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Synthesis and characterization of functionalized phosphenium ions, stabilized by two intramolecular dative P ← N bonds

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Abstract

$ArPH_2$ (Ar = $[C_6H_3(CH_2NMe_2)_2$-2,6]) **3** undergoes hydride abstraction on treatment with trityl cation to give the stabilized phosphenium ion $[ArPH]^+BF_4^-$ **4a**. The same cation was prepared by reaction of **3** with $BrCCl_3$ (**4b**) and also by lithiation of **3** followed by treatment with I_2 (**4c**). ArLi reacts with PX_3 (X = Cl or Br) to give the stabilized phosphenium ion $[ArPX]^+X^-$ which affords **3** by $LiAlH_4$ reduction. In contrast, DIBAL-H reduction of $[ArPX]^+X^-$ gives $[ArPH]^+X^-$. This last reaction constitutes a transformation of a stabilized and functionalized phosphenium ion into a different ion. Confirmation of the structure of these salts was given by single-crystal X-ray diffraction analysis of $[ArPH]^+PF_6^-$ **4e**. © 1997 Elsevier Science S.A.

Keywords: Stabilized phosphenium ion; X-ray structure analysis; DIBAL-H

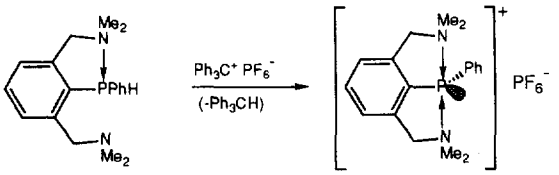
1. Introduction

Phosphenium ions R_2P^+ are reactive species which can be stabilized by the presence of strong π-donor substituents, classically two dialkylamino groups (for reviews on phosphenium ions, see Ref. [1]), or by a bulky substituent providing stabilization close to the phosphorus atom [2]. Another approach to stabilize phosphenium ions is to substitute them by chelating ligands [3–10]. We have recently explored this possibility using the potentially terdentate aryldiamine ligand $[C_6H_3(CH_2NMe_2)_2$-2,6] [11] (Ar) and we have reported the synthesis and the characterization of the salt **2** containing two P–C bonds [12] and stabilized by intramolecular coordination of both amino groups to the phosphorus centre.

We have now extended this method to the formation of functionalized phosphenium ions, stabilized by the same ligand. In this paper, we present the synthesis, characterization and X-ray structure analysis of a stabilized phosphenium ion bearing a P–H σ bond. Stabilized phosphenium ions with a P–X σ bond (X = Cl or Br) are also described.

2. Results and discussion

In a previous paper [12] we showed that phosphane **1** undergoes hydride abstraction by reaction with $Ph_3C^+PF_6^-$ to form the stabilized phosphenium ion **2** (Eq. (1)).



1 2 (1)

We have now prepared as a starting material the phosphane **3** [13] (Scheme 1) by $LiAlH_4$ reduction of diethyl{2,6-bis[(dimethylamino)methyl]phenyl}phosphonate It is to be noted that the ^{31}P NMR chemical shift of **3** (−147.8 ppm, $CDCl_3$) is upfield with respect to that of phenylphosphane (−108.1 ppm [14], $CDCl_3$) thus suggesting N → P intramolecular interactions. However, because of the symmetry of the molecule, further indication concerning the coordination mode cannot be inferred from the ^1H NMR spectrum and it is not known

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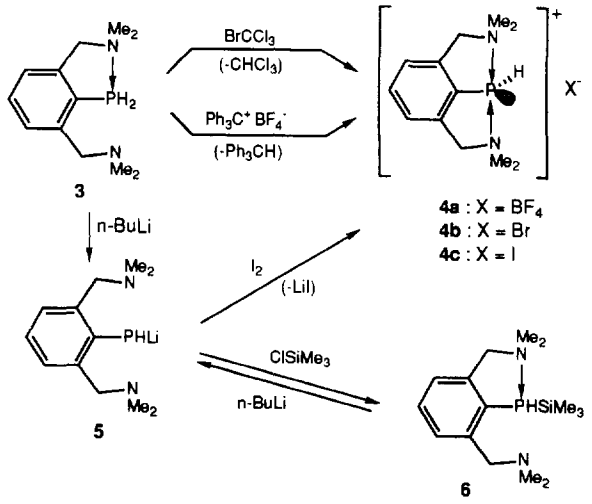
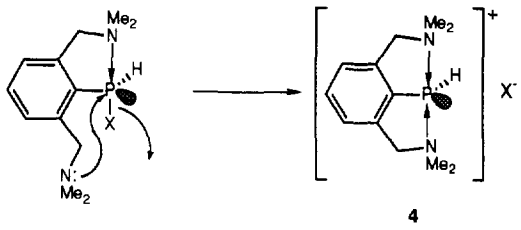


Scheme 1.



Scheme 2.

whether one or both NMe_2 groups are coordinated. In any case, **3** undergoes quantitative hydride abstraction on treatment with $Ph_3C^+BF_4^-$. This behaviour is due to the 'extra' coordination at phosphorus, the trityl cation usually adding to phosphanes to afford the corresponding phosphonium ions [15]. A white powder, stable in air, insoluble in hexane, diethyl ether and tetrahydrofuran but soluble in dichloromethane and chloroform resulted from this reaction (Scheme 1). The ^{31}P NMR spectrum of this species (**4a**) displays a doublet at $\delta = 36.6$ ppm with a $^1J(P,H)$ of 240 Hz. This ^{31}P NMR resonance is shifted considerably downfield with respect to that of the starting phosphane which appears as a triplet ($\delta = -147.8$ ppm, $^1J(P,H) = 207.5$ Hz, $CDCl_3$). The positive-ion FAB mass spectrum shows the parent ion at $m/z = 223$ corresponding to $(M - BF_4)^+$.

Two other salts have been prepared for which the positive-ion FAB mass spectra show also the parent ion at $m/z = 223$ and the ^{31}P NMR data of which (Table 1) are almost identical to those of **4a**: the bromide salt **4b**, by reaction of **3** with $BrCCl_3$ and the iodide salt **4c** by lithiation of **3** followed of treatment by I_2 (Scheme 1). It is to be noted that the lithium derivative **5** was characterized by reaction with trimethylchlorosilane giving rise to the silylphosphane **6** in 81% yield.

^1H NMR spectra of **4a** (in CD_3CN), **4b** (in $CDCl_3$) and **4c** (in $CDCl_3$) exhibit two resonances for the N-methyl groups and an AB system for the benzylic protons (Table 1). This set of signals is consistent with the coordination of both nitrogen atoms to the phosphorus centre, the two CH_2NMe_2 'arms' being equivalent. The diastereotopy of the methyl groups of each NMe_2 unit as well as that of methylene protons indicates that the lone pair at phosphorus is stereochemically active. It is to be noted that the ^1H NMR spectrum of **4a** in $CDCl_3$ shows two quite distinct resonances of equal intensity for the N-methyl protons and a slightly broadened singlet for the methylene protons (Table 1). The ^1H NMR spectra (in $CDCl_3$) of **4a**, **4b**, and **4c** display also a doublet assigned to the PH proton. Overall these data are consistent with the structure described in Scheme 1 in which both NMe_2 groups are coordinated to the phosphorus centre.

