Dicoordinated Phosphorus Compounds: a Novel 4,5-Disubstituted 1,2,4,3-Triazaphosphole. X-Ray Molecular Structures of a 2-*N*-BF_3 Complex of 4,5-Diisopropyl-1,2,4,3-triazaphosphole and of its Tetramer. Conformation in the Crystalline Form and in Solution

Moncef Haddad,[a] Françoise Dahan,[b] Jean-Pierre Legros,[b] Lucien Lopez,[c] Marie-Thérèse Boisdon[c] and Jean Barrans*[,c]

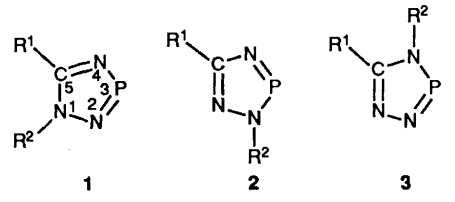
[a] *Institut Universitaire Technique, 8000 Nabeul, Tunisia*

[b] *Laboratoire de Chimie de Coordination du CNRS, Unité n° 8241, liée par convention à l'Université Paul Sabatier et à l'Institut National Polytechnique, 205, route de Narbonne, 31077 Toulouse Cedex, France*

[c] *Université Paul Sabatier, URA-CNRS 454, 118 Route de Narbonne, 31062 Toulouse Cedex, France*

The synthesis of the title compound is described. It may be stabilised by the reaction of its tetramer with BF_3. The tetramer displays several isomers and conformers in solution; one of them has been isolated and its crystal structure determined. The crystal structure of the 2-*N*-BF_3 complex of the parent 4,5-diisopropyl-1,2,4,3-triazaphosphole has also been obtained.

Several years ago, the first cyclic and P=N dicoordinated phosphorus compounds, namely the 1,2,4,3-triazaphospholes, were prepared in our laboratory.[1] Three isomeric forms are possible (**1**–**3** below). Derivatives of **1** and **2** are well known,[1,2]



1 **2** **3**

whereas no isomer of type **3** has yet been isolated; only the 5-phenyl-4-*H*-1,2,4,3-triazaphosphole was observed in a mixture of tautomers.[2c]

This lack is surprising. Therefore we have tried to obtain these isomers **3** from the reaction of tris(dimethylamino)phosphine with suitable amidrazones **4**: $R^1C(NHR^2)$=N-NH_2 or their salts **4**·HX.

Results and Discussion

Synthesis of Oligomers **8**.—A large number of amidrazones have been described in the literature.[3–10] Most of the 3-*N*-substituted ones bear aromatic R^1 and R^2 groups.[3] Only one compound with R^1 = alkyl (NO_2CH_2) has been prepared.[10]

Therefore, in order to obtain triazaphospholes **3**, we prepared new amidrazones **4a–i**, chiefly with R^1 = alkyl.

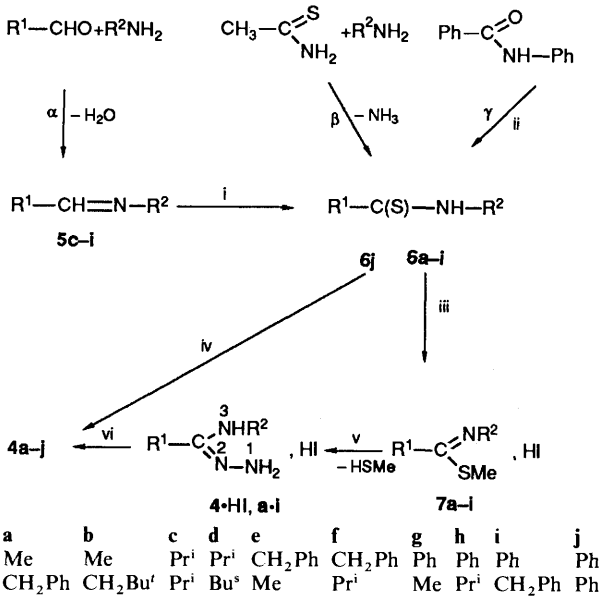
Synthetic methods involving several steps were derived from literature procedures: mainly from reaction of anhydrous hydrazines with methylthioimidate hydriodides used to obtain unsubstituted[6,7b] and disubstituted[7] amidrazones.

The starting materials were imines (α), thioacetamides (β) or *N*-phenylbenzamide (γ) (Scheme 1).

According to the literature,[11] aliphatic imines **5c–f** were prepared in the absence of solvent, while aromatic imines **5g–i** were obtained in benzene solution.[12]

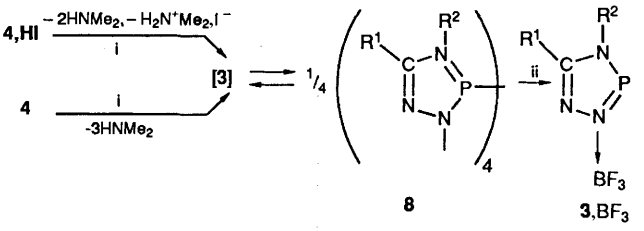
Sulfur reacted with **5** leading to *N*-substituted thioamides **6** by analogy with the Willgerodt–Kindler reaction.[13,14] The thioamides **6a** and **6b** were prepared from thioacetamide.[15]

Thioimidates **7** were obtained according to Bernsthen's method.[16] Finally, anhydrous hydrazine reacting with these derivatives gave amidrazone hydriodides **4**·HI; a strong base was required to obtain the free amidrazones **4**. Furthermore,



	a	b	c	d	e	f	g	h	i	j
R^1	Me	Me	Pr^i	Pr^i	CH_2Ph	CH_2Ph	Ph	Ph	Ph	Ph
R^2	CH_2Ph	CH_2Bu^t	Pr^i	Bu^s	Me	Pr^i	Me	Pr^i	CH_2Ph	Ph

Scheme 1 Preparation of 3-*N*-substituted amidrazones. *Reagents and conditions:* i, $\frac{1}{8}$ S_8; ii, P_2S_5; iii, MeI; iv, NH_2NH_2, H_2O; v, NH_2NH_2; vi, base.



Scheme 2 Preparation of tetramers **8** and complexes **3**·BF_3. *Reagents and conditions:* i, $P(NMe_2)_3$; ii, BF_3·Et_2O.

hydrazine hydrate reacting with thiobenzamide **6j** afforded amidrazone **4j** directly.[3]

Then, tris(dimethylamino)phosphine reacted with amidrazone hydriodides **4**·HI or amidrazones **4**, to afford a three-coordinated phosphorus species **8** which was shown to be an oligomeric form of the 4,5-disubstituted 1,2,4,3-triazaphosphole **3**.

