Reactions of the Hexachlorocyclodiphosphazane $[MeNPCl_3]_2$ with Primary Aromatic Amines: Formation of Highly Basic Bisphosphinimines†

Ramaswamy Murugavel,[a] Santhanathan S. Kumaravel,[a] Setharampattu S. Krishnamurthy,*[a] Munirathinam Nethaji[a] and Jayaraman Chandrasekhar[b]

[a] *Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012, India*

[b] *Department of Organic Chemistry, Indian Institute of Science, Bangalore-560 012, India*

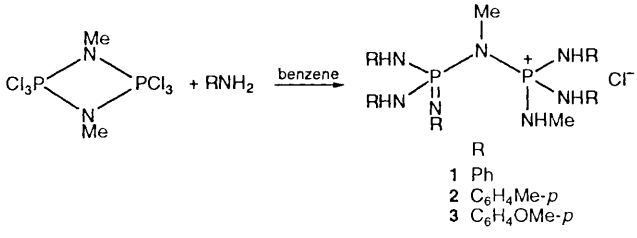
Reactions of hexachlorocyclodiphosphazane $[MeNPCl_3]_2$ with primary aromatic amines afforded the bisphosphinimine hydrochlorides $[(RNH)_2(RN)PN(Me)P(NHMe)(NHR)_2]^+Cl^-$ (R = Ph **1**, C_6H_4Me-4 **2** or C_6H_4OMe-4 **3**). Dehydrochlorination of **2** and **3** by methanolic KOH yielded highly basic bisphosphinimines $[(RNH)_2(RN)PN(Me)P(NMe)(NHR)_2]$ (R = C_6H_4Me-4 **4** or C_6H_4OMe-4 **5**). Compounds **1**–**5** have been characterised by elemental analysis and IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy. The structure of **2** has been confirmed by single-crystal X-ray diffraction. The short P–N bond lengths and the conformations of the PN_4 units can be explained on the basis of cumulative negative hyperconjugative interactions between nitrogen lone pairs and adjacent P–N σ* orbitals. *Ab initio* calculations on the model phosphinimine $(H_2N)_3P{=}NH$ and its protonated form suggest that (amino)phosphinimines would be stronger bases compared to many organic bases such as guanidine.

Phosphinimines or iminophosphoranes of the type $R_3P{=}NR'$ which may be regarded as the monomers of λ^5-cyclodiphosphazanes $[R_3PNR']_2$ are less studied compared to their counterparts phosphine oxides and phosphine sulfides.[1] Apart from being useful synthons for several cyclic phosphazenes and metallophosphazenes,[2] the co-ordination chemistry of phosphinimines would also be of considerable interest.[3] Multiply aminated phosphinimines behave as exceptionally strong bases and this property has been recently exploited by Schwesinger and Schlemper[4] in a variety of organic reactions. To our knowledge, crystal structures of only two bisphosphinimine diphosphazane derivatives, *viz.* $[(NH_2)Ph_2P{=}N{-}PPh_2(NH_2)]^+Cl^-$ and $[(NH_2)_3P{-}N{=}P(NH_2)(NHMe)_2]^+Cl^-$ have been reported[5,6] but in both cases the structure is poorly refined.

Bisphosphinimine derivatives are accessible from the reactions of ammonia or primary alkayl amines with hexachlorocyclodiphosphazanes,[7] $[RNPCl_3]_2$. In this paper we report the reactions of $[MeNPCl_3]_2$ with aromatic primary amines to yield highly basic bis(iminophosphoranyl)methylamines as their hydrochloride adducts by a selective cleavage of one of the P–N bonds of the P_2N_2 ring. The structure of one of these compounds, *viz.* $[(RNH)_2(RN)PN(Me)P(NHMe)(NHR)_2]^+Cl^-$ (R = C_6H_4Me-4) has been determined by X-ray crystallography. These hydrochlorides could be converted into their neutral bases only under forcing conditions testifying to the strong basic character of the latter. In order to understand the electronic structures and to quantify the high basicity of (amino)phosphinimines, we have also carried out *ab initio* molecular-orbital calculations on the model phosphinimine, $(NH_2)_3P{=}NH$ and its protonated form, $[P(NH_2)_4]^+$.

Results and Discussion

Syntheses and Spectra of Bisphosphinimine Hydrochlorides.—



Scheme 1

The reactions of hexachlorocyclodiphosphazane,[8] $[MeNPCl_3]_2$ with primary aromatic amines in boiling benzene give air- and moisture-stable bis(iminophosphoranyl)methylamine hydrochlorides, $[(RNH)_2(RN)PN(Me)P(NHMe)(NHR)_2]^+Cl^-$ (R = Ph **1**, C_6H_4Me-4 **2** or C_6H_4OMe-4 **3**) in good yield (Scheme 1). The compounds can be purified by recrystallisation from dichloromethane–light petroleum (1 : 1). The recrystallised samples are only sparingly soluble in common organic solvents but are readily soluble in a methanol–benzene mixture. The composition and structure of the products have been established by elemental analysis and IR and NMR (^1H, ^{13}C and ^{31}P) spectroscopy. The yield of the products, melting points, analytical data and selected spectroscopic data are listed in Table 1.

The infrared spectra of **1**–**3** do not show the characteristic P_2N_2 ring vibration at *ca.* 850 cm^{-1} indicating that ring cleavage has occurred. The ^{31}P NMR spectrum in each case shows an AX pattern revealing the non-equivalence of the two phosphorus nuclei. The doublet at δ *ca.* 15 is assigned to the phosphorus bearing the protonated nitrogen and the signal at δ *ca.* 0 is assigned to the phosphorus bearing the imine nitrogen. This assignment is based on the chemical shifts of the free bisphosphinimines (see below).

