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N → P intramolecular stabilization of phosphenium ions and preparation of hypercoordinated phosphanes with unusual properties

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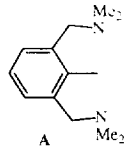
Abstract

The reaction of ArLi **1** (Ar = $[C_6H_3(CH_2NMe_2)_2$-2,6]) with Ph_2PCl affords the phosphane **2** which, on treatment with HCl, gives rise to the monoprotonated ammonium salt **3**, even in the presence of an excess of HCl. **2** reacts with MeI to give exclusively the phosphonium salt **4**. Reaction of **1** with $PhPCl_2$ gives the stabilized phosphenium ion $[ArPPh]^+Cl^-$ **6**. This ion is reduced by $LiAlH_4$ in ArPHPh **9**, which undergoes hydride abstraction on treatment with trityl cation, giving the same ionic phosphorus species. This unusual reaction is an example of increased reactivity of a P–H bond resulting from hypercoordination at the phosphorus atom.

Keywords: Stabilized phosphenium ions; Hypercoordinated phosphane; Pincer ligand; Hexacoordinated phosphonium salt

1. Introduction

van Koten and coworkers [1] have shown that the tridentate pincer ligand **A** is very useful for stabilizing species in unusual oxidation states [2,3] and for the isolation of reactive intermediates [4]. We have recently pointed out that **A** is very efficient at generating hypercoordinated silicon species with unusual properties [5,6] and for stabilizing silylium ions thus providing a novel and general route to siliconium ions [7]. Because of the analogies between the chemistry of hypercoordinated silicon and phosphorus species [8], it was of interest to explore the possibility of obtaining stabilized phosphenium ions [9,10] in this way.



A

In this paper, we report the unusual reactivities of two phosphanes containing the ligand **A**, and the preparation and characterization of phosphenium ions stabilized by bis-chelation of the amino groups of the ligand **A**.

2. Results and discussion

2,6-Bis(dimethylaminomethyl)phenyllithium **1** [2] reacts with Ph_2PCl to give the phosphane **2**, identified by elemental analysis (C, H, P) and solution state NMR studies ($CDCl_3$, ^1H, ^{13}C, ^{31}P) (cf. Experimental). It is to be noted that the ^{31}P NMR chemical shift of **2** (−16.6 ppm) is upfield with respect to that of the triphenylphosphane ($\delta = -5.6$ ppm) [11], which indicates a weak N → P interaction.

Treatment of **2** with HCl (Scheme 1) gives rise to the corresponding monoprotonated ammonium salt **3**, even in the presence of an excess of HCl. Neither protonation of the second amino group nor protonation at phosphorus was observed. The ^{31}P chemical shift for **3** displays a slightly upfield resonance (−20.9 ppm) with respect to the signal of the starting phosphane **2** (−16.6 ppm). The room temperature ^1H NMR spectrum exhibits a sharp signal for the NMe_2 groups, a sharp signal for the methylene protons, and a broad signal for the NH^+ proton. As the temperature is decreased, each of these peaks broadens and splits into two resonances of equal intensity at 168 K (Fig. 1). The magnetic equivalence of the two NMe_2 groups at room temperature is consistent

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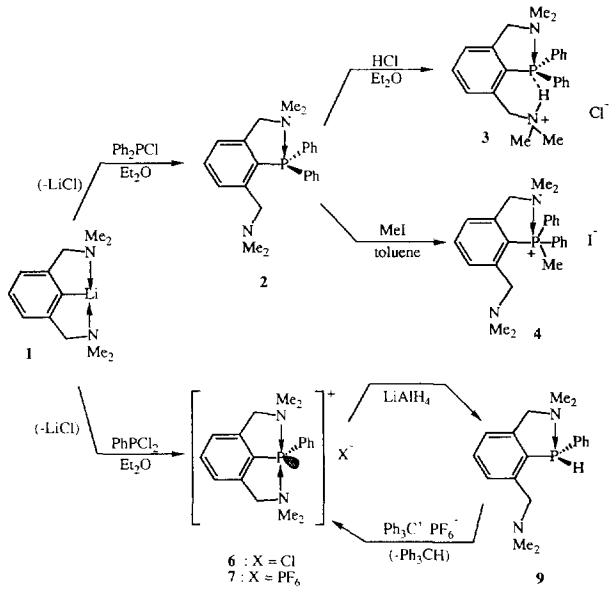


Scheme 1.

with a rapid coordination–decoordination process involving the two units along with transprotonation from one group to the other. At 168 K (250 MHz) this process is slow (on the NMR time scale) and the two NMe_2 units appear dissociated, each exhibiting a broad signal. Interestingly, at 168 K the NH^+ group appears as a doublet with a $^1J(P,H)$ coupling constant of 110 Hz, indicating the formation of a hydrogen bond with the phosphorus atom. The low temperature ^{31}P NMR (81 MHz) spectrum of **3** was studied down to 183 K, at which temperature only broadening and a slight upfield shift of the signal were observed ($\delta = -24.0$ ppm). Thus under these experimental conditions (81 MHz), the $^1J(P,H)$ coupling constant has not been observed by ^{31}P proton coupled NMR. The $\Delta G^{\neq}$ corresponding to the breaking of the NH bond was estimated to be 39.2 kJ mol^{-1} from the coalescence temperature (193 K) of the N-methyl signals. The non-protonation of the second NMe_2 group could result from the existence of the coordination–decoordination process around the phosphorus center which should hinder protonation. This interpretation is supported by the upfield ^{31}P NMR chemical shift of **3** (−20.9 ppm) with respect to that of PPh_3 (−5.6 ppm) [11] at room temperature, indicative of a weak intramolecular N → P interaction. The protonation at nitrogen and not at phosphorus can be explained by the greater basicity of the CH_2NMe_2 group than the $ArPPh_2$ group.

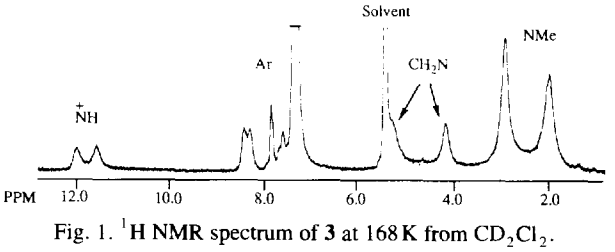


Fig. 1. ^1H NMR spectrum of **3** at 168 K from CD_2Cl_2.

