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Monocyclic and Polycyclic Phosphanes[†,‡,1]

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Contents

I. Introduction and Scope of the Review

Cyclic polyphosphorus compounds with a framework of trivalent phosphorus atoms are derivatives of the corresponding phosphorus hydrides (phosphanes) and are generally designated as cyclophosphanes. These compounds have been the subject of numerous investigations in the past two decades. The reasons for the relatively late development of this branch of phosphorus chemistry are the facts that many cyclophosphanes are difficult to prepare in the pure state and that their structural characterization is also not simple. However, the use of modern laboratory techniques and separation procedures as well as, above all, the methodological advances in nuclear magnetic resonance spectroscopy have now enabled these problems to be more or less solved. Hence, numerous novel cyclic polyphosphorus compounds have been discovered recently. This newly-opened area of "element-near" phosphorus chemistry has many close relationships with the chemistry of carbon. It comprises the fields of small ring compounds through to atomic assemblies of medium size and thus represents a significant link between PH_3 and its derivatives on the one hand and the high molecular modifications of the element phosphorus on the other hand.

The first cyclophosphane, a compound with the formal composition "PhP," was described more than

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[†] Dedicated to Professor Heinrich Nöth, University of Munich, on the occasion of his 65th birthday.

[‡] The term "phosphane" defines a phosphorus hydride or its derivative according to current IUPAC nomenclature; in the United States the equivalent term "phosphine" is more commonly used.

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Marianne Baudler was born in Stettin (Germany, now Poland), studied in Dresden and Göttingen, and received her Ph.D. degree from the University of Göttingen. Graduate study was conducted under the supervision of Professor F. Fehér. Thereafter she joined the Cologne University faculty where she became Professor of Analytical Chemistry (1963) and—after refusing a call of the Technical University of Berlin—Full Professor of Inorganic and Analytical Chemistry (1968). She is the author of approximately 260 publications in the area of nonmetal chemistry, particularly phosphorus chemistry. Her further research interests are concerned with modern spectroscopic methods for structure elucidation. Professor Baudler received the Alfred Stock Award of the Gesellschaft Deutscher Chemiker (1986) and is a member of the Deutsche Akademie der Naturforscher Leopoldina, Halle, and of the Akademie der Wissenschaften, Göttingen.

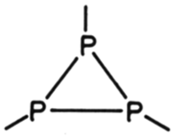
Klaus Glinka was born in 1941 in Gumbinnen (Eastern Prussia), Germany. He studied at the University of Cologne and received his doctoral degree on the synthesis and mass spectrometric investigation of multisulfur compounds in 1970 under the supervision of F. Fehér. In 1971 he joined the staff of the Institut für Anorganische Chemie der Universität Köln serving as an instructor, operator, and organizer. Currently he is following his interests in the history of the Chemical Department in Cologne since 1901 and its ancient predecessors.

100 years ago by Köhler and Michaelis,[2] although its molecular size and cyclic structure were not recognized at that time. The compound was finally identified much later as the cyclopentaphosphane $(PPh)_5$ by an X-ray crystal structure analysis.[3,4] Haiduc[5] has published a comprehensive survey of the initial developments and early controversies in the field of monocyclic phosphanes through to the middle of 1969. Since then several reviews of the various areas of cyclic polyphosphorus compounds have appeared.[6-12] The present article is intended to give a summary of the progress made in the field of mono- and polycyclophosphanes during the last 25 years; the literature up to the end of 1991 has been covered. In addition, the present article contains some previously unpublished results from our laboratories in Cologne. The review published by von Schnering and Hönle[13] in 1988 on metal polyphosphides provides excellent complementary reading to the present paper.

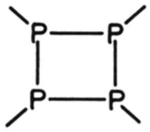
II. Neutral Monocyclic Phosphanes

A. General Comments

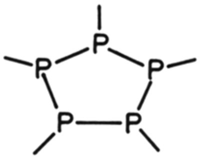
Four basic ring structures made up of trivalent phosphorus atoms form the skeletons of all known neutral monocyclophosphanes as well as those of the corresponding polyphosphides (see section III).



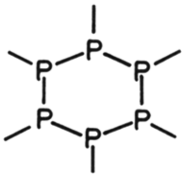
cyclotriphosphane
triphosphirane



cyclotetraphosphane
tetraphosphetane



cyclopentaphosphane
pentaphospholane



cyclohexaphosphane
hexaphosphorinane

According to current nomenclature rules,[14] the two names given under each formula are equivalent. In the present article the upper names are used exclusively for the homocyclic compounds $(PR)_n$ (n = 3–6, R = H or an organic group).

In those cases where the substituents on the cyclophosphane skeletons are hydrogen atoms, the existence of larger rings cannot be discounted since all members of the series P_nH_n with n = 3–10 have been detected by mass spectrometry in the thermolysis products from the diphosphane P_2H_4.[9,15] The first member P_3H_3 was separated from the corresponding phosphane mixture in small amounts by gas chromatography;[16] however, its isolation in preparatively useful amounts is impaired by an extremely rapid oligomerization to the thermodynamically stable five-membered ring compound P_5H_5. Russian workers have reported on the formation of cyclotetraphosphane, P_4H_4, by the electrolysis of white phosphorus in an acetic acid medium;[17] further investigations on this compound are, however, still necessary.

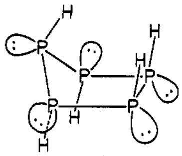
Cyclopentaphosphane, P_5H_5, can be isolated and structurally characterized by spectroscopic methods. It is formed as the major product in the low-temperature vacuum pyrolysis of phosphane mixtures containing a high proportion of P_3H_5 and P_4H_6.[9] In addition, P_5H_5

$$P_3H_5 + P_4H_6 \rightarrow P_5H_5 + 2PH_3 \qquad (1)$$

is formed in a complicated reaction by methanolysis of tetrakis(trimethylsilyl)cyclotetraphosphane.[18]

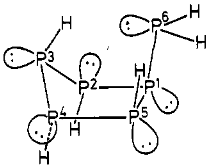
$$(Me_3SiP)_4 \xrightarrow[-Me_3SiOMe]{+MeOH} P_5H_5 \qquad (2)$$

The product was shown to be cyclopentaphosphane by mass spectrometry and, above all, by the AA′BB′C spin system observed in its $^{31}P\{^1H\}$-NMR spectrum.[9] From calculated ^{31}P-NMR parameters, it was deduced that the compound exists as the configurational isomer 1 with the maximum *trans* orientation of the neighboring free electron pairs or hydrogen atoms, respectively. This conclusion is compatible with the crystal structure analyses of $(PCF_3)_5$[19] and $(PPh)_5$,[3,4] which proved that these two long-known pentaorganocyclopentaphosphanes have the same configuration.



1

The parent compound, P_6H_6, of the cyclohexaphosphanes is still unknown. A compound with this composition was indeed detected by mass spectrometry 25 years ago among the thermolysis products of higher, open-chain phosphanes.[20] However, a complete analysis of the respective ^{31}P spin system showed that the compound was in fact 1-phosphinocyclopentaphosphane (2) with the configuration shown.[21]



2

Of particular relevance in this context is the large, positive long-range coupling constant $^2J(P^2,P^6)$ which indicates that the free electron pairs of the respective P atoms are directed toward each other.[22-24] The *cis* arrangement of the substituents at P^1 and P^5 is substantiated by the magnitude of the absolute value of the corresponding $^1J(P,P)$ coupling constant. Furthermore, no evidence for the constitutional isomer with a *six*-membered phosphorus ring and an *all-trans* orientation of hydrogen atoms or free electron pairs, respectively, was obtained from the hydrolysis of $(PCl)_6$ which proceeds through disproportionation to furnish PH_3 and phosphorous acid.[25]

In the cases of alkyl- and aryl-substituted monocyclophosphanes, each substituent favors a certain ring size corresponding to the compound with the highest thermodynamic stability. Hence only *one* P_n ring compound each has been prepared to date for a series of substituents. When sufficient kinetic stabilization is present, however, other oligomers with different ring sizes are also capable of existence and can be prepared by special synthetic methods.

The determination of the ring size of monocyclophosphanes presented a problem for a long time because the various methods for determining the relative molecular masses often gave contradictory results.[5] This situation changed, however, in the middle of the 1970s when a simple NMR method for determining the ring size of cyclophosphanes was discovered; this method is based on a correlation of the $\delta(^{31}P)$ shift values with the number of P atoms in the ring[26-29] (section II.C.2).

B. Methods of Preparation

The methods for the preparation of monocyclophosphanes can be classified into two groups: (i) methods that are unspecific with regard to ring size and which usually give rise to the thermodynamically more stable product, and (ii) methods that are specific for a certain ring size.

In addition, numerous other reactions leading to monocyclophosphanes have been reported.

1. Methods Unspecific as to Ring Size

Well-proven preparative methods of this type are illustrated by the examples shown in eqs 3–8.

(a) Reaction of a primary phosphane with a dichloro(organo)phosphane:[1]

$$RPH_2 + RPCl_2 \rightarrow 2/n(PR)_n + 2HCl \qquad (3)$$

(b) Reaction of a dihalo(organo)phosphane with a reducing agent; the reduction can be performed with mono- or divalent metals such as lithium,[30] sodium,[31] magnesium,[25,32] mercury,[33] or with organic compounds such as 1,3,1′,3′-tetraethylbis(2,2′-imidazolides),[35] or by electrochemical methods.[36,37]

$$RPHal_2 + 2M^I \rightarrow 1/n(PR)_n + 2M^IHal \qquad (4)$$

In some cases metal hydrides[38,39] or tertiary phosphanes[40] have also been employed with success.

$$RPCl_2 + 2LiH \rightarrow 1/n(PR)_n + 2LiCl + H_2 \qquad (5)$$

$$2RPCl_2 + LiAlH_4 \rightarrow 2/n(PR)_n + AlCl_3 + LiCl + 2H_2 \qquad (6)$$

$$RPCl_2 + Bu_3P \rightarrow 1/n(PR)_n + Bu_3PCl_2 \qquad (7)$$

(c) Reaction of white phosphorus with an alkylmagnesium bromide and an alkyl bromide (molar ratio 1:1:2).[41]

$$P_4 + 2RMgBr + 2RBr \rightarrow 4/n(PR)_n + 2MgBr_2 \qquad (8)$$

The monocyclophosphanes listed in Table I have been prepared by the methods a–c.

2. Methods Specific as to Ring Size

Well-established routes to monocyclophosphanes of specific ring size are the reactions d–h, as illustrated by eqs 9–11.

(d) Metal–halogen exchange of a potassium polyphosphide with 1,2-dibromoethane.

$$K(PEt)_nK + BrCH_2CH_2Br \rightarrow (PEt)_n + 2KBr + C_2H_4 \qquad (9)$$

This reaction has been used with success for the preparation of ethyl-substituted cyclotetra- and cyclopentaphosphanes (n = 4 and 5).[50]

(e) [2 + 1]-Cyclocondensation of a 1,2-diorgano-1,2-bis(trimethylsilyl)diphosphane with a dichloro(organo)phosphane (R^1 = Ph, R^2 = Ph,[28,51] Me, Et,[51] Pr^i, Bu^i [52]).

$$Me_3Si(R^1)PP(R^1)SiMe_3 + R^2PCl_2 \rightarrow (R^1P)_2PR^2 + 2Me_3SiCl \qquad (10)$$

This reaction path leads to cyclotriphosphanes with identical ($R^1 = R^2$) or mixed substituents ($R^1 \neq R^2$). An extension of the corresponding reaction principle is

Table I. Synthesis of Monocyclic Phosphanes

compound	method of synthesis	yield, %	bp, °C/Torr	mp, °C	ref
Cyclohexaphosphanes					
$(PPh)_6$	(a)			197–201	29, 41
				183–186	27
$(PCl)_6$	(b) LiH	42			25
$(PBr)_6$	(b) Mg				25
Cyclopentaphosphanes					
$(PPh)_5$	(a)	93		153–155	32
	(b) $LiAlH_4$	58		148–150	32
	(b) Mg	84		148–152	32, 29
	(b) cath. red.	80		150–151	36, 37
$(PHex^c)_5$	(b) Na	7		165–167	34
$(PBu^n)_5$	(a)	82	170°/0.02		32
	(c)	11	170°/0.05		29
$(PPr^n)_5$	(a)	92	140–145°/0.03		32
	(c)	5–20	142°/0.03		29
$(PEt)_5$	(b) Li	81	124–129°/0.05		32
	(c)	5–20	125°/0.05		29
	(d)	94	160–162°/0.3		50
$(PMe)_5$	(b) Li	67	135–136°/3		29
Cyclotetraphosphanes					
$(PHex^c)_4$	(a)	79		219–220	42
	(a)	77		222–224	32
	(b) Mg			214–216	29
$(PBu^t)_4$	(b) Na	63		167–169	43
	(b) Mg			161–162	29
	(b) [a]	57			35
$(PBu^s)_4$	(b) Mg		150°/0.05		29
$(PPr^i)_4$	(b) Mg	80		23–24	32
	(c)		95°/0.05		29
$(PC_3F_7^n)_4$	(b) Hg		118–120°/16		44, 29
$(PC_2F_5)_4$	(b) Hg			23.5	45, 29
$(PNPr^i_2)_4$	(b) Mg	40–57		197–198	68
Cyclotriphosphanes					
$(PHex^c)_3$	(b) Na	18		79	34
$(PBu^s)_3$	(b) Mg	24	98–112°/0.1		46
$(PBu^t)_3$	(b) Mg	35–60	84°/0.1		47, 48
$(PPr^i)_3$	(b) Mg	38	38–40°/0.0005		46
$(PC_3F_7^i)_3$	(b) Hg	100		20	49
$(PC_3F_7^n)_3$	(b) Hg		108–110°/30		29, 44
$(PC_2F_5)_3$	(b) Hg		72–74°/51		29, 44, 45

[a] 1,3,1′,3′-Tetraethylbis(2,2′-imidazolidene).

provided by the [3 + 1]-cyclocondensation of $Me_3Si(Ph)PP(Ph)P(Ph)SiMe_3$ with $PhPCl_2$ or Bu^tPCl_2 which gives rise to the corresponding cyclotetraphosphanes.[53]

(f) [2 + 1]-Cyclocondensation of a 1,2-dipotassium 1,2-diorganodiphosphide with a dichloro(organo)phosphane (R^1 = Ph, R^2 = Pr^i;[52] R^1 = Bu^t, R^2 = Pr^i [54]).

$$K(R^1)PP(R^1)K + R^2PCl_2 \rightarrow (R^1P)_2PR^2 + 2KCl \tag{11}$$

Attack of the nucleophilic phosphide on the already formed three-membered ring compound must be avoided by means of a heterogeneous reaction in a nonpolar solvent. The corresponding [3 + 1]-cyclocondensation of $K(Ph)PP(Ph)P(Ph)K$ with $PhPCl_2$ or Bu^tPCl_2 produces the cyclotetraphosphanes $(PPh)_4$ or $(PPh)_3PBu^t$, respectively, in high yields.[53]

(g) Reductive cyclization of an α,ω-dihalophosphane with lithium hydride.[55]

$$I(PBu^t)_3I + 2LiH \rightarrow (PBu^t)_3 + 2LiI + H_2 \tag{12}$$

This reaction corresponds to the classical synthesis of cyclopropanes by dehalogenation of 1,3-dihalopropanes; however, it has no preparative significance.

