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THREE-MEMBERED PHOSPHORUS RING COMPOUNDS (1)

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Abstract - The synthesis of novel homo- and heterocyclic three-membered phosphorus ring compounds is described. Such strained ring systems are not in all cases hyperreactive substances, but may exist as isolable compounds. The structures are based on ^{31}P NMR spectroscopic data and on single crystal X-ray structure analysis.

INTRODUCTION

In the past two decades, a great number of new cyclic phosphorus compounds could be synthesized. Nevertheless, monocyclic three-membered phosphorus ring systems without additional stabilization by coordination are almost unknown. This is particularly true for compounds with more than one phosphorus atom in a three-membered ring. Of all known elements, carbon shows, of course, the greatest ability to form cyclic compounds of ring size three. Cyclopropane was already detected nearly 100 years ago and the number of its homo- and heterocyclic derivatives is considerable. Although it is well known that a significant discontinuity in chemical properties and reactivity occurs between the first-row elements of the periodic table and those of subsequent rows, it had to be expected from the oblique relation between phosphorus and carbon that phosphorus also has a certain ability to form three-membered ring compounds with directly bonded phosphorus atoms. Besides, elemental white phosphorus consists of P_4 molecules that are composed of four condensed three-membered rings. Therefore, it seemed a challenging problem to find out whether monocyclic three-membered phosphorus ring compounds can also be sufficiently stabilized for chemical preparation and investigation.

HOMOCYCLIC THREE-MEMBERED PHOSPHORUS RING COMPOUNDS

The simplest phosphorus three-membered ring compound is the phosphorus hydride, cyclotriphosphane P_3H_3 (Table 1). Already in 1965 we could detect small amounts of this compound - together with other novel phosphorus hydrides - in the volatile hydrolysis products of calcium phosphide by mass spectroscopy (Ref. 2). It may be seen that cyclotriphosphane is the first member of the homologous series of monocyclic phosphanes P_nH_n. In addition, there exist the open-chain phosphanes P_nH_{n+2} and various series of cyclic phosphanes with lower hydrogen content and condensed ring systems. The two double underlined triphosphanes and tetraphosphanes could be separated in pure form by gas chromatography (Ref. 3). However until now, we were not able to isolate cyclotriphosphane on a preparative scale because of its high reactivity.

In contrast to the rather unstable phosphorus hydrides P_nH_n, their derivatives, in which the hydrogen atoms are substituted by organyl groups, are generally much less reactive. Consequently, some of these organyl-cyclophosphanes have already been known for a long time (Ref. 4). The general procedures for their preparation are the reaction of a primary phosphine with an organyl-dichlorophosphine or the dehalogenation of a dichlorophosphine by an alkali metal and by lithiumhydride, respectively. As may be seen on Table 2, where the ring size n is given for various substituents R, mostly five- or four-membered cyclophosphanes are formed in these reactions for thermodynamic and kinetic reasons. In the case that R equals phenyl for instance, the five-membered ring compound is the cyclophosphane with the highest stability. Besides, a cyclohexaphosphane of somewhat lower stability exists. The corresponding compounds where n equals four and three, however, were still unknown.

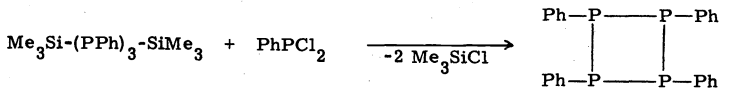
TABLE 1. Novel phosphorus hydrides

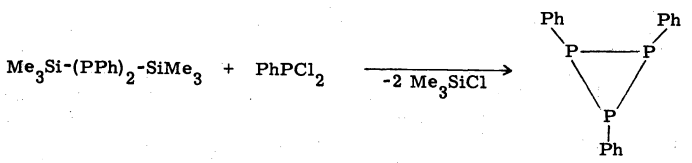
	P_nH_{n+2}	P_nH_n	P_nH_{n-2}	P_nH_{n-4}	P_nH_{n-6}	P_nH_{n-8}	Others
Triphosphane	$\underline{\underline{P_3H_5}}$	$\underline{\underline{P_3H_3}}$					
Tetraphosphane	$\underline{\underline{P_4H_6}}$	$\underline{\underline{P_4H_4}}$	P_4H_2				
Pentaphosphane	P_5H_7	P_5H_5	P_5H_3				
Hexaphosphane	P_6H_8	P_6H_6	P_6H_4	P_6H_2			
Heptaphosphane	$[P_7H_9]$	P_7H_7	P_7H_5	P_7H_3			
Octaphosphane		P_8H_8	$[P_8H_6]$	P_8H_4			
Nonaphosphane		P_9H_9		P_9H_5	P_9H_3		
Decaphosphane		$[P_{10}H_{10}]$	$[P_{10}H_8]$		$P_{10}H_4$	$P_{10}H_2$	
Undecaphosphane						$P_{11}H_3$	$P_{11}H_6$
Dodecaphosphane						$P_{12}H_4$	
Tridecaphosphane						$P_{13}H_5$	
Tetradecaphosphane							$P_{14}H_4$

TABLE 2. Ring size n of cyclophosphanes $(PR)_n$

R \ n	6	5	4	3
Ph	X	X		
Et		X		
Me		X		
t-Bu			X	
i-Pr			X	
c-C_6H_{11}			X	

Already in 1975 we have found that both compounds can easily be prepared in an almost quantitative reaction by a cyclocondensation of the appropriate α,ω-bis(trimethylsilyl)-phenylphosphane with phenyldichlorophosphine under elimination of trimethylchlorosilane (Refs. 5,6). The pure cyclotetraphos-

