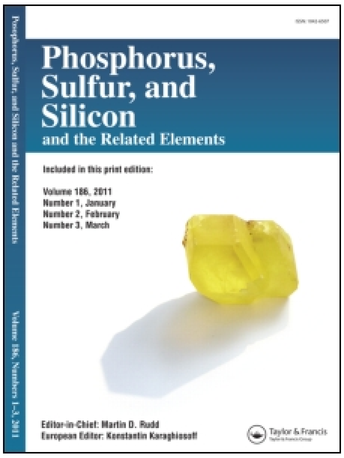

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NITROGEN, PHOSPHORUS, SULFUR-BUILDING STONES OF RINGS AND CAGES

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NITROGEN, PHOSPHORUS, SULFUR—BUILDING STONES OF RINGS AND CAGES

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A review of recent developments in the chemistry of compounds with ring and cage structures made of nitrogen, phosphorus and sulfur atoms is given. Both synthetic and theoretical aspects are considered.

I would like to focus my talk on some recent successes in the synthesis involving ring formation reactions in which rings containing phosphorus, carbon, and sulfur are formed. To begin, however, I would like to consider the simplest polycyclic system which is formed by phosphorus atoms, namely white phosphorus.

A. THE MOLECULE OF WHITE PHOSPHORUS

The remarkable stability of the tetrahedral P_4 molecule constitutes one of the peculiarities of the chemistry of phosphorus.[1] Despite the strain expected for 60° bond angles, one finds a phosphorus-phosphorus bond energy of around 200 kJ/mol in the P_4 molecule which may be considered as typical for phosphorus-phosphorus bonds.[1] Virtually no strain should be present in the cubic P_8 molecule which, however, has never been prepared.[2] Trinquier and others find P_4 to be 125 kJ/mol more stable than 2 P_2,[3] as compared to the experimental value of 232 kJ/mol. The same authors calculated P_8 to be 42 kJ/mol more stable than 2 P_4.[4] The authors argued, however, convincingly that this result merely reflects basis set problems. Similar results were published by Janoschek and myself in 1979.[5] A more accurate treatment of the relative stability of P_2, P_4, and P_8 has been achieved by Ahlrichs et al. very recently.[2]

The authors included effects of valence electron correlation for the smaller systems P_2 and P_4 by means of the recently developed coupled pair functional (CPF) method.[2] On the SCF level one finds a pronounced influence of f functions: ΔE increases from 151 kJ/mol with 1d to 182 kJ/mol with 2d1f. The relatively large effect of f functions indicates bond strain in P_4.[2] As far as the equilibrium distance is concerned the 2d1f CPF result with 221 pm is in perfect agreement with the only available experimental value of 221 ± 2 pm.[6]

Finally, we ought to try to understand the relative strength of the P—P bonds in P_4 despite unfavorable bond angles. The Mulliken population analysis indicates just small promotions from the atomic $3s^23p^3$ configuration to 3d orbitals. Ahlrichs, however, points to the population analysis based on occupation numbers, which characterizes covalent bonds by means of shared electron numbers.[2] For P_4, one gets a shared electron number of 1.36. This two center contribution is typical for strong

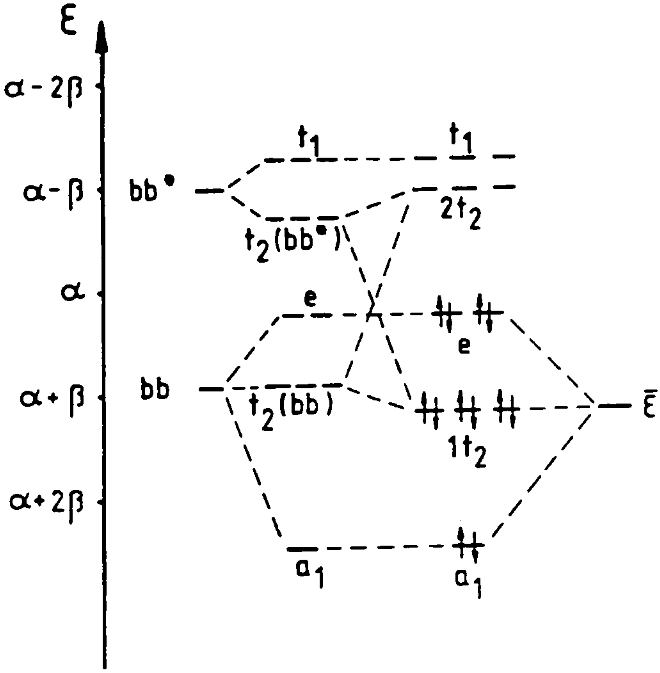


FIGURE 1 MO diagram of P_4 (T_d) within the extended Hückel approach. bb and bb* denote bonding and antibonding banana bond. $\bar{\varepsilon}$ denotes the weighted average of orbital energies of occupied MO's.[2]

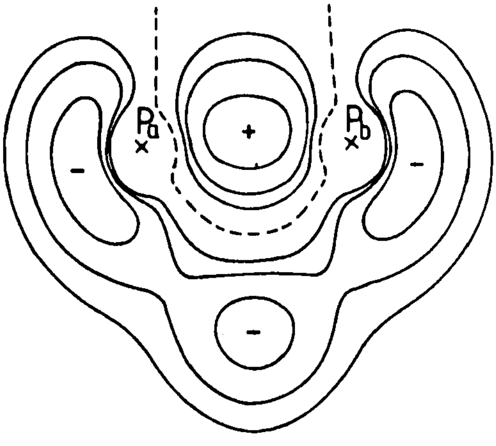


FIGURE 2 Contour lines of the highest occupied t_2 MO of P_4 in the plane going through the center of the tetrahedron and two corners occupied by P_a and P_b. P_c and P_d are above and below the plane in the lower part of the figure. The lines plotted correspond to 0 (dashed), ±0.04, ±0.06, ±0.09, in au.[2]

covalent single bonds. The three-center and four-center terms are unusually large and of the bonding type. The large three-center number found for P_4 proves that valence molecular orbitals are composed of different atomic orbital contributions such that corresponding bonding and anti-bonding three body effects do not cancel. If we assume that bonding of phosphorus mainly involves 3p atomic orbitals, the s atomic orbitals can be considered to be frozen. The six localized banana bonds reduce to a_1, t_2(bb), and e in T_d symmetry as shown in Figure 1. Contour lines of the $1t_2$ molecular orbital are shown in Figure 2. The nodal surface passing through the center of the tetrahedron, causes antibonding between the P_aP_b and P_cP_d subunits of the tetrahedron.[2] The outer region, however, shows no node and implies bonding interactions between the two P_2 subunits. A similar state of affairs is encountered for three-membered rings. P_3 rings occur not only in P_4 but in many other molecules like the cyclotriphosphanes or P_4S_3. Quite a different situation is found in cubic P_8. It is higher in energy than 2 P_4 which is attributed to the repulsion of parallel PP bonds.[2]

B. POLYCYCLIC ORGANOPHOSPHANES

Up to approximately 20 years ago, compounds with the phosphorus ring framework were only sporadically known. Since 1965 with mass spectroscopic studies, a large number of binary compounds of phosphorus and hydrogen have been found, among them ring compounds or cages made of phosphorus atoms. The various modifications of elemental phosphorus show that phosphorus has a marked ability to form element-to-element bonds, and further, to form rings. The latter ability is not only the case for the above mentioned molecule of white phosphorus. Amorphous red phosphorus also contains rings, as is shown in the oxidation with sodium chlorite by which small quantities of the six-membered ring acid are formed (Figure 3).[7] The structure of crystalline red phosphorus is likewise characterized by rings of varying sizes. In spite of this knowledge, there were only approximately 60 compounds known, in which direct phosphorus-phosphorus bonds were present, and only a smaller portion of these compounds had a ring structure.[8] The area of homocyclic compounds with low valence phosphorus has in recent years become better understood by the illuminating work of Marianne Baudler, so that we have today a

