Coordination compounds with 3-, 4- and 6membered heterocycles containing phosphorus

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Abstract: Cyclic phosphorus ylids such as 3 and 4 form coordination compounds both with main group and transition group metals. While 3 functions exclusively as a monodentate ligand, 4 can be monodentate or bidentate. In many reactions of 3 with carbonyl metals, organometallic compounds, and metal halides the cyclic structure is retained, in other cases it is opened. After reviewing the syntheses of 3, 4 and a phosphirane examples of reactions with metal compounds and their products are described and discussed. Special attention is given to the formation of C-C bonds in some of the reactions.

INTRODUCTION

The paper reviews our work on coordination compounds with 3-, 4-, and 6-membered heterocycles containing phosphorus as ligands. Using a procedure which allowed us to prepare the first diphosphoranyl acetylene, namely bis[difluoro bis(diethylamino)] phosphoranyl acetylene, 1, by oxidative fluorination of acetylene bis[phosphonic bis(diethylamino)]amide, 2, with sulfurtetrafluoride (ref. 1), we were able to synthesize many alkyl and aryl difluorodiamino phosphoranes (ref. 2), members of a class of compounds which have been widely unknown when we started this work.

$$[(H_3C)_2N]_2F_2P - C \equiv C - PF_2[N(CH_3)_2]_2 \qquad [(H_3C)_2N]_2P - C \equiv C - P[N(CH_3)_2]_2$$
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λ^5 -DIPHOSPHETES, λ^5 -TRIPHOSPHABENZENES

When alkyl difluorodiamino phosphoranes are reacted with a two-fold molar excess of butyllithium as seen in eq. 1 the primarily formed alkylene fluorodiamino phosphorane reacts further to diphosphetes (diphosphacyclobutadienes; ref. 3). Starting with methyl difluorobis(dimethylamino) phosphorane the reaction with butyllithium yields 1,1,3,3-tetrakis(dimethylamino)- $1\lambda^5,3\lambda^5$ -diphosphete, 3, which is unsubstituted at the endocyclic carbon atoms (ref. 4):

$$\begin{array}{c} (H_{3}C)_{2}N \\ (H_{3}C)_{2}N - P - CH \\ \\ -LiF \\ -2 \text{ n-C}_{4}H_{10} \end{array} \qquad (1)$$

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Figure 1 shows the molecular structure of compound 3. The ring with C_i symmetry is completely planar with equal phosphorus-carbon bond length of 172.5 pm. This bond length lies in the range of phosphorus-carbon double bond lengths in phosphaalkenes with typical values between 168 and 172 pm (ref. 5) or in the range of phosphorus-carbon bond lengths in substituted alkylidene phosphoranes (ref. 6).

Fig. 1 Molecular structure of 1,1,3,3-tetrakis(dimethylamino)- $1\lambda^5$,3 λ^5 -diphosphete 3.

Results of calculations, which were made on 1,1,3,3-tetraamino- $1\lambda^5,3\lambda^5$ -diphosphete, show that the highest occupied molecular orbitals are located at the carbon atoms. They lie considerably higher on the energy scale than the four linear combinations of the nitrogen atoms. An MNDO calculation shows that the phosphorus atoms carry nearly a full positive charge, whereas the negative charge on the carbon atoms amounts to -0.73 (ref. 7). Therefore, the molecule can best be described by formula 3a, and all chemical reactions of diphosphetes can best interpreted by this electron distribution.

$$(H_{3}C)_{2}N \xrightarrow{P} \xrightarrow{\Theta} CH \qquad HC \xrightarrow{P} CH_{3}$$

Although 3 is the main product of the reaction between methyl difluorobis(dimethylamino) phosphorane and butyllithium, the corresponding six-membered ring, 1,1,3,3,5,5-hexakis(dimethylamino)- $1\lambda^5$,3 λ^5 , $5\lambda^5$ -triphosphabenzene, 4, is formed as a by-product. While 3 solidifies only in the refrigerator, 4 is a solid which forms needles melting at 89°C. The six-membered ring is completely planar with equal bond lengths of 169 pm between all carbon and phosphorus atoms (ref. 8).

