

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

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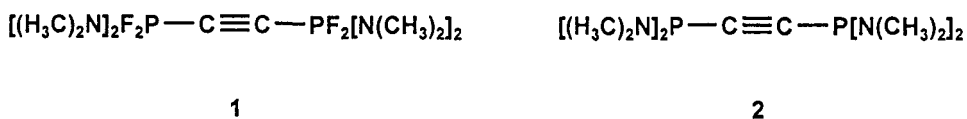
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Abstract: Cyclic phosphorus ylids such as **3** and **4** form coordination compounds both with main group and transition group metals. While **3** functions exclusively as a monodentate ligand, **4** can be monodentate or bidentate. In many reactions 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[diffuoro bis(diethylamino)] phosphoranyl acetylene, **1**, by oxidative fluorination of acetylene bis[phosphonic bis(diethylamino)]amide, **2**, with sulfur tetrafluoride (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.



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):

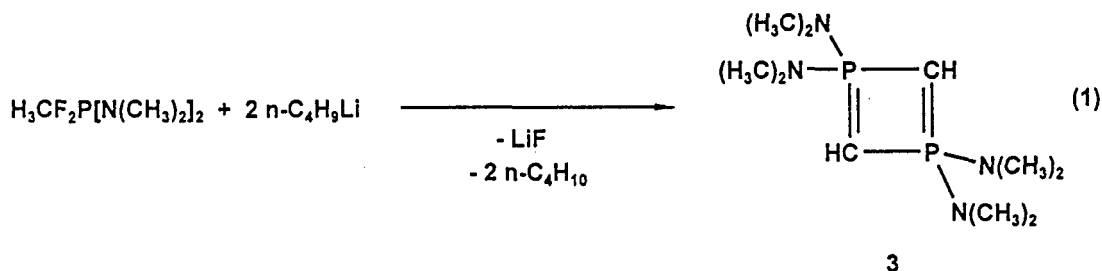


Figure 1 shows the molecular structure of compound **3**. The ring with C_i symmetry is completely planar with equal phosphorus-carbon bond length of 172.5 pm. This bond length lies in the range of phosphorus-carbon double bond lengths in phosphalkenes with typical values between 168 and 172 pm (ref.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

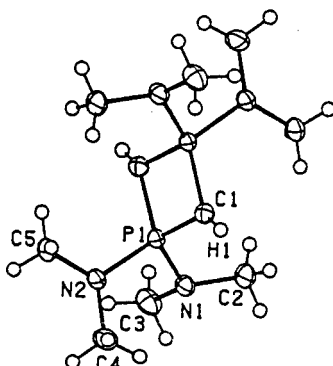
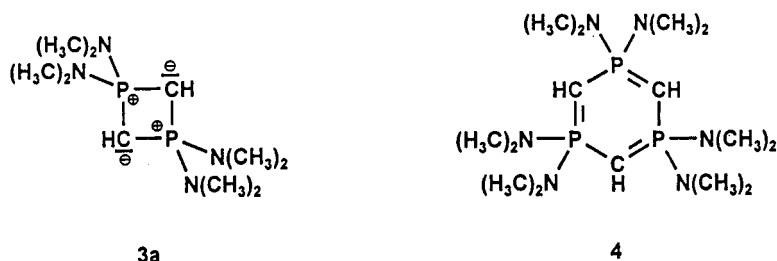


Fig. 1 Molecular structure of 1,1,3,3-tetrakis(dimethylamino)- $1\lambda^5,3\lambda^5$ -diphosphete **3**.

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 be interpreted by this electron distribution.



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)- $1\lambda^5,3\lambda^5,5\lambda^5$ -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 CH_2 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).

from the coordinated carbon atom to the one opposite to it. Optimization 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).