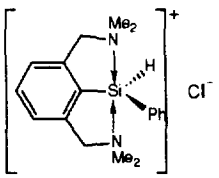
The formation of salts **4b** and **4c** can be explained by postulating the intermediate ArPHX (X = Br or I) which undergoes displacement of the halide by intramolecular coordination of the second amino group to the phosphorus centre (Scheme 2). This last step corresponds to nucleophilic activation of a nucleophilic substitution at phosphorus, a process which has been previously studied [16]. It is worth noting that the formation of the five-coordinate silyl cation **7** [17] was explained in the same way. Interestingly the ^1H NMR spectrum of **7** exhibits also the same set of signals as **4a–4c** for both

Table 1
Selected NMR data for salts **4a-4d** at 297 K in $CDCl_3$ (250 MHz)

Salt	^{31}P NMR		^1H NMR					
	δ (ppm)	$^1J_{(P,H)}$ (Hz)	$\delta(CH_3)_A$ [b] (ppm)	$^3J_{(H,P)}$ (Hz)	$\delta(CH_3)_B$ [b] (ppm)	$\delta(H)_A$ [b]	$\delta(H)_B$ [b] (ppm)	$^2J_{(H,H)}$ (Hz)
4a	36.6 (d)	240	2.69 (d)	4.2	2.75 (s)		4.09 (broad)	
4a [a]			2.49 (d)	4.3	2.50 (s)	3.89 (d)	3.97 (d)	15.0
4b	36.7 (d)	243	2.70 (d)	4.1	2.85 (s)	4.09 (d)	4.24 (d)	15.0
4c	37.0 (d)	246	2.74 (d)	4.0	2.95 (s)	4.11 (d)	4.30 (d)	14.9
4d	37.3 (d)	234	2.69 (d)	4.1	2.85 (s)	4.10 (d)	4.23 (d)	15.0
4e	37.6 (d)	243	2.70 (d)	4.0	2.78 (s)	4.07 (d)	4.14 (d)	15.2

[a] 200 MHz in CD_3CN. [b] See Scheme 1.

CH_2NMe_2 'arms' (an AB system for the benzylic protons and two signals of equal intensity for the methyl protons).



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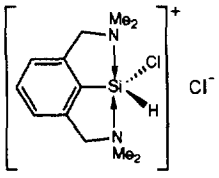

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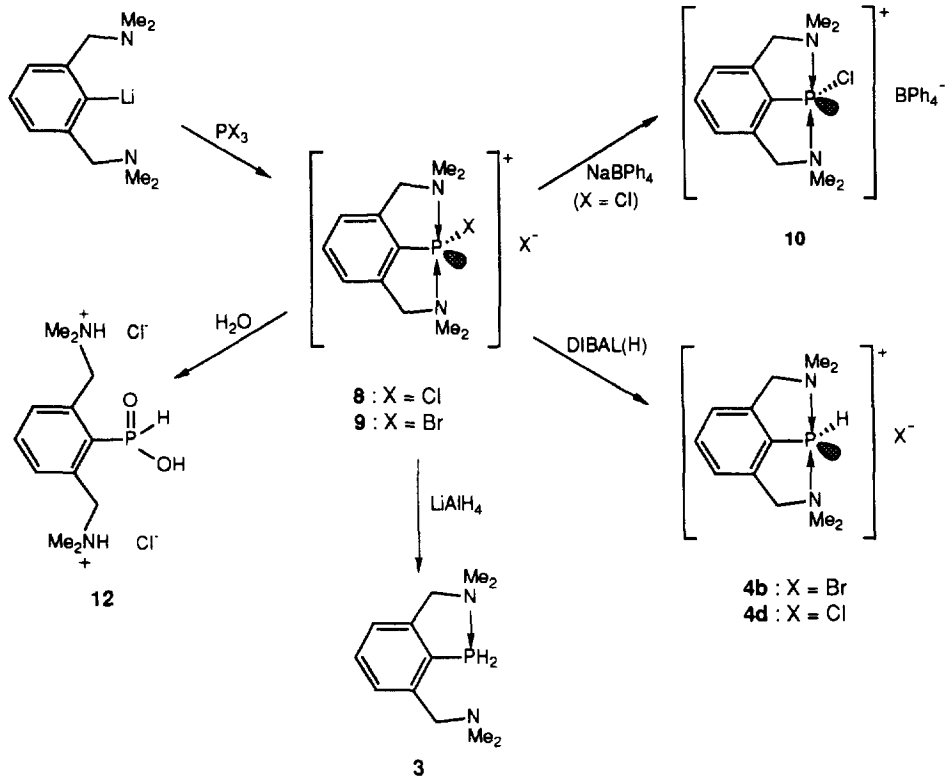
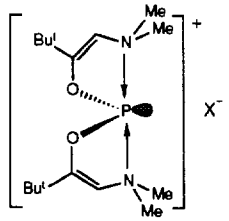
A stabilized phosphenium ion with a P–Si bond could not be obtained by lithiation of the silyl phosphane **6** with *n*-BuLi, followed by the addition of iodide. Instead, the iodide salt **4c** was obtained in 70% yield indicating that *n*-BuLi induces the cleavage of the P–Si bond leading to the lithium derivative **5** (Scheme 1).

2,6-Bis(dimethylaminomethyl)phenyllithium [18] reacts with PCl_3 and PBr_3 to afford respectively the phosphorus species **8** and **9** (Scheme 3). Both compounds were isolated as extremely air- and moisture-sensitive yellow powders, soluble in polar aprotic solvents and halogenated solvents. Treatment of **8** with one molar equivalent of sodium tetraphenylborate yields **10** (Scheme 3) which is also extremely air- and moisture-sensitive. Interestingly the ^{31}P NMR chemical shifts of **8** (131.5 ppm) and **10** (131.9 ppm) are very similar in solution, which indicates their ionic nature. The ^1H NMR spectra of **8**, **9** and **10**, display at room temperature one doublet ($^3J(P,H) = 3$ Hz) for the methyl protons and one singlet for the benzylic protons. Lowering the temperature of the NMR samples resulted in broadening and decoalescence of the N-methyl and methylene signals. At 158 K for **8**, 173 K for **9** and 238 K for **10** (400 MHz, CD_2Cl_2) the ^1H NMR spectra exhibit two signals for the N-methyl protons and a well-resolved AB system for the benzylic protons. Thus, at low temperature, the ^1H NMR spectra of **8**, **9** and **10** exhibit the same set of signals for the CH_2NMe_2 groups as those of compounds **4a–4c**, which suggests that **8**, **9** and **10** have a structure similar to those of **4a–4c** in which both NMe_2 groups are coordinated to the phosphorus centre, this one being covalently bonded to one X atom. The equivalence of the two methyl groups on each NMe_2 unit observed at room temperature for **8** and **9** is interpreted as the result of a rearrangement process involving attack of X^- to the phosphorus atom with inversion of configuration (Scheme 4). The activation energy for this process was estimated [19] to be 36 kJ mol^{-1} for **8** ($T_c = 178$ K, $\Delta\nu = 90$ Hz) and 40 kJ mol^{-1} for **9** ($T_c = 193$ K, $\Delta\nu = 42$ Hz). It is to be



Scheme 3.

noted that a similar rearrangement process was observed for the siliconium ion **11** [20].