The ^1H NMR spectrum of **2** consists of a doublet at δ 1.80 and a triplet at δ 2.97 in the NMe region indicating the presence of two different NMe groups, one attached to two phosphorus atoms and the other to only one phosphorus. The high shielding

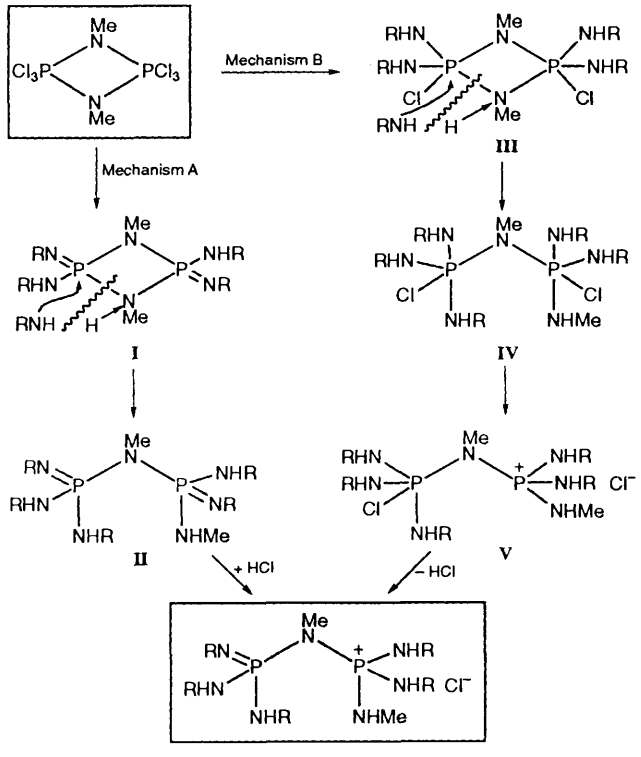
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI units employed: cal ≈ 4.184 J; Hartree ≈ 4.36 × 10^{-18} J.

of the *N*-methyl protons resonating at δ 1.80 may be ascribed to protonation as well as to the 'ring current' of the phenyl group on N(6) (see below). At −40 °C, this signal splits into a doublet of doublets [^3J(PH) = 14, ^3J(HH) = 5 Hz] indicating that the terminal NMe group is protonated. The ^{13}C NMR characteristics are similar to those of the ^{1}H NMR spectrum. For example, the spectrum of **2** shows two different signals for $N^{13}CH_3$ at δ 23.8 and 27.8. The upfield resonance at δ 23.8 is assigned to the terminal $-NH^{13}CH_3$ nuclei. A ^2J(PC) coupling is not observed for either of the $^{13}CH_3$ nuclei.

The spectral data indicate that a double Kirsanov reaction accompanied by the cleavage of one of the ring P–N bonds has occurred. The highly basic nature of the resultant product leads to the formation of the hydrochloride adduct. The structure of the *p*-toluidino derivative **2** has been confirmed by single-crystal X-ray crystallography (see below).

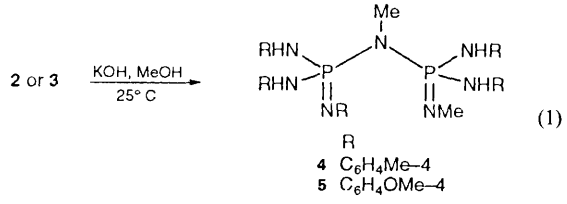
One can envisage two possible mechanisms for the formation of the bisphosphinimine hydrochlorides **1**–**3** from $[MeNPCl_3]_2$ as shown in Scheme 2. Mechanism A involves the formation of a fully amino or imino substituted cyclodiphosphazane intermediate **I** which undergoes a selective cleavage of one of the P–N bonds of the P_2N_2 ring to yield a linear bisphosphinimine intermediate **II**. This intermediate **II** takes up a molecule of HCl formed in the reaction to yield the final product. In the alternative mechanism (Mechanism B), ring cleavage occurs at an early stage of the replacement of chlorine atoms from an intermediate such as **III** to give **IV** which can also exist in the ionic form **V**. This ionic intermediate can lose a molecule of HCl to give the final product.



Scheme 2

The main difference between the two mechanisms lies in the stage of chlorine replacement at which the ring cleavage occurs. Treatment of bis(imino)aminocyclodiphosphazane $[PhNP(NMe_2)(=NPh)]_2$ with *p*-toluidine in boiling toluene does not result in ring cleavage to yield a product such as **II** (Scheme 3).[9] Hence, it is reasonable to assume that ring cleavage occurs in the amination reactions of $[MeNPCl_3]_2$ during an early stage of replacement of chlorine atoms (Mechanism B).

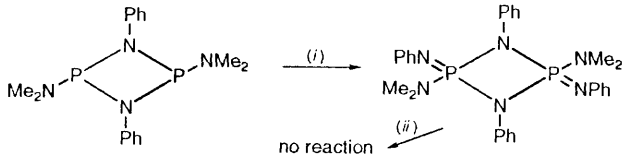
Dehydrochlorination Reactions.—Attempts to dehydrochlorinate the bisphosphinimine hydrochlorides **1**–**3** by treatment with NEt_3 or 1,4-diazabicyclo[2.2.2]octane (dabco) in boiling toluene for 72 h were unsuccessful. When the reactions of $[MeNPCl_3]_2$ with aromatic amines were carried out in the presence of a tertiary base (NEt_3 or dabco) only the hydrochloride adducts **1**–**3** were formed. Dehydrochlorination of **1** or **2** could be effected using methanolic KOH [equation (1)] or



(1)

less efficiently by stirring a benzene solution of **1** or **2** with stoichiometric amounts (1 : 1) of sodium hydride.

