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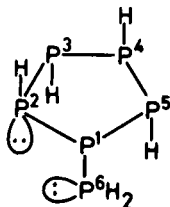
RECENT RESULTS ON PHOSPHORUS RINGS AND CAGES

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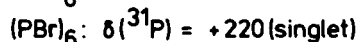
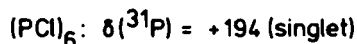
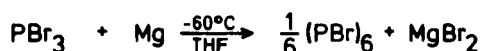
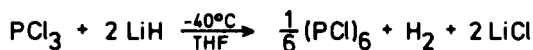
Abstract Various new phosphorus six- and three-membered ring compounds, cyclic polyphosphides with isolated anions, and polycyclic organophosphanes have been synthesized and structurally characterized.

Monocyclic organophosphanes P_nR_n have already been known for a long time.¹ For sterically unperturbed compounds the ring size n is five. Smaller ring sizes can be stabilized by bulky substituents. The only neutral six-membered monocycle of trivalent phosphorus so far known is hexaphenylcyclohexaphosphane.²⁻⁴ We have recently been able to enrich the corresponding phosphorus hydride P_6H_6 in the thermolysis products of higher open-chain phosphanes at 25-35°C.⁵ The structure elucidation was achieved by complete analysis of its proton-decoupled ^{31}P -NMR spectrum on the basis of double resonance experiments. According to the data obtained, P_6H_6



has the constitution of a phosphinocyclopentaphosphane in the configuration shown. Particularly informative in this respect is the large, positive, long-range coupling $^2J(P^2P^6)$ as an indication that the lone electron pairs of these phosphorus atoms are directed toward each other. Evidence for the existence of the constitutional isomer with a six-membered ring of phosphorus atoms and an all-trans arrangement of the hydrogen atoms was not found.

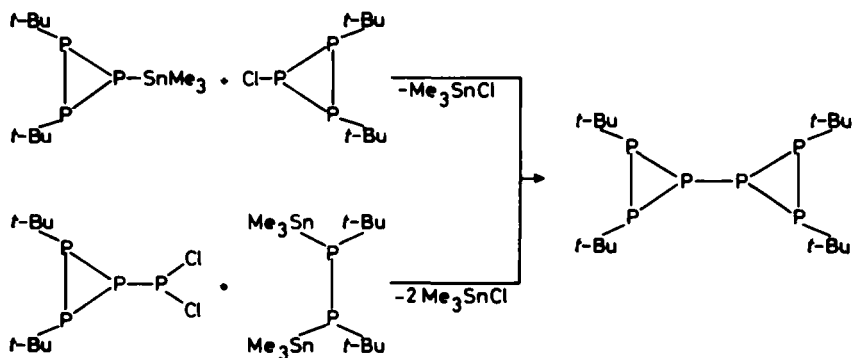
"Actual" cyclohexaphosphanes, however, could be detected in the corresponding phosphorus chloride and bromide compounds. Hexachlorocyclohexaphosphane and hexabromocyclohexaphosphane are formed in the partial



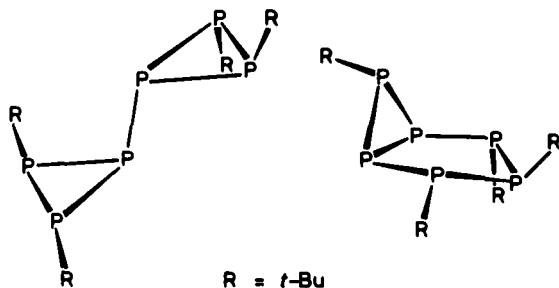
dehalogenation reaction of phosphorus trichloride and phosphorus tribromide, respectively, by lithium hydride or magnesium in polar solvents.⁶ As the first perhalogenated cyclophosphanes they are only stable in diluted solutions at low temperature and could be characterized by means of mass spectroscopy and ^{31}P nuclear magnetic resonance. In the reaction of P_6Cl_6 with phenyllithium the well-known hexaphenylcyclohexaphosphane is formed. These results indicate that the ring size six of neutral phosphorus monocycles is obviously stabilized by electronegative substituents.