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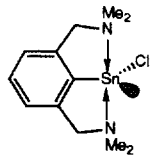

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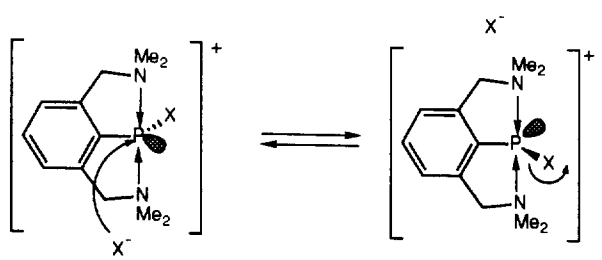
As for **10**, the equivalence of the two methyl groups on each NMe_2 unit observed at room temperature, in spite of the absence of X^- (X = Cl, Br) as counteranion, might be due to an intermolecular exchange reaction of chlorine atoms between two cations. This process should require an activation energy higher than that operating on **8** and **9**. Indeed the $\Delta G^{\ddagger}$ for this process was estimated to be 52 kJ mol^{-1} (T_c = 253 K, $\Delta\nu$ = 103 Hz). At low temperature in all cases these exchange processes are slowed down (on the NMR time scale) so that the methyl groups on each NMe_2 unit and the benzylic protons become diastereotopic.

When **8** is left in the air, atmospheric moisture induces its complete hydrolysis over 2 h with protonation of the two amino groups due to the formation of two molar equivalents of HCl giving rise to **12** quantitatively. The identity of **12** was established by elemental analysis, high resolution mass spectrometry and ^1H, ^{13}C and ^{31}P NMR spectroscopy.

Other diagnostic data for the structural elucidation of **8** and **9** was given from the study of their reactivity toward reducing agents (Scheme 3). $LiAlH_4$ reduction of **8** and **9** affords the phosphane **3**. In contrast, while the reduction of $PhPCl_2$ with two molar equivalents of $(i\text{-}C_4H_9)_2AlH$ gives quantitatively phenylphosphane, treatment of **8** and **9** even with a large excess of DIBAL-H (five molar equivalents) did not afford the phosphane **3**. Instead, in both cases, colourless, air-stable solids were obtained. The product resulting from the DIBAL-H reduction of **9** is the ionic compound **4b** previously obtained by reaction of **3** with $BrCCl_3$ (Scheme 1) and that resulting from the DIBAL-H reduction of **8** is the ionic compound **4d** which also exhibits almost the same ^1H and ^{31}P NMR spectra as **4b** (Table 1). Their positive-ion FAB mass spectra show the parent ion at m/z = 223.



Scheme 4.

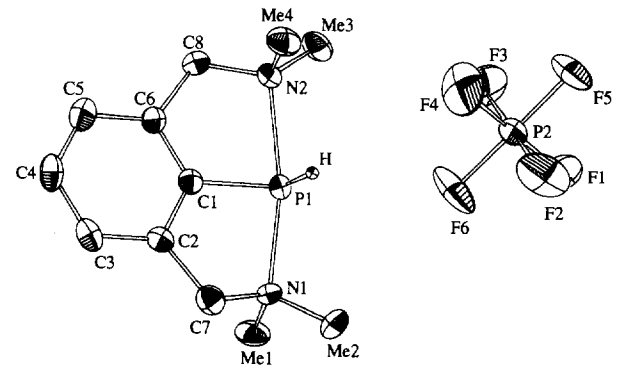


Fig. 1. ORTEP drawing of the molecular structure of **4e** showing the numbering scheme. The thermal ellipsoids and spheres are at the 30% probability level.

Treatment of the chloride **4d** with KPF_6 afforded the corresponding hexafluorophosphate salt $ArPH^+PF_6^-$ **4e**, the ^1H NMR spectrum of which is very similar to those of the salts **4a–4c** (Table 1). The ^{31}P NMR spectrum of **4e** exhibits two signals of equal intensity, one doublet at δ = 37.6 ppm (^1J(P,H) = 243 Hz) and one heptuplet at δ = −143.7 ppm (^1J(P,F) = 712.7 Hz) assigned to PF_6^- [14]. The positive ion FAB mass spectrum shows the

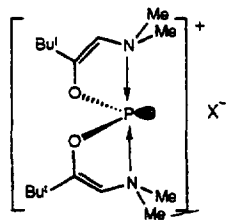
Table 2
Summary of crystal data, intensity measurements and refinement for compound **4e**

Formula	$C_{12}H_{20}F_6N_2P_2$
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	9.190(3)
b (Å)	9.813(2)
c (Å)	17.992 (4)
β (deg)	94.10 (2)
Volume (Å^3)	1618.3 (7)
Mol. wt.	368.24
Z	4
d_{calcd} (g cm^{-3})	1.511
Crystal size (mm^3)	0.15 × 0.40 × 0.30
Crystal colour	colorless
Recrystallization solvent	CH_2Cl_2
M.p. (°C)	198-200
Method of data collection	$\omega-\theta$
Measurement temperature (K)	162
Radiation (graphite-monochoromated)	Mo Kα
μ (cm^{-1})	3.18
2θ limits (deg)	50
No. of unique reflections	2670
No. of observed reflections	1588
Final no. of variables	182
R	0.044
R_w	0.047
Residual electron density	0.41

Table 3
Interatomic distances (Å) and main bond angles (deg) for compound **4e**

P1-C1	1.810(4)	N1-Me1	1.492(5)
P1-H	1.31(2)	N1-Me2	1.488(6)
P1-N1	2.068(4)	C6-C8	1.507(6)
P1-N2	2.082(3)	C8-N2	1.486(5)
P1 , F6	3.476(4)	H , F6	2.81(1)
P1 , F3	4.340(4)	H , F4	3.50(1)
P1 , F4	4.504(4)	H , F3	3.93(1)
		N2-Me3	1.490(6)
C1-C2	1.390(5)	N2-Me4	1.493(5)
C2-C3	1.394(6)		
C3-C4	1.390(6)	P2-F1	1.576(3)
C4-C5	1.397(6)	P2-F2	1.555(4)
C5-C6	1.390(6)	P2-F3	1.577(3)
C6-C1	1.380(6)	P2-F4	1.582(4)
C2-C7	1.500(6)	P2-F5	1.579(3)
C7-N1	1.491(5)	P2-F6	1.590(3)
C1-P1-N1	82.8(2)	C2-C7-N1	106.8(3)
C1-P1-N2	82.4(2)	C7-N1-P1	108.6(3)
C1-P1-H	99.4(8)	P1-C1-C6	118.2(3)
H-P1-N1	89.3(7)	C1-C6-C8	113.8(4)
H-P1-N2	85.4(6)	C6-C8-N2	106.7(3)
N1-P1-N2	163.3(2)	C8-N2-P1	104.9(2)
P1-C1-C2	119.4(3)	C2-C1-C6	122.4(4)
C1-C2-C7	114.5(4)		