This oligomerization was previously observed with other

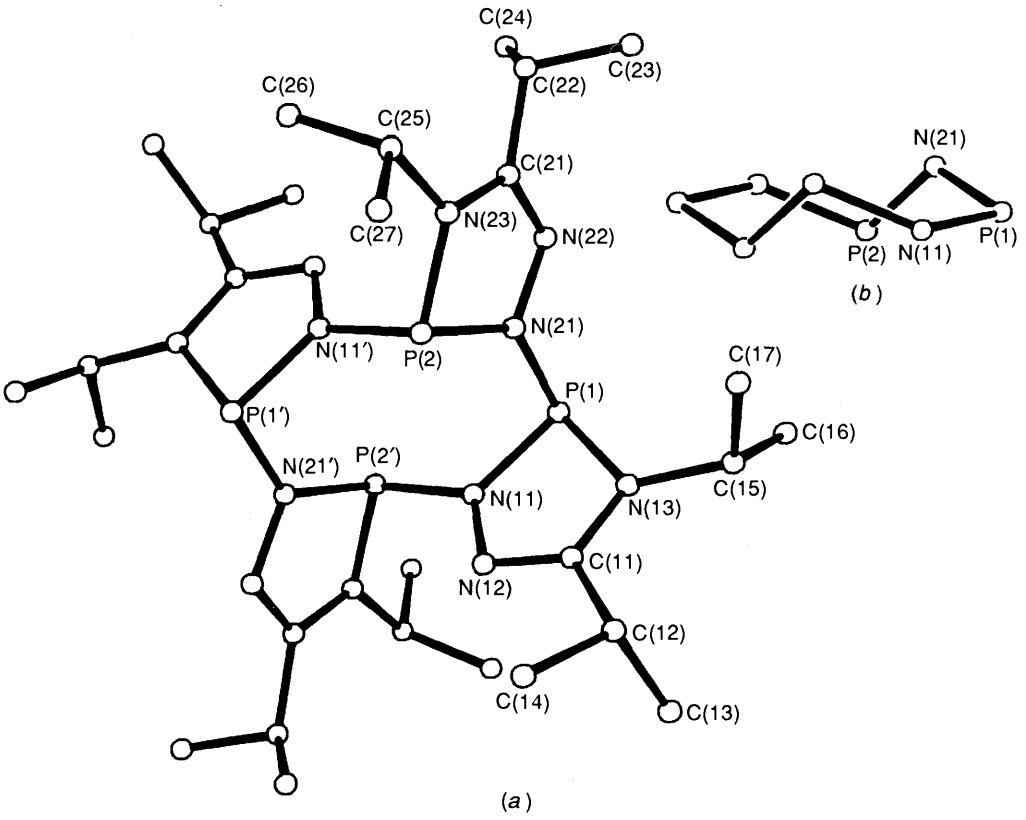


Fig. 1 (*a*) Perspective drawing of the tetramer **8c** with atomic labelling scheme. Hydrogen atoms omitted, arbitrary isotropic temperature factor given to all atoms. (*b*) Side view of the eight-membered ring emphasising the 'twisted-chair' conformation.

Table 1 Selected bond lengths/Å and angles/° with esds in parentheses for **8c**. Primes indicate inversion through a centre of symmetry

Atom 1	Atom 2	Distance		Atom 1	Atom 2	Distance	
P(1)	N(11)	1.707(3)		N(11)	N(12)	1.424(4)	
P(1)	N(13)	1.711(3)		N(12)	C(11)	1.296(5)	
P(1)	N(21)	1.712(3)		N(13)	C(11)	1.386(5)	
P(2)	N(11)′	1.716(3)		N(21)	N(22)	1.423(4)	
P(2)	N(21)	1.707(3)		N(22)	C(21)	1.278(6)	
P(2)	N(23)	1.714(4)		N(23)	C(21)	1.403(6)	
Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N(11)	P(1)	N(13)	86.1(2)	N(11)	N(12)	C(11)	107.5(3)
N(11)	P(1)	N(21)	101.6(2)	P(1)	N(13)	C(11)	112.4(2)
N(13)	P(1)	N(21)	105.3(2)	P(1)	N(21)	P(2)	129.7(2)
N(11)′	P(2)	N(21)	104.2(2)	P(1)	N(21)	N(22)	114.4(3)
N(11)′	P(2)	N(23)	103.5(2)	P(2)	N(21)	N(22)	115.3(3)
N(21)	P(2)	N(23)	86.5(2)	N(21)	N(22)	C(21)	107.9(4)
P(1)	N(11)	P(2)′	122.4(2)	P(2)	N(23)	C(21)	111.3(3)
P(1)	N(11)	N(12)	115.4(2)	N(12)	C(11)	N(13)	115.9(4)
P(2)	N(11)	N(12)	121.3(2)	N(22)	C(21)	N(23)	116.6(4)

P=N dicoordinated phosphorus compounds;[17,18] in some cases, equilibria between oligomers and dicoordinated phosphorus monomers have been observed by variable-temperature ^{31}P NMR experiments.[17]

Conformation of **8c**.—In DCI mass spectra of several compounds **8**, tetrameric, trimeric, dimeric and monomeric lines were observed; the monomer (generated from the oligomer under ionisation conditions) gave the strongest peak. However, no characteristic monomer signal has ever been observed in ^{31}P NMR spectra of **8c** solutions, either in xylene (at room temperature or at 130 °C), or in pyridine at 100 °C,[17] but only a complex system between 60 and 80 ppm.

Crystal Structure of **8c**.—The single-crystal structure of **8c** determined by X-ray diffractometry clearly shows independent centrosymmetric tetrameric molecules of **3c**. The eight-membered ring is not crown-shaped but looks like the 'twisted-chair' conformation of cyclooctane[19] as in the case of the other tetramers.[17b] A drawing of the tetramer structure showing the labelling scheme is given in Fig. 1. Selected bond lengths and angles are reported in Table 1. All the P–N bond lengths are very similar (1.71 Å), longer than the triazaphosphole ones ($\Delta d \simeq 0.06$ Å). Although the 'twisted-chair' shape of the tetraphosphazane ring is analogous to that observed in the tetramer formed from ethylenediamine,[17b] the sum of the NPN angles around the phosphorus atom in the triazaphospholanyl ring **8c** (293.6°) is smaller than that measured in the former (299°).

The tetramer molecule **8c** has twelve potential chiral centres:

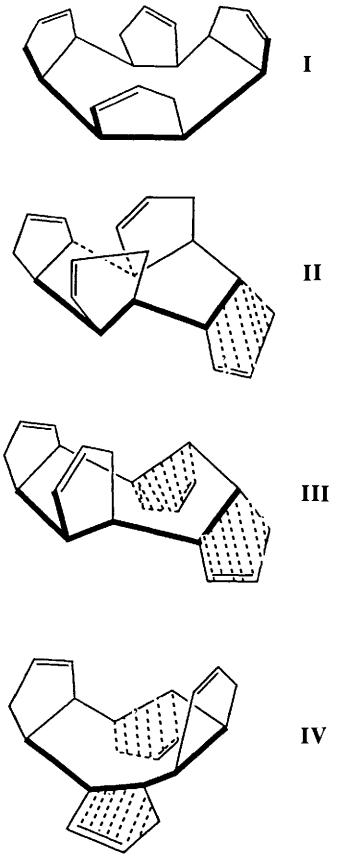


Fig. 2 Models of four possible conformers

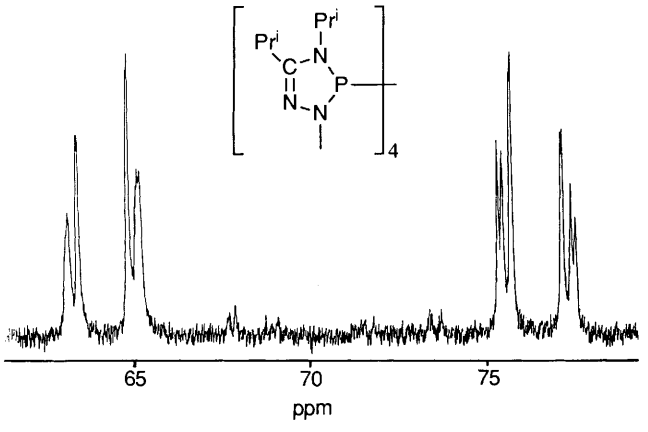


Fig. 3 ^{31}P NMR spectrum of **8c** (C_6D_6)

Table 2 ^{13}C NMR data for **8c** [δ (J)][a]

C_{cycle}	NCH	CCH	$NCHCH_3$	$CCHCH_3$
157 (8.4)			25.37 (12.2)	22.5
154.44 (7.93)	45.9 (14.9)	26.5 (4.6)	24.72 (9.5)	21.9
154.16 (7.82)	46.13 (14.9)		24.61 (9.4)	21.4
			24.37 (11.6)	

[a] Solvent C_6D_6. J in Hz.

the four phosphorus atoms and the eight tricoordinated nitrogen atoms. However, the crystal structure of **8c** shows that the sum of the bond angles around the nitrogen atoms is 360°, and therefore the eight nitrogen atoms cannot be chiral. Therefore there are only four chiral centres (the phosphorus atoms) and therefore sixteen enantiomers are possible. On account of equivalence, this number is reduced to eight.