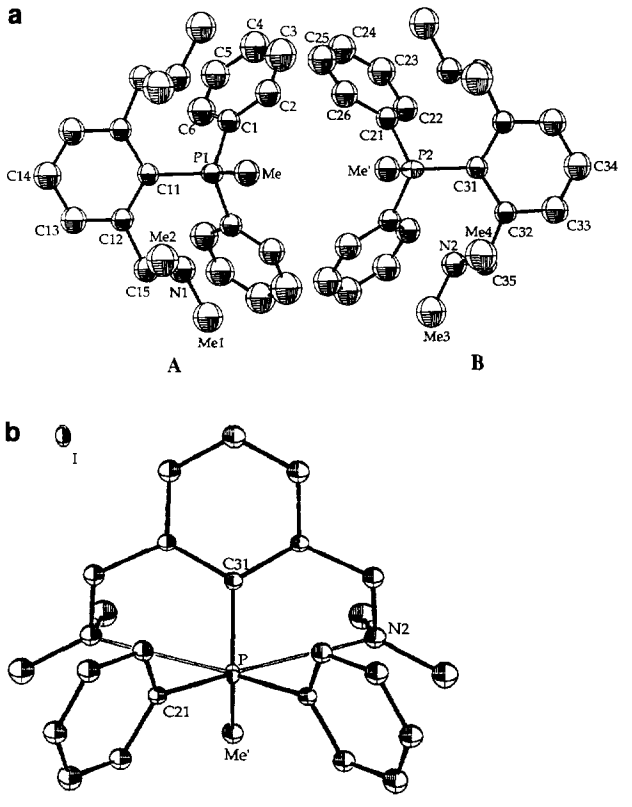


Fig. 2. (a) ZORTEP drawing of the molecular structure of **4** showing the numbering scheme. The thermal ellipsoids and spheres are at the 50% probability level. The mirror plane is perpendicular to the plane of the figure and goes through atoms C14, C15, P2 and C34. (b) Another view of the molecule **B** of compound **4** showing the two N–P interactions and the position of the iodine ion. Ellipsoids enclose 10% of the electron density.

2 reacts with MeI to give exclusively the corresponding phosphonium salt **4**, identified by solution NMR studies (^1H, ^{13}C, ^{31}P) in $CDCl_3$ and by the positive-ion FAB mass spectrum. Crystals of **4** suitable for X-ray structure analysis were grown from an ethanolic solution. The ZORTEP [12] drawing of **4** is displayed in Fig. 2(a) and (b). Bond distances and selected bond angles are listed in Tables 1 and 2 and other crystallographic details are given in Tables 3 and 4. The molecular structure of **4** was first solved with the space group $Pna2_1$ (two independent molecules, $R = 0.036$), then with the space group *Pnma* which led to a higher R factor but to better internal consistency and quite a lower σ value for the final refined atomic coordinates. There are eight molecules in the unit cell which actually correspond to four times two independent half-molecules A and B. The rigorous mirror plane of the crystal gives the remaining half of each molecule. Molecule A is not the mirror image of molecule B, the overall shapes of A and B being only similar but not identical (Tables 1 and 2). Indeed, most typical bond and angle

Table 1
Interatomic distances (Å) for compound **4**

Molecule **A**		Molecule **B**	
P1–Me	1.81(1)	P2–Me′	1.78(1)
P1–C1	1.80(1)	P2–C21	1.81(1)
P1–C11	1.81(1)	P2–C31	1.80(1)
P1 · · · N1	3.14(1)	P2 · · · N2	3.16(1)
C1–C2	1.40(1)	C21–C22	1.40(1)
C2–C3	1.43(1)	C22–C23	1.35(2)
C3–C4	1.34(2)	C23–C24	1.36(2)
C4–C5	1.39(2)	C24–C25	1.37(2)
C5–C6	1.37(2)	C25–C26	1.39(2)
C6–C1	1.41(1)	C26–C21	1.38(1)
C11–C12	1.43(1)	C31–C32	1.43(1)
C12–C13	1.37(1)	C32–C33	1.39(1)
C13–C14	1.37(1)	C33–C34	1.39(1)
C12–C15	1.50(1)	C32–C35	1.52(1)
C15–N1	1.47(1)	C35–N2	1.45(1)
N1–Me1	1.46(2)	N2–Me3	1.48(2)
N1–Me2	1.46(1)	N2–Me4	1.42(1)

values are rather close. The lone pairs of both NMe_2 groups are directed symmetrically towards the phosphorus atoms with a mean distance of 3.15 Å (Table 1), this distance being inferior to the sum of the van der Waals radii of phosphorus and nitrogen atoms (3.4 Å) [13]. The two nitrogen atoms of the same molecule are in a disposition with a mean value of the N–P–N′ angle of 111.6°. The tetrahedral geometry of the phosphorus atom is maintained with an average C–P–C angle of 107.5° for A and 107.6° for B. Thus the geometry around the phosphorus atom is that of a slightly distorted bicapped tetrahedron.

Compound **4** shows fluxional behavior in solution. At room temperature the ^1H NMR spectra in CD_2Cl_2 display a single resonance for the NMe_2 groups and a single resonance for the benzylic protons. Lowering the temperature results in broadening and decoalescence of the NMe_2 and methylene protons. At 203 K (400 MHz) the spectrum exhibits two single resonances for the NMe_2 groups and an AB pattern for the benzylic protons (Fig. 3). This spectrum is consistent with the structure observed in the solid state, which shows a symmetric distribution of the phenyl groups around the phosphorus atom as well as a symmetrical *cis* coordination of the two NMe_2 groups. The $\Delta G^{\neq}$ for the coordination–decoordination process was estimated to be 43.0 kJ mol^{-1} from the coalescence temperature (T_c = 213 K) of the methyl protons.

During crystallization of **4** very few crystals different from the others in form and aspect were found. The X-ray crystal structure determination of one of them has revealed that it corresponds to the ammonium salt **5**, the ZORTEP drawing of which is displayed in Fig. 4. Bond distances and main bond angles are listed in Tables 5 and 6 and other crystallographic details are given in Tables 3 and 7. In this molecule there is no N–P interaction, the Me_2N–P distance being 3.879 Å. The geometry of the phosphorus atom is pyramidal, the average C–P–C angles being 104.6° (compared with 103.4° in triphenylphosphane [14]). The striking feature