Analytical and spectroscopic data for the bisphosphinimines **4** and **5** are listed in Table 1. The ^{1}H NMR spectrum of **4** resembles that of its hydrochloride adduct **2**, except for a shift in the resonance of the protons of the terminal NMe group. The chemical shift of the protons of this methyl group moves downfield from δ 1.80 to δ 2.21 on dehydrochlorination. When



Scheme 3 (*i*) PhN_3; (*ii*) RNH_2, toluene, heat

Table 1 Analytical and NMR spectroscopic data for compounds **1**–**5**

Compound	Yield (%)	M.p./°C	Analyses[a] (%) C	H	N	Cl	NMR δ_H(NMe)(J_{PH}/Hz)	δ_C	δ_P(J_{PP}/Hz)
1	74	215–216	62.6	6.0	16.1	—	1.79 (d, 14)	—	17.9 (d, 12)
			(62.4)	(5.9)	(15.9)		2.97 (t, 11.5)		2.2 (d, 12)
2	60	234–235	64.7	6.9	14.3	5.1	1.80[b] (d, 14)	23.8	18.9 (d, 13.5)
			(64.8)	(6.7)	(14.3)	(5.2)	2.97 (t, 11.5)	27.8	1.6 (d, 13.5)
3	65	>230	58.1	6.1	12.8	4.4	1.80 (d, 14.3)	23.8	14.9 (d, 10.0)
			(58.0)	(6.0)	(12.8)	(4.6)	3.02 (t, 11.4)	27.0	0.6 (d, 10.0)
4	70	110–115	68.5	7.0	15.4		2.21 (d, 11.4)	26.2	8.0 (s)
			(68.5)	(6.9)	(15.1)		2.80 (t, 9.4)	28.5	1.8 (s)
5	60	100–104	63.6	6.5	14.3		2.53 (d, 12.3)	—	6.6 (s)
			(63.7)	(6.5)	(14.1)		2.73 (t, 10.7)		1.2 (s)

[a] Required values in parentheses. [b] At −40 °C, ^3J(HH) = 5 Hz.

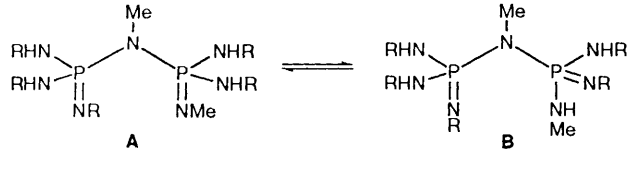
the spectrum is recorded at −40 °C, this resonance does not split further in contrast to the observed splitting of the doublet into a doublet of a doublets at −40 °C for the hydrochloride adducts. This observation shows that the terminal NMe group bears the proton in **2**. Moreover, the methyl protons of the *p*-tolyl group which give rise to a singlet in the spectrum of **2** are in two distinct environments in the free bisphosphinimine. The ^{1}H NMR spectrum of **5** resembles the spectrum of **4**; the two NMe groups in the molecule resonate at δ 2.53 and 2.73 as a doublet and a triplet respectively. The corresponding resonances for the hydrochloride adduct **3** are observed at δ 1.80 and 3.02 respectively.

The ^{13}C NMR spectrum of **4** shows two resonances for the NMe carbon atoms at δ 26.2 and 28.5. On deprotonation, the ^{13}C NMR resonance of the terminal NMe carbon of **2** shifts from δ 23.8 to δ 26.2 while the resonance of the bridging NMe carbon remains more or less unaltered. As in the proton NMR spectrum, two resonances are observed for the CH_3 groups of the *p*-tolyl groups.

The ^{31}P NMR spectrum of **4** shows two single lines in contrast to the AX pattern observed for **2**. The doublet at δ 18.9 for **2** is shifted by ≈11 ppm and appears as a singlet at δ 8 in the spectrum of **4**. The chemical shift of the other signal (δ 1.8) is close to that observed for **2** (δ 1.6). This observation supports the assignments made for the two different phosphorus nuclei in the hydrochloride adducts **1**–**3**. When the spectrum is recorded at lower temperatures, the two-line spectrum progressively splits and yields a coupled spectrum at −70 °C. It is reasonable to assume that an intermolecular tautomeric exchange of the proton between the NR and NMe groups occurs and this exchange process causes the observed dynamic behaviour in the variable-temperature phosphorus spectrum. The absence of splitting of the NMe signal in the ^{1}H NMR spectrum of the free phosphinimines at −40 °C (unlike in the case of their hydrochlorides) indicates that the structure of the molecule is frozen as tautomer **A** at low temperatures.

Crystal and Molecular Structure of Compound **2**.—The structure of compound **2** has been confirmed by single-crystal X-ray diffraction. A perspective view of the molecule with the atom numbering scheme is shown in Fig. 1. Selected structural parameters are listed in Table 2. The unit-cell packing diagram and the hydrogen-bonding network are shown in Fig. 2.

The P–N bond lengths in the molecule vary over a wide range. The P(2)–N(7) bond is the shortest (1.543 Å); this value is shorter than the P=N double bond distance in the methylene bridged bisphosphinimine (p-$MeC_6H_4N{=}PPh_2)_2CH_2$ (1.567 Å)[10] but longer than that in the bis(imino)cyclodiphosphazane, $[(NMe_2)(=NPh)PNPh]_2$ (1.518 Å).[9] The remaining P–N distances involving P(2) are significantly longer. The bond lengths around P(1) are symmetrical and shorter. Interestingly, the P–N bond lengths in the molecule as a whole are quite short (av. 1.622 Å). This value is much less than a normal P–N single bond distance (1.75–1.80 Å).[11] The central P(1)–N(1)–P(2) angle of 131.9° is the largest observed among diphosphazane derivatives with a three-co-ordinate nitrogen atom.[12,13] In spite of having such a large P–N–P angle, N(1) maintains a trigonal-planar geometry. Moreover all the other three-co-ordinate nitrogen atoms (average sum of the angles 358.1°) have a near planar distribution of bonds around them as generally observed for a nitrogen atom attached to a λ^3- or λ^5-phosphorus.[13] The chloride ion is at the centre of an extensive intra- and inter-molecular hydrogen-bonding network and forms four hydrogen bonds with a tetrahedral geometry around it (Fig. 2).