(h) Cyclocondensation of an open-chain 1,2,3-triorganotriphosphane with diphosphorus tetraiodide.[56]

$$2H(PBu^t)_3H + P_2I_4 + 4Et_3N \rightarrow (PBu^t)_3PP(PBu^t)_3 + 4Et_3NHI \tag{13}$$

The *tert*-butyl-substituted 1,1′-bicyclotetraphosphane in which two P_4 ring units are linked to each other through a σ-bond can be obtained by this route.

3. Miscellaneous Reactions

In addition to the procedures mentioned in sections II.B.1 and 2, monocyclophosphanes are also formed in a number of other reactions, and some of them are of interest for the preparation of specific compounds.

For example, the unexpected transformation of $K(PHex^c)_3K$ in carbon disulfide solution constitutes a good method for the preparation of $(PHex^c)_3$.[34]

Tetrakis(trimethylsilyl)cyclotetraphosphane can be obtained by the reaction of trimethylsilylphosphane with di-*tert*-butylmercury.[18]

$$4Me_3SiPH_2 + 4Bu^t_2Hg \rightarrow (Me_3SiP)_4 + 4Hg + 8Bu^tH \tag{14}$$

The corresponding cyclopentaphosphane is formed as a by product. This reaction type resembles the formation of $(PMe)_5$ from methylphosphane and dibenzylmercury[57] and is based on earlier methods for the synthesis of cyclopentaphosphanes by way of organomercury compounds.[58]

The synthesis of $(PCF_3)_4$ by heating CF_3PF_2 in the presence of a tetraalkyllead compound is mentioned in a patent.[59]

The reaction of $LiP(SiMe_3)_2{\cdot}2THF$ with CH_3PCl_2 produces a triphosphane from which upon thermolysis (120 °C, 60 h), the mixed-substituted trimethylsilyl/methylcyclopentaphosphanes $P_5(SiMe_3)_{5-n}Me_n$ (n = 2–4) are formed. Reaction of the same lithium salt with $PhPCl_2$ gives rise to the corresponding mixed-substituted trimethylsilyl/phenylcyclopentaphosphanes.[60,61] The mixed-substituted cyclotetraphosphane $(Me_3SiPPBu^t)_2$ and cyclotriphosphane $(PBu^t)_2PSiMe_3$ were obtained from the reactions of the above-mentioned lithium salt with Bu^tPCl_2 (molar ratios 2:1 and 1:1, respectively);[60,61] the same cyclotriphosphane is also accessible from $(PBu^t)_2PK$ and Me_3SiCl.[9,62] The cyclotetraphosphane $(Me_3SiPPBu^t)_2$ was converted mainly to the mixed-substituted trimethylsilyl/*tert*-butylcyclopentaphosphanes by irradiation.[60,61] The constitutionally isomeric compound $(Me_3SiP)_2(PBu^t)_2$ was prepared by condensation of the open-chain triphosphane $(Me_3Si)_2PP(SiMe_3)P(SiMe_3)Bu^t$ with Bu^tPCl_2.[63] The mixed-substituted cyclotetraphosphane $(PSiMe_3)_3PBu^t$ was obtained using the same reaction principle but starting from the triphosphane $P_3(SiMe_3)_5$.[64]

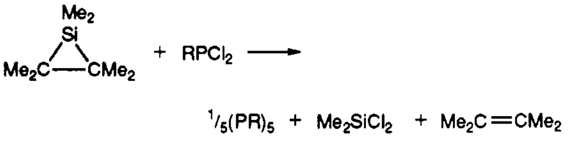
The reaction of $LiP(SiMe_3)_2{\cdot}2THF$ with PCl_3 and $LiBu^t$ was used for the preparation of the cyclotetraphosphane $(PBu^t)_3PSiMe_3$; in addition the two constitutional isomers of the cyclotetraphosphane $P_4(SiMe_3)_2(Bu^t)_2$ were formed.[65] $(PBu^t)_3PSiMe_3$ can also be prepared by the reaction of white phosphorus with $LiBu^t$ and Me_3SiCl (molar ratio 1:2:2).[66,67]

As to be expected, the halogenated silylphosphane $Me_3Si(Bu^t)PCl$ is not stable and decomposes with formation of the cyclophosphanes $(PBu^t)_3$ and $(PBu^t)_4$.[69]

The action of a tertiary amine on 1,2-diiodo-1,2-diphenyldiphosphane produced $(PPh)_5$ in 90% yield.[70]

The reaction of magnesium with Me_3SiCl and Bu^tPCl_2 not only gave rise to the expected diphosphane $Me_3Si(Bu^t)PP(Bu^t)SiMe_3$ but also to the cyclophosphanes $(PBu^t)_4$[71] and $(PBu^t)_3$;[72] the latter product can be isolated in the pure state.

Hexamethylsilirane was cleaved by treatment with $RPCl_2$ (R = Ph, Et, Me), and the dichloroorganophosphane underwent conversion to the corresponding cyclopentaphosphane.[73]



(15)

$(PPh)_5$ together with $(PPh)_4CH_2$, Et_2NH, and CH_3NEt_2 were formed by the reaction of $[(Et_2N)_2CH]_2PhP$ with phenylphosphane at higher temperatures.[74]

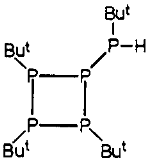
Formation of $(PPh)_4$ and $(PPh)_5$ can be observed on disproportionation of the open-chain phenylphosphanes $H(PPh)_nH$ (n = 2–4).[75–77] The same cyclophosphane mixture was obtained by the reaction of $(Me_3Sn)_2PhP$ with $PhPCl_2$.[78] The reaction of $MePh_2P$ with $PhPF_2$ resulted in the formation of $(PPh)_5$ together with $MePh_2PF_2$.[79]

The methyl-substituted cyclopentaphosphane was produced via the unstable intermediate MePHCl when $MePH_2$ was allowed to react with S_2Cl_2 (molar ratio 2:1).[80]

Finally, the difluorophosphane $2\text{-}MeOC_6H_4PF_2$, obtained by Cl/F exchange from the corresponding chlorophosphane, underwent a spontaneous redox reaction at room temperature to furnish $2\text{-}MeOC_6H_4PF_4$ and $(2\text{-}MeOC_6H_4P)_4$, which could be isolated in the pure state.[81]

4. Preparation of Monocyclic Phosphanes with Side Chains

Phosphanes with the composition P_nR_n (R = H or organic group) with $n > 3$ do not necessarily possess a monocyclic skeleton of n phosphorus atoms but may also occur as smaller monocyclic rings with one or more P_m side chains (m = 1, 2). Some examples are the previously mentioned phosphorus hydride P_6H_6 (**2**)[21] as well as the organo-, trimethylsilyl-, or halo-substituted compounds **3**–**8**.



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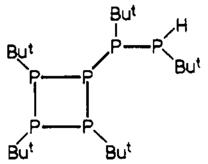

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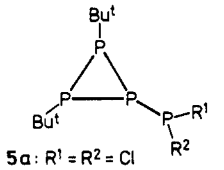
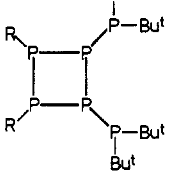
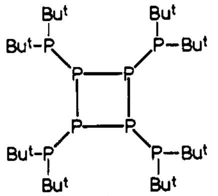


5a: R¹ = R² = Cl
5b: R¹ = Buᵗ, R² = Cl
5c: R¹ = Buᵗ, R² = I
5d: R¹ = Buᵗ, R² = SiMe₃



6a: R = Buᵗ
6b: R = SiMe₃



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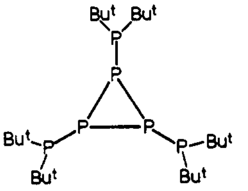


8

Compounds **3**[82] and **4**[83] were formed by the thermolysis of 1,2-di-*tert*-butyldiphosphane[84] via the intermediacy of 1,2,3-tri-*tert*-butyltriphosphane.[85] At 170 °C, the amount of **3** reached a maximum after about 20 h and then decreased in favor of the formation of **4** upon further reaction. The side chain was not lengthened by reaction of **4** with $H_2(PBu^t)_2$; instead the retroreaction to **3** according to eq 19 occurred at higher concentrations of the diphosphane.

$$2H_2(PBu^t)_2 \rightarrow H_2(PBu^t)_3 + Bu^tPH_2 \qquad (16)$$

$$2H_2(PBu^t)_3 \rightarrow \underset{\mathbf{3}}{P_5Bu^t_4H} + Bu^tPH_2 + Bu^tH \qquad (17)$$

$$\underset{\mathbf{3}}{P_5Bu^t_4H} + H_2(PBu^t)_2 \rightarrow \underset{\mathbf{4}}{P_6Bu^t_5H} + Bu^tPH_2 \qquad (18)$$

$$\underset{\mathbf{3}}{P_5Bu^t_4H} + H_2(PBu^t)_3 \rightleftharpoons \underset{\mathbf{4}}{P_6Bu^t_5H} + H_2(PBu^t)_2 \qquad (19)$$

The four-membered ring structures for **3** and **4** were elucidated by ^{31}P-NMR spectroscopy; hence these compounds are 1-(*tert*-butylphosphino)- and 1-(1,2-di-*tert*-butyldiphosphino)-2,3,4-tri-*tert*-butylcyclotetraphosphanes, respectively. Compound **3** is thus a constitutional isomer of 1,2,3,4-tetra-*tert*-butylcyclopentaphosphane,[86] which is formed by hydrolysis of $K(Bu^t)_4P_5$ and—like the starting material—contains a five-membered phosphorus ring skeleton. Since the formation of four-membered ring units is generally favored in the case of *tert*-butyl-substituted cyclophosphanes,[9] compound **3** not surprisingly possesses a higher thermodynamic stability than the other isomer.[86]

The cyclotriphosphanes **5a–c** carrying a phosphino group as substituents are accessible by reactions of the functionalized cyclotriphosphane $(PBu^t)_2PSnMe_3$ with PCl_3 or Bu^tPX_2 (X = Cl, I), respectively.[87] In contrast, use of the corresponding silyl compound $(PBu^t)_2PSiMe_3$ preferentially gave rise to *tert*-butylphosphanes with four- and five-membered ring skeletons.

$$(PBu^t)_2PSnMe_3 + PCl_3 \rightarrow \underset{\textbf{5a}}{(PBu^t)_2PPCl_2} + Me_3SnCl \quad (20)$$

$$(PBu^t)_2PSnMe_3 + Bu^tPX_2 \rightarrow (PBu^t)_2PP(Bu^t)X + Me_3SnX \quad (21)$$

5b: X = Cl
c: X = I

Compound **5d** as well as the three-membered ring compounds $P_3[P(SiMe_3)_2](Bu^t)Cl$, $P_3[P(SiMe_3)_2](SiMe_3)Cl$, and $P_3[P(Bu^t)SiMe_3](Bu^t)Cl$, possessing two different substituents on the ring in addition to the phosphino group, were formed by the thermal decomposition of silylated, PCl-containing isotetraphosphanes via cleavage of Me_3SiCl.[89]

The cyclotetraphosphanes **6a** and **6b** with two di-*tert*-butylphosphino substituents were obtained by cleavage of chlorotrimethylsilane from the open-chain triphosphanes $Bu^t_2PP(SiMe_3)P(Bu^t)Cl$ and $Bu^t_2PP(Cl)P(SiMe_3)_2$, respectively. In the case of **6b**, the constitutional isomer with alternating Bu^t_2P and Me_3Si groups was formed concomitantly.[88] The formation of compounds **6** proceeds by way of the intermediates $Bu^t_2PP{=}PBu^t$ and $Bu^t_2PP{=}PSiMe_3$, respectively, which experience stabilization through dimerization (for further information, see ref 129). The cyclotetraphosphanes **6a** and **6b** were also formed by the thermal decomposition of the isotetraphosphanes $(Bu^t_2P)_2PP(Bu^t)Cl$ and $(Bu^t_2P)_2PP(SiMe_3)_2$ through elimination of Bu^t_2PCl and $Bu^t_2PSiMe_3$, respectively.[89] The cyclotriphosphane $P_3(PBu^t_2)_2Bu^t$ containing two di-*tert*-butylphosphino groups was formed analogously by cleavage of chlorotrimethylsilane from the isopentaphosphane $Bu^t_2PP[P(Bu^t)Cl]P(SiMe_3)PBu^t_2$.[128]

The formation of the cyclophosphanes **7** and **8** in which all substituents are di-*tert*-butylphosphino groups was observed in the thermolysis of the partially silylated triphosphanes $Bu^t_2PP(SiMe_3)P(SiMe_3)_2$, $Bu^t_2PP(SiMe_3)P(Bu^t)SiMe_3$, and $Bu^t_2PP(SiMe_3)PBu^t_2$ as well as the corresponding tetraphosphane $Bu^t_2P[P(SiMe_3)]_2PBu^t_2$.[90] Tetrakis(di-*tert*-butylphosphino)cyclotetraphosphane (**7**) can be obtained in the pure state by the reaction of $Bu^t_2PP(Li)PBu^t_2{\cdot}THF$ with 1,2-dibromoethane and subsequent low-temperature crystallization.[91] Small P_n rings are, in general, stabilized by the presence of di-*tert*-butylphosphino substituents.

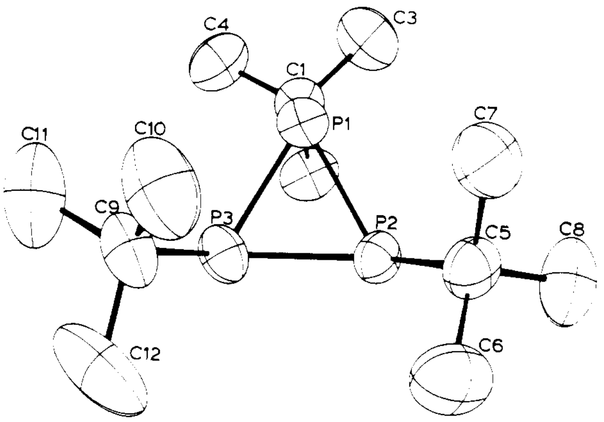


Figure 1. Structure of one of the two independent molecules of $(PBu^t)_3$ (without hydrogen atoms) in the crystal.[99]

C. Structures and Physical Properties

1. Crystal Structure Determinations

The crystal structures of various monocyclophosphanes have been determined. The results are summarized in Table II.

In the various modifications of $(PPh)_6$, the P_6 ring—like the C_6 ring of cyclohexane—exists in the chair form; the phenyl groups occupy equatorial positions. Also, the P_5 rings in the cyclopentaphosphanes $(PPh)_5$ and $(PCF_3)_5$ are not planar and exhibit a somewhat twisted envelope conformation. The P–P bond lengths differ only slightly while the endocyclic ∠PPP bond angles vary over a larger range.

All cyclotetraphosphanes possess a folded P_4 ring with endocyclic ∠PPP bond angles of 80–87° and torsional angles of ±25–46°. The constitutions of mixed-substituted cyclotetraphosphanes are determined by the steric interactions between the substituents. Thus, the compound $P_4Bu^t_2(PBu^t_2)_2$ (**6a**) exists exclusively as the 1,2-di-*tert*-butyl-3,4-bis(di-*tert*-butylphosphino) derivative, whereas $P_4(SiMe_3)_2(PBu^t_2)_2$ (**6b**) exists simultaneously as the isomer with an alternating arrangement of the substituents.[88] Steric hindrance between two *trans*-oriented *tert*-butyl groups on the same side of the ring is apparently larger than that between correspondingly positioned trimethylsilyl and di-*tert*-butylphosphino groups; this can be attributed to the different lengths of the P–C bond as compared to the P–Si and P–P bonds. The quasi-equatorial arrangement of all substituents results in a quasi-axial placement of the free electron pairs.

