Structurally diverse penta- and hexacoordinate phosphorus compounds from the reaction of diethyl or diisopropyl azodicarboxylates with phosphorus(III) compounds†

K. V. P. Pavan Kumar, N. Satish Kumar and K. C. Kumara Swamy*

Received (in Montpellier, France) 19th October 2005, Accepted 27th January 2006
First published as an Advance Article on the web 7th March 2006
DOI: 10.1039/b514839a

The reaction of diethyl azodicarboxylate (DEAD) or diisopropyl azodicarboxylate (DIAD) with cyclic phosphites/phosphoramidites has been examined in an effort to delineate the structural preferences in spirocyclic penta- and tricyclic hexacoordinate (amino)oxyphosphoranes. It is shown that the familiar Bent's or apicophilicity rules referred to in standard books give an oversimplified picture. Thus the reaction of $CH_2(6\text{-}t\text{-Bu-4-Me–}C_6H_2O)_2PCl$ (**19**) with DEAD/DIAD leads to the chlorophosphoranes $CH_2(6\text{-}t\text{-Bu-4-Me–}C_6H_2O)_2PCl$[N(COOR)–N=C(OR)O–] [R = Et (**21a**), *i*-Pr (**21b**)]. Treatment of **21a–b** with pyrazole or imidazole leads to $CH_2(6\text{-}t\text{-Bu-4-Me–}C_6H_2O)_2P(NRR')$[N(COOR)–N=C(OR)O–] [NRR′ = pyrazolyl (**12a–b**), imidazolyl (**13a–b**)] that have trigonal bipyramidal phosphorus with 'reversed apicophilicity'. Compound $S(6\text{-}t\text{-Bu-4-Me–}C_6H_2O)_2P(NH\text{–}i\text{-Pr})$ (**20b**) affords the pentacoordinate derivative $S(6\text{-}t\text{-Bu-4-Me–}C_6H_2O)_2P(NH\text{–}i\text{-Pr})$[N(COOR)–N=C(OR)O–] (**15**), but $S(6\text{-}t\text{-Bu-4-Me–}C_6H_2O)_2PCl$ (**20a**) gives the hexacoordinate phosphorane $S(6\text{-}t\text{-Bu-4-Me–}C_6H_2O)_2PCl$[N(COOR)–N=C(OR)O–] (**16**) with the shortest known S→P coordinate bond. Compound **15** also exhibits the 'reversed apicophilicity' phenomenon, but the disposition of substituents is different from that in **12–13**. The compound $S(6\text{-}t\text{-Bu-4-Me–}C_6H_2O)_2PPh$[N(COOR)–N=C(OR)O–] (**17**) is prepared similarly. Reaction of **16** with imidazole gives $S(6\text{-}t\text{-Bu-4-Me–}C_6H_2O)_2P$(imidazolyl)[N(COOR)–N=C(OR)O–] (**18**). Both **17** and **18** show distorted octahedral geometry with S→P coordination, but the sulfur is *trans* to the phenyl/imidazolyl group (while it is *cis* to –Cl in **16**). The variable temperature ^{31}P NMR spectra of **15** exhibit four totally distinct signals showing a dynamic behaviour with isomeric pentacoordinate species present. Theoretical calculations suggest that the compound as isolated is the favoured one for $S(6\text{-}t\text{-Bu-4-Me–}C_6H_2O)_2P\{(N\text{-}t\text{-Bu})[N(CO_2Et)NH(CO_2Et)]\}$ (**2**, previously reported) as well as **15** and **16**.

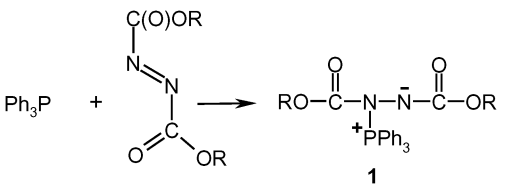
Introduction

The great success of the Mitsunobu esterification reaction in a variety of synthetic applications rests on the redox couple triphenylphosphine–dialkyl azodicarboxylate [ROOCN=NCOOR, R = Et (DEAD), *i*-Pr (DIAD)] in which the Morrison–Brunn–Huisgen [MBH] betaine **1** plays a key role [eqn (1)].[1] Several studies have also shown that the reactions of other P^{III} compounds with dialkyl azodicarboxylates do not necessarily go through betaines of type **1** and could involve pentacoordinate phosphorus.[2,3] In this connection, we have shown that these reactions can lead to a structurally diverse class of compounds like **2–7** (Chart 1), depending upon the substituents on phosphorus.[4] Some significant findings include the following:

(i) Whereas the *tert*-butylamino compound **2** has a tetracoordinate phosphinimine structure in the solid state, the analogous methylamino compound **3** is pentacoordinate.[5]

(ii) Although isocyanate (–NCO) and isothiocyanate (–NCS) groups are isoelectronic, reaction of the P^{III}–NCO precursor leads to a spirocyclic phosphinimine **6** but that of the P^{III}–NCS precursor leads to the pentacoordinate derivative **7**.

(iii) Even among the pentacoordinate phosphoranes **3**, **5** and **7**, there is a significant structural variation as regards the disposition of substituents and all of these show the 'reversed apicophilicity' phenomenon. In these compounds there are four different types of substituents [(a) oxygen atoms of the eight-membered ring, (b) nitrogen of the five-membered ring, (c) oxygen of the five-membered ring and (d) the fifth substituent] and hence positional isomerism can give input into our knowledge of the apicophilicity in trigonal bipyramidal phosphorus.



(1)

1

Because of its role as an intermediate/transition state species in reactions at a tetrahedral P^V centre, pentacoordinate

School of Chemistry, University of Hyderabad, Hyderabad-500046A. P., India. E-mail: kckssc@uohyd.ernet.in; Fax: +91-40-23012460; Tel: +91-40-23134856

† Electronic supplementary information (ESI) available: X-Ray structure determination data as cif files and details of theoretical calculations (2 pages). See DOI: 10.1039/b514839a

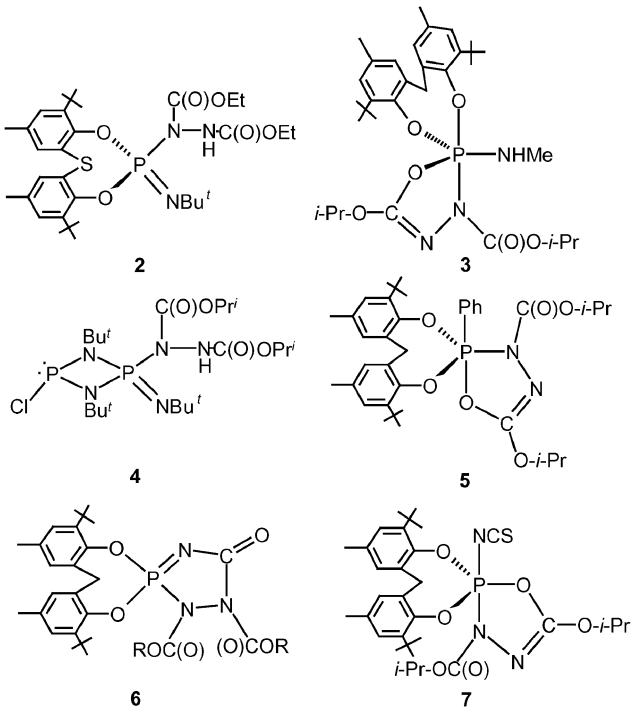


Chart 1

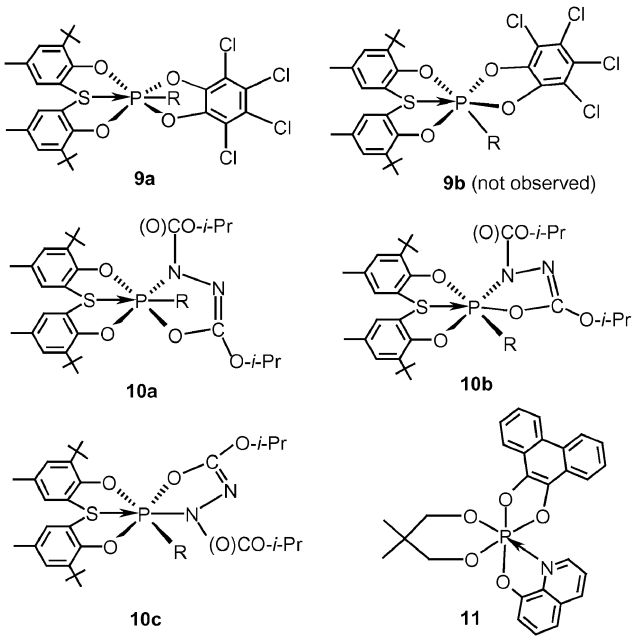


Chart 2

phosphorus has attracted the attention of both experimental and theoretical chemists.[6–8] A knowledge of relative preferences of substituents for the apical position (apicophilicity) at trigonal bipyramidal phosphorus may be useful in ascertaining the stereochemistry of products in reactions involving such intermediates/transition state species.[9,10] Interesting cases of reversed 'apicophilicity', apart from those mentioned above, have been reported recently.[11] In this context, we felt that it is important to investigate the positional preferences observed for substituents in **3**, **5** and **7** in greater detail.[4] Such a study may also throw light on the applicability of Bent's rule as described in textbooks for pentacoordinate phosphorus.[12] It may be noted that according to Bent's rule or in terms of the 3c–4e bonding picture for the apical bonds in the more common trigonal bipyramidal phosphorus, more electronegative substituents prefer apical sites (*i.e.* more apicophilic).

Replacement of the CH_2 moiety in the (eight-membered) dioxaphosphocin ring by a donor atom like sulfur can lead to neutral hexacoordinate phosphorus compounds with S→P donor–acceptor bonds (*e.g.* **9a**; the other isomer **9b** is not observed, Chart 2).[4b,13,14] In the case of compounds of type **10**, there are at least three possible isomers (**10a–c**). Finally, a donor site at the fifth substituent [like nitrogen on an oxinate group] can also, in principle, lead to hexacoordinate phosphorus with N→P bonds (*e.g.* **11**).[14a,15] Although a sizeable number of neutral hexacoordinate compounds are known, positional isomerism is not commonly observed. Possibility of finding positional isomers such as **10a–c** is another aspect we have been interested in. Studies such as these will allow one to ascertain the ease with which phosphorus achieves the hexacoordinate state in neutral compounds and to establish a lower limit to phosphorus electrophilicity leading to an increase in coordination number.[13a,b,d–f] It has also been suggested that in biological systems also, hexacoordinate phosphorus species could be involved.[16]

In this paper, we focus primarily on the synthesis and structures of compounds **12–18** (Chart 3) in which the phosphorus is formally hypervalent. Phosphorus in compounds **12–15** is pentacoordinate with **12**, **13** and **15** showing the 'reversed apicophilicity' phenomenon and thus demonstrating the limitations of Bent's rule. Variable temperature ^{31}P NMR spectra for **12b**, **15** and **18** are discussed in the context of penta-/hexacoordination. In **16–18** it is hexacoordinate *but with the sixth substituent positioned in different ways with respect to coordinated sulfur*. Theoretical calculations have been performed to ascertain the most stable configuration at phosphorus for the amino compounds **15**, **18** and the previously reported compound **2**; the results suggest that structures as observed in this study are the thermodynamically stable ones.

Results and discussion

Compounds **12–18** were synthesized by the routes shown in Scheme 1. The [4 + 2] cycloaddition of DEAD/DIAD to the P^{III} precursor (with XPO_2 skeleton) leads to an XPO_3N skeleton at phosphorus and is analogous to that of the addition of diketones (*e.g.* *o*-chloranil) to P^{III} compounds wherein an XPO_4 framework is generated.[11h] Synthesis of **13b** has also been accomplished by reacting the respective P^{III} precursor CH_2(6-*t*-Bu-4-Me–$C_6H_2O)_2$P(imidazolyl) (**22**) with DIAD (not shown in Scheme 1). Crystal data for **12a**, **13b** and **14–18** are given in Table 1.