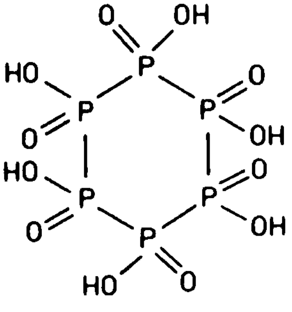


FIGURE 3 Blaser's "P ring acid".[7]

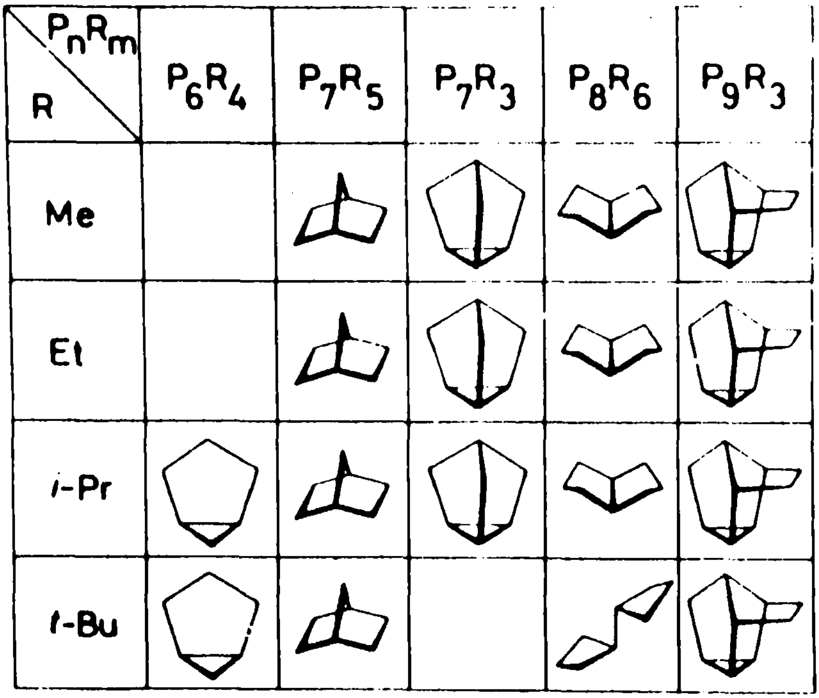


FIGURE 4 Polycyclic organophosphanes of the compound classes P_6R_4, P_7R_5, P_7R_3, P_8R_6, P_9R_3 (structures of the phosphorus skeletons).[9]

systematic picture of the structure of polycyclic phosphanes.[9,10] In most cases, these cyclic structures were constructed from acyclic precursors. In Figure 4 we see the polycyclic organophosphanes of the P_6R_4, P_7R_5, P_7R_3, P_8R_6, and P_9R_3 class. Baudler assumes that the corresponding polycyclic phosphorus hydrides, which are not accessible by direct structural investigation, possess the same structure.[9]

The same is valid for six more classes of compounds which one can see in Figure 5, and which have likewise been systematically studied in regard to the dependence of substituents and the phosphorus ring system.[9,10] Due to less steric interaction among substituents on these tricyclic and polycyclic phosphanes, no differences in the phosphorus ring system appear in any case so that the designated structures are also representative for the corresponding hydrogen derivatives.[9] Only in regard to the pentaorgano nanophosphanes are two constitutional isomers *a* and *b* formed in each case; the ethyl compound could be separated by Baudler.[11] Although a great number of the extended or higher numbered ring systems of polycyclic organophosphanes can be isolated in pure form, only a few representatives of the small polycyclic organophosphanes indeed have been structurally elucidated without, however, successful isolation. A derivative of the polyphosphane P_4H_2, in which H is substituted by dimethylamino groups, was synthesized by Niecke a few years ago starting with diphosphanes.[12] It appeared then for us quite tempting to undertake a synthesis of organobicyclotetraphosphanes directly from white phosphorus in which indeed four three-membered rings are united in a tetrahedron. Until now, however, experiments undertaken to break one bond of the tetrahedron, leaving the remaining

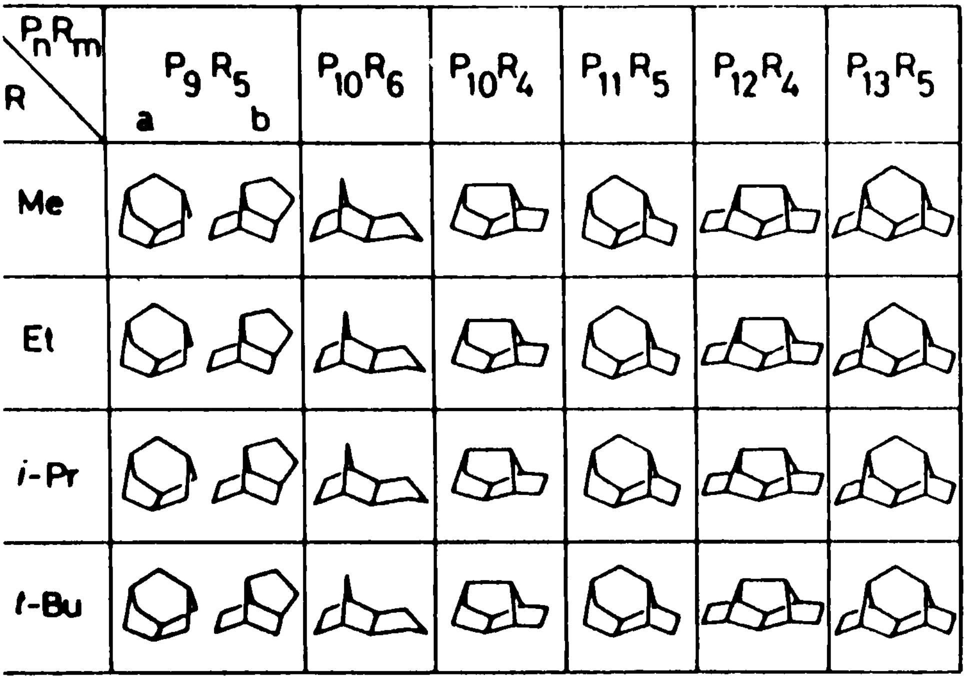
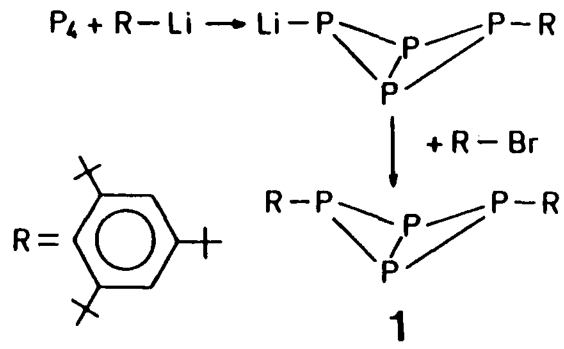


