305)         1.54         3.13           TABLE 2         VR         9.10         0.10         0.06         0.0         0.06         0.0         0.			1		(53.72)	(10.52)	(8.06)	415 (335)	1.24	1.55
VIIb $Et_2N$ $84$ Iquid $(43.37)$ $(10.11)$ $(10.64)$ $9.34$ $470$ (305) $1.54$ $3.13$ TABLE 2TABLE 2 $(10.89)$ $(8.84)$ $(8.84)$ $(70$ (305) $1.54$ $3.13$ TABLE 2DIFFERENCES IN $\nu$ (P=O) AND $\nu$ (P-N) BETWEEN X_2 P(O)NHMe (Ia-VIIa) AND X_2 P(O)NMeAIEt_2 (Ib-VIIb) (cm^{-1}) a $a$ $a_{2}$ Com-X $\nu^A$ (P=O) of $\nu^B$ (P=O) of $\Delta\nu$ (P=O) $\nu^A$ (P=O) of $\nu^A$ (P-N) of $\nu^B$ (P-N) ofCom-X $\nu^A$ (P=O) of $\nu^B$ (P=O) of $a^0$ (P=O) $a^0$ (P=O) $a^0$ (P=O)Ia, bIa-VIIaIb-VIIb $a^0$ (P=O) $a^0$ (P=O) $a^0$ (P=O)Ia, bMeO1260,12351216,1175 $-36$ , -46 $896$ $940$ $60$ IIa, bi-PrO1260,12361216,1175 $-36$ , -46 $890$ $940$ $60$ IIa, bi-PrO1256,12351216,1190 $-36$ , -46 $890$ $940$ $60$ Va, bi-BuO1260,12361216,1190 $-36$ , -46 $890$ $940$ $60$ VIa, bi-PrO1250,12361216,1190 $-36$ , -46 $890$ $940$ $60$ VIa, b $M_{2}N$ 1220,1100 $-20$ , $-36$ $-26$ , $-46$ $890$ $940$ $60$ VIa, b $E_2N$ 1220,12061200,1170 $-20$ , $-36$ $845$ $940$ $60$	VIb	Me <sub>2</sub> N	60	110-120 (0.3	43.53	10.01	11.26	474 (249)	1.91	3.61
VIID         E2_N         84         Iquid         50.31         10.66         9.34 $4^{(0}$ (300)         1.64         3.13           TABLE 2         TABLE 2           TABLE 2           DIFFERENCES IN $\nu$ (P=O) AND $\nu$ (P–N) BETWEEN X <sub>2</sub> P(O)NHMe (Ia–VIIa) AND X <sub>2</sub> P(O)NMeAIEt <sub>2</sub> (Ib–VIIb) (cm <sup>-1</sup> ) a $4^{(0)}$ ( $0.8, 4^{(0)}$ ) $0.4^{(P-N)}$ )           Com-         X $\nu^A$ (P=O) of $\Delta\nu$ (P=O) of $\Delta\nu$ (P=O) of $\nu^A$ (P=O) of $\nu^A$ (P=O) of $\nu^B$ (P=O) of $\nu^A$ (P=N) of $\nu^B$ (P-N) of $\nu^P$ (P-N) of </td <td></td> <td>:</td> <td>ļ</td> <td>:</td> <td>(43.37)</td> <td>(10.11)</td> <td>(10.84)</td> <td></td> <td></td> <td>6 1 0</td>		:	ļ	:	(43.37)	(10.11)	(10.84)			6 1 0
TABLE 2       (10.89)       (10.89)       (10.89)       (10.89)       (10.89)       (10.81)         TABLE 2         DIFFERENCES IN $\nu$ (P=O) AND $\nu$ (P=O) and $\Sigma_2$ P(O)NMeAlEt <sub>2</sub> (Ib-VIIb) (cm <sup>-1</sup> ) a         Com-       X $\nu^A$ (P=O) of $\nu^B$ (P=O) of $\Delta \nu$ (P=O) $\nu^A$ (P=O) of $\nu^B$ (P=O) of $\Delta \nu$ (P=O)         Com-       X $\nu^A$ (P=O) of $\nu^B$ (P=O) of $\Delta \nu$ (P=O) $\nu^A$ (P=O) $\nu^A$ (P=O)         Table 1         In -VIIa       Ib-VIIb $\mu^B$ (P-N) of $\nu^B$ (P-N)         Ia, b       MeO       1260, 1243       1220, 1190 $-40, -63$ 880       940       60         Ia, b       EtO       1260, 1236       1216, 1186 $-39, -66$ 896       940       60         Ia, b       EtO       1260, 1236       1216, 1186 $-25, -46$ 896       940       60         VIa, b       Hauo       1216, 1190 $-25, -46$ 896       940       60       60         VIa, b       Et2N       1216, 1190 $-20, -36$ 860       940       60       60       60       60       60       60       60       60       60 <t< td=""><td>AIID</td><td>Et2N</td><td>84</td><td>pinbir</td><td>20,91</td><td>10.66</td><td>9.34</td><td>470 (30D)</td><td>1,04</td><td>3.13</td></t<>	AIID	Et2N	84	pinbir	20,91	10.66	9.34	470 (30D)	1,04	3.13
TABLE 2DIFFERENCES IN $\nu$ (P=O) AND $\nu$ (P–N) BETWEEN X_2P(O)NHMe (Ia–VIIa) AND X_2P(O)NMe AIEt_2 (Ib–VIIb) (cm <sup>-1</sup> ) aCom-X $\nu^A$ (P=O) of $\nu^P$ (P=O) of $\nu^P$ (P=N) of $\Delta \nu$ (P-N) of $\Delta \nu$ (P-N) ofDIFFERENCES IN $\nu$ (P=O) AND $\nu$ (P=O) of $\nu^B$ (P=O) of $\nu^B$ (P=O) of $\Delta \nu$ (P-N) of $\Delta \nu$ (P-N) of $\Delta \nu$ (P-N) ofDoundIa–VIIaIb–VIIb $\mu^B$ (P=O) of $\nu^B$ (P=O) of $\Delta \nu$ (P-N) of<					(61.13)	(10.89)	(8.84)			
TABLE 2DIFFERENCES IN $\nu$ (P=O) AND $\nu$ (P=N) BETWEEN X2P(O)NHMe (Ia-VIIa) AND X2P(O)NMeAIEt2 (Ib-VIIb) (cm^{-1}) aCom-X $\nu^{A}$ (P=O) of $\nu^{B}$ (P=O) of $\nu^{B}$ (P=O) of $\nu^{A}$ (P=N) of $\nu^{B}$ (P=N) of $\nu^{B}$ (P=N) of $\nu^{B}$ (P=N) of $\nu^{B}$ (P=N) of $\nu^{A}$ (P=N)Com-X $\nu^{A}$ (P=O) of $\nu^{A}$ (P=O) of $\nu^{A}$ (P=O) of $\nu^{A}$ (P=O) $\nu^{A}$ (P=O) of $\nu^{A}$ (P=N) of $\nu^{B}$ (P=N) of $\nu^{A}$ (P=N)DoundIa - VIIaIb-VIIb $\nu^{B}$ (P=O) $\nu^{A}$ (P=O)Ia, bMeO1260, 12431220, 1190 $-40, -53$ Ia, bFFO1266, 12361216, 1175 $-39, -66$ $890$ Ia, bFFO1266, 12361216, 1175 $-36, -66$ $890$ Va, bFAMO1256, 12361216, 1175 $-36, -46$ $890$ $940$ VIa, bMe2N1216, 1190 $-20, -36$ $860$ $940$ $60$ VIa, bMe2N1216, 1170 $-20, -36$ $860$ $940$ $60$ VIa, bE42N1220, 12061200, 1170 $-20, -36$ $860$ $940$ $60$						-	-			-
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	<b>TABLE 2</b>									
$ \begin{array}{ccccc} Com- & X & \nu^{A}(P=O) \ of & \nu^{B}(P=O) \ of & \Delta\nu(P=O) \\ pound & & \mu^{A}(P=O) \ of & \mu^{A}(P=O) \ of & \mu^{A}(P=O) \ of & \mu^{A}(P=N) \ of & \lambda^{D}(P-N) \ of & \mu^{B}(P-N) \ of & \mu^{A}(P-N) \ of & \mu^{A}$	DIFFEREN	CES IN V(P=	-0) AND ν(Ρ	-N) BETWEEN X	2 P(O)NHMe (la-1	VIIa) AND X <sub>2</sub> P(O).	NMeAlEt <sub>2</sub> (Ib-VII	b) (cm <sup>-1</sup> ) a		
poundIa-VIIaIb-VIIb $=\nu B(P=0)$ -Ia-VIIaIb-VIIb $=\nu B(P-N)$ -Ia, bMeO1260, 12431220, 1190 $-40, -53$ 88094060IIa, bFPrO1266, 12431220, 1190 $-40, -53$ 88094060IIa, bFPrO1266, 12351215, 1180 $-33, -65$ 87092056Va, bFMO1266, 12351215, 1175 $-35, -66$ 89593338Va, bFAMO1256, 12351215, 1190 $-35, -45$ 89594056Va, bMe2 N1215, 11901190, 1155 $-25, -35$ 84594056VIa, bE42 N1220, 12051200, 1170 $-20, -35$ 85089545	Com-	×	Au	1 Jo (D=0)	B(P=O) of	∆⊎(P=O)	PA(P-N) of	ν <sup>B</sup> (P-N) of	Δν(P-	-N)
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IIIa, bi-PrO1260, 12361215, 1175 $-35, -60$ 89593338IVa, bi-BuO1240, 12301215, 1185 $-25, -45$ 89094050Va, bi-AmO1250, 12351215, 1190 $-35, -45$ 88594056VIa, bMe2N1215, 11901190, 1155 $-25, -35$ 84590560VIa, bEt_2N1220, 12051200, 1170 $-20, -35$ 85089545	IIa, b	EtO	12	54, 1235	1215, 1180	-39,55	870	920	50	
IVa, b i-BuO 1240, 1230 1215, 1185 –25, -45 890 940 50 Va, b i-AmO 1250, 1235 1215, 1190 –35, -45 885 940 55 VIa, b Me <sub>2</sub> N 1215, 1190 1190, 1155 –25, -35 845 905 60 VIIa, b Et <sub>2</sub> N 1220, 1205 1200, 1170 –20, -35 850 850 895 45	IIIa, b	-PrO	12	50, 1235	1216, 1175	-35, -60	895	933	38	
Va, b     i-AmO     1250, 1235     1215, 1190     -35, -45     885     940     55       Vla, b     Me <sub>2</sub> N     1215, 1190     1190, 1155     -25, -35     845     905     60       Vla, b     E4 <sub>2</sub> N     1220, 1205     1200, 1170     -20, -35     850     895     45	IVa, b	i-BuO	12	.40, 1230	1215, 1185	-26, -46	890	940	20	
VIa, b Me <sub>2</sub> N 1215, 1190 1190, 115525,35 845 905 60 VIIa, b Et <sub>2</sub> N 1220, 1205 1200, 117020,35 850 850 895 45	Va, b	i-AmO	12	50, 1235	1216, 1190	-36, -46	885	940	55	•
VIIa, b Et <sub>2</sub> N 1220, 1205 1200, 1170 –20, –35 850 895 45	Vla, b	Me <sub>2</sub> N	12	15, 1190	190, 1155	-25, -35	845	906	60	
	VIIa, b	Et <sub>2</sub> N	12	20, 1205	1200, 1170	-20, -35	850	895	46	

