

Synthesis, structure and properties of pentavalent three-coordinate phosphorus compounds

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Abstract - Compounds with a $-P\leftarrow$ skeleton have been rare until recently, as they are in general highly reactive. Nevertheless, considerable progress has been achieved in this field lately, especially regarding phosphodiimidic amides, diiminophosphoranes and imino(methylene)phosphoranes. Synthetic routes to the title compounds and new aspects of their reactivity are described. The utility of three-coordinate phosphorus(Y) compounds as ligands has been demonstrated by the fact that they are able to stabilize unusually coordinate state of metals.

INTRODUCTION

One of the trends in the current development of organophosphorus chemistry is a shift in the center of gravity of the investigations toward the area of highly reactive compounds showing unusual electronic and steric structure, as considered from the viewpoint of classical concepts. Among these are compounds of pentavalent three-coordinate phosphorus ($\sigma^3\lambda^5$ -phosphoranes). For a long time it has been presumed that these unusually hybridized phosphorus compounds can exist only as short-lived intermediates. The first stable compound of pentavalent three-coordinate phosphorus, $(Me_3Si)_2N-P(=NSiMe_3)_2$ was obtained in 1973 by imination of phosphenimidic amide $(Me_3Si)_2N-P=NSiMe_3$ with trimethylsilylazide (ref. 1,2). Several years later the stable $\sigma^3\lambda^5$ -phosphoranes namely $(Me_3Si)_2N-P(=S)=NBu^t$ and $Bu^t(Me_3Si)N-P(=S)=NBu^t$ (ref. 3,4) have been synthesized and a general method for the preparation of phosphodiimidic amides has been found. The discoveries initiated an extensive development of the chemistry of pentavalent three-coordinate phosphorus compounds.

This report represents new results in the chemistry of $\sigma^3\lambda^5$ -iminophosphoranes. Main attention is devoted to a consideration of methods for the synthesis of $Z-P(=NR)=X$ compounds and their reactions with organometallic reagents.

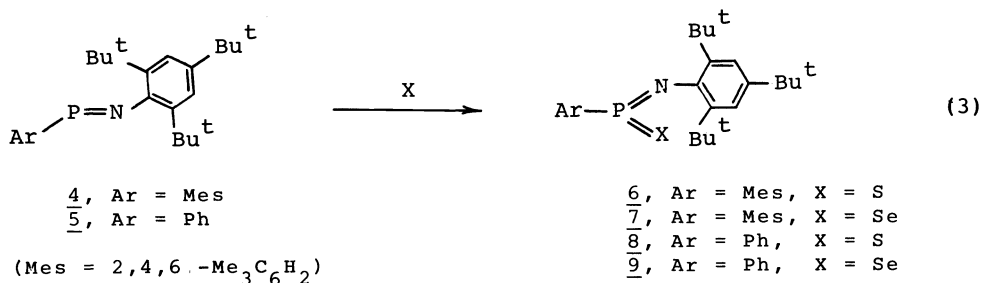
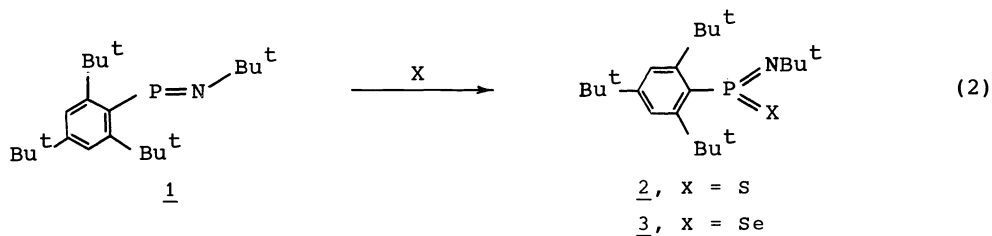
SYNTHESIS AND STRUCTURE OF $\sigma^3\lambda^5$ -IMINOPHOSPHORANES