Now a few words on three-membered phosphorus homo- and heterocycles. Since 1970 a considerable number of kinetically stable triorganocyclotriphosphanes has been

synthesized by different groups.⁷ Nevertheless, the synthetic potential of phosphorus three-membered ring compounds has scarcely been exploited. Starting from



functionalized cyclotriphosphanes with trimethylstannyl and chloro substituents, we have recently succeeded in linking two P₃ ring skeletons via a σ -bond.⁸ The resulting 1,1'-bicyclotriphosphane can also be obtained by an [1+2]-cyclocondensation of a dichlorophosphino-cyclotriphosphane with an 1,2-bifunctional diposphane. The crystalline compound is stable at room temperature.

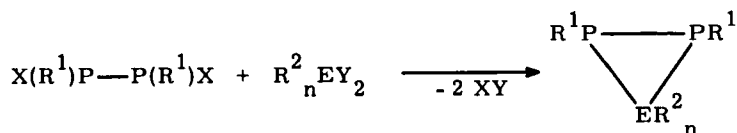


According to spectroscopic investigations, of the two possible configurational isomers, which differ from each other in the relative arrangement of the trans-oriented tert-butyl groups at the two three-membered rings, the sterically more favorable all-trans isomer with C₂ symmetry is present as an enantiomeric pair.

The 1,1'-bicyclotriphosphane is a constitutional isomer of the bicyclo[3.1.0]hexaphosphane formed by dehalogenation of a mixture of tert-butyldichlorophosphane and phosphorus trichloride with magnesium. On warming up to 128°C, the left phosphorus skeleton can be converted into the right one.

In order to link three P_3 rings through one atom, a central atom larger than phosphorus is necessary. Hence, the first tris(cyclotriphosphanyl) compound $[(t\text{-BuP})_2P]_3\text{Sb}$ could be obtained by reacting the stan-nyl substituted cyclotriphosphane with antimony trichloride in the molar ratio of 3:1.⁹ The compound is formed as a mixture of two configurational isomers, of which the symmetric one precipitates from the reaction mixture at low temperature. It is a yellow solid, which is stable below -30°C in the absence of air and light. At higher temperatures or upon exposure to daylight decomposition occurs, leading mainly to the 1,1'-bicyclotriphosphane and elemental antimony.

Following the synthesis of homocyclic triorgano-cyclotriphosphanes, numerous three-membered phosphorus heterocycles have also been prepared with carbon, silicon, germanium, tin, boron, nitrogen, arsenic, antimony, sulfur, and selenium as heteroatoms.⁷ The synthesis of the P_2E ring skeletons - E is the heteroatom -