<sup>a</sup> In 2% benzene solution.

TABLE 1

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TABLE 3     MIAL SPECTR. A OF X2 FUOIMMEATE? 4       NMA SPECTR. A OF X2 FUOIMMEATE? 4     MIAL SPECTR. A OF X2 FUOIMMEATE? 4       Com-     X     P-M-CH3     J(PNCH) b     AICH2     AICH2CH3     J(HCCH1)     P-M-R     J(P-Hg)       Com-     X     P-M-CH3     J(PNCH) b     AICH2     AICH2CH3     J(HCCH1)     P-M-R     J(P-Hg)       Com-     X     P-M-CH3     J(PNCH1) b     AICH2     AICH2     AICH2     J(P-Hg)       Ib     Meio     7.46     17.22     9.718     8.60     7.5     6.20 dq, 8.98 t     7.5       Ib     HPO     7.48     17.22     9.71     8.58     7.5     6.20 dq, 8.98 t     7.5       Ib     HPO     7.40     17.22     9.71     8.53     7.5     6.20 dq, 8.98 t     7.5       Ib     HPO     7.40     17.23     9.71     8.53     7.5     6.20 dq, 8.98 t     7.5       VIb     H2/N     7.76     6.20     7.5     5.96 dd, 8.30-8.00 m     6.6       VIb     H2/N     7.56     7.5     5.96 dd, 8.30-8.00 m     6.7       VIb     H2/N     7.76     7.56     7.56     7.56     7.56       VIb     H2/N     7.56     7.5     7.56     7.56						 			
TABLE 3       TABLE 3       MIR RECTRA OF X2P(KO)NM6AIER2 4       NMR RECTRA OF X2P(KO)NM6AIER2 4       Com-     X     P-MCH3     J(PCH1)     AICH2     AICH2     AICH2       ID     7.66     9.73     8.60     7.5     6.20     6.0       ID     Eto     7.46     17.22     9.71     8.58     7.5     6.20     6.0       ID     Hero     7.46     17.22     9.71     8.58     7.5     6.20     6.0       VID     Hero     7.46     17.22     9.71     8.58     7.5     6.30     6.0       VID     Hero     7.46     17.23     9.71     8.56     7.5     5.96     6.13       VID     EfAN     7.68     4.5     7.5     5.36     7.6     6.0    <				() 					
TABLE 3         TABLE 3           NMR STECTRA OF X2F(O)NM6AER3_4         A           NMR STECTRA OF X2F(O)NM6AER3_4         A(CH2)           NMR STECTRA OF X2F(O)NM6AER3_4         A(CH2)           NMR STECTRA OF X2F(O)NM6AER3_4         A(CH2)           Com-         X         P-N-CH3           NMR STECTRA OF X2F(O)NM6AER3_4         A(CH2)           Com-         X           NMR STECTRA OF X2F(O)NM6AER3_4         A(CH2)           Com-         X           Dound         X           Ib         MeO           7.66         9.78           B         8.60         7.5           B         8.60         7.5           ND         7.43         17.2           9.74         8.58         7.5           B         5.46 m, 8.38 f         7.5           VD         1.40         17.2           9.74         8.58         7.5         5.56 d4, 8.30-8.00 m           VD         1.40         17.2         9.71         8.53 d4, 8.30-8.00 m           VD         1.40         17.2         9.74         8.50         7.5           VD         1.40         17.2         9.75         5.35 d4, 8.30-8.00 m </td <td></td> <td></td> <td></td> <td></td> <td></td> <td>-</td> <td>- 12</td> <td></td> <td></td>						-	- 12		
TABLE 3         TABLE 3           TABLE 3         MM. SPECTRA OF X <sub>2</sub> P(O)NMeAlEt <sub>2</sub> d           NM. SPECTRA OF X <sub>2</sub> P(O)NMeAlEt <sub>2</sub> d         AICH2           NM. SPECTRA OF X <sub>2</sub> P(O)NMeAlEt <sub>2</sub> d           NM. SPECTRA OF X <sub>2</sub> P(O)NMeAlEt <sub>2</sub> d           NM. SPECTRA OF X <sub>2</sub> P(O)NMeAlEt <sub>2</sub> d           Com-         K           P-N-CH3         J(PCH1)           AICH2         AICH2CH3           Jin         Set 0           No.         7.60           Ib         Meto           T.46         17.20           9.77         8.56           T.5         6.20 dq, 8.98 t           Nb         1.720           9.71         8.58           T.5         6.26 dd, 8.30 - 8.00 m           Vb         1.740           V10         7.40           V11         Et <sub>2</sub> N           V11         Et <sub>2</sub> N           V12         9.73           8.50         7.5           Y13         9.73           Y14         17.20           Y15         9.73           Y16         7.5           Y16         7.5           Y16         7.5           Y16		(gH-				· _ ·			
TABLE 3           TABLE 3           TABLE 3           MIN. SFECTRA OF X <sub>2</sub> P(D)MeAlEls <sub>2</sub> 4           Com-           X         P-N-CH3         X(PNCH) <sup>b</sup> AlCH2         AlCH2         P-O-R         P-N-R           Dound         X         P-N-CH3         X(PNCH) <sup>b</sup> AlCH2         AlCH2         P-O-R         P-N-R           Dound         X         P-N-CH3         X(PNCH) <sup>b</sup> AlCH2         AlCH2         P-O-R         P-N-R           Dound         X         P-N-CH3         X(PNCH) <sup>b</sup> AlCH2         AlCH2         AlCH2         P-O-R         P-N-R           Dound         Meo         7.60         16.5         3.78         8.60         7.5         6.75 d         B.18         7.5         6.20 dq, 8.98 t           IIb         EPO         7.46         8.65         7.5         5.95 dd, 8.30 - 8.00 m         7.65 d           VIb         El_2N         7.16         17.23         9.71         8.16         7.5         5.95 dd, 8.30 - 8.00 m           VIb         El_2N         7.56         5.95 dd, 8.30 - 8.00 m         7.65 dd, 9.12 d         7.65 dd           VIb         El_2N		J(P-	11.8	7.5		6.0	8.9	11.3	9.8