Two structural characteristics are apparent for the two cyclotriphosphanes $(PR)_3$ that have so far been analyzed by X-ray crystallography. (See, for example, the structure of $(PBu^t)_3$ in Figure 1.) The bond lengths between P atoms with *cis*-oriented organic groups and the ∠PPC bond angles at these atoms are always significantly larger than the corresponding values for the *trans*-substituted P atoms; these phenomena can be attributed to interactions between the substituents or between the free electron pairs, respectively (see also section II.C.5).

2. NMR Data

In the last two decades, pulsed Fourier-transform NMR spectroscopy has proved to be the most important method for the structural characterization of cyclo-

Table II. Crystal and Molecular Data of Monocyclic Phosphanes

compound	space group	cell dimensions	Z	molecular data	ref(s)
$(PPh)_6$	$P2_1/c$ monoclinic	$a = 12.31$ Å $b = 6.16$ Å $c = 24.86$ Å $\beta = 117.64°$	2		4
$(PPh)_6$	$P\bar{3}c1$ trigonal	$a = 13.026$ Å $b = 11.547$ Å	2	P–P, 2.237 Å P–C, 1.843 Å ∠PPP, 94.6° ∠PPC, 98.5°	92, 93
$(PPh)_6$	$P\bar{1}$ (Ci no. 2) triclinic	$a = 10.551$ Å $b = 14.717$ Å $c = 13.000$ Å $\alpha = 106.26°$ $\beta = 116.80°$ $\gamma = 91.59°$	2	P–P, 2.233 Å P–C, 1.843 Å ∠PPP, 95.5° ∠PPC, 98.2°	93, 94
$(PPh)_5$	$P2_1/n$ monoclinic	$a = 9.742$ Å $b = 10.139$ Å $c = 27.488$ Å $\beta = 90°$	4	P–P, 2.217 Å P–C, 1.843 Å ∠PPP, 107.24, 94.05, 100.25, 95.05, 103.4° ring torsion angles, ±2.2–60.6° ∠PPC, 102.01°	3
$(PCF_3)_5$	$P2_1/n$ monoclinic	$a = 9.87$ Å $b = 9.78$ Å $c = 16.67$ Å $\beta = 103°$	4	P–P, 2.223 Å P–C, 1.91 Å ∠PPP, 93.9, 102.7, 98.0, 103.3, 108.3° ring torsion angles, ±18–58°	19
$(PCF_3)_4$	$P4_2/nmc$ tetragonal	$a = 10.100$ Å $b = 10.100$ Å $c = 6.397$ Å	2	P–P, 2.213 Å P–C, 1.867 Å ∠PPP, 84.7° ring torsion angle, ±34.0°	95
$(PC_6F_5)_4$	$C2/c$ monoclinic	$a = 21.426$ Å $b = 7.627$ Å $c = 18.826$ Å $\beta = 120.45°$	4	P–P, 2.236 Å P–C, 1.838 Å ∠PPP, 85.24° ring torsion angle, ±32.1° ∠PPC, 101.05°	96
$(PHex^c)_4$	$P\bar{4}2_1c$ tetragonal	$a = 10.158$ Å $b = 10.158$ Å $c = 12.695$ Å	2	P–P, 2.224 Å P–C, 1.874 Å ∠PPP, 85.5° ring torsion angle, ±31.4° ∠PPC, 102.72°	97
$(PBu^t)_4$	$P2_1/c$ monoclinic	$a = 9.391$ Å $b = 14.029$ Å $c = 16.854$ Å $\beta = 95.80°$	4	P–P, 2.212 Å P–C, 1.884 Å ∠PPP, 87.30° ring torsion angle, ±24.5° ∠PPC, 104.05°	98
$(2\text{-MeOC}_6H_4P)_4$	$P2_1/n$ monoclinic	$a = 11.923$ Å $b = 15.172$ Å $c = 15.417$ Å $\beta = 100.30°$	4	P–P, 2.225 Å P–C, 1.830 Å ∠PPP, 84.1°	81
$[PN(SiMe_3)_2]_4$	$P\bar{1}$ (no. 2) triclinic	$a = 12.109$ Å $b = 17.490$ Å $c = 22.715$ Å $\alpha = 86.88°$ $\beta = 84.88°$ $\gamma = 83.29°$	4	P–P, 2.234 Å P–N, 1.731 Å ∠PPP, 79.8° ring torsion angle, ±45.7° ∠PPN, 109.8°	129
$P_4Bu^t_2(PBu^t_2)_2$	$P2_1/a$ monoclinic	$a = 17.620$ Å $b = 16.872$ Å $c = 11.705$ Å $\beta = 109.18°$	4	P–Pendocyclic, 2.229 Å P–Pexocyclic, 2.218 Å P–C, 1.897 Å ∠PPPendocyclic, 85.0° ring torsion angle, ±33.0°	88
$(PBu^t)_3$	$P\bar{1}$ triclinic	$a = 6.256$ Å $b = 17.415$ Å $c = 17.806$ Å $\alpha = 62.07°$ $\beta = 79.89°$ $\gamma = 79.66°$	4	P–P, 2.185–2.218 Å P–C, 1.896 Å ∠PPP, 59.5–60.9° ∠PPC, 105–124°	99
$P_3[(Me_3Si)_2CH]_3$	$Pbca$ orthorhombic	$a = 19.021$ Å $b = 13.069$ Å $c = 28.877$ Å	8	P–P, 2.201–2.220 Å P–C, 1.863 Å ∠PPP, 60.0° ∠PPC, 105–111°	100

phosphanes in solution. As may be seen from Figure 2, endocyclic bond angles of ≈100° (ring size $n = 5$), ≈95° ($n = 6$), ≈86° ($n = 4$), and 60° ($n = 3$) can be correlated with ^{31}P-NMR signals of +10, −20, −60, and −140 ppm, respectively (negative sign for high-field shifts).[26–29,99] On decoupling of all other NMR-active nuclei, the ^{31}P-NMR spectra of uniformly substituted monocyclophosphanes $(PR)_n$ are characterized by a singlet for ring sizes $n = 4$ and 6, an A_2B spin system for $n = 3$, and an AA′BB′C spin system for $n = 5$.

The ^{31}P-NMR parameters of uniformly substituted cyclotriphosphanes $(PR)_3$ are listed in Table III, those

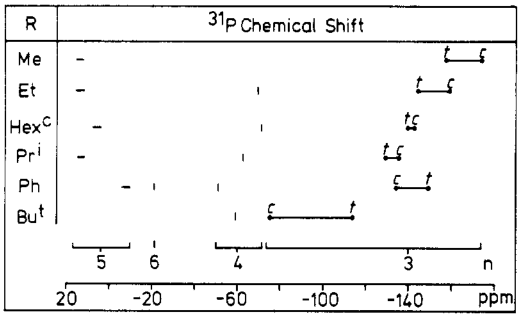
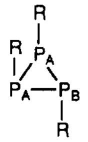


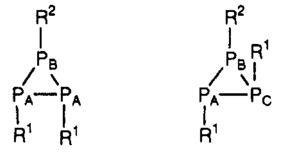
Figure 2. Dependence of ^{31}P chemical shifts of organocyclophosphanes $(PR)_n$ on the ring size n and the substituents R; c and t designate $\delta^{31}P_{cis}$ and $\delta^{31}P_{trans}$ of the cyclotriphosphanes.

Table III. ^{31}P-NMR Parameters of the Cyclotriphosphanes $(PR)_3$



R	δ_A	δ_B	J_{AB}, Hz	ref(s)
Me	-171.0	-157.3	-170.8	101
Et	-157.3	-145.0	-178.5	101
Hex^c	-141.7	-138.9	-185.0	34
Pr^i	-132.3	-128.6	-184.8	46
Ph	-131.7	-147.2	-186.9	51
Bu^t	-71.9	-108.1	-201.1	72, 99

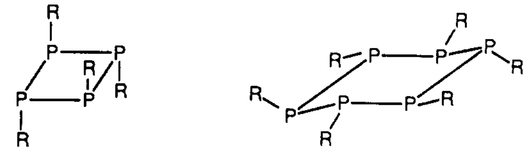
Table IV. ^{31}P-NMR Parameters of the Cyclotriphosphanes $(PR^1)_2PR^2$



a (A_2B) **b** (ABC)

R^1	R^2		δ_A	δ_B	δ_C	J_{AB}, Hz	J_{AC}, Hz	J_{BC}, Hz	ref
Bu^t	Pr^i	**a**	-68.5	-127.8		-192.1			54
		b	-109.0	-112.5	-99.5	-188.7	-205.1	-262.2	
Ph	Bu^i	**a**	-137.4	-162.9		-185.6			52
		b	-149.9	-148.7	-140.9	-180.0	-195.3	-216.0	
Ph	Pr^i	**a**	-140.3	-134.1		-189.9			52
		b	-152.3	-123.6	-136.9	-185.3	-184.1	-226.9	
Ph	Et	**a**	-138.7	-151.8		-186.3			51
		b	-148.3	-141.6	-138.8	-182.7	-184.8	-220.0	
Bu^t	SiMe$_3$	**a**	nonexistent						87
		b	-113.1	-224.7	-90.7	-157.5	-222.4	-309.5	
Bu^t	SnMe$_3$	**a**	nonexistent						87
		b	-116.6	-241.5	-100.5	-154.5	-229.2	-292.9	
Bu^t	H	**a**	nonexistent						148
		b	-136.3	-270.8	-149.2	-144.1	-223.7	-226.6	
Bu^t	Cl	**a**	nonexistent						87
		b	-91.0	-11.4	-95.0	-185.4	-204.6	-241.0	

Table V. ^{31}P-NMR Parameters of the Cyclotetraphosphanes $(PR)_4$ and of the Cyclohexaphosphanes $(PR)_6$



R	$\delta^{31}P$	J_{PP}, Hz	ref(s)	R	$\delta^{31}P$	J_{PP}, Hz	ref(s)
CF$_3$	-76.7	-100.6	109	Ph	-22.2	-106	28, 108
Et	-68.7	-112.6	109	Cl	+194	nd^a	25
Pr^i	-62.4	-123.3	109	Br	+220	nd^a	25
Bu^t	-58.4	-148.4	109				
Hex^c	-69.5	-116.3	109				
Ph	-48.7	nd^a	28, 53				
2-MeOC$_6$H$_4$	-55.6	nd^a	81				
SiMe$_3$	-177.9	nd^a	18, 53				

^{a} nd = not determined.

of mixed-substituted compounds of the type $(PR^1)_2PR^2$ in Table IV.

The ^{31}P-NMR spectra of all cyclotriphosphanes are characterized by high-field chemical shifts in comparison to open-chain triphosphanes or cyclophosphanes of other ring sizes.[7,26,28,29] The $\delta(^{31}P)$ values are influenced by the three-membered ring structure in the same way as the $\delta(^{13}C)$ values of the cyclopropanes.[102] The considerably more apparent "effect of the small ring" in the phosphorus compounds can be attributed to the predominantly s character and hence larger shielding effect of the free electron pairs on the phosphorus atoms of the cyclotriphosphane ring.[28]

Apart from the internal ring angles, the δ values are also influenced to a considerable extent by the exocyclic ∠PPC bond angles.[99] The changes in these parameters on going from the small methyl substituents to the bulky *tert*-butyl substituents cause a significant low-field shift of the signals for the *cis*-substituted P atoms from -171 ppm for $(PMe)_3$ to -72 ppm for $(PBu^t)_3$ (Table III); at the same time, the relative resonance positions of the P_{cis} and P_{trans} atoms are reversed.[99,103]

In the cases of the mixed-substituted cyclotriphosphanes $(PR^1)_2PR^2$, two isomers are observed. The symmetrical isomer **a** with like substituents on one side of the ring exhibits an A_2B spin system in the $^{31}P\{^1H\}$-NMR spectrum while the asymmetrical isomer **b** shows an ABC spin system (Table IV). When neither R^1 nor R^2 is a bulky group, the two isomers are formed in the statistical ratio (**a**:**b** = 1:2).[7] On the other hand, when R^1 is considerably more bulky than R^2, the asymmetrical isomer **b** is definitely preferred for steric reasons.[87]

In general, the $\delta(^{31}P)$ values of cyclophosphanes are also influenced[99] by the size of the dihedral angle between the free electron pairs of adjacent P atoms[99,103] and by β-effects of the substituents.[104]

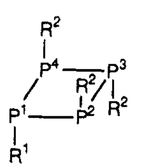
The dihedral angle is also the determining factor for the size of the $^1J(P,P)$ coupling constants of cyclophosphanes[99,103,105,106] which are always negative.[107] *Cis*-substituted P atoms exhibit larger absolute values for the $^1J(P,P)$ coupling constants than *trans*-substituted P atoms. Furthermore, the magnitude of the absolute value of the coupling constants increases with increasing bulkiness of the substituents.[99]

The ^{31}P-NMR parameters of uniformly substituted cyclotetraphosphanes $(PR)_4$ and of the cyclohexaphosphane $(PPh)_6$ are given in Table V, those of the mixed-substituted cyclotetraphosphanes $(PR^1)(PR^2)_3$ and $(PR^1)_2(PR^2)_2$ in Tables VI and VII, respectively. Table VIII contains the ^{31}P data of those cyclopentaphosphanes $(PR)_5$ for which the spectra have been fully analyzed.