Table 2
Selected bond angles (°) for compound **4**

Molecule **A**		Molecule **B**	
Me–P1–C1	109.5(4)	Me′–P2–C21	109.9(4)
Me–P1–C11	115.5(6)	Me′–P2–C31	115.1(6)
C1–P1–C′1	100.0(6)	C21–P2–C′21	102.1(6)
C1–P1–C11	110.6(4)	C21–P2–C31	106.6(4)
C1–P1 · · · N1	172.9(3)	C21–P2 · · · N2	174.6(4)
C15–N1–Me1	111.9(8)	C35–N2–Me3	109.4(8)
C15–N1–Me2	111.8(8)	C35–N2–Me4	113.4(8)
Me1–N1–Me2	108.7(9)	Me3–N2–Me4	108.2(9)
P1–C11–C12	121.5(5)	P2–C31–C32	121.5(5)
C12–C11–C′12	116.9(10)	C32–C31–C′32	116.9(11)
C11–C12–C15	124.0(8)	C31–C32–C35	124.3(8)
C11–C12–C13	120.0(9)	C31–C32–C33	120.6(9)
C13–C12–C15	116.1(8)	C33–C32–C35	115.(8)
C12–C15–N1	113.0(8)	C32–C35–N2	111.8(8)
P1–C1–C2	119.1(7)	P2–C21–C22	119.4(7)
P1–C1–C6	120.4(7)	P2–C21–C26	121.0(7)
C2–C1–C6	119.9(8)	C22–C21–C26	119.4(9)
N1 · · · P · · · N′1	113.3(3)	N2 · · · P · · · N′2	110.4(9)

Table 3
Summary of crystal data, intensity measurements and refinement for compounds **4** and **5**

	4	**5**
Formula	$C_{25}H_{32}N_2IP$	$C_{25}H_{32}N_2IP \cdot H_2O$
Crystal system	orthorhombic	monoclinic
Space group	*Pnma*	$P2_1/a$
a (Å)	15.64(1)	13.997(3)
b (Å)	20.461(4)	11.040(4)
c (Å)	15.476(4)	16.905(3)
β (°)		90.79(2)
V (Å^3)	4953(4)	2612(1)
MW	518.42	536.44
Z	8	4
d_{calc} (g cm^{-3})	1.390	1.364
Crystal size (mm^3)	0.55×0.40×0.25	0.65×0.50×0.15
Crystal color	colorless	colorless
Recrystallized solvent	EtOH	EtOH
M.p. (°C)	220–222	179–181
Method of data collection	ω/θ	ω/θ
Temperature of measurements (K)	293	293
Radiation (graphite-monochromated)	Mo Kα	Mo Kα
μ (cm^{-1})	13.54	12.89
2θ limits (°)	4–46	4–48
No. of unique reflections	3260	3515
No. of observed reflections	2320	2233
Final no. of variables	157	186
R	0.0575	0.0567
R_w	0.0661	0.0619
Residual electron density	0.86	1.05

Table 4
Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\times 10^3$) for compound **4**

Atom	x	y	z	s.o.f.	U_{iso}
I	9784.3(4)	9899.9(3)	2365.0(4)	1	[a]
P1	7483(2)	2500	59(2)	0.5	[a]
Me	7886(6)	2500	−1036(8)	0.5	49(4)
C1	6756(5)	3175(5)	200(5)	1	38(2)
C2	6433(6)	3305(5)	1023(6)	1	48(2)
C3	5796(6)	3798(5)	1122(7)	1	59(3)
C4	5496(7)	4104(6)	418(7)	1	61(3)
C5	5796(7)	3967(6)	−410(7)	1	65(3)
C6	6426(6)	3508(5)	−522(6)	1	54(3)
C11	8289(8)	2500	898(7)	0.5	37(3)
C12	8629(5)	1903(4)	1240(5)	1	37(2)
C13	9185(6)	1920(5)	1925(6)	1	55(3)
C14	9437(11)	2500	2280(9)	0.5	61(4)
C15	8454(6)	1241(5)	863(6)	1	48(3)
N1	8581(5)	1217(4)	−76(5)	1	50(2)
Me1	8312(8)	590(6)	−440(8)	1	73(3)
Me2	9473(7)	1333(7)	−313(9)	1	81(4)
P2	2701(2)	2500	−51(2)	0.5	[a]
Me′	3802(8)	2500	−332(9)	0.5	53(4)
C21	2470(6)	3187(5)	646(5)	1	39(2)
C22	1619(7)	3326(6)	866(6)	1	61(3)
C23	1439(7)	3805(6)	1438(7)	1	64(3)
C24	2076(8)	4164(6)	1796(8)	1	73(3)
C25	2913(8)	4045(7)	1589(8)	1	80(4)
C26	3119(7)	3548(5)	1014(6)	1	55(3)
C31	1974(8)	2500	−948(8)	0.5	37(3)
C32	1673(5)	1904(5)	−1324(5)	1	39(2)
C33	1036(6)	1912(5)	−1946(6)	1	55(3)
C34	704(10)	2500	−2238(9)	0.5	58(4)
C35	2041(6)	1233(5)	−1125(6)	1	49(3)
N2	2965(5)	1229(4)	−1175(5)	1	55(2)
Me3	3290(8)	582(6)	−894(7)	1	70(3)
Me4	3284(9)	1356(7)	−2021(8)	1	83(4)

[a] The anisotropic thermal parameters ($U_{11,22,33,23,13,12}$) for these atoms are as follows: I, 0.0519(5), 0.0257(5), 0.0644(5), 0.0005(3), −0.0028(3), −0.0004(3); P1, 0.043(2), 0.023(2), 0.041(2), 0.0, 0.002(2), 0.0; P2, 0.027(2), 0.030(2), 0.053(2), 0.0, −0.001(2), 0.0.

of this structure is that one of the methyl groups of the $N(1)Me_3^+$ unit is directed towards the lone pair of the phosphorus atom, this methyl group being close to the phosphorus atom at 3.44(1) Å.

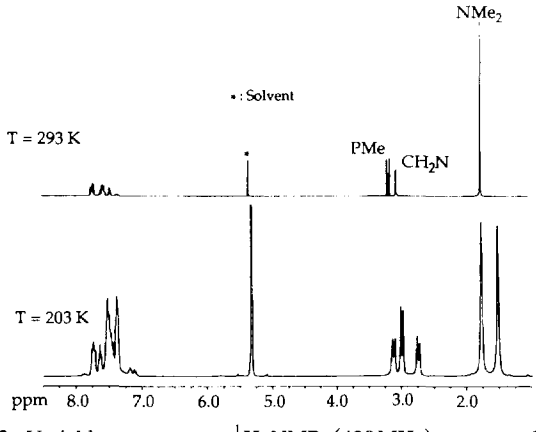


Fig. 3. Variable temperature ^1H NMR (400 MHz) spectra of **4** in CD_2Cl_2.

