

# Cyclic hexacoordinate phosphorus compounds

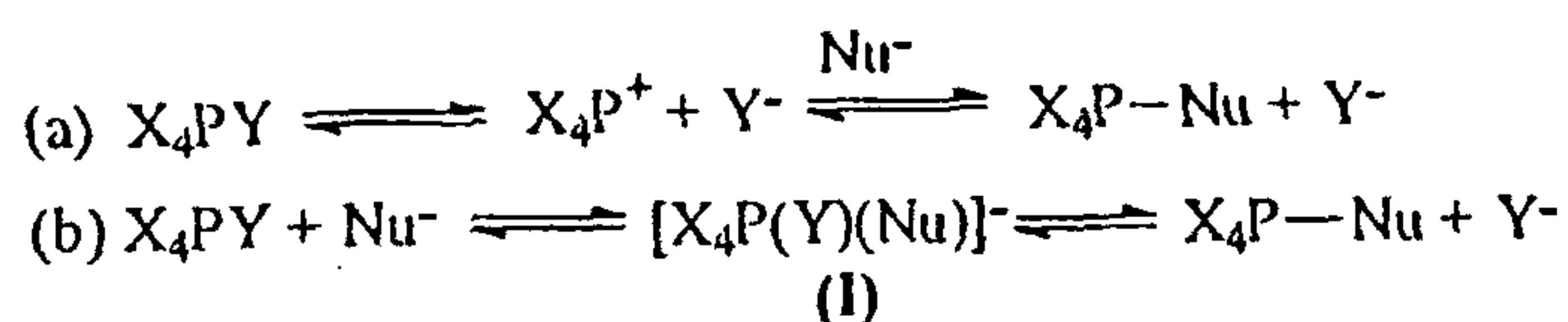
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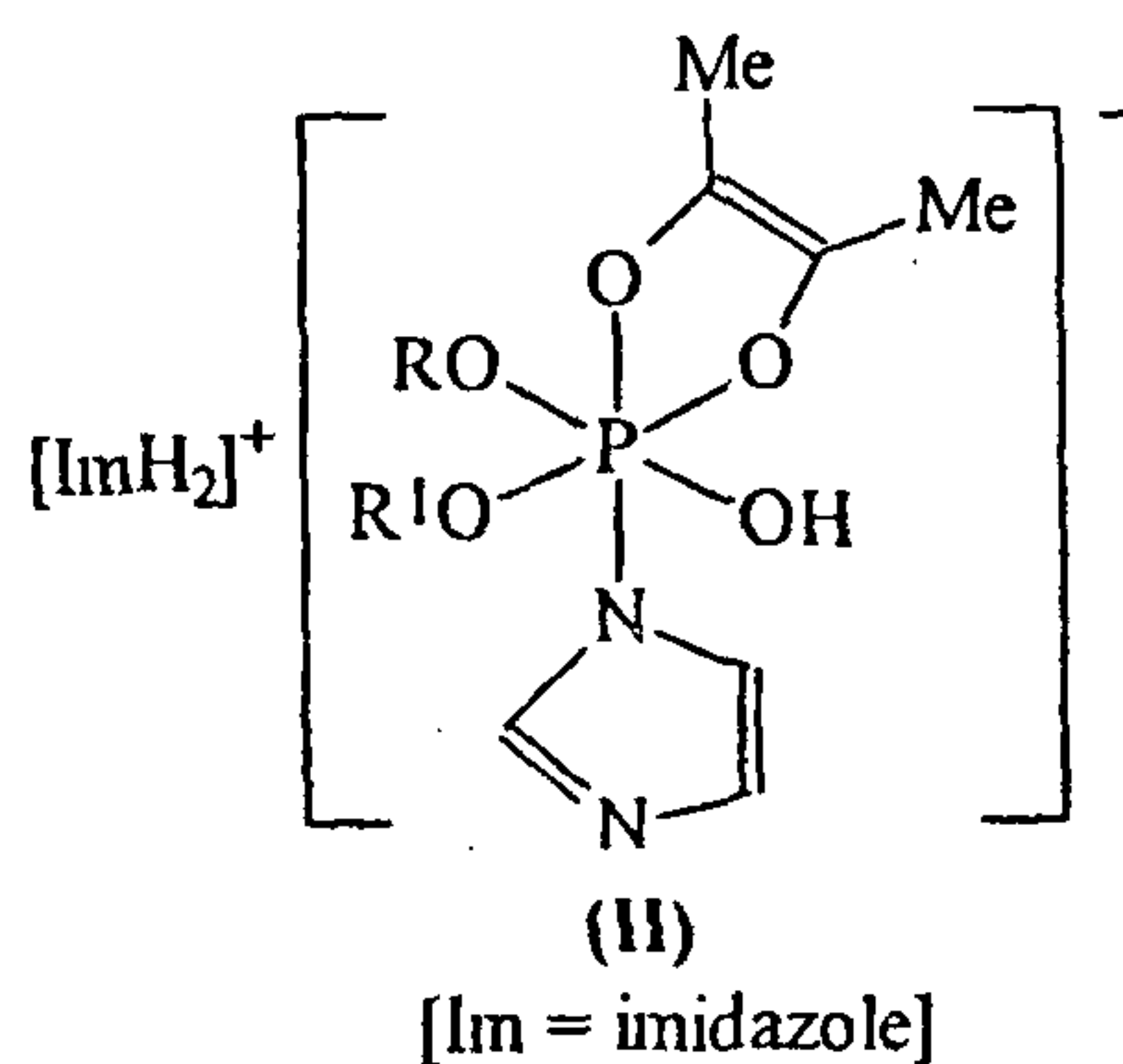
New developments on anionic, cationic and neutral hexacoordinate phosphorus compounds in which phosphorus is a part of a ring are described. Relevance of these species to an understanding of the reaction mechanisms at both tetra-coordinate and pentacoordinate phosphorus(V) centres is highlighted.

THE pentacoordinate state for phosphorus is now well-documented particularly in the context of reactions at a tetrahedral P(V) centre<sup>1</sup>. While considering the substitution at pentacoordinate phosphorus (X<sub>4</sub>PY) itself, two different pathways (a) and (b) can be envisaged<sup>2</sup>. The associative mechanism (b) would entail an anionic hexacoordinate species (I). This type of mechanism is very likely for pentacoordinate phosphorus because of its Lewis acidity, provided that no steric inhibition operates. The existence of a species such as (I) has been



previously established by Westheimer<sup>3a</sup> as well as Trippett<sup>3b</sup>. In addition to these, Ramirez and coworkers have proposed involvement of the hexacoordinate species (II) in the nucleophilic catalysis of the phosphorylation of alcohols R<sup>1</sup>OH by the cyclic phosphate (RO)P(O)[OC(Me)=C(Me)O] in the presence of imidazole<sup>4</sup>. It is also likely that in reactions involving phosphates in biological systems (e.g. activation of tyrosine in the tyrosyl-tRNA synthetase system or in the hydrolysis of *cycl*-3',5'-AMP), donor action by oxygen/nitrogen may lead to a transient hexacoordinate species<sup>5,6</sup>. Thus, a study of hexacoordinate phosphorus holds some relevance to the mechanisms of reactions involving tetra- or pentacoordinate phosphorus centres. It can be expected that electronegative substituents increase the Lewis acidity of the phosphorus centre and hence promote intramolecular acid-base adduct forma-

tion with an increase in the coordination number of the central atom. Thus a significant number of studies on



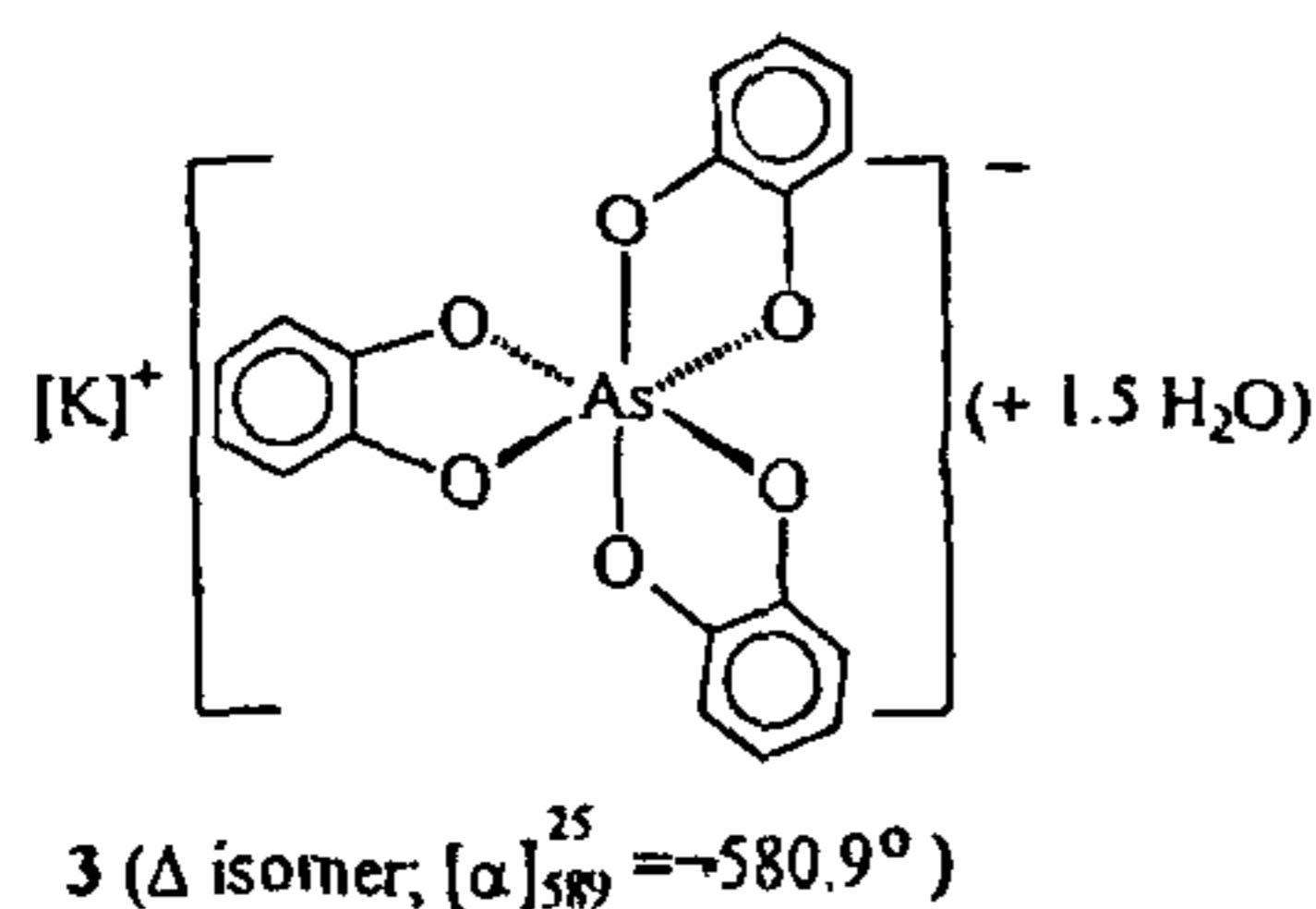
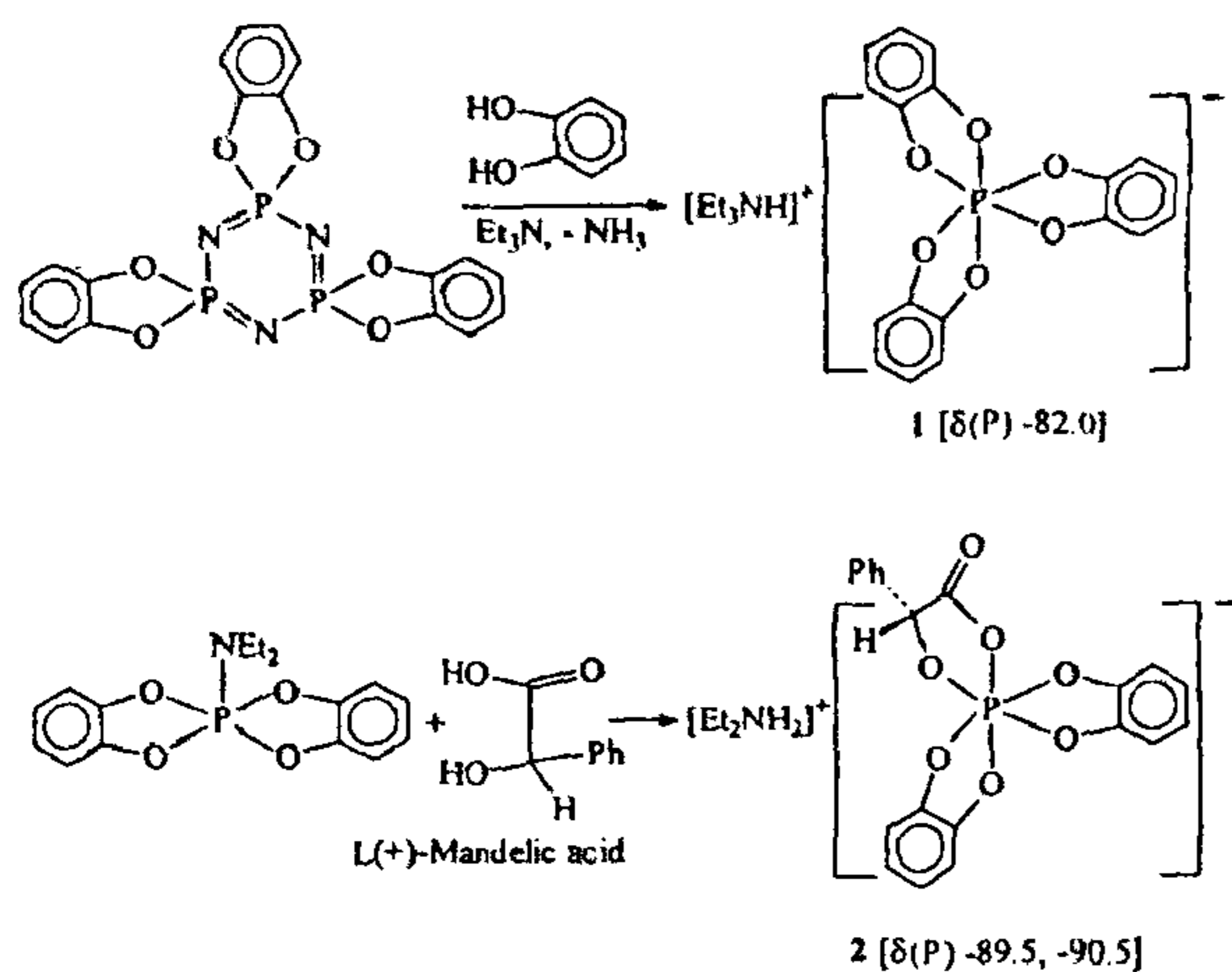
systems with phosphorus bearing the more electronegative oxygen or fluorine substituents have been carried out; the donor site is very often nitrogen although examples with sulfur, oxygen or phosphorus as the coordinating atoms are also known. The purpose of this report is to highlight some important developments in this area, with some input from our own work which includes the X-ray structure of the new phosphorane (NC<sub>9</sub>H<sub>6</sub>O)P(OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)(O<sub>2</sub>C<sub>2</sub>Ph<sub>2</sub>) (**24a**); for an exhaustive treatment of earlier work the reviews by Cavell<sup>7</sup> and Holmes<sup>6</sup> may be referred to. Where appropriate, some reference to arsenic systems will also be made.