3. UV, PE, ESR, and Vibrational Spectra

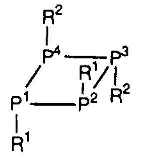
The UV spectra of monocyclophosphanes $(PR)_n$ with n = 3–5[32,45,111] depend on the size of the ring. In earlier

Table VI. ^{31}P-NMR Parameters of the Cyclotetraphosphanes $(PR^1)(PR^2)_3$



R^1	R^2	δ_1	$\delta_{2,4}$	δ_3	$J_{1,2/1,4}$, Hz	$J_{2,3/3,4}$, Hz	$J_{1,3}$, Hz	ref(s)
Pr^i	Bu^t	−77.9	−52.3	−53.8	−138.5	−145.5	+14.8	54
Bu^t	Ph	−11.3	−68.3	−52.7	−126.6	−114.9	+78.8	53
Br	Bu^t	+73.0	−12.9	−59.8	−196.5	−154.9	+38.2	48
Bu^t	SiMe$_3$	−26	−168	−221	−96	−49	15	64
SiMe$_3$	Bu^t	−200	−66	−15	−108	−146	9	67
H	Bu^t	−182	−74	−19	−93	−137	19	67, 148
Li	Bu^t	−212	−54	+9	−192	−164	6	67

Table VII. ^{31}P-NMR Parameters of the Cyclotetraphosphanes $(PR^1)_2(PR^2)_2$



R^1	R^2	$\delta_{1,2}$	$\delta_{3,4}$	$J_{1,2}$, Hz	$J_{1,4/2,3}$, Hz	$J_{3,4}$, Hz	$J_{1,3/2,4}$, Hz	ref
Pr^i	Bu^t	−73.1	−48.3	−128.5	−135.5	−142.2	+15.0	54
Bu^t	SiMe$_3$	−23.5	−212.5	−141	−98	−54	+8	63

publications,[32,111] the intense UV absorptions were interpreted in terms of an extensive delocalization of the free electron pairs on phosphorus in the free d orbitals of neighboring phosphorus atoms. However, on the basis of UV photoelectron spectroscopic investigations, the existence of significant conjugation effects in cyclophosphanes seems to be doubtful since the average ionization energies of the free electron pairs of phosphorus in tertiary phosphanes, diphosphanes, and monocyclophosphanes are very similar.[112,113]

PE spectroscopy also represents a useful method for determining the ring size of cyclophosphanes in the gas phase. Detailed PE spectroscopic investigations in combination with model calculations have provided information on the electronic structures of cyclotriphosphanes and heterocyclic, three-membered ring compounds of phosphorus.[114,115]

The ESR spectra of γ-irradiated single crystals of $(PHex^c)_4$ reveal the formation of oriented radicals as a result of the cleavage of a cyclohexyl group.[116]

The IR spectra of various monocyclophosphanes have been reported.[32,34,39,72,117-119] A symmetrical stretching vibration of the P_n ring between 390 and 425 cm^{-1} and a corresponding asymmetrical vibration between 465 and 490 cm^{-1} were observed in the Raman spectra of alkyl-substituted compounds.[117,120] The vibrational spectra of the phenyl compounds $(PPh)_5$ and $(PPh)_6$ as well as their perdeuterated derivatives have also been investigated.[121]

4. Electrochemical Properties

On electrochemical reduction of $(PPh)_5$, two electrons are transferred to the five-membered ring; this is followed by a rapid ring degradation.[122]

The electrochemical oxidation of the cyclotetraphosphanes $(PR)_4$ (R = NPr^i_2, $N(SiMe_3)_2$, Bu^t) occurs in two steps.[123] In the first step, a stable, violet-colored radical cation $(PR)_4^{\bullet+}$ is formed; this reaction is reversible. On further oxidation of the amino-substituted compounds, the corresponding dications $(PNR_2)_4^{2+}$ are formed which, in contrast to the stable S_4^{2+} ion,[124] undergo rapid rearrangement to the diaminophosphenium cations $^{\cdot}P(NR_2)_2^+$ and white phosphorus. These subsequent reactions take place under cyclovoltammetric conditions even at −100 °C. In comparison to the NR_2-substituted cyclotetraphosphanes, the *tert*-butyl compound is considerably more resistent to oxidization.

5. Theoretical Studies

In the last 10 years a number of different calculations on the molecular and electronic structures of the parent compounds $(PH)_n$ with $n = 3$–6 have been performed.[125-127] One unanimous result is that the P_5 ring in $(PH)_5$ exhibits the highest relative stability. The calculated strain energies of $(PH)_3$ and $(PH)_4$ are 6.7 and 4.3 kcal mol^{-1}, respectively,[127] and are thus markedly lower than those of the corresponding carbocyclic compounds $(CH_2)_3$ and $(CH_2)_4$ (respective strain energies of ca. 27 kcal mol^{-1} each).[130,131] The strain energies

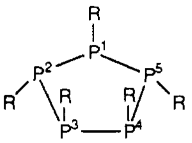
$$^{3}/_{5}(PMe)_5 \rightleftharpoons (PMe)_3 \qquad \Delta H^\circ = 7.8 \pm 0.2\ \text{kcal mol}^{-1}$$

$$^{4}/_{5}(PMe)_5 \rightleftharpoons (PMe)_4 \qquad \Delta H^\circ = 6.0 \pm 0.3\ \text{kcal mol}^{-1}$$

are comparable with the experimentally determined enthalpies of reaction for the ring transformations on the assumptions that the five-membered ring in $(PMe)_5$ is free of ring strain and that no steric interactions between the substituents are present.[101] Accordingly, bond-angle deformations at trivalent phosphorus result, in general, in an appreciably lower strain energy than those at carbon. In the case of $(PH)_3$ a three-center shared electron number (SEN)[132,133] of 0.2 was found for the P_3 ring;[127] this is an indication for the presence of stabilizing multibonding effects similar to those in the P_4 molecule.[134] About one-third of the ring strain in $(PH)_3$ can be attributed to next neighbor interactions as a consequence of the repulsion between the free electron pairs of the *cis*-configurated P atoms.[127] This interaction is also reflected in the structural data for the triorganocyclotriphosphanes that have been analyzed by X-ray crystallography to date. The distance between P atoms with *cis*-oriented substituents, or free electron pairs, is always about 0.02 Å longer than between *trans*-configurated P atoms (see also section II.C.1). The fact that the three-membered phosphorus ring is a relatively stable structural unit is also revealed by the calculated bond length[127] of 2.209 Å between *trans*-configurated P atoms in $(PH)_3$; this value is in the range for normal P–P single bonds (2.21 Å).[135] The barrier to inversion for *one* P atom in $(PH)_3$ is smaller than that in PH_3 and is further lowered considerably by the substitution of the hydrogen atom at the P atom in question by a CH_3 or an SiH_3 group.[136]

For the ground-state structure of $(PH)_4$ an almost planar P_4 ring with an *all-trans* arrangement of the hydrogen atoms or free electron pairs, respectively, at the P atoms (D_{2d} symmetry) was calculated.[125,127,137] The ring strain of 4.3 kcal mol^{-1} may not be neglected and can be attributed to repulsion between parallel P–P bonds separated by the normal single bond dis-

Table VIII. ^{31}P-NMR Parameters of the Cyclopentaphosphanes $(PR)_5$



R	δ_1	$\delta_{2,5}$	$\delta_{3,4}$	$J_{1,2/1,5}$, Hz	$J_{1,3/1,4}$, Hz	$J_{2,5}$, Hz	$J_{2,4/3,5}$, Hz	$J_{2,3/4,5}$, Hz	$J_{3,4}$, Hz	ref
H	−9.9	−31.7	−36.4	−219.4	+31.6	+44.3	+27.5	−220.6	−234.6	9
Me	+16.9	+16.3	+14.6	−248.6	+23.3	−3.6	−8.1	−236.4	−310.3	105
CF_3	+7.5	+10.0	−1.1	−214.5	+36.9	+0.8	−5.3	−223.3	−343.2	106
Et	+19.8	+14.5	+13.9	−260.0	+22.5	−4.0	−9.1	−245.2	−318.1	110

tance.[127,134] The presence of substituents with large spatial requirements and larger group electronegativities favor a folding of the P_4 ring. The diversity of the conformations of the cyclotetraphosphanes $(PR)_4$ determined by X-ray crystallography to date (see Table II) is thus the result of a combination of steric and electronic effects.[129,137]

According to contemporary calculations, the five-membered ring in $(PH)_5$ has either a somewhat distorted envelope form (C_1 symmetry)[125] or a symmetrical envelope conformation (C_s symmetry).[127] It possesses a larger flexibility than the P_3 and P_4 rings. The stability of $(PH)_5$ is not only larger than that of $(PH)_3$ and $(PH)_4$ but also larger than that of P_2H_4 and P_3H_5.[127] It is thus not surprising that the thermolysis of diphosphane preferentially gives rise to $(PH)_5$ and polycyclic phosphanes P_nH_m ($m < n$) containing five-membered ring elements in their structure and to a much lesser extent to higher homologues of the open-chain phosphanes P_nH_{n+2}.[9,11]

The predicted stability of $(PH)_6$ in the chair conformation analogous to cyclohexane is somewhat lower than that of $(PH)_5$ but larger than that of $(PH)_4$;[125] this is in accord with the observed conversion of $(PPh)_6$ into $(PPh)_5$ on warming.[138]

D. Chemical Properties

Earlier results on the chemical properties of the monocyclophosphanes $(PR)_n$ (n = 4, 5) known at that time are summarized in the reviews by Haiduc[5] and Maier.[6] More recent investigations have concerned above all the cyclotriphosphanes $(PR)_3$ as well as ring transformation and ring degradation reactions. With a few exceptions, which will be discussed in section D.1, reactions of monocyclophosphanes lead, at least temporarily, to cleavage of the P_n ring.

1. Reactions with Retention of Ring Size

Monocyclic organophosphanes $(PR)_n$ (n = 3–5) are, in general, readily oxidized by atmospheric oxygen. In principle, two primary steps have to be taken into consideration in this process: either the oxygen reacts with insertion into individual P–P bonds such as in the formation of P_4O_6 from P_4 or by exocyclic addition onto the intact P_n skeleton.

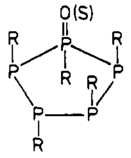
Corresponding investigations have shown that the alkyl-substituted compounds $(PBu^t)_4$, $(PMe)_5$, and $(PEt)_5$ react with a less than equivalent amount of dry atmospheric oxygen at room temperature to furnish cyclophosphane monoxides smoothly.[139,140]

Sulfur reacts with $(PR)_5$ under the same conditions to yield the monosulfides $(PMe)_5S$ (**11a**) and $(PEt)_5S$ (**11b**),[141] while the reactions with $(PHex^c)_4$ and $(PBu^t)_4$ proceed under modified conditions to furnish the monosulfides $(PHex^c)_4S$ (**12a**)[182] and $(PBu^t)_4S$ (**12b**).[142]

$$2(PBu^t)_4 + O_2 \xrightarrow[C_6H_6]{20\ °C} \underset{\textbf{9}}{2(PBu^t)_4O} \qquad (22)$$

$$2(PR)_5 + O_2 \xrightarrow[C_6H_6]{20\ °C} \underset{\substack{\textbf{10a}:\ R = Me\\ \textbf{b}:\ R = Et}}{2(PR)_5O} \qquad (23)$$

IR and NMR spectroscopic investigations as well as an X-ray crystallographic analysis of **12b** have demonstrated that the oxygen and sulfur atoms take up exocyclic positions on the P_n skeleton of the parent compound. The spatial arrangements of the four-membered ring compounds **9** and **12** are unambiguous as a result of the *trans*-oriented organic groups whereas, in the case of the five-membered ring compounds **10** and **11** and on the assumption that only *one cis* arrangement between adjacent organic groups is present, three configurational isomers are possible in each case.



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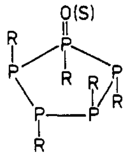

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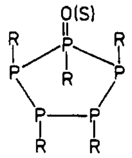
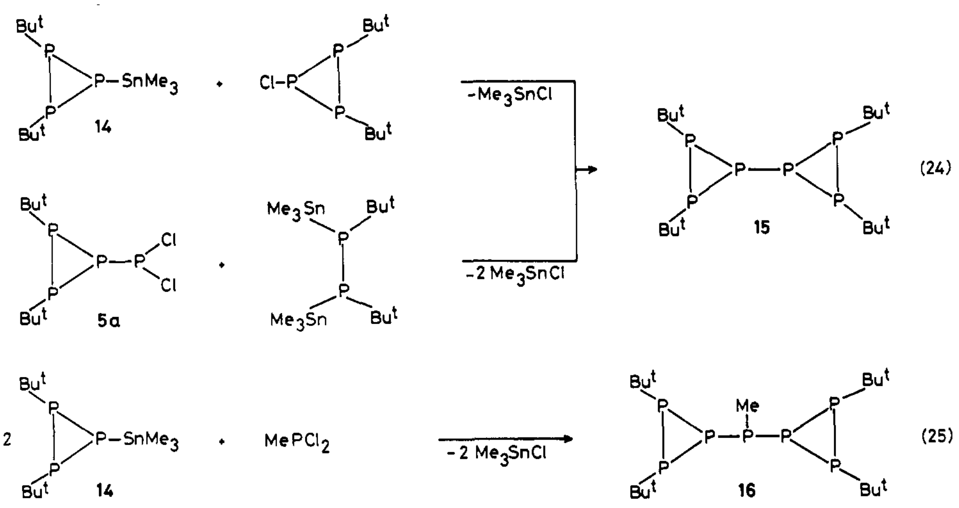


C

In the case of the monoxide **10b**, the two unsymmetrical molecules **A** and **B** are formed in a ratio of approximately 1:1.[139] For the monosulfide **11b**, in contrast, the isomer **B** in which the sulfur has only *one cis* relationship to an adjacent ethyl group is formed exclusively as a result of steric factors.[141] Thus, the cyclophosphane skeleton initially remains intact upon attack by oxygen or sulfur irrespective of the size of the P_n ring and the spatial demands of the substituents R. The formation of more highly oxidized or sulfur-richer products only takes place on continuation of the respective reaction.

Mixed-substituted cyclopentaphosphanes of the type $P_5(R^1)_{5-n}(R^2)_n$ (n = 1–4) are formed within days or weeks by the reaction of $(PPh)_5$ with $(PR)_5$ (R = Me, Et) in tetrahydrofuran at room temperature in the dark.[143] In view of the mild conditions, a radical reaction course via free phosphanediyls (phosphinidenes) :P–R is extremely improbable. The formation of the compounds $P_5Ph_{5-n}Me(Et)_n$ by way of an intermolecular reaction under participation of $\rangle\bar{P}{-}\bar{P}\langle$ groups either by a four-center mechanism or through three-membered

Scheme I

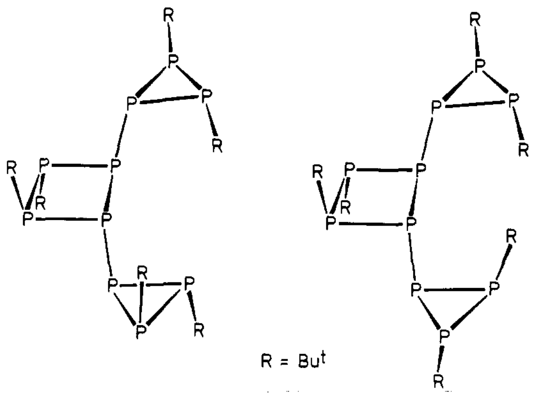


ring intermediates containing a pentavalent phosphorus atom (phosphorane mechanism) is much more reasonable.

Monocyclophosphanes with bulky organic substituents and single functional groups are suitable starting materials for substitution reactions with retention of the P_n ring size. Accordingly, the cyclotriphosphanes $(PBu^t)_2PSiMe_3$ (13) and $(PBu^t)_2PSnMe_3$ (14) were prepared from the phosphide $KP(PBu^t)_2$[87] by reaction with chlorotrimethylsilane and trimethyltin chloride, respectively.[87] The latter product 14 proved to be an excellent starting material for further elaboration of the chemistry of the P_3 ring.

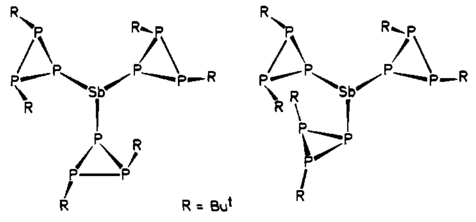
For example, compound 14 reacts with PCl_3 or Bu^tPX_2 (X = Cl, I) according to eqs 20 or 21, respectively, to furnish the phosphino-substituted cyclotriphosphanes **5a–c**.[87] Condensation of 14 with another functionally substituted cyclotriphosphane yields the 1,1′-bicyclotriphosphane 15 which is stable at room temperature under protection from air. An alternative preparation of 15 is the [1 + 2]-cyclocondensation of the phosphino-substituted cyclotriphosphane **5a** with a 1,2-difunctional diphosphane[144] (Scheme I). When 14 is allowed to react with dichloroorganophosphanes such as $MePCl_2$ in a molar ratio of 2:1, two P_3 ring units are linked together through an isolated P atom.[145] The bis(cyclotriphosphanyl)methylphosphane 16 can be prepared in the pure state at low temperatures but, as a consequence of its relatively "open" skeletal structure, decomposes via ring rearrangement and disproportionation at above −30 °C.