Pentacoordinate compounds 12a, 13b, 14, and 15

Fig. 1–4 depict molecular structures of the pentacoordinate compounds **12a**, **13b**, **14**, and **15**, while Table 2 shows the corresponding bond parameters. Compounds **12a**, **13b** and **15**

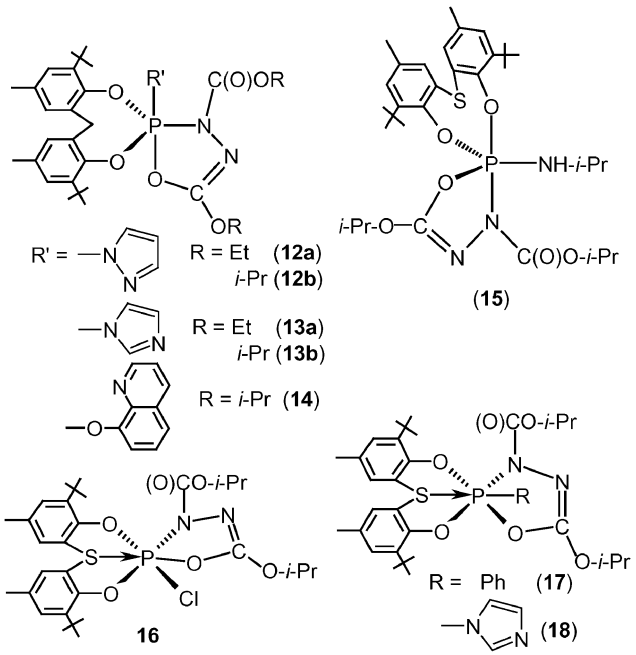
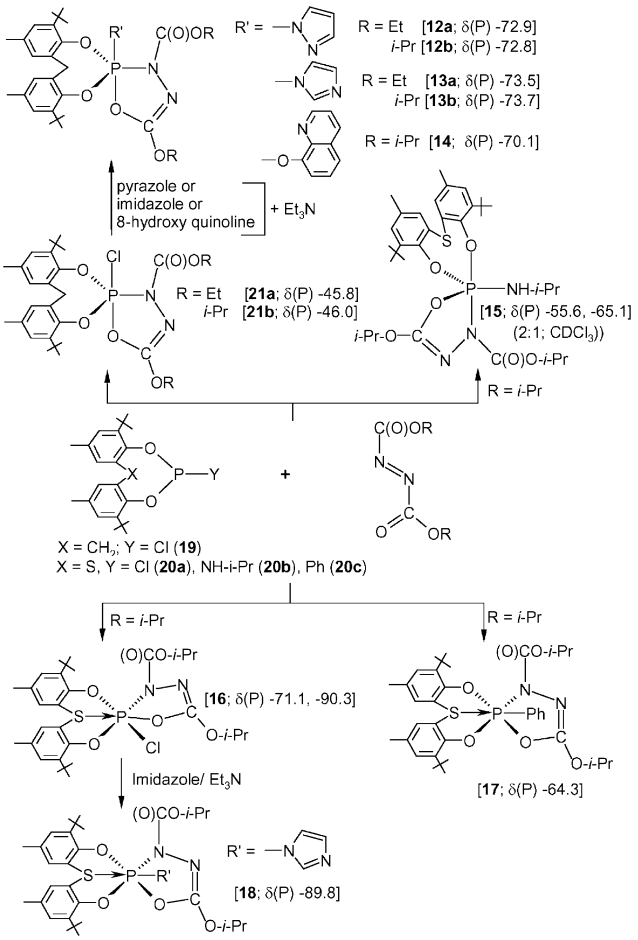


Chart 3

have the PO_3N_2 skeleton, while **14** has a PO_4N skeleton. Solid-state structures confirm that all these compounds possess essentially trigonal bipyramidal (TBP) geometry, with a maximum deviation observed for **15**. The oxinate nitrogen in **14** does not participate in an N→P interaction, which is unlike those in compounds of type **11** alluded to in the Introduction, probably as a result of steric congestion. Despite the fact that the flexible eight-membered 1,3,2-dioxaphosphocin ring is happy with either a-e or e-e occupancy in trigonal bipyramidal geometry,[11a–c,g,h,j,17] it occupies only e-e positions in compounds **12a** and **13b** leaving an apical site to the less electronegative imidazolyl/pyrazolyl nitrogen. Such a feature is in contrast to Bent's rule or the terms of the 3c–4e bonding picture for the apical bonds, according to which more electronegative substituents are expected to prefer apical sites.[12,18] As



Scheme 1

Table 1 Crystal data for compounds **12a**, **13b**·$C_6H_5CH_3$, **14**·$C_6H_5CH_3$, **15**, **16**, **17**·CH_3CN, and **18**[a]

Compound	**12a**	**13b**·$C_6H_5CH_3$	**14**·$C_6H_5CH_3$	**15**	**16**	**17**·CH_3CN	**18**
Empirical formula	$C_{32}H_{43}N_4O_6P$	$C_{41}H_{55}N_4O_6P$	$C_{47}H_{58}N_3O_7P$	$C_{33}H_{50}N_3O_6PS$	$C_{30}H_{42}ClN_2O_6PS$	$C_{38}H_{50}N_3O_6PS$	$C_{33}H_{45}N_4O_6PS$
Formula weight	610.67	730.86	807.93	647.79	625.14	707.84	656.76
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	*Pnma*	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a/Å	9.4608(12)	17.235(3)	16.7166(11)	11.9655(9)	10.4788(7)	9.274(2)	19.6085(11)
b/Å	17.042(2)	18.659(4)	15.0867(19)	22.0001(17)	10.8660(7)	17.798(3)	19.8928(11)
c/Å	20.513(3)	13.113(3)	19.0574(14)	13.9870(11)	16.3413(11)	24.057(7)	19.3009(11)
α/°	90	90	90	90	92.567(1)	90	90
β/°	98.124(2)	90	106.401(13)	94.2570(10)	103.1120(10)	96.367(15)	111.8530(10)
γ/°	90	90	90	90	111.9970(10)	90	90
V/Å^3	3274.1(7)	4217.0(15)	4610.7(7)	3671.8(5)	1662.80(19)	3946.2(16)	6987.7(7)
Z	4	4	4	4	2	4	8
D_{calc}/g cm^{-3}]	1.239	1.151	1.164	1.172	1.249	1.191	1.249
μ/mm^{-1}	0.132	0.113	0.110	0.175	0.268	0.169	0.186
F(000)	1304	1568	1728	1392	664	1512	2800
Data/restraints/parameters	5771/0/398	5200/388/339	8091/6/564	6468/0/411	5836/0/382	6872/0/455	12295/0/835
S	1.043	0.980	1.020	1.014	0.962	1.046	1.031
R_1 [$I > 2\sigma(I)$]	0.0473	0.0487	0.0724	0.0404	0.0418	0.0575	0.0484
wR_2 [all data]	0.1431	0.1640	0.2228	0.1163	0.1125	0.1938	0.1445
Max./min. residual electron density [eÅ^{-3}]	0.559/−0.374	0.191/−0.198	0.366/−0.352	0.233/−0.302	0.321/−0.198	0.626/−0.356	0.662/−.0.369

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{0.5}$.

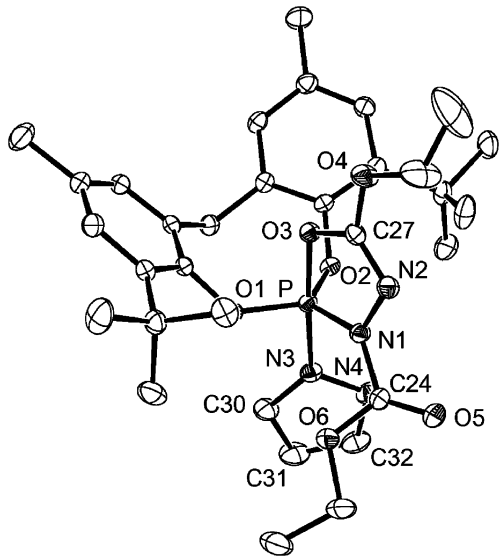


Fig. 1 Molecular structure of **12a** showing the numbering scheme on selected atoms.

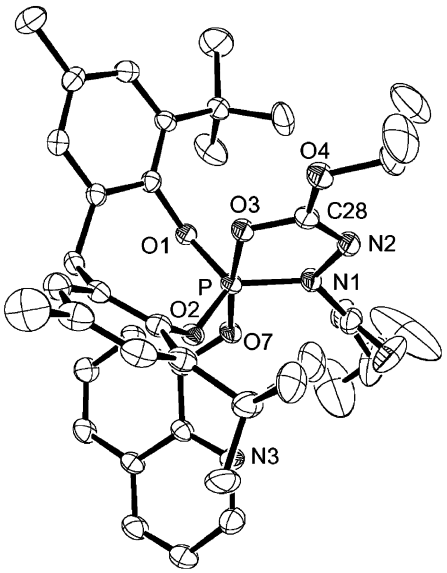
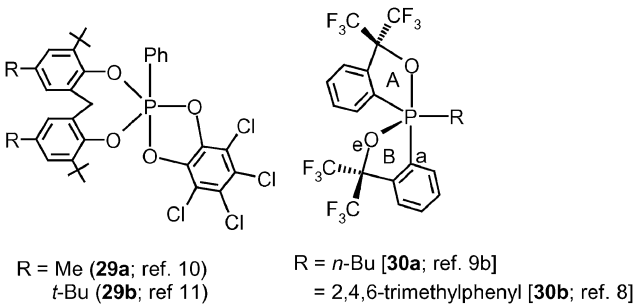


Fig. 3 Molecular structure of **14** · $C_6H_5CH_3$ showing the numbering scheme on selected atoms. The disorder at the *tert*-butyl carbons is not shown.

regards **15**, the equatorial occupancy of the NH–*i*-Pr group is on expected lines; however the N(apical)-O(equatorial) disposition of the five-membered ring is apparently not consistent with apicophilicity rules.[9,10a] Compared to the previously noted antiapicophilicity of carbon (see below), these results are less dramatic but nevertheless are not on expected lines.[10] The same isomer of **15** was obtained from the reaction of **16** with an excess of isopropylamine, thus suggesting that it is the favoured one; the powder X-ray pattern obtained for the bulk of the sample was essentially identical to the simulated one based on the single crystal data (using the Mercury program). The results, nevertheless, are consistent with our previous observations on the *o*-chloranil system (*cf*. Chart 4) in that secondary amino groups are more apicophilic compared to primary amino groups in these pentacoordinate compounds. Thus these results contradict the most often assumed tenet that high apicophilicity is favoured by small size and *vice versa*.[9,10a]

That a less electronegative atom like aromatic carbon can occupy an apical position in preference to a more electronegative oxygen also has recent precedence in compounds of type **29** and **30** (*cf*. five-membered ring B).[11a,d,e,g] This feature, together with our results above, suggests that one needs to be cautious in using the 'apicophilicity' rules for trigonal bipyramidal phosphorus in larger molecules.



