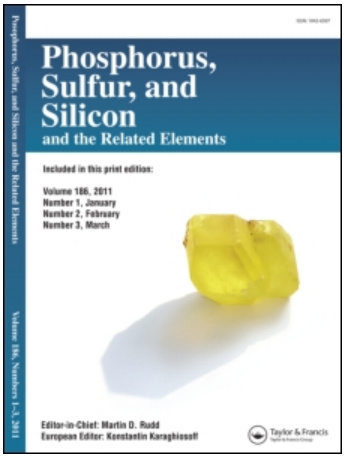

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SYNTHETIC, SPECTROSCOPIC AND CRYSTALLOGRAPHIC STUDIES OF HETEROFUNCTIONAL DIPHOSPHAZANE LIGANDS

R. P. Kamalesh Babu[a]; K. Aparna[a]; S. S. Krishnamurthy[a]; M. Nethaji[a]
[a] Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India

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SYNTHETIC, SPECTROSCOPIC AND CRYSTALLOGRAPHIC STUDIES OF HETEROFUNCTIONAL DIPHOSPHAZANE LIGANDS

R. P. KAMALESH BABU, K. APARNA, S. S. KRISHNAMURTHY* and M. NETHAJI

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

Dedicated to Professor Reinhard Schmutzler on the occasion of his 60th birthday

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New unsymmetrical diphosphazanes of the type $X_2PN(Pr^i)PYY'$ {X = Ph, YY' = $O_2C_{12}H_8$ (**1a**), $O_2C_{20}H_{12}$ (**1b**); X = Ph, Y = Ph, Y' = OC_6H_4Me-4 (**1c**), OC_6H_4Br-4 (**1d**), $OC_6H_3Me_2$-3,5 (**1e**), $N_2C_3H_3$ (**1f**), $N_2C_3HMe_2$-3,5 (**1g**), OC_5H_4N-2 (**1h**)} are prepared and converted into their mono- and di-oxides or sulfides. These can function as heterofunctional ligands through P, S, N or O donor sites. These compounds have been characterized by NMR spectroscopic studies. Variable temperature $^{31}P\{^1H\}$ NMR measurements on some of these compounds reveal the presence of different types of conformers in solution. Single crystal X-ray diffraction studies have been carried out for $Ph_2P(S)N(Pr^i)PPh(N_2C_3HMe_2$-3,5) (**2g**) and $Ph_2P(O)N(Pr^i)P(O)Ph(OC_5H_4N$-2) (**5h**).

Key words: Unsymmetrical diphosphazanes; their monosulfides, monoxides and dioxides; syntheses; NMR spectra; crystal structures.

INTRODUCTION

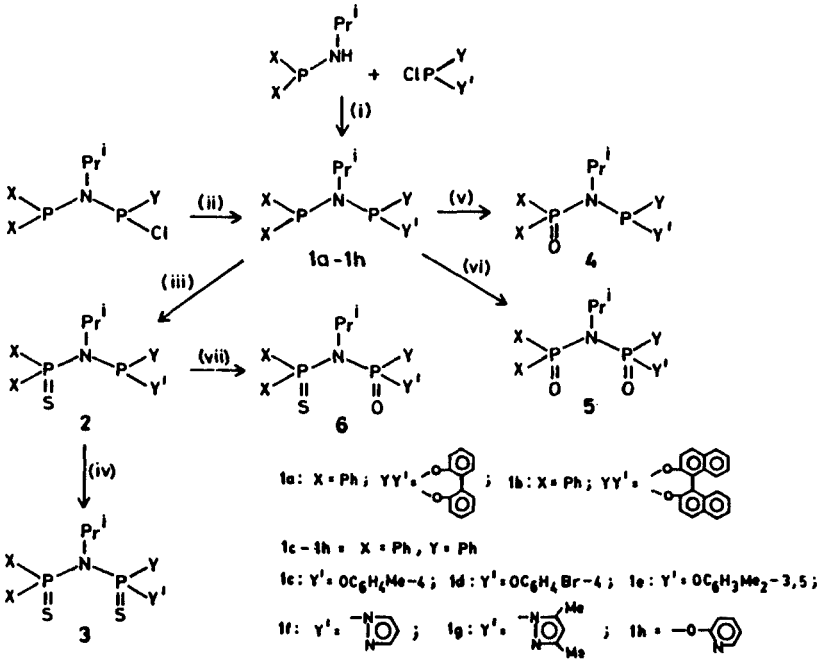
Polydentate ligands containing soft and hard donor sites are of considerable current interest in connection with the development of novel homogeneous catalysts.[1] For instance, chelating ligands with P,O-donor sites have been used in stereoselective hydrogenations,[2] hydrosilylations[3] and hydroformylations.[4] These ligands would be useful in studying f-element coordination chemistry.[5] Chelating ligands with phosphorus and oxygen donor sites can form a bridge between d-block and f-block elements and can give rise to novel heterobimetallic complexes.[6] The "short-bite" ligands $X_2PN(R)PX_2$, known as diphosphazanes offer considerable scope and versatility in designing homo and heterobimetallic complexes.[7] The substituents on the phosphorus atoms can be easily altered to generate unsymmetrical diphosphazanes.[8,9] These unsymmetrically substituted diphosphazanes possess non-equivalent phosphorus nuclei and hence it is possible to obtain $J(^{31}P\text{-}^{31}P)$ directly from the ^{31}P NMR spectrum. This advantage has been exploited by Keat and co-workers[8] as well as McFarlane and co-workers[9] to study the various conformational aspects of diphosphazanes. Continuing our interest in the synthesis of new unsymmetrical diphosphazane ligands and a study of their ligating behaviour towards transition metals[10], we have prepared a series of hybrid diphosphazanes containing P, S, N, and O donor sites and characterized them spectroscopically. The results of these studies are reported in this paper. The structure of a diphosphazane monosulfide $Ph_2P(S)N(Pr^i)PPh(N_2C_3HMe_2$-3,5) (**2g**) and diphosphazane dioxide $Ph_2P(O)N(Pr^i)P(O)Ph(OC_5H_4N$-2) (**5h**) have been confirmed by X-ray crystallography.

RESULTS AND DISCUSSION

Preparative Aspects

Diphosphazanes: The unsymmetrical diphosphazanes $X_2PN(Pr^i)PYY'$ (**1a**, **1b**) {X = Ph; YY' = $O_2C_{12}H_8$ (**1a**) and YY' = $O_2C_{20}H_{12}$ (**1b**)} are prepared by the reaction of (isopropylamino)diphenylphosphine with [1,1'-biphenyl]-2,2'-phosphorochloridite or [1,1'-binaphthyl]-2,2'-phosphorochloridite, respectively, in the presence of triethylamine as hydrogen chloride acceptor. This method is analogous to the preparation of the unsymmetrical diphosphazane $Ph_2PN(Pr^i)P(O_2C_6H_4)$ (**1i**).[10a] The unsymmetrical diphosphazanes $X_2PN(Pr^i)PYY'$ (**1c–1h**) {X = Ph, Y = Ph; Y' = OC_6H_4Me-4 (**1c**), OC_6H_4Br-4 (**1d**), $OC_6H_3Me_2$-3,5 (**1e**), $N_2C_3H_3$ (**1f**), $N_2C_3HMe_2$-3,5 (**1g**), OC_5H_4N-2 (**1h**)} are prepared from the reaction of the chloro diphosphazane $Ph_2PN(Pr^i)PPhCl$ (prepared by the method of Keat and co-workers)[8] with the respective phenol or the pyrazole derivative in the presence of triethylamine (Scheme 1).