parent ion at $m/z = 223$. Single crystals of **4e** suitable for an X-ray analysis were grown slowly from a CH_2Cl_2 solution at room temperature. An ORTEP drawing of **4e** is shown in Fig. 1. A summary of the crystallographic data is presented in Table 2, and the selected bond distances and angles are given in Table 3. The X-ray structure clearly demonstrates the ionic structure of **4e**. There is no interaction between the cationic phosphorus species and the PF_6^- anion: the shortest phosphorus–fluorine distance is 3.476 Å which is greater than the sum of the van der Waals radii of both elements (3.27 Å) [21] and the shortest hydrogen–fluorine distance is 2.81(2) Å which is also greater than the sum of van der Waals radii of the corresponding elements (2.67 Å) [21]. Both amine 'arms' are coordinated to the phosphorus centre with N–P bond distances of 2.082 and 2.068 Å. These distances are longer than the N–P σ bond distance 1.769 Å [22] but notably shorter than the sum of van der Waals radii of nitrogen and phosphorus atoms (3.4 Å) [21]. They are very close to those observed for the compound **13** [9] (2.053 and 2.056 Å) in which two intramolecular N → P interactions occur. The P–H bond is orientated almost orthogonally to the plane of the aryl ligand [C1–P–H angle being of 99.4(8)°]. Hence the phosphorus atom is pseudo five-coordinated, taking into account the phosphorus lone pair, and the geometry of the cation is that of a distorted trigonal bipyramid in which both dimethylamino groups occupy the axial positions, C1, H and the phosphorus lone pair occupying the equatorial sites. Of further interest, the N1–P–N2 angle of 163.3 (2)° deviates notably from the ideal value (180°) for a trigonal bipyramid but is nevertheless much larger than the N–Sn–N angle observed in the tin compound **14** [23] (143.04°) described by van Koten and coworkers with the same bis-chelating ligand.



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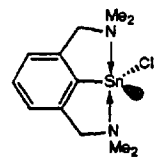

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3. Conclusions

In this paper we describe the preparation of the first stabilized phosphenium ion with a P–H σ bond by using the potentially terdentate aryldiamine ligand [11] $C_6H_3(CH_2NMe_2)_2$-2,6 (Ar). This ligand allowed also the preparation of stabilized phosphenium ions with a P–X σ bond (X = Cl or Br). Thus the reaction of ArLi with PCl_3 affords the ionic species $[ArP–Cl]^+Cl^-$ and not the covalent one $ArPCl_2$ [13], whereas the same reaction with $SbCl_3$ gave the covalent species $ArSbCl_2$ [13]. Furthermore, the transformation of salts **8** and **9** into the stabilized phosphenium ion with a P–H bond was achieved via DIBAL-H reduction showing thus the unusual transformation of a stabilized and functionalized phosphenium ion into another ion.

4. Experimental

4.1. General

All reactions were carried out under an argon atmosphere using Schlenk tube techniques. All solvents were purified by distillation (CH_2Cl_2 and CH_3CN from P_2O_5; diethyl ether from sodium–benzophenone) prior to use and were stored under an argon atmosphere. Chlorodiethylphosphate and chlorotrimethylsilane were distilled over Mg under argon prior to use.

IR spectra were recorded on a Perkin Elmer 1600 Fourier transform spectrometer, mass spectra were registered on a Jeol JMS-D100 and a Jeol JMS-SX102 spectrometer. ^1H, ^{31}P, ^{13}C, ^{15}N and ^{29}Si NMR spectra were obtained using a Brucker 250-AC or a Brucker 200-SY spectrometer. ^1H, ^{13}C and ^{29}Si chemical shifts are relative to Me_4Si, ^{31}P chemical shifts to H_3PO_4 and ^{15}N chemical shifts to nitromethane. Elemental analyses were carried out by the "Centre de microanalyse du CNRS".

4.2. Diethyl{2,6-bis[(dimethylamino)methyl]phenyl}-diethylphosphonate

24.6 mmol of 2,6-bis[(dimethylamino)methyl]phenyllithium [18] in ether (60 ml) was added dropwise at 0 °C to a solution of chlorodiethylphosphate (3.0 ml, 24.6 mmol) in ether (60 ml). The reaction mixture was stirred at room temperature for 2 h. After hydrolysis of the reaction mixture with 40 ml of distilled water, the aqueous layer was extracted with ether (2 × 20 ml). The organic layers were collected, dried over $MgSO_4$ and filtered. After removal of the solvent under vacuum the residual viscous oil was distilled and 5.0 g (15.5 mmol, 63%) of diethyl{2,6-bis[(dimethylamino)methyl]-phenyl}phosphonate was isolated as a yellow oil. B.p. 130–132 °C (0.03 mm Hg); ^{31}P NMR (101.25 MHz, $CDCl_3$): $\delta = 19.0$ (s); ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.26$ (t, $^3J(H,H) = 7.1$ Hz, 6H; C–CH_3), 2.19 (s, 12H; NCH_3), 3.80 (s, 4H; CH_2N), 4.10 (m, 4H; OCH_2), 7.39 to 7.46 (m, 1H; Ar), 7.53 to 7.58 (m, 2H; Ar); ^{13}C NMR (62.89 MHz, $CDCl_3$, {H}): $\delta = 16.32$ (d, $^3J(C,P) = 6.3$ Hz, C–CH_3), 45.45 (s, NCH_3), 61.41 (d, $^2J(C,P) = 5.2$ Hz, OCH_2), 62.36 (d, $^2J(C,P) = 2.7$ Hz, NCH_2), 125.92 (d, $J(C,P) = 179.0$ Hz, Ar), 128.91 (d, $J(C,P) = 14.4$ Hz, Ar), 131.26 (d, $J(C,P) = 3.3$ Hz, Ar), 145.18 (d, $J(C,P) = 11.5$ Hz, Ar); ^{15}N NMR (20.28 MHz, $CDCl_3$, {H}, CH_3NO_2): $\delta = -351.7$ (s); MS (FAB positive mode, *m*-nitrobenzylalcohol (NBA)): *m/z* (%): 329 (100) $[M + H]^+$; $C_{16}H_{29}N_2O_3P$ calcd.: C, 58.53; H, 8.84; N, 8.53; O, 14.63; P, 9.47; found: C, 58.44; H, 8.69; N, 8.32; O, 15.07; P, 9.57.

4.3. 2,6-Bis[(dimethylamino)methyl]phenyl]phosphane (3)

A suspension of $LiAlH_4$ (0.80 g, 21 mmol) in ether (80 ml) was added dropwise at room temperature to a solution of diethyl{2,6-bis[(dimethylamino)methyl]phenyl}phosphonate (4.48 g, 13.6 mmol) in ether (60 ml). The reaction mixture was stirred at room temperature for 2 days and refluxed for 1 h. 0.8 ml of distilled water, 0.8 ml of 15% NaOH solution and 0.8 ml of distilled water were successively added. After filtration of the salts, the solution was dried over $MgSO_4$ and filtered. The solvent was then removed and the crude product was distilled under vacuum to give 2.30 g (10.3 mmol, 75%) of **3** as colourless oil. B.p. 75–80 °C (0.05 mm Hg). [Ref. [13] 100 °C (76 mm Hg)]; ^{31}P NMR (101.25 MHz, $CDCl_3$): $\delta = -147.8$ (t, $^1J(P,H) = 207.5$ Hz) [Ref. [13] $\delta = -146$ (t, $^1J(P,H) = 206$ Hz) ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.12$ (s, 12H; NCH_3), 3.37 (s, 4H; CH_2N), 3.67 (d, $^1J(P,H) = 207.8$ Hz, 2H; PH_2), 7.06 to 7.12 (m, 3H; Ar); IR (Nujol): 2267.4, 2324.8 cm^{-1} (PH_2); MS (FAB positive mode, *o*-nitrophenyloctylether (NPOE)): *m/z* (%): 223 (65) $[M - H]^+$, 58 (100) $[CH_2{=}NMe_2]^+$; $C_{12}H_{21}N_2P$ calcd.: C, 64.28; H, 9.37; N, 12.50; found: C, 64.29; H, 9.90; N, 12.30.