$X = K; Y = Cl; E = C, Si, Ge, Sn, B, As, Sb$

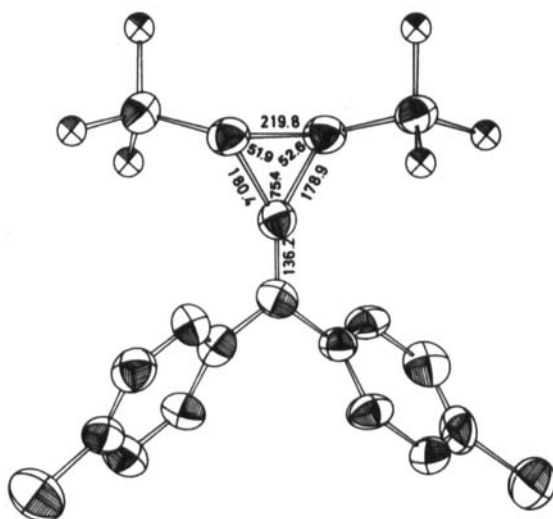
$X = Cl; Y = Me_3Sn; E = S, Se, N$

$K(t\text{-Bu})P-P(t\text{-Bu})K$

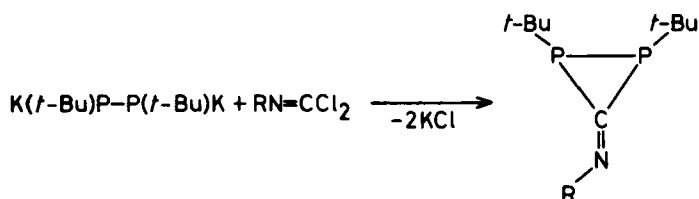
$Cl(t\text{-Bu})P-P(t\text{-Bu})Cl$

generally is done through the [2+1]-cyclocondensation of a bifunctional 1,2-diorganodiphosphane with a geminal nonmetal or metal compound. In particular, 1,2-dipotassium-di-tert-butyldiphosphide and 1,2-dichloro-di-tert-butyldiphosphane have proved well suited synthons for the preparation of kinetically stable phosphorus three-membered ring heterocycles.

Among the three-membered ring heterocyclophosphanes the compounds with carbon as a hetero ring atom - the diphosphiranes - are of particular interest because of their close relationships to cyclopropanes. After it had turned out that the replacement of a tert-butyl substituted phosphorus atom in tri-tert-butylcyclotriphosphane by a $>CR_2$ group does not significantly reduce the stability of the three-membered ring skeleton, we were particularly interested in P_2C heterocycles with an exocyclic double bond, that means with a sp^2 hybridized carbon atom. Since the corresponding cyclopropanes generally are highly reactive, such compounds should be rather unstable. Applying our proven synthetic approach, starting from 1,2-di-potassium-di-tert-butyldiphosphide and 1,1-dichloroolefines, first various methylenediphosphiranes $(t-BuP)_2C=CR_2$ could be prepared.¹⁰ These compounds are unexpectedly stable and less reactive than cyclopropanes with an exocyclic methylene group. The X-ray structure analysis of the 4-chlorophenyl derivative revealed a very small bond angle of only 52° at the phosphorus, whereas the endocyclic angle of 75° at the carbon is significantly larger than in methylenecyclopropanes, where its value is $62-64^\circ$.



In an analogous way also diphosphiraneimines could be obtained using isocyanide dichlorides as synthetic reagents.¹¹ Because of the higher reactivity and worse



$R = 2,4\text{-}t\text{-Bu}_2\text{C}_6\text{H}_3$ $\delta(^{31}\text{P}) = -130,3, -172,1$ (26°C)

$^1J(\text{PP}) = -38,1 \text{ Hz}$

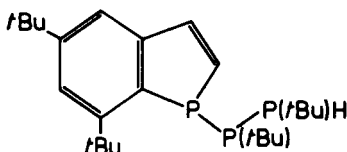
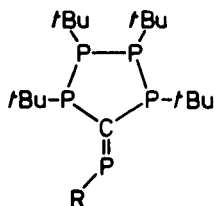
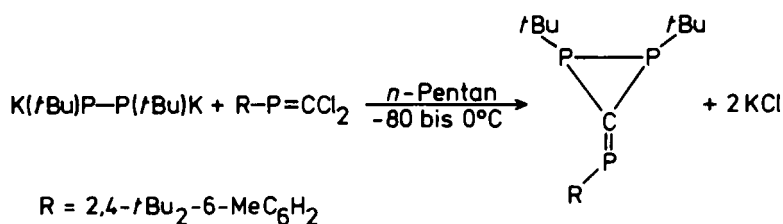
$R = 2\text{-}t\text{-BuC}_6\text{H}_4$ $\delta(^{31}\text{P}) = -129,9, -170,8$ (25°C)

$^1J(\text{PP}) = -38,3 \text{ Hz}$

steric shielding of the exocyclic imino group, an aryl substituent with one alkyl group in ortho-position is needed in this case for kinetic stabilization. If this is a tert-butyl group, the compounds are stable at room temperature and can be isolated in their pure form. Two alkyl groups in ortho-position, however, block the formation of diphosphiraneimines, since the conjugation of the C=N double bond and the aryl group is abolished due to a torsion of the C₆ ring relatively to the P₂C=N

