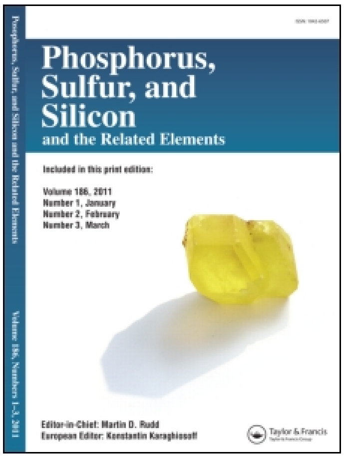

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Fluoroalkylated silylaminophosphanes and bicyclic diphosphanes: Reactivity and structures

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FLUOROALKYLATED SILYLAMINOPHOSPHANES AND BICYCLIC DIPHOSPHANES : REACTIVITY AND STRUCTURES

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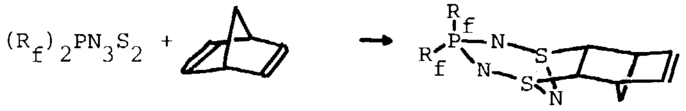
Abstract Phosphorus compounds containig electron withdrawing groups were prepared by degradation reactions of cyclic sulfur-nitrogen chlorides with perfluoroalkylated silylaminophosphanes and by the base catalysed attack of hexafluoroacetone on $P(CN)_3$ and $P(NCS)_3$. New results in the coordination chemistry of bicyclic diphosphanes towards transition metal carbonyls are reported and the improved oxidation of a diphosphane by the SO_2/Zn^{2+} system is discussed.

Silylaminophosphanes of the general type $R^1R^2P-N(SiMe_3)_2$ are intensively investigated during the last five years.[1] They can be easily prepared on a large scale and offer two sites of reactivity, the phosphorus lone pair and the nitrogen-silicon bond, the reactivity of which is a well understood area. If $R=CF_3$ and C_2F_5, the donor capability at the phosphorus atom is markedly changed, because of ths electron withdrawing effect. Halogenation by chlorine and bromine takes place smoothly at lower temperatures. Reaction-products are the halogenated monophosphazenes $(R_f)_2P(X)=NSiMe_3$ (1,2) (X=Cl, Br), which are precursors for oligomeric or polymeric fluoroalkylated phosphazenes.[2] However formation of the phosphonium salt by reaction with methyliodide cannot be achieved. We found that cyclic sulfur-nitrogen chlorides are reductively degraded by silylaminophosphanes, thus leading to 1,1-bis(perfluoroalkyl)cyclo-1-phospha-3,5-dithia-2,4,6-triazenes.

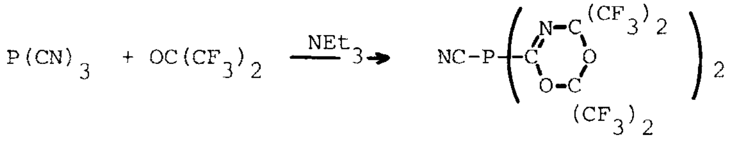
$$S_3N_2Cl_2,\ S_4N_4Cl_2 \xrightarrow{(R_f)_2PN(SiMe_3)_2} (R_f)_2PN_3S_2 + \quad (1)$$

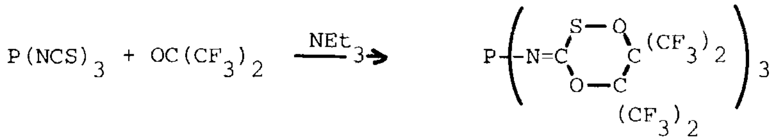
Because of their low melting points and high volatilities, the ring compounds could not be structurally investigated, but reaction with norbornadiene forms stable crystalline adducts allowing the X-ray structure determination.



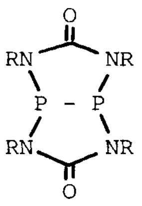
This class of compounds was first reported by R.Appel et al.[3] (R=NHSiMe$_3$). Three more derivatives (R=Me, Ø, OC$_6$H$_5$) were prepared by T. Chivers et al.[4], who reacted S_4N_4 with diphosphanes. When a pure sample of (CF$_3$)PN$_3$S$_2$ is allowed to stand for several days, it decomposes, forming S_4N_4 and an 1,3-diphosphadithiatetrazene with an unusual roof-like structure.