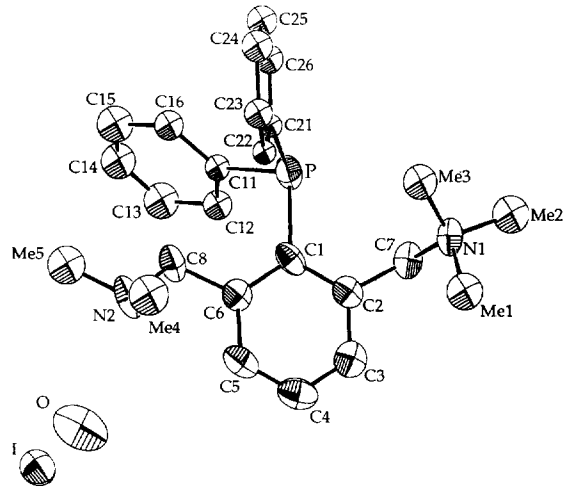
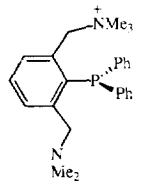


Fig. 4. ZORTEP drawing of the molecular structure of **5** showing the numbering scheme. The thermal ellipsoids and spheres are at the 50% probability level; however, the isotropic thermal parameters for the phenyl carbon atoms C11–C16 and C21–C26 have been decreased in the ratio 2:1 for the sake of clarity.

Table 5
Interatomic distances (Å) for compound **5**

P–C1	1.847(10)	N2–Me5	1.47(1)
P–C11	1.848(11)	C11–C12	1.36(2)
P–C21	1.817(10)	C12–C13	1.47(2)
C1–C2	1.42(1)	C13–C14	1.27(2)
C2–C3	1.39(1)	C14–C15	1.26(3)
C3–C4	1.38(2)	C15–C16	1.46(2)
C4–C5	1.39(2)	C16–C11	1.38(2)
C5–C6	1.38(1)	C21–C22	1.38(1)
C6–C1	1.42(1)	C22–C23	1.38(2)
C2–C7	1.51(1)	C23–C24	1.41(2)
C7–N1	1.53(1)	C24–C25	1.32(2)
N1–Me1	1.50(1)	C25–C26	1.39(2)
N1–Me2	1.50(1)	C26–C21	1.39(2)
N1–Me3	1.52(1)	P,N1	3.879(8)
C6–C8	1.53(1)	P,Me3	3.437(11)
C8–N2	1.46(1)	P,N2	4.669(8)
N2–Me4	1.47(2)	I···O	3.622(9)

The reaction of **2** with MeI was monitored by ^{1}H NMR spectroscopy. Initially, the ^{1}H NMR spectrum of the reaction mixture displays a doublet at $\delta = 3.2$ ppm, assigned to the P–Me group, indicating the direct formation of the phosphonium salt **4**. However, the formation of both salts **4** and **5** followed by fast rearrangement of **5** into **4** due to the geometry of **5** favorable to this transformation is a hypothesis which cannot be ruled out.



5

The reaction of **1** with $PhPCl_2$ does not afford the expected phosphane $(Ar)_2PPh$, but rather an extremely air and moisture sensitive white powder, from which crystals suitable for X-ray analysis could not be obtained. This powder was identified as the salt **6** (Scheme 1) from the following data: the ^{31}P chemical shift is +93.2 ppm in solution; the ^{1}H NMR spectrum (Fig. 5)

Table 6
Selected bond angles (°) for compound **5**

C1–P1–C11	102.9(4)	P–C11–C16	121.6(9)
C11–P–C21	104.7(5)	C16–C11–C12	122.8(11)
C21–P–C1	106.3(4)	P–C21–C22	124.2(8)
P–C1–C2	117.3(6)	P–C21–C26	117.0(8)
P–C1–C6	124.0(7)	C26–C21–C22	118.5(10)
C6–C1–C2	118.2(2)	C2–C7–N1	116.7(7)
P–C11–C12	115.4(9)	C2–C8–N2	115.2(8)

Table 7
Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\times 10^3$) for compound **5**

Atom	x	y	z	U_{iso}
I	1215.0(5)	12221.8(7)	3878.3(4)	[a]
P	6975(2)	8644(2)	2051(2)	[a]
C1	6360(6)	8893(8)	2997(6)	[a]
C2	6906(7)	8749(8)	3701(5)	[a]
C3	6459(8)	8726(9)	4432(6)	[a]
C4	5483(8)	8864(9)	4476(7)	[a]
C5	4937(7)	9064(9)	3795(6)	[a]
C6	5363(6)	9077(8)	3062(5)	[a]
C7	7970(6)	8525(8)	3718(6)	[a]
N1	8614(5)	9641(7)	3801(4)	[a]
Me1	8360(8)	10353(10)	4524(6)	61(3)
Me2	9611(8)	9173(11)	3903(7)	62(3)
Me3	8538(8)	10468(9)	3088(6)	54(3)
C8	4718(6)	9224(9)	2333(6)	[a]
N2	3833(5)	9889(8)	2464(5)	[a]
Me4	4018(9)	11166(11)	2656(7)	74(4)
Me5	3250(8)	9809(11)	1738(7)	66(3)
C11	6119(8)	7688(10)	1490(6)	57(3)
C12	5935(9)	6585(12)	1814(8)	78(4)
C13	5276(12)	5793(16)	1368(10)	115(5)
C14	4959(13)	6198(16)	710(10)	110(5)
C15	5106(14)	7191(16)	364(11)	121(6)
C16	5749(9)	8045(12)	764(8)	80(4)
C21	6959(7)	10090(9)	1538(6)	48(2)
C22	6593(7)	11148(9)	1849(6)	52(3)
C23	6714(9)	12242(13)	1470(8)	78(3)
C24	7186(10)	12264(15)	739(9)	93(4)
C25	7514(10)	11251(13)	428(8)	87(4)
C26	7419(9)	10143(12)	814(7)	73(3)
O	2299(7)	9297(8)	3518(6)	[a]

[a] The anisotropic thermal parameters for these atoms are given in the supplementary material.

shows an AB pattern which was assigned to the methylene protons and two signals of equal intensity for the two NMe_2 groups; the ^{15}N NMR spectrum displays only one doublet ($\delta = -326$ ppm, $^1J_{P-N} = 2.65$ Hz) [15] for both nitrogens, deshielded relative to that of the NMe_2 groups of phosphane **2** ($\delta = -351$ ppm); the positive-ion FAB mass spectrum shows the parent ion at $m/z = 299$ corresponding to $(M-Cl)^+$.