FIGURE 5 Polycyclic organophosphanes of the compound classes P_9R_5, $P_{10}R_4$, $P_{11}R_5$, $P_{12}R_4$, $P_{13}R_5$ (structures of the phosphorus skeletons).[9]

three intact, have failed. As has been shown by Rauhut and Semsel,[13] in connection with the reaction of elementary white phosphorus with phenyllithium, the reaction mixture was hydrolyzed to give phenylphosphine, diphenylphosphine, and so on. No products from this reaction in which the P—P bond is retained were observed. Firstly, in the course of this year, we were successful in finding a reagent which selectively opens one of the bonds of the tetrahedral white phosphorus—even if only to a small extent.[14] One reacts white phosphorus with a mixture of tri-*t*-butylphenyllithium and tri-*t*-butylphenyl bromide to obtain a mixture of red and yellow crystals which are stable to air. It is a mixture of bisorganobicyclotetraphosphane (or bisorganotetraphosphabicyclobutane) **1** and bisorganodiphosphene, the latter described firstly by Yoshifuji.[15] In so doing, it was for the first time possible successfully to isolate a reaction product from white phosphorus where only one bond of the tetrahedral molecule was opened. Bis(tri-*t*-butylphenyl)bicyclotetraphosphane is an ivory-colored solid, with a slight tendency toward oxidation, and is easily soluble in chloroform. Two multiplets appear in the ^{31}P NMR spectrum, from which one can assign a chemical shift of −272 ppm to the bridgehead atom and −130 ppm to the remaining phosphorus atoms to which the organic portion is attached. In Figure 6, one sees the molecular structure of the compound. The tri-tert-butylphenyl moieties are arranged in *cis*-conformation. While all P—P bond distances are similarly large, as in the molecule of white phosphorus, or the P—P distances in other molecules, the distance between the bridgehead atoms of 216.6 pm is substantially smaller. The latter observation corresponds to what is expected. Schoeller and Lerch[16] have analyzed the electronic



nature of tetraphosphabicyclobutane; they have found the central bond to exhibit considerable "olefinic character". Tetraphosphabicyclobutane possesses two high energy levels, and two low energy levels of a_1 and b_1 symmetry. In agreement with the bonding situation in inorganic three-membered ring systems, the presence of these orbitals causes changes in the geometry by substituents. π-donors strengthen the bridgehead bond and weaken the P—P bonds to the peripheral atoms, π-acceptors do the opposite.[16] As we are concerned with π-donors, and considering the predictions from theory, we expect that the distance between both bridgehead atoms is diminished; tetraphosphabicyclobutane should, from this point of view, be an interesting molecule for cycloaddition reactions. This aspect seems the more interesting, since the molecule possesses a symmetric and anti-symmetric HOMO and a low lying LUMO of like symmetries.[16]

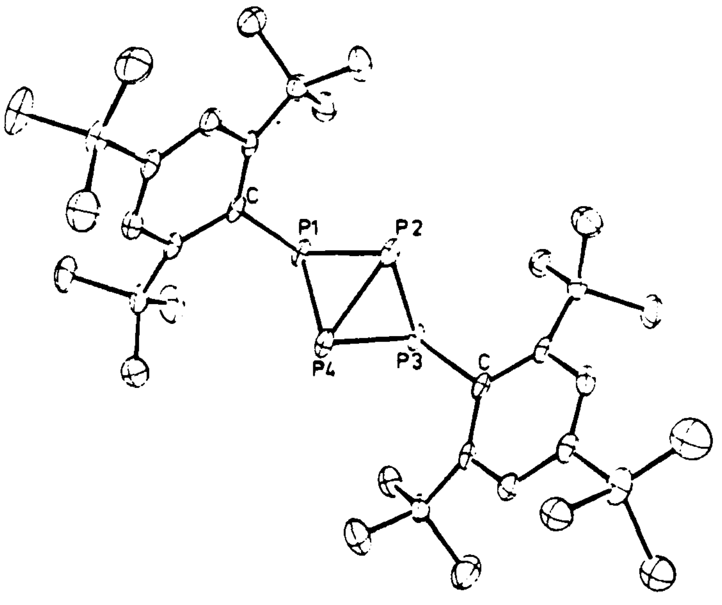


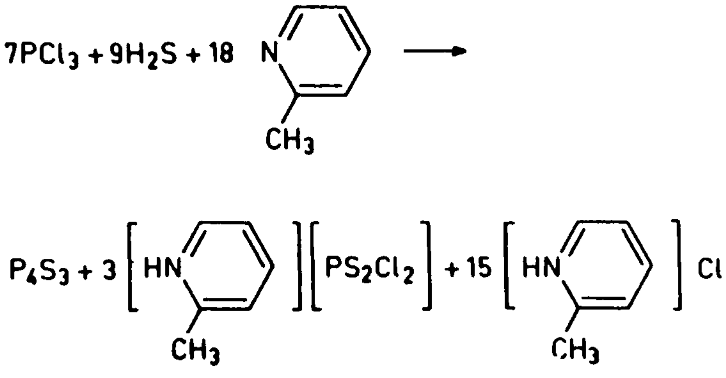
FIGURE 6 Molecular structure of bis(tri-*t*-butyl)bicyclotetraphosphane.

The second reaction product, which we isolated and have already mentioned, is bis(tri-*t*-butylphenyl)diphosphene. It is identical to the structural results of Yoshifuji.[15] Presumably, it is a secondary reaction product of the tetraphosphabicyclobutane which undergoes further reaction in the reaction mixture containing tri-*t*-butylphenyllithium and tri-*t*-butylphenyl bromide. In this connection I should mention a paper by Jutzi and Wippermann[17] which appeared a few months ago. These authors investigated the reaction of dichloro- or dibromopentamethylcyclopentadienylphosphane with reducing agents such as lithium, potassium, or magnesium in tetrahydrofuran and identified a number of reaction products by NMR spectroscopy. Among the reaction products observed in the reaction of dibromopentamethylcyclopentadienylphosphane with magnesium powder were the diphosphene, the cyclotriphosphane, and the bicyclotetraphosphane derivatives, although none of these species has been isolated. The bicyclotetraphosphane which we isolated[14] is stable in air. Attempts partially to oxidize the compound with elementary sulfur or sulfur tetrafluoride, or other experiments, as methylation, failed to produce definitive products. That is, bicyclotetraphosphane behaves, in this respect, as elemental white phosphorus since it too has restricted partial oxidation retaining all bonds. Although the existence of P_4O has been postulated by various authors[18]—as yet, one cannot verify this information.

Not understood is the observation that other phosphorus atoms with coordination number 3 cannot be oxidized easily. Although in the molecule P_4S_3, the phosphorus atom located at the top of the cage and connected to three sulfur atoms should be readily oxidized, oxidation products as P_4S_3O or P_4S_4 have not been synthesized. On the other hand, it is surprising how easily the three-membered phosphorus ring at the base of the P_4S_3 molecule is formed, not only in the thermal route to P_4S_3, but also in solution.

C. THE REACTION BETWEEN PCl_3 AND H_2S

In the theoretical studies concerning the stability of molecular phosphorus, it was shown that the behavior of the three-membered ring compounds is similar to that of the P_4 molecule in regard to bonding relationships and exhibit comparatively great stability for analogous reasons. The latter is the case with the P_7^{3-} anion or with the long-known P_4S_3 system. Thus, as we recently found, the homocyclic phosphorus three-membered ring of the P_4S_3 molecule is easily formed in solution.[19] This reaction had been described as early as 1829 for the first time, namely the reaction between phosphorus trichloride and hydrogen sulfide. Only in 1961 could the two reaction products P_4S_5 and P_4S_7 be identified.[20] We investigated the reaction anew, especially in regard to the question whether the hydrogen sulfide in this reaction functions as a reducing agent or if it is involved in the formation of the low oxidation state phosphorus sulfide with a disproportionation of the +III phosphorus in PCl_3. I would not wish to enter in a too detailed discussion concerning these investigations, but only briefly to mention our results. One reacts equimolar amounts of PCl_3 and hydrogen sulfide in the presence of twice as much 2-methylpyridine, thus one finds in the phosphorus resonance spectrum the well-known resonance lines of the tetraphosphorus trisulfide besides an intensive singlet with a