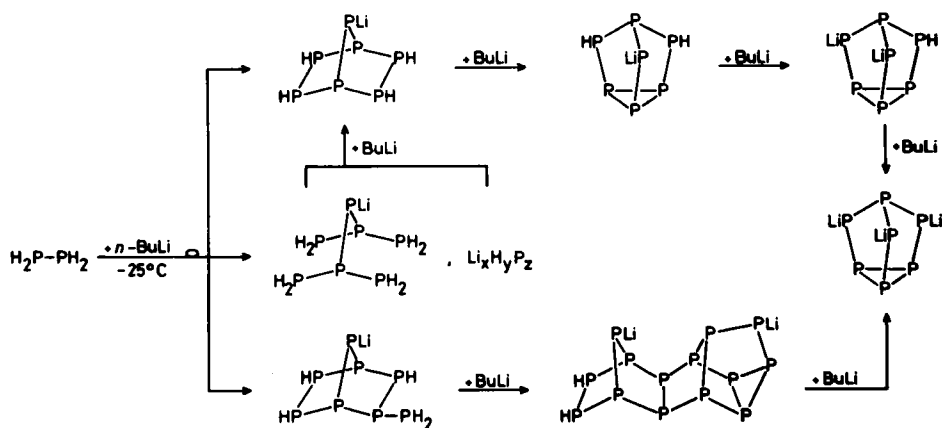
plane. Thermolysis of the diphosphiraneimines produces the corresponding isonitrile and tetra-tert-butylcyclo-tetraphosphane, probably via the formation of di-tert-butylidiphosphene as an intermediate.

With an optimum steric shielding of the exocyclic double bond we have also succeeded very recently in synthesizing the first phosphinidenediphosphirane $(t\text{-BuP})_2\text{C}=\text{PR}$ with $\text{R} = 2,4\text{-}t\text{Bu}_2\text{-6-MeC}_6\text{H}_2$.¹² The cor-



responding dichloromethylidenephosphane $\text{RP}=\text{CCl}_2$ has been prepared by the reaction of the monolithiumphosphide with tetrachloromethane and subsequent elimination of hydrogen chloride. Apart from the phosphinidenediphosphirane mainly tert-butylcyclophosphanes of ring sizes four and three 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 completely characterized by various spectroscopic methods.

Furthermore the Cologne group has, for some time, put an emphasis on the field of cyclic polyphosphides with isolated anions, obtainable from solutions. As has already been reported previously,^{7,13} diphosphane reacts with *n*-butyllithium with simultaneous disproportionation to give trilithium heptaphosphide, PH_3 , and *n*-butane. Recently, a series of new cyclic polyphosphides were detected as intermediates in this metalation reaction and most of them were isolated in pure form at lower temperatures.¹⁴⁻¹⁷ The primary step is the formation of lithium trihydrogen diphosphide, which, however, is not stable in the presence of diphosphane. In a rapid series of disproportionation and transmetalation reactions, it is initially converted into the highly reactive, monolithiated, open-chain phosphanes $\text{LiH}_{n+1}\text{P}_n$ and then into cyclic compounds with a greater number of phosphorus atoms. The first NMR-spectroscopically de-

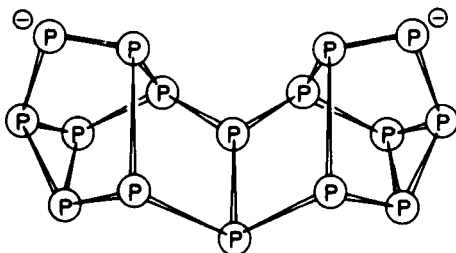
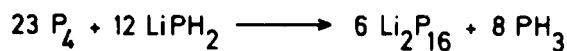


tectable reaction products are the polyphosphides LiH_4P_7 and LiH_5P_8 as well as two precursors of LiH_4P_7 , namely LiH_8P_7 and a not yet identified phosphide $\text{Li}_x\text{H}_y\text{P}_z$. On the whole, a noticeable tendency for the formation of a P_7 skeleton, analogous to that of norbornane, is observ-