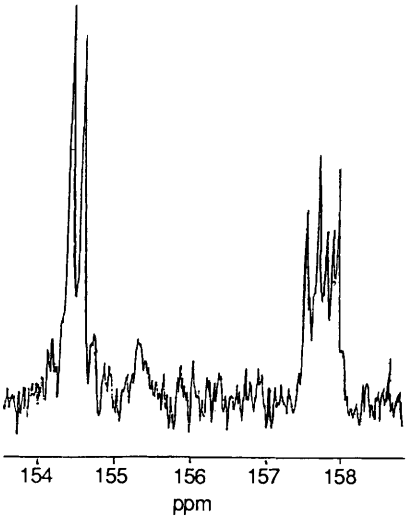


Fig. 4 Partial ^{13}C NMR spectrum of **8c** (C_6D_6)

These eight enantiomers can be regrouped into four models **I–IV** (Fig. 2), each with two enantiomeric forms: **I**, with the four triazaphospholanyl rings towards the same side of the average tetraphosphazane ring plane; **II** with one triazaphospholanyl ring opposite to the three others; **III** with two consecutive rings above and the two others below the average plane of cyclophosphazane with a symmetrical centre; **IV** with the triazaphospholanyl rings in turn above and below the cyclophosphazane ring.

From X-ray diffraction, **8c** exists as the conformer **III**. However, ^{31}P and ^{1}H spectra of **8c** dissolved in C_6D_6 at room temperature were not consistent with a symmetrical molecule. The ^{31}P NMR spectrum showed several groups of signals which could be attributed to different AA'XX' spin systems (Fig. 3). Furthermore in the ^{13}C NMR spectrum, two doublets were expected, corresponding to the carbon atoms of triazaphospholinyl rings, but we observed at least three doublets ($^2J_{PC}$ = 8 Hz) near 155 ppm (Fig. 4), and other signals were also complex (Table 2).

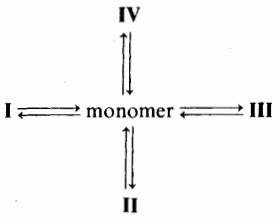
This implies that several isomeric forms of **8c** could exist *in solution*, whereas only one was isolated in the solid state.

A variable temperature ^{31}P NMR experiment was carried out to try to obtain the spectrum of the conformer **8c (III)** alone. Crystals of the conformer **8c (III)** were dissolved in CD_2Cl_2 at −90 °C (at this temperature it was not very soluble). Its ^{31}P NMR spectrum was complex even at this temperature and seemed to be composed of several AA'XX' systems. Only slight modifications appeared when the temperature was progressively increased up to 26 °C. So it seems that the dissolved conformer **8c (III)** is in equilibrium with the monomer, even at −90 °C.

The four conformers of **8c** correspond to different arrangements of the triazaphospholinyl rings around the tetraphosphazane cycle (Fig. 2). As phosphorus inversion is not possible, isomerisation could occur *via* the equilibrium: oligomer $\rightleftharpoons$ monomer, even if no physicochemical method allows us to see it (Scheme 3). Such an equilibrium has previously been observed for oligomers of the type $(R\text{–}P\text{–}NR')_n$ (n = 2–4).[17b,20]

As a result, crystals of **8c** in conformation **III** give, in solution, a mixture of the different conformers.

Triazaphospholes **3**.—Treating tetramers **8** with BF_3·Et_2O afforded the corresponding BF_3-complexed triazaphospholes **3**·BF_3. Several complexes were obtained but only one, **3c**·BF_3 was isolated. The others were detected in CH_2Cl_2 solution by ^{31}P NMR spectroscopy: **3g**·BF_3 (R^1 = Ph, R^2 = Me) $\delta^{31}P$ = 255; **3h**·BF_3 (R^1 = Ph, R^2 = Pr^i) $\delta^{31}P$ = 252; **3i**·BF_3 (R^1 = Ph,



Scheme 3 Equilibrium between the different conformers

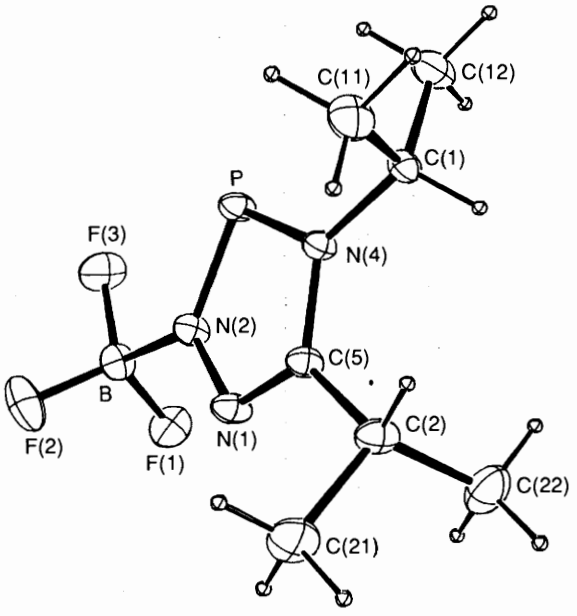


Fig. 5 Molecular structure of **3c**·BF_3 with atomic numbering scheme. Thermal ellipsoids are scaled to enclose 40% probability. Hydrogen atoms are given an arbitrary temperature factor.

R^2 = Benzyl) $\delta^{31}P$ = 251.7; **3j**·BF_3 (R^1 = R^2 = Ph) $\delta^{31}P$ = 251. **8a** and **8b** did not give the complexed monomer with BF_3 even after 12 h of heating at 50 °C. If $AlCl_3$ is used in place of BF_3, **8a** gives the complexed monomer **3a**·$AlCl_3$ (not isolated) δ ^{31}P = 233.

Crystal Structure of **3c**·BF_3.—The molecular structure is shown in Fig. 5; bond lengths and angles are listed in Table 3.

Although the sums of angles around N(2) and N(4) are equal to 360°, the two P–N bonds are rather different; *d* [P–N(2)] = 1.636 Å and *d* [P–N(4)] = 1.669 Å; sp^2 nitrogen hybridisation allows only a partial electronic delocalisation in the ring. This is somewhat different from 1,5- and 2,5-disubstituted 1,2,4,3-triazaphospholes.[21]

^{15}N NMR spectra (Table 4) and X-ray crystallographic analysis of **3c**·BF_3 are consistent with N(2)-complexation.[22,23] The coupling constants $^1J_{PN}$ and $^1J_{PN}$ in **3c**·BF_3 are very different: $^1J_{PN}$ = 112 Hz and $^1J_{PN}$ = 74.8 Hz outlining the double bond character of the PN(2) bond according to the molecular structure.

In conclusion, the 4,5-disubstituted 1,2,4,3-triazaphosphole monomers are isolated only as complexes. It is noteworthy that the phosphorus atom remains dicoordinated and its chemical properties are preserved.[23]

The instability of compounds **3** probably results from a lower electronic delocalisation, so that the PN(2) double bond is more reactive and gives oligomerization.

Experimental

General.—Melting points (uncorrected) were determined using a Büchi-Tottoli apparatus.

^1H, ^{13}C and ^{31}P NMR spectra were recorded with Me_4Si as an internal standard or H_3PO_4 (85% as external standard), on Bruker AC-80 and AC-200 spectrometers, ^{19}F spectra on a Bruker AC-80 spectrometer (CF_3COOH as external standard) and ^{15}N spectra on a Bruker AC-300 spectrometer (NO_2Me as external standard) with 0.08% $Cr(acac)_3$ as relaxing material. *J* values are in Hz. Mass spectra (CDI–NH_3) were obtained with a Varian MAT 311A instrument.