TABLE 3           TABLE 3           MIR SFECTRA OF X2P(0)NMeAIEt <sub>2</sub> a           Com-         X         PNR           NMR SFECTRA OF X2P(0)NMeAIEt <sub>2</sub> a         AICH2         AICH2         AICH2         POR         PNR           NMR SFECTRA OF X2P(0)NMeAIEt <sub>2</sub> a         Com-         X         PNR         AICH2         AICH2         AICH2         AICH2         AICH2         AICH2         AICH2         PNR         P-NR         P-NR         P-NR         P-NR         P-ICH2         P-ICH3         AICH2         AICH2									
TABLE 3         TABLE 3           TABLE 3         VIR. SFECTRA OF X2P(O)NMeAIEF <sub>2</sub> d           NMR. SFECTRA OF X2P(O)NMeAIEF <sub>2</sub> d         AICH2           NMR. SFECTRA OF X2P(O)NMeAIEF <sub>2</sub> d           Com-         X           P-N-CH3         J(PVCH) b           AICH2         AICH2           NMR. SFECTRA OF X2P(O)NMeAIEF <sub>2</sub> d           Com-         X           Me0         7.60           17.2         9.78           8.60         7.5           6.75 d           110         E4O           112.2         9.73           9.74         8.58           110         E4O           7.45         17.2           9.71         8.53           111         8.53           112         9.71           8.50         7.5           5.54 dt, 8.30-8.00 m           VIb         E4_2N           NIb         E4_2N           7.55         9.73           9.73         8.50           7.5         5.54 dt, 7.80-8.00 m           VIb         E4_2N           17.5         9.73           17.5         9.74 <td< td=""><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>÷</td><td></td></td<>								÷	
TABLE 3         TABLE 3         TABLE 3         NMR SPECTRA OF X <sub>2</sub> P(D)NMeAIEls 2         NMR SPECTRA OF X <sub>2</sub> P(D)NMeAIEls 2       Conn       P-M-R         NMR SPECTRA OF X <sub>2</sub> P(D)NMeAIEls 2       AICH2       AICH2       AICH2       AICH2         NMR SPECTRA OF X <sub>2</sub> P(D)NMeAIEls 2       P-M-GH3       AICH2						÷.			.05
TABLE 3       TABLE 3       NMR SPECTRA OF X <sub>2</sub> P(D)NMeAIB? <sub>2</sub> a       NMR SPECTRA OF X <sub>2</sub> P(D)NMeAIB? <sub>2</sub> a       Com-       X     P-M-CH3     J(PNCH) b     AICH2     AICH2CH3     J(PICCH)       Pound     X     P-M-CH3     J(PNCH) b     AICH2     AICH2CH3     J(PICCH)       Dound     X     P-M-CH3     J(PNCH) b     AICH2     AICH2CH3     J(PICCH)       Dound     T.66     17.2     9.718     8.60     7.5     6.75.d       Ib     EtO     7.46     17.2     9.71     8.53     7.5     6.30.d4, R.98.t       Ib     LHO     7.46     17.2     9.71     8.53     7.5     6.30.d4, R.90-8.00 m       VIb     LBuO     7.46     17.2     9.71     8.56     7.5     5.36.d4, 7.80-8.00 m       VIb     Et <sub>A</sub> N     7.18     17.5     9.71     8.56     7.5     5.36.d4, 7.80-8.00 m       VIb     Et <sub>A</sub> N     7.56     7.56     7.56     5.36.d4, 7.80-8.00 m       VIb     Et <sub>A</sub> N     7.56     7.56     5.36.d4, 7.80-8.00 m       VIb     Et <sub>A</sub> N     7.56     7.56     7.56       VIb     Et <sub>A</sub> N     7.56     7.56     7.65		ä						σ	dq, 9
TABLE 3         TABLE 3         NMR SPECTRA OF X <sub>2</sub> P(O)NMeAIEt <sub>2</sub> a         Com-         X       P-N-CH <sub>3</sub> J(PNCH) b       AICH <sub>2</sub> AICH <sub>2</sub> CH <sub>3</sub> J(HCCH)       P-O-R       T         Com-       X       P-N-CH <sub>3</sub> J(PNCH) b       AICH <sub>2</sub> AICH <sub>2</sub> CH <sub>3</sub> J(HCCH)       P-O-R       T         Dound       X       P-M-CH <sub>3</sub> J(PNCH) b       AICH <sub>2</sub> AICH <sub>2</sub> CH <sub>3</sub> J(HCCH)       P-O-R       T         Dound       T       R       B       B       B       G       7.5       G.75d       G         Ib       EtO       7.45       17.2       9.71       8.58       7.5       G.56 dd, 7.80-8.00 m         VID       Et <sub>3</sub> N       7.78       17.2       9.71       8.53       7.5       G.56 dd, 7.80-8.00 m         VID       Et <sub>3</sub> N       7.55       9.71       8.56       7.5       G.56 dd, 7.80-8.00 m         VID       Et <sub>3</sub> N       7.56       9.73       8.56       7.5       G.56 dd, 8.30-8.00 m		Å.		· .	•			.65	.08
TABLE 3         TABLE 3         NIR SPECTRA OF X2P(O)MeAIEt2 a         Sign of the spectra of X2P(O)MeAIEt2 a         NIR SPECTRA OF X2P(O)MeAIEt2 a       AICH2       AICH2       AICH2       IICH2       P-O-R         NIR SPECTRA OF X2P(O)MeAIEt2 a       P-NCH3       AICH2       AICH2       AICH2       IICH2       P-O-R         NIR SPECTRA OF X2P(O)MeAIEt2 a       P-NCH3       AICH2       AICH2       AICH2       AICH2       IICH2       P-O-R         Com-       X       P-NCH3       AICH2       AICH2       AICH2       AICH2       AICH2       AICH3       AICH2       AICH3		H				E	8	•	-
TABLE 3       TABLE 3         TABLE 3       MIR SPECTRA OF X2P(0)NMeAIEt2 d         NMR SPECTRA OF X2P(0)NMeAIEt2 d       AICH2         Com-       X       P-n-CH3         III       Med0       7.60       16.5         III       L-PFO       7.46       17.2         III       L-PFO       7.48       8.58       7.5         VID       L-BH0       7.40       17.2       9.71       8.53       7.5         VID       Me2N       7.78       8.50       7.5       5.36 dd, 8.30-6         VID       Ev2N       7.15       9.78       8.50       7.5       5.31 dd         VID       Ev2N       7.15       9.73       8.60       7.5       5.12 dd       8.12 dd				· ·		8.50	3.90		