R = Me (**29a**; ref. 10)
t-Bu (**29b**; ref 11)

R = *n*-Bu [**30a**; ref. 9b]
= 2,4,6-trimethylphenyl [**30b**; ref. 8]

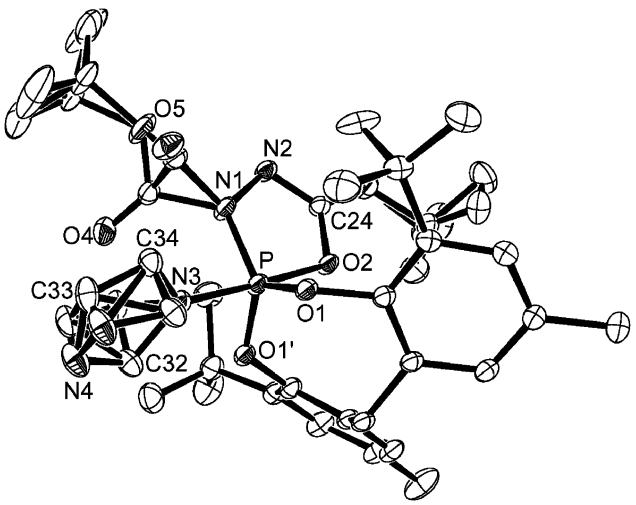


Fig. 2 Molecular structure of **13b** · $C_6H_5CH_3$ showing the numbering scheme on selected atoms; only one of the two positions for the imidazolyl ring and the carboxylate oxygen atoms at N(1) are labelled (see experimental for details).

The P–N(3) bond is significantly longer when the nitrogen is apical (**12a**, **13b**) than when it is equatorial (**15**); this is in line with the formulation of 3c–4e bonds for apical substituents and normal 2c–2e bonds for equatorial substituents.[18b] The P–N(apical) bond lengths in **12a** and **13b** are close to those calculated using the Schomaker–Stevenson empirical expression for a P–N single bond [1.77 Å].[19] Interestingly, the apical P–N(1) bond [1.809 Å] in **15** is significantly longer than even the calculated distance.

The sum of the bond angles at N(3) in the three compounds **12a**, **13b** and **15** is essentially 360° (planar). Although it can be argued that the lone pair of electrons on this nitrogen is involved in π-bonding with phosphorus in compound **15** and hence the planarity, a similar argument does not hold water in the cases of **12a** and **13b** because the nitrogen is apical and the

Table 2 Selected bond lengths (Å) and bond angles (°) with su's for pentacoordinate compounds **12a**, **13b** · $C_6H_5CH_3$, **14** · $C_6H_5CH_3$ and **15**

Compound	**12a**	**13b** · $C_6H_5CH_3$	**14** · $C_6H_5CH_3$	**15**
P–O(1)	1.581(1)	1.587(1)	1.610(3)	1.617(1)
P–O(2)	1.595(1)	1.587(1) [P–O(1′)]	1.602(3)	1.680(1)
P–O(3)	1.727(1)	1.731(2) [P–O(2)]	1.735(3)	1.648(1)
P–N(1)	1.677(2)	1.674(2)	1.681(4)	1.809(2)
P–N(3) [or P–O(7)]	1.763(2)	1.752(2)	1.633(3)	1.619(2)
X_{apical}–P–Y_{apical}	176.56(8) [O(3)–P–N(3)]	177.36(10) [O(2)–P–N(3)]	173.06(18) [O(7)–P–O(3)]	171.72(7) [O(2)–P–N(1)]
ΣN(1) (angle, °)	359.7	353.3	357.0	353.6
ΣN(3) (angle, °)	360.0	359.9	—	360.0

P–N bond is longer (hence expected to have less π-interactions with P).[9] At the moment we do not have a good rationalization for this observation. Theoretical calculations done earlier suggest that π-donors prefer equatorial positions, and that their donor orbitals will preferably lie in the equatorial plane.[7a] Information regarding the site preferences of –NHR and $–NR_2$ groups based on *negative hyperconjugation*[18] involving the nitrogen lone pair and an antibonding orbital of the PO_4N trigonal bipyramid is not available for a more critical assessment of our observation.

The P–O bonds in **12a**, **13b** and **15** also follow the expected general trend with the apical bonds slightly longer than the calculated value (1.72 Å) obtained by using the Schomaker–Stevenson expression. However, in **14**, the P–O(oxinate) apical bond is unexpectedly short [1.633(3) Å] and is about 0.2 Å shorter than that observed for the P–O (chloranil) apical bond in CH_2(6-*t*-Bu-4-Me–$C_6H_2O)_2$P(N=PPh$_3$)(1,2-$O_2C_6Cl_4$).[11g,h] Thus these data increase the observed range of P–O(apical) distances to 1.633–1.832 Å.[4,11g,h,17]

The P···S distance of 3.287 Å in **15** is lower than the sum [3.65 Å] of the van der Waals radii, but for practical purposes the geometry may be treated as only distorted trigonal bipyramid. The conformation of the eight-membered 1,3,2-dioxaphosphocin ring, boat-chair when located diequatorially and tub when located apical-equatorially, has been discussed before.[11h]

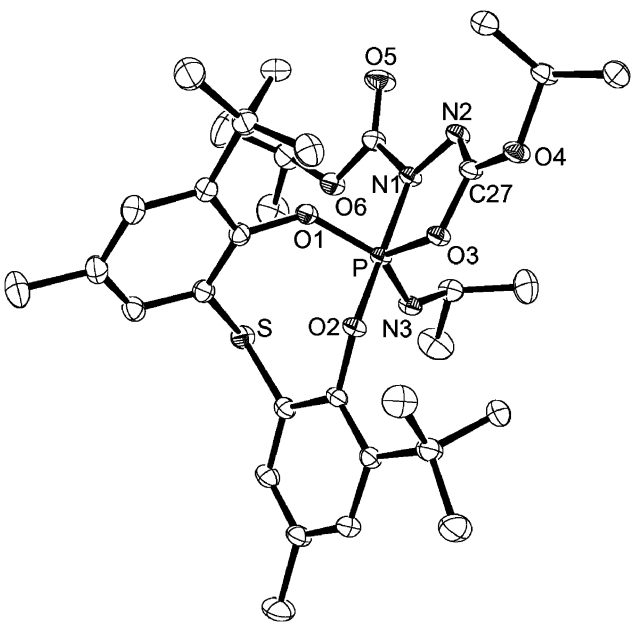
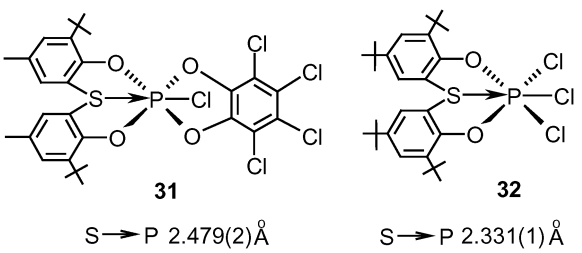


Fig. 4 Molecular structure of **15** showing the numbering scheme on selected atoms.

Hexacoordinate compounds 16–18

Molecular structures of **16**, **17** · CH_3CN and **18** are shown in Fig. 5–7, while selected bond parameters are given in Table 3. The geometry can be considered to be octahedral, with greater distortion for **17** and the least for **16**. The S→P distances are in the range expected for the sulfur coordination to phosphorus; this distance is the shortest in the chloro compound **16**. To our knowledge, this S→P donor–acceptor distance (2.317 Å) in **16** is the shortest known for neutral hexacoordinate phosphorus compounds and is pretty close to the covalent bond distance of 2.13–2.14 Å.[20] This is a bit surprising since, compared to compounds **31**[13c] or **32**[13d] that have PO_4SCl or PO_2SCl_3 skeletons respectively, compound **16** has a PO_3NSCl skeleton; the Lewis acidity at the phosphorus centre (excluding the S→P bond) should have been lower for **16** when compared to **31** and **32**. This, consequently, should have led to a weaker S→P interaction (*i.e.* longer bond) in **16**. It is likely that the presence of a $–CO_2$–*i*-Pr group on nitrogen has played a role in the observed shorter distance.



It can be readily seen that in **17**, **18** and **31** the acyclic substituent (phenyl, imidazolyl or Cl) is the one that is *trans* to the sulfur. This feature contrasts with **16** in which an oxygen atom of the five-membered ring is *trans* to the sulfur, thus hinting at the possibility of positional isomerism in this class of compounds.[21] As suggested by Cavell, the facial coordination observed in these compounds is influenced by the fact that two five-membered rings must be formed and hence the ligand may not be able to span three meridional positions.[13c] The fact that the imidazolyl compound **18** is obtained by starting with the chloro compound **16** also suggests that a pentacoordination–hexacoordination equilibrium may exist in solution to facilitate the ligand reorganization.

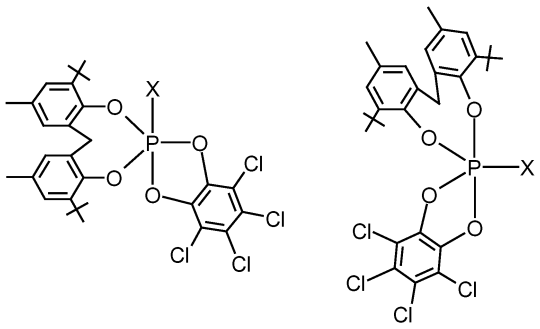


Chart 4

The P–N bond distances in **16–18** are in the range expected for a single bond, but still are lower than the P–N(1) apical bond in **15**. As expected because of the higher coordination number, P–O and P–N distances in **17** are significantly longer than those found in the analogous pentacoordinate compound **5**.[4b] The longer P–C bond in **5** [1.843(2) Å] relative to **17** is consistent with it being at the apical position of the trigonal bipyramid.

In compounds **16–18**, the phosphorus atom is above the mean plane of the four atoms *cis* to sulfur to an extent of 0.112, 0.238 and 0.127 Å, respectively. One can roughly estimate the displacement of these structures from square pyramid (that excludes sulfur coordination) to octahedral (that includes sulfur coordination), based on the value of a 0.431 Å displacement for phosphorus from the mean plane of the basal atoms in a square pyramidal arrangement with basal angles of 150°.[13d] Thus the order of percentage displacement from square pyramid to octahedral geometry would be **16** (~74%) > **18** (~71%) > **17** (~45%); this is in line with the corresponding S→P distances of 2.317, 2.422 and 2.623 Å, respectively.

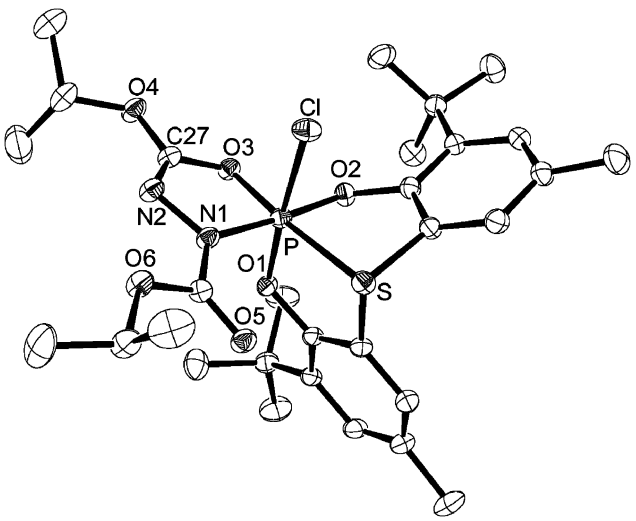


Fig. 5 Molecular structure of **16**. Only selected atoms are labelled.