Microanalyses were carried out by the Central Analytical Service of CNRS and by the analytical service of *ENS Chimie de Toulouse*. Starting products were purified by standard methods.

Aldimines **5c–i**.—(*a*) Aliphatic aldimines $R^1CH{=}NR^2$ (**5c–f**) were prepared[11] *via* a reaction between an aldehyde and a primary amine (slight excess) without solvent. Water separation improved with addition of potassium hydroxide pellets to the mixture. Yields were good when R^1 and R^2 are branched groups (80–90%) but poor when R^1 was benzyl owing to the instability of the imine.

(*b*) Benzaldimines $C_6H_5CH{=}NR^2$ (**5g–i**) were prepared[12] by reacting benzaldehyde with an amine in benzene (1:1.5).

5c R^1 = R^2 = Pr^i (80%) b.p. 22 °C/15 mmHg (lit. 78%, b.p. 124–125 °C[11]); ν_{max}/cm^{-1} 1667.6 (C=N); δ_H(80 MHz; $CDCl_3$) 0.84 (6 H, d, *J* 6.8, CH_3–C–C), 0.94 (6 H, d, *J* 6.4, CH_3–C–N), 2.28 (1 H, d hept., *J* 5.5 and 6.8, C–CH<), 3.04 (1 H, d hept., *J* 0.6 and 6.4, NCH<) and 7.30 (1 H, d, *J* 0.6, CH–C–C<); δ_C(20.15 MHz; $CDCl_3$) 20.96 (*C*H_3–C–C), 26.02 (*C*H_3–C–N), 35.29 (–*C*H–C=N), 62.93 (C–N) and 166.06 (C=N).

5d R^1 = Pr^i, R^2 = Bu^s (90%) b.p. 104 °C (lit. 79%, b.p. 124–125 °C[11]); ν_{max}/cm^{-1} 1668 (C=N); δ_H(80 MHz; $CDCl_3$) 0.66 (3 H, m, *C*H_3CH_2), 0.94 (6 H, br d, *J* = 6.8, CH_3–C–C), 1.00 (3 H, d, *J* 6.3, CH_3–C–N), 1.32 (2 H, CH_2), 2.3 (1 H, m, >*C*H–CH), 2.77 (1 H, m, N–CH<) and 7.32 (1 H, d, *J* 5.6, HC=N); δ_C(20.15 MHz; $CDCl_3$) 12.47, 24.22, 32.47, 69.52 (Bu^s), 21.12, 35.46 (Pr^i) and 162.06 (HC=N).

5e R^1 = Benzyl, R^2 = Me (28% crude) b.p. 54 °C/15 mmHg with decomposition; ν_{max}/cm^{-1} 1672; δ_H(80 MHz; C_6D_6) 3.05 (3 H, m, CH_3), 3.37 (2 H, dq, *J* 5.1 and 0.9, CH_2), 7.1 (5 H, m, Ph) and 7.4 (1 H, m, CH).

5f R^1 = Benzyl, R^2 = Pr^i (55%) b.p. 111–113 °C/20 mmHg, 2 isomers (80:20); ν_{max}/cm^{-1} 1643.8 and 1676; δ_H(80 MHz; $CDCl_3$) 1.08 (2.4 H, d, *J* 6.4, CH_3), 1.47 (0.6 H, d, *J* 6.7, CH_3), 3.7 (1 H, m, –CH<), 4.07 (1.6 H, br s, CH_2), 4.18 (0.2 H, br s, CH_2), 7.31 and 7.23 (5 H, Ph).

Thioamides **6a–i** $R^1C(=S)NHR^2$.—**6a**[13] and **6b** were prepared by refluxing the amine with commercial thioacetamide (Aldrich). In other cases, sulfur and imine were mixed without solvent. When R^1 was a benzyl group (**6e**, **f**), gentle heating was required to start the reaction (30–50 °C), then temperature was controlled by external cooling. Reaction was finished when no sulfur remained (15–60 min); the product was distilled under reduced pressure but it mostly decomposed and yields were poor (< 10%). When R^1 was isopropyl (**6c**, **d**), the reaction mixture was heated until the amine refluxed (30 min); no decomposition was observed when it was distilled under reduced pressure and good yields were obtained (70–90%).

When R^1 was phenyl (**6g–i**), the mixture was heated at 180–190 °C over *ca.* 10 min. After cooling, the solid obtained was carefully washed with hexane, its purity being good enough for the amidrazone synthesis.

6a m.p. 65 °C (lit.,[15a] 65.1–65.3 °C).

6b R^1 = Me, R^2 = CH_2Bu^t m.p. 103–104 °C; δ_H(80 MHz; $CDCl_3$) 0.85 (9 H, s, CH_3), 2.48 (2 H, br s, CH_2), 3.40 (s, CH_3) and 6.6 (br, NH).

6c R^1 = R^2 = Pr^i (90%) b.p. 59 °C/0.05 mmHg (lit.,[15b] 124.5 °C/18 mmHg); ν_{max}/cm^{-1} 3242.6 (NH); δ_H(80 MHz;

Table 3 Bond lengths/Å and angles/° with esds in parentheses for **3c**·BF_3

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
P	N(2)	1.637(1)	C(1)	C(12)	1.516(2)
P	N(4)	1.669(1)	C(2)	C(5)	1.501(1)
N(1)	N(2)	1.363(1)	C(2)	C(21)	1.517(2)
N(1)	C(5)	1.315(1)	C(2)	C(22)	1.529(2)
N(2)	B	1.585(2)	B	F(1)	1.375(2)
N(4)	C(1)	1.495(1)	B	F(2)	1.367(2)
N(4)	C(5)	1.374(1)	B	F(3)	1.390(2)
C(1)	C(11)	1.519(2)			

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N(2)	P	N(4)	89.5(1)	C(5)	C(2)	C(22)	110.1(1)
N(2)	N(1)	C(5)	108.9(1)	C(21)	C(2)	C(22)	111.1(1)
P	N(2)	N(1)	115.9(1)	N(1)	C(5)	N(4)	114.5(1)
P	N(2)	B	123.7(1)	N(1)	C(5)	C(2)	121.5(1)
N(1)	N(2)	B	120.4(1)	N(4)	C(5)	C(2)	123.9(1)
P	N(4)	C(1)	124.4(1)	N(2)	B	F(1)	109.1(1)
P	N(4)	C(5)	111.1(1)	N(2)	B	F(2)	110.0(1)
C(1)	N(4)	C(5)	124.5(1)	N(2)	B	F(3)	103.9(1)
N(4)	C(1)	C(11)	110.2(1)	F(1)	B	F(2)	111.3(1)
N(4)	C(1)	C(12)	110.0(1)	F(1)	B	F(3)	110.7(1)
C(11)	C(1)	C(12)	111.8(1)	F(2)	B	F(3)	111.6(1)
C(5)	C(2)	C(21)	110.5(1)				

Table 4 ^{15}N NMR data of **3c**·BF_3[a]

Nucleus	δ	J_{PN}/Hz
N(1)	−44.43	4.7
N(2)	−77.74	112 (br)
N(4)	−150.33	74.8

[a] Solvent CD_2Cl_2 (ext. ref. NO_2Me).

$CDCl_3$) 0.92 (3 H, d, *J* 6.7, CH_3–C–C), 0.98 (3 H, d, *J* 6.6, CH_3–C–N), 2.59 (1 H, hept., *J* 6.7, CH–C<), 4.39 (d hept., *J* 7.9 and 6.6, >CH–N) and 7.67 (1 H, br, HN<); δ_C(20.15 MHz) 23.33 and 25.00 (CH_3), 45.53 (>*C*–C), 49.15 (>C–N) and 211.66 (>C=).