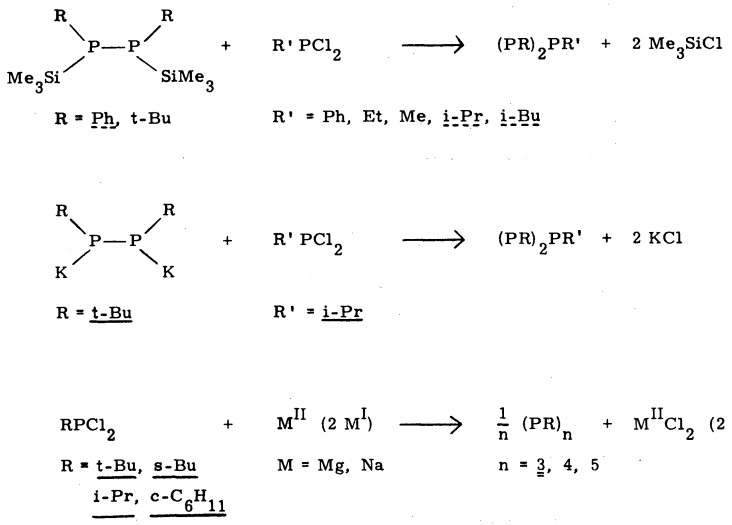




phane is not stable at room temperature, but decomposes slowly under rearrangement into the thermodynamically stable cyclopentaphosphane. The triphenyl-cyclotriphosphane cannot be isolated in a pure state, because the ring interconversion via the cyclotetraphosphane into the cyclopentaphosphane is rather rapid even below room temperature. Nevertheless, the cyclotriphosphane could unambiguously be identified by ^{31}P NMR spectroscopy, because it is characterized by an A_2B spin system at considerably high field.

The first derivative of P_3H_3, the tris(pentafluoroethyl)-cyclotriphosphane, has been reported by Cowley and coworkers (7) in 1970. Through the reaction of pentafluoroethyl-phosphorus-diiodide with mercury in a sealed tube, they obtained a mixture of the corresponding cyclotriphosphane and the cyclotetraphosphane, which could be separated by fractional condensation. The identification of the trimer was based on mass spectrometric and gas-phase molecular weight determinations. A few months later, however, West and coworkers (8) reported the same reaction mixture as being composed of the pentamer and the tetramer. This controversy was not resolved before 1976, when Smith and Mills (9) could prove by ^{31}P NMR spectroscopy that Cowley and coworkers actually had prepared a phosphorus three-membered ring compound.

During the past four years we have found that, depending on the substituents R at the three-membered ring skeleton, cyclotriphosphanes can possess a considerable stability, so that they are formed in various reactions and can often be isolated in a pure state (Refs. 10-17). Three general reactions can be used for the synthesis of triorganyl-cyclotriphosphanes. The



first one we have already seen. However it has to be pointed out that this reaction is not only applicable to the preparation of homogeneously substituted cyclotriphosphanes, as, for instance, triphenyl-cyclotriphosphane (Ref. 6), but that in this way also mixed substituted cyclotriphosphanes $(PR)_2PR'$ can be obtained (Refs. 6,14). This is also true of the second reaction (Ref. 13), which is a [2+1]-cyclocondensation of an 1,2-dipotassium-1,2-diorganyldiphosphide with an organyl-dichlorophosphine. In each case the various compounds prepared and investigated are listed below the reaction equations, where the compounds, which can be isolated in pure form are marked by a solid underline, and those, which can be enriched to at least 80 per cent purity, by a dotted line. The second reaction, however, yields cyclotriphosphanes only, if the salt is almost totally insoluble in the reaction solution, so that a nucleophilic attack at the phosphorus three-membered ring, already formed, is avoided. The third reaction is a simple dehalogenation of an organyl-dichlorophosphine by a metal, as it is also used for the preparation of organyl-cyclophosphanes of larger ring sizes. Consequently, this reaction yields considerable amounts of cyclotriphosphanes only, if the corresponding phosphorus three-membered ring compounds have a remarkable stability. This is the case for R equals t-butyl (Ref. 11), sec-butyl (Ref. 15), i-propyl (Ref. 16) or cyclohexyl (Ref. 12).

However, a mixture of various oligomers is always formed that must be separated by fractional distillation or crystallization.

Other reactions lead to some special cyclotriphosphanes. The first one is

$$(t\text{-BuP})_3X_2 \xrightarrow{LiH} \underline{(t\text{-BuP})_3}$$

X = Hal

$$(PEt)_5 \xrightarrow{\Delta} (PEt)_3 + (PEt)_4 + \ldots$$

$$K_2(c\text{-}C_6H_{11}P)_4 \xrightarrow{CS_2} \underline{(c\text{-}C_6H_{11}P)_3} + (c\text{-}C_6H_{11}P)_4 + \ldots$$

restricted to the t-butyl compound (Ref. 17), because only in this case the corresponding 1,3-dihalogen-triphosphanes could recently be prepared on our lab (Ref. 18). This reaction corresponds exactly to the classical synthesis of cyclopropanes by dehalogenation of 1,3-dichloropropanes. Furthermore, triethyl-cyclotriphosphane is formed by thermolysis of the well-known cyclopentaphosphane, $(PEt)_5$ (Ref. 5), and tricyclohexyl-cyclotriphosphane can also be obtained at a high yield by the action of carbon disulfide on 1,4-dipotassium-tetracyclohexyl-tetraphosphide in a complex reaction (Ref. 12).