## Anionic hexacoordinate phosphorus

Two compounds bearing cyclic substituents are shown in Scheme 1 along with a synthetic route for each<sup>8,9</sup>. While **1** represents one of the first structurally characterized hexacoordinated spirophosphoranes, **2** is an example wherein the diastereomers are readily identified by <sup>31</sup>P NMR. The synthesis of **2** represents a general route to hexacoordinated compounds.

Compound **1** should, in principle, exist in the Λ and Δ forms, but because of configurational lability it has not been resolved into its enantiomers. This feature contrasts with that of the corresponding arsenic analogue **3** which could be obtained in an optically pure Δ form (as a hydrate)<sup>10</sup>. In the case of phosphorus, the tetrachlorocatecholate [P(1,2-O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>3</sub>]<sup>-</sup> {δ(P): -79 to -82

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depending on the cation] is configurationally stable as an amine salt and can be resolved readily; the salts are conveniently prepared by treating tetrachlorocatechol with  $\text{PCl}_5$  in toluene in the presence of a suitable amine<sup>11</sup>. The ammonium salt of this anion (R or S configuration) undergoes diastereoselective ion pairing with racemic  $[\text{Fe}(4,4'\text{-Me}_2\text{-bipy})_3]^{2-}$  (R + S)<sup>12</sup>.

When the pentacoordinate compound **4** is treated with phenol and triethylamine, four distinct hexacoordinate species (**5–8**) are observed (Chart 1) in addition to unreacted **4** and  $\text{PhOP}(1,2\text{-O}_2\text{C}_6\text{H}_4)_2$  (**9**) (ref. 2). Two of these (**7** and **8**) have been independently synthesized from **9**. The exchange of ligands as shown here is probably the reason for the configurational instability of these hexacoordinated compounds.

A remarkable compound in this series is **10** which has six carbons around phosphorus and an extremely high molecular rotation<sup>6b,13</sup>; the symmetrical disposition of the three 5-membered rings around phosphorus is probably the reason for its stability.

### Cationic hexacoordinate phosphorus

There are a few studies on cationic hexacoordinate compounds; an example of this type of species is **11**,

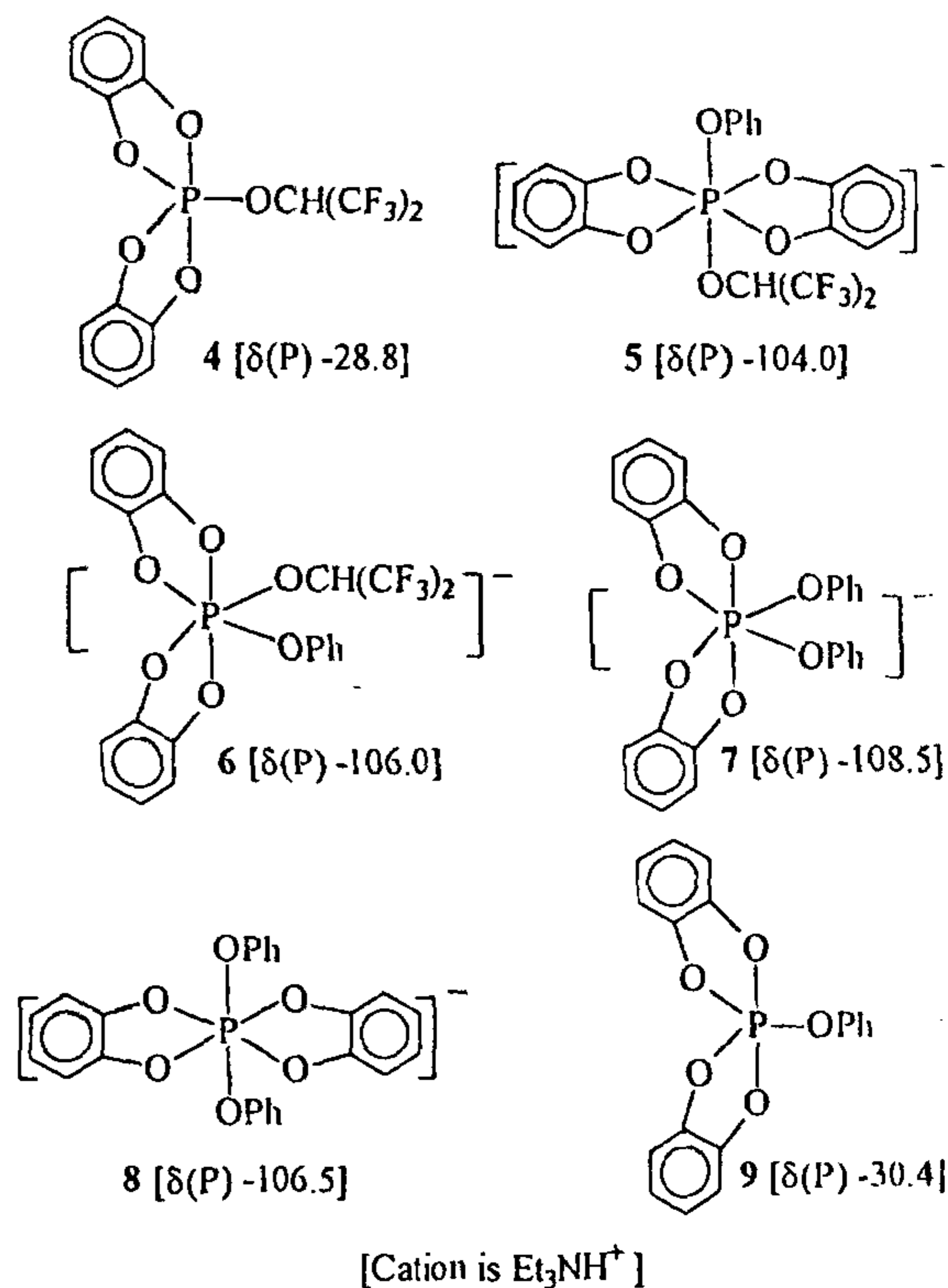
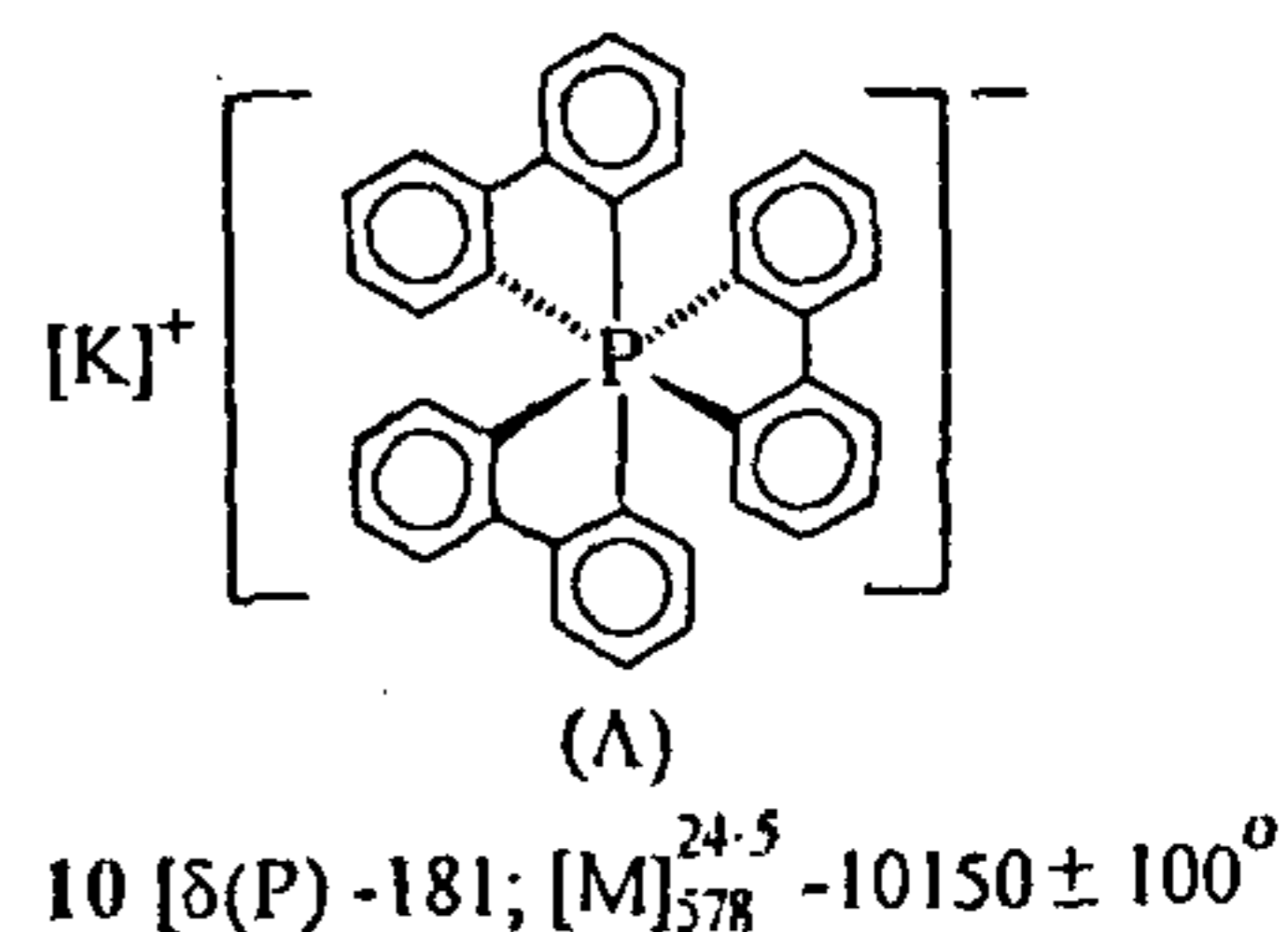