It is of interest to compare the structural parameters of **2** with those of two structurally related compounds **6** and **7**.[5,6] The main difference between the structure of **2** and those of **6** and **7** is the geometry around the central nitrogen atom which is three-co-ordinate and trigonal-planar in **2** but two-co-ordinate in **6** and **7**. The presence of a two-co-ordinate bridging nitrogen atom in **7** also allows for a wider P–N–P angle of 136°. However, the corresponding value for **6** is only 129.1°. Large P–N–P angles ranging up to 148° are observed at the two-co-

Table 2 Selected structural parameters (bond lengths in Å, angles in °) for compound **2** with estimated standard deviations (e.s.d.s) in parentheses

P(2)–N(7)	1.543(5)	P(1)–N(1)	1.664(6)
N(1)–C(11)	1.491(8)	P(1)–N(2)	1.594(6)
N(2)–C(21)	1.451(9)	P(1)–N(3)	1.608(6)
N(3)–C(31)	1.431(9)	P(1)–N(4)	1.598(6)
N(4)–C(41)	1.404(8)	P(2)–N(1)	1.699(7)
N(5)–C(51)	1.410(8)	P(2)–N(5)	1.639(6)
N(6)–C(61)	1.414(8)	P(2)–N(6)	1.628(5)
N(7)–C(71)	1.407(10)	Cl···H(N3)	2.47(6)
N(3)–P(1)–N(4)	119.2(3)	N(1)–P(2)–N(5)	107.8(3)
N(2)–P(1)–N(4)	110.1(3)	P(1)–N(1)–P(2)	131.9(3)
N(2)–P(1)–N(3)	102.0(3)	P(2)–N(1)–C(11)	114.2(4)
N(1)–P(1)–N(4)	103.7(3)	P(1)–N(1)–C(11)	112.7(5)
N(1)–P(1)–N(3)	106.3(3)	P(1)–N(2)–C(21)	125.7(6)
N(1)–P(1)–N(2)	116.1(3)	P(1)–N(3)–C(31)	127.5(5)
N(6)–P(2)–N(7)	120.0(3)	P(1)–N(4)–C(41)	129.7(5)
N(5)–P(2)–N(7)	118.2(3)	P(2)–N(5)–C(51)	129.9(5)
N(5)–P(2)–N(6)	98.0(3)	P(2)–N(6)–C(61)	128.0(5)
N(1)–P(2)–N(7)	103.8(3)	P(2)–N(7)–C(71)	127.7(4)
N(1)–P(2)–N(6)	108.5(3)		
N(1)–P(1)–N(4)–C(4)	172.7(6)	N(4)–P(1)–N(1)–C(1)	175.8(5)
N(2)–P(1)–N(1)–C(3)	168.6(6)	N(3)–P(1)–N(2)–C(2)	166.5(6)
N(1)–P(2)–N(7)–C(7)	177.6(6)	N(7)–P(2)–N(1)–C(1)	160.3(5)
N(6)–P(2)–N(5)–C(5)	161.5(6)	N(5)–P(2)–N(6)–C(6)	177.9(6)

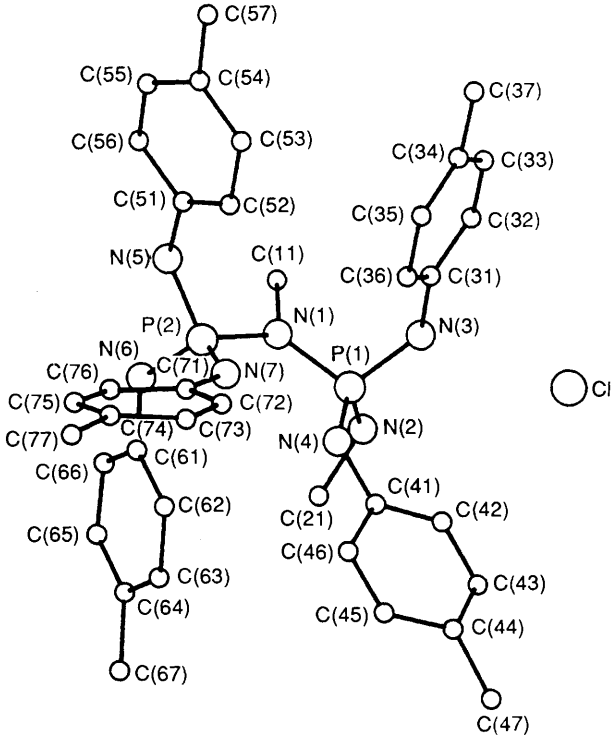


Fig. 1 Molecular structure of compound **2** with atom labelling scheme

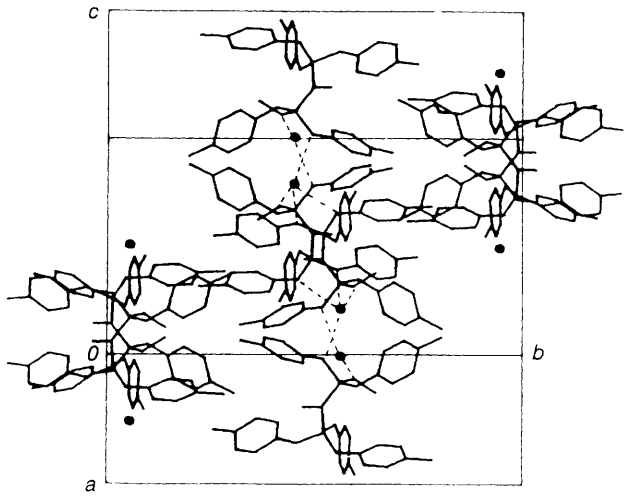
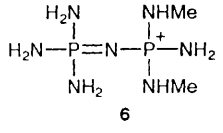
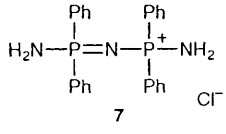