shift of 81.6 ppm, which had been a puzzle for us for some time. Further investigations showed that the singlet derives from dichlorodithiophosphate and that the reaction in part occurs according to the equation: Figure 7 offers a description of the reaction sequence. The reaction begins with the nucleophilic attack by the hydrogen sulfide, or hydrogen sulfide ions, to the phosphorus atom of the PCl_3 molecule with subsequent formation of thiophosphorous acid chloride which reacts further with PCl_3 to form thiodiphosphorous acid tetrachloride. Nucleophilic attack of another hydrogen sulfide molecule at the phosphorus atom follows the cleavage of dichlorodithiophosphate to dichlorophosphane which reacts with another PCl_3 to form the first P—P bond. The reaction sequence is repeated several times with intramolecular HCl cleavage until homocyclic P_3Cl_3 is formed. This then can react with hydrogen sulfide to form the corresponding thiol. The cage molecule P_4S_3 is finally achieved by further reaction with PCl_3 in the presence of base. The successive steps of this reaction, as shown in Figure 7 are not completely verified. The proposed reaction mechanism, however, explains in a straightforward fashion the formation of both major products for the reaction of phosphorus trichloride and hydrogen sulfide under the conditions used in this reaction.

D. POLYCYCLIC POLYPHOSPHIDES

Allow me to return for a moment to the polycyclic phosphane and to say a few words about polycyclic metal polyphosphide before I finalize my coverage of this research area.

Complicated metalpolyphosphides, whose anions represent polycyclic ring systems, have been studied by Baudler, Fritz, v. Schnering, and others. P_2H_4 reacts with butyllithium or lithium dihydrogenphosphide with simultaneous disproportionation to form trilithium heptaphosphide and PH_3, which gives with alkyl halides the corresponding trialkylheptaphosphane P_7R_3. Trilithium heptaphosphide reacts with diphosphane to form the dilithium hydrogen heptaphosphide which is not stable at room temperature, but decomposes by way of a complex disproportion reaction, by which products Li_2P_{16} and Li_3P_{21} among others are formed.[9]

This chemistry was touched upon already in the 60s by Bergerhoff.[21] White phosphorus reacts with potassium dihydrogen phosphide in dimethylformamide to

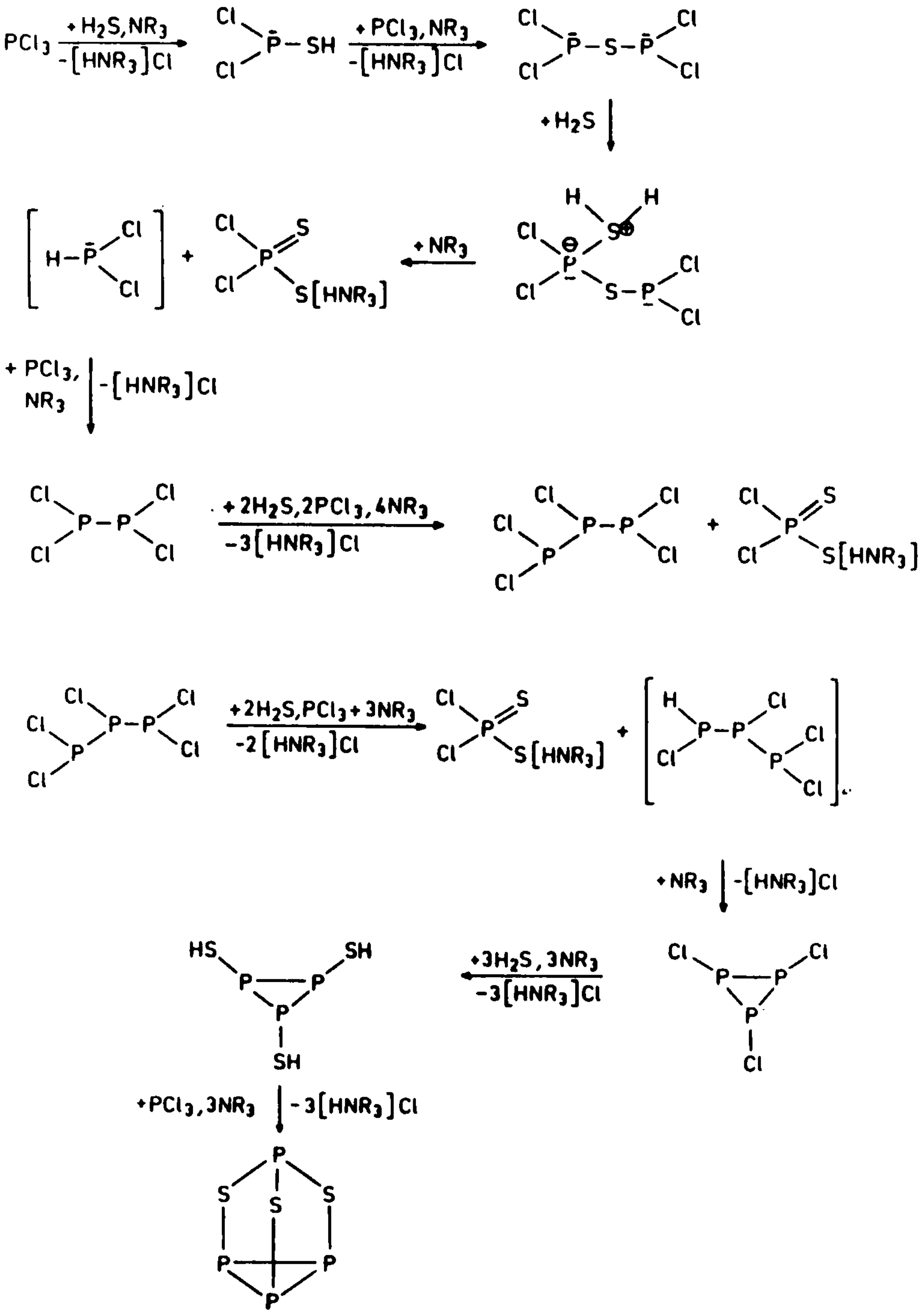


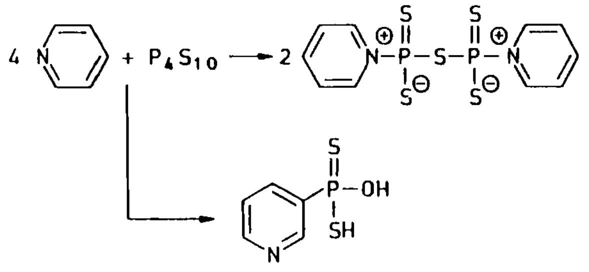
FIGURE 7 Proposed scheme for the reaction between PCl_3 and H_2S.

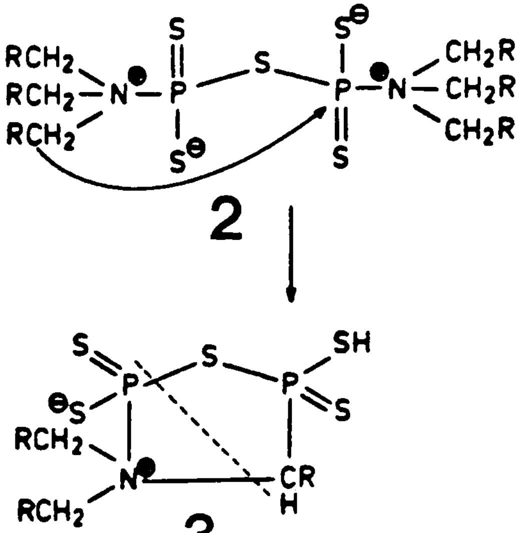
form a dark red liquid, which at that time was studied closely by NMR techniques but gave only broad signals.

