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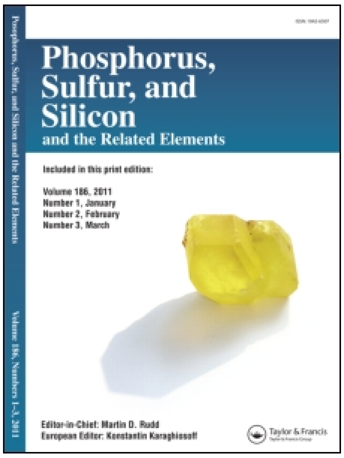

Phosphorus, Sulfur, and Silicon and the Related Elements

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Polyphosphorus Compounds: Recent Synthetic and Structural Results

Marianne Baudler[a]
[a] Institut für Anorganische Chemie der Universität Köln, Köln 41, FRG

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POLYPHOSPHORUS COMPOUNDS: RECENT SYNTHETIC AND STRUCTURAL RESULTS

MARIANNE BAUDLER
Institut für Anorganische Chemie der Universität Köln,
Greinstraße 6, D-5000 Köln 41, FRG

Abstract Various new phosphorus six-, five-, and three-membered ring compounds as well as polycyclic organophosphanes and the silaphosphacubane $(t\text{-BuSiP})_4$ have been synthesized and structurally characterized.

The only neutral six-membered ring compound of trivalent phosphorus so far known is hexaphenylcyclohexaphosphane.[1-3] We have recently been able to prepare hexachlorocyclohexaphosphane and hexabromocyclohexaphosphane by the following reactions:[4]

$$PCl_3 + 2\,LiH \xrightarrow[THF]{-40°C} \tfrac{1}{6}(PCl)_6 + H_2 + 2\,LiCl$$

$$PBr_3 + Mg \xrightarrow[THF]{-60°C} \tfrac{1}{6}(PBr)_6 + MgBr_2$$

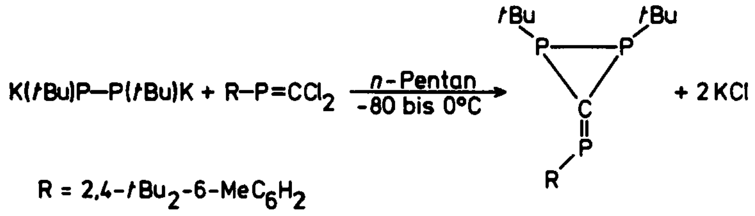
$$(PCl)_6\text{: } \delta(^{31}P) = +194 \text{ (singlet)}$$
$$(PBr)_6\text{: } \delta(^{31}P) = +220 \text{ (singlet)}$$

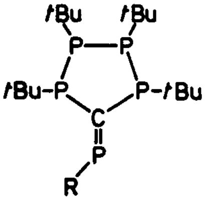
As the first perhalogenated cyclophosphanes they are only stable in diluted solutions at low temperature. With phenyllithium the well-known $(PPh)_6$ is formed. The ring size six of neutral phosphorus monocycles is obviously stabilized by electronegative substituents.

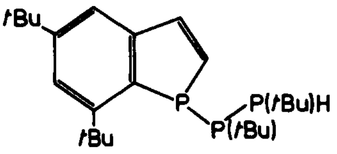
The reaction of alkylsubstituted cyclophosphanes with oxygen and sulfur under mild conditions afforded the monoxides $(t\text{-BuP})_4O$ and $(PEt)_5O$,[5] and the monosulfide $(PEt)_5S$,[6] respectively. According to the IR- and NMR-spectra, oxygen or sulfur is in each case bound exocyclically to the P_n-

skeleton of the parent cyclophosphane. In the case of the five-membered ring compounds various configurational isomers exist. An indication for the existence of constitutional isomers with heterocyclic six-membered rings has not been found.

Following the synthesis of diphosphiranes and methylenediphosphiranes[7] it has been found that a phosphinidenediphosphirane can also be prepared through a [2+1]-cyclocondensation reaction:[8]





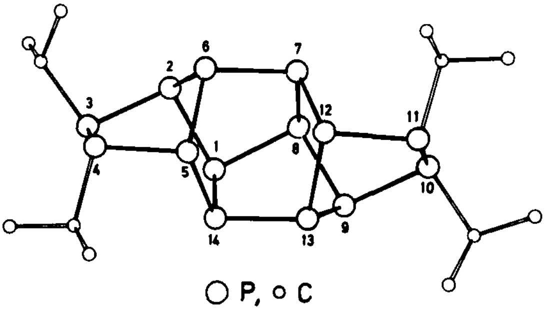


Additionally, tert-butylcyclophosphanes $(t\text{-BuP})_{3,4}$ as well as a phosphinidenetetraphospholane and a diphosphino-substituted phosphindole are formed. The separation of the reaction products could be achieved by means of fractional crystallization and high pressure liquid chromatography. The yellow solid phosphinidenediphosphirane is stable at room temperature and has been structurally characterized by various spectroscopic methods.

Three-membered phosphorus ring compounds of the type $(RP)_2PX$ (X = functional group) are suitable building blocks for the synthesis of novel compounds containing P_3 rings. For example, the condensation of $(t\text{-BuP})_2PSnMe_3$ with $SbCl_3$ leads to a tris(cyclotriphosphanyl) compound, in which three P_3 rings are linked through one antimony atom.[8] If PCl_3 instead of $SbCl_3$ is put into the reaction, a ring enlargement takes place with incorporation of the isolated phosphorus atom, leading to a cyclotetraphosphane with two neighboring cyclotriphosphanyl substituents.[9] Both compounds are formed as a mixture of two configurational isomers.

The increasing information meanwhile availabe on the polycyclic organophosphanes[10] indicates that the formation of constitutional isomers is obviously as common as it is with the polycycloalkanes. Thus, the dehalogenation of $RPCl_2$ in admixture with P_4 leads, in the case of R = Me, Et, i-Pr, to the 3,4,5,8,9,10-hexaorganotricyclo[5.2.1.$0^{2,6}$]decaphosphanes.[11,12] On going to the tert-butyl compound, however, a significant structural change occurs due to steric reasons: $P_{10}(t\text{-}Bu)_6$ has a skeleton consisting of a bicyclic P_6- and a monocyclic P_4 partial structure which are linked through a σ-bond.[13]

An unexpected structure has been found for the hexacyclic tetradecaphosphane $P_{14}(i\text{-}Pr)_4$ which could be prepared by reacting $i\text{-}PrPCl_2$, P_4, and magnesium and subsequently thermolysing the crude reaction product.[14] The P_{14}-skeleton is built up by two P_7-unit groups analogous to that of norbornane, which are linked by three zero bridges. The configurational isomer of the crystal, shown above, is transformed into a mixture of three diastereomers in solution already below room temperature, thus indicating remarkable molecular dynamics.



Very recently, the first silaphosphacubane $(t\text{-}BuSiP)_4$ [15] has been prepared by the reaction of $t\text{-}BuSiCl_3$ with

$LiAl(PH_2)_4$ at -40°C and subsequent removal of the solvent at room temperature. Two different molecules of symmetry $\bar{4}$ and 23 are present in the crystal. The cage, which is highly distorted compared with a cube, is composed of a larger P_4-tetrahedron and a smaller Si_4-tetrahedron, which results in the phosphorus atoms being displaced outwards; the bond angles at silicon and phosphorus are 102° and 77°, respectively. The remarkable thermal stability (m.p. 323-324°C) can be attributed to the similar covalent radii of phosphorus and silicon and to the bulky tert-butyl substituents.

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