Fig. 2 Unit-cell packing diagram of **2** (viewed perpendicular to *bc* plane) showing the hydrogen-bonding network. Hydrogen-bonding distances and symmetries are Cl···N(3) 3.225(7), Cl···N(2)($-x$, y, $\frac{1}{2} - z$) 3.192(6), Cl···N(5)(x, $-y$, $\frac{1}{2} + z$) 3.220(5) and Cl···N(6)(x, $-y$, $\frac{1}{2} + z$) 3.208(5) Å



6



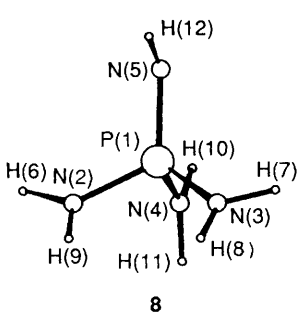
7

ordinate nitrogen atoms of cyclotetra and higher membered cyclophosphazenes and these large values are generally considered to be indicative of delocalisation.[2a,14] This interpretation must be viewed with caution in the light of the large P–N–P angle observed even at a three-co-ordinated nitrogen atom as in **2** (131.9°).

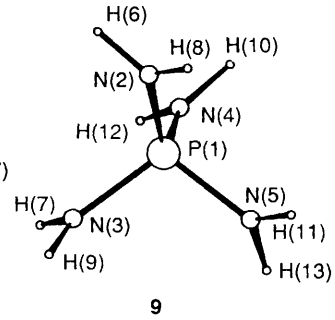
The structures of both **6** and **7** are poorly refined precluding any meaningful comparison of P–N bond lengths. However, there are clearly two distinct types of P–N bonds in both **6** and **7**; the central P–N bonds are shorter than the two terminal P–N bonds. The average values for the central and terminal P–N bond distances of **6** are 1.56 and 1.63 Å respectively; the corresponding values for **7** are 1.57 and 1.65 Å. In contrast to these structures, the terminal P–N distances are shorter than the central P–N distances in **2**.

The Origin of Short P–N *Bonds in Compound* **2**.—The variation of P–N bond lengths in compound **2** can be understood by viewing the molecule as a combination of a phosphinimine $[(R_2N)_3P{=}NR]$ and a phosphonium ion $[P(NR_2)_4]^+$ unit sharing a common –NR group. The exceptionally short P(2)–N(7) length can be be assigned to a formal double bond. The near equivalence of P–N bond lengths about P(1) is consistent with the phosphonium ion character for this subunit. In this formulation, the positive charge would be spread over all the nitrogen substituents making the NHR units poor proton donors. This supposition is supported by the fact that attempts to deprotonate compounds **1**–**3** by heating them under reflux with strong tertiary amine bases, such as triethylamine or dabco in toluene for 72 h have been unsuccessful. The exceptionally high basicity of phosphinimines formed in these reactions is analogous to that of $(NH_2)_2C{=}NH$, which upon protonation forms the symmetrical guanidinium ion in which the positive charge is dispersed over the entire CN_3 framework.

The formal P–N single bonds involving both P(1) and P(2) are remarkably short. An interesting feature of the structure is that around each phosphorus atom, two sets of C–N–P–N′ dihedral angles are close to 180° (Table 2). This geometry is ideal for interactions between each of the nitrogen lone-pair



8



9

Fig. 3 Geometry optimised structures of species **8** and **9**

orbitals and an adjacent P–N σ* orbital of appropriate symmetry.[15] Such cumulative negative hyperconjugative interactions should lead to short P–N bonds.[15,16] This effect appears to be more pronounced in the phosphonium ion part of the molecule than in the phosphinimine part. This kind of cumulative negative hyperconjugative interactions leading to short C–O distances have already been documented for orthocarbonates $C(OR)_4$ (R = aryl) by crystallographic and molecular-mechanics studies.[16]

In order to verify the operation of these interactions *ab initio* calculations have been carried out on the model compound, $(NH_2)_3P{=}NH$ **8** and its protonated form $P(NH_2)_4^+$ **9**. Two sets of calculations were carried out with the 3-21G and 3-21G(*) basis sets by imposing C_s symmetry for the free phosphinimine **8** and an idealised D_{2d} geometry for the phosphonium ion **9**. The optimised structures of **8** and **9** are shown in Fig. 3. The bond distances, bond angles and dihedral angles derived from the optimised geometries of **8** and **9** and the absolute energies are summarised in Table 3. In general, the structures calculated at 3-12G level show longer P–N bond lengths compared to those at 3-21G(*) level. However the bond angles and dihedral angles are not basis-set dependent. The structural data listed in Table 3 clearly indicate that the calculated structures of **8** and **9** satisfactorily reproduce the geometries of the phosphinimine and phosphonium ion part of the bisphosphinimine hydrochloride **2**. In particular, the exceptionally short P(2)–N(7) bond length (1.543 Å) is remarkably close to the formal P=N length computed for **8** at the 3-21G(*) level. This value is also close to that calculated for $H_3P{=}NH$.[17]

In the computed structures of both **8** and **9** as well as in the crystal structure of **2** there are two sets of H–N–P–N′ (or C–N–P–N′) dihedral angles that are close to 180°. Consequently, the lone pair on each of the nitrogen atoms is in the plane of another N–P–N unit, an arrangement ideal for cumulative negative hyperconjugation which leads to short P–N bonds.