The reaction of 14 with PCl_3 in a molar ratio of 3:1 gives rise to a condensation product with the expected composition $P_{10}Bu^t_6$. However, this is not the tris(cyclotriphosphanyl)phosphane $[(PBu^t)_2P]_3P$; instead the cyclotetraphosphane with two adjacent cyclotriphosphanyl substituents, 17, is formed since the isolated P atom is incorporated into one of the three-membered rings for steric reasons.[146] Compound 17 is obtained as a mixture of the two configurational isomers **A** (C_2 symmetry) and **B**, which differ in the mutual orientation of the respective *trans*-oriented *tert*-butyl groups on the two three-membered rings.



A 17 B

In order to link three P_3 ring skeletons to *one* atom, the central atom must apparently be larger than phosphorus. Indeed, the analogous reaction of 14 with $SbCl_3$ does proceed smoothly to furnish the tris(cyclotriphosphanyl)stibane 18 which also exists as two configurational isomers **A** (C_3 symmetry) and **B**.[147] The compound can be prepared in the pure state at lower temperatures but decomposes at above −30 °C or on exposure to daylight to furnish 15, phosphorus–antimony polycyclic compounds, and elemental antimony.



A 18 B

Protolysis of the partially silylated cyclotriphosphane 13 with methanol results in the formation of the corresponding hydrocyclotriphosphane $(PBu^t)_2PH$.[9,148] The four-membered ring compound $(PBu^t)_3PH$ can be prepared analogously from the cyclotetraphosphane $(PBu^t)_3PSiMe_3$ (19).[67]

The reaction of alkali metals or organolithium compounds with monocyclic organophosphanes is generally accompanied by P–P bond cleavage and the formation of open-chain phosphides[6] (see also section II.D.3). When the P_n ring is more or less sterically shielded by *tert*-butyl substituents, the ring cleavage reaction may be partially or even completely suppressed.

Thus, the reaction of $(PBu^t)_3$ with potassium in a molar ratio of PBu^t:K = 1:0.44 yields, in addition to

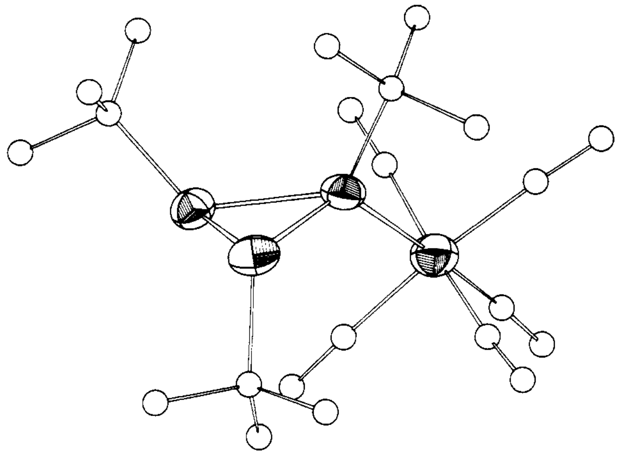
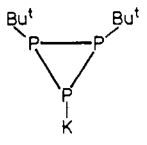


Figure 3. Structure of one of the two independent molecules of $(PBu^t)_3Cr(CO)_5$ (without hydrogen atoms) in the crystal.[150]

$K(Bu^t)PP(Bu^t)_2$ and other *tert*-butyl phosphides, the monometalated cyclotriphosphane **20** which is a suitable starting material for other functionalized cyclotriphosphanes such as **13** and **14**.[87] The cyclic tetraphosphide **21** can be obtained from the reaction of the partially silylated cyclotetraphosphane **19** with butyllithium by elimination of Bu^nSiMe_3.[67]



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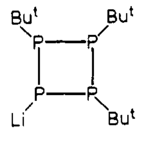


21

In general, compounds with trivalent phosphorus atoms serve as excellent ligands in complex chemistry. Organocyclotriphosphanes accordingly react with metal carbonyls by way of ligand exchange reactions to furnish mixed mono- and dinuclear carbonyl(cyclotriphosphane)–metal complexes.[149]

$$(PR)_3 + M(CO)_5THF \xrightarrow[-THF]{} (PR)_3M(CO)_5 \quad (26)$$

$$R = Pr^i, Bu^t;\ M = Cr, W$$

$$(PR)_3 + 2M(CO)_5THF \xrightarrow[-2THF]{} (PR)_3[M(CO)_5]_2 \quad (27)$$

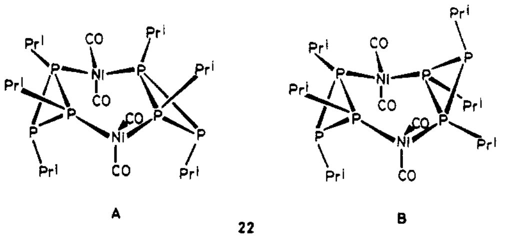
$$R = Pr^i;\ M = Cr$$

Both series of compounds are remarkably stable toward thermal stress and oxidation. The structures were deduced from the $^{31}P\{^1H\}$-NMR spectra[149] and, in the cases of $(PBu^t)_3Cr(CO)_5$[150] (Figure 3) and $(PPr^i)_3W(CO)_5$,[151] also by single-crystal X-ray analyses. The first $M(CO)_5$ group is arranged in a *trans* position to the *cis*-oriented organic substituents and the second $M(CO)_5$ group is positioned *trans* to the first. The cyclotriphosphane ligand serves—in contrast to the complex $(PPh)_3[Mn(CO)_2Cp]_3$[152] obtained by a different route—as a 2- or 4-electron donor. The π-acceptor capability of $(PR)_3$ is similar to that of PPh_3.

A different type of binuclear complex in which the P_3 rings are linked as four-electron ligands with the ML_n fragments to form a six-membered P_4M_2 metallacycle is obtained from the reaction of $(PPr^i)_3$ with $Ni(CO)_4$.[153]

$$2(PPr^i)_3 + 2Ni(CO)_4 \xrightarrow[-4CO]{} \underset{\mathbf{22}}{(CO)_2Ni(\mu\text{-}P_3Pr^i_3)_2Ni(CO)_2} \quad (28)$$

The formation of **22** proceeds through the mononuclear complex $(PPr^i)_3Ni(CO)_3$ which can be detected in the ^{31}P-NMR spectrum at the beginning of the reaction. The complex **22** is formed as a mixture of the isomers **A** and **B** that differ in the mutual orientations of the three-membered phosphorus rings. Isomer **A** rearranges in solution above 0 °C to **B** until an approximately 1:1 equilibrium has been achieved.[154]



A 22 B

2. Rearrangements to Rings of Different Sizes

Triorganocyclotriphosphanes are only metastable in comparison with the corresponding cyclophosphanes where $n > 3$. Thus, they undergo rearrangement to the respective, more stable four- or five-membered ring products[156] at varying rates—depending on the substituents R and the polarity of the solvent.[28,51,101] The reaction course does not involve a radical process via free phosphanediyls (phosphinidines) :P–R but most probably, in analogy to the formation of mixed-substituted cyclopentaphosphanes, an intermolecular reaction takes place following a four-center or phosphorane mechanism (see section II.D.1).

The first indications for a ring rearrangement reaction of cyclophosphanes were obtained in the $(PPh)_n$ system, namely the thermal conversion of $(PPh)_6$ into $(PPh)_5$[138] and the oligomerization of $(PPh)_3$ in solution at room temperature to give $(PPh)_5$ via $(PPh)_4$.[28,51] Considerable confusion about the ring sizes and their rearrangement reactions existed for some time in the case of the C_2F_5-substituted cyclophosphanes before their unambiguous clarification.[29,45,157,158]

As shown by ^{31}P-NMR spectroscopy, the cyclotriphosphanes $(PR)_3$ (R = Me, Et, Ph) exist at higher temperatures in a thermodynamic equilibrium with the corresponding cyclotetraphosphanes and cyclopentaphosphanes; in the case of R = Ph, $(PPh)_6$ is also formed.[101] From the temperature dependence of the equilibrium constants, the enthalpies of reaction given in section II.C.5 were determined in the case of the $(PMe)_n$ system for the rearrangements five-membered ring → three-membered ring and five-membered ring → four-membered ring. Although cyclotriphosphanes with small substituents R, such as $(PMe)_3$ or $(PH)_3$, exhibit relatively low strain energies because of the absence of steric interactions, their rates of oligomerization are particularly high. The reason for this is the unsatisfactory steric shielding of the P_3 ring skeleton. In contrast, cyclotriphosphanes with bulky substituents R are often remarkably resistant to oligomerization reactions in spite of their higher strain energies. This

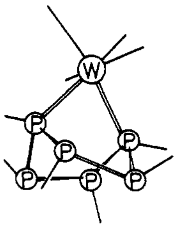


Figure 4. Coordination sphere in the complex $(PMe)_6W(CO)_4$.[164]

is due to the well-known kinetic stabilization of small ring compounds by voluminous substituents.[101,159]

Changes in ring size also occur in metalation reactions of organocyclophosphanes. Hence, in the reaction of $(PBu^t)_4$ with potassium, the monometalated cyclotriphosphane $KP(PBu^t)_2$ (**20**) and the cyclic pentaphosphide $KP(PBu^t)_4$ are formed in addition to the open-chain phosphides $K(PBu^t)_nK$ (n = 2–4, see section II.D.3).[87,160] On the other hand, the triphosphide $K_2(PPh)_3$—obtained from $(PPh)_5$ and potassium—does not exist as a cyclic dianion as originally assumed[161] but rather has an open-chain phosphorus skeleton.[28,162,163]

The cyclopentaphosphane $(PMe)_5$ reacts with metal hexacarbonyls at higher temperatures and long reaction times via ring expansion to give the carbonyl(cyclophosphane)–metal complexes $(PMe)_6M(CO)_4$ (M = Cr, W) and $(PMe)_9M_2(CO)_6$ (M = Cr, Mo, W).[164] While the dinuclear complexes are assumed to have structures similar to the analogous arsenic compound,[165] X-ray crystallographic analysis has shown that the $(PMe)_6$ ligand in the mononuclear complexes has the boat configuration (see Figure 4).

3. Reactions with Ring Cleavage

Nucleophilic attack at the P–P bond in monocyclophosphanes occurs with numerous reagents such as alkali metals, organoalkali metal derivatives, alkali metal phosphides, amides, and cyanides. The P_n ring is cleaved and then degraded stepwise in all cases; various intermediates can be isolated from some of these reactions. The action of halogens, alkyl halides, phosphorus–halogen compounds, sulfur, and selenium lead mostly to an at least temporary opening of the phosphorus ring. In addition to the previously reviewed work in this field,[6] the results of pertinent investigations carried out in the last two decades will be discussed here.

The reaction of $(PBu^t)_4$ with potassium in boiling tetrahydrofuran furnishes not only the open-chain tetraphosphide $K(PBu^t)_4K$,[43] but also involves further chain degradation steps to give the tri- and diphosphides $K(PBu^t)_nK$ (n = 3, 2).[160] As a consequence of its poor solubility, $K(Bu^t)PP(Bu^t)K$ can easily be separated from the phosphide mixture and serves as an excellent starting material for the synthesis of mixed-substituted cyclotriphosphanes $(PBu^t)_2PR$ and three-membered heterocyclic systems of the type $(PBu^t)_2E$ (E = heteroatom).[7,9]

The combined reaction of the cyclopentaphosphanes $(PR)_5$ (R = Me, Et) with magnesium and PCl_3 results in the formation of polycyclic phosphanes (see section V.B).[9,11,159,166]

The electrochemical reduction of monocyclophosphanes involves transfer of two electrons to the respective P_n ring and, in all cases, a subsequent, rapid ring degradation.[122]

Various open-chain monolithium phosphides of the type $Li(PEt)_nPh$ (n = 1–5) are formed by the reaction of phenyllithium with a mixture of $(PEt)_5$ and $(PEt)_4$ depending on the molar ratio PEt:LiPh.[167] The degradation of $(PPh)_5$ with LiPh was reinvestigated a few years ago, as were the analogous reactions with $LiBu^n$ and LiMe.[168] The reaction patterns are more or less identical. In the case of $LiNR_2$ (R = Et, Pr^i), the phosphides $Li(PPh)_nNR_2$ (n = 2, 3) are formed[169] and with CN^- the monophosphide $P(Ph)CN^-$ is obtained.[170] The corresponding primary products from the reaction of $(PPh)_5$ with NaCp, $Na(PPh)_nCp$ (n = 1–3), undergo stabilization through shifts of protons of the Cp ring.[168]

Cyclotetraphosphanes with two to four adjacent Me_3Si substituents react with LiR (R = Me, Bu^n) via ring opening and formation of terminal, monolithiated tetraphosphides which subsequently undergo isomerization and disproportionation reactions.[171]

The ring degradation of monocyclophosphanes by stoichiometric amounts of halogens to yield the corresponding dihalo(organo)phosphanes has been known for a long time.[6]

$$(PR)_n + nX_2 \rightarrow nRPX_2 \qquad (29)$$
$$n = 3\text{–}5;\ X = Cl, Br, I$$

On iodination or bromination of $(PPh)_5$ in a molar ratio of 2.5:1, it is possible to isolate the intermediates $I(Ph)PP(Ph)I$[172] and $Br(Ph)PP(Ph)Br$, respectively.[173] The latter compound is also accessible from the reaction of $(PPh)_5$ with $PhPBr_2$.[173]

$$(PPh)_5 + 5PhPBr_2 \rightarrow 5(PPh)_2Br_2 \qquad (30)$$

The mild, halogenating ring opening of the cyclotriphosphane $(PBu^t)_3$ has proved to be especially suitable for the preparation of the remarkably stable α,ω-dihalo-substituted, open-chain phosphanes.[48,174] The resultant tri- and diphosphanes are versatile building blocks for novel open-chain and cyclic *tert*-butylphosphanes.

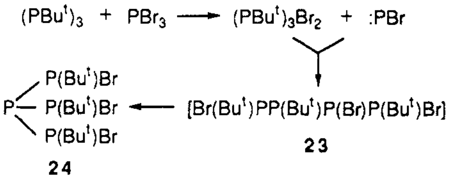
$$(PBu^t)_3 + X_2 \rightarrow X(Bu^t)PP(Bu^t)P(Bu^t)X \qquad (31)$$
$$X = Br, I$$

$$(PBu^t)_3 + PCl_5 \rightarrow Cl(Bu^t)PP(Bu^t)P(Bu^t)Cl + PCl_3 \qquad (32)$$

$$(PBu^t)_3 + 2PCl_5 \rightarrow Cl(Bu^t)PP(Bu^t)Cl + Bu^tPCl_2 + 2PCl_3 \qquad (33)$$

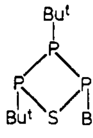
When PBr_3 is used as the halogenating agent for ring opening, a subsequent reaction involving insertion of the intermediarily formed bromophosphanediyl takes place. The thus formed tetraphosphane **23** is, as expected, unstable and rearranges to the isotetraphosphane **24**.[175]

The reaction of $(PCF_3)_4$ with fluoroalkyl iodides R_fI has been investigated in detail.[176–181] It involves ring cleavage and complete chain degradation to furnish $CF_3(R_f)PI$.