6d R^1 = Pr^i, R^2 = Bu^s (70%) b.p. 78 °C/0.05 mmHg; ν_{max}-($CDCl_3$)/cm^{-1} 3243.1 (NH); δ_H(80 MHz; $CDCl_3$) 0.86 (3 H, t, *J* 7, *CH*$_3$–CH_2), 1.15 (3 H, d, *J* 6.5, *CH*$_3$–C–N), 1.17 (6 H, d, *J* 6.7, CH_3–C–C), 1.50 (2 H, m, CH_2), 2.72 (1 H, hept., >CH–C) and 4.55 (1 H, m, >CH–N).

6e R^1 = Benzyl, R^2 = Me (5%) b.p. 135 °C/0.5 mmHg with decomposition (lit.,[13a] m.p. 63 °C); δ_H(80 MHz; $CDCl_3$) 3.08 (3 H, dd, *J* 4.85 and 0.5, CH_3) and 4.10 (2 H, br s, CH_2).

6f R^1 = Benzyl, R^2 = Pr^i [15c] (8%) b.p. 125 °C/0.1 mmHg with decomposition; δ_H(80 MHz; $CDCl_3$) 2 isomers (90:10) 1.13 (5.4 H, d, *J* 6.55, CH_3) and 1.41 (0.6 H, d, *J* 6.25, CH_3), 4.05 (1.8 H, br s, CH_2) and 4.34 (0.2 H, CH_2), 4.57–4.75 (1 H, m, CH) and 7.3 (5 H, m, Ph).

6g R^1 = Ph, R^2 = Me (90%) m.p. 81 °C (lit.,[15d] 60% m.p. 79 °C); **6i** R^1 = Ph, R^2 = Benzyl (87%) m.p. 124 °C (lit.,[15e] 86 °C).

Thioimidate Hydriodides **7** $R^1C(SMe)=NR^2$ HI.—To a solution of the thioamide **5** (0.1 mol) in acetone (50 cm^3), was added methyl iodide (0.1 mol). The mixture was stirred for several hours at 30 °C, until a solid precipitated. This was isolated by filtration, washed with acetone or pentane, then recrystallised from acetone (R′ = aliphatic).

7a R^1 = Me, R^2 = Benzyl (50%) m.p. 138–140 °C (Found: C, 32.95; H, 6.3; N, 4.95. $C_8H_{18}INS$ requires C, 33.45; H, 6.27; N, 4.87%).

7b R^1 = Me, R^2 = CH_2Bu^t (70%) δ_H(80 MHz; $CDCl_3$) 1.04 [9 H, s, (*CH*$_3$)$_3$C], 2.79 (3 H, s, CH_3C), 3.16 (3 H, br s, CH_3S), 3.34 (2 H, d, *J* 6.3, CH_2) and 11.9 (1 H, flat, NH).

7c R^1 = R^2 = Pr^i (88%) m.p. 94–96 °C; two isomers (1:2): ν_{max}/cm^{-1} (KBr) 3410 (br, NH), 1604 and 1591 (C=N); δ_H(250.13 MHz; $CDCl_3$) [1.27 (1 H, d, *J* 6.85) and 1.48 (2 H, d, *J* 7.0), CH_3–C–C], [1.60 (1 H, d, *J* 6.5) and 1.49 (2 H, d, *J* 7.0), CH_3–C–N], [2.97 (1 H, s) and 2.80 (2 H, s), CH_3–S], 3.37 and 3.44 (1 H, 2 hept., >CH–C), [4.22 (0.7 H, hept.) and 4.54 (0.3 H, hept., $^3J_{HNCH} \simeq 8$ and $^3J_{HCCH}$ 6.65), >CH–N], 9.94 and 10.80 (1 H, flat, NH); δ_C(62.90 MHz; $CDCl_3$) 16.46, 18.26, 21.28 and 22.23 (*C*H$_3$C), 20.52 (CH_3S), 35.45 (>*C*–C), 53.26 (>C–N) and 198.94 (>C=).

7d R^1 = Pr^i, R^2 = Bu^s (80%) m.p. 105 °C (Found: C, 35.85; H, 6.75; N, 4.5. $C_9H_{20}INS$ requires C, 35.88; H, 6.64; N, 4.65%); ν_{max}($CDCl_3$)/cm^{-1} 3379.2 (NH); δ_H(80 MHz, C_5H_5N), 0.84 (3 H, dt, *J* 2.4 and 6.9, *CH*$_3$–CH_2), 1.05–1.18 (9 H, m, CH_3), 1.47 (2 H, m, CH_2), 2.21 and 2.36 (1.2 H and 1.8 H, br s, CH_3), 2.97 (1 H, hept., >CH–C), 3.62 (1 H, m, >CH–N) and 13.5 (1 H, v br, NH); δ_C(20.15 MHz; C_5D_5N) 58.02 and 59.74 (CH_3–S) and 174.57 and 178.05 (>C=N).

7e R^1 = Benzyl, R^2 = Me (40%) m.p. 141–143 °C (lit.,[16e] 106 °C) (Found: C, 38.95; H, 4.55; N, 4.3. $C_{10}H_{14}INS$ requires C, 39.09; H, 4.57; N, 4.56%); δ_H(80 MHz, C_5D_5N) 2 isomers (40:60) 2.31 (1.8 H, s, CH_3–S) and 2.37 (1.2 H, s, CH_3–S), 3.21 (1.28 H, br s, CH_3N) and 3.41 (1.2 H, t, *J* 0.85, CH_3N), 3.75 (1.2 H, br s, CH_2) and 4.17 (0.8 H, q, *J* 0.85, CH_2) and 13.5 (1 H, flat, NH).

7f R^1 = Benzyl, R^2 = Pr^i (70%) m.p. 180–181 °C (Found: C, 42.95; H, 5.4; N, 4.2. $C_{12}H_{18}INS$ requires C, 42.98; H, 5.37; N, 4.18%); δ_H(80 MHz; C_5D_5N), 2 isomers (55:45) 1.05 (d, *J* 6.15) and 1.26 (d, *J* 6.25), [6 H, (*CH*$_3$)$_2$–CH–N], 2.30 and 2.36 (3 H, 2 s, CH_3–S), 3.97 (1 H, hept., *J* 6.2), 4.22 and 3.77 (2 H, 2 br s, CH_2) and 7.3 (5 H, m, Ph).

7g R^1 = Ph, R^2 = Me, m.p. 164 °C (lit.,[16f] 128–9 °C); **7h** R^1 = Ph, R^2 = Pr^i, m.p. 187 °C (lit.,[16g] 166 °C); **7i**, R^1 = Ph, R^2 = Benzyl, m.p. 142 °C.

Amidrazone Hydriodides **4**·HI $R^1C(NHR^2)=N-NH^2$·HI. —Anhydrous hydrazine (0.1 mol) was added dropwise to a suspension of **7**·HI (0.1 mol) in methanol (20 cm^3) at 0 °C. The mixture was stirred for 2 h. Anhydrous diethyl ether was added and the amidrazone hydriodide **4**·HI precipitated. The precipitate was filtered and carefully washed with anhydrous diethyl ether, then dried under reduced pressure. When R^1 = alkyl, the solution was concentrated before adding diethyl

ether. **4c,d**·HX crystallised only after several weeks. When R^1 = Benzyl, the amidrazone hydriodide appeared as a wax that decomposed on distillation.

4a·HI R^1 = Me, R^2 = Bz (50%) m.p. 164–170 °C (Found: C, 31.45; H, 6.4; N, 12.6. $C_7H_{18}N_3I$ requires C, 31.00; H, 6.64; N, 15.50%).