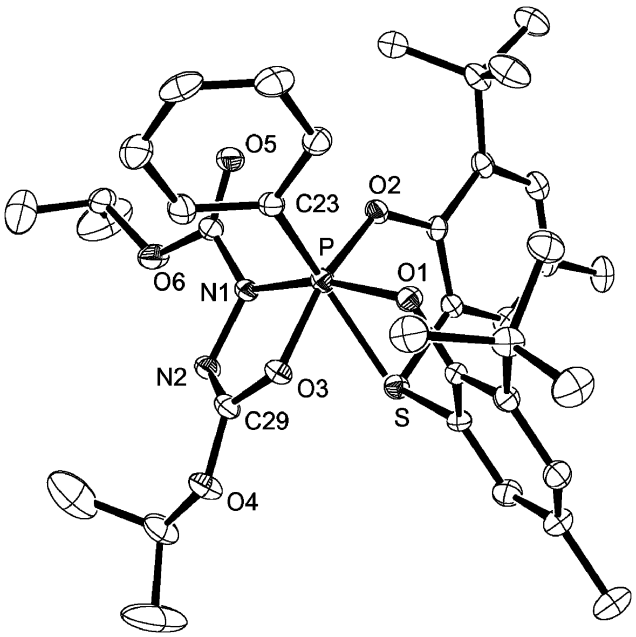


Fig. 6 Molecular structure of **17** · CH_3CN. Solvent atoms are omitted and only selected atoms are labelled.

Solution state NMR spectroscopy

The ^{31}P NMR ($CDCl_3$) spectra confirm that the pentacoordinate structure is preserved in solution for **12a**, **13b**, **14**, and **15**. Compounds **12–14** and **17–18** show a single line, whereas compounds **15–16** show two or more lines at 20 °C. The lower frequency for **17** (δ_P −64.3) relative to **5** (δ_P −51.7) clearly shows that hexacoordination is retained in solution for the former compound; it should be noted that while a higher coordination number moves the δ_P value to lower frequency, formation of five-membered rings (*cf.* **17**) in place of an eight-membered ring (**5**) has an opposite effect.[15a] Similarly, **18** has a significantly more negative δ_P value compared to CH_2(6-*t*-

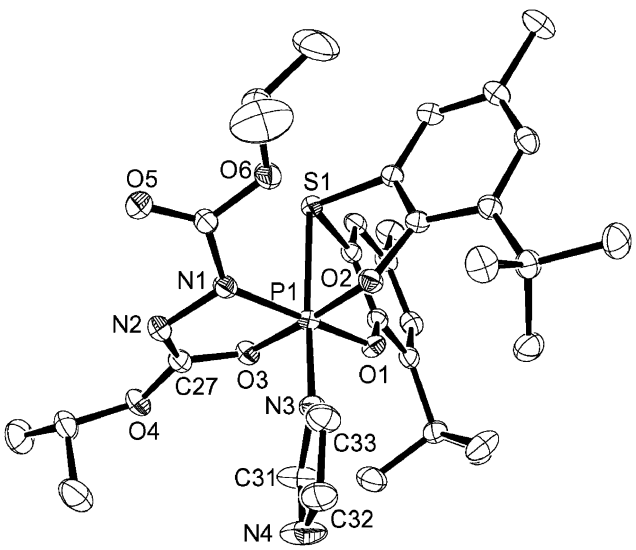


Fig. 7 Molecular structure of **18**. Only selected atoms are labelled. There are two molecules in the asymmetric unit, but only one is shown; the other one has similar bond parameters.

Table 3 Selected bond lengths (Å) and bond angles (°) with su's for hexacoordinate compounds **16**, **17** · CH_3CN, and **18**

Compound	**16**	**17** · CH_3CN	**18**
P–O(1)	1.668(1)	1.701(3)	1.639(2)
P–O(2)	1.674(1)	1.667(3)	1.676(2)
P–O(3)	1.667(1)	1.715(3)	1.721(2)
P–N(1)	1.771(2)	1.791(4)	1.789(2)
P–R	2.219(1) (R = Cl)	1.820(4) (R = Phenyl-C)	1.747(2) (R = imidazolyl-N)
P–S	2.317(1)	2.628(2)	2.422(1) (both)
O(1)–P–O(2)	91.03(7)	89.76(15)	92.90(9)
O(1)–P–O(3)	93.70(7)	87.81(14)	175.27(8)
O(1)–P–N(1)	91.83(8)	162.45(16)	95.53(9)
O(1)–P–R [R = Cl, C(23) or N(3)]	174.03(6)	95.11(17)	90.79(9)
O(1)–P–S (S1)	89.24(5)	81.40(10)	86.67(6)
O(2)–P–O(3)	89.91(7)	164.98(15)	86.16(8)
O(2)–P–N(1)	176.02(8)	93.47(16)	168.94(9)
O(2)–P–Cl (C(23), N(3))	90.00(6)	97.06(17)	93.31(9)
O(2)–P–S	86.75(5)	84.42(11)	84.29(6)
O(3)–P–N(1)	87.14(7)	84.61(15)	84.86(9)
O(3)–P–Cl (C(23), N(3))	92.18(6)	97.92(17)	93.89(9)
O(3)–P–S	175.59(6)	80.57(10)	88.62(6)
N(1)–P–Cl (C(23), N(3))	87.44(6)	101.59(18)	93.73(10)
N(1)–P–S	96.06(6)	81.76(12)	89.04(7)
(C(23), N(3) Cl–P–S	84.95(3)	176.22(15)	176.41(8)
ΣN(1) (angle, °)	359.8	358.0	

Bu-4-Me–$C_6H_2O)_2$P(imidazolyl)[N(COO–*i*-Pr)–N=C(O–*i*-Pr)O–] (**13b**: δ_P −73.5). Observation of two ^{31}P NMR signals for **16** [δ −71.1, −90.3] that appear at very much lower frequencies compared to **21b** [δ −46.0; pentacoordinate] clearly suggest that both the signals for **16** are due to hexacoordinate isomers. We ascribe these to S-*trans*-O (observed in the solid state) and S-*trans*-Cl [*cf*. compound **18**] isomers.

The ^{31}P NMR $\Delta\delta$ values for the pentacoordinate/hexacoordinate pairs **21b**/**16** (≥ 25.0 ppm), **13b**/**18** (16.1 ppm), and **5**/**17** (12.6 ppm) also indicate that S→P bond strength should be in the order **16** > **18** > **17**; this is what is actually observed [S→P distances are, respectively, 2.317(1), 2.628(2), and 2.422(1) Å].

For **13b**, **15** and **18** we have recorded the variable temperature ^{31}P NMR spectra in toluene-d_8. Compound **13b** did not exhibit any significant change in its ^{31}P NMR spectra; in the ^{1}H NMR spectra, the *tert*-butyl protons showed one peak at >20 °C, but at lower temperatures gave two peaks. Corresponding changes for the methyl as well as the isopropyl CH_3 protons were also observed. We ascribe these features to freezing of bond rotation (at the eight-membered/five-membered ring) with no significant change in the local environment at phosphorus. The lower frequency ^{31}P NMR chemical shift of **18** relative to **13b** ($\Delta\delta$ ∼ 16.1 ppm) throughout the temperature range studied clearly shows that hexacoordination is retained in solution for **18**. The latter compound showed two *tert*-butyl, two methyl and four isopropyl methyl signals till 40 °C; at higher temperatures only two isopropyl methyl signals were seen with no change for the methyl or *tert*-butyl signals.

The ^{31}P NMR spectra of **15**, however, changed with temperature [Fig. 8]. At low temperatures three peaks at δ −63.7, −63.4 and −54.5 are observed in toluene-d_8.[22] As the temperature is raised, the two lower frequency peaks merge and broaden, and a new peak at δ −39.2 ± 1.0 appears. At 353 K the spectra show only two peaks, one at δ −39.2 ± 1.0 and the other at −54.5; upon cooling to 20 °C the original pattern was observed. We consider first the structural possibilities **I–VII** (Chart 5); a third hexacoordinate form (*cf*. **10c**) and the pentacoordinate form **IV** have not been observed in the solid state (X-ray structure) so far. Based on the chemical shift values, we rule out the hexacoordinate (**V–VI**; also see **10c**) and tetracoordinate forms (**VII**). The two closely placed peaks at δ −64.7 and −64.4 suggest that the local environment at phosphorus is not changed significantly for these isomers; based on our previous studies,[4,11h] we ascribe these to the NH–*i*-Pr (equatorial) isomers of **III** (R = *i*-Pr; R′ = NH–*i*-Pr) having the boat-chair or tub conformation. It can be noted that the ^{31}P NMR spectrum of closely related CH_2(6-*t*-Bu-4-Me–$C_6H_2O)_2$P(NH–*i*-Pr)[N(COOR)–N=C(OR)O–] (**33**), prepared *in situ* in an NMR tube from its P^{III} precursor, showed two closely spaced resonances at δ −65.3 and −65.7 (*ca*. 1 : 4 ratio).[23] The remaining two signals for **15** with a large $\Delta\delta$ are then ascribable to any two among **I–II**. Currently we do

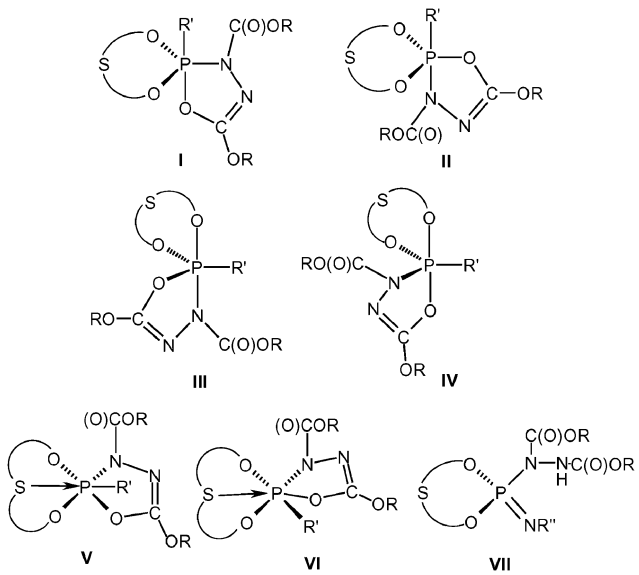
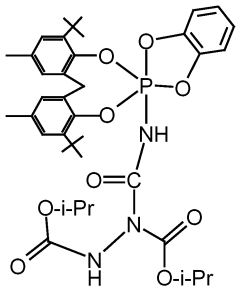


Chart 5

not have a way to distinguish these; we only note that in the structure of compound **34**,[4b] the NHR group is apical and hence it is possible to have NH–*i*-Pr apical. The ^{1}H NMR spectrum also showed multiple signals that changed with temperature, but was more complicated for a detailed analysis.



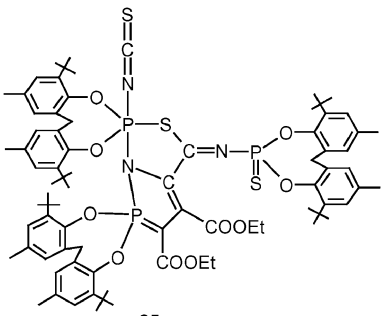
34

Theoretical calculations

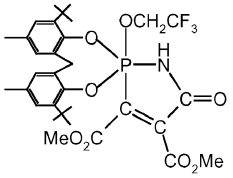
From what has been discussed above, it is clear that, depending on the substituents, the reaction of cyclic phosphites with DEAD/DIAD leads to tetra- (structure **VII**), penta- (structures **I–III**; structure **IV** is not observed by X-ray so far) or hexacoordinate (structures **V–VI**) compounds (Chart 5). In an effort to ascertain relative stabilities of various configurations, particularly for **2**, **15**, **16** and **18**, we did geometry optimization using the known coordinates from the available X-ray structures at the B3LYP/6-31G* level using the Gaussian 03 program package (see ESI for details†).[30] For compound **2** which had unusual solution and solid state behaviour [tetracoordination in solid state (X-ray) and pentacoordination in solution state (^{31}P NMR)],[4b] optimization showed clearly that tetracoordination (**VII**) is more stable than the penta- or hexacoordination by at least 17 kJ mol^{-1}. For compound **15** also, theoretically calculated energies justify what is experimentally found, albeit marginally. The observed pentacoordinate isomer **III** is marginally more stable than the tetra- or hexa- or other pentacoordinate structures by $\geq$7 kJ mol^{-1}. Calculated energies for compounds **16** and **18** suggest that the hexacoordinate isomers (**V** and **VI**) are more stable than their pentacoordinate isomers. Between the two hexacoordinate isomers, the observed structure **VI** is the most stable one for **16**; this isomer is marginally more stable (by *ca.* 2.5 kJ mol^{-1}) than the observed structure **V** (X-ray) for **18**. Thus, within the errors associated with calculations, although assessing the stability of individual isomers with a particular coordination number is difficult, prediction of the stability of isomers with different coordination numbers is possible.