(34)

The action of sulfur on monocyclophosphanes does not only result in cyclophosphane monosulfides with exocyclic bonded sulfur (section II.D.1). On the contrary, an extensive insertion of the sulfur into the P_n ring with formation of phosphorus–sulfur heterocycles takes place. This process presumably proceeds through an intermediate opening of the phosphorus ring. Of the various compounds formed depending on the PR:S ratio and further to the earlier results,[6] some additional products have now been structurally elucidated. Moreover, pertinent investigations on the reactivity of monocyclophosphanes toward selenium have been performed.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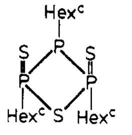
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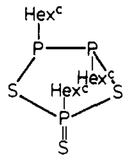
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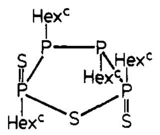
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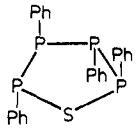
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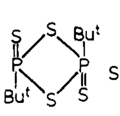
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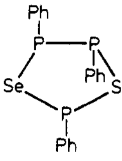
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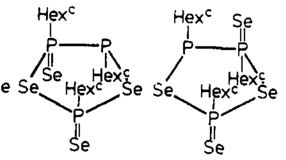

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Under suitable conditions, the reaction of $(PBu^t)_3$ with sulfur gives rise to $(PBu^t)_3S$ (**25**) which has a heterocyclic, four-membered ring structure.[183] The corresponding selenium derivative $(PBu^t)_3Se$ has an analogous structure.[183] The reaction of $(PHex^c)_3$ with sulfur under appropriate conditions gives rise to two constitutionally isomeric compounds **26** and **27** with the composition $(PHex^cS)_3$.[182,183] The compound **26** has the same ring skeleton as **25** but with two additional, exocyclic sulfur atoms while **27** has the same structure as the long-known[6] phenyl derivative $(PPhS)_3$; the structure of the latter, however, was only recently elucidated unambiguously.[184] The reaction of $(PHex^c)_4$ with sulfur gives rise to products with intact P_4 ring skeletons as well as the relatively unstable compound $(PHex^c)_4S_3$ (**28**) with a heterocyclic P_4S ring and two exocyclic sulfur atoms.[182] $(PMe)_4Se_3$, recently obtained from $(PMe)_5$ and selenium, has an analogous structure.[185] A compound, $(PPh)_4S$ (**29**),[6] with the same five-membered ring skeleton as **28** but with exclusively λ^3-phosphorus atoms was prepared earlier from $(PPh)_5$ and sulfur but its structure was only recently determined unequivocally by ^{31}P-NMR spectroscopy.[186] The corresponding selenium compound $(PPh)_4Se$ has an analogous constitution.[187,188] Similar to $(PR)_5$ (R = Ph, Me) and in contradiction to previous results,[43] $(PBu^t)_4$ also reacts with excess sulfur through insertion into all P–P bonds to form the dimer of dithiophosphonic acid anhydride $(PBu^tS_2)_2$ (**30**).[160]

Reactions with selenium do not always give rise to products corresponding to those obtained with sulfur. Thus, $(PPh)_5$ also furnishes the compound $(PPh)_3Se_2$ (**31**)[187-189] with a five-membered ring skeleton like that of **27** but with exclusively λ^3-phosphorus; the sulfur analogue is still unknown. And, in the case of the reaction of $(PHex^c)_3$ with excess selenium, the compound $(PHex^c)_3Se_4$ (**32**) is obtained as a mixture of the isomers **A** and **B**,[183] presumably by way of the analogue of **27**.

The combined action of sulfur and alcohols on cyclopentaphosphanes was claimed in a patent as a method for the preparation of the dithiophosphonic esters RP(S)(OR′)SH.[190]

The well-known cleavage of cyclophosphanes by tertiary phosphanes[6] has been reinvestigated in detail recently for the case of the reactions of $(PCF_3)_n$ (n = 4, 5) with PMe_3 which give rise to the phosphane–phosphinidine complex Me_3PPCF_3.[191]

On treatment of $(PPh)_5$ with $(CF_3S)_2$ or $(CF_3Se)_2$, ring degradation with insertion of a PPh group into the S–S or Se–Se bond, respectively, occurs.[192]

The action of Me_3SnH on $(PCF_3)_4$ also results in complete degradation of the cyclotetraphosphane.[193]

$$(PCF_3)_4 + 4Me_3SnH \rightarrow$$
$$2Me_3SnP(H)CF_3 + (Me_3Sn)_2PCF_3 + H_2PCF_3 \quad (35)$$

Carbon tetrachloride reacts with $(PPh)_5$ and $(PHex^c)_4$ to furnish $PhP(Cl)CCl_3$ and $Cl(Hex^c)PP(Hex^c)CCl_3$, respectively. The tris(amino)phosphonium salts $[RP(NR^1R^2)_3]Cl$ are formed when a primary or secondary amine is added to the system $(PR)_n/CCl_4$.[194]

An equilibrium mixture in which 1,2-diphenyldiphosphane can be detected by NMR spectroscopy is obtained when $(PPh)_5$ and $PhPH_2$ are mixed.[195]

$$(PPh)_5 + 5PhPH_2 \rightleftharpoons 5H(Ph)PP(Ph)H \quad (36)$$

Under pyrolysis conditions in the mass spectrometer, heating of $(PPh)_5$ up to 400 °C gives rise to free phenylphosphanediyl (phenylphosphinidine, :PPh) which can be trapped by suitable reaction partners.[196-198]

A gravimetric method for the analysis of $(PPh)_5$ involves cleavage of this compound by $TeCl_4$ and separation of the stoichiometric amount of tellurium.[199]

$$(PPh)_5 + 5TeCl_4 \rightarrow 5Te + 5PhPCl_4 \quad (37)$$

III. Monocyclic Phosphorus Anions with Coordination Number ≤ 3

A. Anions with Coordination Number 3

A monocyclic anion with exclusively hydrogen atoms as substituents is the tetrahydrocyclopentaphosphide ion which is present in the compound $LiH_4P_5{\cdot}n$ solvent (**33**). This product is formed by metalation of P_2H_4 at −78 °C with either $LiBu^n$ or $LiPH_2$ in tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) (see section IV).[11,200] Upon suitable performance of the reaction, compound **33** can be isolated at low temperature as a lemon-yellow solid that decomposes above −30 °C. The structure as the monolithium salt of $(PH)_5$ was confirmed by a complete analysis of the $^{31}P\{^1H\}$-NMR spectrum.[201]

Organo-substituted, monocyclic anions are formed in metalation reactions of organocyclophosphanes in which the P_n ring is shielded to a large extent by bulky substituents so that the cleavage reaction is suppressed. On formation of the respective cyclic phosphide, the ring size may be retained or changed (see section II.D). Thus, the cyclic triphosphide $KP(PBu^t)_2$ (**20**) is formed together with other, open-chain products by treatment of $(PBu^t)_3$ with potassium.[87] The same compound **20** can also be obtained from the corresponding reaction of $(PBu^t)_4$ in which, above all, the cyclic pentaphosphide $KP(PBu^t)_4$ as well as the cyclotetraphosphide $KP(PBu^t)_3$ are additionally formed.[87]

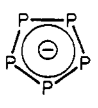
The reactions of organolithium derivatives with partially silylated cyclophosphanes carrying bulky organic groups provide another access to organo-substituted, monocyclic phosphides. Thus, the remarkably stable cyclotetraphosphide **21** was prepared from the cyclotetraphosphane **19** (see section II.D.1).[67] Compound **21** and the lithium cyclotriphosphide $LiP(PBu^t)_2$, corresponding to the potassium salt **20**, are the main products of the reaction of white phosphorus with $LiBu^t$ (molar ratio 1:2) at room temperature.[66]

The formation of the cyclic pentaphosphide $KP(PPh)_4$ has been observed in the reaction of white phosphorus with the open-chain phosphide $K(PPh)_4K$.[202]

B. Anions with Lower Coordination Numbers

Alkali metal phosphides of the composition $M^I_4P_6$ (M^I = K,[203] Rb,[204,205] Cs[205]) are accessible from reactions of the corresponding metal with red phosphorus at higher temperatures and, according to crystal structure analyses, contain isolated P_6 rings. These rings are planar or only slightly corrugated and possess D_{6h} symmetry. With regard to phosphorus, each P atom has the coordination number 2 and is additionally surrounded by six M^I atoms in a trigonal prism. The P–P bond lengths are distinctly shorter (2.15 Å) than normal single bonds (2.21 Å[135]) which is indicative of some multiple-bond character (10π-electron system).[13,203] The planar structure of the P_6^{4-} ion has also been the subject of extended Hückel MO calculations.[206] The main product of the reaction of Me_3SnCl with K_4P_6 in DME is the tricyclic phosphane $P_7(SnMe_3)_3$ (see section V) together with $P(SnMe_3)_3$.[203] The singlet at $\delta = +473$ in the ^{31}P-NMR spectrum of the respective reaction solution does not correspond to the P_6^{4-} ion—as originally assumed[203,207]—but belongs to the pentaphosphacyclopentadienide ion **34** (see below) formed therefrom.[11,208]

The monocyclic anions **34–36** containing phosphorus atoms with the coordination number 2 are formed by the nucleophilic cleavage of white phosphorus with sodium (P/Na = 3:1) in boiling diethylene glycol dimethyl ether (diglyme).[208] Further polyphosphides (above all Na_2P_{16}, Na_3P_{21}, Na_3P_{19}; see section IV) are additionally formed.



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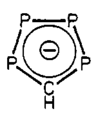

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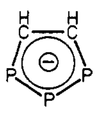


36

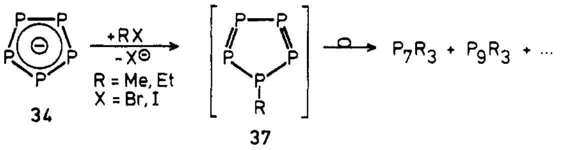
The particularly interesting species, the pentaphosphacyclopentadienide ion (cyclo-P_5^-; **34**) is also accessible in tetrahydrofuran from the reaction of white phosphorus with $LiPH_2$[208] as well as with, in the presence of 18-crown-6, sodium[209] or $NaPH_2$.[210] An especially convenient approach to **34** is the degradation of red phosphorus with KPH_2 (P/KPH_2 = 1.9:1) in boiling dimethylformamide (DMF) which, under appropriate conditions, provides almost exclusively the polyphosphides KP_5 and K_2HP_7.[211] After separation of by products, pure solutions of M^IP_5 in THF (M^I = Li[208]), in THF/18-crown-6 (M^I = Na[209,210]), or in DMF (M^I = K[211]), respectively, are obtained. Upon concentration of the 10^{-2} to 10^{-3} molar solutions or upon addition of less polar solvents, increased decomposition occurs with the preferred formation of $M^I_2P_{16}$ and $M^I_3P_{21}$. The KP_5/DMF solution is stable for several weeks at room temperature under protection from air.

The M^IP_5 solutions are gold-orange to red in color and are extremely sensitive to oxidation. In their ^{31}P-NMR spectra, they exhibit a characteristic low-field singlet at $\delta = +470$; the position of this signal is only slightly dependent on the solvent and the counterion. The composition of the NaP_5/diglyme solution has been substantiated by the analytically determined Na:P ratio of 1:5.[208] Furthermore, **34** can also be observed directly in the negative-ion FAB mass spectra of NaP_5/18-crown-6/THF solutions.[209] The existence of the cyclo-P_5^- ion (6π-electron system) stabilized by mesomerism in analogy to the cyclopentadienide ion was further confirmed by the appearance of the UV spectrum of **34**.[209]

The occurrence of the P_5^- species has up to now only been observed in a negative-ion mass spectrum of red phosphorus at 325 °C[212] and in the sandwich and triple decker complexes $[(\eta^5\text{-}P_5)M(\eta^5\text{-}C_5Me_4R)]$ (M = Fe, Ru; R = Me, Et) and $[(\eta^5\text{-}C_5Me_5Cr)_2(\mu,\eta^5\text{-}P_5)]$, respectively, described by Scherer.[213] The latter compounds were obtained from white phosphorus by cothermolysis with appropriate substrate complexes. The formation of **34** in reactions subsequent to 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 leading to the formation of phosphorus-richer polyphosphides from phosphorus-poorer polyphosphides (see section IV). The fact that **34** is also one of the main products of the nucleophilic cleavage of red phosphorus may be attributed, on the one hand, to the structural features of P_{red}[214] and, on the other hand, to the noteworthy tendency for the formation of the free cyclo-P_5^- ion and its high stability. This stability and the aromatic character of **34** are fully substantiated by theoretical investigations based on MNDO[215] and *ab initio* MO calculations.[216,217]

The chemistry of **34** is characterized both by analogies with and by differences to the chemistry of the $C_5H_5^-$ ion. Thus, **34** reacts with alkyl halides to form, above all, P_7R_3 and P_9R_3. The nonaromatic primary product **37** is apparently so unstable that it rearranges spontaneously into the thermodynamically more favored alkylpolyphosphanes. Dimers of **37** have not been observed.[209]

LiP_5 reacts with LiC_5Me_5 and $FeCl_2$ in a one-pot process to furnish the mixed sandwich complex **38** which was previously prepared by Scherer via cothermolysis of white phosphorus and $[(\eta\text{-}C_5Me_5)Fe(CO)_2]_2$.[218,219]

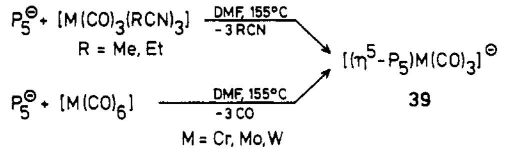


(38)

$$\text{LiP}_5 + \text{LiC}_5\text{Me}_5 + \text{FeCl}_2 \xrightarrow[-2\,\text{LiCl}]{\text{THF}} \underset{\mathbf{38}}{[(\eta^5\text{-P}_5)\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)]} \qquad (39)$$

Attempts to prepare metallocene analogues with two P_5 ligands have all led to high molecular products that are amorphous to X-rays.[220] The formation of such products may be attributed to the additional coordination capacity of the λ^3-phosphorus resulting from the presence of the free electron pair.[221]

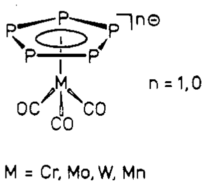
Thermal ligand exchange reactions of the tris(nitrilo)tricarbonyl or hexacarbonyl complexes of chromium, molybdenum, or tungsten with **34** (preferably as KP_5/DMF solutions) have given rise to the corresponding tricarbonyl(pentaphosphacyclopentadienyl)metalate ions **39**.[220] Their formation proceeds through intermediates which have not been characterized but they can be detected by ^{31}P NMR spectroscopy in the first stages of the process, especially at room temperature. The reaction of **34** with bromo(pentacarbonyl)manganese(I) gave rise to the neutral tricarbonyl(pentaphosphacyclopentadienyl)manganese (pentaphosphacymantrene, **40**).[220]



(40)

$$\text{P}_5^{\ominus} + [\text{Mn(CO)}_5\text{Br}] \xrightarrow[-\text{Br}^{\ominus},\,2\,\text{CO}]{\text{DMF, 155}\,^\circ\text{C}} \underset{\mathbf{40}}{[(\eta^5\text{-P}_5)\text{Mn(CO)}_3]} \qquad (41)$$

All spectroscopic findings are in favor of structures analogous to those of the corresponding cyclopentadienyl complexes for **39** and **40**.[220] A singlet in the region characteristic for pentaphosphametallocenes is observed in each of the ^{31}P-NMR spectra;[213] for the metalate ions **39** the position of the signal is practically independent of the counterion. The strongly negative coordination shift as compared to free **34** (between 300 and 365 ppm) is a general and characteristic feature for π-phospha–arene complexes.[222] Since the positions of the $\nu(CO)$ bands are shifted appreciably in the IR spectra in comparison to those of the respective (C_5H_5) complexes (in the case of **39** for M = W, to higher, in the case of **40** to lower wave numbers), **34** and $C_5H_5^-$ apparently possess significantly different donor/acceptor properties.