TABLE 3       TABLE 3         TABLE 3       TABLE 3         NMR SPECTRA OF X2P(0)NMeAlEt2 a         NMR SPECTRA OF X2P(0)NMeAlEt2 a         Com-       X         P-M-CH3       JCPNCH) b       AlCH2         Ib       MeO       7.60       16.5       9.78       8.60       7.5       6.76 d         Ib       MeO       7.60       16.5       9.78       8.60       7.5       6.20 dq.8.         Ib       EtO       7.16       17.2       9.73       8.58       7.5       6.20 dq.8.         Ib       LPOO       7.46       17.2       9.74       8.56       7.5       6.30 dq.7.         Ib       LPOO       7.46       17.2       9.74       8.53       7.5       6.30 dq.7.         IIIb       LPOO       7.46       17.2       9.71       8.53       7.5       6.30 dq.7.         VIb       Me2N       7.78       9.73       8.65       7.5       6.30 dq.8.         VIb       Me2N       7.78       9.17.3       9.73       8.12 d       9.12 d         VIb       Et2N       7.5       9.75       9.12 d       9.12 d       9.12 d         VIb       Et2N	and and a second se Second second			98 t	33 d	80-	30-1		
TABLE 3         TABLE 3         TABLE 3         TABLE 3         NIMR SPECTRA OF X2P(O)NMeAlEt 2         Com-       X         NIMR SPECTRA OF X2P(O)NMeAlEt 2         Com-       AICH2       AICH2CH3       J(HCCH)       P-O-         Com-       X       PM-CH3       J(PNCH)       AICH2       AICH2CH3       J(HCCH)       P-O-         Ib       MeO       7.66       9.78       8.60       7.5       6.75 d       6.76 d         Ib       EtO       7.45       17.2       9.74       8.54       8.3       5.46 r         Ib       HeO       7.45       17.2       9.74       8.53       7.5       6.26 d         Ib       HeO       7.46       17.2       9.74       8.60       7.5       6.26 d         VIb       HeIO       7.16       17.2       9.73       8.60       7.5       6.26 d       6.26 d         VIb       Me2N       7.76       9.78       8.60       7.5       6.12 d       6.12 d         VIb       EtAN        9.73       8.60		H	<u> </u>	q, 8,	n, 8,1	d, 7.	190	-	
TABLE 3         TABLE 3         NMR SPECTRA OF X2 P(0)NMeAlEt2 $a$ Com-         X         P-N-CH3         OR         P-N-CH3         OR         DOUND         P-N-CH3         NME SPECTRA OF X2 P(0)         P-N-CH3         OUT         P-N-CH3         OP N         PN-CH3         N         N         NO         PN-CH3         NO         PN-CH3         NED         IID         NGCH2         NEO         N         IID         IID         IID         IID         <th colspan="</td> <td></td> <td>-</td> <td>75 d</td> <td>20 d</td> <td>46 n</td> <td>25 d</td> <td>96 d</td> <td></td> <td></td>		-	75 d	20 d	46 n	25 d	96 d		
TABLE 3         TABLE 3         NMR SPECTRA OF X2P(0)NMeAlEt2 a         NMR SPECTRA OF X2P(0)NMeAlEt2 a       AICH2       AICH2CEH3       J(HCCH)         Dound       T.60       T.60       16.5       9.718       8.60       7.5         Ib       MeO       7.56       17.22       9.73       8.68       7.5         IIb       I-PrO       7.45       17.22       9.71       8.53       7.5         Vb       I-BuO       7.46       17.22       9.71       8.56       7.5         Vb       I-AmO       7.46       17.23       9.73       8.56       7.5         Vb       Me2N       7.56       9.73       8.56       7.5         VIIb       E42N       7.56       9.73       8.56       7.5         VIIb       E42N       7.56       9.73       8.56       7.5		ų.	9	9	õ	ý a	ഫ്ക		
TABLE 3       TABLE 3         TABLE 3       NMR SPECTRA OF $X_2 P(O)$ NMe AIEt <sub>2</sub> a         NMR SPECTRA OF $X_2 P(O)$ NMe AIEt <sub>2</sub> a       AICH2       AICH2       AICH2       AICH2         Dound       X       P-N-CH3       J(PNCH) b       AICH2       AICH2       J(HOC         Ib       MeO       7.60       16.5       9.78       8.60       7.5         Ib       MeO       7.46       17.2       9.73       8.58       7.5         Ib       EtO       7.46       17.2       9.74       8.53       7.5         Ib       L-BuO       7.46       17.2       9.71       8.56       7.5         Vb       L-BuO       7.46       17.2       9.71       8.56       7.5         Vb       Me2N       7.78       17.2       9.73       8.56       7.5         V1b       Me2N       7.55       9.73       8.56       7.5         V1b       Et <sub>2</sub> N       7.55       9.73       8.50       7.5         V1b       Et <sub>2</sub> N       7.55       9.73       8.50       7.5         V1b       Et <sub>2</sub> N       7.55       9.73       8.50       7.5		(H)							
TABLE 3     TABLE 3       TABLE 3     NMR SPECTRA OF X2 P(O)NMEAIEt2 a       NMR SPECTRA OF X2 P(O)NMEAIEt2 a     J(PNCH) b       AICH2     AICH2       Dound     X       P-N-CH3     J(PNCH) b       AICH2     AICH2CH3       Jh     MeO       Tobund     T.60       Ib     MeO       Tobund     T.60       Ib     MeO       Tobund     T.60       Ib     MeO       Table     9.78       B.60     7       Ib     EtO       Table     17.2       Pib     17.2       Vb     1.40       Table     1.7.3       Vb     1.40       Table     1.7.3       Vb     1.40       Table     1.7.3       Vb     1.7.5       Vb     Me2N       Table     1.7.5       V1b     Et2N       Table     1.7.5       V1b     Et2N       Table     1.7.3       9.78     9.73       8.50     7       7.46     1.7.3       9.78     9.78       8.50     7       7.46     1.7.3       9.78     9.73		(HCC	ц	ц,	9	ц.	ц.	ъ.	ю.