Summary and implications

An important implication of the compounds discussed above (**3**, **5**, **7**, **12a**, **13b**, **15**, **23–30**) and from our other studies (see **35–36**)[24] is that Bent's rule, as described in standard textbooks, for pentacoordinate phosphorus is to be used cautiously. The limitation of Bent's rule perhaps stems from the fact that it deals with only the atoms directly connected to phosphorus. In the vast majority of pentacoordinate phosphorus compounds with trigonal bipyramidal geometry, the constraints imposed by the secondary atoms will play a significant role in determining the 'apicophilicity' of a group. In addition, as observed elsewhere also, the preference for a majority of 4–7 membered rings to span apical–equatorial positions in trigonal bipyramidal geometry could undermine Bent's rule.[25,26] Thus the familiar steric or electronegativity rule for the apicophilicity may not be followed in several cases.



35



36

The presence of several isomers in solution (^{31}P NMR) for compounds which showed a fixed geometry in the solid state (*e.g.* **15**) clearly shows that the energy difference among various isomeric forms is not very large. Isolation of the same isomer from different routes and the homogeneity of the sample by powder diffraction also suggest that the ones

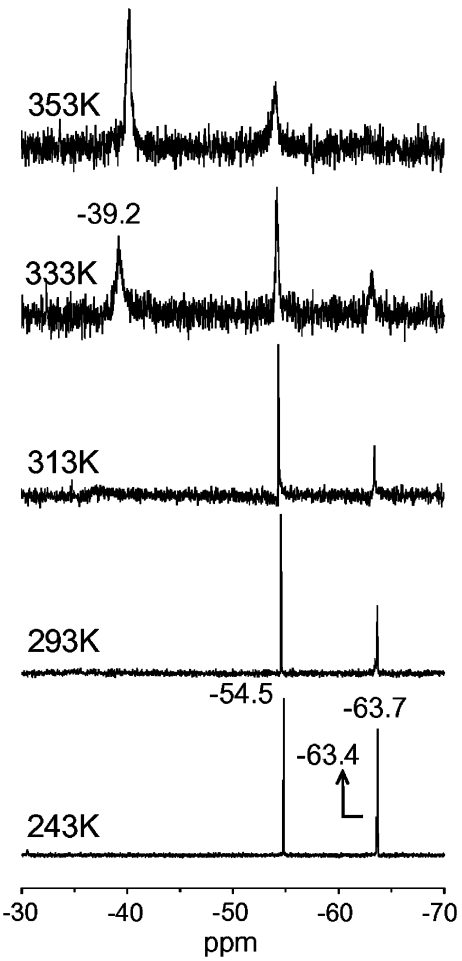


Fig. 8 Variable temperature ^{31}P NMR spectra for **15** in toluene-d_8.

isolated are thermodynamically favoured. The usefulness/limitation of DFT calculations in this context is also highlighted; it is shown that the theory developed till to-date is insufficient to explain all the bonding features.

As regards hexacoordinate compounds, observation of positional isomers in which the bridgehead sulfur is coordinated *trans* to the oxygen of the DIAD residue (compound **16**) or to the nitrogen/carbon of the amino or phenyl substituent (compounds **17–18**) suggests that in favourable cases, isomeric neutral hexacoordinate compounds may be isolatable; an indication to this effect is given by the ^{31}P NMR spectrum of **16** which shows two signals in the hexacoordinate region. The S→P donor–acceptor distance (2.317 Å) in **16** is the shortest known for neutral hexacoordinate phosphorus compounds and is very close to the covalent bond distance of 2.13–2.14 Å. The results suggest that in biological systems also, hexacoordinate phosphorus species could be involved when a suitable donor site close to phosphorus is available.[16]

Experimental

Materials and methods

Chemicals were procured from Aldrich/Fluka or from local manufacturers; they were purified when required. Solvents were purified according to standard procedures.[27] All reactions, unless stated otherwise, were performed in a dry nitrogen atmosphere. ^{1}H, ^{13}C and ^{31}P{H} NMR spectra were recorded on a Bruker 200 MHz or 400 MHz spectrometer in $CDCl_3$ or $C_6D_5CD_3$ solutions (unless stated otherwise), with shifts referenced to $SiMe_4$ (δ = 0) or 85% H_3PO_4 (δ = 0). Variable temperature ^{1}H and ^{31}P NMR spectra were recorded in $C_6D_5CD_3$. IR spectra were recorded on a JASCO FT/IR-5300 spectrophotometer. Elemental analyses were carried out on a Perkin-Elmer 240C or Thermo Finnigan EA1112 analyzer. Powder XRD data was obtained from INEL (France) using an X-ray diffractometer with 120 CPS detector (λ_{Co} = 1.788 97 Å).

The chloro precursors CH_2(6-*t*-Bu-4-Me–C_6H_2O)$_2$PCl (**19**),[11h] S(6-*t*-Bu-4-Me–C_6H_2O)$_2$PCl (**20a**)[13d] and S(6-*t*-Bu-4-Me–C_6H_2O)$_2$PPh (**20c**)[28] were prepared by literature procedures. The P^{III} precursors CH_2(6-*t*-Bu-4-Me–C_6H_2O)$_2$PNRR′ (R = H, R′ = *i*-Pr; δ_P 141.3 and R, R′ = imidazolyl; δ_P 125.1) were prepared by the reaction of **19** with the respective amine. We have previously reported the synthesis of **21b**;[4a] compound **21a** was synthesized similarly [mp 179–181 °C; δ_H (200 MHz; $CDCl_3$) 1.30 (3 H, t, *J* 7.2 Hz, CH_2CH_3), 1.38 (18 H, s, *t*-Bu-*H*), 1.44 (3 H, t, *J* 7.2 Hz, CH_2CH_3), 2.32, 2.34 (6 H, 2 × s, 2 × ArCH_3), 3.43 (1 H, dd, *J* 2.9 and 13.7 Hz, ArCH_AH_X), 4.35, 4.45 (4 H, 2 × qrt, *J* 7.2 Hz each, CH_2CH_3), 5.34 (1 H, dd, J_{PH} 5.8 and *J* 13.7 Hz, ArCH_AH_X) and 7.04, 7.17 (4 H, 2 × br s, 4 × Ar–*H*); δ_C (50 MHz; $CDCl_3$) 14.2, 14.6 (2 × s, 2 × CH_2CH_3), 21.2 (s, ArCH_3), 30.9 (s, C(CH_3)$_3$), 32.9 (s, *C*(CH_3)$_3$), 34.9 (s, ArCH_2), 62.3, 66.3 (2 × s, 2 × OCH_2CH_3), 127.1, 129.6, 134.6, 134.7, 135.1, 140.1, 140.2, 148.0, 148.4, 149.9 and 153.4, 153.6; δ_P (80 MHz; $CDCl_3$) −45.8].

Syntheses

The P^{III} precursor S(6-*t*-Bu-4-Me–C_6H_2O)$_2$P(NH–*i*-Pr) (20b). To a stirred solution of **20a** (0.90 g, 2.12 mmol) in toluene (60 cm^3) at 0 °C was added isopropylamine (0.25 g, 4.25 mmol) in toluene over a period of 5 min. The mixture was stirred overnight at room temperature, filtered and the filtrate concentrated to *ca.* 2 cm^3 and heptane (*ca.* 0.5 cm^3) was added. Crystals of the **20b** (0.65 g, 70%) were obtained at 5 °C after 12 h (found C 67.36, H 8.01, N 3.11, S 7.10. $C_{25}H_{36}NO_2PS$: calc. for C 67.38, H 8.14, N 3.14, S 7.19%); mp 148–150 °C; ν_{max}(KBr)/cm^{-1} 3360, 1595, 1427 and 1005; δ_H (200 MHz; $CDCl_3$) 1.29 (6 H, d, *J* 6.0 Hz, CH(CH_3)$_2$), 1.42 (18 H, s, *t*-Bu-*H*), 2.25 (6 H, s, 2 × ArCH_3), 3.31 (1 H, br, PN*H*), 3.35 (1 H, m, NHC*H*(CH_3)$_2$) and 7.08–7.29 (4 H, m, 4 × Ar–*H*); δ_C (50 MHz; $CDCl_3$) 20.6 (s, ArCH_3), 26.8 (d, J_{PC} 5.5 Hz, NHCH(CH_3)$_2$), 30.2 (s, C(CH_3)$_3$), 35.0 (s, *C*Me$_3$), 44.1 (d, J_{PC} 38.4 Hz), 123.3, 128.9, 131.4, 133.7, 140.2 and 153.3; δ_P (80 MHz; $CDCl_3$) 137.5.

CH_2(6-*t*-Bu-4-Me–C_6H_2O)$_2$P[N(COOEt)NC(OEt)–O–](NN=CHCH=CH–) (12a). To a stirred solution of **21a** (0.58 g, 1.0 mmol) in dichloromethane (10 cm^3) was added triethylamine (0.10 g, 0.14 cm^3, 1.0 mmol) and pyrazole (0.07 g, 1.0 mmol) at 0 °C. The mixture was stirred at room temperature for 24 h, dichloromethane removed *in vacuo*, dry toluene (15 cm^3) added and the mixture was filtered. Concentration of the filtrate to 2 cm^3, followed by the addition of heptane (4 cm^3) afforded crystals of **12a** (0.58 g, 89%) after keeping at 0 °C for *ca.* 24 h (found: C 62.61, H 6.89, N 9.08. $C_{32}H_{43}N_4O_6P$: calc. for C 62.94, H 7.10, N 9.18%); mp 146–149 °C; ν_{max}(KBr)/cm^{-1} 1771, 1671, 1439, 1263, 1209, 1130 and 1071; δ_H (200 MHz; $CDCl_3$) 0.91, 1.07 (6 H, 2 × t, *J* 6.9 Hz each, CH_2CH_3), 1.42 (18 H, s, *t*-Bu-*H*), 2.34 (6 H, s, 2 × ArCH_3), 3.53 (1 H, d, *J* 13.6 Hz, ArCH_AH_X), 3.65 (2 H, qrt, *J* 6.9 Hz, CH_2CH_3), 3.90 (2 H, qrt, *J* 6.9 Hz, CH_2CH_3), 4.21 (1 H, dd, J_{PH} 4.8 and *J* 13.6 Hz, ArCH_AH_X), 6.32 (1 H, br s, pyrazolyl–*H*), 7.06, 7.17 (4 H, 2 × br s, 4 × Ar–*H*) and 7.72 and 8.22 (2 H, 2 × d, *J* ∼ 3.0 Hz each, 2 × pyrazolyl–*H*); δ_C (50 MHz; $CDCl_3$) 13.6, 14.1 (2 × s, CH_2CH_3), 21.1 (s, ArCH_3), 30.8 (s, C(CH_3)$_3$), 34.1 (s, *C*Me$_3$), 34.9 (s, ArCH_2), 64.1, 64.6 (2 × s, 2 × OCH_2CH_3), 105.1, 105.2, 125.3, 127.1, 128.3, 129.1, 133.0, 133.1, 134.3, 134.4, 134.6, 140.0, 140.1, 141.1, 141.4, 147.6, 147.9, 153.7 and 154.0; δ_P (80 MHz; $CDCl_3$) −72.9.

