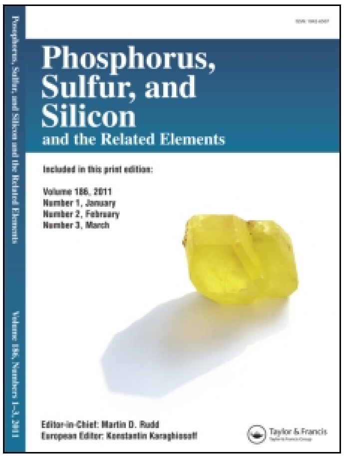

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REACTIONS OF PHOSPHORUS-PHOSPHORUS BONDED MIXED-VALENCE DIPHOSPHORUS COMPOUNDS

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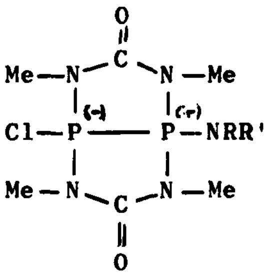
Abstract : A novel type of mixed valence diphosphorus compound, involving the grouping $Cl-\underset{|}{P}-\underset{|}{P}-NEt_2$, with the two phosphorus atoms doubly bridged by N.N'-dimethylurea, has become readily available. Reactions of this type of compound have furnished a variety of new structural elements, involving two directly bonded phosphorus atoms in two different oxidation states and / or coordination numbers.

The reaction of N.N'-dimethyl-N.N'-bis(trimethylsilyl) urea with aminodichlorophosphines, $RR'NPCl_2$, has provided an easy access to a novel class of diphosphorus compounds, 1 (c.f. ref. 1),



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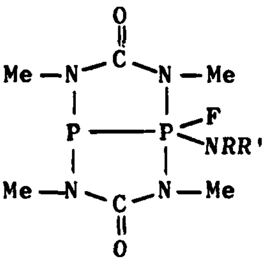
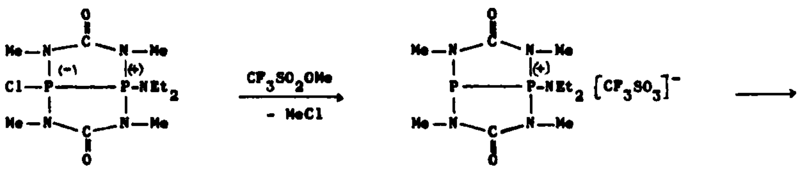


2

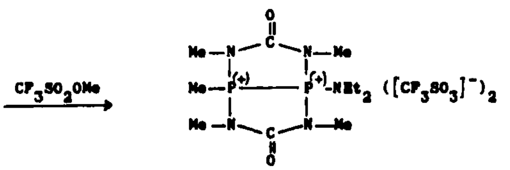
(R,R' = Me_2, Et_2, $(CH_2)_4$, $(CH_2)_5$, $(CH_2CH_2)_2O$, etc.). Reaction of 1 with sodium fluoride in acetonitrile has furnished the new class of compounds, $\lambda^3P\lambda^5P$-bonded fluorophosphoranes, 2. Compounds of types 1 and 2 display several sites of reactivity, especially at the two phosphorus atoms and, potentially, at the phosphorus-phosphorus bond. The compounds, 1 and 2 with RR' = Et_2 have been chosen for a study of some of their chemical reactions.

New diphosphorus systems have been created, e.g. by the oxidative addition of tetrachloro-o-benzoquinone to the lower-valent phosphorus atom in 1 (RR' = Et_2) (→$\lambda^5P\lambda^4P^{(+)}$), or by the reaction of 1 (RR' = $(CH_2)_5$) with chlorine (→$\lambda^6P^{(-)}\lambda^4P^{(+)}$). The reaction of 1 with two equivalents of CF_3SO_2OMe was found to produce the novel structural element, $\lambda^4P^{(+)}\lambda^4P^{(+)}$, i.e. a diphosphorus compound with positive charges at two neighbouring phosphorus atoms,



$\delta(\lambda^4P)$ 42.7 ; $\delta(\lambda^3P)$ 16.2

$^1J(PP)$ 170.6 ; δ_F $(CFCl_3)$ - 78.8.