With the exception of the transition metal complexes containing $\leftarrow P \rightarrow M$ fragment all the presently known stable pentavalent three-coordinate phosphorus compounds can be related to one of the following three classes: metaphosphoric (phosphenic) acid derivatives, metaphosphonic acid derivatives, and compounds with double bond between a carbon atom and three-coordinate phosphorus ($\sigma^3\lambda^5$ -methylene phosphoranes). Strategy of the synthesis of $Z-P(=X)=Y$ compounds is based in most cases on the introduction of $=NR$, $=CR_2$ groupings, or oxygen, sulfur, selenium atoms to the two-coordinate phosphorus. In general, two approaches are principally possible for the synthesis of $\sigma^3\lambda^5$ -phosphoranes with unlike groupings (X, Y) at the phosphorus atom.



This methodology was used for the synthesis of the first examples of sterically protected stable imino(oxo-, thioxo-, and selenoxo-)iminophosphoranes (ref. 6).

Treatment of iminophosphine 1 in benzene with 1 equiv. of sulfur at 50°C gives after evaporation the compound 2 in 62 % yield. Similar reaction 1 with selenium affords 3 (72 %). Interaction of iminophosphines 4, 5 with sulfur and selenium results in the formation of iminophosphoranes 6-9. The thioxo- (or selenoxo)iminophosphoranes form pale yellow crystals highly sensitive to atmospheric moisture but fairly stable at 20°C.



In contrast to sulfur and selenium, molecular oxygen does not react with the iminophosphine 1. However the oxidation of 1 with ozone in dichloromethane at -78°C leads to the imino(oxo)phosphorane Ttb-P(=O)=NBu^t (Ttb = 2,4,6-tri-tert-butylphenyl). The latter observation provides an interesting contrast with diphosphene TtbP=PTtb in which the P=P bond is cleaved by ozone under the same conditions (ref. 7).

Whereas λ^3 -iminophosphines 1, 4 and 5 give stable imino(thioxo-, selenoxo-)phosphoranes, interaction of λ^5 -Bu-P=N-Ttb with sulfur and selenium results in oligomeric products. The latter reveal according to the NMR data (Fig. 1) a remarkable ability to dissociate into the $\delta^3\lambda^5$ -phosphoranes under heating.

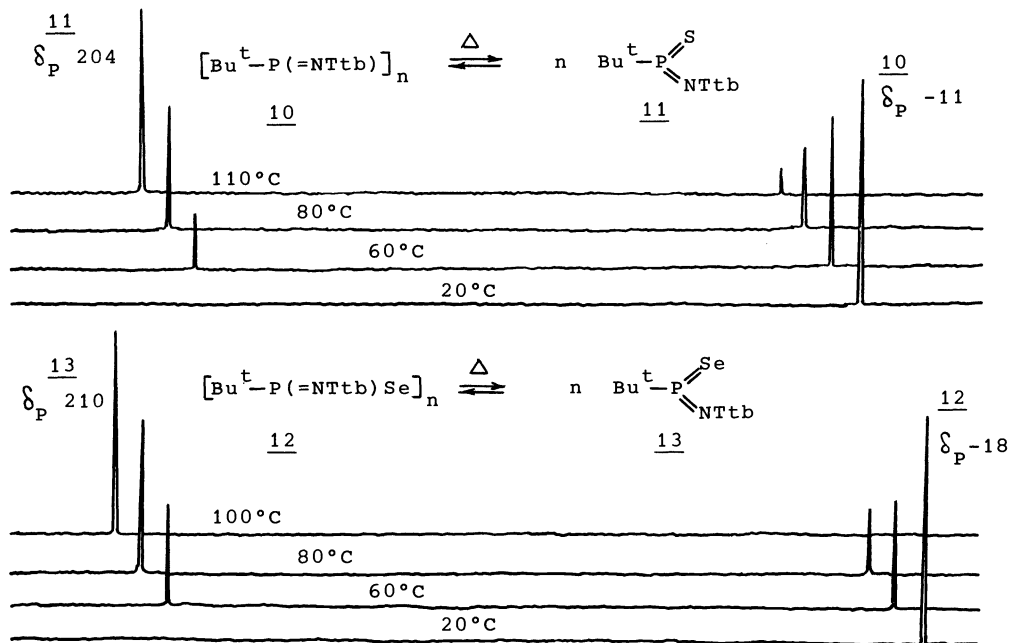
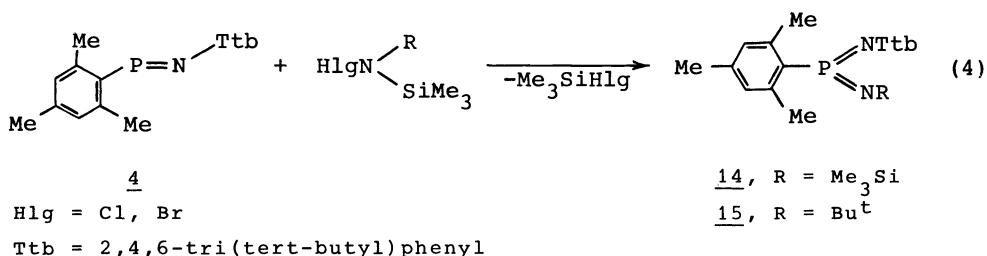