CH_2(6-*t*-Bu-4-Me–C_6H_2O)$_2$P[N(CO_2–*i*-Pr)NC(O–*i*-Pr)O–](NN=CHCH=CH–) (12b). The procedure was the same as in the preparation of **12a** using 1.0 mmol each of **21b** and pyrazole. Crystallization was done using a mixture of toluene (2 cm^3) and heptane (4 cm^3) to afford **12b** (0.49 g, 78%) (found: C 63.98, H 7.38, N 8.80. $C_{34}H_{47}N_4O_6P$ calc. for C 63.93, H 7.41, N 8.77%); mp 176–178 °C; ν_{max}(KBr)/cm^{-1} 1753, 1667, 1605, 1414, 1263, 1209, 1107 and 947; δ_H (200 MHz; $CDCl_3$) 0.77, 1.06 (12 H, 2 × d, *J* 5.9 Hz each, 2 × CH(CH_3)$_2$), 1.41 (18 H, s, *t*-Bu-*H*), 2.32 (6 H, s, 2 × ArCH_3), 3.50 (1 H, d, *J* 16.0 Hz, ArCH_AH_X), 3.70–3.83 (1 H, m, C*H*Me$_2$), 4.21 (1 H, dd, J_{PH} 3.0 and *J* ∼ 16.0 Hz, ArCH_AH_X), 4.58–4.71 (1 H, m, C*H*Me$_2$), 6.32 (1 H, br s, pyrazolyl–*H*), 7.04–7.28 (4 H, m, 4 × Ar–*H*), 7.68 and 8.20 (2 H, 2 × d, *J* ∼ 2.5 Hz each, 2 × pyrazolyl–*H*); δ_C (50 MHz; $CDCl_3$) 21.0, 21.4, 21.5, 21.8, 22.0 (5 lines, ArCH_3 + CH(CH_3)$_2$), 30.6, 31.1 (2 × s, 2 × C(CH_3)$_3$), 34.0 (s, *C*Me$_3$), 34.9 (s, ArCH_2), 71.7, 72.8 (2 × s, 2 × O*C*HMe$_2$), 105.3, 127.0, 127.8, 128.8, 133.2,

134.2, 134.4, 140.2, 141.1, 141.4, 148.5, 153.0, 153.2, 154.2 and 154.4; δ_P (80 MHz; $CDCl_3$) −72.8.

CH_2(6-*t*-Bu-4-Me–C_6H_2O)$_2$P[N(COOEt)NC(OEt)–O–](NCH=NCH=CH–) (13a). The procedure was the same as in the preparation of **12a** using 1.0 mmol each of **21a** and imidazole. Crystallization was done using a mixture of toluene (2 cm^3) and heptane (4 cm^3) to afford **13a** (0.54 g, 83%) (found: C 62.54, H 6.93, N 8.95. $C_{32}H_{43}N_4O_6P$: calc. for C 62.94, H 7.10, N 9.18%); mp: 137–138 °C; ν_{max}(KBr)/cm^{-1} 1763, 1665, 1439, 1267, 1206, 1127 and 1067; δ_H (200 MHz; $CDCl_3$) 0.92, 1.13 (6 H, 2 × t, *J* 6.8 Hz each, 2 × CH_2CH_3), 1.41 (18 H, br s, *t*-Bu-*H*), 2.33, 2.34 (6 H, 2 × s, 2 × $ArCH_3$), 3.43 (1 H, d, *J* 13.7 Hz, $ArCH_AH_X$), 3.67 (2 H, qrt, *J* 6.8 Hz, CH_2CH_3), 4.18 (1 H, dd, J_{PH} 4.6 and *J* 13.7 Hz, $ArCH_AH_X$), 4.38 (2 H, qrt, *J* 6.8 Hz, CH_2CH_3), 6.92 (1 H, br s, imidazolyl–*H*), 7.06, 7.18 (4 H, 2 × br s, 4 × Ar–*H*) and 7.48, 8.22 (2 H, 2 × br s, 2 × imidazolyl–*H*); δ_C (50 MHz; $CDCl_3$) 13.5, 14.0 (2 × s, CH_2CH_3), 21.0 (s, $ArCH_3$), 30.8, 31.0 (2 s, $C(CH_3)_3$), 33.8 (s, $C(CH_3)_3$), 34.9 (s, $ArCH_2$), 64.7, 64.8 (2 s, OCH_2CH_3), 120.9, 121.0, 121.3, 127.4, 128.2, 128.9, 129.0, 129.2, 129.3, 132.9, 133.0, 134.7, 134.8, 139.5, 147.3, 147.6 and 155.7; δ_P (80 MHz; $CDCl_3$) −73.5.

CH_2(6-*t*-Bu-4-Me–C_6H_2O)$_2$P[N(CO_2–*i*-Pr)NC(O–*i*-Pr)O–](NCH=NCH=CH–) (13b). The procedure was the same as in the preparation of **12a** using 1.0 mmol each of **21b** and imidazole. Crystallization was done using a mixture of toluene (1 cm^3) and heptane (2 cm^3) to afford **13b** (0.54 g, 85%) (found: C 64.34, H 7.55, N 8.61. $C_{34}H_{47}N_4O_6P$ calc. for C 63.93, H 7.41, N 8.77%); mp 190–193 °C; ν_{max}(KBr)/cm^{-1} 1755, 1663, 1262, 1101, 1013 and 947; δ_H (200 MHz; $CDCl_3$) 0.78 (6 H, d, *J* 5.9 Hz, $CH(CH_3)_2$), 1.12 (6 H, br, $CH(CH_3)_2$), 1.41 (18 H, s, 2 × *t*-Bu-*H*), 2.32 (6 H, s, 2 × $ArCH_3$), 3.52 (1 H, dd, *J* 1.4 and 13.6 Hz, $ArCH_AH_X$), 3.83 (1 H, m, $CHMe_2$), 4.17 (1 H, dd, *J* 3.9 and 13.6 Hz, $ArCH_AH_X$), 4.69 (1 H, m, $CHMe_2$), 6.98–7.32 (5 H, m, 4 Ar–*H* + 1 imidazolyl–*H*) and 7.46, 8.18 (2 × H, br s, 2 × imidazolyl–*H*). Variable temperature δ_H (200 MHz; $C_6D_5CD_3$) at selected temperatures: 298 K: δ 0.75 (6 H, d, *J* 6.3 Hz, $CH(CH_3)_2$), 1.11 (6 H, d, *J* 6.3 Hz, $CH(CH_3)_2$), 1.58 (18 H, s, *t*-Bu-*H*), 2.17 (6 H, s, 2 × $ArCH_3$), 3.26 (1 H, d, *J* 13.3 Hz, $ArCH_AH_X$), 3.83 (1 H, m, $CHMe_2$), 4.23 (2 H, m, $CHMe_2$ + $ArCH_AH_X$), 4.72 (1 H, m, $CHMe_2$), 7.00–7.32 (5 H, m, 4 × Ar–*H* + 1 × imidazolyl–*H*) and 7.82, 8.56 (2 H, br s, 2 × imidazolyl–*H*). 263 K: δ 0.72 (6 H, d, *J* 6.3 Hz, $CH(CH_3)_2$), 1.06 (6 H, 4 lines, $CH(CH_3)_2$), 1.54, 1.60 (18 H, 2 × s, 2 × *t*-Bu-*H*), 2.13, 2.21 (6 H, 2 × s, 2 × $ArCH_3$), 3.18 (1 H, d, *J* ~ 13.0 Hz, $ArCH_AH_X$), 4.14 (1 H, dd, *J* ~ 3.0 and ~ 13.0 Hz, $ArCH_AH_X$), 4.35, 4.72 (2 H, 2 × m, 2 × $CHMe_2$), 6.90–7.23 (4 H, m, 4 × Ar–*H*) and 7.45, 7.84, 8.61 (2 H, br s, 2 × imidazolyl–*H*). δ_C (50 MHz; $CDCl_3$) 21.0, 21.2, 21.5, 21.8, 21.9 (5 lines, $ArCH_3$ + $CH(CH_3)_2$), 30.9, 31.1 (2 × s, $C(CH_3)_3$), 33.7 (s, $C(CH_3)_3$), 34.9 (s, $ArCH_2$), 72.7, 73.2 (2 × s, $OCHMe_2$), 120.7, 121.1, 125.3, 127.3, 127.8, 128.6, 128.9, 129.0, 129.2, 133.1, 134.7, 135.1, 139.5, 140.5, 147.7 and 155.1 (all Ar-*C*), δ_P (80 MHz; $CDCl_3$) −73.7.

CH_2(6-*t*-Bu-4-Me–C_6H_2O)$_2$P[N(CO_2–*i*-Pr)NC(O–*i*-Pr)O–](8-OC_9H_6N) (14). The procedure was the same as in the preparation of **12a** using 1.0 mmol each of **21b** and 8-hydroxyquinoline. Crystallization was done using a mixture of toluene and heptane (2 cm^3 + 1 cm^3) to afford **14** (0.57 g, 80%) (found: C 67.22, H 7.10, N 5.95. $C_{40}H_{50}N_3O_7P$ calc. for C 67.11, H 7.04, N 5.87%); mp: 152–154 °C; ν_{max}(KBr)/cm^{-1} 1752, 1667, 1468, 1385, 1271, 1209, 1107 and 932; δ_H (200 MHz; $CDCl_3$) 0.87 (6 H, br s, $CH(CH_3)_2$), 1.20 (6 H, d, *J* ~ 5.9 Hz, $CH(CH_3)_2$), 1.35 (18 H, s, *t*-Bu-*H*), 2.30 (6 H, s, $ArCH_3$), 3.39 (1 H, d, *J* ~ 16.0 Hz, $ArCH_AH_X$), 3.92 (1 H, br m, $CHMe_2$), 4.02 (1 H, br, $ArCH_AH_X$), 4.15 (1 H, br m, $CHMe_2$) and 6.78–8.04 (10 H, m, Ar–*H* + oxinato–*H*); δ_C (50 MHz; $CDCl_3$) 20.9, 21.5, 21.7, 22.0 (4 × s, $ArCH_3$ + $CH(CH_3)_2$), 30.8, 31.1 (2 × s, $C(CH_3)_3$), 34.2 (s, CMe_3), 34.9 (s, $ArCH_2$), 70.6, 70.7, 72.5, 72.7 (4 × s, 4 × $OCHMe_2$), 120.3, 121.4, 123.3, 125.3, 126.1, 126.7, 127.1, 128.2, 128.8, 129.1, 129.5, 133.4, 135.1, 140.2, 140.4 and 149.3; δ_P (80 MHz; $CDCl_3$) −70.1 (br). X-Ray structural analysis was performed on the sample crystallized from toluene.