Diphosphazane monosulfides: Heterofunctional diphosphazane monosulfides with a phosphorus and a sulfur donor site are obtained by heating the diphosphazanes with sulfur (1:1/8) under reflux in dry tetrahydrofuran (Scheme 1). Only the mono-



SCHEME 1

sulfides in which the PPh_2 phosphorus is attached to sulfur atom are obtained in all these reactions. This is not surprising in view of the greater nucleophilicity of diphenyl substituted phosphorus compared to PPh(OAr) or PPh(pyrazolyl) phosphorus. The symmetrical diphosphazane $Ph_2PN(Pr^i)PPh_2$[11] also gives the monosulfide $Ph_2P(S)N(Pr^i)PPh_2$ (**2j**).

Diphosphazane disulfides: The diphosphazane disulfides can be obtained by treating the diphosphazane precursors with an excess of sulfur in boiling benzene for 48 hours. However, attempts to prepare the disulfide of **1g** under similar conditions proved unsuccessful; only the monosulfide **2g** and some minor unidentified products are obtained.

Diphosphazane monoxides: Diphosphazane monoxides are obtained by their oxidation with trimethylamine-N-oxide. Only one diphosphazane monoxide (**4g**) is isolated in a pure form and completely characterized; others have been identified by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. As observed for the monosulfides, only the PPh_2 moiety is oxidized.

Diphosphazane dioxides and mixed oxide sulfides: Diphosphazane dioxides can be easily prepared by the treatment of the respective diphosphazanes with hydrogen peroxide solution in acetone.

The monosulfides **2a** and **2j** are oxidized using hydrogen peroxide to give the mixed diphosphazane oxide sulfides (**6a** and **6j**).

Spectroscopic Aspects

The ^1H NMR spectra shows two different resonances for the two methyl groups of the isopropyl substituent owing to the presence of an adjacent chiral phosphorus center in compounds **1c–1h**. The spectra of the diphosphazane **1b**, because of the 1,1′-binaphthyl substituent, shows two different resonances for the methyl groups. By contrast the spectrum of **1a** shows only a doublet for the two methyl groups.

The $^{13}C\{^1H\}$ NMR spectra of some of the diphosphazanes have been studied and the observed resonances can be easily assigned (Table I). It is worth noting that the *ipso* carbons of the Ph_2P moiety couples with both the phosphorus and resonates as a doublet of doublets, whereas the *ipso* carbons of the PYY′ moiety appear only as a doublet without coupling to the other phosphorus nucleus.

The $^{31}P\{^1H\}$ NMR spectra for all these compounds at ambient temperature show a simple AX pattern owing to the non-equivalence of the phosphorus nuclei. The $^{31}P\{^1H\}$ NMR chemical shifts along with their coupling constant values are listed in Table II. The ^{31}P chemical shifts for these diphosphazanes vary from 27–156 ppm depending on the nature of the substituents attached to the phosphorus atoms. The chemical shift of the PPh_2 phosphorus also shows a significant change upon changing the substituents on the other phosphorus atom. The magnitude of the coupling constant ($^2J_{PP}$) values lies between 14 to 30 Hz. The P(V) resonances are less dependent on the nature of the substituents present; the P═S phosphorus resonates between 55–70 ppm and the chemical shift of P═O phosphorus lies between 0–35 ppm.

TABLE I

$^{13}C\{^1H\}$ NMR values of some of the diphosphazanes[a]

Diphosphazane	Chemical shift values (ppm)
$Ph_2PN(Pr^i)PPh(OC_6H_4Me\text{-}\underline{4})$ **(1c)**	157.0 (d, J_{PC} = 11.7 Hz, *ipso* carbon of phenoxy), 144.4 (d, J_{PC} = 17.2 Hz, *ipso* carbon of phenyl (PYY')), 142.8 (dd, J_{PC} = 16.8, 4.2 Hz, *ipso* carbon of phenyl (PXX)), 142.2 (dd, J_{PC} = 14.2, 8.0 Hz, *ipso* carbon of phenyl (PXX)), 139.9 (s, 4-carbon of phenoxy), 136.6–121.4 (m, other phenyl carbons), 52.4 (d, J_{PC} = 20.0 Hz, $CH(Pr^i)$), 27.1 (d, J_{PC} = 9.2 Hz, $Me(Pr^i)$), 26.5 (d, J_{PC} = 10.9 Hz, $Me(Pr^i)$), 22.7 (s, Me(phenoxy)).
$Ph_2PN(Pr^i)PPh(OC_6H_4Br\text{-}\underline{4})$ **(1d)**	158.3 (d, J_{PC} = 11.8 Hz, *ipso* carbon of phenoxy), 143.5 (d, J_{PC} = 13.0 Hz, *ipso* carbon of phenyl (PYY')), 142.3 (dd, J_{PC} = 15.3, 5.2 Hz, *ipso* carbon of phenyl (PXX)), 141.9 (dd, J_{PC} = 16.6, 7.5 Hz, *ipso* carbon of phenyl (PXX)), 137.0–123.0, (m, other phenyl carbons), 117.0 (s, 4C phenoxy), 52.8 (d, J_{PC} = 18.5 Hz, $CH(Pr^i)$), 27.2 (dd, J_{PC} = 9.0, 3.2 Hz, $Me(Pr^i)$), 26.5 (d, J_{PC} = 9.9 Hz, $Me(Pr^i)$).
$Ph_2PN(Pr^i)PPh(OC_6H_3Me_2\text{-}\underline{3},\underline{5})$ **(1e)**	159.0 (d, J_{PC} = 11.0 Hz, *ipso* carbon of phenoxy), 144.5 (d, J_{PC} = 15.8 Hz, *ipso* carbon of phenyl (PYY')), 143.0 (m, *ipso* carbons of phenyls (PXX)), 141.7 (s, 3,5 carbons of phenoxy), 136.3–119.4 (m, other phenyl carbons), 52.8 (d, J_{PC} = 18.3 Hz, $CH(Pr^i)$), 27.3 (d, J_{PC} = 8.5 Hz, $Me(Pr^i)$), 26.7 (d, J_{PC} = 10.3 Hz, $Me(Pr^i)$), 23.7 (s, Me (phenoxy)).
$Ph_2PN(Pr^i)PPh(N_2C_3HMe_2\text{-}\underline{3},\underline{5})$ **(1g)**	154.9 (s, 5C-pyrazolyl), 150.1 (d, J_{PC} = 25.2 Hz, 3C-pyrazolyl), 144.0 (m, *ipso* carbons of phenyl (PXX)), 141.7 (d, J_{PC} = 9.1 Hz, *ipso* carbon of phenyl (PYY')), 137.3–127.8 (m, other phenyl carbons), 108.4 (s, 4C-pyrazolyl), 55.2 (dd, J_{PC} = 25.0, 6.0 Hz, $CH(Pr^i)$), 26.6 (d, J_{PC} = 13.9 Hz, $Me(Pr^i)$), 26.1 (d, J_{PC} = 11.8 Hz, $Me(Pr^i)$), 16.3 (s, pyrazolyl Me-$\underline{5}$), 14.3 (d, J_{PC} = 20.5 Hz, pyrazolyl Me-$\underline{3}$).