Treatment of **6** with $NaPF_6$ gives rise to the corresponding hexafluorophosphate salt **7** (Scheme 1), which

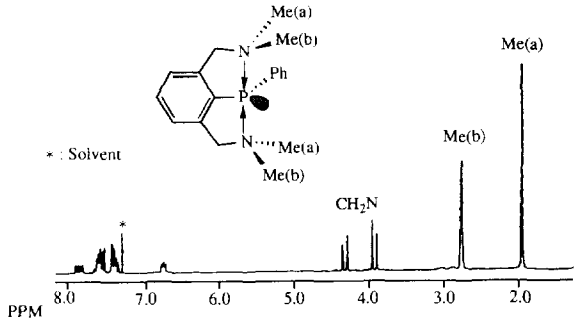
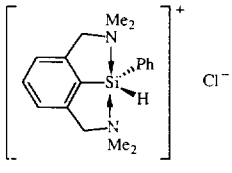


Fig. 5. ^{1}H NMR spectrum of **6** at room temperature from $CDCl_3$.

exhibits ^{1}H and ^{15}N NMR spectra almost identical to those of **6**. Furthermore, the ^{31}P NMR spectrum obtained by the INVGATE method (recycle time 20 s) displays two signals of equal intensity, one at $\delta = +95.5$ ppm very close to that observed for **6** and the other at $\delta = -143.6$ ppm characteristic of PF_6^- [11]. The positive-ion FAB mass spectrum also shows the parent ion at $m/z = 299$.

Overall these data are consistent with structure **6** (Scheme 1), analogous to that proposed for the siliconium ion **8** [7] in which the two $N(CH_3)_2$ groups are coordinated to the phosphorus center giving rise to diastereotopy of the methyls. Confirmation of the ionic structure of **6** was provided by conductivity measurements from which the equivalent conductance Λ of **6** was found to be 25 S cm^2 equiv.$^{-1}$ in CH_2Cl_2.

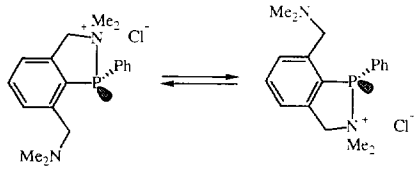


8

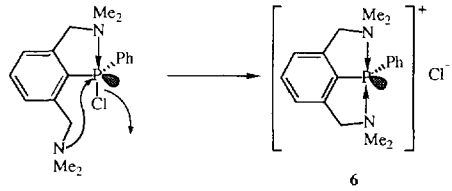
We assume that compound **6** cannot exist as an ammonium salt (Scheme 2) containing a tricoordinate phosphorus center, analogous to that observed for some non-functional silyl cations [16,17]. Indeed, if such were the case we should observe in the ^{1}H NMR spectrum one resonance for both $N(CH_3)_2$ groups at room temperature because of the dynamic coordination–decoordination process of the two NMe_2 goups, whereas at low temperature when this process is slow a completely different spectrum would be exhibited.

The formation of **6** results from initial substitution of a chloride ion by the lithium derivative **1** leading to the ArPhPCl intermediate, followed by displacement of the second chloride ion by intramolecular coordination of the second amino group to the phosphorus center (Scheme 3). This last step corresponds to nucleophilic activation of a nucleophilic substitution at phosphorus, a process which has been studied previously [8].

Other cationic phosphorus species intramolecularly coordinated by one [18–22] or two [23] donor groups have been described, but in most cases the stabilized



Scheme 2.



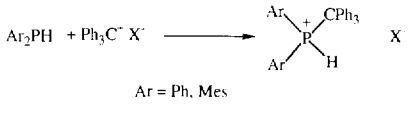
6

Scheme 3.

phosphenium salt had at least one heteroatom–phosphorus bond [18–20,22,23].

$LiAlH_4$ reduction of **6** affords the phosphane **9** (Scheme 1), the ^{31}P NMR chemical shift of which ($\delta = -77.5$ ppm, $^{1}J_{P-H} = 225$ Hz) is upfield with respect to that for Ph_2PH [11] ($\delta = -41.0$ ppm), thus suggesting an intramolecular N → P interaction. The room temperature ^{1}H NMR spectrum shows the magnetic equivalence of the two CH_2NMe_2 units, each unit appearing as a singlet assigned to the NMe_2 protons and an AB pattern assigned to the methylene protons. The equivalence of the NMe_2 groups results from dynamic coordination, the NMe_2 groups displacing each other [5,24] (rapidly on the ^{1}H NMR time scale). During this dissociative process there is simultaneous formation of one N → P interaction and cleavage of the other with rotation around the CH_2–N bond and inversion at nitrogen resulting in equivalence of the NMe_2 groups. The non-equivalence of the methylene protons indicates that there is no rotation (on the NMR time scale) around the P–C_{ipso} bond.

Interestingly, the increase in coordination number of the phosphorus atom in **9** gives rise to unusual properties of the P–H bond. Thus, **9** undergoes hydride abstraction by reaction with $Ph_3C^+PF_6^-$ (Scheme 1), reforming the cation as the stabilized phosphenium salt **7** for which the ^{1}H and ^{31}P NMR data as well as the positive-ion FAB mass spectrum are essentially identical to those for **6**. It is worth noting that hydride abstraction does not occur in the case of 'classical' secondary phosphanes; instead there is quaternization of the phosphane [25] (Eq. (1)). Thus this reaction is the first example of increased reactivity of a P–H bond owing to extra coordination around the phosphorus atom by chelation of the amino group. The modification of reactivity of a bond because of 'extra' coordination is a well known phenomenon in silicon chemistry [26], but has not previously been observed in phosphorus chemistry.



(1)

3. Conclusion

This study has shown that the phosphanes **2** and **9** bearing the potentially bis-chelating ligand **A** have their own characteristic reactivity, different from that of corresponding tricoordinated phosphanes. We have previously shown the ability of the ligand **A** to stabilize silylium ions. We now show the ability of this same ligand to stabilize phosphenium ions. This is another example of analogy between the chemistry of hypercoordinated silicon and phosphorus species.

4. Experimental

All the reactions were carried out under a dry argon atmosphere using standard Schlenk techniques. ^{1}H, ^{31}P, ^{13}C and ^{15}N NMR spectra were obtained using a Bruker 200-SY or 250 AC spectrometer. Chemical shifts for ^{13}C and ^{1}H NMR spectra are relative to Me_4Si and were calibrated by measurement of the chemical shifts of the deuterated solvents. Chemical shifts for ^{31}P and ^{15}N NMR spectra were calibrated with respectively external 85% H_3PO_4 and nitromethane. IR spectra were recorded with a Perkin–Elmer 1600 spectrophotometer. Mass spectra were obtained with a Jeol JMSD-100 instrument. Elemental analyses were performed at the Centre de Microanalyse du CNRS. All solvents were freshly distilled and stored under N_2.