If however the ratio of reaction partners is suitably chosen, very simply polycyclic polyphosphides can be obtained in this way. We found that by using a ratio of potassium phosphide to white phosphorus of 2:1 nearly only heptaphosphide anion is formed.[22] In phosphorus-rich reaction mixtures one finds extended polyphosphides. If one chooses a reaction ratio of 1:1, then the anion P_{21}^{3-} in quite high concentration is formed.[22] The latter are two examples, which show, at least in part, that polyphosphanes or polyphosphides can be obtained directly from elementary phosphorus.

E. THE REACTION BETWEEN TERTIARY AMINES AND P_4S_{10}

The new ring system which I have mentioned previously is formed by the reaction of P_4S_{10} and triethyl, tri-*n*-butyl, tri-isobutyl, and other amines. The base can act as the reaction medium, or an inert solvent like toluene may be used. We had earlier investigated the reaction between pyridine, and substituted pyridines, with P_4S_{10}. As a first reaction product, bis(pyridinium)perthiophosphoric-betain can be isolated.[23] If the reaction is heated at boiling for a few more days, phosphorus-carbon bonds are formed. The reaction product after aqueous work-up is pyridyl-3-dithiophosphoric acid.[24] If one reacts one of the above mentioned tertiary amines with P_4S_{10}, similar reactions take place whereby a new cyclic system is formed.[25] The primary reaction is the adduct **2** of the tertiary amine and P_4S_{10} which for the case of pyridine can be easily isolated.[23] Then follows an attack of the α-carbon atom at the more distant phosphorus atom leading to ring closure. From the phosphorus NMR spectra of the reaction mixture it is fairly easy to conclude that the formation of an intermediate product has taken place. An AB, or nearly AX system, can be assigned to the proposed formula **3**. It contains the important feature of the end product, namely the atomic sequence C—P—S. This portion of the intermediate product represents half of the six-membered ring **4**, which is then isolated as the final product. It is the salt of dithiooxodithiaphosphorinane-dithiol. The free acids are formed by either the thermolysis of the ammonium salts, or by the effect of hydrochloric acid. If one heats the dialkylammonium salt in a vacuum at a temperature of 190°, there forms a colorless sublimate which is easily soluble in nonpolar solvents. From the phosphorus and proton NMR spectra one can provide a structure **5**. The structure could be confirmed by an X-ray analysis (Figure 8). The





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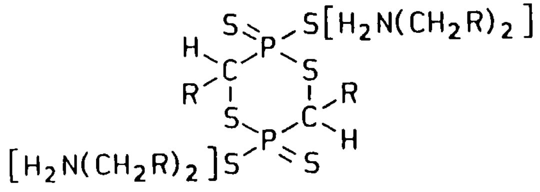

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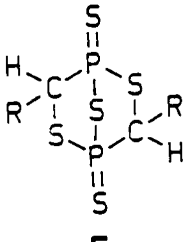
$R = C_2H_5, n\text{-}C_3H_7, i\text{-}C_3H_7$



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molecule possesses a bicyclic structure with a sulfur bridge between the phosphorus atoms. It is important to emphasize that in this reaction a transalkylation occurs whereby the alkyl groups from nitrogen are transferred to phosphorus.

F. DIPHOSPHACYCLOBUTADIENE

Finally, I would like to speak about four-membered ring systems. Tetraalkyl- and tetraaryl-tetraphosphanes have been known for a long time. They can be obtained

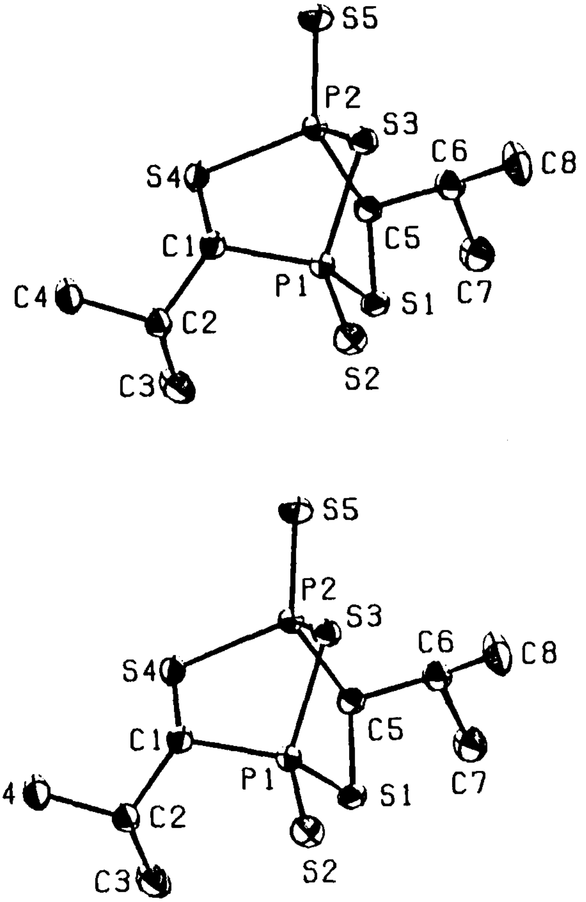
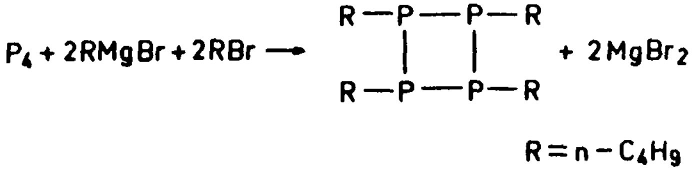
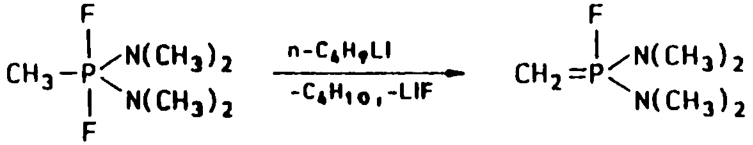


FIGURE 8 Molecular structure of 5.

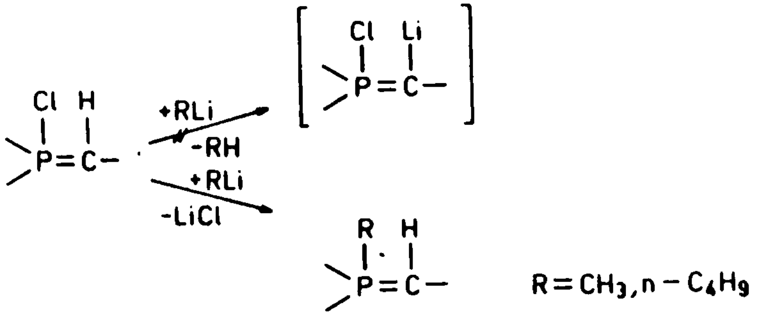
from white phosphorus by way of a reaction of organomagnesium compounds and alkyl halides.[26] Phosphorus atoms together with their ligands can be substituted by CR_2 groups.[27]



For a long time, a system was unknown in which a four-membered ring compound contains two double bonds, which would be represented as a phosphorus derivative of cyclobutadiene. In connection with such compounds we undertook the investigation of the chemical behavior of alkyl or aryldifluorodiaminophosphoranes. The latter are compounds of the general formula $RPF_2(NR_2)_2$. We prepared a number of these compounds by fluorination of alkyl or aryldiaminophosphanes with SF_4.[28] We were next concerned with the question of whether cleavage of HF could be obtained from completely alkylated alkyldifluorodiaminophosphorane ylids. The latter reaction was in fact the case. If one adds an equimolar amount of butyllithium in hexane to a solution of methyldifluorobis(dimethylamino)phosphorane in pentane