4b·HI R^1 = Me, R^2 = CH_2Bu^t (70%) m.p. 200 °C (Found: C, 34.4; H, 4.8; N, 15.4. $C_9H_{14}IN_3$ requires C, 37.11; H, 4.81; N, 14.43%); ν_{max}/cm^{-1} 1684 (C=N); δ_H(80 MHz; C_5D_5N) 2.26 (3 H, s, CH_3), 4.76 (2 H, s, CH_2), 7.17–7.42 (5 H, m, Ph) and 8.3 (4 H, v br, NH); δ_C(20.15 MHz; C_5D_5N) 14.69 (CH_3), 45.18 (CH_2), 126.48, 127.31, 128.6 and 135.86 (Ph) and 165.19 (C=N).

4c·HI R^1 = R^2 = Pr^i (69%) (Found: C, 27.3; H, 6.3; N, 15.0. $C_7H_{18}IN_3$ requires C, 31.00; H, 6.64; N, 15.50%); ν_{max}/cm^{-1} 1640 (C=N); δ_H(80 MHz; C_5D_5N) 1.225 (3 H, d, *J* 6.3, CH_3), 1.28 (3 H, d, *J* 6.8, CH_3), 3.17 (1 H, hept., >CH–C), 4.08 (1 H, hept., >CH–N) and 7.70 (3 H, HN); δ_C(50.3 MHz; DMSO) 18.43, 20.34, 22.70 (CH_3), 43.07, 45.10 (>CH–), 168.91 and 170.27 (>C=N–).

4d·HI R^1 = Pr^i, R^2 = Bu^s (75%) m.p. 68 °C (Found: C, 32.3; H, 7.1; N, 14.6. $C_8H_{20}IN_3$ requires C, 33.68; H, 7.02; N, 14.74%); δ_H(80 MHz; C_5D_5N) 0.81 (3 H, t, *J* 7, CH_3CH_2), 1.16–1.33 (9 H, m, CH_3CH), 1.5 (2 H, m, CH_2), 3.19 (1 H, m, >CHC), 3.82 (1 H, m, >CHN) and 7.4 (4 H, br NH); δ_C(50.32 MHz; C_5D_5N) 11.14 (CH_3CH_2), 20.20 and 20.37 [$(CH_3)_2C$], 21.92 (CH_3C), 28.61 (>CHC–), 30.29 (CH_2), 52.01 (>CH–N) and 170.66 (>C=N–).

4f·HI R^1 = Benzyl, R^2 = Pr^i (50%) wax (Found: C, 44.45, H, 5.5, N, 9.4. $C_{11}H_{18}IN_3$ requires C, 41.38; H, 5.64; N, 13.17%); δ_H(80 MHz; $CDCl_3$) two isomers (15:85) 1.08 (5.1 H, d, *J* 6.4, CH_3) and 1.47 (0.9 H, d, *J* 6.7, CH_3), 4.07 and 4.22 (2 H, CH_2), 7.31 (5 H, Ph).

4g·HI R^1 = Ph, R^2 = Me (75%) m.p. 138–141 °C (lit.,[9] 151–152 °C) (Found: C, 34.55; H, 4.35; N, 15.45. $C_8H_{12}IN_3C$, 34.65; H, 4.33; N, 15.16%).

4h·HI R^1 = Ph, R^2 = Pr^i (68%) m.p. 120–123 °C (Found: 38.0; H, 5.2; N, 13.8. $C_{10}H_{17}IN_3$ requires C, 39.34; H, 5.24; N, 13.77%); δ_H(80 MHz; C_5D_5N) 1.17–1.31 (6 H, CH_3), 3.82 (1 H, m, CH) and 7.43 (5 H, Ph).

4i·HI R^1 = Ph, R^2 = Benzyl (78%) m.p. 160–163 °C (Found: C, 46.55; H, 4.55; N, 12.0. $C_{14}H_{16}N_3I$ requires C, 47.59; H, 4.53; N, 11.89%).

Amidrazones **4c, g, j** $R^1C(NHR^2)$=N–NH_2.—Addition of a stoichiometric amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to a suspension of amidrazone hydriodide in dry benzene afforded the free base. After filtration of HI·DBU, the amidrazone **4** was purified by distillation.

4c R^1 = R^2 = Pr^i (80%) b.p. 35–40 °C/0.05 mmHg; δ_H(80 MHz; $CDCl_3$) 1.10 (3 H, d, *J* 6.8, CH_3–C–C), 1.25 (3 H, d, *J* 6.3, CH_3–C–N), 2.58 (1 H, hept., >CH–C), 3.61 (1 H, hept., >CHN) and 3.44 (3 H, br, NH).

4g R^1 = Ph, R^2 = Me (70%) b.p. 82 °C/0.07 mmHg (Found: C, 64.95; H, 7.65; N, 25.55. $C_8H_{11}N_3$ requires C, 64.43; H, 7.38; N, 28.11%); δ_H(80 MHz; $CDCl_3$) 2.61 (3 H, s, CH_3), 4.07 (3 H, br, NH) and 7.30 (5 H, Ph).

4j.[3]

Oligomers **8**.—A mixture of **4**·HI (or **4**) (0.1 mol) and $P(NMe_2)_3$ (0.1 mol) in refluxing benzene (150 cm^3) was stirred under a slow stream of argon until dimethylamine [0.2 (or 0.3) mol] was evolved. Dimethylamine hydriodide was removed by filtration of the hot mixture. Then the filtrate was concentrated under reduced pressure to give **8** on cooling.

8a R^1 = Me, R^2 = Benzyl (50%) m.p. 208–210 °C (Found: C, 54.95; H, 5.3; N, 21.75; P, 17.15. $C_9H_{10}N_3P$ requires C, 56.54; H, 5.23; N, 21.99; P, 15.78%); δ_H(80 MHz; C_5D_5N) 2.05 and 1.89 (3 H, CH_3), 4.82–4.52 (2 H, m, CH_2), 7.18–7.30 (5 H, m, Ph); δ_C(50.3 MHz, C_5D_5N) 13.03 (d, *J* 5.5, CH_3), 46.6–47.7 (m with 2 d upon it) 47.26 (*J* 10.0) and 47.65 (*J* 4.9), [128.0–130.6 (m) and 139.77 (broad d, *J* 5.1), Ph] and 152.96 (d, *J* 8.0, C_{cycle}); δ_P 69–85 (several systems AA′XX′); *m*/*z* 192 (100, M/4 + 1), 383 (18.28, M/2 + 1), 574 (0.02, 3 M/4 + 1), 765 (0.02, M + 1), 766 (0.02, M + 2).

8b R^1 = Me, R^2 = CH_2Bu^t δ_P 61–89 (m).

8c R^1 = R^2 = Pr^i (90% raw) m.p. 245 °C (Found: C, 48.45; H, 8.3; N, 25.0; P, 18.45. $C_7H_{14}N_3P$ requires C, 49.12; H, 8.19; N, 24.56; P, 18.13%). Several isomers were detected from NMR spectra: δ_H(250 MHz; CD_2Cl_2) 1.1 and 1.25 (6 H, 2 d, *J* 6.8, CH_3–C–C), 1.25 and 1.4 (6 H, 2 d, *J* 6.9, CH_3–C–N), 2.65 (1 H, 2 hept., *J* 6.8, >CH–C), 3.82 (1 H, d hept., J_{HP} 6.6 and J_{HH} 6.8); δ_P(C_6D_6, 81.01 MHz) AA′XX′ systems 75.83 and 63.67 (J_{PNP} + J'_{PNP} = 116.5), 75.70 and 63.78 (J_{PNP} + J'_{PNP} = 168); δ_C(50.32 MHz; C_6D_6) (see Table 2); *m*/*z* 172 (100, $M^+/4$ + 1), 343 (17.6, $M^+/2$ + 1), 514 (0.16, $3M^+/4$ + 1), 685 (0.36, M^+ + 1), 686 (0.25, M^+ + 2) and 687 (0.10, M^+ + 3).