Proton Affinity.—The calculated energies of **8** and **9** can be used to obtain the proton affinity of the free bisphosphinimine **8** which is remarkably high (283.2 and 281.4 kcal mol^{-1} at 3-21G and 3-21G(*) levels respectively). The basicity of **8** is in fact higher than that of organic super bases such as guanidine whose calculated proton affinity at the 3-21G level is only 254.6 kcal mol^{-1}. Although the calculated proton affinity of this model compound **8** refers to the gas phase, the result is consistent with the very high basicity of the bisphosphinimines as reflected in the ready formation of their hydrochloride adducts **1**–**3**. The calculated proton affinity of **8** is also in accord with the high pK_a measured for the bisphosphinimines $[(NMe_2)_3P{-}N{=}P(NMe_2)_2(NR)]$ (R = Me, 32.7; Bu^t, 33.4; $C_8H_{17}{}^t$, 33.2) in acetonitrile.[4a,b]

Phosphinimines of the type $R_3P{=}NR$ (R = alkyl or aryl) are not as basic as **8**. For example, the proton affinity of $H_3P{=}NH$ has been calculated to be 246.9 kcal mol^{-1} at the 6-31G* level.[18] The increase in basicity on going from $R_3P{=}NR$ (R = alkyl or aryl) to $(NH_2)_3P{=}NR$ is similar to the trend observed for the series $H_2C{=}NH$, $(NH_2)HC{=}NH$ and $(NH_2)_2C{=}NH$ for which

Table 3 Selected structural parameters (bond lengths in Å, angles in °) of species **8** and **9** derived from *ab initio* calculations[a]

$(NH_2)_2P{=}NH$ **8**	3-21G	3-21G(*)
P(1)–N(2)	1.703	1.673
P(1)–N(3)	1.703	1.673
P(1)–N(4)	1.681	1.653
P(1)–N(5)	1.611	1.541
N–H (NH_2) (av.)	0.997	0.998
N(5)–H(12)	1.012	1.004
N(2)–P(1)–N(3)	97.91	97.64
N(2)–P(1)–N(4)	106.73	107.35
N(2)–P(1)–N(5)	119.68	119.53
N(4)–P(1)–N(5)	105.05	104.62
P(1)–N(2)–H(6)	124.81	125.25
P(1)–N(2)–H(8)	118.83	118.87
H(6)–N(2)–H(8)	116.23	115.76
P(1)–N(4)–H(10)	122.28	122.97
P(1)–N(4)–H(11)	118.82	118.81
H(10)–N(4)–H(11)	118.89	118.22
P(1)–N(5)–H(12)	115.49	122.07
N(3)–P(1)–N(2)–H(6)	3.0	0.8
N(3)–P(1)–N(2)–H(8)	178.8	176.7
N(4)–P(1)–N(5)–H(12)	180.0	180.0
N(5)–P(1)–N(4)–H(10)	180.0	180.0
$[P(NH_2)_4]^+$ **9**		
P(1)–N(2), N(3), N(4), N(5)	1.665	1.632
N(2)–H(6)	1.001	1.003
N(2)–H(8)	1.002	1.005
	112.5	112.7
N(2)–P(1)–N(3), N(2)–P(1)–N(4)	112.5	112.7
N(3)–P(1)–N(5), N(4)–P(1)–N(5)	103.5	103.2
N(2)–P(1)–N(5), N(3)–P(1)–N(4)		
N–P–N–H dihedral angles	180.0	180.0
	or 0.0	or 0.0

[a] The calculated absolute energies (in Hartrees) of **8** and **9** at 3-21G(*) level are −559.777 24 and −560.225 64 respectively.

the calculated proton affinities (using the 4-31G basis set) are 228, 249 and 264 kcal mol^{-1} respectively. Protonated $(NH_2)_3P{=}NR$ may thus be viewed as an inorganic tetrahedral analogue of the planar guanidinium ion.

Conclusion

A simple two-step synthetic route for (amino)bisphosphinimines from hexachlorocyclodiphosphazanes has been developed. The structural features of the bisphosphinimine hydrochloride $[(RNH)_2(RN)PN(Me)P(NHMe)(NHR)_2]^+Cl^-$ (R = C_6H_4Me-4) **2** as revealed by X-ray crystallography are reproduced by the computed geometries of the model phosphinimine $(H_2N)_3P{=}NH$ and its protonated form $[P(NH_2)_4]^+$. Cumulative negative hyperconjugative interactions are invoked to explain the short P–N bonds in **2**. The calculated proton affinity of $(H_2N)_3P{=}NH$ indicates that (amino)phosphinimines are more basic than strong organic nitrogen bases such as guanidine. Bisphosphinimines reported here may also function as potential bidentate ligands in transition-metal chemistry.[3]

Experimental

General.—All the experimental manipulations were performed under a dry N_2 atmosphere. Melting point determinations, elemental analysis and IR and NMR spectroscopy were performed as described previously.[19] The λ^5-cyclodiphosphazane, $[MeNPCl_3]_2$ was prepared from methylamine hydrochloride and phosphorus pentachloride.[8]