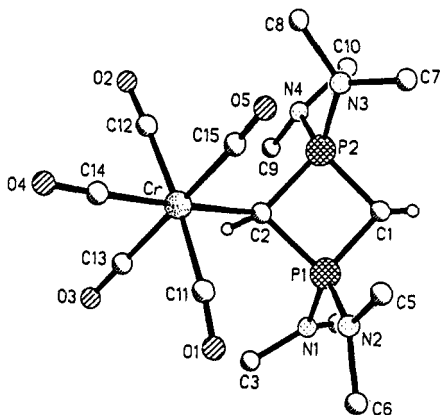
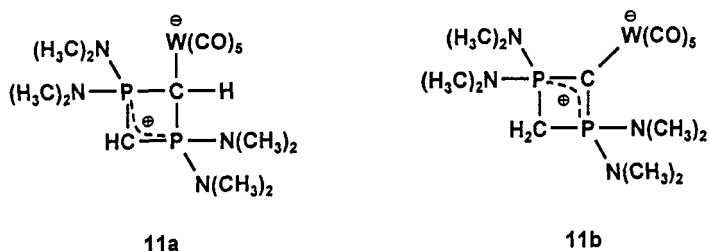
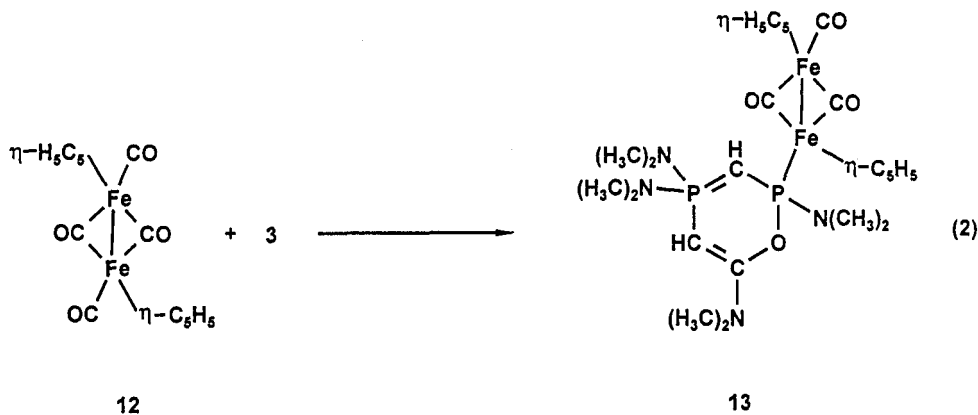


Fig. 2 Molecular structure of $1\lambda^5,3\lambda^5$ -diphosphete pentacarbonyl chrom **10**.

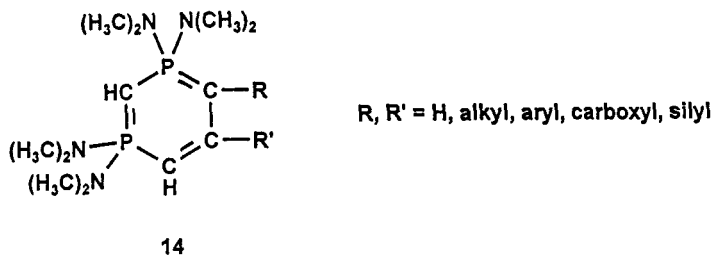


A surprising result was obtained from experiments to substitute one or more carbonyl groups in the binuclear cyclopentadienyl carbonyl iron complex **12** (see eq. 2; ref. 16). The expected compound or compounds in which one or more carbonyl groups were expected to be substituted by **3** were not obtained. 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 transferred from phosphorus to carbon. The mechanism of the reaction has not been elucidated yet.