Fig. 1. Temperature variations of the ^{31}P NMR spectra of the compounds 10 and 12 in o-dichlorobenzene medium.

We developed a general method for the synthesis of compounds $Z-P(=NR^1)=NR^2$ involving reaction of two-coordinate phosphorus compounds with N-haloamines. Using this approach we succeeded in obtaining the first representatives of $\sigma^3\lambda^5$ -diiminophosporanes (ref. 8).



The diiminophosporanes 14, 15 are yellow-coloured crystalline substances, readily soluble in organic solvents and thermally stable at 150°C. An X-ray crystal structure of 14 (Fig. 2) shows that diiminophosporane adopts a planar structure (mean deviation of the central atoms, P(1), N(1), N(2), C(1) is 1 pm). Compared with the typical values of a single bond, the P=N distances have been shortened from 177 to 154.9 and 153.3 pm.

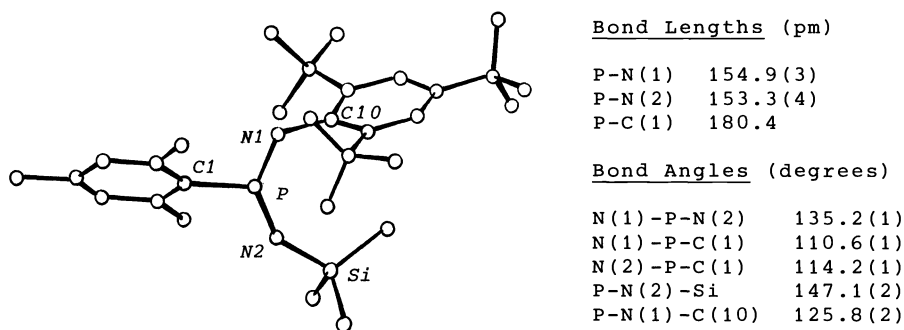
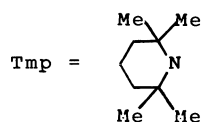
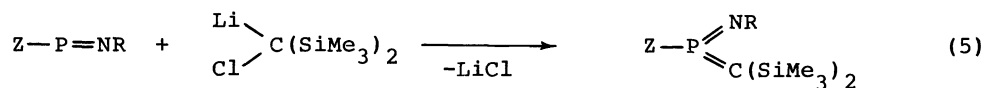
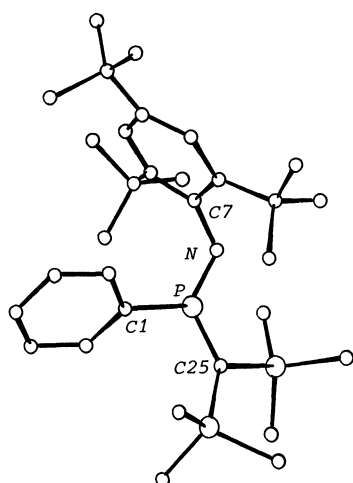


Fig. 2. Molecular structure of diiminophosporane 14.