[a]Recorded at 50 MHz in CH_2Cl_2 solvent; s = singlet, d = doublet, dd = doublet of doublets, m = multiplet.

Variable Temperature ^{31}P NMR Studies

Variable temperature ^{31}P NMR studies have been carried out for the diphosphazanes **1c** and **1g** as well as their monosulfides (**2c** and **2g**) to study the nature of the conformers present in solution. The ^{31}P NMR data for these compounds at different temperatures are given in Table III.

The ^{31}P NMR spectrum of $Ph_2PN(Pr^i)PPh(OC_6H_4Me\text{-}\underline{4})$ (**1c**) at 296 K shows a broad peak at 41 ppm which arises from the PPh_2 phosphorus and a sharp doublet at 129.6 ppm from $PPh(OC_6H_4Me\text{-}\underline{4})$. At 250 K, both the resonances are broadened and upon further decrease in temperature, two new pairs of resonances are seen. The ratio of the major set of doublets to the minor set of doublets is 2:1. The spectra at various temperatures are shown in Figure 1. A similar behaviour is observed for $Ph_2PN(Pr^i)PPh(N_2C_3HMe_2\text{-}\underline{3},\underline{5})$ (**1g**) but in this case the ratio of the intensities of two sets of doublets at low temperature is 12:1. In the case of di-

TABLE II

^{31}P NMR data for diphosphazanes and their derivatives[a]

Diphosphazane	PNP **1a–1j**	P(S)NP **2a–2j**	P(O)NP **4a–4j**	P(O)NP(O) **5a–5j**
$Ph_2PN(Pr^i)P(O_2C_{12}H_8)$ **(1a)**	148.6 (d) 27.9 (d) $^2J_{PP}$ = 25.4 Hz	145.0 (d) 59.0 (d) $^2J_{PP}$ = 82.0 Hz	116.9 (d) 49.4 (d) $^2J_{PP}$ = 59.0 Hz	31.8 (d) 4.8 (d) $^2J_{PP}$ = 14.3 Hz
$Ph_2PN(Pr^i)P(O_2C_{20}H_{12})$ **(1b)**	148.3 (d) 28.3 (d) $^2J_{PP}$ = 26.0 Hz	—	—	35.4 (d) 7.3 (d) $^2J_{PP}$ = 13.0 Hz
$Ph_2PN(Pr^i)PPh(OC_6H_4Me\text{-}\underline{4})$ **(1c)**	127.4 (d) 39.5 (br) $^2J_{PP}$ = 21.2 Hz	121.0 (d) 67.6 (d) $^2J_{PP}$ = 22.0 Hz	120.0 (d) 29.0 (d) $^2J_{PP}$ = 68.5 Hz	30.2 (d) 16.6 (d) $^2J_{PP}$ = 11.0 Hz
$Ph_2PN(Pr^i)PPh(OC_6H_4Br\text{-}\underline{4})$ **(1d)**	129.1 (d) 39.4 (br) $^2J_{PP}$ = 22.1 Hz	122.6 (d) 67.9 (d) $^2J_{PP}$ = 26.0 Hz	121.6 (d) 30.0 (d) $^2J_{PP}$ = 73.0 Hz	29.5 (d) 16.8 (d) $^2J_{PP}$ = 10.9 Hz
$Ph_2PN(Pr^i)PPh(OC_6H_3Me_2\text{-}\underline{3},\underline{5})$ **(1e)**	126.3 (d) 38.6 (br) $^2J_{PP}$ = 22.7 Hz	120.2 (d) 67.7 (d) $^2J_{PP}$ = 28.7 Hz	119.0 (d) 32.8 (br) $^2J_{PP}$ = 72.0 Hz	29.7 (d) 15.6 (d) $^2J_{PP}$ = 13.0 Hz
$Ph_2PN(Pr^i)PPh(N_2C_3H_3)$ **(1f)**	85.6 (d) 43.3 (br) $^2J_{PP}$ = 26.4 Hz	—	—	32.3 (d) 15.3 (d) $^2J_{PP}$ = 10.1 Hz
$Ph_2PN(Pr^i)PPh(N_2C_3HMe_2\text{-}\underline{3},\underline{5})$ **(1g)**	71.6 (d) 43.8 (br) $^2J_{PP}$ = 29.8 Hz	70.0 (d) 65.3 (d) $^2J_{PP}$ = 111.0 Hz	64.2 (d) 33.9 (d) $^2J_{PP}$ = 110.0 Hz	30.7 (d) 19.1 (d) $^2J_{PP}$ = 10.0 Hz
$Ph_2PN(Pr^i)PPh(OC_5H_4N\text{-}\underline{2})$ **(1h)**	126.4 (d) 40.2 (br) $^2J_{PP}$ = 21.8 Hz	—	116.9 (d) 30.5 (d) $^2J_{PP}$ = 81.5 Hz	30.4 (d) 16.1 (d) $^2J_{PP}$ = 14.0 Hz
$Ph_2PN(Pr^i)P(O_2C_6H_4)$ **(1i)**	155.8 (d)[b] 28.9 (d) $^2J_{PP}$ = 14.0 Hz	—	—	34.7 (d) 1.5 (d) $^2J_{PP}$ = 10.5 Hz
$Ph_2PN(Pr^i)PPh_2$ **(1j)**	48.8 (br)[c]	67.5 (d) 54.4 (d) $^2J_{PP}$ = 63.0 Hz	46.0 (d) 30.5 (d) $^2J_{PP}$ = 70.0 Hz	28.0 (s)
$Ph_2P(S)N(Pr^i)P(S)Ph(OC_6H_4Me\text{-}\underline{4})$ **(3c)**		86.3 (d), 68.3 (d), $^2J_{PP}$ = 9.9 Hz		
$Ph_2P(S)N(Pr^i)P(O)Ph_2$ **(6j)**		67.2 (br), 28.9 (br)		
$Ph_2P(S)N(Pr^i)P(O)(O_2C_{12}H_8)$ **(6a)**		68.8 (d), 7.4 (d), $^2J_{PP}$ = 7.0 Hz		

[a]Recorded at 81 MHz in CH_2Cl_2 solvent; d = doublet, br = broad. [b]Reference 10a. [c]Reference 8.