TABLE 3       TABLE 3         TABLE 3       MMR SFECTRA OF $X_2P(0)$ NMeAlEt <sub>2</sub> a         NMR SFECTRA OF $X_2P(0)$ NMeAlEt <sub>2</sub> a         Neto       7.60       16.5       9.78       8.60         Ib       MeO       7.45       17.2       9.74       8.54         IIb       Eto       7.45       17.2       9.74       8.56         VIb       Me2N       7.78       17.2       9.771       8.56         VIb       Et <sub>2</sub> N       7.56       17.3       9.773       8.50		Ţ.	7	2	80	7	2	2	-
TABLE 3       TABLE 3         TABLE 3       TABLE 3         NMR SPECTRA OF $X_2 P(0)$ NMeAlEt <sub>2</sub> a       AlcH <sub>2</sub> NM and belowing       T-60       16.5       9.78       8.60         Ib       MeO       7.60       16.5       9.77       8.68         Ib       MeO       7.60       16.5       9.77       8.68         Ib       MeO       7.45       17.2       9.77       8.56         Ib       Ho       7.45       17.2       9.74       8.56         Ib       Ho       7.45       17.2       9.71       8.56         Vb       i-BuO       7.46       17.2       9.71       8.56         Vb       i-AmO       7.46       17.2       9.74       8.56         Vb       i-AmO       7.46       17.2       9.74       8.56         Vb       i-AmO       7.46       17.2       9.74       8.50         Vb       i-AmO       7.46       17.2       9.74       8.50         Vb       i-AmO       7.46       17.2       9.74       8.50         Vb       i-AmO       7.46       17.2       9.73       8.50         Vlb		2 CH							
TABLE 3       TABLE 3         TABLE 3       TABLE 3         NMR SPECTRA OF $X_2 P(O)NMeAlEt_2$ d         NME SPECTRA OF $X_2 P(O)NMeAlEt_2$ d         NME SPECTRA OF $X_2 P(O)NMeAlEt_2$ d         NME SPECTRA OF $X_2 P(O)NMeAlEt_2$ d         N       MeO         N       MeO         N       Hb         MeO       7.60         112.0       17.2         N       117.2         VI       17.5         Y       17.5		ICH	.60	•58	.54	.53	.50	.05	.50
TABLE 3TABLE 3TABLE 3NMR SPECTRA OF $X_2P(0)$ NMeAlEt2 $a$ NMR SPECTRA OF $X_2P(0)$ NMeAlEt2 $a$ NMR SPECTRA OF $X_2P(0)$ NMeAlEt2 $a$ LibMeOT.607.6016.59.7811bi-PrO7.4517.29.7311bi-PrO7.4617.29.71Ybi-AmO7.40YbKe2N7.55Yb17.39.73		4	. 00	æ	æ	80			
TABLE 3TABLE 3TABLE 3NMR SPECTRA OF $X_2 P(0)$ NMeAlEt2 aNMR SPECTRA OF $X_2 P(0)$ NMeAlEt2 aNMR SPECTRA OF $X_2 P(0)$ NMeAlEt2 aCom-XP-N-CH3 $J(PNCH)^b$ AlCHpound7.60IbMeOTo b7.60IbMeOTo b17.29.78IbEtO7.4517.29.74Vbi-PuOTABLE3VIbMe2NTable3VIbEt2NTable3Table3Table3Table3		5							
TABLE 3       TABLE 3         TABLE 3       NMR SPECTRA OF X2P(0)NMeAlEt <sub>2</sub> d         NMR SPECTRA OF X2P(0)NMeAlEt <sub>2</sub> d       1000000000000000000000000000000000000		VICH	.78	.73	.74	12.1	.68	.78	.73
TABLE 3       TABLE 3         TABLE 3       NMR SPECTRA OF X2P(0)NMeAlEt2 a         NMR SPECTRA OF X2P(0) NMeAlEt2 a       J(PNCH)         Com-       X       P-N-CH3       J(PNCH)         Ib       MeO       7.60       16.5       17.2         Ib       MeO       7.45       17.2       17.2         Ib       i-PrO       7.45       17.2       17.2         Ib       i-PuO       7.45       17.2       17.2         Vb       i-AmO       7.46       17.2       17.3         Vb       i-AmO       7.46       17.3       17.3         VIb       Et2N       7.55       17.3       17.3         VIb       Et2N       7.55       17.3       17.3			6	6	6	ся <u>.</u>	0	с <b>р</b>	°.
TABLE 3       TABLE 3         TABLE 3       TABLE 3         NMR SPECTRA OF X2P(O)NMeAlEt2 a         NMR SPECTRA OF X2P(O) 106 A         Dound       X         P-N-CH3       J(PN(0))         Pound       T.60       16.5         Ib       MeO       7.60       16.5         Ib       MeO       7.60       16.5         Ib       MeO       7.60       16.5         Ib       MeO       7.60       16.5         Ib       HvO       7.45       17.2         IIb       I-BuO       7.45       17.2         Vb       I-BuO       7.40       17.3         VIb       Me2N       7.76       17.3         VIb       Et2N       7.55       17.5         VIb       Et2N       7.55       12.0		7 (HC	_	<u> </u>	. <i>.</i> .				
TABLE 3TABLE 3NMR SPECTRA OF X2P(0)NMeAIEt2 aNMR SPECTRA OF X2P(0)NMeAIEt2 aCom-XP-N-CH3DoundT.60IbMeOT.60IbMeOT.65IbMeOT.45IbIbuOT.45IbIbuOT.45VIbE42NVIbE42NT.55		(PNC	16.5	17.2	11.2	17.2	17.3	17.5	17.3
TABLE 3TABLE 3NMR SPECTRA OF X2P(O)NMeAIENMR BFECTRA OF X2P(O)NMeAIENMR beconcolCom-Com-Com-DoundIbMeOT.60IbMeOT.60IbMeOT.60IbMeOT.60IbNumber 10Number 11Number 11	9 5	9							
TABLE 3TABLE 3NMR SPECTRA OF X2P(0)NMCom-XP-N-Com-XP-N-Com-XP-N-DoundXP-N-DoundXP-N- <trr>P-N-<t< td=""><td>AlEt</td><td>ЧĊН</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></t<></trr>	AlEt	ЧĊН							
TABLE 3       TABLE 3       TABLE 3       NMR SPECTRA OF X <sub>2</sub> P(O       Com-       Com-       Dound       Ib       MeO       Ib       MeO       Ib       Ib       Ib       Vb       Ib       Vb       Ib       VIb       EtO       Vb       IbuO       VIb       Et2N	WN(	-2 -	.60		1.45	1.43	7.40	7.78	7.55
TABLE 3 TABLE 3 NMR SPECTRA OF X: Com- X Com- X Com- C Ib MeO Ib MeO Ib MeO Ib EtO Vb I-BuO Vb I-BuO Vb I-BuO VIb Me2N VIIb Et2N	P(0)	1		•	•-	•-	• -		
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TABLE 3 TABLE 3 NMR SPECTI Com- Com- IIb IIb Vb Vb VIb VIb VIb	0 <b>Y</b> 1	×	MeO	EtO	l-PrO	l-But	i-Am	Me <sub>2</sub> ]	Et <sub>2</sub> )
TABLE 3 TABLE 3 NMR SPI Com- Com- Ib VMb Vb Vb Vb VIb	CTR 1			· ·			:		
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	TAB	Com	9	qu	qui	ΙVb	d V	VIP	VIIb
		- - 1			s i		•	- 	-