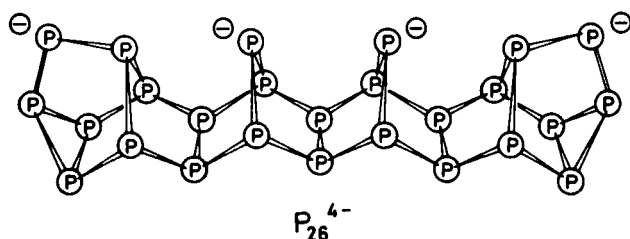
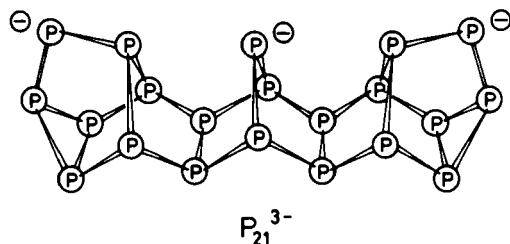
ed. By adding further amounts of butyllithium, LiH_8P_7 and $\text{Li}_x\text{H}_y\text{P}_z$ are converted into LiH_4P_7 , which then temporarily remains unchanged, whereas LiH_5P_8 reacts further to furnish the insoluble polycyclic tetradecaphosphide $\text{Li}_2\text{H}_2\text{P}_{14}$. As soon as its formation is complete, LiH_4P_7 also reacts further to give the tricyclic heptaphosphide LiH_2P_7 , which is then gradually transformed into the final product Li_3P_7 . During the last step in the reaction this compound is also formed by degradation of the tetradecaphosphide.

The compositions and structures of the new polyphosphides have been established by complete analyses of their proton-decoupled ^{31}P -NMR spectra or in the case of the tetradecaphosphide by a two-dimensional phosphorus-NMR spectrum. It is particularly interesting that the polycyclic P_{14} skeleton is formed in the course of the transformation of a bicyclic P_7 skeleton with a side chain to a tricyclic P_7 skeleton with a cage structure. The $\text{P}_{14}\text{H}_2^{2-}$ ion is a typical conjuncto-phosphane, which is made up of a P_7 partial structure analogous to that of norbornane and a P_9 partial structure analogous to that of deltacyclane joined through a common two-atom bridge; thus, a central P_8 partial structure analogous to that of pentalane is formed.

The dilithium hydrogen heptaphosphide, a further intermediate, is not stable at room temperature but decomposes in a complex disproportionation reaction in which, among other products, dilithium hexadecaphosphide is formed.^{7,18} The constitution of the P_{16}^{2-} ion in solution is identical with that found by von Schnering et al.^{19,20} for solid $(\text{Ph}_4\text{P})_2\text{P}_{16}$ by means of X-ray structural analysis. Thus, the P_{16} skeleton represents a conjuncto-phosphane made up of two P_9 structural ele-



ments, analogous to that of deltacyclane, joined through a common two-atom bridge. Dilithium hexadecaphosphide can also be prepared more simply and in high yield by the nucleophilic cleavage of white phosphorus with lithium dihydrogenphosphide in a molar ratio of 1.92:1.²¹