TABLE III

Variable temperature ^{31}P NMR data for some diphosphazanes[a]

Compound	Temperature (K)	δ Ph_2P (ppm)	δ PYY′ (ppm)	$^2J_{PP}$ (Hz)
$Ph_2PN(Pr^i)PPh(OC_6H_4Me\text{-}4)$	296	41.0 (br)	129.6 (d)	19.6
(**1c**)	250	37.0 (br)	130.0 (br)	—
	230[b]	36.0 (d)	131.0 (d)	24.5
		52.0 (br)	129.0 (br)	—
	195[b]	36.0 (d)	133.0 (d)	32.0
		52.0 (d)	130.0 (d)	15.4
$Ph_2PN(Pr^i)PPh(N_2C_3HMe_2\text{-}3,5)$	295	44.0 (br)	74.0 (d)	33.0
(**1g**)	260	44.0 (br)	74.0 (br)	—
	245[b]	43.2 (d)	74.0 (d)	29.0
		57.0 (br)	69.0 (br)	—
	220[b]	43.0 (d)	74.0 (d)	33.5
		57.0 (d)	69.0 (d)	17.0
$Ph_2P(S)N(Pr^i)PPh(OC_6H_4Me\text{-}4)$	295	70.0 (d)	123.0 (d)	21.2
(**2c**)	230	70.0 (br)	122.0 (br)	—
	205[b]	70.0 (d)	119.0 (br)	47.5
		68.0 (d)	124.0 (d)	104.0
$Ph_2P(S)N(Pr^i)PPh(N_2C_3HMe_2\text{-}3,5)$	293	67.6 (d)	72.6 (d)	111.0
(**2g**)	193	67.2 (d)	72.0 (d)	118.4

[a]Recorded at 81 MHz in CH_2Cl_2 solvent; br = broad, d = doublet.

[b]The first set of values correspond to the major conformer **D**, the ratio of major to minor conformer **C** is 2:1 for **1c**, 12:1 for **1g** and 10:1 for **2c**.

phosphazane monosulfide, $Ph_2P(S)N(Pr^i)PPh(OC_6H_4Me\text{-}4)$ (**2c**), the P(III) resonance is broad even at 230 K and below this temperature, minor sets of doublets are observed. The spectrum of the diphosphazane monosulfide $Ph_2P(S)N(Pr^i)$-$PPh(N_2C_3HMe_2\text{-}3,5)$ (**2g**), remains almost the same over the temperature range 293–193 K and no new set of doublets are observed; the only difference is a slight increase in $^2J_{PP}$ from 111 Hz to 118 Hz.

We have shown previously[10a] that for an unsymmetrically substituted diphosphazane of the type $X_2PN(R)PY_2$, we have to consider four idealized conformations **A**–**D** as shown in Scheme 2. Molecular models indicate that when R is bulky (e.g., Bu^t) steric interactions with groups XX or YY will destabilise conformer **A** and it has been suggested[8] that other conformers will predominate. However conformation **B** requires a close approach of the groups XX or YY; for example with X=Y=Cl, the distance between X and Y is 260 ppm[9] which is sufficiently less than the van der Waals diameter of Cl to preclude this conformation. An enlargement of the PNP bond angle would make this less unfavourable but generally in diphosphazanes, the PNP bond angle lies around 120°.

The solid state structures of $Ph_2P(S)N(Pr^i)PPh(N_2C_3HMe_2\text{-}3,5)$ (**2g**), $Ph_2P(O)N$-$(Pr^i)P(O)Ph(OC_5H_4N\text{-}2)$ (**5h**) (see below) and $Ph_2PN(Pr^i)P(O_2C_6H_4)$[10a] show the presence of the diphenyl substituents on phosphorus atom *trans* to the isopropyl group on the nitrogen atom which corresponds to conformer **D**. As noted above there is no significant change in the ^{31}P NMR spectrum of diphosphazane monosulfide **2g** from 293–193 K; one may therefore conclude that only one rigid conformer is present in solution, which can be assigned to conformer **D** based on the crystal structure evidence. If we consider the case of the monosulfide **2c**, we have

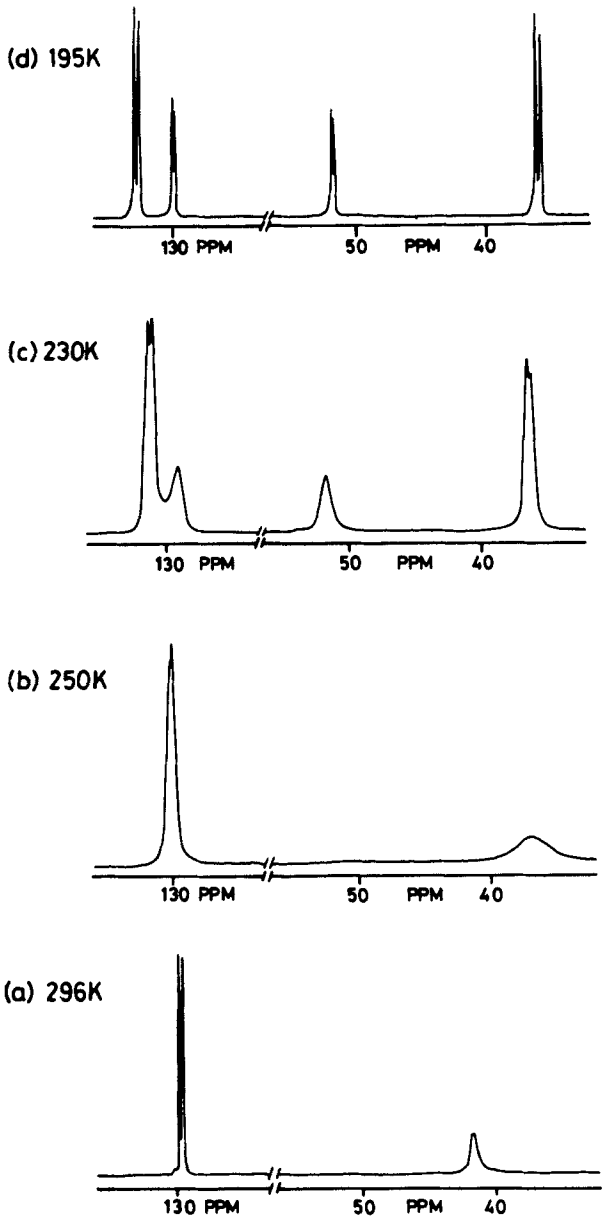
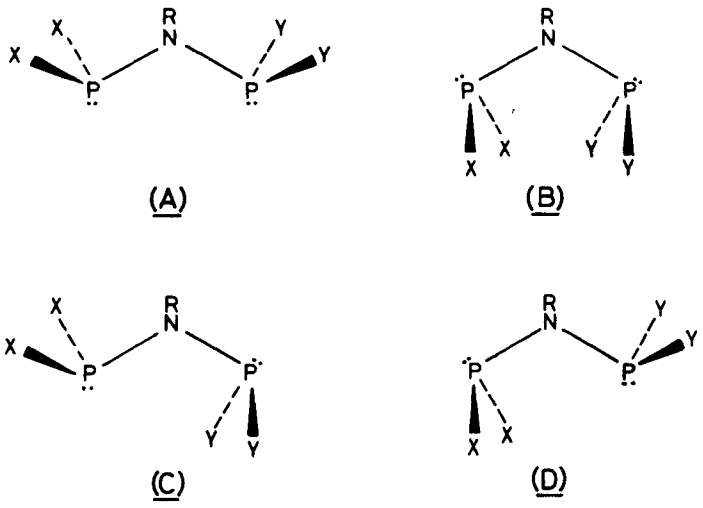


FIGURE 1 Variable temperature $^{31}P\{^{1}H\}$ NMR spectra of $Ph_2PN(Pr^i)PPh(OC_6H_4Me\text{-}\underline{4})$ (1c) (solvent CH_2Cl_2; 80.1 MHz).