There are two methods for the synthesis of $\sigma^3\lambda^5$ -imino(methylene)phosporanes. The first one is based on reactions of two-coordinate phosphorus compounds with aliphatic diazocompounds (ref. 9), the second one developed by us includes interaction of $\sigma^3\lambda^5$ -iminophosphines and phosphenimidous amides with α -halogen substituted organolithium compounds (ref. 10). Equation (5) exemplifies the reactions of iminophosphines with $\text{LiC}(\text{Cl})(\text{SiMe}_3)_2$. The constitution of imino(methylene)phosporanes has been confirmed by an X-ray structure determination of the compound 19 (Fig. 3). The phosphorus atom shows a plane-trigonal distribution of bonds (sum of the valence angles 359.9°). The phosphorus-carbon double bond length (164 pm) is shorter than that of a typical phosphorus-carbon single bond (185 pm). It is consistent with the view that the phosphorus is approximately sp^2 hybridized.



- $\underline{16}$, Z = $(\text{Me}_3\text{Si})_2\text{N}$, R = Me_3Si
 $\underline{17}$, Z = $\text{Bu}^t(\text{Me}_3\text{Si})\text{N}$, R = Bu^t
 $\underline{18}$, Z = Tmp, R = Me_3Si
 $\underline{19}$, Z = Ph, R = Ttb

Bond Lengths (pm)

| | |
|---------|----------|
| P-N | 152.2(2) |
| P-C(1) | 180.5(3) |
| P-C(25) | 163.9(3) |

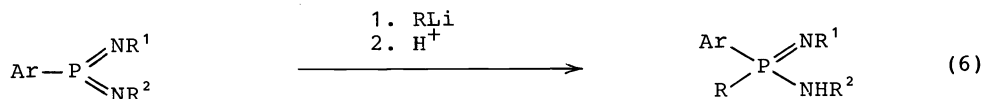
Bond Angles (degrees)

| | |
|--------------|----------|
| C(1)-P-N | 117.0 |
| C(1)-P-C(25) | 117.0 |
| N-P-C(25) | 125.9(2) |
| P-N-C(7) | 124.4(2) |

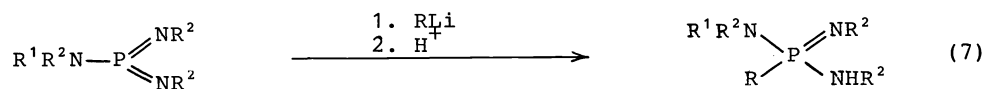
Fig. 3. Molecular structure of imino(methylene)phosphorane 19.**REACTIONS OF $\sigma^3\lambda^5$ -IMINOPHOSPHORANES**

Pentavalent three-coordinate phosphorus derivatives are versatile reagents and ligands for the synthesis of many important classes of compounds. We report here several illustrative examples from areas of current interest in our laboratory involving reactions of $\sigma^3\lambda^5$ -iminophosphoranes with organometallic compounds.

Diiminophosphoranes and phosphodiimidic amides vigorously add organolithium compounds at -78°C in inert solvent medium to form pentavalent four-coordinate phosphorus derivatives (ref. 11).