All cyclotriphosphanes are characterized by ^{31}P NMR chemical shifts at considerably high field compared to open-chain triphosphanes and cyclic phosphanes of larger ring sizes (Refs. 5,6,9,10,12,13-16,19). Obviously, this is the effect of the small ring and the consequence of the predominant s-character and, therefore, good shielding of the free electron pair at the phosphorus atoms. The homogeneously substituted cyclotriphosphanes in each case exhibit an A_2B spin system as it is shown on Fig. 1 for the t-butyl compound,

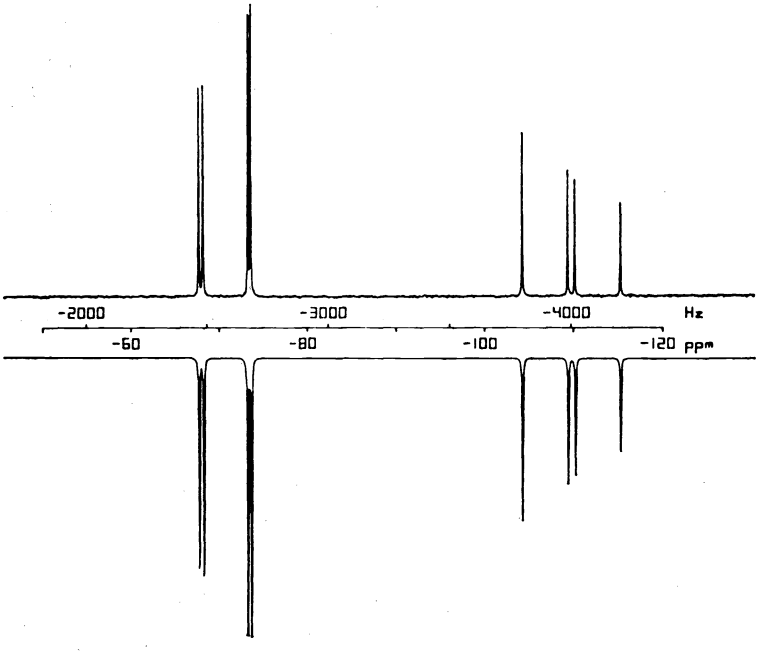


Fig. 1 Experimental and calculated $^{31}P\{^1H\}$-NMR spectrum of $(t\text{-BuP})_3$

together with the simulated spectrum. This A_2B system indicates that two organyl groups lie on one side and the third one on the other side of the P_3-ring. This structure was confirmed by an X-ray analysis of the t-butyl compound, carried out by Dr. Krüger at the Max-Planck-Institute in Mülheim (Fig. 2). In Table 3 the ^{31}P NMR parameters of several cyclotriphosphanes

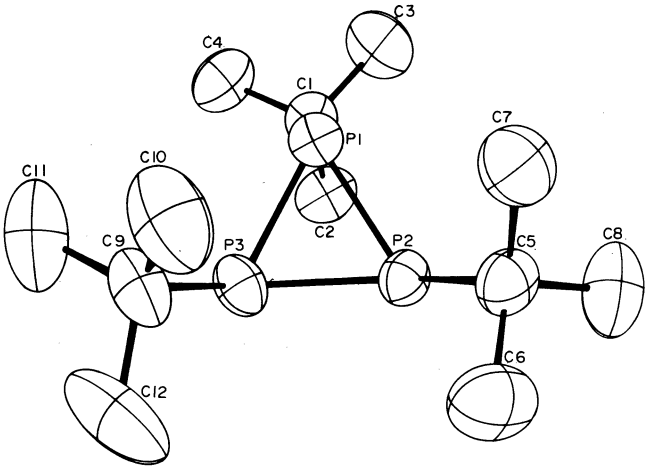
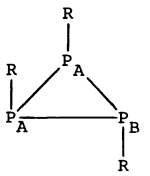


Fig. 2 Crystal structure of $(t\text{-BuP})_3$

TABLE 3. ^{31}P NMR parameters of $(PR)_3$



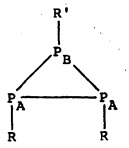
R	$\delta(P_A)$ [ppm]	$\delta(P_B)$ [ppm]	J_{AB} [Hz]
C_2H_5	-157.3	-145.0	-178.5
$c\text{-}C_6H_{11}$	-141.7	-138.9	-185.0
$i\text{-}C_3H_7$	-132.3	-128.6	-184.8
C_6H_5	-131.7	-147.2	-186.9
$t\text{-}C_4H_9$	-71.9	-108.1	-201.1

are compiled. It may be seen that the chemical shifts as well as the coupling constants are considerably effected by the bulkiness of the substituents. The strongest effect, of course, occurs at the phosphorus atoms whose substituents lie on the same ring side. The eclipsed conformation of this part of the molecule leads to an increase of the exocyclic C-P-P bond angles which causes deshielding of the P atoms and hence a downfield shift, which is accompanied by an increase of the negative coupling constant.

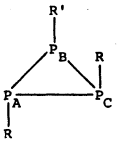
In the case of mixed substituted cyclotriphosphanes (Table 4) with two different organyl groups, two diastereomers are formed (Refs. 6,13,14). The symmetric one a with identical organyl groups on one ring side shows an A_2B spin system in the ^{31}P NMR spectrum, whereas the asymmetric isomer b is characterized by an ABC system. In the table the corresponding ^{31}P NMR parameters are compiled. As could be found for all compounds investigated, both isomers always appear simultaneously, often at the statistically expected ratio.