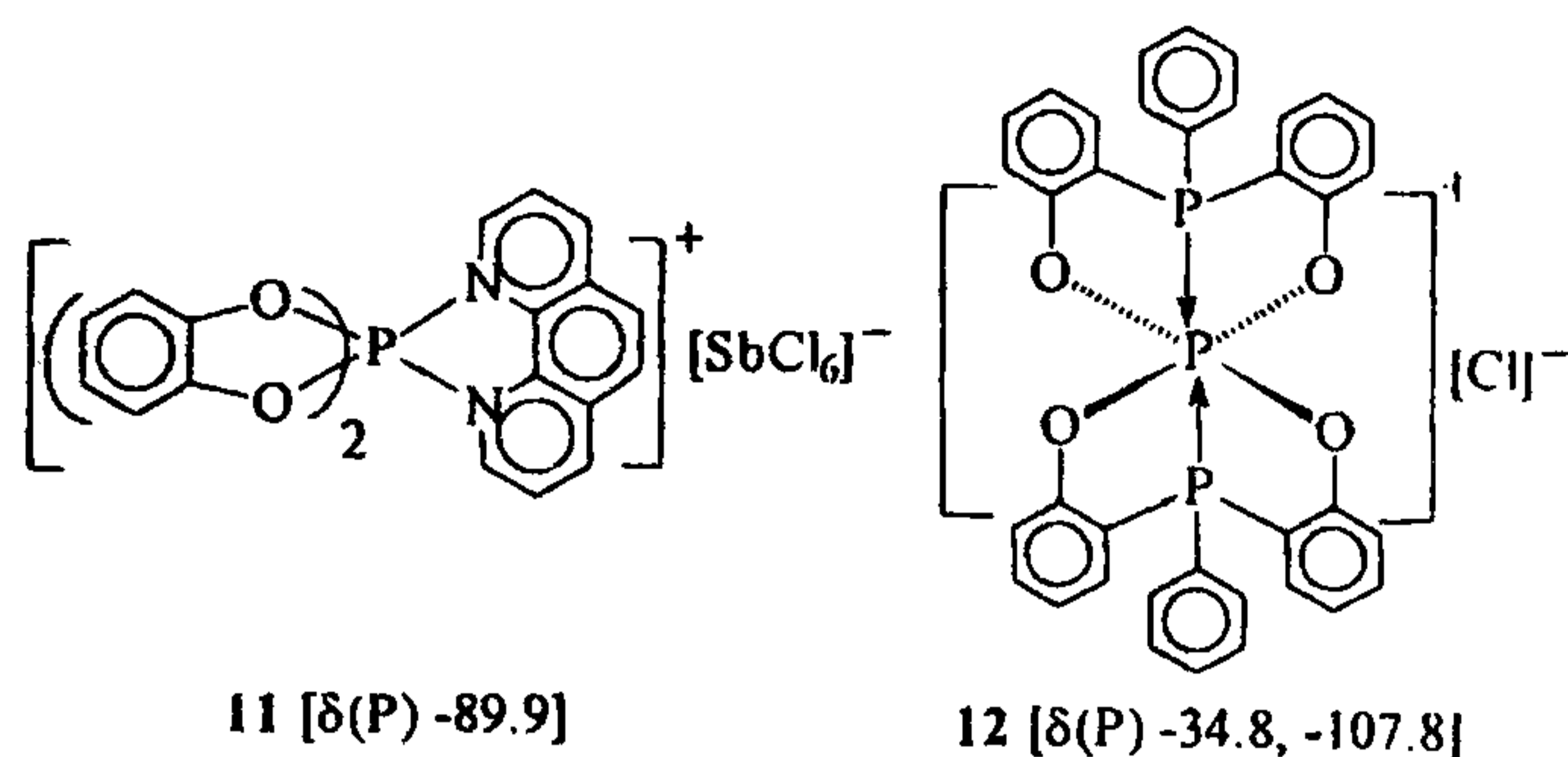
Chart 1.



prepared by treating  $[(\text{C}_6\text{H}_4\text{O}_2)_2\text{P}]^+[\text{SbCl}_6]^-$  with 1,10-phenanthroline<sup>14</sup>. Another unique compound **12** with two P(III)  $\rightarrow$  P(V) bonds has been recently reported by Cavell and coworkers<sup>15</sup>. Since it is unlikely that such cationic species are involved in nucleophilic substitution reactions of pentacoordinate compounds of our interest, this topic is not being elaborated on.

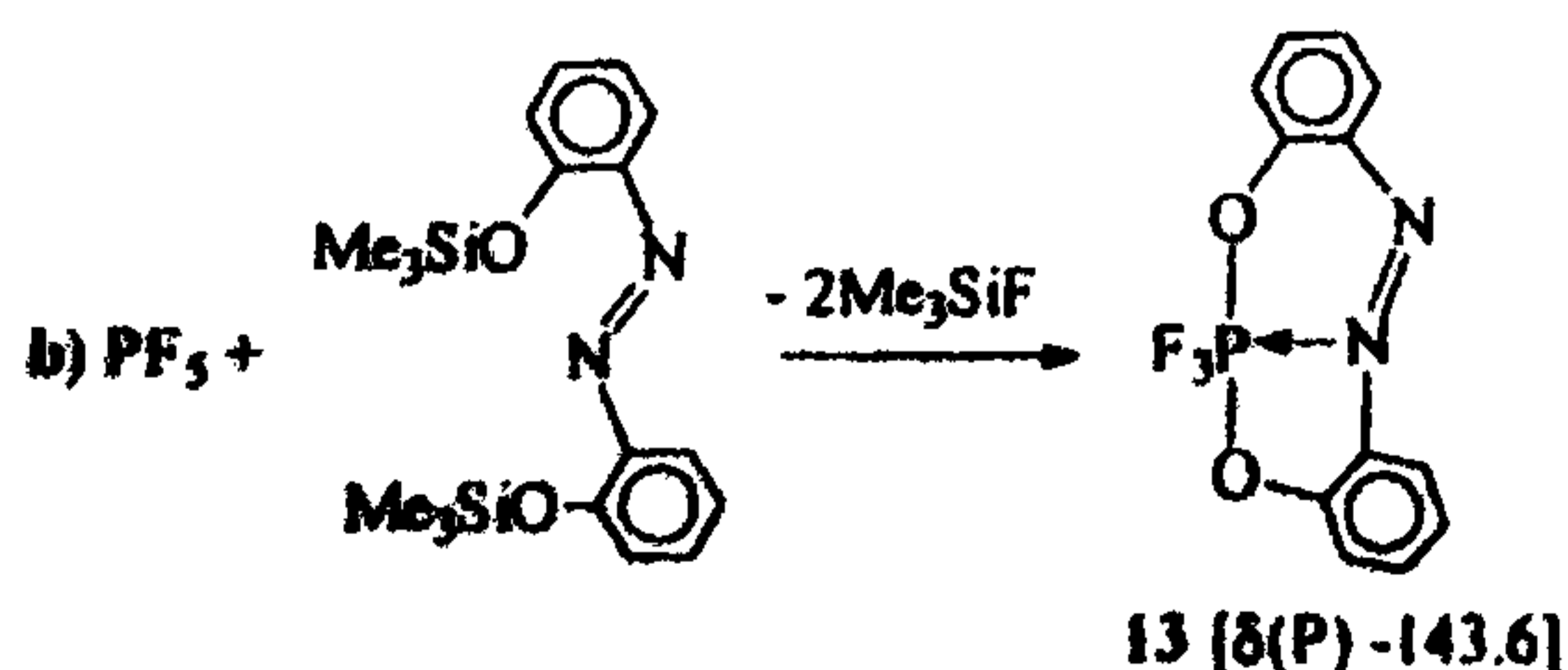
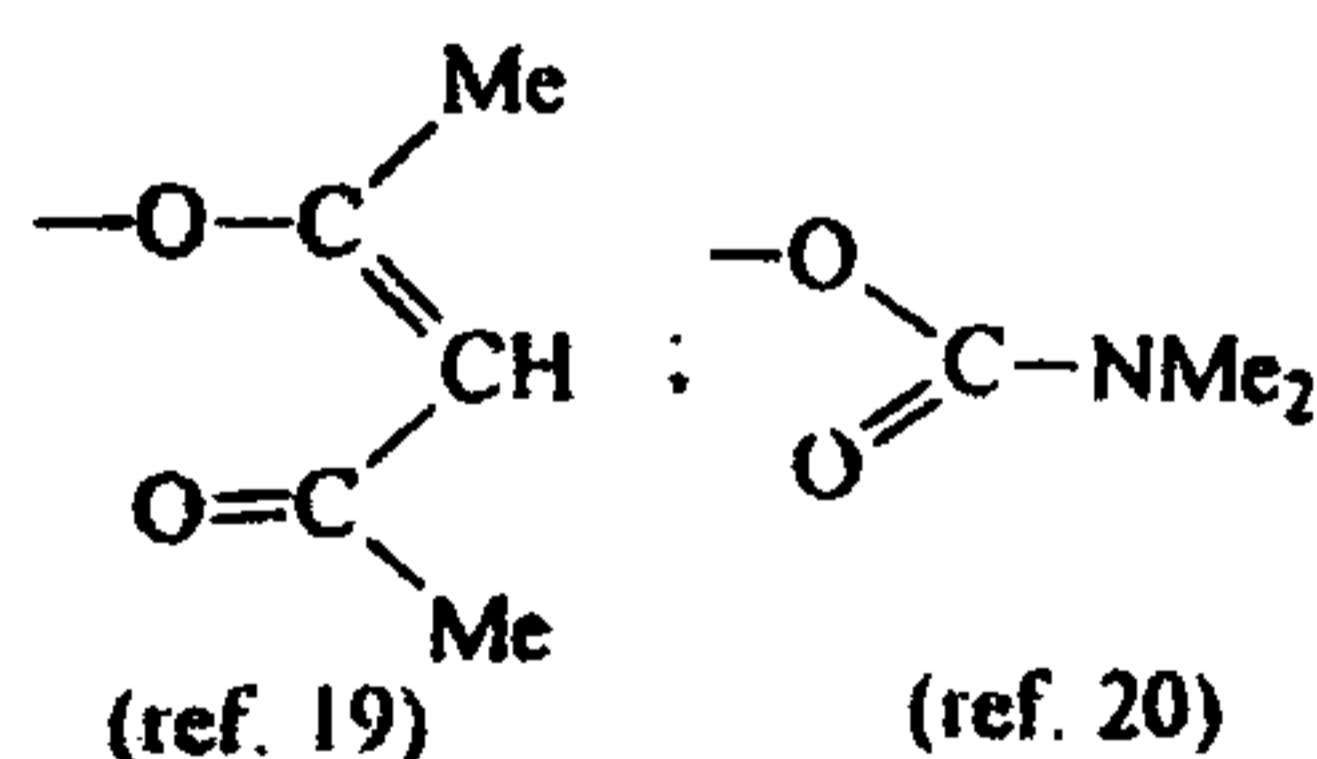
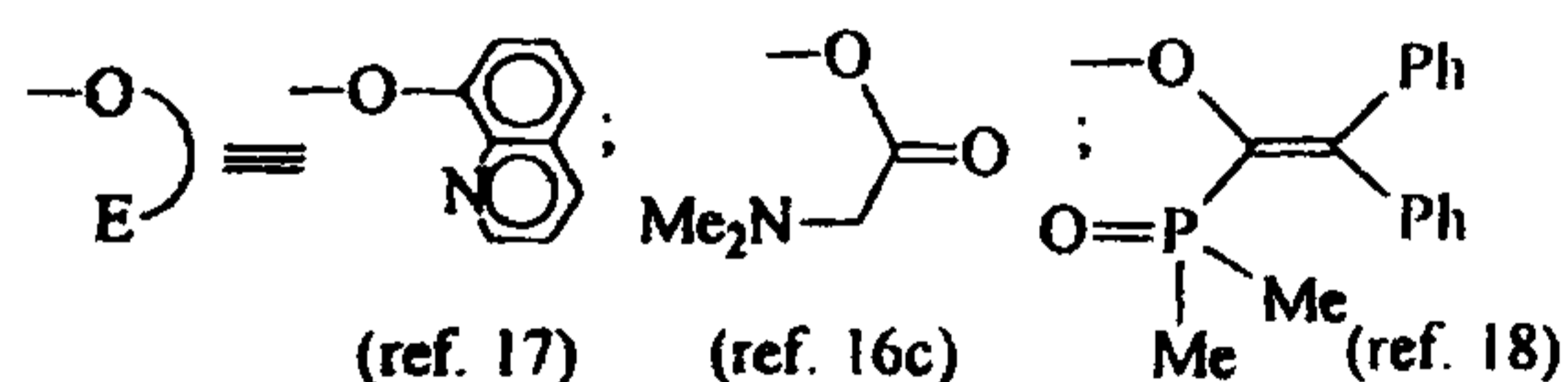
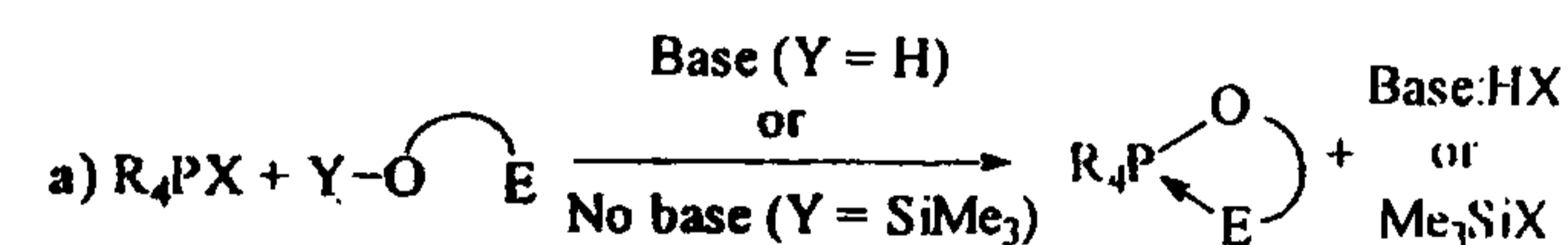
### Neutral hexacoordinate phosphorus