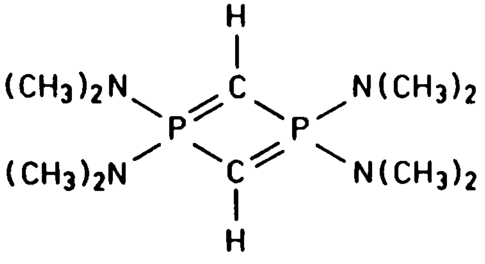


between the temperature of −80° and room temperature, an exothermic reaction follows immediately with separation of a precipitate of lithium fluoride. From the solution, one can isolate a colorless liquid which contains mainly P-fluoro-ylids. We were able to prepare numerous examples of the class of P-fluoro-ylids which have been unknown until now.[29] I will not continue further in detail on this topic. The reaction between P-chloro-ylids and lithium alkyls, as methyllithium or butyllithium,



were earlier investigated as a few trials. The reactions take a course whereby the chlorine atom is replaced and the phosphorus—carbon bond is formed. The possible cleavage of an existing C—H bond to liberate a hydrogen does not play a role due to the overwhelming rate of the coupling process. The reaction of methylenefluorobis(dimethylamino)phosphorane with lithium alkyls was of interest to us due to the minor steric interaction at carbon and the higher stability of the P—F bond.

We reacted methyldifluorobis(dimethylamino)phosphorane with twice the molar quantity of butyllithium at −95° in *n*-pentane.[30] The major product of the reaction shows a singlet in the ^{31}P NMR spectrum with a chemical shift of 49 ppm. The crystalline compound is very sensitive towards moisture and atmospheric oxygen. The proton NMR spectrum of the compound makes it possible to identify the isolated compound as the first known example of the parent diphosphacyclo-



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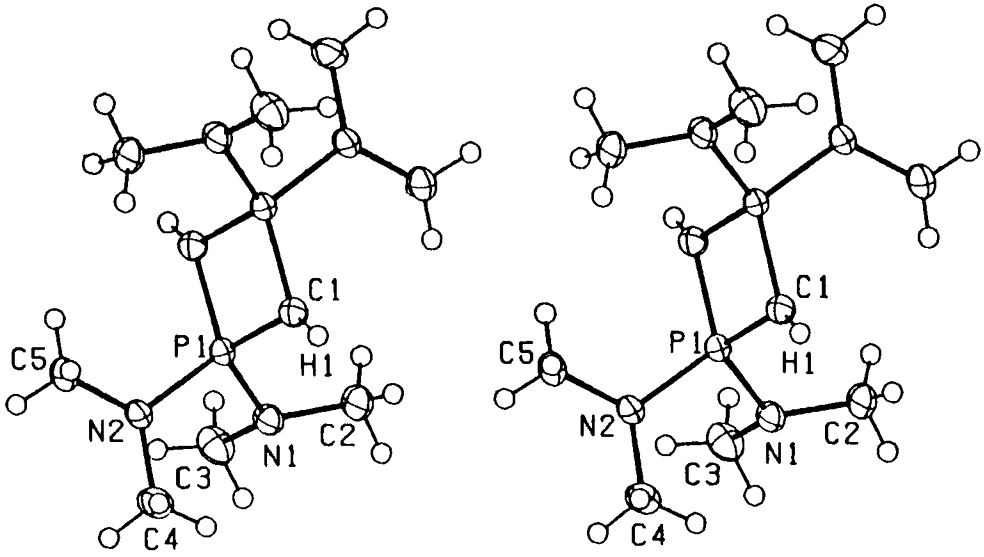
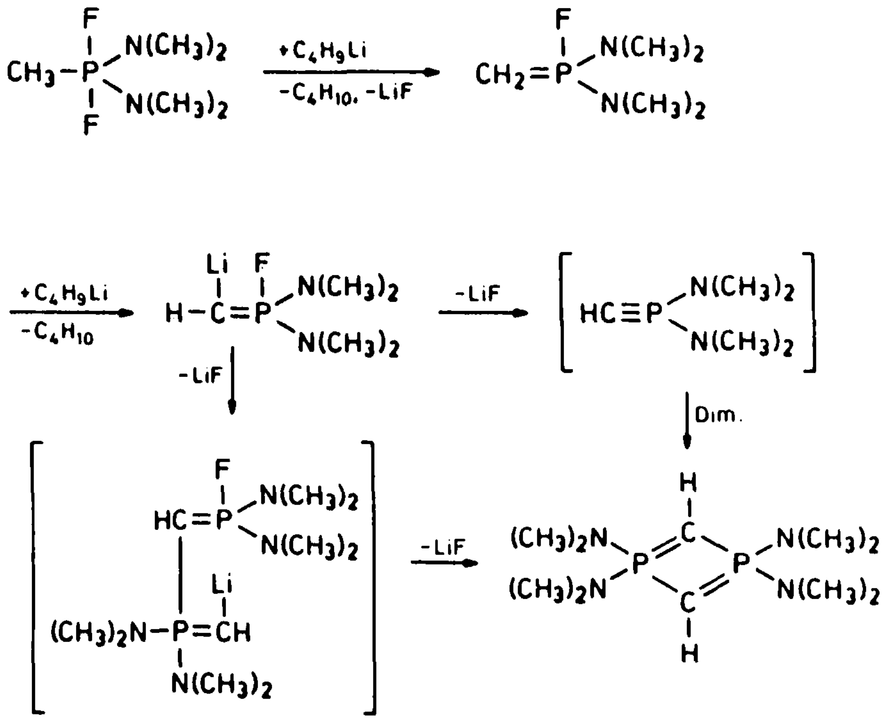
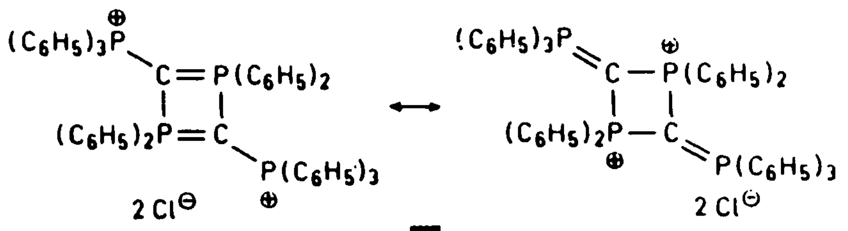


FIGURE 9 Molecular structure of $\{-HC{=}P[N(CH_3)_2]\}_2$

butadiene **6**—that is where the substituents on the carbons are protons. The spectroscopic data are compatible with a four-membered ring system, in which the carbon atoms exist as localized ylidic anions or which is characterized by delocalized double bonds. The X-ray structural analysis shows that a planar ring structure exists with a four-membered ring, built of alternating phosphorus and carbon atoms. Figure 9 shows the molecular structure of the diphosphacyclobutadiene **6**. The four-membered ring of C_i symmetry is completely flat with exactly equal P—C bond distances of 172.5 pm. This value lies in the region of P=C double bonds in the phosphaalkenes with typical values ranging between 168 and 172 pm or within the region of P—C bonds in substituted alkylidenephosphoranes and is distinctly smaller than those in 1,2-diphosphetenes with sp^2 hybridized carbons where the distance amounts to 185 pm. The intramolecular contact spacing between the two carbons and the two phosphorus atoms are, at 73% and 65%, respectively, of the van der Waals radii, extremely short and can be explained due to a high ring strain. One observes a distorted tetrahedral environment at the phosphorus atom, while the carbon atoms approach near planarity. The first step proceeds with the attack of butyllithium at the α-methylene group with the formation of a metal ylid. Then either a double intermolecular cleavage of lithium fluoride with formation of a second phosphorus carbon bond or an intramolecular elimination of lithium fluoride, whereby a system with a P≡C triple bond forms which then dimerizes in a subsequent step. In contrast to 1,2- and 1,3-diphosphetenes, four-membered ring compounds with only one double bond in the ring, about which much has been described since 1964, the series of the diphosphetes or diphosphacyclobutadienes had only a single known representative, namely 1,1,3,3-tetraphenyl-2,4-bis(triphenylphosphine)-4λ^5-3λ^5-diphosphacyclobutadiendichloride **7**, which was obtained by Appel,[30] and the X-ray work accomplished by J. Weiss.[31] The great stability of this



compound with a melting point of 385° is attributed by the authors to substitution of positively charged phosphonium groups, the π-electron density outside of the ring in the external phosphorus-carbon bond is therefore electron-withdrawing.