At present we are studying the chemical behaviour of these cyclotriphosphanes in more detail. Mild halogenation leads via ring opening to 1,3-dihalogen-1,2,3-triorganyl-triphosphanes (Ref. 18). The reaction of cyclohexyl-cyclotriphosphane with sulfur in the molar ratio 1:1 to 1:3 at -10°C gives two isomeric compounds, whose structures could be elucidated by ^{31}P NMR spectroscopy (Ref. 20). The five-membered ring compound totally resembles the reac-

TABLE 4. ^{31}P NMR parameters of $(PR)_2PR'$



a (A_2B)

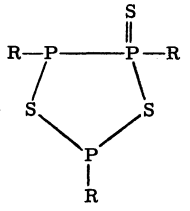


b (ABC)

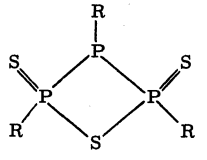
R	R'		$\delta(P_A)$ [ppm]	$\delta(P_B)$ [ppm]	$\delta(P_C)$ [ppm]	J_{AB} [Hz]	J_{AC} [Hz]	J_{BC} [Hz]
$t\text{-}C_4H_9$	$i\text{-}C_3H_7$	a	-68.5	-127.8		192.1		
		b	-109.0	-112.5	-99.5	∓188.7	∓205.1	∓262.2
C_6H_5	$i\text{-}C_4H_9$	a	-137.4	-162.9		185.6		
		b	-149.9	-148.7	-140.9	∓180.0	∓195.3	∓216.0
C_6H_5	$i\text{-}C_3H_7$	a	-140.3	-134.1		189.9		
		b	-152.3	-123.6	-136.9	∓185.3	∓184.1	∓226.9
C_6H_5	C_2H_5	a	-138.7	-151.8		186.3		
		b	-148.3	-141.6	-138.8	∓182.7	∓184.8	∓220.0

tion product of pentaphenyl-cyclopentaphosphane with sulfur at the ratio 1 P : 1 S (Ref. 21). In contrast to this, the four-membered isomer is the

$$(c\text{-}C_6H_{11}P)_3 + 3/8\ S_8 \xrightarrow[-10^{\circ}C]{THF} (c\text{-}C_6H_{11}PS)_3$$



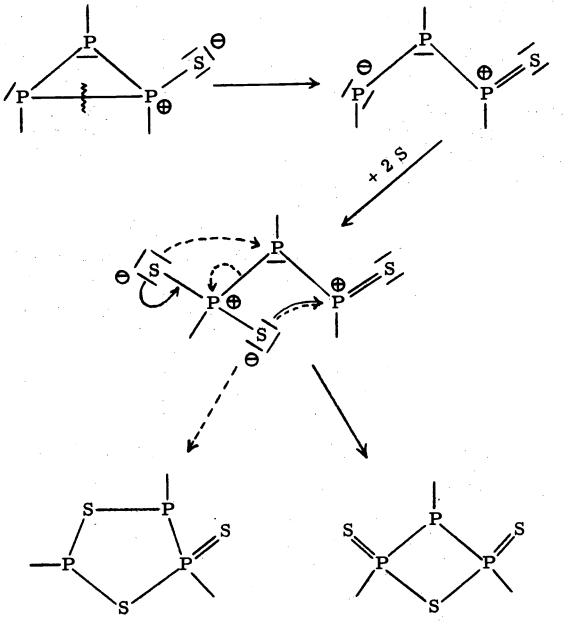
ABX



A_2B

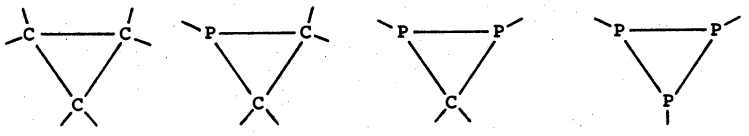
first representative of a novel heterocyclic P_3S ring system. The compound is stable at room temperature under inert conditions, but decomposes in solution within a few days. No conversion into the five-membered cycle could be observed. The reaction of cyclohexyl-cyclotriphosphane with sulfur probably proceeds via the following steps. After the first attack of sulfur on one of the two phosphorus atoms with cis-standing cyclohexyl groups, the respective phosphorus-phosphorus bond is immediately split off. Therefore a cyclotriphosphane-monosulfide with a sulfur atom in an exocyclic position could not be detected. Subsequently, a synchronous attack of two sulfur atoms occurs under formation of the two isomeric phosphorus sulfur heterocycles which were actually found.

Following the synthesis of several pure cyclotriphosphanes, such as tri-t-butyl-, tri-sec-butyl-, tri-i-propyl-, tricyclohexyl- and di-t-butyl-i-propyl-cyclotriphosphane, the question arose, whether also three-membered phosphorus heterocycles are accessible. During the last three years we succeeded in synthesizing such compounds with carbon, silicon, germanium, boron, arsenic and sulfur as hetero-ring atoms. Of particular interest, of



course, are the compounds with two phosphorus and one carbon atom in a three-membered ring, the diphosphiranes. As can be seen, the diphosphirane is the

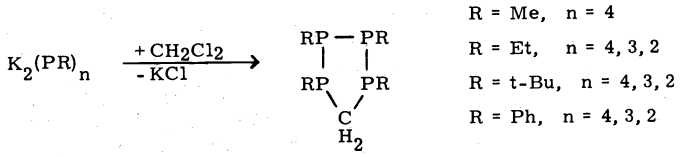
Cyclopropane	Phosphirane	Diphosphirane	Cyclotriphosphane



known	known	unknown	known

only three-membered ring system between cyclopropane and cyclotriphosphane which was still unknown. The first monophosphiranes were already synthesized more than 10 years ago (Refs. 22-24).