8d R^1 = Pr^i, R^2 = Bu^s (70%) m.p. 239 °C (Found: C, 51.15; H, 8.7; N, 22.6; P, 15.3. $C_8H_{16}N_3P$ requires C, 51.89; H, 8.65; N, 22.70; P, 16.76%); δ_H(80 MHz; C_6D_6) 0.76 (3 H, dt, *J* 1.3 and 7.2, CH_3–CH_2), 1.10–1.38 [6 H, m, $(CH_3)_2C$–C], 1.44 (3 H, br d, *J* 6.9, CH_3–C–N), 1.70 (2 H, m, CH_2), 2.40 (1 H, m, >CH–C) and 3.26 (1 H, m, >C–N); δ_C(50.3 MHz; C_6D_6) 11.09 and 11.51 (CH_3CH_2), 20.94–24.34 (m, CH_3), 26.47 (CH_2), 30.8 and 32.7 (m, >CHC), 51.9 (m, >CHN), 154.56 and 158.09 (m, C_{cycle}); δ_P(81.01 MHz; C_6D_6) two systems AA′XX′: 74.0 and 61.7 (J_{PNP} + J'_{PNP} = 171), 74.33 and 62.35 (J_{PNP} + J'_{PNP} = 137).

8f R^1 = Benzyl, R^2 = Pr^i (60%) m.p. 230–233 °C (Found: C, 58.85; H, 6.25; N, 19.15; P, 13.8. $C_{11}H_{14}N_3P$ requires C, 60.27; H, 6.39; N, 19.18; P, 14.15%); δ_H(80 MHz; $CDCl_3$) 0.84–1.25 (6 H, m, CH_3), 3.4–4 (3 H, m, $CHCH_2$) and 7.0–8.7 (5 H, m, Ph); δ_C(50.32 MHz; C_5D_5N) 24.75, 25.45 and 25.66 (m, CH_3), 33.71 (d, *J* 5.1, CH_2), 47.48 (d, 14.3) and 47.62 (d, *J* 14.5, >CN), 127.36, 129.64, 137.77 and 153.3 (m, Ph); δ_P(81.01 MHz; C_6D_6) 78–60 (complex systems); *m*/*z* 220 (100, M/4 + 1), 435 (11.64, M/2 + 1), 658 (0.07 3M/4 + 1) and 878 (0.05 M + 2).

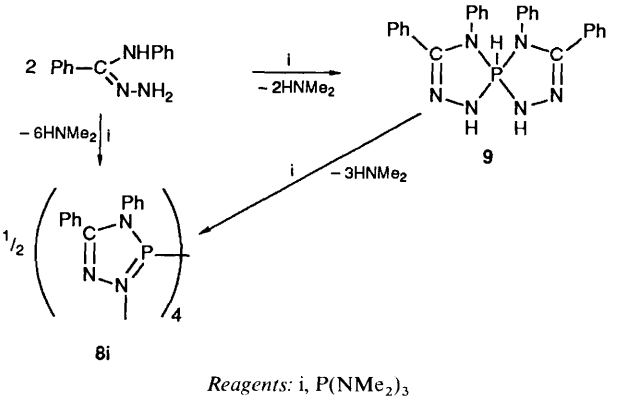
8g R^1 = Ph, R^2 = Me (70%) m.p. 88 °C; δ_P 70–80 (m).

8h R^1 = Ph, R^2 = Pr^i (65%) m.p. 98 °C (Found: C, 57.95; H, 6.0; N, 19.45; P, 14.5. $C_{10}H_{12}N_3P$ requires C, 58.54; H, 5.85; N, 20.49; P, 15.12%); δ_H(80 MHz; $CDCl_3$) 1.17, 1.19, 1.25 and 1.31 (6 H, d, *J* 6.7, 6.3, 6.5 and 6.6), 3.82 (1 H, m, >CH–), 7.43 (5 H, m, Ph); δ_P(32.44 MHz; $CDCl_3$) AA′XX′ spin system: δ_A = 76.6, δ_X = 64 (J_{PNP} + J'_{PNP} = 146 Hz).

8i R^1 = Ph, R^2 = Benzyl (74%) m.p. 90 °C; δ_P 71 (m).

8j R^1 = Ph, R^2 = Ph (80%) m.p. 137 °C; δ_P 70–80 (m).*

* During the synthesis of the oligomer **8j** (R^1 = R^2 = Ph), the formation of a spirophosphorane **9** was observed. After an increasing step, the ratio **9**:**8j** decreased; finally only **8j** remained. Using a 2:1 ratio of amidrazone and aminophosphine, **9** was isolated: m.p. 234 °C; δ_P = 54.9 ($^1J_{PH}$ = 570 Hz). It seemed that the rate of formation of **9** was greater than that of the oligomer. Afterwards, **9** reacted with the remaining $P(NMe_2)_3$ to afford **8j**.



Reagents: i, $P(NMe_2)_3$

Table 5 Non-hydrogen atom fractional coordinates with esds in parentheses for **8c**. Letters a and b following atom number refer to statistically disordered positions.

Atom	*x*	*y*	*z*
P(1)	0.489 49(5)	0.140 58(6)	0.460 0(1)
P(2)	0.425 45(5)	−0.023 92(6)	0.416 2(1)
N(11)	0.549 7(2)	0.074 9(2)	0.455 8(3)
N(12)	0.570 6(2)	0.053 7(2)	0.336 0(3)
N(13)	0.505 7(2)	0.159 7(2)	0.308 8(3)
N(21)	0.428 5(2)	0.075 6(2)	0.457 7(3)
N(22)	0.374 7(2)	0.106 5(2)	0.514 4(4)
N(23)	0.348 0(2)	−0.017 1(2)	0.437 8(3)
C(11)	0.544 9(2)	0.102 7(2)	0.258 5(4)
C(12)	0.561 2(2)	0.098 4(3)	0.124 4(4)
C(13)	0.579 3(3)	0.013 8(4)	0.085 4(5)
C(14)	0.609 7(3)	0.157 2(4)	0.093 5(6)
C(15)	0.470 5(2)	0.218 6(2)	0.233 9(4)
C(16)	0.466 0(3)	0.298 6(3)	0.301 9(5)
C(17)	0.409 6(3)	0.186 2(4)	0.196 9(6)
C(21)	0.332 3(2)	0.054 1(3)	0.500 8(5)
C(22a)	0.273 7(5)	0.067 1(9)	0.577(1)
C(22b)	0.264 2(5)	0.071 3(9)	0.528(2)
C(23a)	0.229 0(9)	0.111(1)	0.489(2)
C(23b)	0.253 6(8)	0.162 8(8)	0.511(2)
C(24a)	0.278 8(6)	0.118(1)	0.695(1)
C(24b)	0.266 1(8)	0.041(1)	0.662(2)
C(25)	0.306 2(3)	−0.085 1(3)	0.415 0(8)
C(26)	0.321 3(3)	−0.126 2(4)	0.294 3(8)
C(27)	0.305 7(3)	−0.145 2(4)	0.518 8(8)

4,5-Disubstituted-1,2,4,3-triazaphospholes N-Boron Trifluoride **3**·BF_3.—BF_3·Et_2O (0.20 mol) was added to the oligomer **8** (0.05 mol) dissolved in dichloromethane (10 cm^3) or dry benzene. The reaction was slightly exothermic. After cooling, the solution was concentrated. The precipitate obtained was filtrated and recrystallised from benzene.