The introduction of bulky groups (RO = i-PrO, i-BuO, i-AmO or  $Et_2N$ ) on the phosphorus atom decreased the degree of association. The steric effect of the substituent on phosphorus is explained in terms of the dissociative equilibrium between the intermolecularly coordinated dimer and the intramolecularly coordinated monomer (eqn. 3).

In this connection, the preparation of the di-tert-butyl N-methylphosphoramidate derivative,  $(t-BuO)_2 P(O)NMeAlEt_2$ , failed. Evolution of excess ethane occurred (ca. 1.5 ~ 1.7 times the theoretical value).

#### IR and NMR spectra of Ib-VIIb

As shown in Table 2, the stretching frequency of P=O bond in Ib–VIIb, showed values lower than in the original dialkyl N-methylphosphoramidates Ia–Va or in the tetraalkylphosphorodiamidic N-methylamides (VIa, VIIa)  $(\Delta\nu(P=O) \text{ ca.} -20 \text{ to } -60 \text{ cm}^{-1})$ , which suggests the coordination of oxygen atom of P=O bonds to diethylaluminium group. The stretching frequency of the P–N bond (850 to 950 cm<sup>-1</sup>) [10] shifted to higher values on introduction of the diethylaluminium moiety  $[\Delta\nu(P-N) \text{ ca. } 40 \text{ to } 60 \text{ cm}^{-1}]$ . These two shifts of P=O (lower) and P–N (higher) stretching frequencies can be explained in terms of structure B or D, in which  $(p-d)\pi$  bonding between phosphorus and nitrogen atoms is involved. When electronegative groups (RO or R<sub>2</sub>N) are linked to the phosphorus atom, it is reported that the contraction of 3d orbitals increases their availability to  $(p-d)\pi$  bonding [11].



The NMR spectroscopic results are summarized in Table 3. Changes of coupling constant, J(PNCH), by introduction of the diethylaluminium group, provide important information about the P-N bond. Dialkyl N-methylphosphoramidates or tetraalkylphosphorodiamidic N-methylamides  $X_2P(O)NHMe$  (X = RO, R<sub>2</sub>N) (Ia-VIIa) showed J(PNCH) values around 10 to 12 Hz. These values increased to 16 to 17 Hz for the organoaluminium homologs  $X_2P(O)NMeAlEt_2$  (Ib-VIIb) as shown in Table 3. The increase of J(PNCH) by diethylaluminium group reflects the contribution of  $(p-d)\pi$  interaction between phosphorus and

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TABLE 4

Cerbonyl compounds	Products (% yield)	[(MeO) <sub>2</sub> P(O)NMe- AlEt <sub>2</sub> ] <sub>2</sub> (Ib)	[(EtO)2P(O)NMeAl- Et2]2 (IIb)
PhCH=O p-MeOC <sub>6</sub> H <sub>4</sub> CH=O	PhCH=NMe (RO) <sub>2</sub> P(O)OAlEt <sub>2</sub> p-MeOC <sub>6</sub> H <sub>4</sub> CH=NMe (RO) <sub>2</sub> P(O)OAlEt <sub>2</sub>	74 98 70 88	70 86 71 76
Ph-N=C=O <sup>a</sup> Ph <sub>2</sub> C=O	Ph-N=C=N-Me Ph-NHCONH-Me (RO) <sub>2</sub> P(O)NMeCONHPi Ph <sub>2</sub> C=NMe	60 40 1 0	36 9 55 30

REACTION PRODUCTS OF ID, IID WITH CARBONYL COMPOUNDS

<sup>a</sup> Demetallated with dilute hydrochloric acid and yield was obtained by NMR analysis.

nitrogen atoms (cf.  $P^{v}=N-CH; J(PNCH)$  20 to 30 Hz) [12, 13]. The change in coupling constants is also consistent with the strong interaction of oxygen with the aluminium atom.

# Iminocarbonylation reactions of $(RO)_2 P(O)NMeAlEt_2$ with aromatic aldehydes and ketone

When diethylaluminium dimethyl (and diethyl) N-methylphosphoramidate (Ib and IIb), reacted with aromatic aldehydes, the corresponding N-arylidenemethylamines were obtained in 70 to 80% yield along with diethylaluminium dialkyl phosphate (80 to 90% yield) (eqn. 4) as summarized in Table 4. The reaction between IIb and benzophenone was extremely slow even at  $80^{\circ}$ , probably due to a steric effect.



(R = Me, Et)

Reactions of  $X_2P(O)NMeAlEt_2$  [X = MeO (Ib), EtO (IIb) and  $Me_2N$  (VIb) with phenyl isocyanate

Phenyl isocyanate showed remarkable differences in reactivity which depended upon the degree of association of the starting aluminium compound. The reaction of dimeric compounds  $(RO)_2P(O)NMeAlEt_2$  (Ib, IIb) (R = Me, Et), with phenyl isocyanate did not proceed at room temperature. On heating up to 80°, a subsequent elimination reaction occurred immediately. In the case of IIb, three products were present: methylphenylcarbodiimide (36%; elimination product), N-methyl-N'-phenylurea (9%; hydrolysis product of carbodiimide) and  $(EtO)_2P(O)NMeCONHPh$  (55%; hydrolysis product of the corresponding 1/1 insertion intermediate) (see Table 4). The presence of both elimination (methylphenylcarbodiimide and its urea derivative) and insertion products [(EtO)<sub>2</sub>P(O)-NMeCONHPh] indicates the addition—elimination process shown in eqn. 5.