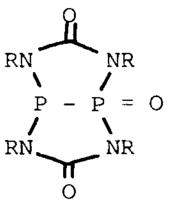
Hexafluoroacetone has prooved once more[5] to be a versatile reagent in fifth group chemistry. In a base catalysed reaction with As(CN)$_3$ a 14-membered heterocyclic ring consisting of As, O, N and C-atoms is formed. P(CN)$_3$and P(NCS)$_3$ also do not follow the established patterns of reactivity. Oxidative addition at phosphorus described by Ramirez[5] or insertion of the keton into the phosphorus carbon bond reported by Pudovik[6] were not observed. We found, that hexafluoroacetone adds across the pseudohalide, forming six-membered C,N,O- and C,O,S- containig heterocyclic rings.



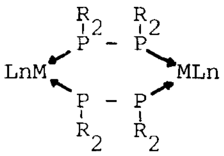


Recently we have reported the one-step reaction of N,N'-bissilylated ureas with PCl_3 to form new bicyclic compounds containing phosphorus-phosphorus bonds.[7] Depending not on the substituents on the nitrogen atoms but on the reaction conditions, the compounds contain a λ^3P-λ^3P- or a λ^3P-λ^4P bond.

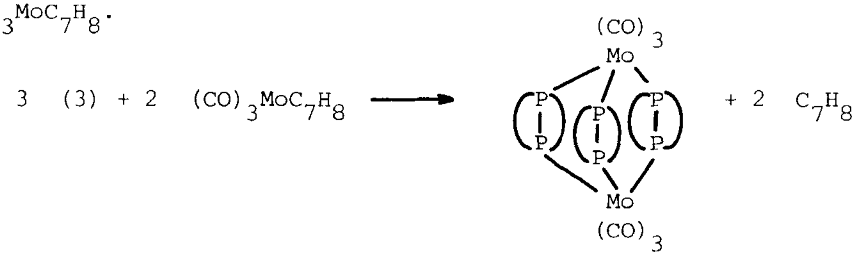

(3)


(4)

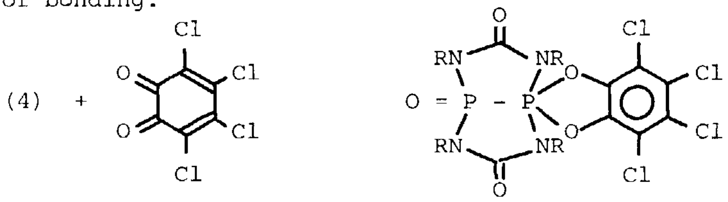
The preparation of polynuclear transition metal carbonyl complexes containing diphosphane ligands is of special interest, because such ligands may confer stability to the cluster and prevent it from fragmentation into monomeric units. The presence of more than one metal atom improves the catalytic potential in reactions in which multicenter interaction is important.[8] Elegant syntheses of homodinuclear six-membered rings of type (5) with diphosphane ligands were described by Vahrenkamp et al.[9]


(5)

We report the preparation of a binuclear molybdenum tricarbonyl complex with three diphosphane ligands by reacting (3) with $(CO)_3MoC_7H_8$.



The coordination chemistry of (4) was investigated by reacting it with $(CO)_5CrTHF$ in a 1:1 and with $(CO)_4CrC_7H_8$ in a 1:2 molar ratio. (4) can be oxidized by reacting it with tetrachloro-o-benzoquinone in a molar ratio of 1:1 to yield the corresponding λ^4P-λ^5P-diphosphorane. Up to now there are only two compounds known to contain this kind of bonding.[10]



In the course of our investigations on transition metal complexes of sulfur-nitrogen compounds, we observed the enhanced oxidizing capability of SO_2 in the presence of Zn^{2+}. Tetraphenyldiphosphane is smoothly oxidized and coordinated by $Zn(SO_2)_n(AsF_6)_2$ (n=2-4) without rupture of the P-P bond. Oxidations of phosphanes with SO_2, catalysed by PBr_3, reported by Fluck et al.,[11] always require long reaction times. The ease of the oxygen transfer under Zn^{2+} catalysis can be explained as due to the coordinationof SO_2 via oxygen to the metal center, thus weakening the opposite sulfur-oxygen bond

$$Zn(SO_2)_n(AsF_6)_2 + 3\ P_2\O_4 \longrightarrow Zn\ O_2P_2\O_4\ {}_3(AsF_6)_2 + S_n$$

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