M = Cr, Mo, W, Mn

The anions **35** and **36** occur solely in the reaction of white phosphorus with sodium in boiling diglyme,[208] thus their formation is the result of a participation of the solvent in the reaction process. Since they cannot be separated either from the polyphosphides formed as main products or from **34**, the structures given for **35** and **36** are based on a complete analysis of the AA′BB′ and AB_2 spin systems, respectively, observed at low field in the $^{31}P\{^1H\}$-NMR spectrum and on the splitting observed under ^1H coupling conditions.[208,223] A constitutional isomer of the ring system **36** exists in the compound lithium 3,5-di(*tert*-butyl)-1,2,4-triphosphacyclopentadienide·3DME.[224] The concomitant, spontaneous formation and remarkable thermal stabilities of **34**–**36** reflect the significant stability of anionic, P-containing five-membered rings with delocalized 6π-electron systems.

IV. Isolated Polycyclic P_n^{m-} and $H_xP_n^{(m-x)-}$ Anions

The syntheses and structural elucidations of metal phosphides and polyphosphides were recently reviewed comprehensively.[13] Thus, only those polyphosphides and hydrogen polyphosphides with isolated polycyclic anions of the types P_n^{m-} and $H_xP_n^{(m-x)-}$ will be discussed in this Section. Selection criteria are that the compounds are closely related to the polycyclic phosphorus hydrides and organophosphanes and that they can be prepared in solution (and not solely by solid phase reactions). The nomenclature used is analogous to that of the phosphanes, i.e. heptaphosphane(5) for P_7H_5, heptaphosphane(3) for P_7H_3. The corresponding anionic derivatives accordingly (even if only formally) have a $P_7(5)$ or a $P_7(3)$ skeleton and thus are unambiguously characterized with regard to their composition and constitution (see also section V).

A. Hydrogen Polyphosphides and Polyphosphides by Metalation of Diphosphane

Diphosphane reacts with *n*-butyllithium or lithium dihydrogen phosphide in THF or DME via disproportionation to furnish trilithium heptaphosphide (**41**) and phosphane as the final products; in the former reaction, *n*-butane is also produced.[225]

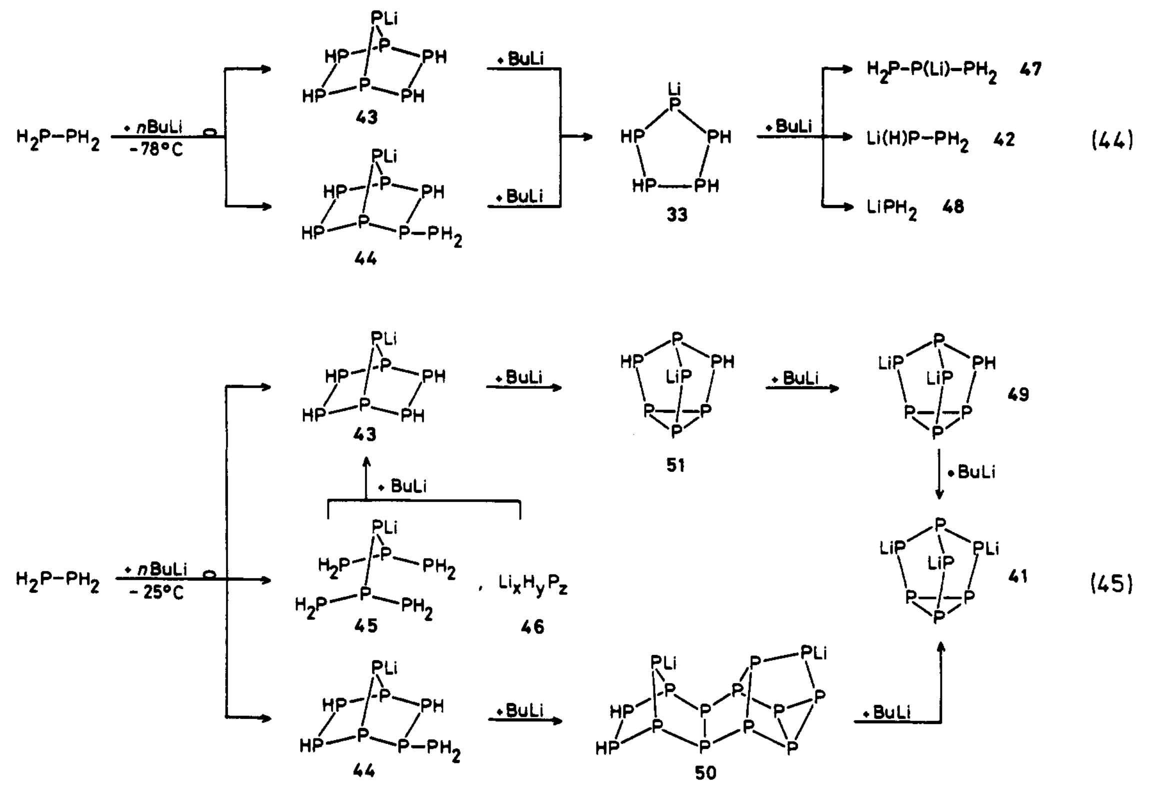
$$9P_2H_4 + 3LiBu^n \xrightarrow[-20\,^\circ C]{THF} \underset{\mathbf{41}}{Li_3P_7} + 11PH_3 + 3Bu^nH \qquad (42)$$

$$9P_2H_4 + 3LiPH_2 \xrightarrow[-20\,^\circ C]{DME} \underset{\mathbf{41}}{Li_3P_7} + 14PH_3 \qquad (43)$$

Recently, several novel metal hydrogen polyphosphides (partially metalated higher phosphanes) have been detected as intermediates and some of them have even been isolated in the pure state at low temperatures.[9,11,200,226–229] On the basis of the formation and degradation of the intermediates—depending on the reaction temperature—the detailed reaction sequences shown in eqs 44 and 45 (Scheme II) can be derived for the reaction of P_2H_4 with $LiBu^n$.

In each case, the primary step is the formation of lithium trihydrogen diphosphide (**42**) which, however, is not stable in the presence of diphosphane. In a series of rapid disproportionation and transmetalation reactions **42** is transformed initially into the highly reactive,

Scheme II



monolithiated, more phosphorus-rich, open-chain phosphanes $LiH_{n+1}P_n$ and then through cyclic compounds to phosphides no longer having sufficient nucleophilicity for attack on diphosphane. Since the reaction sequence temporarily comes to a standstill at this point, these phosphides are the first reaction products to be detected.

$$P_2H_4 + LiBu^n \rightarrow \underset{\textbf{42}}{LiH_3P_2} + Bu^nH \qquad (46)$$

When the metalation reaction is carried out at −78 °C, the major such phosphides are lithium tetrahydrogen heptaphosphide (**43**) and lithium pentahydrogen octaphosphide (**44**) whereas, at −25 °C, two potential precursors of **43**, namely lithium octahydrogen heptaphosphide (**45**) and a not yet identified phosphide **46** are formed additionally. On the whole, a clear tendency for the formation of a $P_7(5)^-$ skeleton analogous to norbornane can be recognized which apparently exhibits a comparatively low nucleophilicity.

The reaction continues only after addition of further metalating reagent. At −78 °C, further **43** is mainly formed at first which, in turn and like **44**, reacts further to give lithium tetrahydrogen cyclopentaphosphide (**33**). This latter product is finally degraded to yield the phosphides **47**, **42**, and **48**. The tricyclic heptaphosphide **41** is not formed at this temperature; however, **33** does disproportionate at above −30 °C to form dilithium hydrogen heptaphosphide (**49**) together with PH_3 and P_2H_4, a reaction that is attributable to the particular stability of the $P_7(3)$ skeleton.

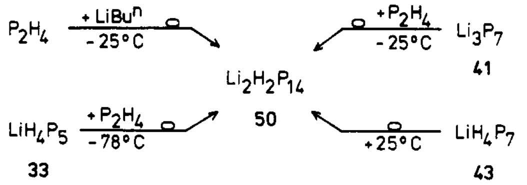
At −25 °C, further **43** is initially formed from the precursors **45** and **46**. Compound **43** remains unchanged up to a P_2H_4/$LiBu^n$ ratio of 8:1 while **44** reacts to furnish the polycyclic phosphide **50**, an orange-red solid which, being insoluble in THF, precipitates from the reaction mixture. After this, **43** also reacts further to yield lithium dihydrogen heptaphosphide (**51**), the first product possessing the tricyclic $P_7(3)$ skeleton. Continued metalation then leads to **49** and on to the final product **41** which is additionally formed in the other last reaction step by degradation of **50**. The differing courses of the reactions at −25 and −78 °C can be attributed to the increasing solubility of PH_3 in THF with decreasing temperature; thus PH_3 can participate to a greater extent in the reaction at −78 °C.

The compositions and structures of the novel hydrogen polyphosphides **43**, **44**, **49**, **50**, and **51** containing isolated, polycyclic $H_xP_n^{(m-x)-}$ ions were elucidated unequivocally by complete analyses of their $^{31}P\{^1H\}$-NMR spectra or by two-dimensional $^{31}P\{^1H\}$-NMR spectra. Compound **45** is an open-chain phosphide possessing a doubly branched $P_7(9)$ skeleton. The polyphosphide **33** with its monocyclic anion has been discussed in section III.A.

The heptaphosphide **43** is formed in the metalation of P_2H_4 with $LiBu^n$ when the ratio of the reaction partners is within the range 120:1 to 6:1.[200] It is stable in the presence of P_2H_4 and thus only reacts further with $LiBu^n$ after all the diphosphane has been consumed. Compound **43** separates at −25 °C from reaction mixtures having a P_2H_4/$LiBu^n$ ratio of 8:1 as an orange-red oily phase above the solid **50** and can be isolated in 60–70% purity (together with **44** and/or **51**).[228] Like all other polyphosphides with isolated anions, **43** is highly sensitive to oxidation and hydrolysis; decomposition also proceeds in solution at above about −10 °C. Its lower nucleophilicity in comparison to **42** and the more phosphorus-rich subsequent products $LiH_{n+1}P_n$ (see above) is also reflected in the low-field position of the signal for the phosphidic P^- atom (δ = −20). The anionic charge is apparently partially delocalized over the branched $P_7(5)$ skeleton in **43**. The hydrogen atoms are arranged in an *all-trans* orientation.

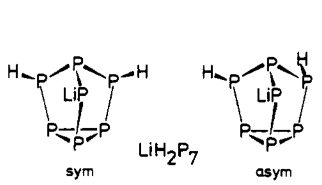
The octaphosphide **44** is also a major product of the metalation of P_2H_4 by $LiBu^n$ over a wide range of stoichiometries.[200] In reactions with a molar ratio of $P_2H_4/LiBu^n$ of 35:1 at −25 °C, it comprises about 60 mol % of the reaction mixture. The constitution and configuration were elucidated by a complete analysis of the $^{31}P\{^1H\}$-NMR spectrum[229] on the basis of selective population transfer experiments.[230] The PH_2 group is arranged in an *endo* position and the substituents on the $P_7(5)$ skeleton occupy *all-trans* positions. The ^{31}P-NMR signal of the phosphidic P^- atom ($\delta = -57$) indicates that the delocalization of the negative charge in **44** is less than that in **43**.

Of particular interest is the tetradecaphosphide **50**, whose polycyclic molecular skeleton is formed in the course of the transformation of a bicyclic P_7 skeleton with a side chain (**44**) to a tricyclic P_7 skeleton (**41**). The same compound is also accessible from a sort of retroreaction of **41** with P_2H_4 and is formed additionally in the reaction of **33** with P_2H_4 and on the disproportionation of **43**.[227] Since difficultly separable by products are formed in all cases, the adduct $Li_2H_2P_{14}{\cdot}6THF$ can only be obtained in 80–90% purity. On the basis of structural elucidation by NMR spectroscopy, the $H_2P_{14}^{2-}$ ion is a typical conjuncto-phosphane made up of a norbornane-type $P_7(5)$ and a deltacyclane-type $P_9(3)$ partial skeleton which are annelated at the two-atom bridges; in this manner, a central pentalane-type $P_8(6)$ partial skeleton has been constructed.



(47)

The two tricyclic hydrogen heptaphosphides **51** and **49** are further intermediates of the metalation of P_2H_4 by $LiBu^n$ at −25 °C. At a reactant ratio of $P_2H_4/LiBu^n$ = 8:1 the lithium dihydrogen heptaphosphide (**51**) is formed for the first time in addition to **43** and **50**. Compound **51** occurs as a mixture of the symmetrical (sym) and asymmetrical (asym) configurational isomers.[9,200]



The same product is formed in the stepwise protonation of **41** as well as in the partial metalation of P_7H_3 (**52**) with $LiPH_2$; the best preparative route, however, is the reaction of **52** with **41** at −78 °C. Compound **51** can be isolated as a light-orange, amorphous solvent adduct[231] which decomposes below room temperature with cleavage of PH_3 and formation of more phosphorus-rich polyphosphides (see below).

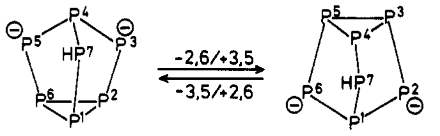
$$\underset{\mathbf{52}}{2P_7H_3} + \underset{\mathbf{41}}{Li_3P_7} \rightarrow \underset{\mathbf{51}}{3LiH_2P_7} \tag{48}$$

Dilithium hydrogen heptaphosphide (**49**) is the sole THF-soluble product of the metalation of P_2H_4 with $LiBu^n$ at a molar ratio of 5.5:1 and is formed together with the solid tetradecaphosphide **50**. The recommended preparative route to **49** is the reaction of **41** with P_2H_4 at −25 °C which gives rise to crystalline $Li_2HP_7{\cdot}n$THF.[9,226]

$$\underset{\mathbf{41}}{2Li_3P_7} + 9P_2H_4 \rightarrow \underset{\mathbf{49}}{3Li_2HP_7} + 11PH_3 \tag{49}$$

Compound **49** is also formed during the protolysis of **41** under modified stoichiometric conditions and in the metalation of **52** with $LiPH_2$ or **41**. Furthermore, **49** is a product of the disproportionation of **33** (section III.A) as well as of the nucleophilic cleavage of white phosphorus (section IV.B). Below −15 °C and under an inert atmosphere, **49** is stable for longer times whereas, at room temperature, decomposition to yield more phosphorus-rich polyphosphides occurs (see below).

The ^{31}P-NMR parameters obtained from a spectral analysis indicate that the $P_7(3)$ skeleton of **49** is markedly distorted in comparison with that of **41**. A special structural feature of **49** revealed by temperature-dependent NMR studies is its fluctuating anion. As a result of its similarity with the hydrocarbon dihydrobullvalene,[232] the HP_7^{2-} ion is capable to undergo a degenerate Cope rearrangement[233] and can be described at room temperature by two structurally identical valency tautomers.[226] As can be seen, opening of the bond between P^2 and P^6 in the three-membered ring and formation of a bond between the bridging atoms P^3 and P^5 with concomitant migration of the two negative charges to the atoms P^2 and P^6 regenerate the unchanged HP_7^{2-} ion. On the other hand, in **49** there is no evidence for an intra- or intermolecular metal/hydrogen exchange.