SCHEME 2

a less bulky substituent at one of the phosphorus centers and hence at room temperature we observe only a time averaged conformer as a result of fast P—N bond rotation. As the temperature is decreased, the rate of rotation decreases and two sets of doublets are observed. The major set of peaks can be assigned to the conformer **D** and the minor set of peaks to conformer **C**. The variable temperature ^{31}P NMR spectra for **1c** and **1g** can also be explained similarly. The ratio of the two conformers is 2:1 for **1c** whereas for **1g** the ratio is 12:1. The large difference can be explained by the greater steric bulk at the PYY′ phosphorus in **1g** leading to the predominance of one of the conformers.

Crystal Structures of $Ph_2P(S)N(Pr^i)PPh(N_2C_3HMe_2$-3,5) (**2g**) *and* $Ph_2P(O)N(Pr^i)$-$P(O)Ph(OC_5H_4N$-2) (**5h**)

The structures of the diphosphazane monosulfide **2g** and the diphosphazane dioxide **5h** have been determined by single crystal X-ray diffraction studies. A perspective view of **2g** and **5h** are shown in Figures 2 and 3, respectively. The corresponding bond lengths and bond angles are listed in Table IV. In both these compounds the geometry around the nitrogen atoms is planar; the P(III) phosphorus atom is trigonal pyramidal and the P(V) phosphorus atom is tetrahedral.

The diphosphazane **2g** adopts the conformation **D** (Figure 2) in which the isopropyl group on the nitrogen atom is *trans* to the phenyl groups of the Ph_2PS and *cis* to the pyrazolyl and phenyl groups of $PPh(N_2C_3HMe_2$-3,5). The lone pair on the phosphorus (P2) is *trans* to the sulfur atom. The PNP bond angle in **2g** is 112.9° which is less than the usual PNP bond angle observed for diphosphazanes.[10a] The P—N bond lengths (1.705 and 1.718 Å) are nearly equal despite the presence of different substituents on phosphorus atoms. The P—N(pyrazolyl) bond length is slightly longer (1.740 Å).

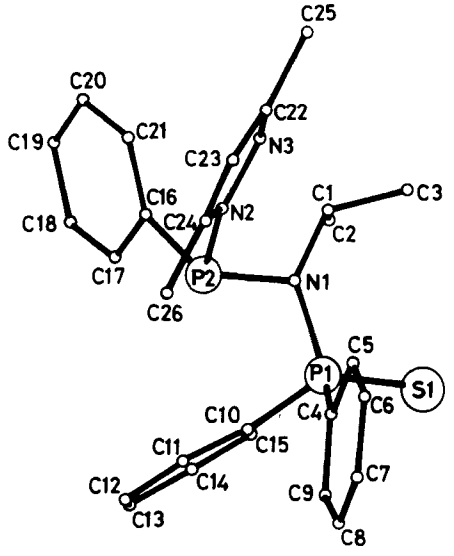


FIGURE 2 PLUTO diagram of $Ph_2P(S)N(Pr^i)PPh(N_2C_3HMe_2\text{-}3,5)$ (**2g**).

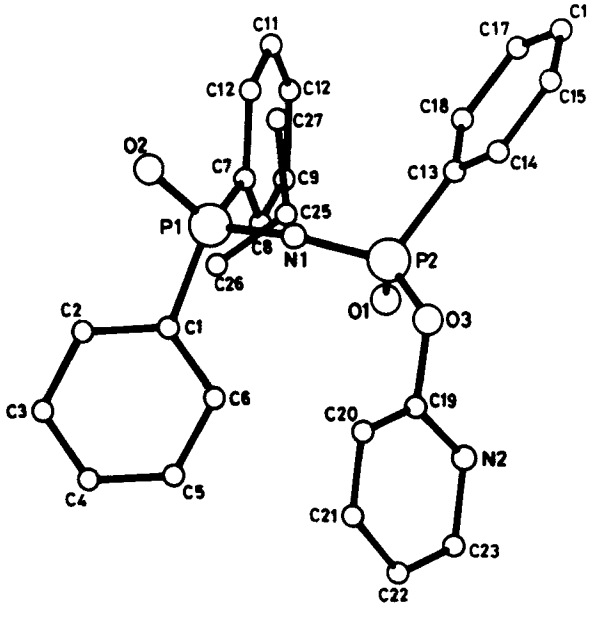


FIGURE 3 PLUTO diagram of $Ph_2P(O)N(Pr^i)P(O)Ph(OC_5H_4N\text{-}2)$ (**5h**).

The diphosphazane dioxide **5h** also adopts the conformer **D**. As observed in **2g**, the phenyl groups of $Ph_2P(O)$ are oriented *trans* to the isopropyl group on nitrogen and the PYY′ group is present *cis* to the Pr^i group. The oxygen atoms are oriented *trans* to each other. The PNP bond angle is 124.1°. The two P—N bond lengths are distinctly different; the one connecting the pyridinol substituted phosphorus is

TABLE IV

Selected bond distances (Å) and bond angles (°) in $Ph_2P(S)N(Pr^i)PPh(N_2C_3HMe_2\text{-}3,5)$ (**2g**) and $Ph_2P(O)N(Pr^i)P(O)Ph(OC_5H_4N\text{-}2)$ (**5h**)

2g		**5h**	
(a) Bond lengths (Å)			
P1—S1	1.946 (1)	P1—O2	1.470 (3)
P1—N1	1.705 (2)	P1—N1	1.703 (2)
P1—C4	1.816 (3)	P1—C1	1.812 (3)
P1—C10	1.818 (2)	P1—C7	1.807 (3)
P2—N1	1.718 (3)	P2—O1	1.461 (2)
P2—N2	1.740 (2)	P2—N1	1.664 (3)
P2—C16	1.831 (3)	P2—O3	1.599 (2)
N1—C1	1.497 (4)	P2—C13	1.788 (3)
N2—N3	1.378 (3)	O3—C19	1.399 (4)
		N1—C25	1.514 (4)
(b) Bond Angles (°)			
C4—P1—C10	107.2 (1)	C1—P1—C7	109.9 (1)
N1—P1—C10	105.9 (1)	N1—P1—C7	107.4 (1)
N1—P1—C4	105.7 (1)	N1—P1—C1	108.1 (1)
S1—P1—C10	111.02 (8)	O2—P1—C7	109.6 (1)
S1—P1—C4	110.58 (9)	O2—P1—C1	110.7 (1)
S1—P1—N1	115.96 (7)	O2—P1—N1	111.1 (1)
N2—P2—C16	102.7 (1)	N1—P2—C13	109.3 (1)
N1—P2—C16	102.2 (1)	O3—P2—C13	98.9 (1)
N1—P2—N2	103.4 (1)	O3—P2—N1	105.9 (1)
P1—N1—P2	112.9 (1)	O1—P2—C13	114.8 (1)
P2—N1—C1	121.7 (2)	O1—P2—N1	111.9 (1)
P1—N1—C1	124.5 (2)	O1—P2—O3	115.0 (1)
P2—N2—N3	124.1 (2)	P2—O3—C19	122.5 (2)
		P1—N1—P2	124.1 (1)
		P2—N1—C25	117.0 (2)
		P1—N1—C25	118.6 (2)

shorter (1.664 Å) compared to the other P—N bond length (1.703 Å) owing to the electron withdrawing effect of the pyridinol group and consequent strengthening of the "negative hyperconjugative interactions" in the P—N segment connected to this phosphorus.[12]