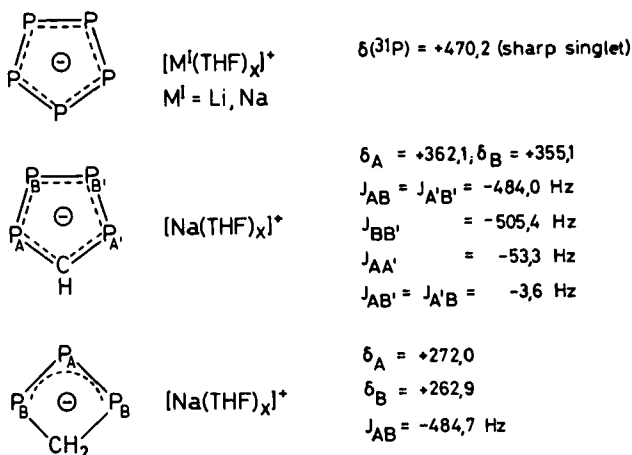


Likewise, both the room temperature decomposition of Li_2HP_7 and the cleavage of white phosphorus with LiPH_2 or sodium under different stoichiometric conditions give rise to the henicosaphosphides $\text{M}_3^{\text{I}}\text{P}_{21}$ and the

hexacosaphosphides $M^I_4P_{26}$, of which the compounds Na_3P_{21} and Li_4P_{26} have been isolated in pure form as solvent adducts with 15 and 16 moles of tetrahydrofuran, respectively.^{22,23} According to detailed ^{31}P -NMR spectroscopic investigations, they contain the isolated anions P_{21}^{3-} and P_{26}^{4-} , which are made up of two P_9 terminal groups, analogous to that of deltacyclane, and one or two, respectively, P_7 middle groups, analogous to that of norbornane. Noteworthy of the phosphorus-rich phosphides with conjuncto-phosphane skeletons is the preference for P_9 terminal groups analogous to that of deltacyclane, whereas covalent, polycyclic organophosphanes P_nR_m ($m < n$) usually contain terminal, two-atom bridges with trans-oriented substituents. Apparently, two-atom bridges with negative charges on neighboring phosphorus atoms are energetically so unfavorable in polyphosphides that the system spontaneously stabilizes itself by closure of a zero bridge to form the three-membered ring of the partial structure analogous to deltacyclane. This explains why the corresponding polyphosphides with isolated P_n^{m-} ions do not exist for all covalent phosphanes P_nR_m ($R = H, \text{ alkyl, aryl}$).

Reacting trisodium henicosaphosphide with excess alkyl halides or trimethylchlorosilane affords the partially substituted henicosaphosphides $NaP_{21}R_2$ with trans-oriented substituents R on the terminal P_9 groups.²⁴ A substitution at the phosphidic phosphorus atom of the P_7 middle group does not occur for steric reasons. Protonating agents such as acetylacetone, in contrast, attack primarily at the central P^- atom, the site of greatest nucleophilicity, so that the hydrogen henicosaphosphide Na_2HP_{21} is accessible in this manner.²⁵

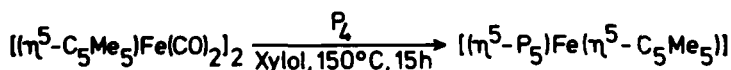
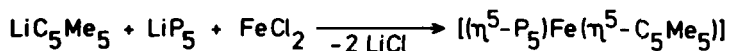
In the reaction of white phosphorus with sodium powder in the atomic ratio of 3:1 in boiling diglyme, small amounts of three further compounds are formed in addition to those polyphosphides obtained when the reaction is performed in tetrahydrofuran or 1,2-dimethoxyethane.²⁶ These products are characterized by ³¹P-NMR signals at low field in the region typical for diphos-



phenes and phosphaaalkenes. With $LiPH_2$ in tetrahydrofuran, only lithium pentaphosphide is formed and, after separation of the other polyphosphides, it can be obtained as a pure solution in tetrahydrofuran.²⁶ The formation of the heterocyclic anions in the reaction with sodium is indicative of the participation of the solvent diglyme in the course of the reaction. The novel polyphosphides are remarkably stable in solution; neither at room temperature nor after short-heating can the start of decomposition be detected by ³¹P-NMR spectroscopy. In contrast, a conversion to phosphorus-rich polyphosphides, especially $M^I_2P_{16}$ and $M^I_3P_{21}$, takes place on complete removal of the solvent. The constitutional assignments for the three anions are based on their NMR data and, in the case of the pentaphosphacyclopentadienide ion, also