Table 4 Atomic coordinates of the non-hydrogen atoms of compound **2**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cl	0.0878(1)	0.0553(1)	0.3508(1)
P(1)	0.1618(1)	0.0548(1)	0.1667(1)
P(2)	0.2230(1)	0.0150(1)	0.0482(1)
N(1)	0.1673(3)	0.0117(2)	0.1006(3)
N(2)	0.0804(3)	0.0895(2)	0.1458(3)
N(3)	0.1614(3)	0.0136(2)	0.2330(3)
N(4)	0.2343(3)	0.0985(2)	0.1826(3)
N(5)	0.2265(3)	−0.0498(2)	0.0164(3)
N(6)	0.1700(3)	0.0455(2)	−0.0313(2)
N(7)	0.3019(3)	0.0428(2)	0.1012(3)
C(11)	0.1004(4)	−0.0305(3)	0.0729(4)
C(21)	0.0579(5)	0.1409(3)	0.0999(5)
C(31)	0.2128(5)	−0.0342(3)	0.2656(4)
C(32)	0.2909(5)	−0.0352(3)	0.2718(4)
C(33)	0.3381(5)	−0.0831(5)	0.3034(5)
C(34)	0.3112(7)	−0.1290(4)	0.3294(5)
C(35)	0.2356(8)	−0.1259(4)	0.3239(5)
C(36)	0.1847(5)	−0.0797(3)	0.2916(4)
C(37)	0.3632(7)	−0.1803(4)	0.3644(5)
C(41)	0.2546(4)	0.1481(3)	0.2274(3)
C(42)	0.2194(4)	0.1625(3)	0.2763(4)
C(43)	0.2437(5)	0.2126(3)	0.3184(4)
C(44)	0.3020(5)	0.2482(3)	0.3140(4)
C(45)	0.3352(4)	0.2330(3)	0.2644(4)
C(46)	0.3125(4)	0.1835(3)	0.2223(4)
C(47)	0.3236(6)	0.3034(3)	0.3589(5)
C(51)	0.2790(4)	−0.0957(3)	0.0499(4)
C(52)	0.2712(4)	−0.1446(3)	0.0066(4)
C(53)	0.3216(5)	−0.1913(3)	0.0345(5)
C(54)	0.3790(5)	−0.1908(3)	0.1036(6)
C(55)	0.3871(5)	−0.1422(4)	0.1464(5)
C(56)	0.3386(5)	−0.0941(3)	0.1192(4)
C(57)	0.4357(5)	−0.2422(4)	0.1340(6)
C(61)	0.1423(4)	0.1029(3)	−0.0441(4)
C(62)	0.1873(4)	0.1479(3)	−0.0033(4)
C(63)	0.1598(5)	0.2036(3)	−0.0185(4)
C(64)	0.0886(6)	0.2156(3)	−0.0754(5)
C(65)	0.0440(5)	0.1708(4)	−0.1184(5)
C(66)	0.0699(4)	0.1141(3)	−0.1023(4)
C(67)	0.0564(4)	0.2798(3)	−0.0935(6)
C(71)	0.3706(4)	0.0538(3)	0.0870(3)
C(72)	0.3746(4)	0.0535(3)	0.0177(4)
C(73)	0.4463(5)	0.0639(3)	0.0106(4)
C(74)	0.5151(4)	0.0764(3)	0.0708(5)
C(75)	0.5116(4)	0.0770(4)	0.1388(4)
C(76)	0.4408(4)	0.0652(3)	0.1470(4)
C(77)	0.5926(5)	0.0894(4)	0.0623(5)

Syntheses of Compounds **1**–**3**.—Aniline (11.2 g, 120 mmol) in benzene (20 cm^3) was added dropwise with stirring to $[MeNPCl_3]_2$ (3.33 g, 10 mmol) in benzene (50 cm^3) at 25 °C (**CAUTION**: benzene is a suspected carcinogen and appropriate precautions should be taken while carrying out the experiment). The reaction mixture was heated under reflux for 1 h and filtered. The solvent was removed *in vacuo* and the residue washed with cold methanol to obtain $[(RNH)_2(RN)PN(Me)P(NHMe)(NHR)_2]^+Cl^-$ **1** (R = Ph). The *p*-toluidino and *p*-anisidino derivatives $[(RNH)_2(RN)PN(Me)P(NHMe)(NHR)_2]^+Cl^-$ (R = C_6H_4Me-4 **2** or C_6H_4OMe-4 **3**) were prepared by a procedure similar to that described above for **1**. The infrared spectra of **1**–**3** in Nujol mulls showed a broad band at 3050–3150 cm^{-1} attributable to ν(N–H).

Dehydrochlorination of Compounds **2** *and* **3**.—Dehydrochlorination of compounds **2** or **3** were effected by the treatment of solutions of these in benzene–methanol (3:1) (1 g in 25 cm^3) with 1 equivalent of KOH in methanol (10 cm^3) and stirring for 30 min. The precipitated KCl was filtered off and the solution evaporated to dryness. The residue was extracted with benzene

to obtain compound **4** or **5**. The free bisphosphinimines were very hygroscopic and reformed the phosphinimine-phosphonium ion upon exposure to atmospheric moisture (NMR evidence); ν(N–H) for **4** 3162 cm^{-1}.

When the dehydrochlorination was effected by stirring **2** with NaH in benzene, **4** was isolated only in 25–30% yield. The ^{31}P NMR spectrum of the reaction mixture showed the presence of many monophosphazene species apart from **4**.

X-Ray Structural Determination of Compound **2**.—Suitable crystals for X-ray diffraction study were grown as parallelopipeds from dichloromethane–light petroleum at 0 °C.

Crystal data. $C_{37}H_{46}ClN_7P_2$, M = 686.2, monoclinic, space group $C2/c$, crystal size, 0.2 × 0.2 × 0.15 mm, a = 18.222(3), b = 23.250(3), c = 19.444(14) Å, β = 113.16(2)°, U = 7574 $Å^3$. The unit-cell parameters were derived and refined by using 25 randomly selected well centred reflections in the range 25 < 2θ < 40°, Z = 8, D_c = 1.202 g cm^{-3}, $F(000)$ = 2904, λ(Mo-Kα) = 0.7107 Å, μ(Mo-Kα) = 1.8 cm^{-1}, T = 292 K.