EXPERIMENTAL

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk-line techniques.[13] Solvents were distilled under nitrogen over appropriate drying agents prior to use. $Ph_2PN(Pr^i)$-PPhCl was prepared by a literature method[8]; Ph_2PCl (Aldrich) was used as supplied. Infrared spectra were recorded on a BIO-RAD FT-IR spectrophotometer. NMR spectra were recorded on a Bruker ACF200 spectrometer operating at 200.1 MHz (^1H), at 81 MHz (^{31}P) and at 50 MHz (^{13}C). Peak positions are relative to $SiMe_4$ as an internal reference (^1H, ^{13}C) or to 85% H_3PO_4 ($^{31}P\{^1H\}$) as an external standard. Elemental analyses were performed on a Heraeus CHN-O Rapid instrument.

The melting point, micro analyses data and ^1H NMR data for all the compounds are tabulated in Table V.

[1,1'-biphenyl]-2,2'-phosphorochloridite and [1,1'-binaphthyl]-2,2'-phosphorochloridite. For the preparation of these compounds, we have adopted the method reported for the preparation of 1,2-phenylene phosphorochloridite.[14]

TABLE V

Melting point, analytical and ^1H NMR data for diphosphazane ligands[a]

Compound	M.p. °C	Elemental analyses found (calcd) (%) C	H	N	δ-^1H NMR ppm[b] $CH_3(Pr^i)$	$CH(Pr^i)$
$Ph_2PN(Pr^i)P(O_2C_{12}H_8)$ **(1a)**	120	70.4 (70.9)	5.6 (5.5)	2.9 (3.1)	1.26	3.9
$Ph_2PN(Pr^i)P(O_2C_{20}H_{12})$ **(1b)**	203	74.4 (75.4)	5.1 (5.3)	2.3 (2.5)	1.27, 1.16	3.6
$Ph_2PN(Pr^i)PPh(OC_6H_4Me\text{-}\underline{4})$ **(1c)**	74	74.6 (73.5)	6.6 (6.4)	3.7 (3.1)	1.28, 1.06 2.3[c]	3.8
$Ph_2PN(Pr^i)PPh(OC_6H_4Br\text{-}\underline{4})$ **(1d)**	86	63.2 (62.1)	4.9 (4.9)	3.1 (2.7)	1.30, 1.05	3.8
$Ph_2PN(Pr^i)PPh(OC_6H_3Me_2\text{-}\underline{3},\underline{5})$ **(1e)**	63	73.8 (73.9)	6.8 (6.6)	3.5 (2.9)	1.31, 1.06 2.24[c]	3.8
$Ph_2PN(Pr^i)PPh(N_2C_3H_3)$ **(1f)**	103	68.7 (69.1)	5.8 (6.1)	10.3 (10.1)	1.28, 1.15	4.2
$Ph_2PN(Pr^i)PPh(N_2C_3HMe_2\text{-}\underline{3},\underline{5})$ **(1g)**	100	70.0 (70.1)	6.9 (6.6)	9.3 (9.4)	1.32, 1.18 2.30, 1.89[d]	4.2
$Ph_2PN(Pr^i)PPh(OC_5H_4N\text{-}\underline{2})$ **(1h)**	83	69.5 (70.3)	5.7 (5.9)	6.5 (6.3)	1.36, 1.08	3.8
$Ph_2P(S)N(Pr^i)P(O_2C_{12}H_8)$ **(2a)**	180	66.1 (66.2)	4.9 (5.2)	2.6 (2.9)	1.29	4.0
$Ph_2P(S)N(Pr^i)PPh(OC_6H_4Me\text{-}\underline{4})$ **(2c)**	149	69.9 (68.7)	6.2 (5.9)	3.5 (2.9)	1.48, 1.29 2.35[c]	3.9
$Ph_2P(S)N(Pr^i)PPh(OC_6H_4Br\text{-}\underline{4})$ **(2d)**	156	57.8 (58.5)	4.5 (4.7)	2.7 (2.5)	1.46, 1.27	4.0
$Ph_2P(S)N(Pr^i)PPh(OC_6H_3Me_2\text{-}\underline{3},\underline{5})$ **(2e)**	140	70.5 (69.2)	6.6 (6.2)	3.9 (2.8)	1.48, 1.29 2.35[c]	3.9
$Ph_2P(S)N(Pr^i)PPh(N_2C_3HMe_2\text{-}\underline{3},\underline{5})$ **(2g)**	160	66.7 (65.4)	6.4 (6.1)	9.2 (8.8)	1.29, 1.22 2.34, 1.80[d]	4.6
$Ph_2P(S)N(Pr^i)P(S)Ph(OC_6H_4Me\text{-}\underline{4})$ **(3c)**	153	63.8 (64.5)	5.3 (5.6)	2.5 (2.7)	1.79, 1.70 2.18[c]	4.3
$Ph_2P(O)N(Pr^i)PPh(N_2C_3HMe_2\text{-}\underline{3},\underline{5})$ **(4g)**	115	66.6 (67.7)	5.9 (6.3)	8.3 (9.1)	1.31, 1.18 2.30, 1.88[d]	4.2
$Ph_2P(O)N(Pr^i)P(O)(O_2C_{12}H_8)$ **(5a)**	140	64.1 (66.2)	5.3 (5.2)	3.0 (2.9)	1.55	4.2
$Ph_2P(O)N(Pr^i)P(O)Ph(OC_6H_4Me\text{-}\underline{4})$ **(5c)**	155	67.8 (68.7)	5.7 (5.9)	3.2 (2.9)	1.59, 1.40 2.27[c]	4.0
$Ph_2P(O)N(Pr^i)P(O)Ph(OC_6H_4Br\text{-}\underline{4})$ **(5d)**	140	58.5 (58.5)	4.5 (4.7)	2.6 (2.5)	1.57, 1.34	3.9
$Ph_2P(O)N(Pr^i)P(O)Ph(OC_6H_3Me_2\text{-}\underline{3},\underline{5})$ **(5e)**	145	68.8 (69.2)	6.1 (6.2)	2.7 (2.8)	1.59, 1.41 2.26[c]	4.0
$Ph_2P(O)N(Pr^i)P(O)Ph(N_2C_3HMe_2\text{-}\underline{3},\underline{5})$ **(5g)**	135	63.6 (65.4)	5.9 (6.1)	7.8 (8.8)	1.48, 1.33 2.30, 1.76[d]	4.4
$Ph_2P(O)N(Pr^i)P(O)Ph(OC_5H_4N\text{-}\underline{2})$ **(5h)**	147	64.1 (65.5)	5.2 (5.5)	5.0 (5.9)	1.64, 1.43	4.1
$Ph_2P(O)N(Pr^i)P(O)(O_2C_6H_4)$ **(5i)**	160	60.3 (61.0)	5.2 (5.1)	3.3 (3.4)	1.11	3.3
$Ph_2P(O)N(Pr^i)P(O)Ph_2$ **(5j)**	205	71.2 (70.6)	5.5 (5.9)	2.9 (3.1)	1.40	3.7
$Ph_2P(S)N(Pr^i)P(O)(O_2C_{12}H_8)$ **(6a)**	145	63.8 (64.1)	4.7 (4.9)	3.1 (2.8)	1.25	4.5

[a]Recorded at 200.1 MHz in $CDCl_3$ solvent.
[b]$CH_3(Pr^i)$ resonances are doublets with $^3J_{HH} \sim 7$ Hz, $CH(Pr^i)$ resonances are multiplets.
[c]CH_3 on the aryl ring.
[d]Pyrazolyl methyls.