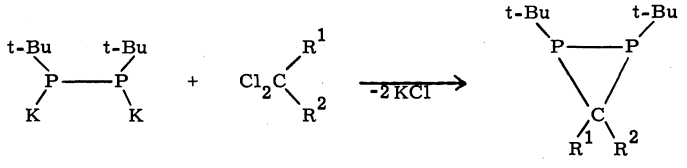
Previous investigations on the synthesis of cyclocarbaphosphanes had shown that the reaction of α,ω-dimetallated or -disilylated organyl-phosphanes with



carbon dihalides in tetrahydrofurane always leads to five-membered cyclocarbaphosphanes, independent of the chain-length n of the starting bifunctional organyl-phosphane (Ref. 25). Even if diphosphanes are used as starting compounds, almost exclusively five-membered heterocycles are obtained. Obviously, reaction products of smaller ring sizes than five rearrange themselves very easily in the presence of the nucleophilic salts or the polar solvent tetrahydrofurane into the thermodynamically and kineti-

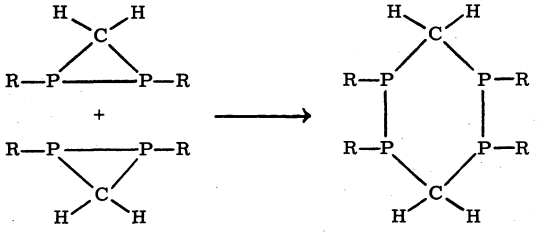
cally stable five-membered rings. Hence, it should be possible to obtain the primary metastable three-membered carbon heterocycle, if these ring interconversion reactions could be suppressed. Moreover, bulky substituents should additionally stabilize the diphosphirane skeleton.

As a result of this synthetic concept, the [2+1]-cyclocondensation of 1,2-dipotassium-1,2-di-t-butyl-diphosphide with dichloromethane, 1,1-dichloro-



Compound	$R^1 = H$, $R^2 = H$	$R^1 = H$, $R^2 = CH_3$	$R^1 = CH_3$, $R^2 = CH_3$
$\delta(^{31}P)$ [ppm]	-168,8	-127,6 -136,7 Centre: -132,2	-91,7
$\delta(^{13}C)$ for Ring-C [ppm]	6,2	21,0	36,2

ethane or 2,2-dichloropropane in pentane at 0°C actually gives the 1,2-di-t-butyl-diphosphirane, the 1,2-di-t-butyl-3-methyl-diphosphirane and the 1,2-di-t-butyl-3,3-dimethyl-diphosphirane, respectively, in rather good yields (Ref. 26). Besides, the homocyclic tetra-t-butyl-cyclotetraphosphane and - in the reaction with methylene chloride - also five-membered cyclocarbaphosphanes are formed. The three diphosphiranes could be isolated in pure form by high vacuum fractional distillation. They are colourless liquids, not self-inflammable but easily oxidized by contact with air. The dimethyl compound is surprisingly stable under inert conditions and can be heated for a short time up to 200°C without noticeable decomposition. The compound with two hydrogen atoms at the ring carbon, however, already dimerizes at room temperature quantitatively within a few days, resulting in

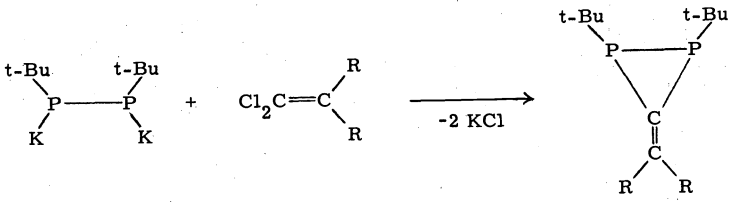


$R = t\text{-}C_4H_9$

$\delta(^{31}P) = -168,8$ ppm $\qquad$ $\delta(^{31}P) = -26,2$ ppm

the six-membered cyclodicarbaphosphane with two opposite CH_2-groups. This process can be stopped by dilution with an inert solvent or by cooling to -78°C. The difference in reactivity of these two diphosphiranes is due to differences in their endocyclic and exocyclic bond angles as can be seen from the NMR parameters. The three diphosphiranes were characterized in all details through chemical analysis, cryoscopic and mass spectrometric molecular weight determinations as well as by ^{31}P, ^{13}C and proton NMR spectra. The corresponding results - especially the ^{31}P chemical shifts, which lie in the high field region of cyclotriphosphanes - unambiguously confirm the three-membered diphosphirane structure.

During the past months, we were also able to synthesize diphosphiranes with an exocyclic C=C double bond. Through the reaction of 1,2-dipotassium-1,2-di-t-butyl-diphosphide with several 1,1-dichloroolefines, the 1,2-di-t-



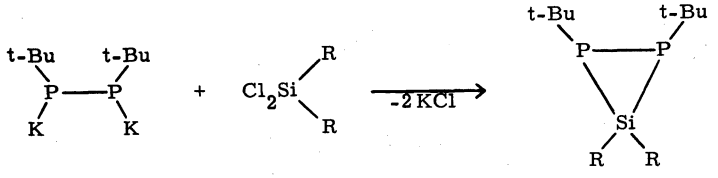
R = H : $\delta(^{31}P)$ = -143,2 ppm

R = CH_3 : $\delta(^{31}P)$ = -139,8 ppm

R = 4-ClC_6H_4 : $\delta(^{31}P)$ = -149,9 ppm

butyl-3-methylene-diphosphirane, -3-dimethylmethylene-diphosphirane and -3-bis(4-chlorophenyl)methylene-diphosphirane were prepared (Ref. 27). The hydrogen-substituted compound already decomposes in the reaction mixture at -60°C, so that it could only be enriched up to 70 per cent purity. The other two methylene-diphosphiranes have a considerably higher relative stability and could be isolated in a pure state by high vacuum distillation or fractional crystallization.