S(6-*t*-Bu-4-Me–C_6H_2O)$_2$PNHiPr[N(CO_2–*i*-Pr)NC(O–*i*-Pr)O–] (15). To a solution of **20b** (0.69 g, 1.53 mmol) in dry toluene (15 cm^3), DIAD (0.31 g, 1.53 mmol) was added dropwise over a period of 3 min by syringe and the mixture stirred for 24 h at room temperature. The solvent was removed and the residue was crystallized from heptane (*ca.* 2 cm^3) containing traces of dichloromethane to afford **15** (0.77 g, 78%) (found: C 59.93, H 7.75, N 6.52. $C_{33}H_{50}N_3O_6PS$ calc. for C 61.18, H, 7.78; N 6.48%). The same compound was also obtained by reacting **16** with isopropylamine; mp: 119–121 °C; ν_{max}(KBr)/cm^{-1} 3383, 1728 and 1676; δ_H (400 MHz; $CDCl_3$) 1.00–1.48 (30 H, many lines, $CH(CH_3)_2$ + *t*-Bu-*H*), 2.22, 2.32 (6 H, 2 × s, 2 × $ArCH_3$), 2.95 and 3.30 (together 1 H, m, $NHCH(CH_3)_2$), 3.50 and 3.68 (together 1 H, br, –N*H*), 4.45 and 4.90 as well as 5.05, 5.16 (total 2 H, two sets of m, $CHMe_2$) and 7.00–7.40 (4 H, many lines, 4 × Ar–*H*). Two major groups of signals are thus seen; δ_C (50 MHz; $CDCl_3$) 20.7, 21.8, 22.2, 26.4, 29.7, 30.3, 30.5, 34.6, 34.9, 44.5, 45.9, 68.3, 72.4, 73.0, 128.5, 129.0, 130.0, 131.5, 133.4, 133.6 and 135.7. The *C*=O signals were too broad. δ_P (160 MHz; $CDCl_3$) −55.6 and −65.1 (1 : 2); a minor signal (*ca.* 5% of the other two put together) at −64.7 was also observed. Variable temperature ^{31}P NMR ($C_6D_5CD_3$) spectra are shown in Fig. 8. The corresponding ^1H NMR spectra were recorded but a detailed analysis was not possible due to the broadness and multiplicity of the peaks.

S(6-*t*-Bu-4-Me–C_6H_2O)$_2$PCl[N(CO_2–*i*-Pr)NC(O–*i*-Pr)O–] (16). To a stirred solution of **20a** (0.92 g, 2.2 mmol) in toluene (20 cm^3) at −78 °C was added DIAD (0.45 g, 2.2 mmol) dropwise through a syringe over a period of 5 min. The reaction mixture was brought to room temperature and stirred for 12 h; later the solvent was evaporated and residue crystallized from a heptane–dichloromethane (2 + 0.5 cm^3) mixture to afford **16** (0.95 g, 70%) (found: C 57.78, H 6.81, N 4.62, S 5.04. $C_{30}H_{42}ClN_2O_6PS$ calc. for C 57.64, H 6.77, N 4.48, S 5.13%); mp: 156–158 °C; ν_{max}(KBr)/cm^{-1} 1747, 1651, 1593, 1372 and 1224; δ_H (400 MHz; $CDCl_3$) 0.92–1.60 (30 H, many lines, $CH(CH_3)_2$ + *t*-Bu-*H*), 2.35 (6 H, br, 2 × $ArCH_3$), 4.90–5.20 (2 H, m, 2 × $CHMe_2$) and 7.20–7.44 (4 H, m, 4 × Ar–*H*); δ_C (50 MHz; $CDCl_3$) 20.7, 20.9, 21.0, 21.8, 21.9, 29.2,

29.5, 30.4, 31.2, 34.5, 35.8, 69.3, 69.7, 70.4, 72.2, 73.1, 73.9, 121.6, 125.5, 127.7, 128.1, 129.8, 130.3, 130.8, 131.2, 131.6, 132.1, 133.2, 134.5, 134.7, 135.0, 135.3, 137.3. 137.5, 141.0, 147.3, 150.1, 150.1, 153.1,160.5 and 173.1; δ_P (160 MHz; $CDCl_3$) −71.1 and −90.3 (br). The compound hydrolyzes rapidly and a peak at δ −7.0 appears within $\frac{1}{2}$ h.

S(6-*t*-Bu-4-Me–$C_6H_2O)_2$P[N(CO_2–*i*-Pr)NC(O–*i*-Pr)O](Ph) (17). To a stirred solution of **20c** (0.94 g, 2.0 mmol) in toluene (20 cm^3) was added DIAD (0.40 g, 2.0 mmol) dropwise over a period of 0.5 h. Upon stirring for two days and removal of all the solvent, **17** (1.07 g, 80%) was obtained as a light yellow solid (found: C 64.21, H 7.10, N 4.82. $C_{36}H_{47}N_2O_6PS$ calc. for C 64.84, H 7.11, N 4.20%). The compound was crystallized from an acetonitrile–dichloromethane (2 : 1) mixture; mp 148–150 °C; ν_{max}(KBr)/cm^{-1} 1714, 1655 and 1103; δ_H (200 MHz; $CDCl_3$) 0.95, 1.13, 1.15 and 1.26 (12 H, d each, $J \sim 6.3$ Hz, 2 × HC(CH_3)$_2$), 1.20 and 1.40 (18 H, 2 × s, 2 × C(CH_3)$_3$), 2.22 and 2.28 (6 H, 2 × s, 2 × Ar–CH_3), 4.62–4.80 (2 H, m, 2 × CH(CH_3)$_2$) and 7.10–7.45, 8.10–8.17 (9 H, 2 × m, Ar–*H*). The CH_3CN peak in the spectrum of crystals appeared at δ 1.91; δ_C (50 MHz; $CDCl_3$) 20.6, 20.7, 21.5, 21.7, 21.9 (5 × s, ArCH_3 + OCH(CH_3)$_2$), 29.5 and 30.6 (2 × s, C(CH_3)$_3$), 34.7, 35.2 (2 × s, C(CH_3)$_3$), 69.1 and 72.6 (2 × s, 2 × O–CH(CH_3)$_2$), 117.6, 117.9, 122.8, 122.9, 127.1, 127.4, 129.4, 129.8, 129.9, 130.6, 130.8, 131.0, 131.3, 131.7, 132.0, 136.6, 137.7, 137.9, 138.6, 138.8, 141.3, 151.1, 151.4, 151.7, 152.9, 153.1, 154.4 and 154.6; δ_P (80 MHz; $CDCl_3$) −64.3.

S(6-*t*-Bu-4-Me–$C_6H_2O)_2$P[N(CO_2–*i*-Pr)NC(O–*i*-Pr)O–](NCH=NCH=CH–) (18). To a stirred solution of **16** (1.38 g, 2.19 mmol) in dichloromethane (20 cm^3) was added imidazole (0.15 g, 2.19 mmol) and triethylamine (0.22 g, 2.19 mmol) in dichloromethane dropwise over a period of 0.5 h. at 0 °C. The mixture was stirred at room temperature for 12 h, dichloromethane was removed *in vacuo*, dry toluene (15 cm^3) was added and the mixture was filtered. The residue was crystallized from a dichloromethane–hexane (4 : 1) mixture (2 cm^3) to afford **18** (0.54 g, 85%) (found: C 64.34, H 7.55, N 8.61. $C_{34}H_{47}N_4O_6P$ calc. for C 63.93, H 7.41, N 8.77%); mp 192–195 °C; ν_{max}(KBr)/cm^{-1} 1716, 1651 and 1599; δ_H (400 MHz; $CDCl_3$) 1.03, 1.10, 1.17 and 1.25 (12 H, d each, J 6.4 Hz, 2 × CH(CH_3)$_2$), 1.34 and 1.41 (18 H, 2 × s, 2 × *t*-Bu-*H*), 2.23 and 2.31 (6 H, 2 × s, 2 × ArCH_3), 4.83 (2 H, m, 2 × OCH(CH_3)$_2$), 7.20–7.57 (5 H, m, Ar–*H* + imidazolyl–*H*) and 7.46 and 8.23 (2 H, 2 × s, 2 × imidazolyl–*H*); δ_C (50 MHz; $CDCl_3$) 20.8, 21.5, 21.6 (3 lines, ArCH_3 + CH(CH_3)$_2$), 29.5, 29.8 (2 × s, C(CH_3)$_3$), 34.8, 35.0 (2 × s, C(CH_3)$_3$), 69.8, 73.1 (2 × s, OCHMe$_2$), 118.1, 118.2, 120.3, 120.4, 121.4, 121.5, 128.0, 128.1, 128.2, 128.3, 131.7, 131.8, 131.9, 132.2, 137.5, 137.6, 138.2, 138.3, 140.2, 140.3, 149.8, 150.0, 151.1, 151.2 and 154.4; δ_P (160 MHz; $CDCl_3$) −89.8.

X-Ray structural analysis

X-Ray data were collected on an Enraf-Nonius-MACH3 at 293 K (**14**, **17**) or a Bruker AXS SMART diffractometer (**12a**, **13b**, **15**, **16** and **18**) at 296 K using Mo-K_α (λ = 0.71073 Å) radiation and capillary mounting. The structures were solved by direct methods;[29] all non-hydrogen atoms were refined anisotropically. For the hydrogen atoms bonded to carbon, the riding model was used. The hydrogen atoms bonded to nitrogen were located in a difference map. The structure of **13b** shows that the imidazolyl and the DIAD residues are disordered; the structure was also solved in the lower space group $Pna2_1$ but at the final stages, refinement did not converge. The *R* value for **17** is a bit high because of the only moderate quality of the data.

CCDC reference numbers: 280917–280923. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b514839a

Acknowledgements

This work was supported by the Department of Science and Technology (DST), New Delhi. The National Single Crystal Diffractometer Facility at the University of Hyderabad funded by DST (New Delhi), and the UPE and the CAS programs of the UGC for other equipment are gratefully acknowledged. We also thank Dr Regine Herbst-Irmer (Göttingen) for help in the refinement of the X-ray structure of **13b** and Mr P. Parameswaran for help with theoretical calculations.

References

1 Selected reviews: (*a*) O. Mitsunobu, *Synthesis*, 1981, 1–28; (*b*) D. L. Hughes, *Org. React.*, 1992, **42**, 335–656; (*c*) D. L. Hughes, *Org. Prep. Proced. Int.*, 1996, **28**, 127–164; (*d*) J. A. Dodge and S. A. Jones, *Recent Res. Dev. Org. Chem.*, 1997, **1**, 273–283.

2 (*a*) R. Hulst, A. van Basten, K. Fitzpatrick and R. M. Kellogg, *J. Chem. Soc., Perkin Trans. 1*, 1995, 2961–2963; (*b*) Z. Li, Z. Zhou, L. Wang, Q. Zhou and C. Tang, *Tetrahedron: Asymmetry*, 2002, **13**, 145–148.

3 For earlier literature on the formation of pentacoordinate compounds from the reactions of P^{III} species with DEAD/DIAD, see: (*a*) B. A. Arbuzov, N. A. Polezhaeva and V. S. Vinogradova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 2525–2529; (*b*) H. Gonclaves, J. R. Domroy, Y. Chapleur, B. Castro, H. Faudet and R. Burgada, *Phosphorus, Sulfur Relat. Elem.*, 1980, 147–152; (*c*) J. P. Majoral, R. Kraemer, T. ŃGando M'Pondo and J. Navech, *Tetrahedron Lett.*, 1980, **21**, 1307–1310.

4 (*a*) N. S. Kumar, P. Kommana, J. J. Vittal and K. C. Kumara Swamy, *J. Org. Chem.*, 2002, **67**, 6653–6658; (*b*) N. S. Kumar, K. P. Kumar, K. V. P. P. Kumar, P. Kommana, J. J. Vittal and K. C. Kumara Swamy, *J. Org. Chem.*, 2004, **69**, 1880–1889.

5 For other examples and reactions involving these compounds, see: K. P. Kumar, M. Chakravarty and K. C. Kumara Swamy, *Z. Anorg. Allg. Chem.*, 2004, **630**, 2063–2070.

6 Selected references: (*a*) D. J. H. Smith, in *Comprehensive Organic Chemistry*, ed. D. H. R. Barton and V. D. Ollis, Pergamon, Exeter, 1979, vol. 2, pp. 1233–1256; (*b*) W. S. Sheldrick, *Top. Curr. Chem.*, 1978, **73**, 1–48; (*c*) R. R. Holmes, *Pentacoordinated Phosphorus–Reaction Mechanisms*, ACS Monograph 176, vol. II, American Chemical Society, Washington, DC, 1980; (*d*) F. Bangerter, M. Karpf, L. A. Meier, P. Rys and P. Skrabal, *J. Am. Chem. Soc.*, 1998, **120**, 10653–10659; (*e*) A. E. Wróblewski and J. G. Verkade, *J. Am. Chem. Soc.*, 1996, **118**, 10168–10174; (*f*) M. L. Bojin, S. Barkallah and S. A. Evans Jr, *J. Am. Chem. Soc.*, 1996, **118**, 1549–1550; (*g*) A. Núñez and O. Núñez, *J. Org. Chem.*, 1996, **61**, 8386–8390; (*h*) J. Michalski, A. Skowronska, R. Bodalski, in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, ed. J. G. Verkade and L. D. Quin, VCH, Deerfield Beach, Florida, 1987, ch. 8, pp. 255–296.