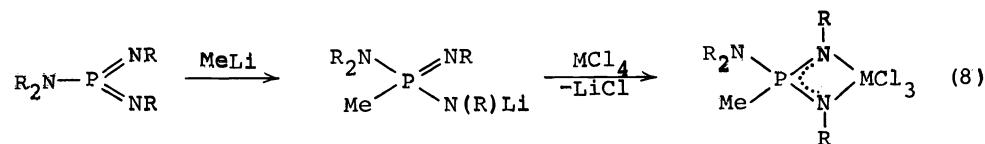


Ar = Mes, Ph; $\text{R}^2 = \text{Bu}^t, \text{Ttb}, \text{Me}_3\text{Si}$
 R = Me, Bu^t , Ph



$\text{R}^1, \text{R}^2 = \text{Bu}^t, \text{Me}_3\text{Si}$
 R = Me, Bu^t , Ph

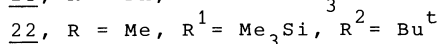
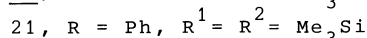
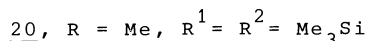
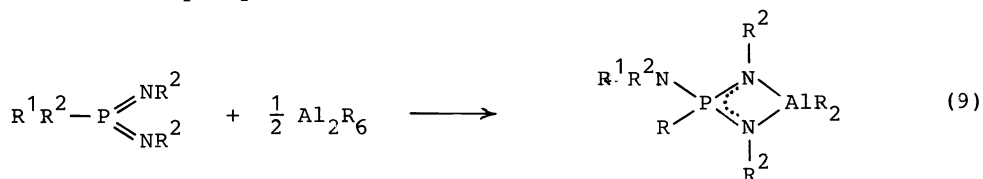
Reactions (6), (7) represent a new method of $\text{P}^{\text{V}}\text{-C}$ bond formation. Their synthetic importance lies in the fact that they open up a route to species being perspective as interesting chelate ligands. As examples, we can cite the syntheses of complexes, containing penta-coordinate titanium, zirconium and tin (ref. 12, 13).



R = Me_3Si

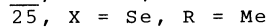
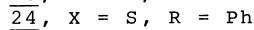
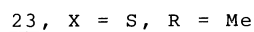
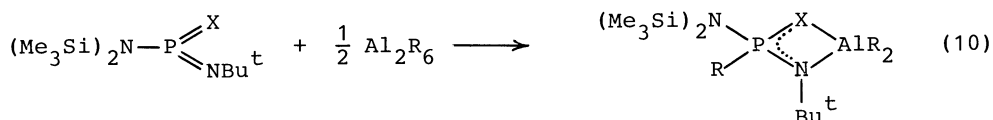
M = Ti, Zr, Sn

$\sigma^3\lambda^5$ -Iminophosphoranes react with organoaluminium compounds in a peculiar manner. Treatment of phosphodiimidic amides with trimethylaluminium or triphenylaluminium results in the formation of the four-membered ring heterocycles (ref. 14). The reactions presumably proceed by electrophilic attack by the trimethyl- or triphenylaluminium on the imide nitrogen atom of the phosphodiimidic amide with subsequent migration of the Me or Ph group from the aluminium atom to the phosphorus atom.

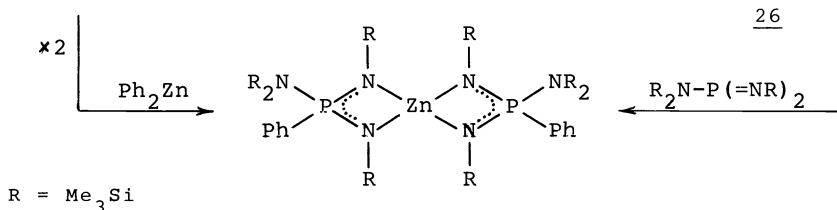
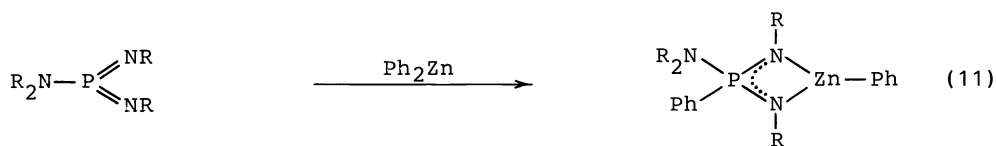