In a similar reaction of 1,2-dipotassium-1,2-di-t-butyl-diphosphide with



R = CH_3 : $\delta(^{31}P)$ = -132,7 ppm

$\delta(^{29}Si)$ = -31,3 ppm

R = C_6H_5 : $\delta(^{31}P)$ = -122,4 ppm

$\delta(^{29}Si)$ = -41,8 ppm

dimethyl-dichlorosilane or diphenyl-dichlorosilane, the first two diphosphasiliranes, compounds with two phosphorus atoms and one silicon atom in a three-membered ring, could be prepared (Ref. 28). Immediately after the combination of the reactants, the relative portions of the diphosphasiliranes in the reaction mixture amount to about 80 mole per cent, but decrease with increasing reaction time. In addition, four-, five-, and six-membered phosphorus-silicon-heterocycles as well as tetra-t-butyl-cyclotetraphosphane are formed. Both diphosphasiliranes could be isolated in pure form by high vacuum fractional distillation. The relatively low yields of only 10 or 27 per cent, however, indicate that under these conditions considerable thermal decomposition already occurs. The dimethyl compound, which is a colourless viscous liquid, is much more reactive than the corresponding diphosphirane with a P_2C ring. It has a considerable tendency to dimerize and is also self-inflammable in contact with air, especially in the presence of cell tissue. The -3,3-diphenyl-diphosphasilirane, however, which forms colourless crystals with a melting point of 73°C, has a considerably higher relative stability. It does not show any tendency to dimerize, is not inflammable in air and can be stored in a normal refrigerator for several weeks without decomposition. This difference in stability is obviously due to the better shielding of the silicon atom by the larger phenyl groups. The structure of the two diphosphasiliranes can immediately be deduced from their NMR parameters. Whereas the phosphorus chemical shifts lie exactly in the region of cyclotriphosphanes, the ^{29}Si signals are comparable to that of hexamethyl-silacyclopropane, which appears at -49,3 ppm against tetramethylsilane (Ref. 29). The slight downfield shift of the diphospha-

siliranes in the ^{29}Si spectrum is probably due to the greater flexibility of phosphorus to form small bond angles compared to carbon, so that the silicon is somewhat less exposed to ring strain in the phosphorus than in the carbon three-membered heterocycle. Fig. 3 shows the result of an X-ray

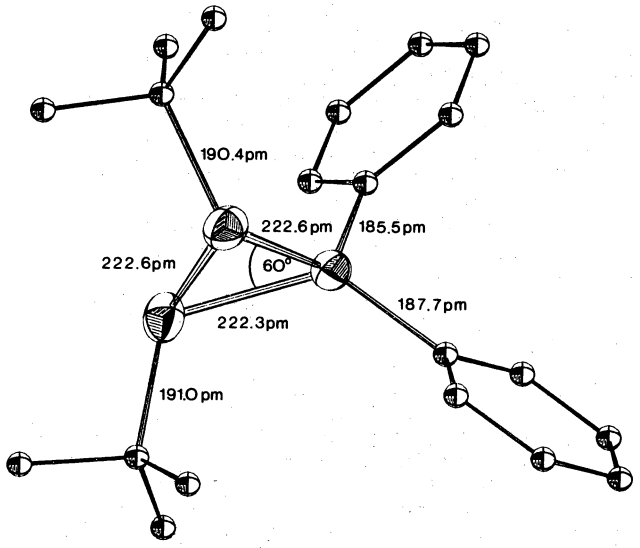
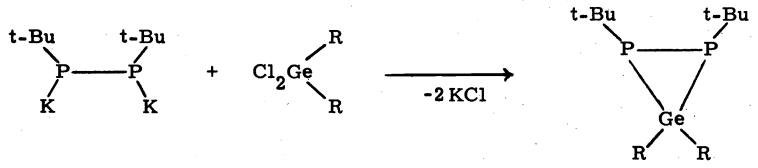


Fig. 3 Crystal structure of $(t\text{-BuP})_2SiPh_2$

structure analysis of the 1,2-di-t-butyl-3,3-diphenyl-1,2,3-diphosphasilirane, carried out by Professor Tebbe (30) in Köln. As may be seen, the phosphorus-phosphorus and phosphorus-silicon bond distances are practically identical and hence the endocyclic bond angles at the phosphorus as well as at the silicon are 60° within the standard deviations. Obviously, the substitution of one >P(t-Bu)-ring member in tri-t-butyl-cyclotriphosphane by a $>SiPh_2$-group does not cause a noticeable distortion of the equilateral three-membered ring. This is astonishing in so far, as silicon generally shows a much greater tendency to keep the tetrahedral angle than phosphorus, as is well known.

Following the synthesis of the relatively stable di-t-butyl-diphenyl-diphosphasilirane, the question arose, whether also three-membered phosphorus heterocycles with elements of the fourth period of the periodic table can be prepared and investigated. Indeed, through the [2+1]-cyclocondensation of



$R = C_2H_5$: $\delta(^{31}P) = -126,8$ ppm

$R = C_6H_5$: $\delta(^{31}P) = -113,3$ ppm

our key compound with diethyl-germanium-dichloride or diphenyl-germanium-dichloride we succeeded in synthesizing the first two diphosphagermiranes (Ref. 31). The cyclisation reactions in this case must be carried out at -60° and -40°C, respectively, because of the increased reactivity of these heterocycles in the reaction mixture. Under these conditions, the diphosphagermiranes are immediately formed in relative amounts between 80 and 97 mole percent. In addition, some tetra-t-butyl-cyclotetraphosphane was found. After rapid removal of the non-reacted salt, the reaction solutions can be warmed up to room temperature without noticeable decomposition. The ethyl-substituted compound could be entirely purified by low temperature crystal-

lization, whereas the phenyl compound could only be enriched to 93 per cent purity because of difficulties in removing residual amounts of the homocyclic tetraphosphane. Both diphosphagermiranes were thoroughly characterized by chemical analysis and spectroscopic methods. They are relatively stable substances, but extremely sensitive to air. The phenyl-substituted compound shows some tendency to dimerize at room temperature in contrast to the corresponding compound with a P_2Si ring. This process is accelerated by polar solvents, such as acetonitrile. Although under normal conditions, the -3,3-diethyl-diphosphagermirane is a viscous liquid with a melting point of about -30°C, at low temperature single crystals could be obtained for an x-ray analysis, carried out again by Professor Tebbe (32). According to the