δ_P 21.3 , 42.7 ; $^1J(PP)$ 219

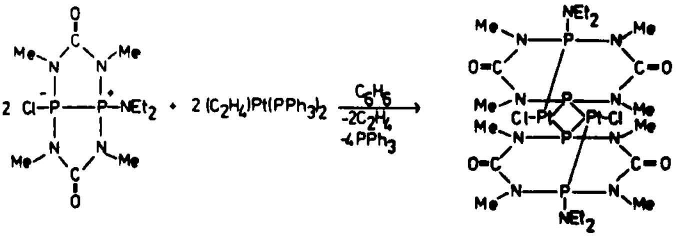
δ_F - 78.8

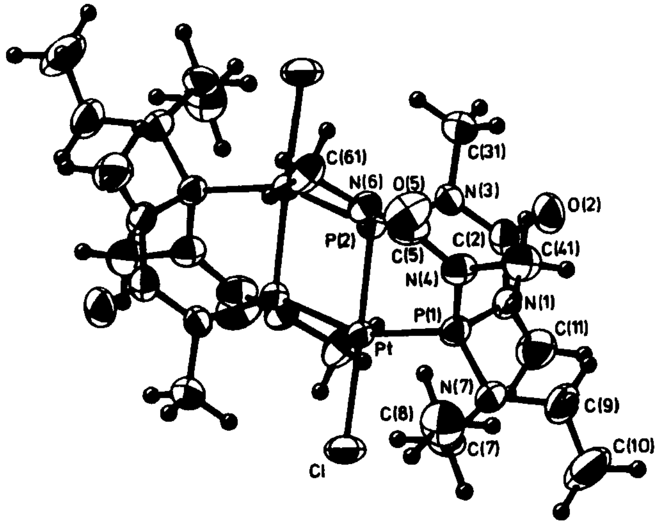
Reactions of the fluorophosphorane, 2 (RR' = Et_2) include abstraction of F^- from λ^5P, e.g. with PF_5 (→$\lambda^3P\lambda^4P^+$); preparation of $Fe(CO)_4$ complexes, involving 2 as a λ^3 donor species ; Staudinger reactions at λ^3P with Me_3SiN_3 or PhN_3 ;

preparation of further unusual diphosphorus compounds from the Staudinger products, e.g. by their reaction with BF_3.

The $\lambda^3P\lambda^5P$ fluorophosphorane, 2 (RR' = Et_2) was found to react with elemental sulfur under forcing conditions, to give a $\lambda^4P(:S)$-substituted fluorophosphorane. Reaction of the latter with PF_5 has given rise to the formation of a hexafluorophosphate with the $\lambda^4P\lambda^4P^{(+)}$ grouping.

The phosphorus-phosphorus bond in 1 (RR' = Et_2) was not left intact during its reaction with $(C_2H_4)Pt(PPh_3)_2$. In a redox reaction, involving two equivalents each of 1 and of $(C_2H_4)Pt(PPh_3)_2$ a novel, binuclear platinum complex was formed . A reaction scheme for the formation of this platinum complex, and a view of its structure are shown in the following ,





The n.m.r. data, especially ^{31}P, for all compounds have been recorded, and will be discussed. In a number of cases single-crystal X-ray structure determinations have been conducted, and detailed structural information is available.

The phosphorus-phosphorus bond lengths in all our new mixed-valence diphosphorus compounds havebeen found quite constant, in the neighbourhood of 220 pm, regardless of the oxidation state and/or coordination number of the two phosphorus atoms. These bond lenghts were observed for a wide variety of new and/or novel diphosphorus compounds, with or without charges at the two phosphorus atoms.

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