4.4. {2,6-Bis[(dimethylamino)methyl]phenyl}phosphorus tetrafluoroborate (4a)

A solution of trityl tetrafluoroborate (2.10 g, 6.36 mmol) in CH_2Cl_2 (20 ml) at −10 °C was added dropwise to a solution of **3** (1.44 g, 6.43 mmol) in CH_2Cl_2 (20 ml). The reaction mixture was stirred at room temperature for 2 h. The solvent was removed under vacuum and the residue was washed with ether (4 × 25 ml) to eliminate Ph_3CH. After filtration, 1.83 g (5.91 mmol, 93%) of **4a** was obtained as a white powder. M.p. 185 °C; ^{31}P NMR (101.25 MHz, $CDCl_3$): $\delta = 36.6$ (d, $^1J(P,H) = 240$ Hz); ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.69$ (d, $^3J(H,P) = 4.2$ Hz, 6H; NCH_3), 2.75 (s, 6H; NCH_3), 4.09 (broad s, CH_2N), 5.96 (d, $^1J(H,P) = 240$ Hz, 1H; PH), 7.10 to 7.45 (m, 3H; Ar); ^1H NMR (250 MHz, CD_3CN): $\delta = 2.49$ (d, $^3J(H,P) = 4.3$ Hz, 6H; NCH_3), 2.50 (s, 6H; NCH_3), 3.89 (d, $^2J(H,H) = 15.1$ Hz, 2H; CH_2N), 3.97(d, $^2J(H,H) = 15.0$ Hz, 2H; CH_2N), 5.68 (d, $^1J(H,P) = 237$ Hz, 1H; PH), 7.00 to 7.45 (m, 3H; Ar); MS (FAB positive mode, NPOE): *m/z* (%): 223 (100) $[M - BF_4]^+$; (FAB negative mode, NPOE): *m/z* (%): 87 (100) $[BF_4^-]$.

4.5. {2,6-Bis[(dimethylamino)methyl]phenyl}phosphorus bromide (4b)

4.5.1. From 3

0.6 ml (6.20 mmol) of bromotrichloromethane was added dropwise at 0 °C by syringe to a solution of **3** (1.40 g, 6.25 mmol) in ether (40 ml). The reaction mixture was stirred at room temperature for 1 h. The solvent was removed under vacuum and the residue was washed with ether (4 × 30 ml). After filtration, 1.82 g (6.00 mmol, 97%) of **4b** was obtained as a white powder. M.p. 195 °C (decomp.); ^{31}P NMR (101.25 MHz, $CDCl_3$): $\delta = 36.7$ (d, $^1J(P,H) = 243$ Hz). ^{13}C NMR (50.32 MHz, $CDCl_3$, {H}): $\delta = 47.70$ (d, $^2J(C,P) = 16.0$ Hz, NCH_3), 48.10 (s, NCH_3), 64.30 (s, NCH_2), 125.10, 131.10, 139.05, 139.20 (Ar); IR (KBr): 2254 cm^{-1} (PH); MS (FAB positive mode, NPOE): *m/z* (%): 223 (100) $[M - Br]^+$; (FAB negative mode, NPOE): *m/z* (%): 79, 81 (100) $[Br^-]$.

4.5.2. From 9

A solution of diisobutylaluminiumhydride (0.7 mmol) in hexane (0.7 ml) was added dropwise at 0 °C to a solution of **9** (0.27 g, 0.66 mmol) in CH_2Cl_2 (12 ml). The reaction mixture was stirred at room temperature for 5 h. The solvent was removed and the crude product was allowed under vacuum (0.02 mm Hg) for 3 days at 90 °C to eliminate the diisobutylaluminium bromide

formed. The residue was washed with ether (2 × 50 ml) to give after filtration 0.18 g (0.59 mmol, 90%) of **4b** as a yellow powder. M.p. 195 °C (decomp.); ^{31}P NMR (101.25 MHz, $CDCl_3$): $\delta = 36.3$ (d, $^1J(P,H) = 241$ Hz); ^{13}C NMR (50.32 MHz, $CDCl_3$, {H}): $\delta = 47.75$ (d, $^2J(C,P) = 15.9$ Hz, NCH_3), 48.10 (s, NCH_3), 64.34 (s, NCH_2), 125.18, 131.15, 139.10, 139.24 (Ar); IR (KBr): 2251 cm^{-1} (PH). MS (FAB positive mode, NPOE): m/z (%): 223 (100) $[M - Br]^+$; (FAB negative mode, NPOE): m/z (%): 79, 81 (100) $[Br^-]$; HRMS (FAB positive mode, NPOE): calcd. $m/z = 223.1364$; found $m/z = 223.1348$.

4.6. {2,6-Bis[(dimethylamino)methyl]phenyl}phosphorus iodide (4c)

7.14 mmol of *n*-BuLi 2.5 M in hexane was added dropwise at 0 °C to 1.6 g (7.14 mmol) of **3** in ether (20 ml). The reaction mixture was stirred at room temperature for 0.5 h to give a yellow solution of **5**. A solution of iodine (1.80 g, 7.14 mmol) in ether (30 ml) was then added dropwise at 0 °C to **5**. The reaction mixture was stirred at room temperature for 1 h and the solvent was removed under vacuum. The white solid obtained was treated with CH_2Cl_2 (20 ml) and LiI was filtered on Celite. The solvent was removed under vacuum to give a white solid which was washed with ether (4 × 20 ml). After filtration, 1.76 g (5.0 mmol, 70%) of crude **4c** was obtained as a white powder. M.p. 186 °C (decomp.). ^{31}P NMR (101.25 MHz, $CDCl_3$): $\delta = 37.0$ (d, $^1J(P,H) = 246$ Hz); ^{13}C NMR (62.89 MHz, $CDCl_3$, {H}): $\delta = 47.60$ (d, $^2J(C,P) = 15.6$ Hz, NCH_3), 47.85 (s, NCH_3), 63.85 (s, NCH_2), 124.63, 129.08, 131.43, 138.37 (Ar); ^{15}N NMR (20.28 MHz, $CDCl_3$, {H}, CH_3NO_2): $\delta = -325.0$ (d, $^1J(N,P) = 6.9$ Hz); IR (KBr): 2258 cm^{-1} (PH); MS (FAB positive mode, NPOE): m/z (%): 223 (100) $[M - I]^+$; (FAB negative mode, NPOE): m/z (%): 127 (100) $[I^-]$. $C_{12}H_{20}IN_2P$ calcd.: C, 41.11; H, 5.77; N, 8.00; found: C, 40.86; H, 5.63; N, 7.77.