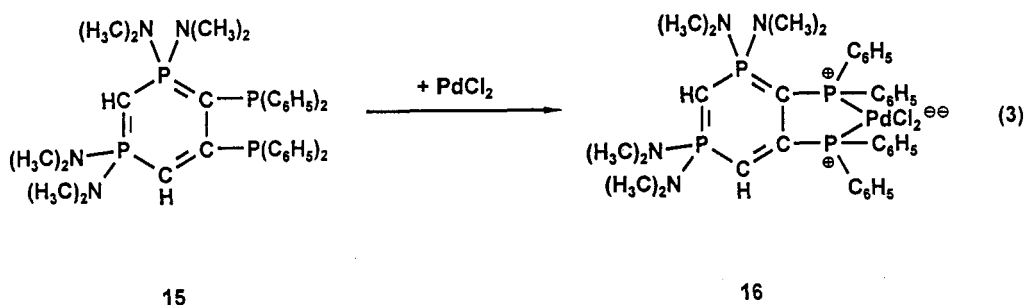


1 λ^5 ,3 λ^5 -DIPHOSPHABENZENES. COORDINATION COMPOUNDS WITH 4 AND 15 AS LIGANDS

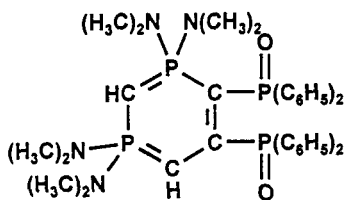
Acetylene and acetylene derivatives can easily be inserted into the four-membered ring of **3**, forming six-membered 1 λ^5 ,3 λ^5 -diphosphabenzenes (**14**) (ref. 17):



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 transition 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).



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.



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.

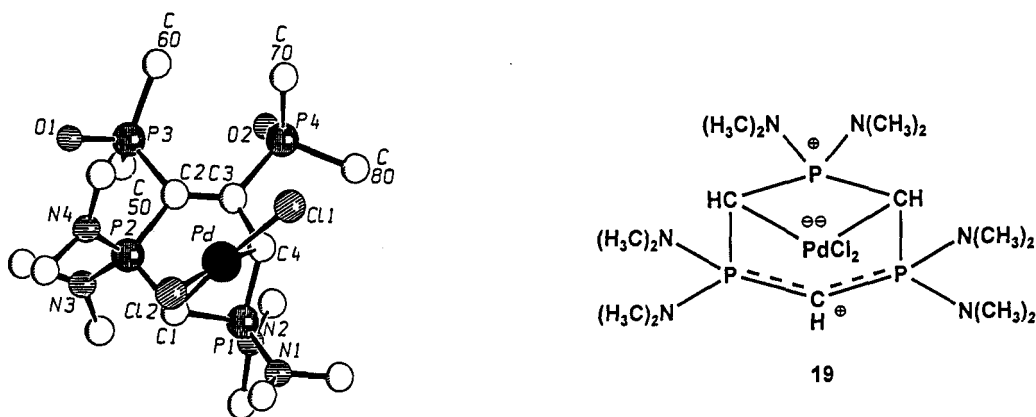
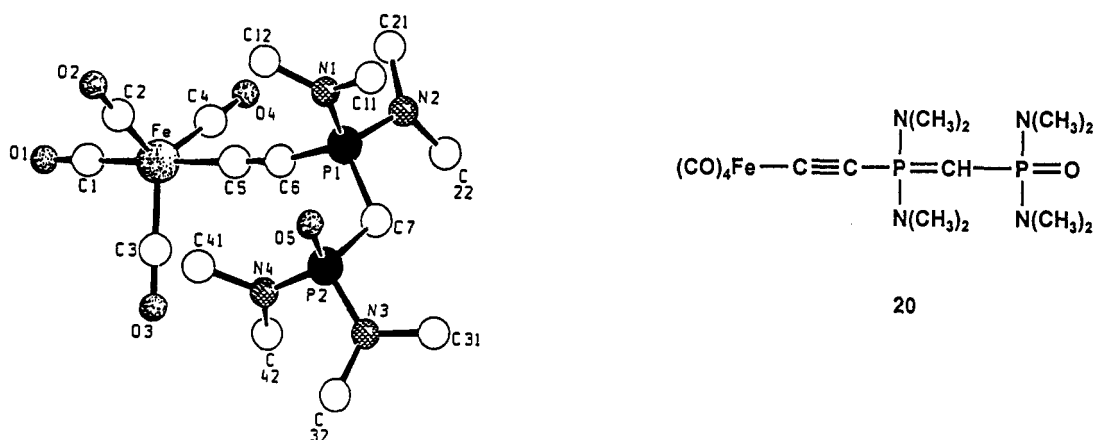