(EtO),P(O)NMeCONHPh (55%)

The hydrolysis product of the 1/1 insertion product is consistent with the conclusion that the Al-N bond of IIb was cleaved exclusively.

The addition reaction of phenyl isocyanate with IIIb or IVb (R = i-Pr or i-Bu) took place at room temperature more readily than with Ib or IIb. It is reasonable to conclude that the active species of the addition reaction should be monomeric, because the content of monomeric species in IIIb or IVb is larger than that in Ib or IIb as shown in Table 1. Therefore the dissociation to the monomeric form is required for Ib (R = Me) or IIb (R = Et) prior to insertion.

The reactivity of VIb to Ph—N=C=O at room temperature was quite low compared with those of Ib—IVb. The addition process took place slowly even at 80°. Hydrolysis of the reaction mixture gave only the 1/1 insertion product,  $(Me_2N)_2P(O)NMeCONHPh$  and no elimination products.

For the formation of P-O-Al bond at the elimination stage, the  $(RO)_2 - P(O)$  group is more effective than  $(R_2N)_2P(O)$  group. This suggests that the acidic character of the phosphorus atom plays an important role in the elimination step, because the acidity of the phosphorus atom in the former is larger than that of the latter.

#### Experimental

### General remarks

Dialkyl N-methylphosphoramidates,  $(RO)_2P(O)NHMe$ , and tetraalkylphosphorodiamidic N-methylamides,  $(R_2N)_2P(O)NHMe$ , were prepared by known methods [9, 14]. The physical data of these new compounds are summarized in Table 5. Commercial Et<sub>3</sub> Al (Ethyl Corp.) was used without further purification. Hydrocarbon solvents were thoroughly dried over sodium wire. All reactions and measurements of physical constants of the products were carried out under dry nitrogen or argon. Molecular weights in benzene solution were

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		10.24 (10.07) 6.65 (7.18) 6.30 (6.27) 5.39 (6.57) 19.36 (18.99)
	(%) H	7.07 (7.25) 9.10 (9.29) 9.59 (9.93) 10.19 (10.43) 10.71 (10.93)
and and an and an and an	found (calcd.)	
	Analysis 1 C	25.92 (25 Known cc 43.80 (43 48.73 (48 52.98 (52 Known cc 48.70 (48
	. (° C/mm)	-91/0.5 -83/0.03 -82/0.03 5-118/0.25 5-117/0.23 5-130/0.35
ИНМе	B.F	889 111 112 121 121 121 121
ATA OF X2P(0)	Yield (%)	73 74 85 97 68 30 30,137-143/3.
ND ANALY TICAL D	x	MeO EtO HPrO HPrO H-BuO H-2N Et2N Et2N 130/15. <sup>b</sup> Lit. [20] b
TABLE 6 PHYSICAL AI	Compound	Ia Ila IIa IVa VIa VIIa VIIa UIt. [19] b.p.

determined cryoscopically. Infrared spectra were recorded with a Japan Spectroscopic Co. Model IR-S and NMR spectra were recorded with a Japan Electron Optics Co. Model C-60HL using TMS as an internal standard. Elemental analyses of organoaluminium compounds were carried out by Alfred Bernhardt Microanal. Lab. in West Germany.

Preparation of diethylaluminium dialkyl N-methylphosphoramidates (Ib–Vb) and tetraalkylphosphorodiamidic N-methylamides (VIb, VIIb)

The preparation of diethylaluminium dimethyl N-methylphosphoramidate (Ib) is described as an example; IIb—VIIb were prepared analogously. Dimethyl N-methylphosphoramidate (Ia)(2.44 g, 17.5 mmol) in 20 ml of benzene was added dropwise to  $Et_3 Al$  (1.99 g, 17.5 mmol) in 20 ml benzene at room temperature. During the addition of Ia evolution of gas was observed. The reaction mixture was heated up to 80° and refluxed for 1 h. After the gas evolution had ceased completely, the solvent was removed, and the product was distilled under reduced pressure to give liquid Ib, b.p.  $135-142^{\circ}/0.28$  mm. Yield 2.81 g (72%) based on  $Et_3 Al$  used. See Tables 1—3 for data.

#### Reaction of Ib with aldehydes

Benzaldehyde. Benzaldehyde (0.416 g, 3.92 mmol) in 10 ml of benzene was added dropwise to Ib (0.871 g, 3.92 mmol) in 10 ml of benzene at room temperature. After 15 h both absorption bands at 1700 cm<sup>-1</sup> [ $\nu$ (C=O)] and 940 cm<sup>-1</sup> [ $\nu$ (P–N)] had not vanished. The reaction mixture was heated to reflux. The two above-mentioned absorption bands completely disappeared, and the appearance of new band at 1650 cm<sup>-1</sup> [ $\nu$ (C=N)] was noted. Removal of the solvent and distillation under reduced pressure gave N-benzylidenemethylamine, b.p. 75–80°/20 mm (lit. b.p. 60°/8 mm) [15], 0.35 g (yield 74%) and a residue, 0.81 g (yield 98%) of diethylaluminium dimethyl phosphate [(MeO)<sub>2</sub>P(O)–O–AlEt<sub>2</sub>]. N-benzylidenemethylamine showed the same infrared and NMR spectra as the authentic compound [16].

*p-Anisaldehyde.* In an analogous manner, reaction of Ib, (0.645 g, 2.90 mmol)in 10 ml benzene and *p*-anisaldehyde (0.395 g, 2.90 mmol) in 10 ml of benzene gave by distillation under reduced pressure *N-p*-methoxybenzylidenemethylamine, b.p.  $63-65^{\circ}/0.08 \text{ mm}$ , 0.30 g (yield 70%). Spectroscopic and physical data of the isolated product were identical with those of an authentic sample. A residue, 0.538 g(yield 88% as diethylaluminium dimethyl phosphate), was also obtained.

#### Reaction of Ib with phenyl isocyanate

Phenyl isocyanate (0.338 g, 2.83 mmol) in 10 ml of benzene was added dropwise to Ib, (0.629 g, 2.83 mmol) in 10 ml of benzene at room temperature. After 16 h, both absorption bands at 2260 cm<sup>-1</sup> [ $\nu$ (NCO)] and 940 cm<sup>-1</sup> [ $\nu$ (PN)] remained. The reaction mixture was heated to 80° and refluxed for 6 h. Both of the above two absorption bands disappeared completely and new bands at 2130 cm<sup>-1</sup> [ $\nu$ (NCN)], characteristic of *N*-methyl-*N'*-phenylcarbodiimide, 1695 and 1650 cm<sup>-1</sup> appeared. After hydrolysis of the mixture with dilute hydrochloric acid the product was extracted with benzene. The benzene solution was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>; removal of the solvent gave 0.511 g of an oil. NMR analysis of this oil showed the presence of *N*-methyl-*N'*-phenylcarbodiimide (60%) and PhNHCONHMe (40%). The authentic sample of carbodiimide was prepared according to ref. 17.

