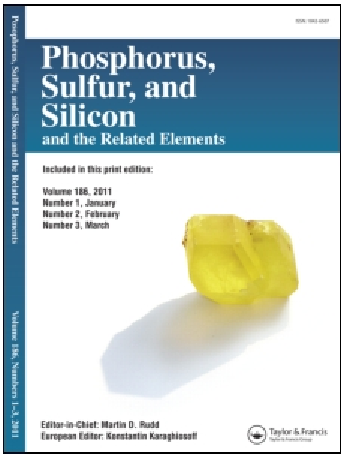

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Polycyclic Organophosphanes and Organosilaphosphanes - Recent Developments

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POLYCYCLIC ORGANOPHOSPHANES AND ORGANOSILAPHOSPHANES - RECENT DEVELOPMENTS

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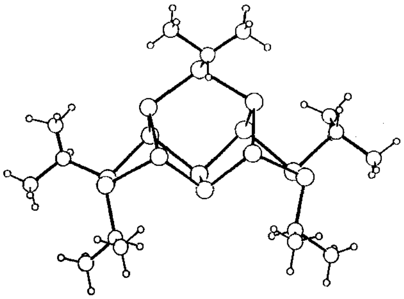
Abstract Various novel polycyclic isopropylphosphanes and tert-butylphosphanes with nine to twenty phosphorus atoms in the molecule have been synthesised and structurally characterised. Moreover, several precursors of the tert-butyl-substituted silaphosphacubane have been identified so that the stepwise construction of this pentacyclic silaphosphane is now clarified.

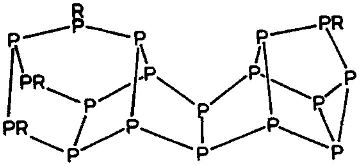
For structural investigations of phosphorus-rich organopolycyclophosphanes, the respective isopropyl derivatives have proved to be particularly suitable. On the one hand, they exhibit the typical skeletal structures of the sterically unhindered members of the individual compound classes and, on the other hand, are more soluble than the methyl or ethyl derivatives. This latter property facilitates their isolation and spectroscopic characterisation. The corresponding compounds $P_nPr^i_m$ with twelve to twenty phosphorus atoms in the molecule were obtained in preparatively interesting amounts by the reaction of Pr^iPCl_2 with P_4 and magnesium and subsequent thermolysis of the thus-formed crude phosphane mixtures.[1] By suitable work-up of the thermolysate in several separation steps, we have recently isolated the compounds $P_{13}Pr^i_5$, $P_{18}Pr^i_4$, $P_{18}Pr^i_6$, and $P_{20}Pr^i_6$ and clarified their structures.[2-5]

The structure of $P_{13}Pr^i_5$ is derived from the P_9R_5 constitutional isomer analogous to noradamantane by condensation of two isopropyl-substituted P_2 bridges and concomitant formation of two new five-membered rings. The resultant P_{13} moiety is a major building block of Hittorf's phosphorus. Thus,



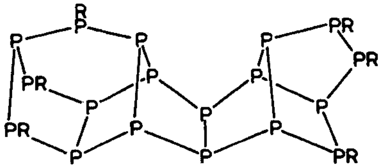
the compound $P_{13}Pr^{i}_{5}$ now constitutes the most phosphorus-rich, unchanged partial structure of the element in the form of a discrete molecule.

The structures of the compounds $P_{18}Pr^{i}_{4}$, $P_{18}Pr^{i}_{6}$, and $P_{20}Pr^{i}_{6}$ exhibit some close relationships. The skeletons of $P_{18}Pr^{i}_{4}$ and $P_{18}Pr^{i}_{6}$ each contain a P_{11} partial structure



$P_{18}R_4$

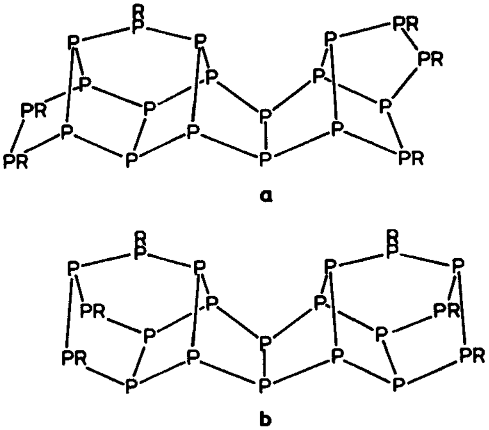
R = *i*-Pr



$P_{18}R_6$

which can be derived from the noradamantane-like P_9 skeleton by condensation of a P_2 bridge. The other structural element in the case of $P_{18}Pr^{i}_{4}$ is a P_9 framework analogous to deltacyclane. In the case of $P_{18}Pr^{i}_{6}$ the other partial structure is the P_9R_5 constitutional isomer analogous to brexane. Both molecules are typical conjuncto-phosphanes in which the partial frameworks are each annelated at their P_2 bridges. In this way a central P_8 partial structure analogous to pentalane is formed.

The eicosaphosphane $P_{20}Pr^{i}_{6}$ exists as two constitutional isomers **a** and **b** in equal proportions. In the case of **a**, the



$P_{20}R_6$
R = *i*-Pr

P_{20} framework consists of a P_{13} structural unit and a P_9 element analogous to brexane; in the case of **b**, it is made up of two P_{11} units identical to those occuring in the P_{18} compounds. The isomer **a** differs from $P_{18}Pr^i{}_6$ only by an additional, isopropyl-substituted P_2 bridge which completes the formation of a new five-membered ring annelated over three P atoms.

A completely different situation exists for the tert-butyl-substituted bi- and tricyclic phosphanes, where significant changes in the phosphorus skeletal structures are effected by steric interactions between the substituents. Thus, the compound $P_8Bu^t{}_6$ possesses the unusual structure of a 1,1'-bicyclotetraphosphane in which two four-membered phosphorus rings are linked to each other by a σ-bond.[6] The next higher homologues $P_9Bu^t{}_7$ and $P_{10}Bu^t{}_8$ follow the same structural principle.[7] In the case of the nonaphosphane, a PBu^t moiety is inserted between the two tert-butyl-substituted P_4 rings and, in the case of the decaphosphane, a chain consisting of two PBu^t moieties is inserted between the two rings. The more phosphorus-rich, tricyclic compound $P_{13}Bu^t{}_9$ is made up of the compounds $P_9Bu^t{}_7$ and $P_8Bu^t{}_6$ with the middle ring being common to both components of the molecule.[8] This tridecaphosphane is the first organophosphane to contain three P_4 rings linked by σ-bonds either directly or through an isolated phosphorus atom. In the case of the dodecaphosphane

$P_{12}Bu^t_8$, the phosphorus skeleton comprises a bicyclic P_8 ring and a monocyclic P_4 ring which can be linked together in various ways.[9] Accordingly, the compound is formed as a mixture of two constitutional isomers in almost equal proportions.

In connection with the tert-butyl-substituted silaphosphacubane $(Bu^tSiP)_4$ recently synthesised by the reaction of tert-butyltrichlorosilane with lithium tetraphosphinoaluminate[10] we have been able to identify various polycyclic precursors of this compound. Of particular interest is the first silaphosphane with a norcubane structure.[11] In contrast to the cubane, one phosphorus atom is lacking at a corner of the cube and the free valencies on the neighbouring silicon atoms are occupied by additional chlorine atoms. In addition to this compound, other precursors of the cubane have also been characterised so that the stepwise construction of this pentacyclic silaphosphane is now fully understood.[12]

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