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The planarity of our diphosphacyclobutadiene and the fact that the phosphorus-carbon bonds are identical within the limits of error, must be surprising, since there is no possibility for electron withdrawal from the ring system. Yet, the structural analysis gives no hints as to the mesomeric exchange between phosphorus atoms and the exocyclic dimethylamino groups.

A 4π-electron ring system possesses antiaromatic character according to the Hückel $(4n + 2)\pi$-electron rule. The expected result is the lowering of symmetry accompanied by distortion of the ring. It is a fact that cyclobutadiene and its tetra-*t*-butyl derivatives possess a planar, rectangular structure with D_{2h} symmetry according to new findings.[33,34] The same symmetry is possessed by our diphos-

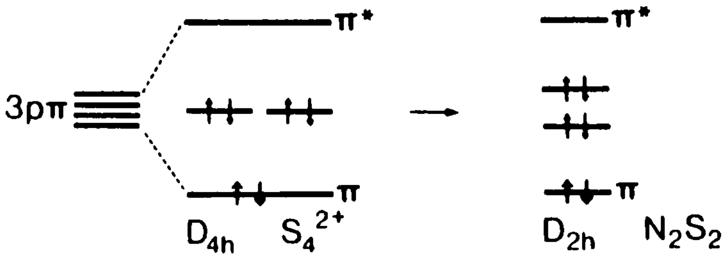
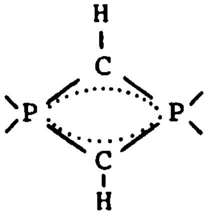
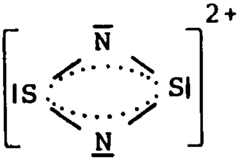


FIGURE 10 Splitting of the 3p atomic orbitals in S_2N_2 as compared to S_4^{2+}.

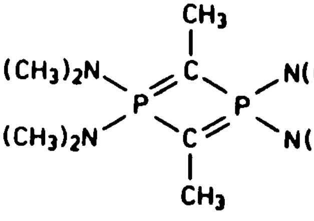
phacyclobutadiene; as is also the case for planar-constructed S_2N_2, whose π-system, however, is made up of 6 electrons.[35,36] Four electrons distribute themselves in two almost degenerate nonbonding π-molecular orbitals (Figure 10). CNDO/2 studies for S_2N_2 lead to 3 localized π-molecular orbitals, two of which are 2π-electron-3-center orbitals over the S—N—S atoms, while the third goes to an antibonding interaction between the sulfur atoms.[37] If two electrons will be withdrawn from this system, so one then achieves an ion which is isoelectronic with our molecule, the unknown $S_2N_2^{2+}$ ion, for which a structure with two localized double bonds is predicted.[38] Calculations suggest that these electrons come from the S—S-π-bond, so that still one 4π-electron system with two 2-electron-3-center bonds remains which is extended over the S—N—S atoms. This way of reviewing things leads qualitatively to the same result as is true for the cyclophosphazene. The phosphorus atoms build from its d_{xz}- and d_{yz}-orbitals two new orbitals which can overlap with the p orbitals of nitrogen. The result is a π-electronic structure with an island-like three-centered bond, whereby the islands are separated from each other in each case at the phosphorus atom, and within the island, delocalized P—N—P systems exist.[39]





If one applies this concept to the system of diphosphacyclobutadiene, one thus obtains two delocalized, yet separated halves with equally long phosphorus—carbon bonds which are filled in each case by two π-electrons as is the case in CNDO/2 calculations for $S_2N_2^{2+}$. The planar geometry is then the optimal arrangement for the formation of π-bonding and correspond to calculated results.

The question concerning the appearance of monomeric λ^5-phosphacetylene as an intermediate in the formation of the diphosphacyclobutadiene requires still a closer look. Understandably, it is of special interest for us: Does the reaction proceed by way of a monomeric λ^5-phosphaacetylene, and is it possible, in addition to the dimer, to obtain a derivative of the long sought after tri-phosphabenzene? We



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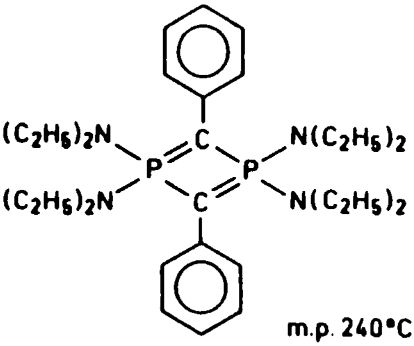
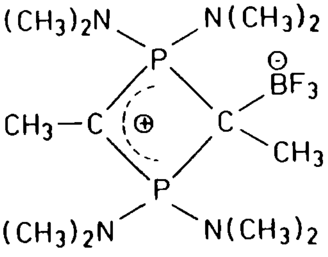


m.p. 240°C

9

thought about this problem that the latter might be a question of substituents on carbon, and attempted to synthesize appropriate derivatives. Meanwhile, we were also successful in synthesizing methylated **8** and phenylated **9** derivatives of diphosphacyclobutadiene at the carbon atom.[40] In both cases, however, was there no indication for the existence of the corresponding triphosphabenzene found. The phenyl-substituted compound is extraordinarily thermally stable. It melts without decomposition at 240°. The diphosphacyclobutadiene should form with powerful electrophilic reagents the corresponding salt, and in so doing, be stabilized. This is in



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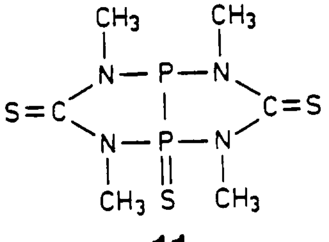
fact the case. The C,C′-dimethyl derivative reacts for example with boron trifluoride with formation of the trifluoroborate salt **10**.[40]

G. TETRAAZADIPHOSPHAPENTALENE SULFIDE AND DIAZADIPHOSPHOLIDINE SULFIDE

As I have touched upon the subject of three- and four-membered ring systems, I wish to conclude my talk with a very short survey concerning five-membered rings where one sees direct phosphorus-phosphorus bonds. Several examples of this ring system have been synthesized in recent years by us in Stuttgart[41,42] and independently by Roesky[43,44] and Schmutzler.[45]