This category constitutes the largest number of compounds studied thus far, and is quite important in connection with the mechanism of reactions at pentacoordinate phosphorus<sup>7</sup>. A large body of early

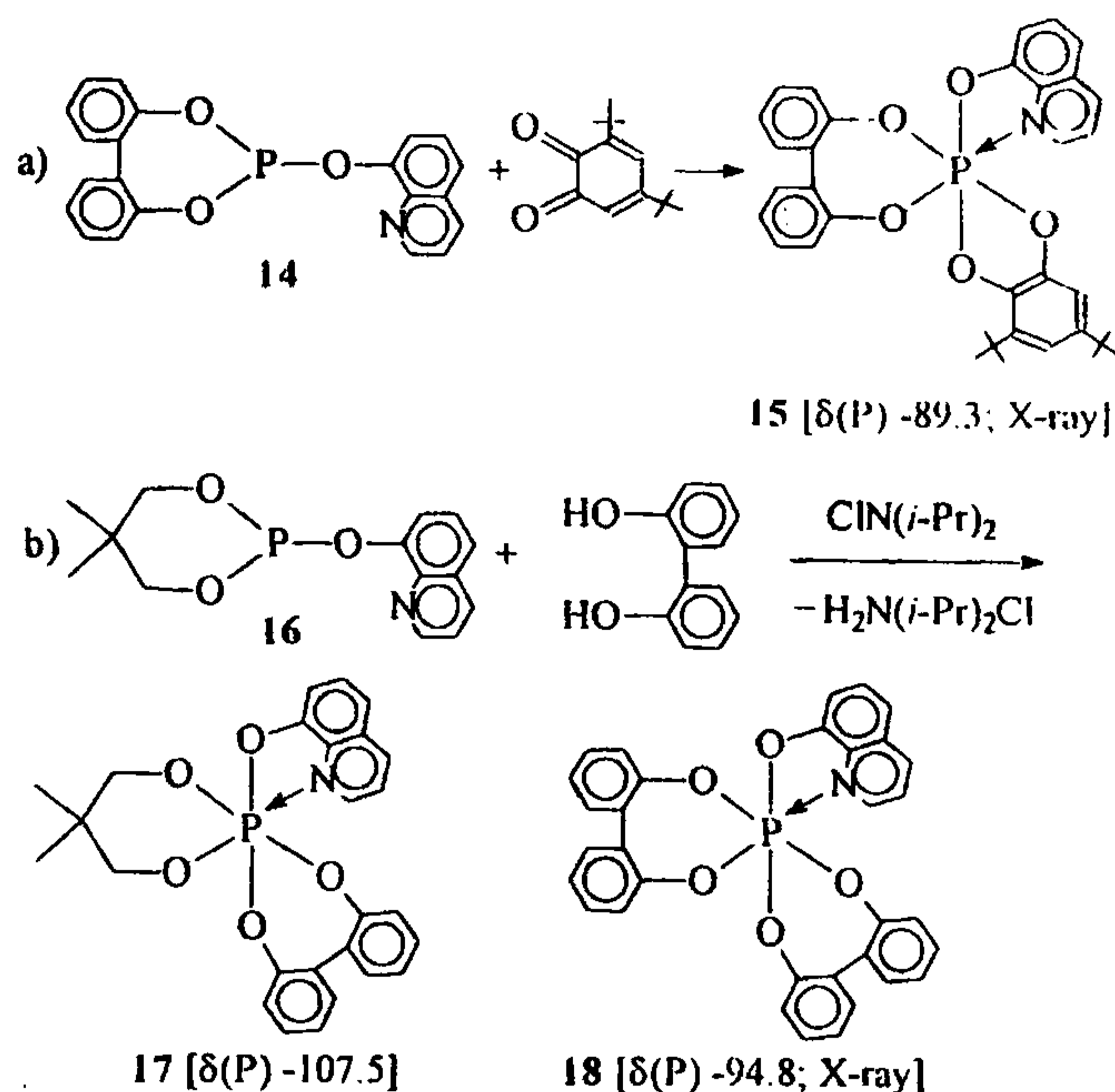


work is available on simple acid-base adducts of the type  $X_5P:Base$ <sup>16</sup>. In general, the coordinating atom at the sixth site can be N, O, P or S. A general route to these hexacoordinate systems is by reacting the compounds  $R_4PX$  with a nucleophile such as  $YO-E$  ( $Y = H$  or  $SiMe_3$ ;  $E = N, S, O, P$ ) by elimination of  $YX$  (Scheme 2)<sup>16-20</sup>. This approach can be extended to replace two  $X$  groups on  $P$  in  $(CF_3)_nPX_{5-n}$  by a tridentate Schiff base; this route has been employed for compound 13 [Scheme 2(b)] (ref. 21).

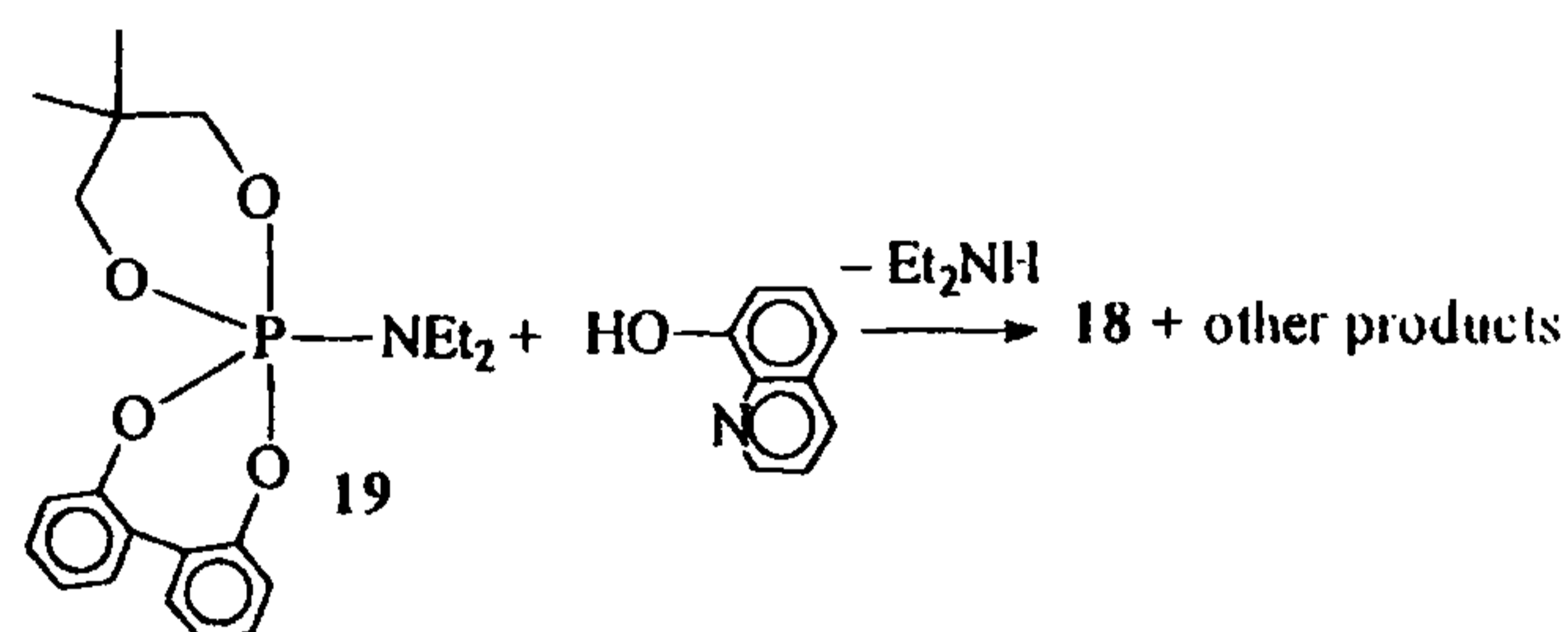
An alternate route, which we have utilized, is to start with a suitable  $P(III)$  precursor possessing a potential donor site (N, O or S) and add to it a quinone or diol, oxidatively (Scheme 3). The latter method (using diol/ $N$ -chlorodiisopropylamine) is interesting in that, in addition to the expected normal product such as 17 (Scheme 3), a ring-exchanged product such as 18 is also obtained from the reaction mixture<sup>22</sup>. In fact, the yield of 18 was increased on using more (~3-fold excess) of



Scheme 2.