REACTIONS OF 3 WITH NON-METALLIC ELECTROPHILES

As mentioned before, the endocyclic carbon atoms in $1,3-\lambda^5$ -diphosphetes are highly nucleophilic. The most simple reaction of 3 with an electrophile is the addition of a proton to give the corresponding cation 5 (ref. 9). The four-membered ring is still planar, but now with two short P-C bonds to the CH group and two long P-C bonds to the CH₂ group. In an analogous way 3 reacts with boron trifluoride to give the zwitterionic product 6, a crystalline compound which is very stable (ref. 10).

$$(H_{3}C)_{2}N \longrightarrow P \longrightarrow CH_{2} \qquad (H_{3}C)_{2}N \longrightarrow P \longrightarrow C \longrightarrow H \qquad (H_{3}C)_{2}N \longrightarrow P \longrightarrow C \longrightarrow S$$

$$HC \longrightarrow P \longrightarrow N(CH_{3})_{2} \qquad HC \longrightarrow P \longrightarrow N(CH_{3})_{2} \qquad H_{2}C \longrightarrow P \longrightarrow N(CH_{3})_{2}$$

$$N(CH_{3})_{2} \qquad N(CH_{3})_{2} \qquad N(CH_{3})_{2} \qquad N(CH_{3})_{2}$$

Similarly, carbon oxide sulfide, carbon dioxide, and carbon disulfide can serve as electron acceptors, all leading to analogous products, although in all cases the addition of COS, CO₂, and CS₂, respectively, is followed by proton migration leading with CS₂ to the first stable product 7 of the reaction (ref. 11).

REACTIONS OF 3 WITH METALLIC ELECTROPHILES

A stable carbon-tin bond is formed in the reaction of tin(II) chloride with 3 (ref. 12). The thermally very stable compound can be isolated. In an analogous reaction 3 can be added to germanium(II) chloride (ref. 12). Similarly, trimethylindium and trimethylaluminium can be reacted with 3 to form the indium and aluminium complexes 8 and 9 (ref. 13). The indium and aluminium atoms have distorted tetrahedral coordination spheres.

The planarity of the four-membered ring of 3 is nearly retained. Both products are crystalline compounds at room temperature. The indium-carbon bond length was measured to be 233 pm which is very large compared with bond lengths characteristic for indium-carbon bonds in compounds with indium of coordination number 4. NMR measurements at room temperature showed that in solution an intermolecular exchange process occurs. 3 is exchanged among the molecules within the time scale of NMR spectroscopy. It can be frozen at 225 K. In contrast to trimethylindium, trimethylaluminium being a much stronger Lewis acid is expected to form a more stable metal-carbon bond when reacted with 3. This is reflected by the fact that the exchange process of the type just discussed is not observed. In addition, the bond length between aluminium and the carbon atom in 9 is in the range of normal aluminium-carbon bond lengths, although with 208 pm somewhat longer than the bonds to the methyl groups. It may be mentioned that experiments to bind a second molecule of trimethylindium or aluminium to 8 or 9, respectively, were not successful. Likewise, experiments to eliminate methane from the complexes resulting in metal-carbon double bonds failed.

Carbonyl groups of metal carbonyls can be substituted by the diphosphete 3. Hexacarbonyl chromium and 3 react to give the very stable compound 10 shown in Fig. 2 (ref. 14). With nonacarbonyl diiron a compound is obtained in which 3 is attached to the iron atom of a tetracarbonyl iron group, while pentacarbonyl iron is eliminated in the reaction (ref. 14). As a further example the reaction of *cis*-cyclooctatetraene pentacarbonyl tungsten with 3 may be mentioned. *Cis*-cyclooctatetraene is substituted by 3 and the $1\lambda^5,3\lambda^5$ -diphosphete pentacarbonyl tungsten 11 is formed (refs. 12, 14). It is isolated as crystalline material with structure 11a or structure 11b, the latter resulting from 11a by proton migration

from the coordinated carbon atom to the one opposite to it. Optimation of the two structures using a pseudopotential method and calculation of the relative energies taking into account the electron correlation has shown that structure 11a with two CH groups in the ring is only 2.4 kcal/mol less stable than structure 11b with the CH₂ group (ref. 15).

Fig. 2 Molecular structure of $1\lambda^5$, $3\lambda^5$ -diphosphete pentacarbonyl chrom 10.

A suprising result was obtained from experiments to substitute one or more carbonyl groups in the binuclear cyclopentadienyl carbonyl iron complex 12 (see eq. 2; ref. 16). The expected compound or compounds in which one or more carbonyl groups were expected to be substituted by 3 were not obtained. From the reaction mixture a dark violet, crystalline, air stable compound could be isolated: the [1.2.4]-oxadiphosphinine complex 13 as shown by chemical analysis, NMR spectroscopy, and X-ray diffraction. The heterocycle has not been known before. Carbon monoxide from 12 has been inserted into the four-membered ring of 3. In addition, a dimethylamino group was transfered from phosphorus to carbon. The mechanism of the reaction has not been elucidated yet.