In a quite direct way, we were able to obtain the tetraazadiphosphapentalene **11** by reaction of N,N′-dimethylthiourea with phosphorus trichloride.[41] One adds the two components in the presence of pyridine with benzene as the reaction medium at reduced temperature; in such a way, the bicyclic compound can be isolated in good yield. The product can be characterized as a stable compound which melts at 173–175° and is resistent to hydrolysis. The compound, on the other hand, can be transformed to the disulfide with sulfur, or, on the other hand, sulfur can be removed with tributylphosphane. The fact that the synthesis proceeds from dimethylthiourea and PCl_3, yet only forms the monosulfide, presented us with somewhat of a puzzle. This question was answered, however, by the investigation of the reaction between dimethylurea and phenyldichlorophosphane.[42] The two compounds react in the presence of pyridine to form the diazadiphospholidine sulfide **12**. The reaction pathway is indicated in Figure 11. Figure 12 shows the molecular structure of compound **11**.[41] Unfortunately, the roof-shape of the molecule is not easily recogniz-



11

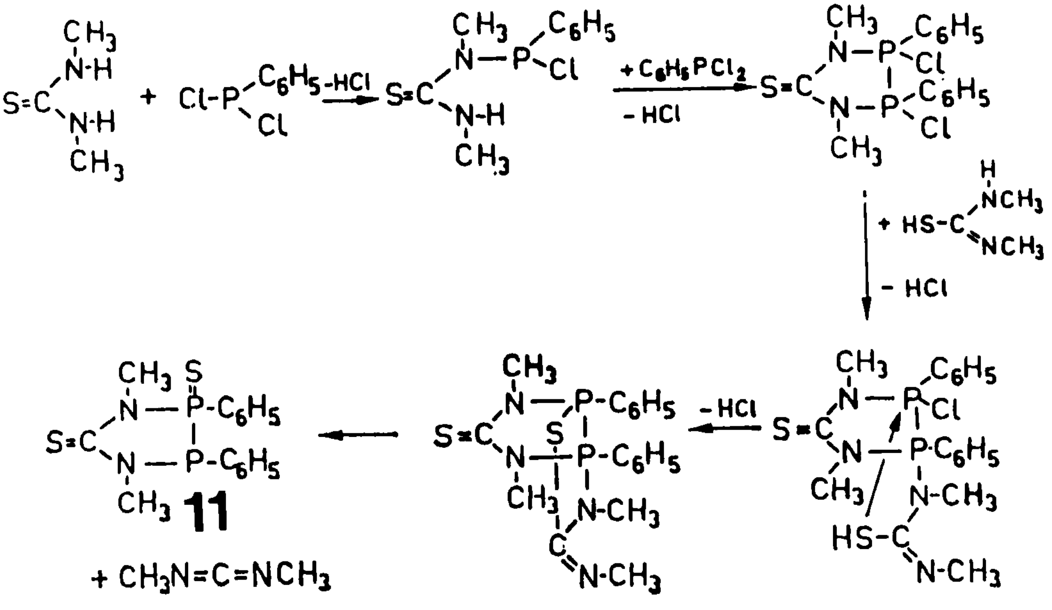


FIGURE 11 Reaction pathway for the formation of compound 11.

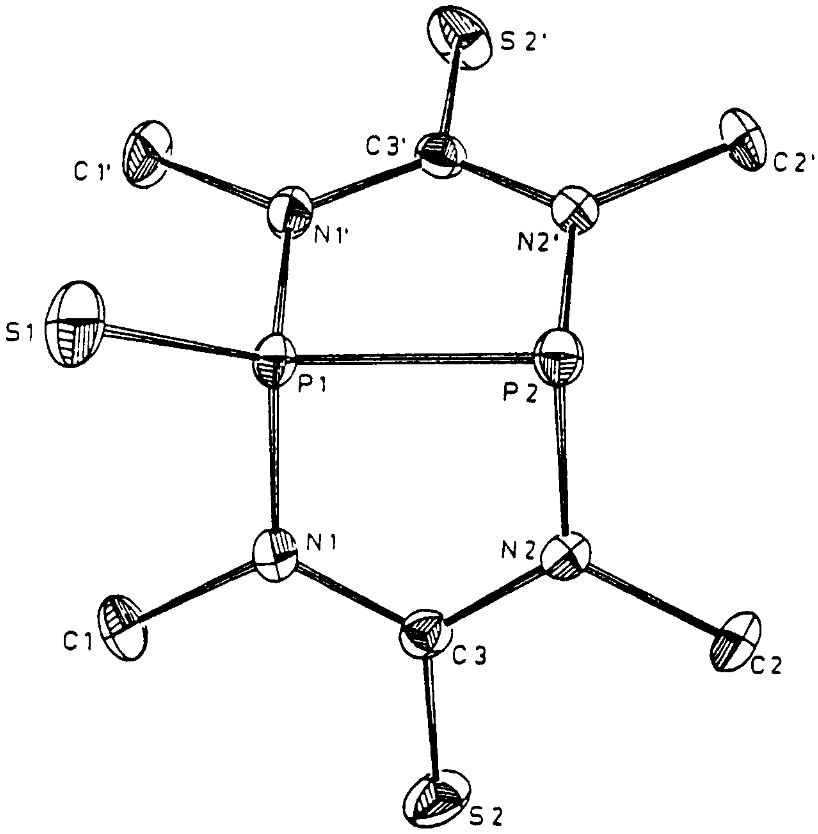
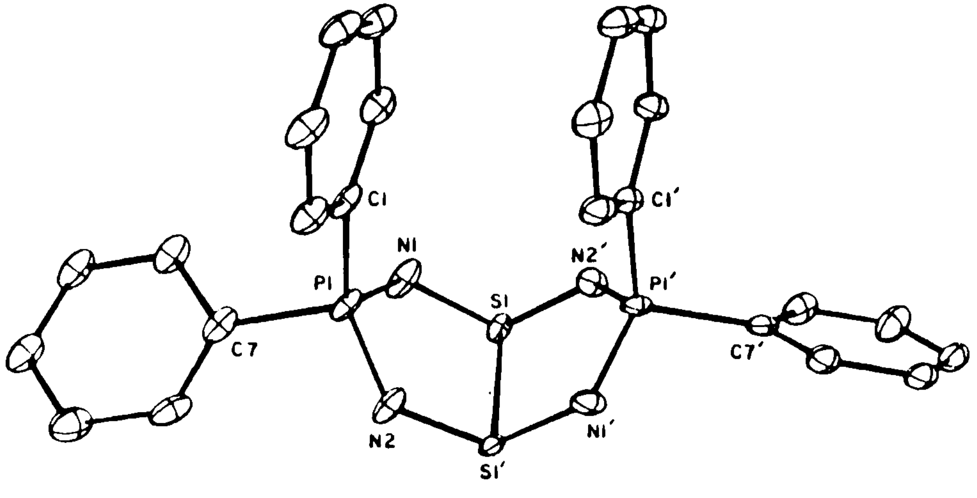


FIGURE 12 Molecular structure of $P_2S_3N_4C_6H_{12}$.



12

FIGURE 13 Molecular structure of 1,5-$(C_6H_5)_2P(NSN)_2P(C_6H_5)_2$.[46]

able. The two five-membered rings are almost flat and form an angle of 105.8°. This structure puts one in mind of a molecule from sulfur-nitrogen chemistry which was described by Chivers and others in 1983, namely a reaction product of tetrasulfurtetranitride and tetraphenyldiphosphine.[46] The molecule **12** (Figure 13) can be considered as possessing bicyclic character in which both five-membered rings possess the S—S bond in common.[46] Although the bond relationships in the two molecules are very different, still the structural analogy is very striking. By the way, B_4H_{10} has a similar structure. It is an example of the great significance of stereochemistry for the existence and stability of a compound. For a long time, this consideration for synthesis was not a respected point of view; only electronic effects were called upon for synthetic methods. In only recent years has experience shown how great a role the stereochemical effects play. In fact, the role of stereochemistry plays a fundamental part in the development of the chemistry of nonmetals with low coordination numbers.

With this remark I would like to conclude my report.

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