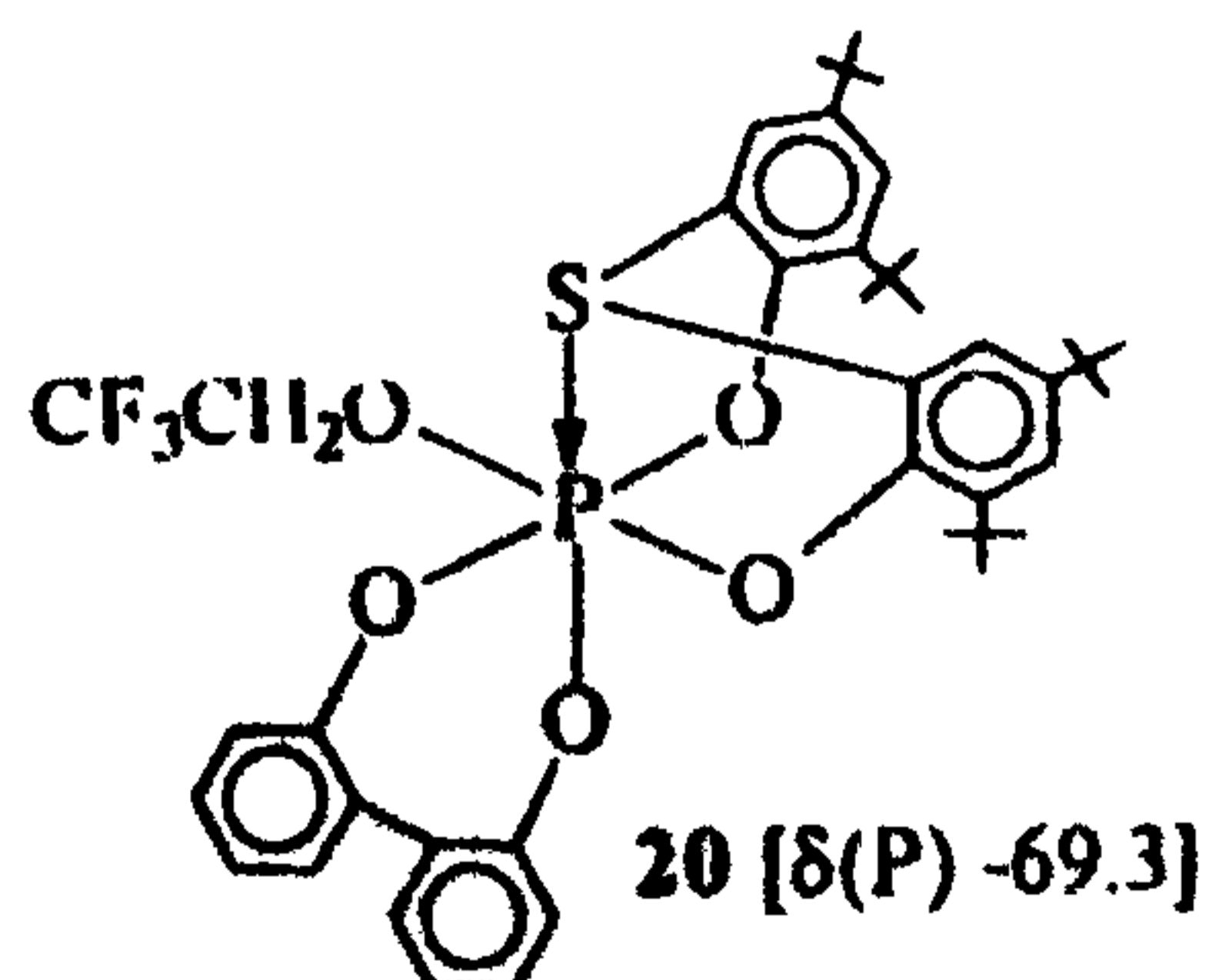


Scheme 3.



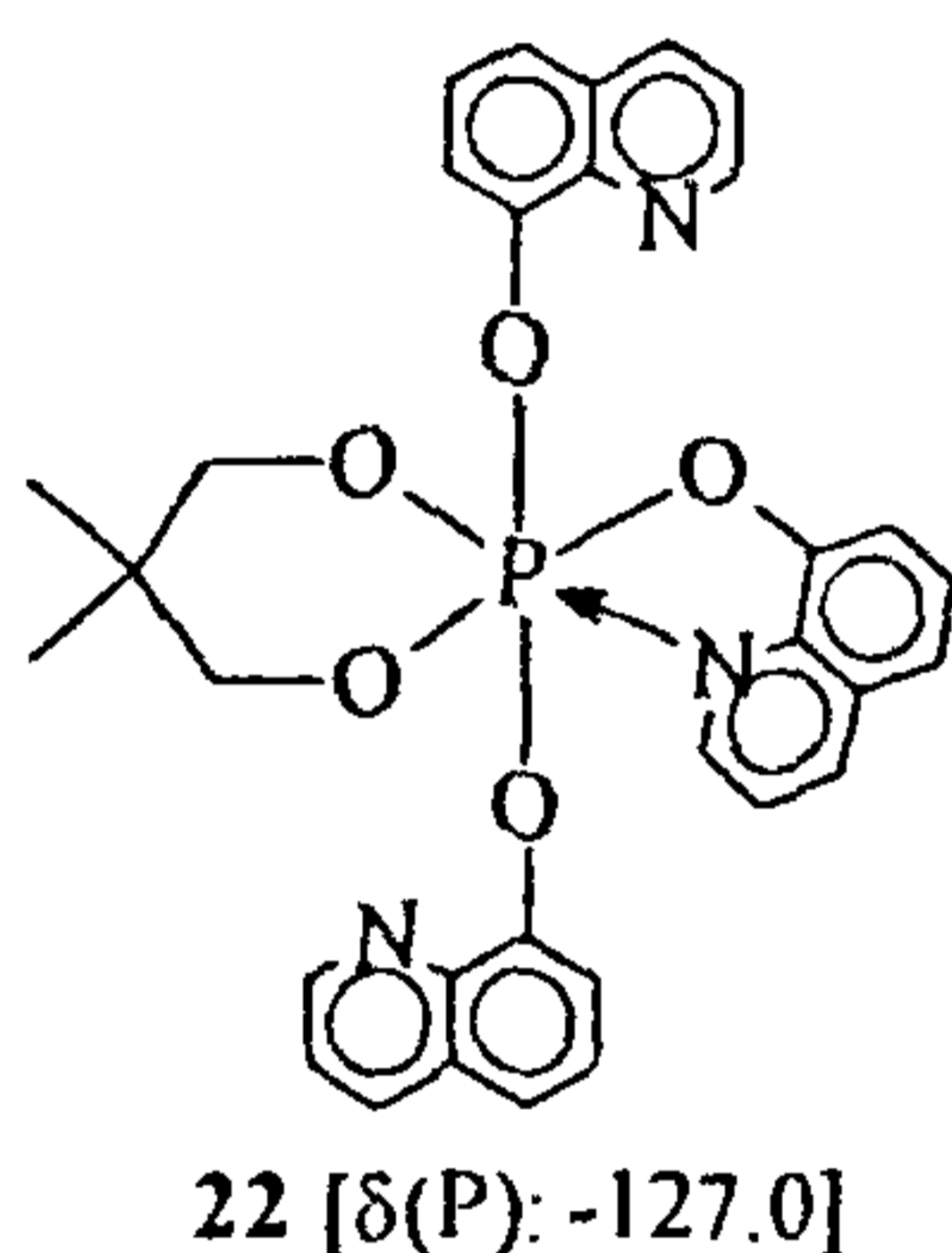
Scheme 4.

biphenol. In a rather surprising reaction, compound 18 was also isolated when the aminophosphorane 19 was treated with 8-hydroxyquinoline (Scheme 4). Here again, exchange of the six-membered phosphorinane ring by the seven-membered phosphepin ring has taken place in addition to the displacement of the diethylamino group by oxinate. Such a feature is reminiscent of the exchange of  $-OCH(CF_3)_2$  for the  $OPh$  group in the anionic compounds alluded to in Chart 1.

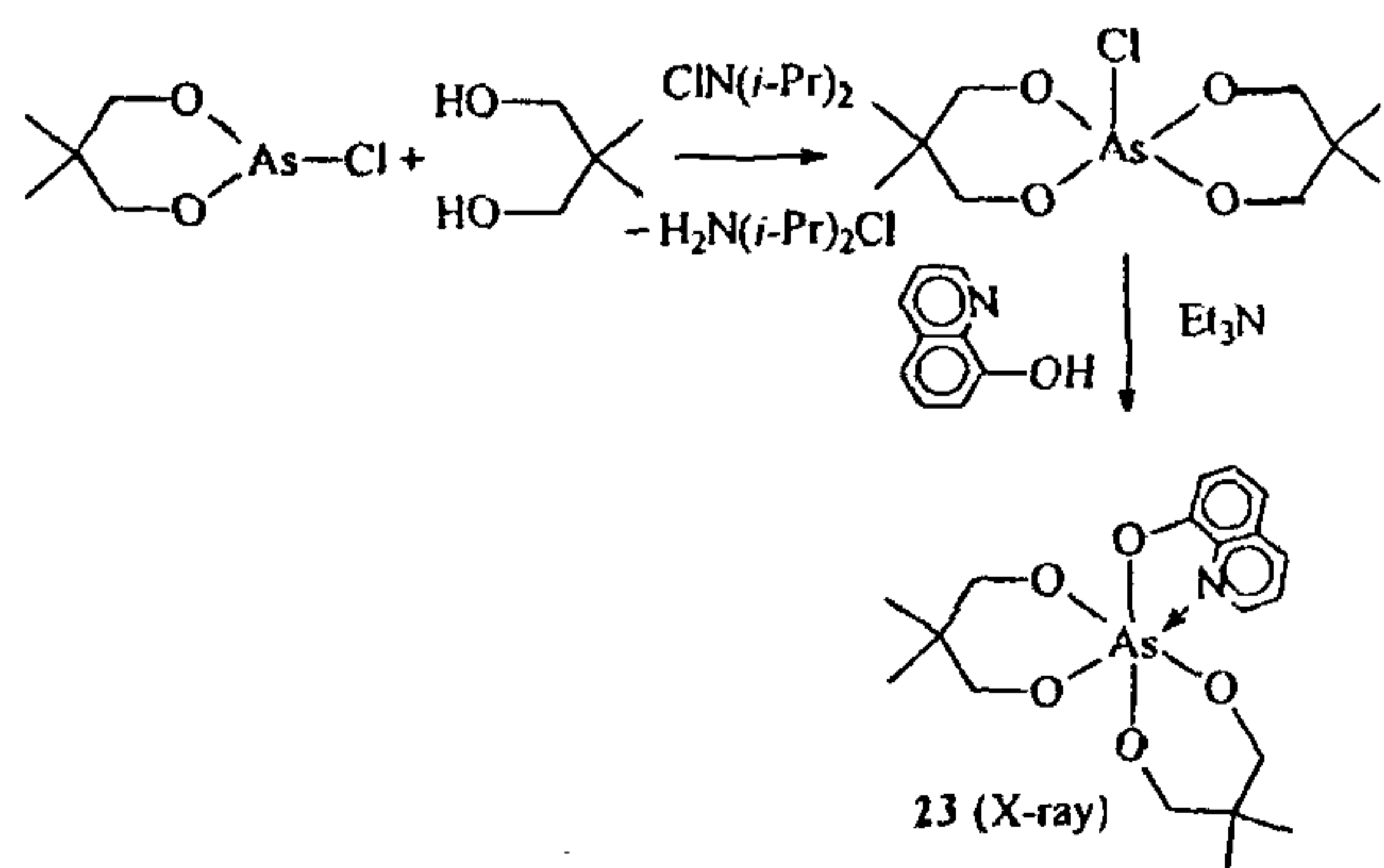


Route (b) has also been utilized by Holmes and co-workers to synthesize S → P bonded compounds such as **20** (ref. 23).