1\(\lambde{s}\), 3\(\lambde{s}\)-DIPHOSPHABENZENES. COORDINATION COMPOUNDS WITH 4 AND 15 AS LIGANDS

Acetylene and acetylene derivatives can easily be inserted into the four-membered ring of 3, forming six-membered $1\lambda^5$, $3\lambda^5$ -diphosphabenzenes (14) (ref. 17):

The first step of the insertion reaction is a [2+2]-cycloaddition followed by spontaneous valence isomerisation. By insertion of bis(diphenylphosphinyl)acetylene the two-dentate ligand 15 is obtained which forms very stable coordination compounds with transitition metals as demonstrated in eq.3 for the reaction with palladium(II) chloride yielding 16 (ref. 18). With nickel(II) chloride the analogous nickel complex is formed (ref. 19).

$$(H_{3}C)_{2}N \ N(CH_{3})_{2} \ (H_{3}C)_{2}N \ N(CH_{3})_{2} \ (H_{3}C)_{2}N \ N(CH_{3})_{2} \ (H_{3}C)_{2}N \ P \ C \ P \ C_{6}H_{5} \ (H_{5}C)_{2}N \ P \ C \ P \ C_{6}H_{5} \ (H_{5}C)_{2}N \ P \ C_{6}H_{5} \ (H_{5}C)_{2}N \ P \ C_{6}H_{5} \ (H_{5}C)_{2}N \ H \ C_{6}H_{5} \ (H_{5}C)_{2}N \ H$$

The two diphenylphosphinyl groups in 15 are very sensitive towards oxidation (ref. 20). In air they react immediately with oxygen, forming the corresponding phosphonyl groups in compound 17. By this reaction the chelating properties of the substituents on diphosphabenzene are lost.

$$(H_{3}C)_{2}N N(CH_{3})_{2}$$

$$| O | | O |$$

$$| C - P(C_{6}H_{5})_{2}$$

$$(H_{3}C)_{2}N - P C - P(C_{6}H_{5})_{2}$$

$$(H_{3}C)_{2}N - O O$$

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The molecule, however, is still able to function as a ligand. With palladium(II) chloride the planar complex 18 is formed in which two of the endocyclic, ylidic carbon atoms are functioning as electron

donors. The result of an X-ray structural analysis is shown in Fig. 3 (ref. 20). One of the endocyclic phosphorus atoms of 18 lies outside the plane of the original six-membered ring.

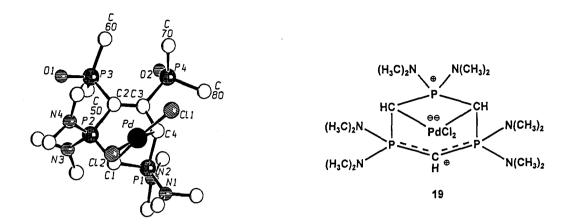


Fig. 3 Molecular structure of the diphosphabenzene palladium(II) complex 18

Also, the endocyclic carbon atoms of $1\lambda^5, 3\lambda^5, 5\lambda^5$ -triphosphabenzene 4 have good electron donor properties. 4 can, for instance, be reacted with palladium(II) chloride-benzonitrile to give the planar coordination compound 19 (ref. 21). As in the diphosphabenzene complex 18 five atoms of the originally planar six-membered ligand are located in a plane, while the phosphorus atom between coordinating carbon atoms is kinked out of the plane.

Reaction of Fe(CO), with 3

While nonacarbonyl diiron and 3 react to give $(1\lambda^5, 3\lambda^5$ -diphosphete)Fe(CO)₄ analogous to 10 (see Fig. 2; ref. 14) in which the four-membered ring of 3 is retained, reaction of pentacarbonyl iron with 3 leads to ring opening (ref. 22). A [2+2]-cycloaddition process may be assumed as the first step of the reaction leading to the formation of a P-O and C-C bond. Finally, the reaction results in the linear product 20.

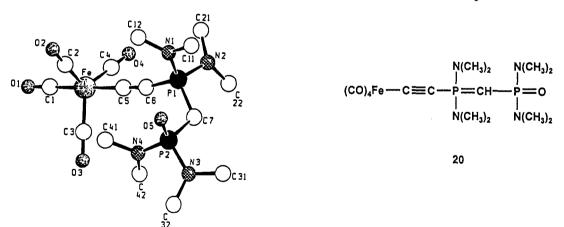


Fig. 4 Molecular structure of the phosphorylmethyl phosphonioethinyl tetracarbonyl iron 20.