Intensity data were collected on an Enraf–Nonius CAD-4 diffractometer using Mo-Kα radiation; ω–2θ scan mode, octants collected $+h$, $+k$, $\pm l$, 2θ range 2–50°, no crystal or intensity decay, 6662 unique reflections of which 2765 with $F_o > 6\sigma F_o$ were considered to be observed. The data were corrected for Lorentz and polarisation effects. Absorption and extinction corrections were not made. The structure was solved by direct methods using SHELXS 86.[20a] The hydrogen atoms were located from successive difference maps and included in subsequent calculations. Least-squares refinement was carried out using SHELX 76.[20b] All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were assigned individual isotropic thermal parameters. The final R and R' values were 0.054 and 0.053, respectively, for 609 refined parameters. The final shift/e.s.d. and residual electron density were 0.002 and 0.27 e $Å^{-3}$ respectively. Final fractional atomic coordinates of the non-hydrogen atoms are given in Table 4.

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

References

1 M. Bermann, *Adv. Inorg. Chem. Radiochem.*, 1972, **14**, 1; M. Bermann, *Top. Phosphorus Chem.*, 1972, **7**, 311.

2 (*a*) S. S. Krishnamurthy and A. C. Sau, *Adv. Inorg. Chem. Radiochem.*, 1978, **21**, 41; (*b*) H. G. Heal, *The Inorganic Heterocyclic Chemistry of Sulfur, Nitrogen and Phosphorus*, Academic Press, New York, 1980; (*c*) H. W. Roesky, K. V. Katti, U. Seske, M. Witt, E. Egert, R. Herbst and G. M. Sheldrick, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 477.

3 E. W. Abel and S. A. Mucklejohn, *Phosphorus Sulfur Relat. Elem.*, 1981, **9**, 235; H. Schimidbaur, *Adv. Organomet. Chem.*, 1970, **9**, 259; K. Dehnicke and J. Strahle, *Polyhedron*, 1989, **8**, 707; K. V. Katti and R. G. Cavell, *Organometallics*, 1989, **8**, 2147; P. Imhoff, C. J. Elsevier and C. H. Stam, *Inorg. Chim. Acta*, 1990, **175**, 209.

4 (*a*) R. Schwesinger and H. Schlemper, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1167; (*b*) R. Schwesinger, *Nachr. Chem. Tech. Lab.*, 1990, **38**, 1214; (*c*) R. Schwesinger, *Chimia*, 1985, **39**, 269.

5 J. W. Cox and E. R. Corey, *Chem. Commun.*, 1969, 205.

6 M. Ziegler, *Z. Anorg. Allg. Chem.*, 1968, **362**, 257.

7 B. S. Drach, I. N. Zhmurova and A. V. Kirsanov, *Zh. Obshch. Khim.*, 1967, **37**, 2524; V. Gutmann, K. Utvary and M. Bermann, *Monatsh. Chem.*, 1966, **97**, 1745.

8 A. C. Chapman, W. S. Holmes, N. L. Paddock and H. L. Searle, *J. Chem. Soc.*, 1961, 1825.

9 S. S. Kumaravel, S. S. Krishnamurthy, T. S. Cameron and A. Linden, *J. Chem. Soc., Dalton Trans.*, 1990, 1119.

10 P. Imhoff, R. v. Asslet, C. J. Elsevier, K. Vrieze, K. Goubitz, K. F. v. Malseen and C. H. Stam, *Phosphorus Sulfur Silicon Relat. Elem.*, 1990, **47**, 401.

11 T. S. Cameron, R. E. Cordes and B. R. Vincent, *Acta Crystallogr., Sect. C*, 1986, **42**, 1242 and refs. therein.

12 R. P. K. Babu, S. S. Krishnamurthy and M. Nethaji, *Heteroatom Chem.*, 1991, **2**, 477.

13 R. Keat, *Top. Curr. Chem.*, 1982, **102**, 89.

14 R. T. Oakley, S. J. Rettig, N. L. Paddock and J. Trotter, *J. Am. Chem. Soc.*, 1985, **107**, 6923.

15 A. A. Korkin, *Russ. Chem. Rev.*, 1992, **61**, 473; A. E. Reed and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1990, **112**, 1434; J. M. Lehn and G. Wipff, *J. Chem. Soc., Chem. Commun.*, 1975, 800; M. Biddlestone, R. Keat, H. G. Parkes, H. Rose, D. S. Rycroft and R. A. Shaw, *Phosphorus Sulfur Relat. Elem.*, 1985, **25**, 25.

16 N. Narasimhamurthy, H. Manohar, A. G. Samuelson and J. Chandrasekhar, *J. Am. Chem. Soc.*, 1990, **112**, 2937.

17 P. V. Sudhakar and K. Lammertsma, *J. Am. Chem. Soc.*, 1991, **113**, 1899.

18 P. Molina, M. Alajarin, C. L. Leonardo, R. M. Claramunt, M. de la Concepcion Foces-Foces, F. H. Cano, J. Catalan, J. L. G. de Paz and J. Elguero, *J. Am. Chem. Soc.*, 1989, **111**, 355.

19 R. Murugavel, S. S. Krishnamurthy and M. Nethaji, *J. Chem. Soc., Dalton Trans.*, 1993, 2569.

20 (*a*) G. M. Sheldrick, SHELXS 86, Program for crystal structure solution, University of Göttingen, 1986; (*b*) G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1976.

Received 24*th June* 1993; *Paper* 3/03626J