In the reaction of (OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)P(OC<sub>9</sub>H<sub>6</sub>N) (**16**) with 2,2-dimethyl-1,3-propanediol in the presence of ClNPr<sub>2</sub>, initially the reaction mixture exhibited a peak at ca. -67.0 ppm ascribable to (OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>P(OC<sub>9</sub>H<sub>6</sub>N) (**21**) with no N → P coordination. Upon attempted crystallization, the air-sensitive product **22** [ $\delta(\text{P})$ : -127.0] was isolated in ca. 10% yield. A partial X-ray structure (the sample was not stable enough to get a good set of data) showed that here again one of the six-membered rings was given up for the two oxinates to give **22**; the low yield of **22** suggests the presence of

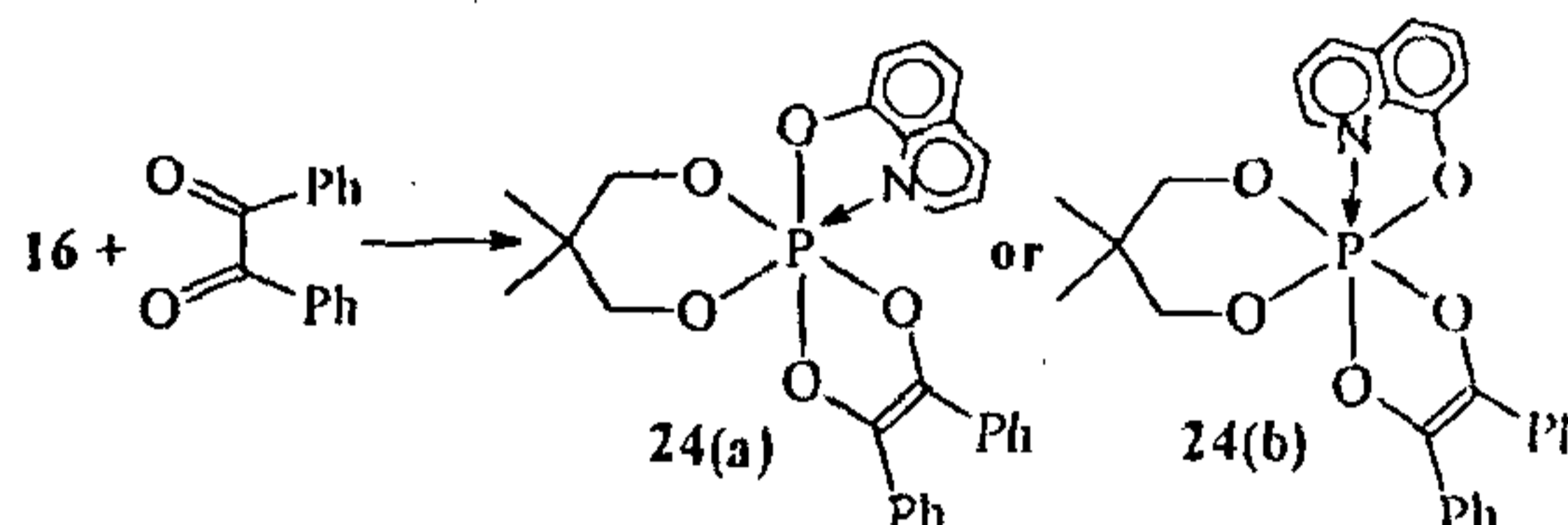


other products also, but they could not be isolated. It is worth mentioning here that although compound **21** could not be isolated due to its instability, the corresponding arsenic derivative could be isolated rather readily<sup>24</sup> (Scheme 5). The greater stability of **23** *vis-à-vis* **21** may be attributed to the greater Lewis acidity of As(V) relative to P(V), which makes hexacoordination more favourable for arsenic.

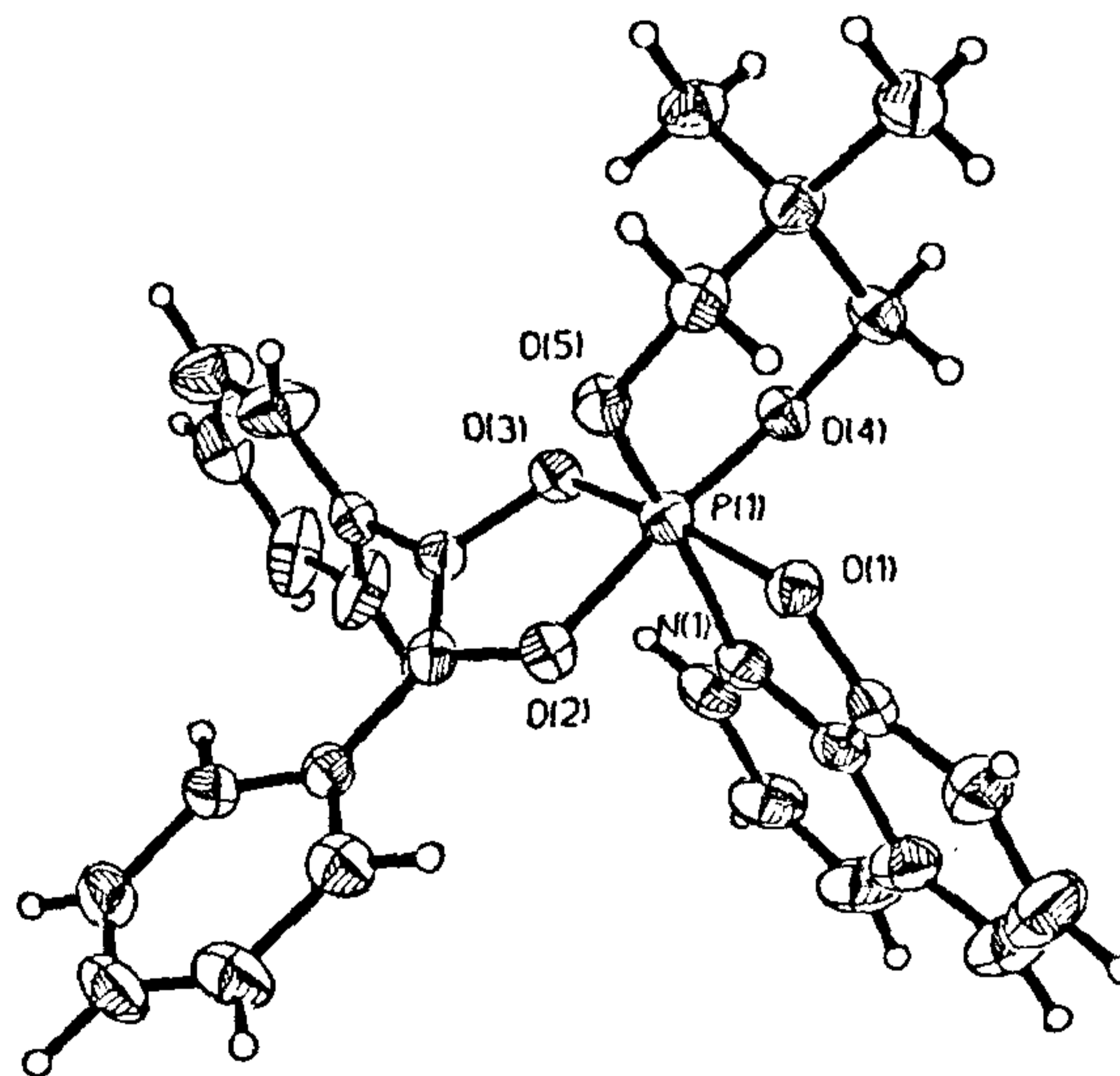


Scheme 5.

In the structure of **15** (Scheme 3) it can be noted that the oxinate nitrogen is *trans* to an oxygen of the seven-membered ring; the other isomer in which it is *trans* to an oxygen of the five-membered ring is not observed. In order to probe this aspect further, we treated **16** with benzil<sup>25</sup> (Scheme 6). Interestingly, of the two possible isomers **24a** and **24b**, we obtained only one isomer **24a** in which the oxinate nitrogen is *trans* to an oxygen of the six-membered ring, as revealed by X-ray crystallography (Figure 1) (refs 26, 27). Although the P-N bond is quite long in this compound, it is well within the sum of the van der Waals radii<sup>28</sup>, and is comparable to that observed in analogous structures<sup>7,22</sup>. A point worth mentioning here is that this bond length [2.026(2) Å] is pretty close to the N → As bond length [2.045(4) Å] observed in the arsenic compound **23** mentioned above.



Scheme 6.



**Figure 1.** An ORTEP drawing of **24a**. Selected bond distances and bond angles: P(1)-O(1) 1.721(2), P(1)-O(2) 1.700(2), P(1)-O(3) 1.678(2), P(1)-O(4) 1.654(2), P(1)-O(5) 1.621(2), P(1)-N(1) 2.026(2) Å. O(5)-P-O(4) 98.71(10), O(5)-P-O(3) 96.60(10), O(4)-P(1)-O(3) 86.93(10), O(5)-P(1)-O(2) 92.31(10), O(4)-P(1)-O(2) 168.79(9), O(3)-P(1)-O(2) 89.80(10), O(5)-P(1)-O(1) 91.61(10), O(4)-P(1)-O(1) 94.23(10) O(3)-P(1)-O(1) 171.44(9), O(2)-P(1)-O(1) 87.46(10), O(5)-P(1)-N(1) 173.94(9), O(4)-P(1)-N(1) 85.40(10), O(3)-P(1)-N(1) 88.03(10), O(2)-P(1)-N(1) 83.77(10), O(1)-P(1)-N(1) 83.61(10).

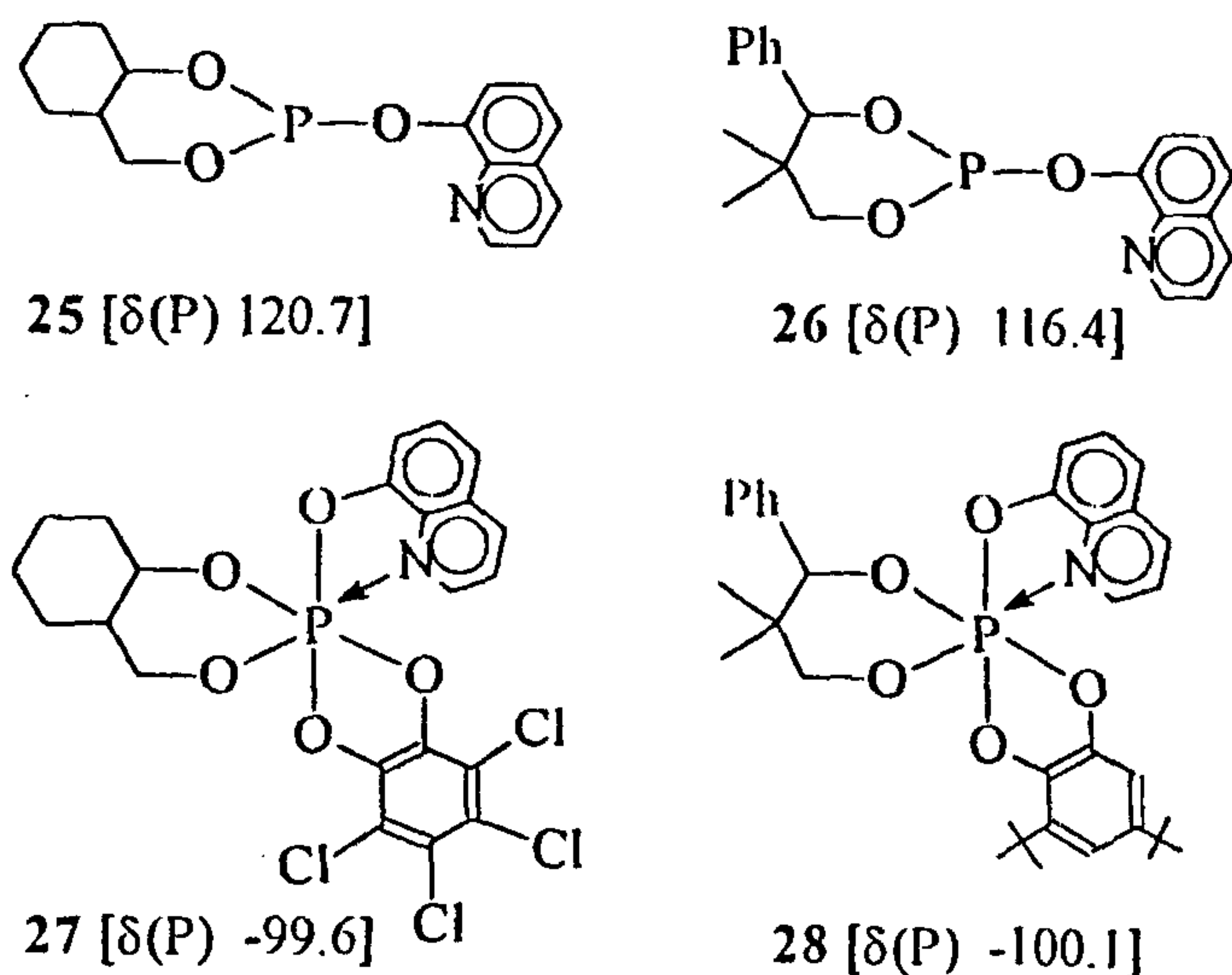
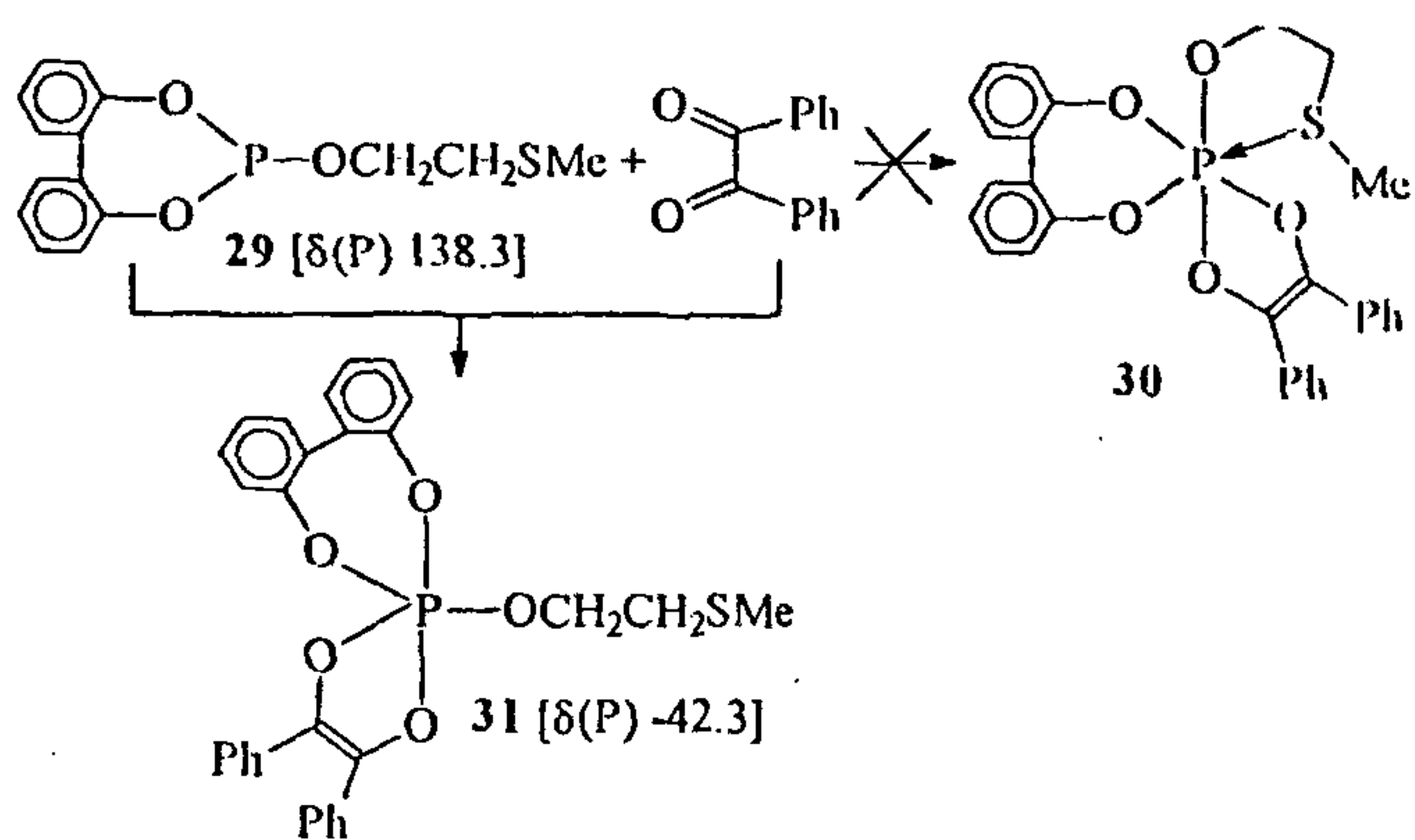