A tetracarbonyl iron complex with a terminal ligand corresponding to the allenylidene ligand C=C=CR₂ has been formed. The structure of the compound is shown in Fig. 4. The most interesting bond length is the one between the two carbon atoms. It was measured to be 121 pm, corresponding exactly to a carbon-carbon triple bond. The arrangement of the atom unit Fe-C-C-P is nearly linear. Similar bond lengths and angles were observed in the manganese complex 21 described by Mitchell, Korte, and Kaska (ref. 23) as well as in triphenylphosphorus allylidene ketene 22 (ref. 24) and thioketene 23 (ref. 25).

$$Br(CO)_4Mn = C = C = P(C_6H_5)_3$$
 $O = C = C = P(C_6H_5)_3$ $S = C = C = P(C_6H_5)_3$

The bond angles are interpretated by the mesomeric formulas a, b, and c:

In formula c the phosphorus atom uses sp² hybrides giving rise to a bond angle smaller than 180°. Formulas a and b indicate linear arrangements. The situation may be compared with nitrosyl complexes in which NO can function as σ acceptor leading to bond angles smaller than 180°. For the metal complexes mentioned above the mesomeric formula b is assumed to have a high statistical weight. The metal-carbon bond to the acetylene ligand is much longer than the one to the carbonyl groups. Therefore the ligand is expected to be a good σ donor but a weaker π acceptor than the carbonyl group. Reaction of 3 with excess pentacarbonyl iron yields compound 24, a crystalline product (ref. 22).

PHOSPHIRANES AS LIGANDS

Phosphiranes are strong ligands in coordination compounds. A new access to phosphiranes has been opened by the reaction of trialkyldifluoro phosphoranes with reagents that abstract hydrogen fluoride. 1-benzyl-2,3-diphenyl phosphirane can be obtained from tribenzyldifluoro phosphorane and lithium bis(trimethylsilyl)amide (ref. 26). With hexacarbonyl tungsten the corresponding phosphirane pentacarbonyl tungsten 25 is formed (ref. 26).

$$(H_{3}C)_{2}N \longrightarrow P \longrightarrow C \longrightarrow Fe(CO)_{4} \qquad (CO)_{5}W \longrightarrow CH_{2}C_{6}H_{5}$$

$$(H_{3}C)_{2}N \longrightarrow P \longrightarrow C \longrightarrow C \longrightarrow Fe(CO)_{4} \qquad (CO)_{5}W \longrightarrow CH_{2}C_{6}H_{5}$$

$$H_{2}C \longrightarrow P \longrightarrow N(CH_{3})_{2} \qquad HC \longrightarrow CH \longrightarrow H_{5}C_{6} \qquad C_{6}H_{5}$$

$$24 \qquad \qquad 25$$

OUTLOOK

By inserting the acetylene group of $1,\omega$ -diacetylenes into $1\lambda^5,3\lambda^5$ -diphosphetes two $1\lambda^5,3\lambda^5$ -diphosphabenzenes connected via methylene groups are formed as shown for the reaction of 1,5-hexadiine with 3 in eq. 4, yielding 26 (ref. 27):

HC=C-(CH₂)₂-C=CH
$$\xrightarrow{+2 \times 3}$$
 HC $\xrightarrow{(H_3C)_2N}$ $\xrightarrow{N(CH_3)_2}$ $\xrightarrow{(H_3C)_2N}$ $\xrightarrow{N(CH_3)_2}$ $\xrightarrow{HC-P}$ $\xrightarrow{(H_3C)_2N}$ $\xrightarrow{N(CH_3)_2}$ $\xrightarrow{(H_3C)_2N}$ $\xrightarrow{N(CH_3)_2}$ $\xrightarrow{(H_3C)_2N}$ $\xrightarrow{N(CH_3)_2}$ $\xrightarrow{N(CH_3)_2}$ $\xrightarrow{(H_3C)_2N}$ $\xrightarrow{N(CH_3)_2}$ $\xrightarrow{N$

Reaction of 3 with 1.7-octadiine leads to a product in which the diphosphabenzene rings are separated by four methylene groups. The endocyclic carbon atoms of the heterocycles are able to function as donor atoms in coordination compounds. Thus, compounds with two coordination centers where the distance is easily variable can be prepared. With longer methylene group chains it may even be possible to link the two heterocycles via a metal center.

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