X-Ray crystallographic analysis of compound 21 shows that four-membered ring is symmetric and virtually planar (mean deviation of central atoms is 3 pm). Endocyclic P-N bonds (161.7 and 162.3 pm) are considerably shortened as compared with exocyclic P-N bond (165.9 pm). The peculiarities of the molecular geometry of 21, in our opinion, are due to the zwitterionic structure of the heterocycle. This conclusion is consistent with the positive (i. e. deshielded) ^{31}P chemical shift (δ_P 21-55 ppm) for complexes 20-22.

In reactions of the $\sigma^3\lambda^5$ -imino(thioxo-, or selenoxo-)phosphoranes with organoaluminium compounds the complexes 23-25 are formed in high yields (ref. 14, 15). Unlike complex 21, the four-membered ring in 24 is planar and has a "butterfly" shape with a dihedral angle between the planes SPN(2) and SAlN(2) of 11° . The endocyclic P-N bond (162.1 pm) is shorter as compared with the exocyclic P-N bond (165.8 pm); phosphorus-sulfur bond length (203.8 pm) is less than the sum of the Van der Waals radii (ref. 16).



The reactions of $\sigma^3\lambda^5$ -iminophosphoranes with organoaluminium compounds are accompanied by an increase in the coordination number of the phosphorus and by replacement of a monodentate ligand for a bidentate one within the coordination sphere of metal. Such reactions are of interest in view of the coordination chemistry, as in some cases they result in the unusually coordinated complexes. Thus, we have isolated the three-coordinate zinc complex 26 from reaction of the phosphodiimidic amide with diphenylzinc (ref. 17).



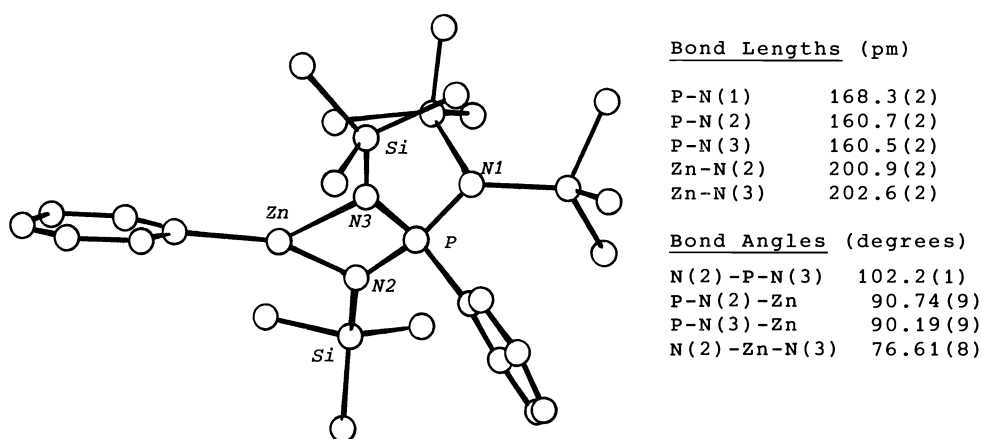


Fig. 4. Molecular structure of complex 26.

The structure of the complex 26 has been confirmed by the NMR data, X-ray crystallographic analysis (Fig. 4), and the chemical transformations. Zinc atom in the molecule 26 has a plane-trigonal distribution of bonds (sum of the valence angles is 359.5°). The four-membered ring is symmetrical and practically planar. The Zn-N and Zn-C bonds are in the normal range for organozinc compounds. Similar to the compounds 21 and 24 complex 26 exhibits visible extension of the exocyclic P-N bond (168.3 pm) as compared with the endocyclic bonds (160.7, 160.5 pm).

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