4.1. {2,6-Bis[(dimethylamino)methyl]phenyl}-diphenylphosphane 2

A freshly prepared THF solution (80 ml) of **1** [2] (18.1 mmol) was added slowly at 0 °C to a solution of chlorodiphenylphosphane (18.1 mmol) in THF (30 ml). There was immediate formation of a white precipitate. The reaction mixture was stirred at room temperature for 2 h. After filtration of the LiCl precipitate, the filtrate was concentrated and distilled to give 4.89 g (72%) of **2**. B.p. 123 °C/0.05 mmHg. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.96 (s, 12H, NCH_3); 3.31 (s, 4H, CH_2N); 7.17 to 7.54 (3m, 13H, Ar). ^{13}C NMR (62.89 MHz, $CDCl_3$, {H}): δ 44.67 (NCH_3); 63.47 (d, $^{3}J_{(P,C)} = 13.5$ Hz, CH_2N); 127.17 (s); 128.11 (d, $J_{(P,C)} = 5.2$ Hz); 128.29 (d, $J_{(P,C)} = 5.8$ Hz); 129.81 (s); 131.47 (d, $J_{(P,C)} = 18.1$ Hz); 133.29 (d, $J_{(P,C)} = 21.4$ Hz); 137.91 (d, $J_{(P,C)} = 15.2$ Hz); 146.85 (d, $J_{(P,C)} = 13.5$ Hz) (Ar). ^{31}P NMR (101.25 MHz, $CDCl_3$, {H}): δ −16.6 (s). ^{15}N NMR (20.28 MHz, $CDCl_3$): δ −352 (d, $^{1}J_{(P,N)} = 3.2$ Hz). Positive-ion FAB MS (GT): m/z = 377 ($(M-Cl)^+$, 100). Anal. Found: C, 76.68; H, 7.78; N, 7.61. $C_{24}H_{29}N_2P$ Calc.: C, 76.59; H, 7.71; N, 7.44%.

4.2. 2-[(Dimethylammonium)methyl]6[(dimethylamino)methyl]phenyldiphenyl phosphane chloride 3

A HCl (1.86 mmol) solution (2 ml) in ether at 0 °C was added dropwise by a syringe to a solution of the phosphane **2** (0.7 g, 1.86 mmol) in 20 ml of ether. There was immediate formation of a white precipitate. The reaction mixture was stirred at room temperature for 1 h. The precipitate was then filtered and washed three times with 10 ml of ether to give 0.65 g (1.58 mmol, 85%) of **3** as a white solid. M.p. 236–238 °C. ^{31}P NMR (101.25 MHz, $CDCl_3$): δ −20.9 (s). ^{31}P NMR (81.00 MHz, CD_2Cl_2, 183 K): δ −24.0 (broad signal). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.26 (s, 12H, NCH_3); 4.42 (s, 4H, CH_2N); 7.13 to 7.39 (2m, 10H, Ar); 7.61 (t, 1H, $^{3}J_{(H,H)} = 7.6$ Hz, Ar); 8.29 (d, 2H, $^{3}J_{(H,H)} = 8.5$ Hz, Ar); 12.60 (s, ^{1}H, NH). ^{1}H NMR (250 MHz, CD_2Cl_2, 168 K): δ 1.74 (s, 6H, NCH_3); 2.69 (s, 6H, NCH_3); 4.00 (s, 2H, CH_2N); 5.11 (s, 2H, CH_2N); 7.28 to 8.41 (3m, 13H, Ar); 11.89 (d, 1H, $^{1}J_{(H,P)} = 109$ Hz, NH). ^{13}C NMR (50.32 MHz, $CDCl_3$, {H}): δ 42.65 (s, NCH_3); 58.49 (d, $^{3}J_{(P,C)} = 21.7$ Hz, CH_2N); 129.90 (s); 130.03 (d, $J_{(P,C)} = 5.7$ Hz); 131.87 (d, $J_{(P,C)} = 17.8$ Hz); 132.50 (d, $J_{(P,C)} = 10.9$ Hz); 133.92 (d, $J_{(P,C)} = 20.7$ Hz); 133.56 (s); 135.92 (d, $J_{(P,C)} = 27.0$ Hz); 138.68 (d, $J_{(P,C)} = 15.1$ Hz) (Ar). Positive-ion FAB MS (GT): m/z = 377 ($(M-Cl)^+$, 100); positive-ion FAB HRMS (*o*-nitrophenyloctyl ether): Found m/z = 377.2056; Calc. m/z = 377.2147 $(M-Cl)^+$.

4.3. 2,6-Bis[(dimethylamino)methyl]phenyldiphenylmethylphosphoniumiodide 4

Iodomethane (0.54 g, 3.8 mmol) was added dropwise by a syringe at room temperature to a solution of the phosphane **2** (1.43 g, 3.8 mmol) in 25 ml of toluene. The reaction mixture was stirred at room temperature overnight. The precipitate was then filtered and washed three times with 10 ml of ether to give 1.50 g (2.9 mmol, 76%) of **4** as a white powder. M.p. 220–222 °C. ^{31}P NMR (101.25 MHz, $CDCl_3$, {H}): δ 16.7 (s). ^{1}H NMR (250 MHz, $CDCl_3$, 293 K): δ 1.75 (s, 12H, NCH_3); 3.04 (s, 4H, CH_2N); 3.35 (d, 3H, $^{2}J_{(H,P)} = 13.9$ Hz, CH_3P); 7.39 to 7.86 (3m, 13H, Ar). ^{1}H NMR (400 MHz, CD_2Cl_2, 203 K): δ 1.51 (s, 6H, NCH_3); 1.76 (s, 6H, NCH_3); 2.74 (d, $^{2}J_{(H,H)} = 15.0$ Hz, 2H, CH_2N); 2.99 (d, $^{2}J_{(H,P)} = 14.0$ Hz, 3H, CH_3P); 3.12 (d, $^{2}J_{(H,H)} = 15.0$ Hz, 2H, CH_2N); 7.10 to 7.76 (6m, 13H, Ar). ^{13}C NMR (50.32 MHz, $CDCl_3$, {H}): δ 10.06 (d, $^{1}J_{(C,P)} = 64.9$ Hz, CH_3P); 44.70 (s, NCH_3); 65.43 (d, $^{3}J_{(P,C)} = 3.0$ Hz, CH_2N); 125.61 (s); 127.38 (s); 129.20 (d, $J_{(P,C)} = 6.0$ Hz); 130.25 (d, $J_{(P,C)} = 19.3$ Hz); 130.49 (d, $J_{(P,C)} = 16.4$ Hz); 132.85 (d, $J_{(P,C)} = 12.0$ Hz); 133.02 (d, $J_{(P,C)} = 2.9$ Hz); 135.15 (d, $J_{(P,C)} = 3.2$ Hz) (Ar). Positive-ion FAB MS (GT): m/z = 391 ($(M-I)^+$, 100); negative-ion FAB MS (GT): m/z = 127 (I^-), 100).