4.7. {2,6-Bis[(dimethylamino)methyl]phenyl}trimethylsilylphosphane (6)

7.14 mmol of *n*-BuLi 2.5 M in hexane was added dropwise at 0 °C to 1.6 g (7.14 mmol) of **3** in ether (30 ml). The reaction mixture was stirred at room temperature for 0.5 h and 0.9 ml (7.14 mmol) of chlorotrimethylsilane was added dropwise at 0 °C. The reaction mixture was stirred at room temperature for 2 h. After filtration of LiCl on Celite and removal of the solvent under vacuum, the residual viscous oil obtained was distilled to give 1.71 g (5.78 mmol, 81%) of **6** as colourless oil. B.p. 115 °C (0.07 mm Hg); ^{31}P NMR (101.25 MHz, $CDCl_3$): $\delta = -158.0$ (d, $^1J(P,H) = 212$ Hz); ^{29}Si NMR (49.69 MHz, $CDCl_3$, {H}): $\delta = 4.0$ (d, $^1J(Si,P) = 6.6$ Hz); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.15$ (d, $^3J(H,P) = 4.2$ Hz, 9H; $SiCH_3$), 2.25 (s, 12H; NCH_3), 3.60 (d, $^1J(H,P) = 212$ Hz, 1H; PH), 3.25 (d, $^2J(H,H) = 13.2$ Hz, 2H; CH_2N), 3.70 (d, $^2J(H,H) = 13.2$ Hz, 2H; CH_2N), 7.05 to 7.29 (m, 3H; Ar); $C_{15}H_{29}N_2PSi$ calcd.: C, 60.81; H, 9.79; N, 9.46; P, 10.47; found: C, 60.72; H, 9.68; N, 9.26; P, 10.59.

4.8. {2,6-Bis[(dimethylamino)methyl]phenyl}phosphorus chloride (4d)

A solution of diisobutylaluminiumhydride (6.5 mmol) in hexane (6.5 ml) was added dropwise at 0 °C to a solution of **8** (1.9 g, 6.48 mmol) in CH_2Cl_2 (25 ml). The reaction mixture was stirred at room temperature overnight. The solvent was then removed and the crude product was heated at 90 °C under vacuum (0.1 mm Hg) for 3 days to eliminate the diisobutylaluminium chloride. The residue was washed with ether (2 × 50 ml) to give after filtration 1.54 g (5.96 mmol, 92%) of **4d** as a beige powder. M.p. 247 °C (decomp.); ^{31}P NMR (101.25 MHz, $CDCl_3$): $\delta = 37.3$ (d, $^1J(P,H) = 234$ Hz); ^{13}C NMR (50.32 MHz, $CDCl_3$, {H}): $\delta = 47.75$ (d, $^2J(C,P) = 15.7$ Hz, NCH_3), 48.05 (s, NCH_3), 64.31 (s, NCH_2), 125.15, 131.10, 139.10, 139.23 (Ar); IR (KBr): 2254 cm^{-1} (PH); MS (FAB positive mode, NPOE): m/z (%): 223 (100) $[M - Cl]^+$; HRMS (FAB positive mode, NPOE): calcd. $m/z = 223.1364$; found $m/z = 223.1298$.

4.9. 2,6-Bis[(dimethylamino)methyl]phenyl}phosphorus hexafluorophosphate (4e)

A solution of **4d** (1.39 g, 5.3 mmol) in CH_3CN (10 ml) was added dropwise at 0 °C to a solution of KPF_6 (0.94 g, 5.1 mmol) in CH_3CN (20 ml). The reaction mixture was stirred 2 h at room temperature. The solvent was removed under vacuum. 15 ml of CH_2Cl_2 was added to the residue to precipitate KCl, which was filtered. After removal of the solvent under vacuum, 1.55 g (4.2 mmol, 83%) of **4e** was obtained as a white powder which was recrystallized from CH_2Cl_2 (7 ml, 2 weeks at room temperature) to give colourless crystals. M.p. 198–200 °C; ^{31}P NMR (101.25 MHz, $CDCl_3$): $\delta = 37.6$ (d, $^1J(P,H) = 243$ Hz, PH), -143.7 (hept., $^1J(P,F) = 713$ Hz, PF_6^-); ^{1}H NMR (250 MHz, CD_3CN): $\delta = 2.64$ (d, $^3J(H,P) = 4.1$ Hz, 6H; NCH_3), 2.65 (s, 6H; NCH_3), 4.03 (d, $^2J(H,H) = 16.0$ Hz, 2H; CH_2N), 4.14 (d, $^2J(H,H) = 156.0$ Hz, 2H; CH_2N), 5.73 (d, $^1J(H,P) = 237$ Hz, 1H; PH), 7.20 (dd, $^3J(H,H) = 7.8$ Hz, $^4J(H,P) = 2.2$ Hz, 2H; Ar), 7.39 (t, $^3J(H,H) = 8.0$ Hz, 1H; Ar); ^{13}C NMR (62.89 MHz, $CDCl_3$, {H}): $\delta = 47.40$ (d, $^2J(C,P) = 15.8$ Hz, NCH_3), 47.75 (s, NCH_3), 63.80 (s, NCH_2), 124.58, 129.15, 131.44, 138.15 (Ar); IR (CH_2Cl_2): 2305 cm^{-1} (PH); MS (FAB positive mode, NPOE): m/z (%): 223 (100) $[M - PF_6]^+$; (FAB nega-

tive mode, NPOE): m/z (%): 154 (100) [PF_6^-]; $C_{12}H_{20}F_6N_2P_2$ calcd.: C, 39.13; H, 5.43; N, 7.61; found: C, 39.22; H, 5.48; N, 7.53.

4.10. {2,6-Bis[(dimethylamino)methyl]phenyl}chlorophosphorus chloride (8)

A freshly prepared Et_2O solution (50 ml) of 2,6-bis[(dimethylamino)methyl]phenyllithium [23] (13.2 mmol) was added slowly at 0 °C to a solution of PCl_3 (1.15 ml, 13.2 mmol) in ether (30 ml). There was immediately formation of a white precipitate. The reaction mixture was stirred at room temperature for 3 h. After filtration of the precipitate, the solid obtained was treated with CH_2Cl_2 (50 ml) to precipitate LiCl. After filtration of LiCl, the solvent was removed and the solid obtained was washed with ether (2 × 20 ml) to give 2.80 g (10.9 mmol, 83%) of a yellow powder. M.p. 154 °C (decomp.); ^{31}P NMR (101.25 MHz, $CDCl_3$): $\delta = 131.5$ (s); ^{31}P NMR (CP/MAS, {H}): $\delta = 132.0$ (s); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 2.85$ (d, ^3J(P,H) = 3.0 Hz, 12H; NCH_3), 4.39 (s, 4H; NCH_2), 7.32 (dd, ^3J(H,H) = 7.6 Hz, ^4J(P,H) = 2.8 Hz, 2H; Ar); 7.45 (dt, ^3J(H,H) = 7.9 Hz, ^5J(P,H) = 1.4 Hz, 1H; Ar); ^{1}H NMR (400 MHz, CD_2Cl_2, −115 °C): $\delta = 2.68$ (s, 6H; NCH_3), 2.79 (s, 6H; NCH_3), 4.09 (d, ^{2}J(H,H) = 15.0 Hz, 2H; CH_2N), 4.30 (d, ^2J(H,H) = 15.0 Hz, 2H; CH_2N), 7.12 (d, ^3J(H,H) = 7.0 Hz, 2H; Ar); 7.34 (t, ^3J(H,H) = 7.0 Hz, 1H; Ar); ^{13}C (62.89 MHz, $CDCl_3$): $\delta = 46.45$ (d, ^2J(C,P) = 12.6 Hz, NCH_3), 61.55 (d, ^2J(C,P) = 6.3 Hz, CH_2N), 125.32, 130.60 (d, ^1J(C,P) = 36.5 Hz), 134.60, 141.71 (Ar); ^{15}N NMR (20.28 MHz, $CDCl_3$, {H}): $\delta = -320.9$ (d, ^1J(N,P) = 15 Hz); MS (FAB positive mode, NBA): m/z (%) 239 (60) [M − 2Cl + OH]$^+$, 257 (100) [M − 2Cl + 2OH + H]$^+$. Elemental analysis could not be carried out because of the extreme air-sensitivity of **8**.