# Reaction of IIb with aldehydes and ketones

Benzaldehyde. When a mixture of benzaldehyde (0.250 g, 2.32 mmol) and IIb, (0.584 g, 2.32 mmol) in 20 ml of benzene was kept at room temperature for 24 h and heated at reflux for 12 h, absorption bands at 1700 cm<sup>-1</sup> [ $\nu$ (C=O)] and 920 cm<sup>-1</sup> [ $\nu$ (PN)] disappeared, and a new absorption band at 1650 cm<sup>-1</sup> [ $\nu$ (C=N)] appeared. The products were PhCH=NMe (0.19 g, 70%) and (EtO)<sub>2</sub> - P(O)-O-AlEt<sub>2</sub> (0.51 g, 92%).

*p-Anisaldehyde*. In an analogous manner a mixture of IIb, (0.871 g, 3.50 mmol) and *p*-anisaldehyde (0.476 g, 3.50 mmol) in 20 ml of benzene was kept at room temperature for 17 h and then refluxed for 4 h. The products were *p*-MeOC<sub>6</sub>H<sub>4</sub>CH=NMe (0.34 g, 71%) and (EtO)<sub>2</sub>P(O)-O-AlEt<sub>2</sub> (0.54 g, 76%).

Benzophenone. A mixture of IIb, (0.664 g, 2.64 mmol) and benzophenone (0.482 g, 2.64 mmol) in 20 ml of benzene was heated at reflux for 5 days. During the heating, the intensity of  $\nu$ (C=O) (1680 cm<sup>-1</sup>) band of the ketone decreased slightly and that the 1640 cm<sup>-1</sup> [ $\nu$ (C=N)] band increased gradually. However, the reaction did not go to completion. The corresponding imino compound, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C=NMe, was obtained in 30% yield on the basis of NMR. NMR (CCl<sub>4</sub>):  $\tau$  6.93 s (NCH<sub>3</sub>), 2.38–3.28 ppm (m, phenyl).

# Preparation of authentic diethylaluminium diethyl phosphate

Diethyl phosphate [18] (1.60 g, 10.3 mmol) in 20 ml of benzene was added to Et<sub>3</sub> Al (1.17 g, 10.3 mmol) in 20 ml of benzene. During the addition of the phosphate, evolution of gas was observed. The reaction mixture was heated to 80°. After gas evolution ceased completely, removal of the solvent and distillation under reduced pressure gave diethylaluminium diethyl phosphate, 1.95 g (yield 80% based on Et<sub>3</sub> Al used), b.p. 108–114°/0.35 mm. (Found: Al, 10.15; active ethyl groups 1.84. C<sub>8</sub>H<sub>20</sub>O<sub>4</sub> Pal calcd.: Al, 11.32%; active ethyl groups 2.00 per mol.) NMR (benzene):  $\tau$  9.75 q (AlCH<sub>2</sub>, 4H, J 7.5 Hz), 9.03 t (P–O– CH<sub>2</sub>–CH<sub>3</sub>, 6H, J 6.8 Hz), 8.51 t (AlCH<sub>2</sub>CH<sub>3</sub>, 6H, J 7.5 Hz), 6.17 dq ppm (P–O–CH<sub>2</sub>–CH<sub>3</sub>, 4H, J(POCH) 7.8 Hz, J (HCCH) 6.8 Hz). IR (benzene:  $\nu$ (P=O) 1280 s and 1262 s,  $\nu$ (P–O–C) 1020–1045 vs cm<sup>-1</sup>.

## Reaction of IIb with phenyl isocyanate

An equimolar mixture of IIb, (0.578 g, 2.30 mmol) and phenyl isocyanate, (0.275 g, 2.30 mmol) in 20 ml of benzene was kept at room temperature for 1 day. However, no reaction occurred. The mixture was heated to 80° and refluxed for 6 h. Both absorption bands at 2260 cm<sup>-1</sup> [ $\nu$ (NCO)] and 920 cm<sup>-1</sup> [ $\nu$ (P-N)] disappeared completely, while new bands at 2130 cm<sup>-1</sup> [ $\nu$ (N=C=N)], 1690 cm<sup>-1</sup> and 1650 cm<sup>-1</sup> appeared. Hydrolysis of the mixture gave an oil, 0.455 g, which contained three components, *N*-methyl-*N'*-phenylcarbodiimide (36%), PhNHCONHME (9%) and the 1/1 insertion product (EtO)<sub>2</sub>P(O)NMe-CONHPh (55%). (EtO)<sub>2</sub>P(O)NMeCONHPh; NMR (CCl<sub>4</sub>):  $\tau$  8.65 t (P-O-CH<sub>2</sub>-CH<sub>3</sub>, *J* 6.8 Hz), 7.05 d (P-N-CH<sub>3</sub>, *J*(PNCH) 6.8 Hz), 5.88 dq (P-O-CH<sub>2</sub>-CH<sub>3</sub>, *J* 6.8 Hz), 7.05 d (P-N-CH<sub>3</sub>, *J*(PNCH) 6.8 Hz), 5.88 dq (P-O-CH<sub>2</sub>-CH<sub>3</sub>, *J*(POCH) 7.5, *J*(HCCH) 6.8 Hz), 2.38-3.32 (phenyl), -0.10 s ppm (P-NH-Me). IR (CCl<sub>4</sub>): 3230 m [ $\nu$ (NH)], 1700 s [ $\nu$ (C=O)], 1276 s [ $\nu$ (P=O)], 1014 s [ $\nu$ (P-O-C)], 873 m cm<sup>-1</sup> [ $\nu$ (P-N)].

# Reaction of VIb with phenyl isocyanate

An equimolar mixture of VIb, (1.21 g, 4.85 mmol) and phenyl isocyanate (0.578 g, 4.85 mmol) in 20 ml of benzene was kept at room temperature for 60 h. No reaction occurred. Heating at reflux for 17 h caused the disappearance of  $\nu(\text{NCO})$  (2260 cm<sup>-1</sup>) and appearance of bands at 1630 cm<sup>-1</sup> and 1660 cm<sup>-1</sup>. Hydrolysis of the mixture as before gave an oil, *N*-tetramethylphosphorodiamidic-*N*-methyl-*N*'-phenylurea, (Me<sub>2</sub>N)<sub>2</sub>P(O)NMeCONHPh, in 73% yield. IR (benzene): 3160 m [ $\nu(\text{NH})$ ], 1690 vs [ $\nu(\text{C=O})$ ], 1260 vs [ $\nu(\text{P=O})$ ] and 985 vs, 970 vs cm<sup>-1</sup> [ $\nu(\text{P=O-C})$ ]. NMR (CCl<sub>4</sub>):  $\tau$  7.38 d [P-N(CH<sub>3</sub>)<sub>2</sub>, 12H, J(PNCH) 9.8 Hz), 7.21 d (P-N-CH<sub>3</sub>, J(PNCH) 7.5 Hz, 3H), 2.45-3.32 m (phenyl, 5H) and -0.62 s (CON<u>H</u>Ph, 1H). (Found: C, 50.56; H, 6.68; N, 19.75. C<sub>12</sub>H<sub>21</sub>N<sub>4</sub>O<sub>2</sub>P calcd.: C, 50.70; H, 7.45; N, 19.71%.)

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