Anal. Found: C, 57.52; H, 6.14; N, 5.19. $C_{25}H_{32}IN_2P$ Calc.: C, 57.91; H, 6.17; N, 5.40%.

4.4. {2,6-Bis[(dimethylamino)methyl]phenyl}phenylphosphorus chloride 6

A freshly prepared THF solution (60 ml) of **1** [2] (13 mmol) was added slowly at 0 °C to a solution of dichlorophenylphosphane (13 mmol) in THF (20 ml). The mixture was stirred at room temperature for 2 h. After filtration of the precipitate, the solid obtained was dissolved in CH_2Cl_2 and LiCl was eliminated by filtration. The solvent was removed and the precipitate obtained was washed with THF to give 3.9 g (11.7 mmol, 90%) of crude **6** as a beige powder. M.p. 166–167 °C (decomp.). ^{31}P NMR (101.25 MHz, $CDCl_3$): δ 93.2 (s). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.95 (s, 6H, NCH_3); 2.75 (d, $^3J_{(P,H)} = 5.0$ Hz, 6H, NCH_3); 3.90 (d, $^2J_{(H,H)} = 15.5$ Hz, 2H, NCH_2); 4.30 (d, $^2J_{(H,H)} = 15.5$ Hz, 2H, NCH_2); 6.72 (t, 1H, $^3J_{(H,H)} = 6.7$ Hz, Ar); 7.31 to 7.87 (3m, 7H, Ar). ^{13}C NMR (50.32 MHz, $CDCl_3$, {H}): δ 46.50 (s, NCH_3); 47.68 (d, $^2J_{(P,C)} = 20.8$ Hz, NCH_3); 62.14 (s, CH_2N); 125.45 (d, $J_{(P,C)} = 2.7$ Hz); 129.50 (d, $J_{(P,C)} = 15.6$ Hz); 129.55 (s); 130.02 (d, $J_{(P,C)} = 17.3$ Hz); 130.50 (d, $J_{(P,C)} = 32.4$ Hz); 132.56 (d, $J_{(P,C)} = 17.9$ Hz); 134.87 (d, $J_{(P,C)} = 54.8$ Hz); 140.90 (d, $J_{(P,C)} = 3.1$ Hz). ^{15}N NMR (20.28 MHz, $CDCl_3$): δ −326 (d, $^1J_{(P,N)} = 2.65$ Hz). Positive-ion FAB HRMS (*o*-nitrophenyloctylether): Found m/z = 299.1712; Calc. $m/z = 299.1677$ $(M-Cl)^+$.

4.5. {2,6-Bis[(dimethylamino)methyl]phenyl}phenylphosphorus hexafluorophosphate 7

(a) *From the phosphane* **9**. A solution of 0.69 g (1.83 mmol) $Ph_3C^+PF_6^-$ in CH_2Cl_2 (15 ml) was added dropwise at −55 °C to a CH_2Cl_2 solution (25 ml) of the phosphane **9** (0.6 g, 2 mmol). After 30 min at −30 °C the reaction mixture became colorless. The solvent was eliminated under vacuum and the white precipitate obtained was washed with Et_2O (4 × 15 ml) to give 0.78 g (96%) of **7**. ^{31}P NMR (101.25 MHz, $CDCl_3$): δ 94.2 (s, P–Ph); −143.7 (hept, $^1J_{(P,F)} = 713$ Hz, PF_6^-). ^{31}P CP/MAS NMR (121.49 MHz, {H}): δ 91.3 (s, P–Ph) and −144.7 (hept, $^1J_{(P,H)} = 712$ Hz, PF_6^-). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.89 (s, 6H, NCH_3); 2.68 (d, $^3J_{(P,H)} = 4.8$ Hz, 6H, NCH_3); 3.85 (d, $^2J_{(H,H)} = 15.5$ Hz, 2H, NCH_2); 4.05 (d, $^2J_{(H,H)} = 15.5$ Hz, 2H, NCH_2); 6.76 (t, 1H, $^3J_{(H,H)} = 6.7$ Hz, Ar); 7.10 to 7.94 (3m, 7H, Ar). Positive-ion FAB MS (*o*-nitrophenyloctyl ether): $m/z = 299$ $(M-PF_6)^+$; negative-ion FAB MS (*o*-nitrophenyloctyl ether): $m/z = 145$ (PF_6^-).

(b) *From the salt* **6**. A solution of 1.9 g (5.68 mmol) **6** in MeCN (7 ml) was added dropwise at 0 °C to an MeCN solution (40 ml) of $NaPF_6$ (1.0 g, 5.95 mmol). After 3 h at room temperature, the NaCl precipitate (0.32 g) was removed by filtration and the solvent was eliminated under vacuum. The residue was taken up in CH_2Cl_2 and the excess $NaPF_6$ was eliminated by filtration. 2.4 g (5.45 mmol, 96%) of a beige powder identified as **7** was obtained. ^{31}P NMR (101.25 MHz, $CDCl_3$): δ 95.5 (s, P–Ph) and −143.6 (hept, $^1J_{(P,F)} = 712$ Hz, PF_6^-). ^{31}P CP/MAS NMR (121.49 MHz, {H}): δ 91.3 (s, P–Ph) and −144.5 (hept, $^1J_{(P,F)} = 713$ Hz, PF_6^-). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.86 (s, 6H, NCH_3); 2.64 (d, $^3J_{(P,H)} = 4.9$ Hz, 6H, NCH_3); 3.83 (d, $^2J_{(H,H)} = 15.5$ Hz, 2H, NCH_2); 4.02 (d, $^2J_{(H,H)} = 15.3$ Hz, 2H, NCH_2); 6.72 (t, 1H, $^3J_{(H,H)} = 6.5$ Hz, Ar); 7.31 to 7.90 (3m, 7H, Ar). Positive-ion FAB HRMS (*o*-nitrophenyloctyl ether): Found $m/z = 299.1574$; Calc. $m/z = 299.1677$ $(M-PF_6)^-$; negative-ion FAB MS (*m*-nitrobenzyl alcohol): $m/z = 145$ (PF_6^-).