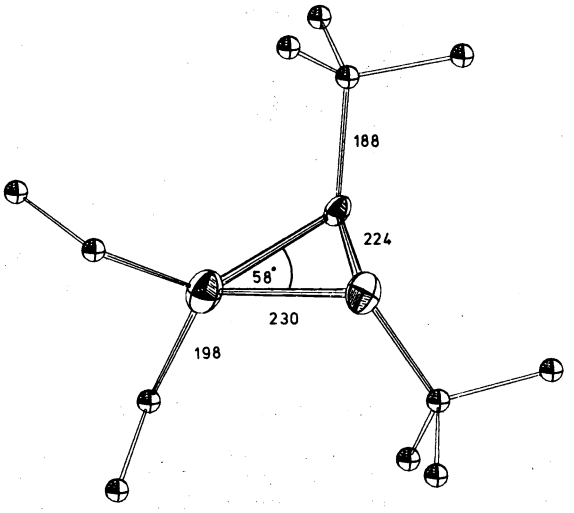
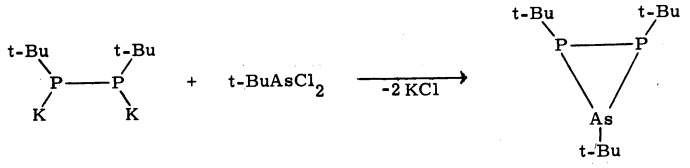
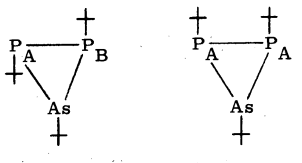


Fig. 4 Crystal structure of $(t\text{-BuP})_2GeEt_2$

larger covalent radius of germanium compared to that of silicon, the phosphorus-germanium bond distances are longer than the phosphorus-phosphorus bond length, causing a somewhat smaller endocyclic bond angle for germanium than for phosphorus. However, the deviations from an equilateral triangle are not very considerable.

There is only a small step in the fourth period from germanium to arsenic, but it seemed to be an open question, whether merely a single substituent at a relatively large heteroatom could sufficiently stabilize a three-membered phosphorus ring system. Our proven synthetic approach, using t-butyl-



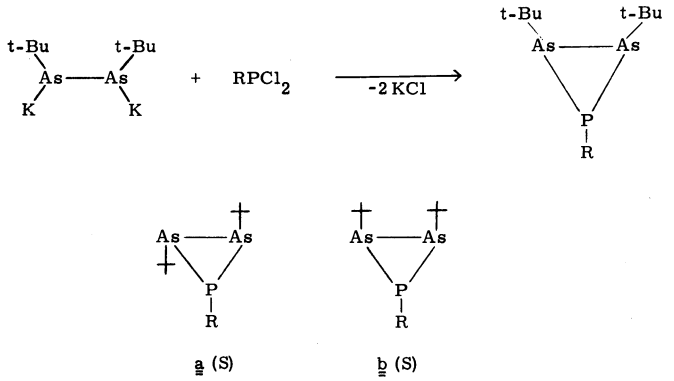


a (AB) b (S)

Isomer	$\delta(P_A)$ [ppm]	$\delta(P_B)$ [ppm]	J_{AB} [Hz]
a	-45,1	-86,0	-230,5
b	-51,5	—	—

arsenic-dichloride as a reactant, actually leads to the tri-t-butyl-diphosphaarsirane (Ref. 33). As in the case of the germanium compound, the cyclization reaction as well as the filtration of excess salt have to be carried out at low temperature. The isolation, however, can subsequently be performed by high vacuum fractional distillation. The heterocycle was obtained at 98 per cent purity and about 30 per cent yield. A slight contamination by the homocyclic t-butyl-cyclotriphosphane could not be avoided due to thermal decomposition. The tri-t-butyl-diphosphaarsirane forms two stereoisomers which can be distinguished by ^{31}P NMR spectroscopy. The asymmetric form $\underline{\underline{a}}$ with trans-standing organyl groups at the phosphorus atoms shows an AB spin system, whereas the symmetric isomer $\underline{\underline{b}}$ exhibits a singulett. Because the phosphorus-phosphorus bond distance is shorter than that of the phosphorus-arsenic bond, the steric interaction of the cis-standing t-butyl groups is stronger in $\underline{\underline{b}}$ than in $\underline{\underline{a}}$. Consequently, isomer $\underline{\underline{a}}$ has a considerably higher relative stability, so that $\underline{\underline{b}}$ gradually rearranges itself into $\underline{\underline{a}}$ even at -25°C in the dark. The diphosphaarsirane is self-inflammable only in contact with cellulose and can be stored at -20°C for weeks without decomposition.

Considering the notable relative stability of tri-t-butyl-diphosphaarsirane, it could be expected that also three-membered phosphorus arsenic heterocycles with only one phosphorus atom could probably be produced. The required

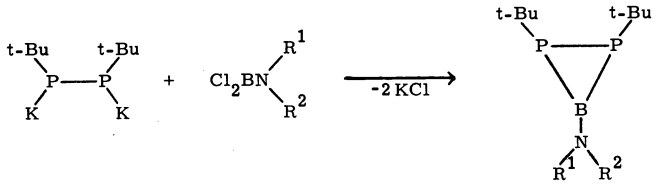


$\underline{\underline{a}}$ (S) $\underline{\underline{b}}$ (S)

R = Et	$\underline{\underline{a}}$:	$\delta(^{31}P)$ = -117,2 ppm
	$\underline{\underline{b}}$:	$\delta(^{31}P)$ = -118,3 ppm
R = i-Pr	$\underline{\underline{a}}$:	$\delta(^{31}P)$ = -81,2 ppm
	$\underline{\underline{b}}$:	$\delta(^{31}P)$ = -91,9 ppm

starting compound, the 1,2-dipotassium-1,2-di-t-butyl-diarsenide, was already described by Tzschach and Kiesel (34). It readily reacts with ethyldichlorophosphine or isopropyldichlorophosphine, giving the corresponding phosphadiarsiranes together with heterocycles of larger ring sizes (Ref. 35). The ethyl-substituted compound could not be worked up because of its thermal instability. The -3-isopropyl-phosphadiarsirane, however, could be isolated in a pure state by short path high vacuum distillation that was repeated and followed by low temperature crystallization. At room temperature, it is a colourless liquid becoming pale yellow when exposed to light for a longer period. Again, both stereoisomers are formed, of which the molecule with trans-standing t-butyl groups shows the greater relative stability.