7 Selected references: (*a*) R. Hoffmann, J. M. Howell and E. L. Muetterties, *J. Am. Chem. Soc.*, 1972, **94**, 3047–3058; (*b*) T. Uchimaru, W. J. Stec and K. Taira, *J. Org. Chem.*, 1997, **62**, 5793–5800; (*c*) H. Wasada and K. Hirao, *J. Am. Chem. Soc.*, 1992, **114**, 16–27; (*d*) H. Wasada and Y. Tsutsui, *Chem. Lett.*,

1995, 825; (*e*) J. A. Deiters and R. R. Holmes, *Organometallics*, 1996, **15**, 3944–3956.
8 For square pyramidal phosphorus see: (*a*) H. Wunderlich, D. Mootz, R. Schmutzler and M. Wieber, *Z. Naturforsch., B: Anorg. Chem. Org. Chem.*, 1974, **B29**, 32; (*b*) R. R. Holmes, *Prog. Inorg. Chem.*, 1984, **32**, 119–235; (*c*) I. V. Shevchenko, A. Fischer, P. G. Jones and R. Schmutzler, *Chem. Ber.*, 1992, **125**, 1325–1332.
9 S. Trippett, *Phosphorus, Sulfur Relat. Elem.*, 1976, **1**, 89–98.
10 (*a*) D. E. C. Corbridge, *Phosphorus 2000: Chemistry, Biochemistry and Technology*, Elsevier, Amsterdam, 4th edn, 2000, ch. 13, pp. 1137–1142; (*b*) M. Nakamoto, S. Kojima, S. Matsukawa, Y. Yamamoto and K.-y. Akiba, *J. Organomet. Chem.*, 2002, **643–644**, 441–452, (apicophilicity scale); (*c*) S. Matsukawa, K. Kajiyama, S. Kojima, S.-y. Furuta, Y. Yamamoto and K.-y. Akiba, *Angew. Chem., Int. Ed.*, 2002, **41**, 4718–4722; (*d*) S. Matsukawa, K. Kajiyama, S. Kojima, S.-y. Furuta, Y. Yamamoto and K.-y. Akiba, *Angew. Chem.*, 2002, **114**, 4912–4916, (apicophilicity scale).
11 (*a*) N. V. Timosheva, T. K. Prakasha, A. Chandrasekaran, R. O. Day and R. R. Holmes, *Inorg. Chem.*, 1995, **34**, 4525–4526; (*b*) T. K. Prakasha, A. Chandrasekaran, R. O. Day and R. R. Holmes, *Inorg. Chem.*, 1995, **34**, 1243–1247; (*c*) N. V. Timosheva, A. Chandrasekaran, T. K. Prakasha, R. O. Day and R. R. Holmes, *Inorg. Chem.*, 1996, **35**, 6552–6560; (*d*) S. Kojima, K. Kajiyama, M. Nakamoto and K.-y. Akiba, *J. Am. Chem. Soc.*, 1996, **118**, 12866–12867; (*e*) K. Kajiyama, M. Yoshimune, M. Nakamoto, S. Matsukawa, S. Kojima and K.-y. Akiba, *Org. Lett.*, 2001, **3**, 1873–1875; (*f*) J. Kobayashi, K. Goto, T. Kawashima, M. W. Schmidt and S. Nagase, *J. Am. Chem. Soc.*, 2002, **124**, 3703; (*g*) S. Kumaraswamy, C. Muthiah and K. C. Kumara Swamy, *J. Am. Chem. Soc.*, 2000, **122**, 964–965; (*h*) P. Kommana, S. Kumaraswamy, J. J. Vittal and K. C. Kumara Swamy, *Inorg. Chem.*, 2002, **41**, 2356–2363; (*i*) S. Kojima, M. Sugino, S. Matsukawa, M. Nakamoto and K.-y. Akiba, *J. Am. Chem. Soc.*, 2002, **124**, 7674–7675, and the references cited therein; (*j*) P. Kommana, N. S. Kumar, J. J. Vittal, E. G. Jayasree, E. D. Jemmis and K. C. Kumara Swamy, *Org. Lett.*, 2004, **6**, 145–148.
12 See, for example: (*a*) J. E. Huheey, E. A. Keiter and, R. L. Keiter, *Inorganic Chemistry—Principles of Structure and Reactivity*, Addison-Wesley Publishing Company (Harper Collins College Publishers), New York, 4th edn, 1993, p. 227; (*b*) G. Wulfsberg, *Inorganic Chemistry*, University Science Books, Sausalito, California (USA), 2000, p. 110.
13 For neutral hexacoordinate compounds with an S→P bond see: (*a*) R. R. Holmes, T. K. Prakasha and R. O. Day, *Inorg. Chem.*, 1993, **32**, 4360–4367; (*b*) T. K. Prakasha, R. O. Day and R. R. Holmes, *J. Am. Chem. Soc.*, 1993, **115**, 2690–2695; (*c*) C. Y. Wong, R. McDonald and R. G. Cavell, *Inorg. Chem.*, 1996, **35**, 325–334; (*d*) D. J. Sherlock, A. Chandrasekaran, R. O. Day and R. R. Holmes, *J. Am. Chem. Soc.*, 1997, **119**, 1317–1322; (*e*) A. Chandrasekaran, R. O. Day and R. R. Holmes, *J. Am. Chem. Soc.*, 1997, **119**, 11434–11441; (*f*) P. Sood, A. Chandrasekaran, R. O. Day and R. R. Holmes, *Inorg. Chem.*, 1998, **37**, 6329–6336.
14 (*a*) C. Y. Wong, D. K. Kennepohl and R. G. Cavell, *Chem. Rev.*, 1996, **96**, 1917–1951; (*b*) R. R. Holmes, *Chem. Rev.*, 1996, **96**, 927–950; (*c*) K. C. Kumara Swamy, S. Kumaraswamy, M. A. Said, R. Herbst-Irmer and M. Pülm, *Curr. Sci.*, 2000, **78**, 473–478.
15 (*a*) M. A. Said, M. Pülm, R. Herbst-Irmer and K. C. Kumara Swamy, *J. Am. Chem. Soc.*, 1996, **118**, 9841–9849, and the references cited therein for earlier work; (*b*) N. V. Timosheva, A. Chandrasekaran and R. R. Holmes, *Inorg. Chem.*, 2004, **43**, 7403–7411.
16 R. R. Holmes, *Acc. Chem. Res.*, 2004, **37**, 746–753.
17 M. A. Said, M. Pülm, R. Herbst-Irmer and K. C. Kumara Swamy, *Inorg. Chem.*, 1997, **36**, 2044–2051.
18 (*a*) A. E. Reed and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1990, **112**, 1434–1445; (*b*) M. Lattman, Hypervalent Compounds, in *Encyclopedia of Inorganic Chemistry*, ed. R. B. King, John Wiley & Sons, Chichester, England, 1994, vol. 3, pp. 1496–1511.
19 See ref. 10, p. 69; we have used the Pauling electronegativity for this calculation.
20 See ref. 10, p. 72 and D. F. Shriver and D. W. Atkins, *Inorganic Chemistry*, Oxford University Press, Oxford, 3rd edn, 1999, pp. 24 and 71.
21 In most of the compounds using the same type of sulfur containing ligand, sulfur is *trans* to the acyclic substituent except in S[4,6-(t-Bu)$_2$C$_6$H$_2$O]$_2$P(OCH$_2$CF$_3$)[2,2′-O$_2$(C$_6$H$_4$)$_2$]. See ref. 13 and T. K. Prakasha, R. O. Day and R. R. Holmes, *Inorg. Chem.*, 1992, **31**, 3391–3397.
22 Previously, we have shown that the ^{31}P NMR spectrum recorded at low temperature immediately upon dissolution also shows the same pattern as the one obtained by dissolving at room temperature and then lowering the temperature. See ref. 4*a*.
23 This compound could be isolated as a solid (mp 114–116 °C). The ^{1}H NMR spectrum for this compound also showed a complex pattern.
24 (*a*) S. Kumaraswamy, P. Kommana, N. S. Kumar and K. C. Kumara Swamy, *Chem. Commun.*, 2002, 40–41; (*b*) S. Kumaraswamy, K. S. Kumar, N. S. Kumar and K. C. Kumara Swamy, *Dalton Trans.*, 2005, 1847–1851.
25 Selected references: (*a*) D. Schomburg, U. Wermuth and R. Schmutzler, *Chem. Ber.*, 1987, **120**, 1713–1718; (*b*) K. C. Kumara Swamy, J. M. Holmes, R. O. Day and R. R. Holmes, *J. Am. Chem. Soc.*, 1990, **112**, 6092–6094; (*c*) J. H. Yu, A. M. Arif and W. G. Bentrude, *J. Am. Chem. Soc.*, 1990, **112**, 7451–7461; (*d*) S. D. Burton, K. C. Kumara Swamy, J. M. Holmes, R. O. Day and R. R. Holmes, *J. Am. Chem. Soc.*, 1990, **112**, 6104–6115; (*e*) R. R. Holmes, K. C. Kumara Swamy, J. M. Holmes and R. O. Day, *Inorg. Chem.*, 1991, **30**, 1052–1062; (*f*) T. K. Prakasha, S. D. Burton, R. O. Day and R. R. Holmes, *Inorg. Chem.*, 1992, **31**, 5494–5499; (*g*) S. Kojima, K. Kajiyama and K.-y. Akiba, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 1785–1797; (*h*) M. Gorg, E. Lork, A. A. Kolomeitsev and G.-V. Röschenthaler, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1997, **127**, 15–25; (*i*) X.-D. Liu and J. G. Verkade, *Inorg. Chem.*, 1998, **37**, 5189–5197, (an unusual salt with fused five-membered rings); (*j*) H. Nakazawa, K. Kawamura, K. Kubo and K. Miyoshi, *Organometallics*, 1999, **18**, 2961–2969, (metallophosphoranes); (*k*) N. Thirupathi, S. S. Krishnamurthy and M. Nethaji, *Inorg. Chem.*, 1999, **38**, 1093–1098; (*l*) R. Sonnenburg, I. Neda, H. Thönnessen, P. G. Jones and R. Schmutzler, *Z. Anorg. Allg. Chem.*, 2000, **626**, 412–420; (*m*) C. Muthiah, M. A. Said, M. Pülm, R. Herbst-Irmer and K. C. Kumara Swamy, *Polyhedron*, 2000, **19**, 63–68.
26 Highly constrained six-membered ring systems are an exception. See: Y. Huang, A. M. Arif and W. G. Bentrude, *J. Am. Chem. Soc.*, 1991, **113**, 7800–7802.
27 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon, Oxford, UK, 1986.
28 S. D. Pastor, J. D. Spivack and L. P. Steinhuebel, *J. Heterocycl. Chem.*, 1984, **21**, 1285–1287.
29 (*a*) G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997; (*b*) G. M. Sheldrick, *SADABS, Program for area detector adsorption correction*, Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996; (*c*) G. M. Sheldrick, *SHELXTL NT Crystal Structure Analysis Package*, Bruker AXS, Analytical X-ray System, WI, USA, 1999, version 5.10.
30 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 (Revision C.02)*, Gaussian, Inc., Wallingford, CT, 2004.