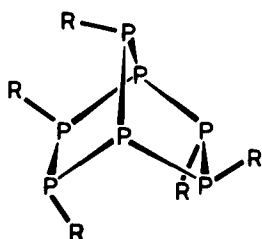
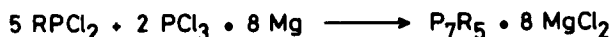
on the negative-ion mass spectrum and the analytically determined Na:P ratio of 1:5 for solutions of NaP_5 . To date, the P_5^- species has only been observed in the negative-ion mass spectrum of red phosphorus at 325°C ²⁷ and in some transition metal complexes, recently prepared by Scherer.^{28,29} The formation of this ion in the subsequent reactions of the nucleophilic cleavage of white phosphorus under conditions that favor the formation of polyphosphides with conjuncto-phosphane skeletons is indicative of its direct participation in the complex reactions involved in the synthesis of phosphorus-richer from phosphorus-poorer polyphosphides. The spontaneous formation and thermal stability are in accord with the most recent MNDO calculations,³⁰ which predict a significant stability for the P_5^- ion.

Studies on the reaction behavior of the alkali-metal pentaphosphacyclopentadienides are in progress. With compounds of the transition metals Fe, Ni, Rh, Mn, Cr, or Mo dark brown to black solids are formed, whose insolubility and relative nonvolatility make their characterization difficult.³¹ However, the black reaction product formed immediately upon reaction with FeCl_2 in THF at room temperature exhibits a characteristic IR band at 815 cm^{-1} , which is evidence for an intact aromatic P_5 ring as structural element. In addition, the mixed pentaphosphacyclopentadienyl-pentamethylcyclopentadienyl sandwich complex could be prepared by direct one-pot synthesis from LiP_5 , LiC_5Me_5 and FeCl_2 ;³¹ the

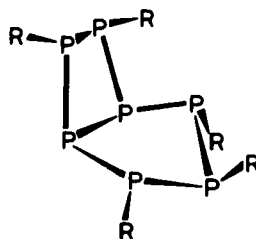


product is identical with the compound recently obtained by Scherer et al.³² by cothermolysis of a mixed pentamethylcyclopentadienyl carbonyl iron complex and white phosphorus. The existence of the free "aromatic" anions P_5^- and P_4CH^- again reveals the close relationship between phosphorus and carbon chemistry.⁷

A further field, intensively studied by the Cologne group, is that of the polycyclic organophosphanes P_nR_m ($m < n$). In addition to results already reported previously,⁷ many new representatives with 4-13 phosphorus atoms in the molecule have been prepared and their structures elucidated during the last few years. The organopolycyclophosphane with the largest phosphorus skeleton so far identified is the compound $P_{24}(i\text{-Pr})_4$ of as yet unknown structure. The increasing information meanwhile available on the polycyclic organophosphanes indicates that the formation of constitutional isomers is probably as common as it is with the polycycloalkanes. In the following a few typical examples shall be discussed in more detail.



$R = \text{Me, Et, } i\text{-Pr}$

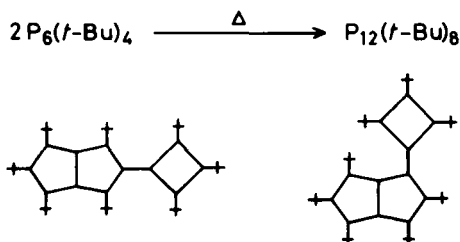


$R = t\text{-Bu}$

As reported previously,^{7,33} the dehalogenation of organodichlorophosphanes in admixture with phosphorus trichloride leads, in the case of small alkyl groups, to the 2,3,5,6,7-pentaorganobicyclo[2.2.1]heptaphosphanes.

Surprisingly, the recently prepared *tert*-butyl compound contains a completely different phosphorus skeleton, consisting of a five-membered ring and an annelated four-membered ring.³⁴ The structure of a 2,3,4,6,7-penta-*tert*-butylbicyclo[3.2.0]heptaphosphane is apparently the result of a destabilization of the P_7 skeleton analogous to that of norbornane owing to increasing steric interactions with increasing steric bulk of the substituents at P_6 and P_7 .