Phosphorus trichloride (0.09 mol) was added dropwise with vigorous stirring to the corresponding phenol (0.05 mol) moistened with 0.1 mL of water. The mixture was refluxed for 5 hours and cooled to room temperature. Hydrogen chloride gas was evolved during the reaction. The cooled viscous liquid was dissolved in 20 mL dry toluene and filtered through glass wool. Solvent and excess PCl_3 were removed under *vacuo* to yield the title compounds. Yield: 95%.

The preparation of these compounds by different procedures is reported elsewhere.[15,16]

$X_2PN(Pr^i)PYY'$ {*X = Ph, YY' = $O_2C_{12}H_8$* (**1a**), *$O_2C_{20}H_{12}$* (**1b**)}. A solution of the aryloxy phosphorus chloride {[1,1'-biphenyl]-2,2'-phosphorochloridite or [1,1'-binaphthyl]-2,2'-phosphorochloridite} (0.05 mol) in 50 mL of toluene was added dropwise to (isopropylamino)diphenylphosphine (0.05 mol, 12.15 g) and triethylamine (0.055 mol, 5.55 g) in 50 mL of toluene at 0°C. The mixture was warmed to room temperature and stirred overnight. Triethylamine hydrochloride was filtered off and the filtrate was passed through a silica gel column. Solvent was removed under *vacuo* from the eluent to obtain a viscous oil. This oil was dissolved in methanol and cooled to 0°C overnight to obtain colorless crystals of the title compounds. Yield: 60–65%.

$X_2PN(Pr^i)PYY'$ (**1c–1h**). (Chlorophenylphosphino)(diphenylphosphino) isopropylamine (0.05 mol) in 25 mL of toluene was added dropwise to a 100 mL toluene solution of the corresponding phenol or secondary amine (0.05 mol) and triethylamine (0.06 mol) at 0°C with stirring. The mixture was heated to 80°C and maintained at this temperature for 4 hours. The mixture was worked up as described above to obtain **1c–1h**. Yield: 65–75%.

$X_2P(S)N(Pr^i)PYY'$ (**2a, 2c, 2d, 2e, 2g, 2j**). Elemental sulfur (1.25×10^{-4} mol) was added to a solution of the diphosphazane (0.001 mol) in 20 mL of tetrahydrofuran. The mixture was heated under reflux for 45 minutes. Solvent was removed under *vacuo* and the resultant oil was dissolved in methanol and cooled to 0°C overnight. Colorless crystals were obtained. Yield: 80–90%.

TABLE VI

Crystal data and intensity collection parameters for $Ph_2P(S)N(Pr^i)PPh(N_2C_3HMe_2\text{-}3,5)$ (**2g**) and $Ph_2P(O)N(Pr^i)P(O)Ph(OC_5H_4N\text{-}2)$ (**5h**)

	2g	**5h**
Formula	$C_{26}H_{29}N_3P_2S$	$C_{26}H_{26}N_2O_3P_2$
Molecular weight	477.58	476.46
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/C$
Z	2	4
a, Å	7.755 (1)	9.668 (1)
b, Å	17.615 (1)	9.665 (1)
c, Å	9.5549 (8)	25.790 (6)
β	108.33 (1)°	95.20 (2)°
V, Å^3	1238.9	2399.9
Crystal dimensions, mm	0.13 × 1.23 × 0.4	0.14 × 0.45 × 0.27
d_c, gcm^{-3}	1.28	1.32
$F(000)$	504	1000
Radiation (graphite monochromator)	Mo – K_α (0.71069 Å)	Mo – K_α (0.71069 Å)
Linear abs. coeff. μ cm^{-1}	2.33	1.68
Scan technique	$\omega/2\theta$	$\omega/2\theta$
θ range	1–25°	1–25°
Total number of reflections	2559	4979
Unique reflections	2257	4233
Observed reflections	2114 ($F_o > 5\sigma(F_o)$)	3252 ($F_o > 3\sigma(F_o)$)
R	0.02	0.0473
R_w	0.0277	0.0532
w	$1.0000/(\sigma^2(F) + 0.000227F^2)$	$1.0000/(\sigma^2(F) + 0.000409F^2)$
Largest peak in final diff. map, e/Å^3	0.23	0.36
$(\Delta/\sigma)_{max}$	0.08	0.09

$R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

$Ph_2P(S)N(Pr^i)P(S)Ph(OC_6H_4Me$-4) (**3c**). A mixture of $Ph_2PN(Pr^i)PPh(OC_6H_4Me$-4) (**1c**) (0.458 g, 0.001 mol) and elemental sulfur (0.096 g, 3.75×10^{-4} mol) in 20 mL of benzene was heated under reflux for 48 hours. The reaction mixture was cooled and passed through a short silica gel column. Solvent was removed from the eluent under *vacuo* and the resultant oil was dissolved in methanol and cooled overnight to 0°C to obtain colorless crystals of the title compound. Yield: 80%.

$X_2P(O)N(Pr^i)PYY'$ (**4a–4j**). To a solution of the diphosphazane (0.001 mol) in 15 mL of tetrahydrofuran was added trimethylamine N-oxide (0.001 mol). The suspension was stirred for 48 hours. Solvent was removed under *vacuo* and the resultant oil was dissolved in methanol to obtain **4a–4j** as colorless crystalline solids. Yield: 60–70%.

$X_2P(O)N(Pr^i)P(O)YY'$ (**5a–5j**). The diphosphazane (0.001 mol) was dissolved in 20 mL of acetone and cooled to 0°C. About 5 mL of 30% hydrogen peroxide solution was added dropwise with stirring. Stirring was continued for 1 hour. Acetone was removed from the reaction mixture and the oily residue was extracted with dichloromethane. The dichloromethane extract was dried over Na_2SO_4 and solvent was removed to obtain a colorless solid or oil. Recrystallisation using dichloromethane/petroleum ether (1:1) afforded crystalline solids. Yield: 80–90%.

$X_2P(S)N(Pr^i)P(O)YY'$ (**6a**, **6j**). These compounds were prepared by the oxidation of their corresponding mono sulfides (**2a**, **2j**) using hydrogen peroxide as described for the preparation of **5a–5j**. Yield: 80%.