4.11. {2,6-Bis[(dimethylamino)methyl]phenyl}bromophosphorus bromide (9)

Starting from PBr_3, 67% of a yellow powder was obtained according to the same procedure as that used to prepare **8**. M.p. 144 °C (decomp.); ^{31}P NMR (101.25 MHz, $CDCl_3$): $\delta = 132.8$ (s); ^{31}P NMR (CP/MAS, {H}): $\delta = 131.2$ (s); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.95$ (d, ^3J(P,H) = 3.0 Hz, 12H; NCH_3), 4.38 (s, 4H; NCH_2), 7.37 (dd, ^3J(H,H) = 7.5 Hz, ^4J(P,H) = 2.8 Hz, 2H; Ar); 7.49 (dt, ^3J(H,H) = 7.9 Hz, ^5J(P,H) = 1.3 Hz, 1H; Ar); ^{1}H NMR (400 MHz, CD_2Cl_2, −100 °C): $\delta = 2.52$ (s, 6H; NCH_3), 2.60 (s, 6H; NCH_3), 3.95 (d, ^2J(H,H) = 15.2 Hz, 2H; CH_2N), 4.16 (d, ^2J(H,H) = 15.2 Hz, 2H; CH_2N), 7.22 (d, ^3J(H,H) = 7.1 Hz, 2H; Ar); 7.43 (t, ^3J(H,H) = 7.1 Hz, 1H; Ar); ^{13}C (62.89 MHz, $CDCl_3$): $\delta = 46.65$ (d, ^2J(C,P) = 13.5 Hz, NCH_3), 61.35 (d, ^2J(C,P) = 6.3 Hz, CH_2N), 125.32, 130.43 (d, ^1J(C,P) = 36.1 Hz), 134.30, 141.61 (Ar); ^{15}N NMR (20.28 MHz, $CDCl_3$, {H}): $\delta = -324.7$ (d, ^1J(N,P) = 13 Hz); MS (FAB positive mode, NBA): m/z (%) 239 (70) [M − 2Br + OH]$^+$, 257 (100) [M − 2Br + 2OH + H]$^+$; (FAB negative mode, NBA): m/z (%) 79,81 (100) [Br^-]. Elemental analysis could not be carried out because of the extreme air-sensitivity of **9**.

4.12. {2,6-Bis[(dimethylamino)methyl]phenyl}chlorophosphorus tetraphenylborate (10)

A solution of sodium tetraphenylborate (0.64 g, 1.87 mmol) in CH_2Cl_2 (5 ml) and CH_3CN (2 ml) was added dropwise at 0 °C to a solution of **8** (0.55 g, 1.87 mmol) in CH_2Cl_2 (7 ml). The reaction mixture was stirred overnight at room temperature. After filtration of NaCl (0.11 g, 1.88 mmol), the solvent was removed under vacuum. The residue was washed with ether (2 × 30 ml) to give 0.95 g (1.64 mmol, 88%) of **10** as a beige powder. M.p. 127 °C (decomp.); ^{31}P NMR (161.97 MHz, CD_2Cl_2): $\delta = 131.9$; ^{1}H NMR (200 MHz, CD_2Cl_2, 293 K): $\delta = 2.58$ (d, ^3J(P,H) = 3.0 Hz, 12H; NCH_3), 3.86 (s, 4H; NCH_2), 6.93 to 7.44 (6 m, 23H; Ar); ^{1}H NMR (400 MHz, CD_2Cl_2, 213 K): $\delta = 2.30$ (d, ^3J(H,P) = 7.0 Hz, 6H; NCH_3), 2.48 (s, 6H; NCH_3), 3.30 (d, ^2J(H,H) = 16.0 Hz, 2H; CH_2N), 3.41 (d, ^2J(H,H) = 16.0 Hz, 2H; CH_2N), 6.96 to 7.60(5 m, 23H; Ar); ^{13}C NMR (50.32 MHz, CD_2Cl_2): $\delta = 46.55$ (d, ^2J(C,P) = 16.0 Hz, NCH_3), 61.61 (d, ^2J(C,P) = 4.1 Hz, NCH_2), 122.45, 125.85, 126.27, 130.90 (d, ^1J(C,P) = 35.7 Hz), 135.23, 136.44, 141.90, 164.02 (q, ^1J(C,B) = 49.2 Hz) (Ar); MS (FAB positive mode, NBA): m/z (%) 239 (80) [M − BPh_4 − Cl + OH]$^+$, 257 (100) [M − BPh_4 − Cl + 2OH + H]$^+$; (FAB negative mode, NBA): m/z (%) 319 (100) [BPh_4^-]. $C_{36}H_{39}BClN_2P$ calcd.: C, 74.93; H, 6.76; N, 4.85; found: C, 74.20; H, 6.83; N, 4.46.

4.13. 2,6-Bis[(dimethylammonio)methyl]phenyl}phosphonic acid dichloride (12)

0.45 g (1.53 mmol) of **10** was placed in a watch glass under a moist atmosphere. After 2 h the sticky oil formed was washed with hexane (3 × 20 ml) and dried under vacuum to give 0.5 g (1.50 mmol, 98%) of **11** as white powder. M.p. 194 °C (decomp.); ^{31}P NMR (101.25 MHz, CD_3CN): $\delta = 10.4$ (d, ^1J(P,H) = 543 Hz); ^{1}H NMR (200 MHz, CD_2Cl_2): $\delta = 2.80$ (d, ^3J(P,H) = 3 Hz, 12H; NCH_3), 4.39 (s, 4H; CH_2N), 4.70 (broad signal, 1H; POH), 7.85 (d, ^1J(H,P) = 543.0 Hz, 1H; PH), 7.59 to 7.77 (2 m, 5H; Ar), 10.70 (broad signal, 2H; NH^+); ^{13}C NMR (50.32 MHz, CD_2Cl_2): $\delta = 42.26$ (s, NCH_3), 59.31 (s, NCH_2), 132.49, 135.33 (d, J(C,P) = 8.5 Hz), 135.81 (d, J(C,P) = 8.7 Hz), 139.42 (d, J(C,P) = 108.7 Hz) (Ar); MS (FAB positive mode, GT):

m/z (%): 257 (100) $[M - H - 2Cl]^+$. HRMS (FAB positive mode, NPOE): calcd. $m/z = 257.1419$; found $m/z = 257.1461$; $C_{12}H_{23}Cl_2N_2O_2P_2 \cdot 2.5H_2O$ calcd.: C, 38.56; H, 7.48; Cl, 18.98; N, 7.48; found: C, 38.64; H, 7.41; Cl, 18.64; N, 6.75.

4.14. Crystal structure of compound 4e

4.14.1. Crystal preparation

Crystals of **4e** were grown by slow evaporation of a dichloromethane solution in a nitrogen atmosphere. Colourless plates were obtained. A plate of dimensions $0.15 \times 0.30 \times 0.40\,mm^3$ was stuck on a glass fibre with mineral oil, immersed in a stream of cold nitrogen on a Nonius CAD 4 automated diffractometer at 162 K.