4.6. {2,6-Bis[(dimethylamino)methyl]phenyl}phenylphosphane 9

A suspension of **6** (1.76 g, 5.2 mmol) in Et_2O (15 ml) was added dropwise at 0 °C to a suspension of $LiAlH_4$ (0.108 g, 2.84 mmol) in Et_2O (20 ml). The reaction mixture was stirred at room temperature for 15 h, and was then hydrolyzed with 15 ml of water. The product was extracted with Et_2O (2 × 20 ml) and the organic layer was dried ($MgSO_4$). After evaporation of the solvent, the residue was distilled to give 1.06 g (3.5 mmol, 68%) of **9** as a pale yellow oil. B.p. 135 °C/0.8 mmHg. ^{31}P NMR (101.25 MHz, $CDCl_3$): δ −77.5 (d, $^1J_{(P,H)} = 225$ Hz). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.13 (s, 12H, NCH_3); 3.25 (d, 2H, $^2J_{(H,H)} = 130$ Hz, CH_2N); 3.65 (d, 2H, $^2J_{(H,H)} = 130$ Hz, CH_2N); 5.52 (d, 1H, $^1J_{(P,H)} = 225$ Hz, PH); 7.18 to 7.31 (2m, 8H, Ar). ^{13}C NMR (62.89 MHz, $CDCl_3$, {H}): δ 44.93 (s, NCH_3); 63.92 (d, $^3J_{(P,C)} = 7.5$ Hz, CH_2N); 127.40 (s); 128.00 (d, $J_{(P,C)} = 6.2$ Hz); 128.13 (s); 128.92 (d, $J_{(P,C)} = 3.0$ Hz); 132.69 (d, $J_{(P,C)} = 17.0$ Hz); 134.53 (d, $J_{(P,C)} = 17.7$ Hz); 136.31 (d, $J_{(P,C)} = 11.4$ Hz); 144.05 (d, $J_{(P,C)} = 9.4$ Hz) (Ar). IR (cm^{-1}, $CHCl_3$): 2214 (w), 2299 (w). Positive-ion FAB (*o*-nitrophenyloctyl ether): $m/z = 299$ $(M-H)^+$. Anal. Found: C, 71.80; H, 7.95; N, 9.71. $C_{18}H_{25}N_2P$ Calc.: C, 71.97; H, 8.38; N, 9.32%.

4.7. Crystal structure determination

4.7.1. Crystal preparation

Colorless crystals of compound **4** were grown by slow evaporation of an ethanol solution. A large number of orthogonal prisms were obtained, along with a few thin, sharp-edged transparent plates. A sample of both types of crystal was sealed inside a capillary and mounted on an Enraf–Nonius CAD4 automated diffractometer at 293 K.

4.7.2. X-ray data collection

Data were collected with graphite-monochromated Mo Kα radiation. Lattice constants (Table 3) came

from the least-squares refinement of 23 reflections obtained in the range $11.8° < 2\theta < 24.1°$ for compound **4** (prisms) and 25 reflections with $11.3° < 2\theta < 45.5°$ for compound **5** (plates). In both cases, the intensities of three standard reflections were monitored at intervals of 60 min; no significant change in these intensities occurred during data collection. The structure amplitudes were obtained after the usual Lorentz and polarization reduction. Only the reflections having $F > 6\sigma(F)$ were considered to be observed. The absorption corrections were neglected.

4.7.3. Structure determination and refinement of 4 (prisms)

Direct methods (SHELXS-86 [27]) succeeded in locating the whole set of non-hydrogen atoms through a single calculation. [The systematic absences were in accordance either with the non-centrosymmetric space group $Pna2_1$ or with the space group *Pnma*. Both groups led easily to a solution with direct methods. Obviously erroneous results were obtained when starting from space group $Pna2_1$ (large σ values, incorrect bond lengths). A correct refinement of the parameters was readily achieved with centrosymmetric group *Pnma*.] After six cycles of least-squares refinement with anisotropic thermal parameters for iodine and phosphorus atoms, the hydrogen atoms were positioned by calculation (SHELX-76 [28]). However, the coordinates of the atoms H15 and H35 failed to be correctly calculated; therefore these two hydrogen atoms were not included in the subsequent refinement cycles. Refinement converged to the final R value of 0.058 (R_w = 0.066).

The final atomic coordinates are listed in Table 4. The labelling scheme is given in Fig. 2. Interatomic distances and main bond angles are listed in Tables 1 and 2 respectively. A full list of bond angles and calculated hydrogen atom coordinates are avaible as supplementary material.

4.7.4. Structure determination and refinement of 5 (plates)

The systematic absences ($h\,0\,l$, $h = 2n + 1$; $0\,k\,0$, $k = 2n + 1$) revealed the space group $P2_1/a$. Direct methods (SHELXS-86) gave only the positions of the iodide anion, the atom of phosphorus, and carbon atoms C1 and C2. A Fourier map phased on P and I atoms revealed the bis-dimethyaminophenyl moiety along with atoms C11 and C12. A subsequent difference Fourier analysis gave all the remaining carbon atoms. After eight cycles of least-squares refinement with anisotropic thermal parameters for both I and P atoms and the contribution of the calculated hydrogen atoms, the difference Fourier map gave a peak in the vicinity of nitrogen atom N2 (2.88(1) Å) and of the iodide ion (3.62(1) Å). The peak was taken as an oxygen (a water molecule coming from the 95% ethanol). The carbon atoms C1 to C8 and the oxygen atom were then refined anisotropically. The final R value was 0.057 (R_w = 0.062). The last difference Fourier calculation clearly revealed a water hydrogen atom (coordinates 0.7853, 0.5689, 0.3245). These coordinates give interatomic distances 0.91 and 2.02 Å for the O–H bond and N2 · · · H hydrogen bonding. The refined I^- · · · O distance (3.622(9) Å) is larger than the sum of the corresponding van der Waals radii (3.50 Å); therefore a second hydrogen bonding was looked for in or around the O · · · I direction. However, no peak fitting such conditions could be detected.

The final atomic coordinates are listed in Table 7. The labelling scheme is given in Fig. 4. Interatomic distances are listed in Table 5, selected bond angles in Table 6. A full list of bond angles, anisotropic thermal parameters and calculated hydrogen atom coordinates are avaible as supplementary material.

5. Supplementary material

Full lists of bond angles for compounds **4** and **5**, lists of calculated hydrogen atom coordinates and a list of anisotropic thermal parameters for compound **5** (5 pages). Ordering information is given on any current masthead page.

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