TABLE VII

Non-hydrogen atomic coordinates and isotropic thermal parameters ($Å^2 \times 10^4$) for $Ph_2P(S)N(Pr^i)PPh(N_2C_3HMe_2$-3,5) (**2g**)

Atom	*X/a*	*Y/b*	*Z/c*	U_{eq}[a]
P1	0.26307 (8)	0.63490 (0)	0.71154 (6)	333 (2)
S1	0.49336 (9)	0.62209 (5)	0.67317 (8)	514 (3)
P2	−0.01983 (8)	0.73173 (5)	0.73791 (6)	347 (2)
N1	0.1869 (3)	0.7259 (1)	0.70790 (2)	336 (6)
N2	0.0197 (3)	0.7959 (1)	0.88310 (2)	417 (8)
N3	0.1103 (3)	0.8638 (1)	0.89000 (2)	447 (8)
C1	0.2691 (4)	0.7928 (2)	0.65590 (3)	390 (8)
C2	0.4537 (4)	0.8140 (2)	0.76090 (4)	550 (11)
C3	0.2666 (5)	0.7840 (2)	0.49450 (3)	566 (13)
C4	0.2780 (3)	0.5984 (2)	0.89270 (3)	376 (9)
C5	0.3245 (4)	0.6460 (2)	1.01490 (3)	476 (9)
C6	0.3534 (5)	0.6155 (2)	1.15470 (3)	612 (13)
C7	0.3376 (4)	0.5383 (2)	1.17290 (3)	584 (12)
C8	0.2929 (4)	0.4916 (2)	1.05270 (4)	572 (11)
C9	0.2641 (4)	0.5207 (2)	0.91230 (3)	488 (10)
C10	0.0826 (3)	0.5829 (1)	0.57790 (3)	366 (8)
C11	−0.0652 (4)	0.5510 (2)	0.60930 (3)	442 (10)
C12	−0.1999 (4)	0.5141 (2)	0.50050 (4)	543 (11)
C13	−0.1901 (4)	0.5100 (2)	0.35910 (3)	597 (11)
C14	−0.0472 (5)	0.5434 (2)	0.32560 (3)	569 (11)
C15	0.0894 (4)	0.5792 (2)	0.43410 (3)	469 (9)
C16	−0.1536 (3)	0.7879 (2)	0.57970 (3)	364 (8)
C17	−0.2271 (4)	0.7465 (2)	0.45050 (3)	517 (10)
C18	−0.3341 (5)	0.7807 (2)	0.32320 (3)	598 (12)
C19	−0.3722 (4)	0.8579 (2)	0.32510 (4)	615 (12)
C20	−0.3048 (5)	0.8988 (2)	0.45150 (4)	600 (12)
C21	−0.1950 (4)	0.8642 (2)	0.57940 (3)	487 (10)
C22	0.1267 (4)	0.8920 (2)	1.02240 (3)	483 (10)
C23	0.0454 (5)	0.8428 (2)	1.09870 (3)	590 (12)
C24	−0.0183 (4)	0.7824 (2)	1.01180 (3)	493 (10)
C25	0.2158 (5)	0.9667 (2)	1.06730 (4)	653 (13)
C26	−0.1108 (5)	0.7121 (2)	1.03850 (4)	682 (14)

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \vec{a}_i \vec{a}_j$.

TABLE VIII

Non-hydrogen atomic coordinates and isotropic thermal parameters (Å^2 × 10^4) for $Ph_2P(O)N(Pr^i)P(O)Ph(OC_5H_4N\text{-}2)$ (**5h**)

Atom	*X/a*	*Y/b*	*Z/c*	U_{eq}[a]
P1	0.06124 (7)	0.69100 (7)	0.41266 (3)	325 (2)
P2	0.32199 (7)	0.71694 (7)	0.36046 (3)	352 (2)
O1	0.2328 (2)	0.7744 (2)	0.31697 (7)	445 (6)
O2	0.0270 (2)	0.6683 (2)	0.46643 (7)	442 (6)
O3	0.4239 (2)	0.5963 (2)	0.34517 (7)	478 (7)
N1	0.2303 (2)	0.6509 (2)	0.4061 (1)	336 (7)
N2	0.3887 (4)	0.5281 (4)	0.2563 (1)	804 (13)
C1	−0.0470 (3)	0.5846 (3)	0.3676 (1)	362 (8)
C2	−0.1624 (3)	0.5266 (3)	0.3873 (1)	439 (10)
C3	−0.2531 (3)	0.4435 (3)	0.3562 (1)	548 (13)
C4	−0.2283 (4)	0.4175 (3)	0.3058 (1)	563 (11)
C5	−0.1138 (4)	0.4727 (4)	0.2860 (1)	604 (13)
C6	−0.0227 (3)	0.5573 (3)	0.3167 (1)	514 (11)
C7	0.0373 (3)	0.8715 (3)	0.3959 (1)	354 (8)
C8	−0.0200 (3)	0.9216 (3)	0.3486 (1)	461 (10)
C9	−0.0409 (4)	1.0629 (3)	0.3417 (1)	594 (12)
C10	−0.0053 (4)	1.1532 (3)	0.3821 (1)	624 (13)
C11	0.0481 (4)	1.1055 (3)	0.4292 (1)	605 (13)
C12	0.0698 (3)	0.9636 (3)	0.4365 (1)	473 (10)
C13	0.4485 (3)	0.8345 (3)	0.3900 (1)	411 (10)
C14	0.5794 (3)	0.7942 (3)	0.4114 (1)	501 (10)
C15	0.6731 (4)	0.8910 (5)	0.4323 (1)	656 (15)
C16	0.6381 (5)	1.0290 (5)	0.4322 (2)	829 (17)
C17	0.5102 (5)	1.0693 (4)	0.4118 (2)	808 (17)
C18	0.4139 (4)	0.9740 (3)	0.3907 (1)	588 (12)
C19	0.3835 (3)	0.4954 (3)	0.3080 (1)	416 (10)
C20	0.3602 (4)	0.3743 (3)	0.3265 (1)	594 (13)
C21	0.3224 (6)	0.2769 (4)	0.2897 (2)	975 (21)
C22	0.3243 (5)	0.2958 (4)	0.2382 (2)	766 (16)
C23	0.3567 (4)	0.4235 (4)	0.2207 (1)	691 (14)
C25	0.3076 (3)	0.5610 (3)	0.4472 (1)	412 (9)
C26	0.2364 (4)	0.4233 (3)	0.4533 (1)	541 (11)
C27	0.3371 (4)	0.6382 (4)	0.4989 (1)	597 (13)

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \vec{a}_i \vec{a}_j$.

Crystal Structure Determination. A summary of the crystal data for compounds **2g** and **5h** and parameters pertinent to the structure determination are given in Table VI. The crystal was coated with a thin film of paraffin oil to protect it from atmosphere during data collection. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation. Cell constants were obtained by least squares refinement of the setting angles of 25 reflections in the range $18 < 2\theta < 26$. In the course of the data collection, no decrease in intensity was observed as monitored by three control reflections measured periodically. Lorentz polarization corrections were applied to the intensity data.

The structure was solved by direct methods using SHELXS-86[17] program and least square refinements were performed by the full-matrix method with SHELX-76.[18] All hydrogen atoms were located from difference Fourier maps. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. Non-hydrogen atom coordinates are given in Tables VII and VIII.

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