Chart 2.



Scheme 7.

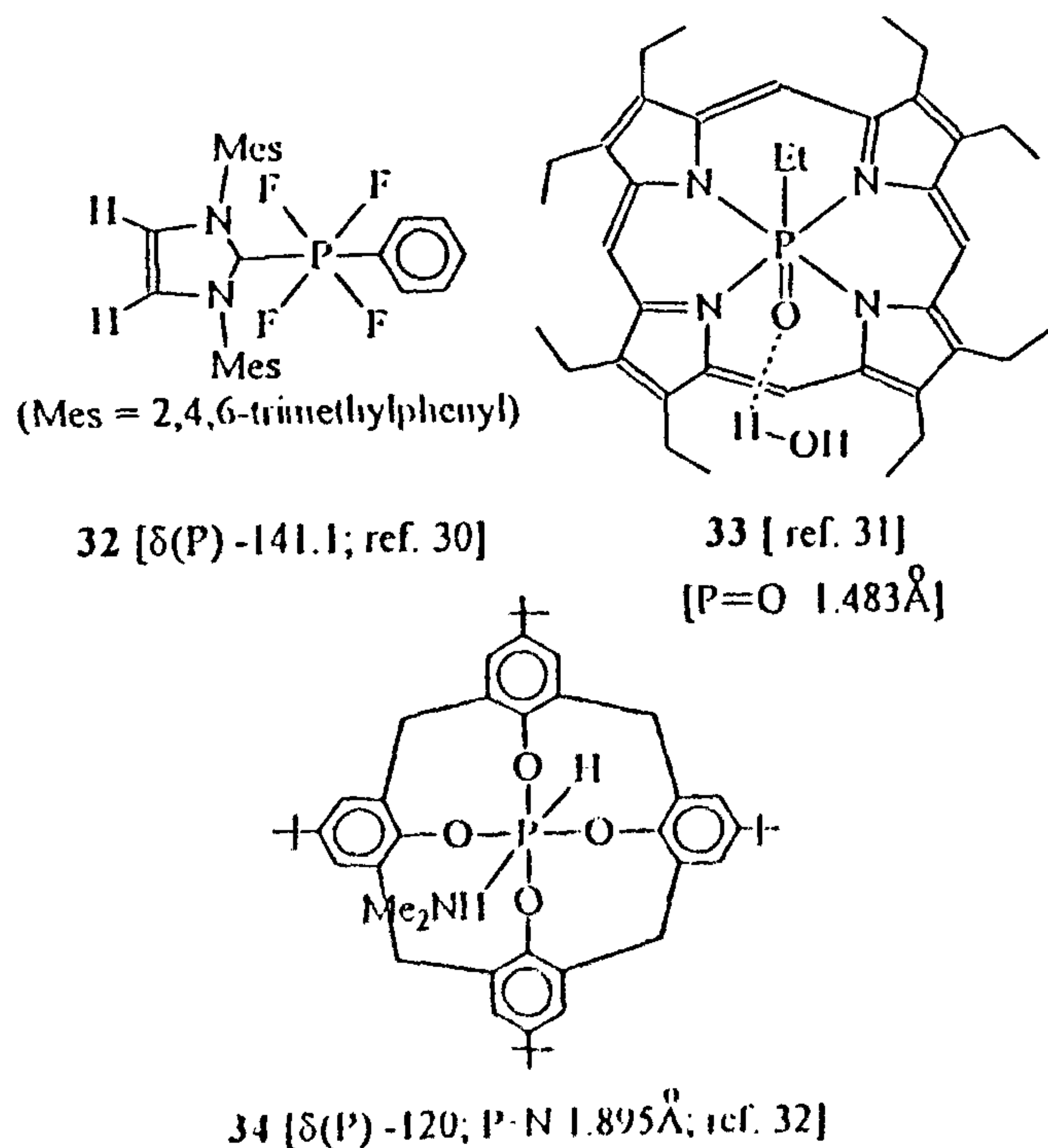
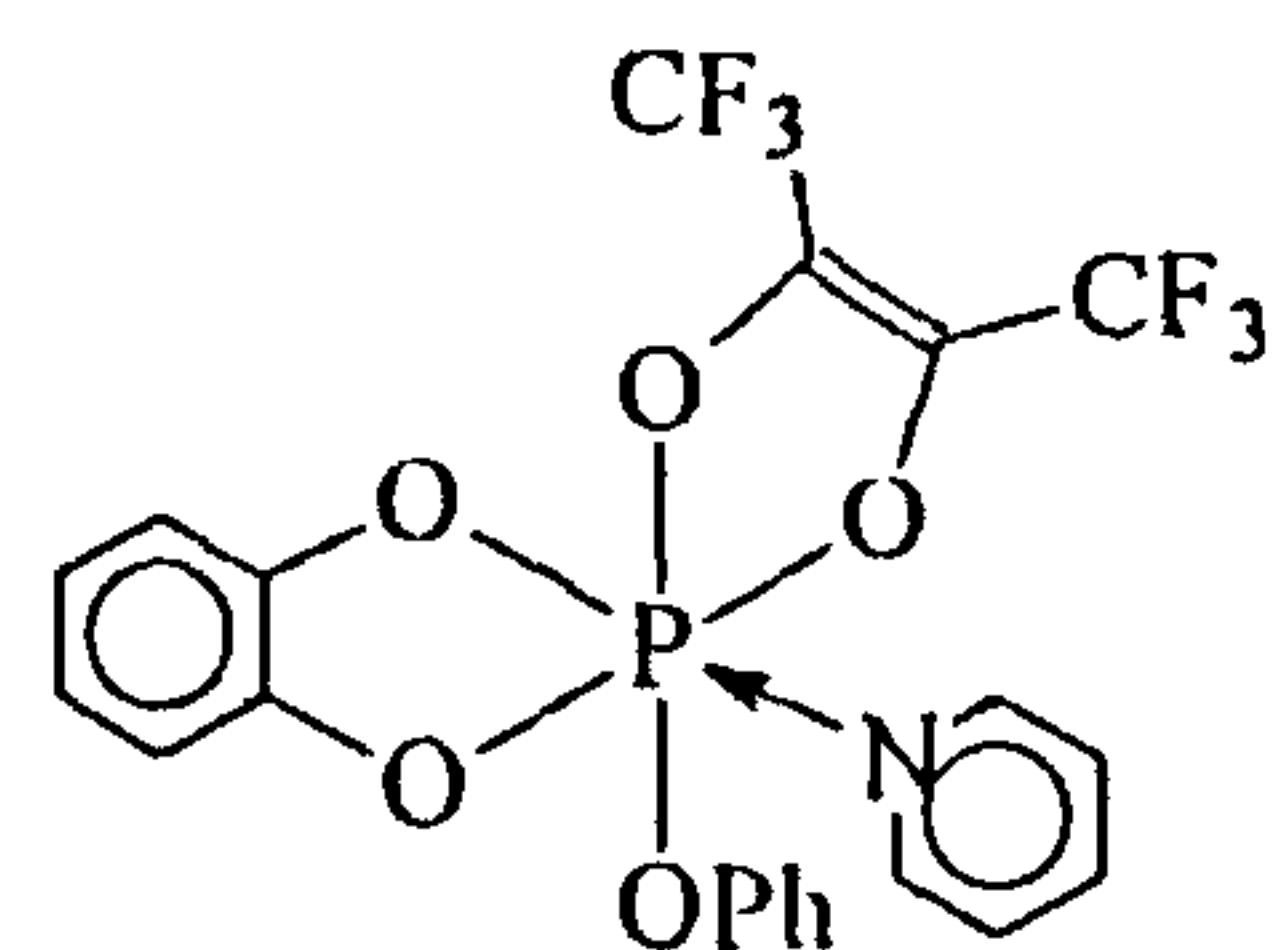


Chart 3.



In the reactions of the phosphites **25** and **26** with chloranil and 3,5-di-*t*-butyl-1,2-benzoquinone respectively, we again observed only one hexacoordinate product in each case, to which we assign the structures **27** and **28** respectively (Chart 2). Treatment of **25** with 3,5-di-*t*-butyl-1,2-benzoquinone however, led to the observation of two hexacoordinate [ $\delta(\text{P})$ : -97.1 and -99.0] and two pentacoordinate [ $\delta(\text{P})$ : -50.3 and -51.6] species, thus showing the presence of isomers.

We also attempted to prepare the  $S \rightarrow P$  bonded compound **30** by treating **29** with benzil (Scheme 7), but observed only **31** in which the sulfur does not coordinate to phosphorus [ $^{31}\text{P}$  NMR]<sup>29</sup>.