Fig. 3 Molecular structure of the diphosphabenzene palladium(II) complex **18**

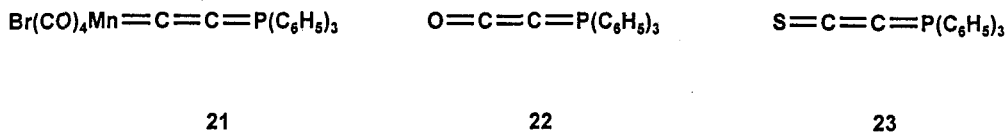
Also, the endocyclic carbon atoms of $1\lambda^5,3\lambda^5,5\lambda^5$ -triphosphabenzene **4** have good electron donor properties. **4** can, for instance, be reacted with palladium(II) chloride-benzonitrile to give the planar coordination compound **19** (ref. 21). As in the diphosphabenzene complex **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 $\text{Fe}(\text{CO})_5$ with **3**

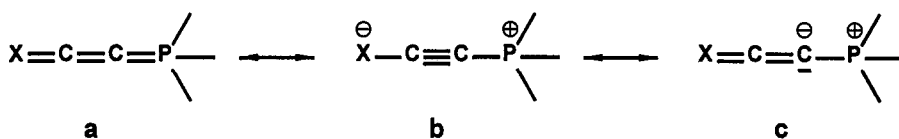
While nonacarbonyl diiron and **3** react to give $(1\lambda^5,3\lambda^5\text{-diphosphete})\text{Fe}(\text{CO})_4$ analogous to **10** (see Fig. 2; ref. 14) in which the four-membered ring of **3** is retained, reaction of pentacarbonyl iron with **3** leads to ring opening (ref. 22). A [2+2]-cycloaddition 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**.



A tetracarbonyl iron complex with a terminal ligand corresponding to the allenylidene ligand $C=C=CR_2$ 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 allenylidene ketene **22** (ref. 24) and thioketene **23** (ref. 25).



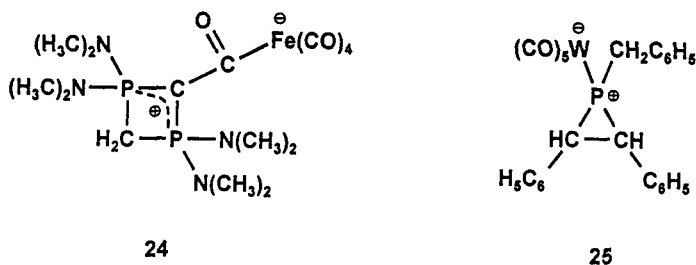
The bond angles are interpreted by the mesomeric formulas **a**, **b**, and **c**:



In formula **c** the phosphorus atom uses sp^2 hybrid orbitals 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).

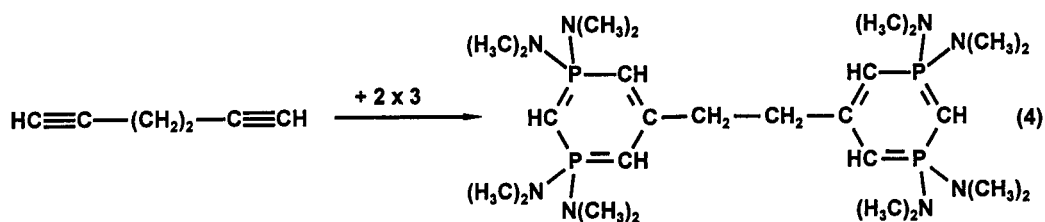
PHOSPHIRANES AS LIGANDS

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 tribenzylidifluoro phosphorane and lithium bis(trimethylsilyl)amide (ref. 26). With hexacarbonyl tungsten the corresponding phosphirane pentacarbonyl tungsten **25** is formed (ref. 26).



OUTLOOK

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



26

Reaction of **3** with 1,7-octadiene 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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