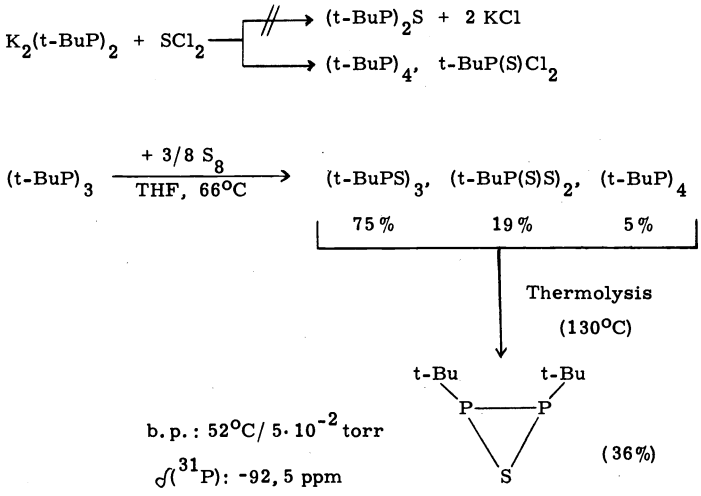
Of special interest in the class of three-membered phosphorus ring compounds are the heterocycles with boron. We have found that our synthetic approach may also be applied to the preparation of diphosphaboriranes, compounds with a $\overline{PPB}$-skeleton. It has to be pointed out, however, that the [2+1]-cyclocondensation reaction runs successfully only with diorganylamino-boron-dichlorides, whereas organyl-boron-dichlorides merely yield phosphorus boron heterocycles of larger ring sizes. Using the aminoboranes shown here, the cyclization reaction is almost quantitative in the temperature range between -40° and -78°C. The various diphosphaboriranes can subsequently be isolated in their pure form by low temperature crystallization at yields up to 80 per cent. A purification by distillation is not possible because of thermal decomposition. When R is an alkyl group, at room temperature the compounds are



R^1	R^2	$\delta(^{31}P)$ [ppm]	$^1J(PP)$ [Hz]	$\delta(^{11}B)$ [ppm]
i-Pr	i-Pr	-159,2 (S)	—	50,7
Et	Et	-152,5 (S)	—	52,6
Me	n-Bu	-148,1 (AB)	75,9	53,2
Me	t-Bu	-151,4 (AB)	77,2	51,2
Me	c-C_6H_{11}	-152,0 (AB)	75,7	51,8

colourless viscous liquids, whereas the methyl-cyclohexyl derivative forms white crystals. The diphosphaborirane structure was unambiguously confirmed by cryoscopic and mass spectrometric molecular weight determinations as well as by other common methods of characterization. The compounds with two unbranched substituents at the nitrogen slowly dimerize at room temperature, resulting in the corresponding six-membered heterocycles with opposite BNR_2-groups. This dimerization is already inhibited by only one substituent with a branching point in α-position. The diphosphaboriranes with two different groups at the nitrogen exhibit in each case an AB spin system in the ^{31}P NMR spectrum due to hindered rotation around the boron nitrogen bond, which has a marked double bond character as found in aminoboranes. In the case of the di-i-propylamino compound, a low temperature splitting of the singulett into an AB system is not caused by a pyramidal inversion of the boron atom (Ref. 36) but has to be attributed to frozen rotation around the nitrogen carbon bonds resulting in two unequivalent isopropyl groups. The high field chemical shifts of all compounds indicate that no notable π back-donation from phosphorus to boron exists.

Very recently, we also succeeded in preparing a three-membered phosphorus heterocycle with sulfur. However, the attempted ring closure with sulfur



dichloride only gave t-butyl-thiophosphonic-acid-dichloride and the homocyclic tetraphosphane. But through the reaction of tri-t-butyl-cyclotriphosphane with sulfur in boiled tetrahydrofurane and subsequent thermolysis of the product mixture at 130°C, followed by high vacuum distillation, the pure 1,2-di-t-butyl-thiadiphosphirane could be obtained at a yield of 36 per cent (Ref. 38). This formation obviously occurs through a ring contraction of phosphorus sulfur heterocycles of larger ring sizes. Under normal conditions the compound is a pale yellow viscous liquid of extremely bad odor, which can be stored in a refrigerator for weeks. During our thorough characterization by all common methods, all results clearly confirmed the three-membered thiadiphosphirane structure. A crystal structure analysis is in progress.

The recent work on three-membered phosphorus homo- and heterocycles has shown that such strained ring systems are not in all cases hyperreactive and exotic substances, but may exist as isolable compounds. If nucleophilic or electrophilic attack is avoided by means of bulky substituents and appropriate reaction conditions, such metastable species can show a considerable kinetic stability. Therefore, also in future interesting preparative results can be expected in this field.

Acknowledgement - I am indebted and grateful to many dedicated and enthusiastic coworkers for their skilful efforts in the laboratory as well as their contributions of new ideas which resulted in rapid development of the area reviewed here. My thanks also go to Professor Tebbe and Dr. Krüger for undertaking the X-ray structural studies. I acknowledge the generous support of Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie.

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