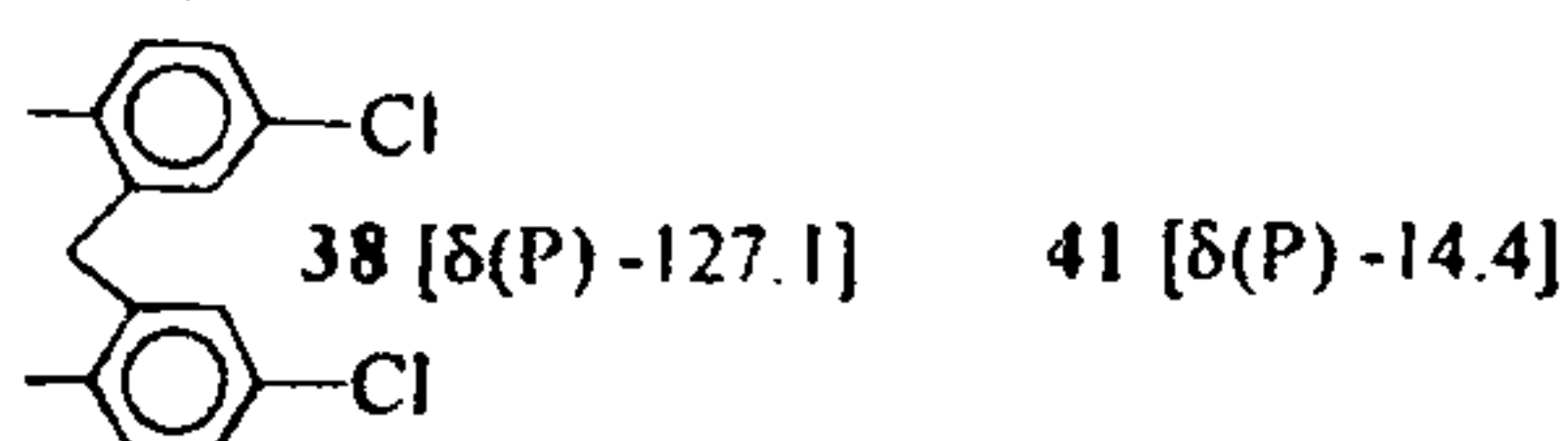
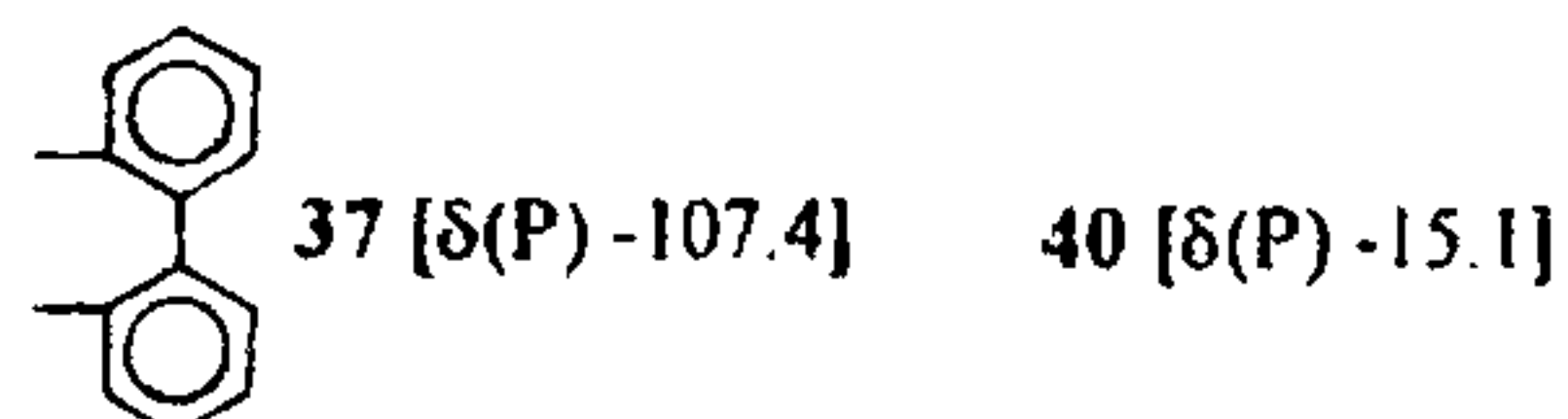
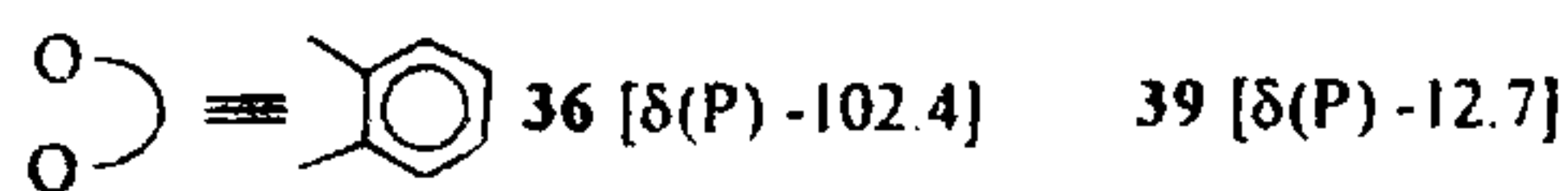
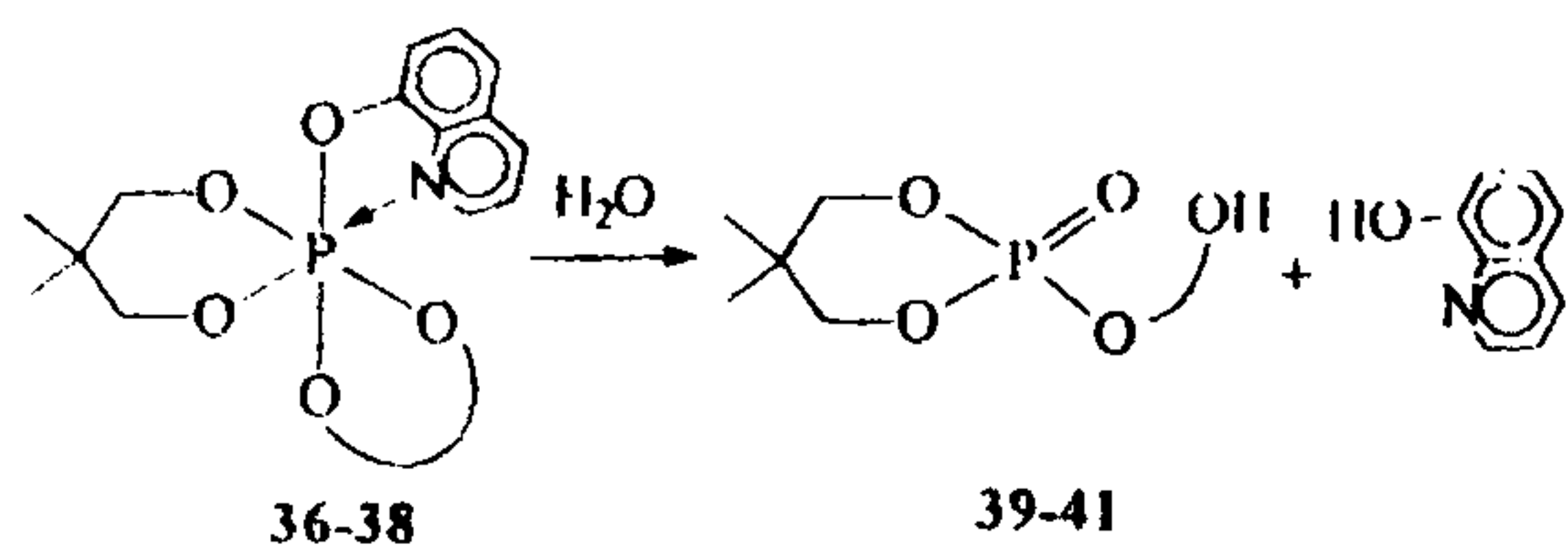
In addition to the above, a few other unique hexacoordinate compounds have been reported (Chart 3). Compound **32** represents a rare example of a 'carbene' complex with the carbene acting as a donor<sup>30</sup>. While the novelty of **33** lies in the presence of a 'P=O' bond in a hexacoordinated environment at phosphorus<sup>31</sup>, the calixarene derivative **34** (ref. 32) may be regarded as the dimethylamine adduct of a hydridophosphorane – the type of species (e.g. **35**) that Ramirez and coworkers have proposed in the base-catalysed reactions of oxyphosphoranes<sup>33</sup>.

### Reactivity of hexacoordinate phosphorus compounds

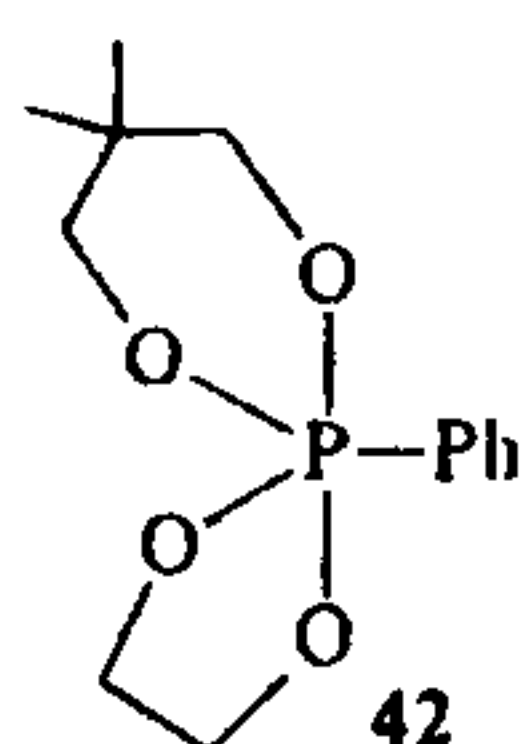
The oxinate compounds **36–38** undergo facile hydrolysis to lead to phosphate esters with the six-membered saturated ring intact (Scheme 8) (ref. 34). Such a feature contrasts with that observed in the acid hydrolysis of the pentacoordinated spirophosphorane **42** where a product with the six-membered phosphorinane ring intact was not seen<sup>35</sup>. Details of the mechanism of hydrolysis of **36–39** are not studied as yet, but it is likely that in the initial step where water approaches the phosphorus compound, the P–N bond gets weakened (or cleaved).

### Summary

We have given here a short account of some novel features of cyclic hexacoordinate phosphorus compounds. We have also described the synthesis and X-ray structure of a new tricyclic hexacoordinate phosphorane; the results show that the donor atoms have specific site preferences around the octahedral phosphorus. The proposed role



Scheme 8.



of hexacoordination on phosphorus in enzymatic reactions<sup>6</sup> is expected to trigger new activity in this area.

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25. Compound **26** was obtained by heating (OCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>O)-P(OC<sub>9</sub>H<sub>6</sub>N)<sup>22</sup> (0.53 g, 1.92 mmol) with benzil (0.40 g, 1.92 mmol) for 10 min at 100°C under neat conditions in an atmosphere of nitrogen. It was crystallized from dichloromethane-hexane (1:1) mixture. Yield: 0.75 g (80%). MP 175°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 1.05, 1.26 (s each, 6H, CH<sub>3</sub>), 3.85–4.25 (m, 4H, OCH<sub>2</sub>), 7.12–8.62 (m, 10H, Ar-H). <sup>31</sup>P NMR: -101.8. Anal. calcd. for C<sub>28</sub>H<sub>26</sub>NO<sub>5</sub>P: C 68.99, H 5.34, N 2.87. Found: C 68.84, H 5.30, N 2.81%.
26. Crystal data: Triclinic, space group P $\bar{1}$ ;  $a = 9.174(6)$ ,  $b = 11.484(7)$ ,  $c = 12.168(8)$  Å,  $\alpha = 107.00(5)$ ,  $\beta = 100.86(4)$ ,  $\gamma = 95.17(3)^\circ$ ,  $V = 1189.5(13)$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.361$ ,  $\mu = 0.156$  mm<sup>-1</sup>,  $2\theta_{\text{max}} = 45^\circ$ , total reflections: 3107, observed reflections: ( $I > 2\sigma(I)$ ) = 2416,  $R_1$  ( $I > 2\sigma(I)$ ): 0.0416; wR2 (all data): 0.1105, max/min residual electron density 0.202/-0.286 eÅ<sup>-3</sup>. The six-membered phosphorinane ring has a chair conformation, while both the five-membered rings are nearly planar. Further data is deposited with CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [CCDC137073].
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