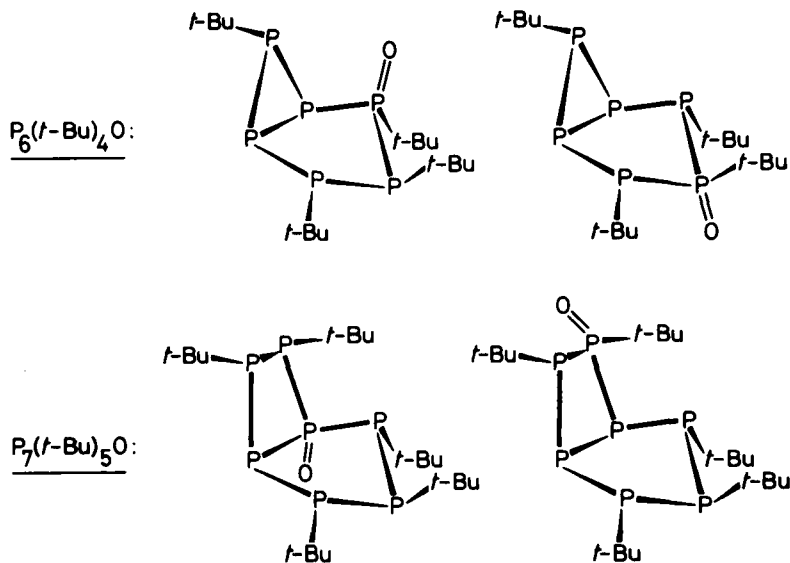
Different structures for one and the same compound can be formed when several skeletons with comparable stabilities are possible for a single compound. Thus, constitutional isomers of conjuncto-phosphanes can vary by different linkage of the same partial skeletons. One example of this is the octa-*tert*-butyldodecaphosphane,



which is formed by thermolytic "dimerization" of the corresponding bicyclo[3.1.0]hexaphosphane and can be isolated as colorless crystals.^{35,36} Its phosphorus skeleton is a ring assembly of a bicyclic and a monocyclic ring system which can be linked in two different ways. Accordingly, the compound is produced as a mixture of two constitutional isomers of comparable abundance, which can be separated by chromatography. Both compounds have similar stabilities.

Constitutional isomers can also be formed in the class of organopolycyclophosphane oxides. Like all other compounds of trivalent phosphorus, polycyclic organo-

phosphanes readily undergo oxidative attack at the lone electron pairs on the phosphorus atoms. Although the resistance toward atmospheric oxygen increases with increasing phosphorus content and increasing bulk of the substituents, rapid oxydation generally takes place in solution. Thus, the bicyclic phosphanes $P_6(t-Bu)_4$ and



$P_7(t-Bu)_5$ react with dry air in solution at room temperature to form the corresponding monoxides, respectively, which can be isolated as pale yellow solids.³⁷ Both compounds are product mixtures of two constitutional isomers. Their structures have been elucidated by complete analyses of their proton-decoupled ^{31}P -NMR spectra. Accordingly, in each case, the oxygen atom is bonded exocyclically to the P_n skeleton of the parent compound and the three- and four-membered ring, respectively, are strongly inclined towards the five membered ring. The attack of the oxygen at a polycyclic organophosphane is obviously mainly determined by steric factors. As can be seen from the observed isomer distribution, for instance in $P_7(t-Bu)_5$ the bonding of oxygen to P^1 and P^7

is apparently equally favorable, but at P^2 or P^4 , in contrast, it is hindered by the endo position of the tert-butyl group at P^7 . The fact that no isomers of $P_6(t-Bu)_4O$ are formed with the oxygen bonded to the three-membered ring is presumably attributable to the predominant s character of the lone electron pairs on the corresponding phosphorus atoms of the parent compound.

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