3c·BF_3 R^1 = R^2 = Pr^i (80%) m.p. 141–143 °C (Found: C, 33.95; H, 6.05; N, 16.9, B, 4.7; P, 12.9. $C_7H_{14}BF_3N_3P$ requires C, 33.15; H, 5.86; N, 17.57; B, 4.60; P, 12.97%); δ_H(80 MHz; C_6D_6) 0.84 (6 H, dd, *J* 6.6 and 0.75, CH_3–C–N), 1.10 (6 H, d, *J* 6.7, CH_3–C–C), 2.43 (1 H, hept., *J* 6.8, >CH–C), 3.59 (1 H, d, hept., *J* 14 and 6.85, >CH–N); δ_{CH_3} from the two Pr^i are exchanged in $CDCl_3$ solution 1.45 (d, *J* 6.8, CH_3–C–C) and 1.71 (dd, *J* 6.6 and 0.8, CH_3–C–N); δ_C(50.32 MHz; CD_2Cl_2) 21.63 (d, *J* 5.0, *C*H_3–C–C), 26.87 (d, *J* 7.55, *C*H_3–C–N), 27.92 (s, >*C*–C), 51.35 (d, *J* 9.2, >C–N), 170.03 (br, C_{cycle}); δ_F(282.4 MHz; C_6D_6) −69.78 (m); δ_P(32.4 MHz; CD_2Cl_2) 253.2 (q, *J* 22); δ_B(25.71, CD_2Cl_2) 2.98 (dq, *J* 11.3); δ_N(CD_2Cl_2) − 150.33 (d, *J* 74.8 N^4), 77.74 (d, *J* 112 N^2) and 44.43 (d, *J* 4.7 N^1).

3f·BF_3 R^1 = Benzyl, R^2 = Pr^i (75%) δ_H(80 MHz; $CDCl_3$) 1.28 (6 H, d, *J* 6.7, CH_3), 3.90 (2 H, br s, CH_2), 4.3 (1 H, m, Ph) and 7.24 (5 H, m, Ph); δ_P(32.44 MHz; $C_2H_4Cl_2$) 254.6.

X-Ray Structure Determination of **8c**.—Crystals were grown by slow evaporation at room temperature of a benzene solution. The selected crystal was sealed under nitrogen in a Lindemann glass capillary tube.

Crystal data. $C_{28}H_{56}N_{12}P_4$, *M* = 684.7, orthorhombic, *a* = 21.876(3), *b* = 16.530(3), *c* = 10.876(2) Å, *U* = 3933 $Å^3$ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections), space group *Pccn*, *Z* = 4, D_c = 1.16 g cm^{-1}, *F*(000) = 1472, μ(Mo-Kα) = 1.9 cm^{-1}.

Data collection and processing. CAD4 diffractometer, graphite-monochromated Mo-Kα radiation, λ = 0.710 69 Å, ω–2θ mode with ω scan width = 0.9 + 0.35 tan θ, ω scan speed 0.9–8.2° min^{-1}; 3452 unique reflections measured in the range $1.5 \leqslant \theta \leqslant 25°$, 1881 reflections with $I > 2\sigma(I)$, three standard reflections monitored every two hours, no decay observed, no absorption correction because of small μ and block-shaped crystal (0.4 × 0.3 × 0.3 mm^3). Space group *Pccn* from systematic absences.

Structure solution and refinement. Direct methods [24] followed by standard full-matrix least-squares refinements and Fourier procedures.[25] Non-hydrogen atoms refined anisotropically. Hydrogen atom contributions to the structure factors calculated from idealised, unrefined positions (C–H = 0.97 Å) and arbitrary isotropic temperature factors (U = 0.1 $Å^2$). Final conventional R and R_w values are 0.049 and 0.064, weighting scheme used is $w = 1/[\sigma^2(F) + 0.001\ F^2]$. The highest and lowest residues in the last difference Fourier map are 0.19 and −0.23 electrons $Å^{-3}$. Scattering factors and anomalous dispersion terms were taken from ref. 25. Non-hydrogen atom positional parameters are listed in Table 5.

From the examination of difference Fourier maps and on the basis of the values of the thermal parameters, the C(23)–C(22)–C(24) isopropyl group was estimated to be statistically disordered over two sets of positions which were each assigned an occupation factor of 0.5. The other isopropyl groups were not considered disordered although their thermal parameters suggest that they probably are to a smaller extent.[26]

X-Ray Structure Determination of **3c**·BF_3—Crystals of the BF_3 complex of 4,5-diisopropyl-1,2,4,3-triazaphosphole were grown from benzene by slow evaporation at room temperature. The large crystals obtained were cut under nitrogen into blocks of suitable size. The selected block was stuck on the end of a glass fibre and quickly mounted on the diffractometer in the dry nitrogen gas flow of a cooling device. Measurements were carried out at 190 K, under the conditions described in ref. 20.

Crystal data. $C_7H_{14}BF_3N_3P$, *M* = 239.0, orthorhombic, *a* = 7.835(4), *b* = 9.867(3), *c* = 14.555(3) Å, *U* = 1125 $Å^3$ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections), space group $P2_12_12_1$, *Z* = 4, D_c = 1.41 g cm^{-1}, *F*(000) = 496, μ(Mo-Kα) = 2.1 cm^{-1}.

Data collection and processing. CAD4 diffractometer, cold nitrogen gas flow low temperature attachment, *T* = 190 K, graphite-monochromated Mo-Kα radiation, λ = 0.710 69 Å, ω–2θ mode with ω scan width = 0.9 + 0.35 tan θ, ω scan speed 0.9–8.2° min^{-1}; 1876 unique *hkl* reflections measured in the range $1.5 \leqslant \theta \leqslant 30°$, 1684 reflections with $I > 2\sigma(I)$, three standard reflections monitored every hour, no decay observed, no absorption correction because of small μ and block-shaped crystal (0.6 × 0.5 × 0.2 mm^3). Space group $P2_12_12_1$ from systematic absences.

Structure solution and refinement. Direct methods [24] followed by standard full-matrix least-squares refinements and Fourier procedures.[26] Non-hydrogen atoms refined anisotropically. All hydrogen atoms located on difference Fourier maps, but idealised, unrefined positions (C–H = 0.97 Å) and common refined isotropic temperature factor (U = 0.048 $Å^2$) used in calculations. Attempts to determine the absolute configuration failed because of the weakness of the anomalous dispersion terms. Final conventional R and R_w values are 0.025 and 0.034, weighting scheme used is $w = 1/[\sigma^2(F) + 0.001\ 26\ F^2]$. The highest and lowest residues in the last difference Fourier map are 0.24 and −0.31 electrons $Å^{-3}$. Scattering factors and anomalous dispersion terms taken from ref. 25. Non-hydrogen atom positional parameters are listed in Table 6. All calculations were performed on a micro VAX 3400 DEC computer.

Additional material availabie from the Cambridge Crystallographic Data Centre (CCDC) comprises H-atom coordinates, thermal parameters and a full table of bond lengths and angles for each of the two compounds **8c** and **3c**·BF_3.*

* For details of the deposition scheme see 'Instructions for Authors (1992),' *J. Chem. Soc., Perkin Trans. 2*, issue 1.

Table 6 Non-hydrogen atom fractional coordinates with esds in parentheses for **3c**·BF_3

Atom	*x*	*y*	*z*
P	0.979 92(4)	0.642 82(4)	0.420 67(2)
N(1)	0.722 4(2)	0.755 6(1)	0.345 92(8)
N(2)	0.869 2(2)	0.778 0(1)	0.393 95(8)
N(4)	0.836 0(1)	0.546 9(1)	0.366 58(8)
C(1)	0.846 0(2)	0.396 0(1)	0.358 70(9)
C(2)	0.557 9(2)	0.568 3(1)	0.278 1(1)
C(5)	0.705 6(2)	0.624 6(1)	0.331 63(9)
C(11)	0.733 3(2)	0.329 7(2)	0.430 8(1)
C(12)	1.030 1(2)	0.349 9(2)	0.366 6(1)
C(21)	0.395 3(2)	0.644 9(2)	0.300 6(1)
C(22)	0.596 5(2)	0.573 7(2)	0.175 2(1)
B	0.928 2(2)	0.927 8(2)	0.417 2(1)
F(1)	0.954 3(1)	0.997 5(1)	0.336 54(7)
F(2)	0.808 4(2)	0.990 4(1)	0.470 79(9)
F(3)	1.081 3(1)	0.910 4(1)	0.464 16(8)

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