4.14.2. X-ray data collection

Data were collected with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Lattice constants (Table 2) come from a least squares refinement of 25 reflections obtained in the range $7.8 < 2\theta < 27.5°$. The intensities of three standard reflections were monitored at intervals of 60 min; significant change in these intensities occurred during data collection. The systematic absences were uniquely defining the space group $P2_1/c$. The structure amplitudes were obtained after the usual Lorentz and polarization reduction. Only the reflections having $F_o \geq 3\sigma(F)$ were considered to be observed. The absorption corrections were neglected ($\mu = 3.2\,cm^{-1}$).

Table 4
Fractional atomic coordinates ($\times 10^4$) for compound **4e**

Atom	x	y	z
P1	848(1)	2105(1)	876(1)
H	1454(15)	1701(15)	1517(13)
C1	64(4)	3695(4)	1164(2)
C2	-1224(4)	3674(4)	1525(2)
C3	-1840(5)	4915(5)	1713(3)
C4	-1138(5)	6123(5)	1553(2)
C5	172(5)	6131(5)	1204(2)
C6	765(5)	4893(4)	1005(2)
C7	-1753(5)	2274(4)	1704(2)
N1	-1120(4)	1320(4)	1168(2)
Me1	-2074(5)	1255(5)	462(2)
Me2	-923(5)	-69(4)	1492(3)
C8	2134(5)	4687(4)	604(3)
N2	2699(4)	3312(3)	817(2)
Me3	3627(5)	2754(5)	243(3)
Me4	3557(5)	3382(5)	1552(2)
P2	5691(1)	1372(1)	8512(1)
F1	6007(3)	2577(3)	9080(2)
F2	6063(4)	2282(4)	7844(2)
F3	5307(4)	449(3)	9188(2)
F4	5374(4)	141(4)	7956(2)
F5	4044(3)	1833(3)	8394(2)
F6	7351(3)	915(4)	8637(2)

4.14.3. Structure determination and refinement

Direct methods (SHELXS-86 program) [24] succeeded in locating the whole set of non-hydrogen atoms through a single calculation. After four cycles of least squares refinement with anisotropic thermal parameters for phosphorus and fluorine atoms, the hydrogen on phosphorus atom was located in a difference Fourier synthesis; the P1–H distance was 1.33 Å. At this stage the other hydrogen atoms were positioned by calculation (SHELX-76 program) [25] and all non-hydrogen atoms were refined anisotropically. Refinement converged to the R value of 0.047.

Individual bond lengths and main bond angles are listed in Table 3. The final atomic coordinates are listed in Table 4. The labelling scheme is given in Fig. 1.

4.14.4. Supplementary material

A full list of the bond angles for compound **4e**, along with a list of anisotropic thermal parameters for all non-hydrogen atoms and a list of calculated hydrogen atoms coordinates are available (3 pages). Ordering information is given on any current masthead page.

References

[1] A.H. Cowley and R.A. Kemp, *Chem. Rev., 85* (1995) 367. M. Sanchez, M.R. Mazières, L. Lamandé and R. Wolf, in M. Regitz and O.J. Scherer (eds.), *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Georg Thieme, Stuttggart, 1990, p. 129.

[2] R.W. Reed, Z. Xie and C. Reed, *Organometallics, 14* (1995) 5002.

[3] (a) W. Becker and R. Schmutzler, *Phosphorus Sulfur, 36* (1988) 231. (b) W. Becker, D. Schomburg and R. Schmutzler, *Phosphorus Sulfur Silicon, 42* (1989) 21.

[4] R. Bartsch, M. Sanchez and R. Wolf, *Phosphorus Sulfur, 35* (1988) 89.

[5] L. Lamandé and A. Munoz, *Tetrahedron Lett., 32* (1991) 75.

[6] C. Payrastre, Y. Madaule, J.G. Wolf, T.C. Kim, M.R. Mazières, R. Wolf and M. Sanchez, *Heteroatom Chem., 3* (1992) 157.

[7] R. Weiss and S. Engel, *Angew. Chem., 104* (1992) 239; *Angew. Chem. Int. Ed. Engl., 31* (1992) 216.

[8] R. Reed, R. Réau, F. Dahan and G. Bertrand, *Angew. Chem., 105* (1993) 464; *Angew. Chem. Int. Ed. Engl., 32* (1993) 399.

[9] Y.V. Balitzky, S.E. Pipko, A.D. Sinitsa, A.N. Chernega and Y.G. Gololobov, *Phosphorus Sulfur Silicon, 75* (1993) 167. S.E. Pipko, Y.V. Balitzky, A.D. Sinitsa and Y.G. Gololobov, *Tetrahedron Lett., 35* (1994) 168.

[10] M. Sanchez, F. Cosledan, J.M. Sotiropoulos, L. Lamandé, A.B. Drapailo, A.O. Gudima and V.D. Romanenko, *Tetrahedron Lett., 36* (1995) 2085.

[11] J.T.B.H. Jastrzebski and G. van Koten, *Adv. Organomet. Chem., 35* (1993) 231.

[12] C. Chuit, R.J.P. Corriu, A. Mehdi and C. Reyé, *J. Organomet. Chem.*, in press.

[13] D.A. Atwood, A.H. Cowley and J. Ruiz, *Inorg. Chim. Acta, 198–200* (1992) 271.

[14] D.G. Gorenstein and D.O. Shah, in *Phosphorus ^{31}P NMR. Principles and Applications*, Academic Press, 1994, p. 553.

[15] J.B. Lambert and J.H. So, *J. Org. Chem., 56* (1991) 5960.

[16] R.J.P. Corriu, J.P. Dutheil and G.F. Lanneau, *J. Am. Chem. Soc., 106* (1984) 1060. R.J.P. Corriu, G.F. Lanneau and D. Leclercq, *Tetrahedron, 45* (1989) 1959. R.J.P. Corriu, G.F. Lanneau and D. Leclercq, *Tetrahedron, 36* (1980) 1617. G.F. Lanneau, *Phosphorus Sulfur, 27* (1986) 43. R.J.P. Corriu, *Phosphorus Sulfur, 27* (1986) 1

[17] C. Chuit, R.J.P. Corriu, A. Mehdi and C. Reyé, *Angew. Chem., 105* (1993) 1372; *Angew. Chem. Int. Ed. Engl., 32* (1993) 1311.

[18] G. van Koten, J.T.B.H. Jastrzebski, J.G. Noltes, A.L. Spek and J.C. Schoone, *J. Organomet. Chem., 148* (1978) 233.

[19] H. Günther, *NMR Spectroscopy*, Wiley, New York, 1980, pp. 240–244.

[20] M. Chauhan, C. Chuit, R.J.P. Corriu, A. Mehdi and C. Reyé, *Organometallics*, in press.

[21] A. Bondi, *J. Phys. Chem., 68* (1964) 441.

[22] E. Hobbs, D.E.C. Corbridge and B. Raistrich, *Acta Crystallogr., 6* (1953) 691. D.W. Cruickshank, *Acta Crystallogr., 17* (1964) 671.

[23] J.T.B.H. Jastrzebski, P.A. van der Schaaf, J. Boersma and G. van Koten, *Organometallics, 8* (1989) 1373.

[24] P. Main, G. Germain and M.M. Wiilfson, MULTAN-80, *A System for Computer Programs for the Automatic Solution of Crystal Structures for X-ray Diffraction Data*, Universities of York, UK, and Louvain, Belgium, 1980.

[25] G.M. Sheldrick, SHELX-76, *A Program for Crystal Structure Determination*, University of Cambridge, UK, 1976.