Compounds in which the hydrogen atoms of **49** and **51** are substituted by trimethylsilyl or organic groups have been obtained by reaction of $(Me_3Si)_3P_7$ (**53**) with **41** or by reaction of white phosphorus with organolithium derivatives, respectively.[234] These derivatives of **49** also exhibit the fluctuating bond phenomenon.

The final product of the metalation of diphosphane with $LiBu^n$ or $LiPH_2$, namely trilithium heptaphosphide (**41**), is also produced in the nucleophilic cleavage of white phosphorus by $LiPH_2$; in fact, this route is preferable for preparative purposes[235] (see section IV.B). Compound **41** is stabilized by the addition of three solvent molecules (THF, DME) and decomposition occurs upon their removal. Reaction with chloro(trimethyl)silane furnishes the silyl derivative **53**,[225] which is also accessible from P_4, Na/K alloy, and Me_3SiCl.[236] Protolysis of **53** under mild conditions yields the phosphorus hydride **52** which can be converted back to **41** by metalation.[225] The reactions of **41** with alkyl halides furnish the corresponding trialkylheptaphosphanes P_7R_3 (see section V).[225]

The structure of the $P_7(3)$ skeleton has been elucidated by von Schnering by X-ray crystallographic analyses of the alkaline earth metal polyphosphides

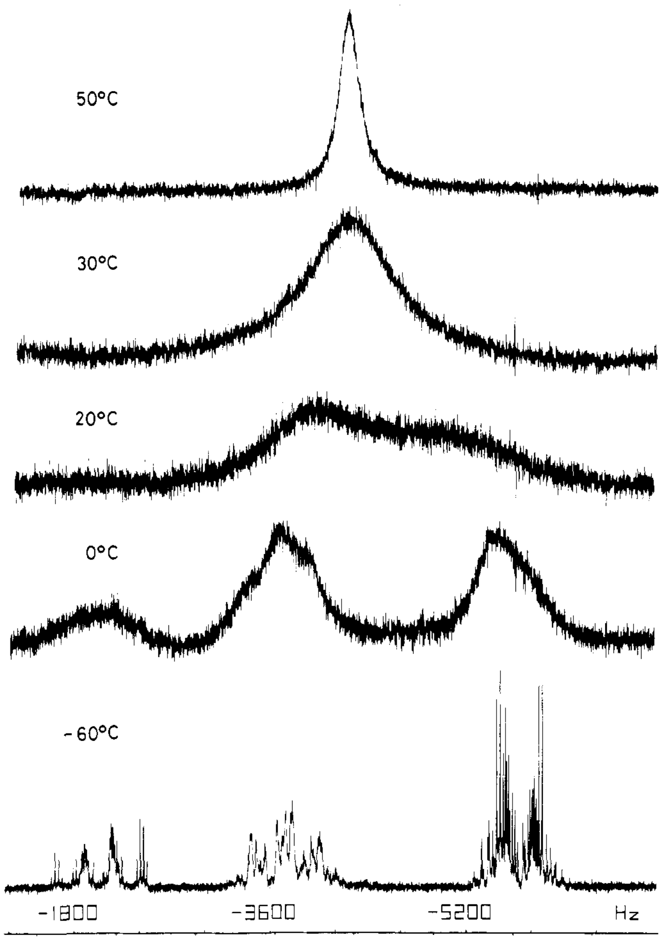
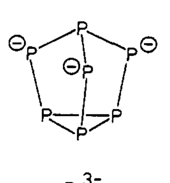
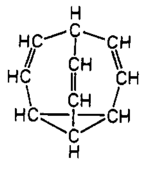


Figure 5. ^{31}P NMR spectrum of Li_3P_7 (**41**) in tetrahydrofuran-d_8 as a function of temperature (36.43 MHz).[9]

Sr_3P_{14}[237] and Ba_3P_{14}[238] as well as the silyl derivative **53**.[239] It consists of a tricyclic cage analogous to that of P_4S_3. The low-temperature ^{31}P-NMR spectrum of **41** (Figure 5) is in accord with this structure and exhibits three signal groups at $\delta = -57$, -103, and -162 in an intensity ratio of 1:3:3. On the basis of a complete spectrum analysis,[240] these correspond to the P atom at the apex, the negatively charged P atoms in the bridges, and the P atoms of the three-membered ring, respectively. On raising the temperature, increasing line broadening up to coalescence of all ^{31}P-NMR signals occurs; on cooling the original low-temperature spectrum reappears. This phenomenon is attributable to a reversible valency tautomerism analogous to that of bullvalene.[241] Indeed, the P_7^{3-} ion and bullvalene ($C_{10}H_{10}$) have three important common structural features; they each contain a three-membered ring which markedly reduces the activation energy for the Cope rearrangement, and in addition a 3-fold axis and three easily mobile electron pairs.



P_7^{3-}



$C_{10}H_{10}$

In the course of the intramolecular rearrangements of P_7^{3-}, P–P bonds are continuously broken and reformed in such a way that, as in the case of the HP_7^{2-} ion (see above), the anion is always regenerated. In a series of such rearrangements, each of the seven phosphorus atoms can occupy each of the possible positions; this gives rise of 7!/3 = 1680 valency tautomers.[225] In analogy to the rearrangement of the two valency tautomers of HP_7^{2-}, each individual Cope rearrangement involves the following transformations: two atoms of the three-membered ring take up negative charges and become bridging atoms, two bridging atoms enter into the three-membered ring, while the apex atom provides the third atom of the three-membered ring and vice versa, namely the third atom of the former three-membered ring becomes the new apex atom. The calculated enthalpy of activation for this process ($\Delta H^{\ddagger} = 14.12$ kcal mol^{-1})[242] is in very good agreement with the results from temperature dependent ^{31}P-NMR spectroscopic investigations.[225] This mechanism has been substantiated further by topological studies.[243] The route for the rearrangement of the phosphorus atoms in P_7^{3-} was directly demonstrated by a two-dimensional ^{31}P-NMR exchange spectrum of **41** recorded at a temperature below the coalescence point where rapid magnetization transfer is already taking place (Figure 6).[244]

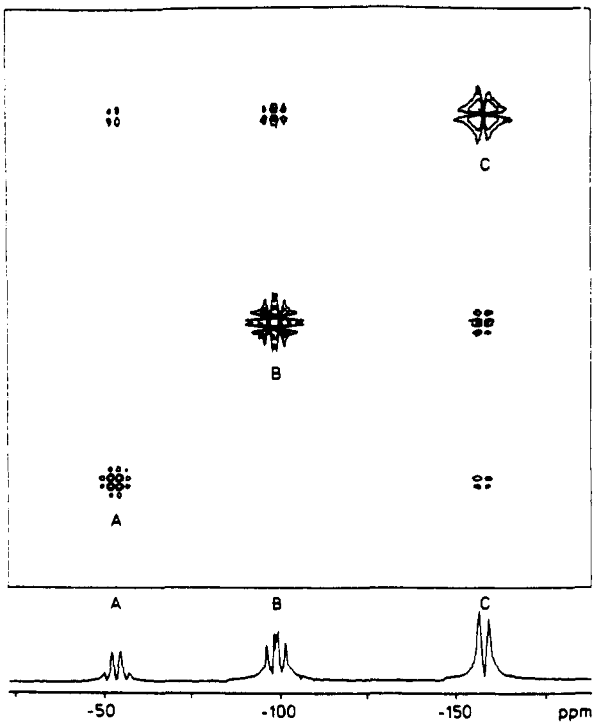


Figure 6. (Above) 2D exchange ^{31}P NMR spectrum of Li_3P_7 (**41**) in THF/THF-d_8 (pulse sequence: 90°, t_1, 90°, t_m, 90°, t_2), mixing time for magnetization transfer $t_m = 0.01$ s $\pm 30\%$, measuring temperature −30 °C, measuring frequency 121.5 MHz, measuring time 2.5 h, and (below) the corresponding 1D-^{31}P NMR spectrum.[244]

As can be seen, magnetization transfer takes place between the signal groups C and B as well as A and C but not between the groups A and B. Thus, the positional exchanges between three-membered ring and bridge atoms as well as between apex and three-membered ring atoms in the manner mentioned above have been proven experimentally. Furthermore, the intensity differences of the cross peaks BC and AC confirm that the number of respective exchange processes is larger in the first case than in the second case (see above). The heptaphosphanortricyclene anion is, therefore, a typical fluctuating molecule. The coalescence temperatures of 41 in 1,2-dimethoxyethane,[234] ethylenediamine,[245] and tetramethylethylenediamine[246] are lower than that in tetrahydrofuran.[225] As to be expected, derivatives of 41 such as P_7H_3, P_7R_3, and $(Me_3Si)_3P_7$ in which the substituents are covalently bonded to the bridging phosphorus atoms do not exhibit any valency isomerization.

B. Polyphosphides by Nucleophilic Cleavage of White Phosphorus

Trilithium heptaphosphide (41) is, as mentioned above (section IV.A), most conveniently synthesized by nucleophilic cleavage of white phosphorus with an excess of lithium dihydrogen phosphide in boiling DME.[235] This gives rise to 41 as the solvent adduct

$$3P_4 + 6LiPH_2 \rightarrow \underset{\textbf{41}}{2Li_3P_7} + 4PH_3 \qquad (50)$$

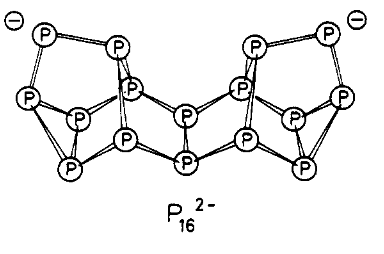
Li_3P_7·3 monoglyme in 95% yield. The formation of the heptaphosphide from white phosphorus, which formally constitutes the insertion of a >PLi group into three of the phosphorus–phosphorus bonds of the P_4 molecule, proceeds through a complicated sequence of reaction steps. Further lithium polyphosphides are formed as intermediates and these can be isolated under modified reaction conditions (see below).

Compound 41 is formed similarly in the reaction of organolithium derivatives with white phosphorus.[66] The nicely crystalline solvent adduct $[Li(tmeda)]_3P_7$ was obtained from $LiCH_2PPh_2$ and P_4 in tetramethylethylenediamine (tmeda) and its crystal structure determined by single-crystal X-ray analysis.[13,246]

The hydrogen heptaphosphides 49 and 51 are not stable at room temperature (see section IV.A) but decompose in a complex disproportionation reaction to furnish, among others, dilithium hexadecaphosphide (54).[9,226,247] Compound 54 can be prepared more simply and in better yield by nucleophilic cleavage of white phosphorus with lithium dihydrogen phosphide in a molar ratio of 1.92:1.[248] The corresponding sodium salt

$$23P_4 + 12LiPH_2 \rightarrow \underset{\textbf{54}}{6Li_2P_{16}} + 8PH_3 \qquad (51)$$

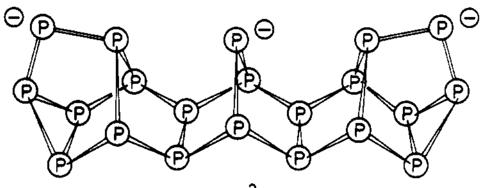
55 can be obtained analogously using sodium powder in the presence of 18-crown-6.[249] Formation of 54 has also been observed in the reaction of white phosphorus with $LiP(SiMe_3)_2$.[250] In all cases, 54 and 55 are formed as solvent adducts, which, on drying or warming, give up some of the solvent while becoming darker in color and less soluble. According to ^{31}P-NMR spectroscopy, isolated P_{16}^{2-} ions are present in solution in each case.



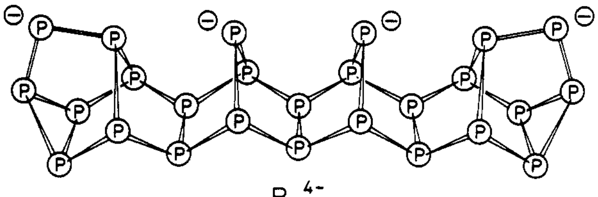
P_{16}^{2-}

The same structure has been found by a crystal structure analysis of $(Ph_4P)_2P_{16}$, formed from Na_3P_7 and $Ph_4P^+Cl^-$ via disproportionation.[13,135,251] Thus, the $P_{16}(2)$ skeleton is a conjuncto-phosphane made up of two deltacyclane-type $P_9(3)$ units annelated at the two-atom bridges. In general, conjuncto-phosphane skeletons are defined as those P_n skeletons for which the partial structures are known from less phosphorus-rich phosphides (sections III and IV) or organophosphanes (section V). The corresponding dialkylhexadecaphosphanes $P_{16}R_2$ (see section V) are formed in the reactions of 54 and 55 with alkyl halides.[252]

Likewise, the cleavage of white phosphorus by lithium dihydrogen phosphide or sodium under different stoichiometric conditions—as well as the room temperature decomposition of the hydrogen heptaphosphide 49—also give rise to the henicosaphosphides $M^I_3P_{21}$ and the hexacosaphosphides $M^I_4P_{26}$ (M^I = Li, Na, K). Of these compounds, Na_3P_{21}·15THF (56) and Li_4P_{26}·16THF (57) have been isolated in the pure state.[253,254] According to their ^{31}P-NMR spectra, these compounds contain isolated P_{21}^{3-} and P_{26}^{4-} anions, respectively, made up of two deltacyclane-type $P_9(3)$ terminal groups and one or two, respectively, norbornane-type $P_7(5)$ middle groups. The anions may also be described as the annelation products of a $P_{14}(4)$ skeleton—like that in 50—with a $P_9(3)$ group or of two $P_{14}(4)$ groups, respectively. Their constitutions have been confirmed by X-ray crystal analyses of the henicosaphosphide $[Li(12\text{-crown-}4)_2]_3P_{21}$·2THF[255] and the hexacosaphosphide Li_4P_{26}·16THF,[254,256] respectively. The former compound was obtained from the reaction of Li_3P_7 with $(CHT)Cr(CO)_3$ (CHT = cycloheptatriene) in the presence of 12-crown-4.[255]



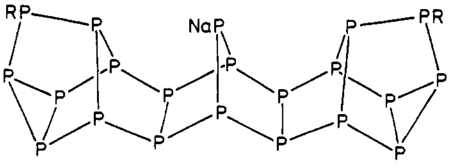
P_{21}^{3-}



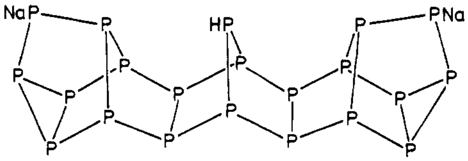
P_{26}^{4-}

Noteworthy of the phosphorus-rich phosphides with conjuncto-phosphane skeletons is the preference for deltacyclane-type $P_9(3)$ terminal groups while covalent, polycyclic organophosphanes P_nR_m ($m < n$) usually possess terminal two-atom bridges with *trans* substituents (section V). In the case of phosphides, it seems that two-atom bridges with negative charges on the adjacent phosphorus atoms (in addition to the free electron pairs) are so energetically unfavorable that the system is spontaneously stabilized by the formation of a zero-atom bridge to give the three-membered ring of the deltacyclane-type partial structure. Hence it is understandable that the corresponding polyphosphides with isolated P_n^{m-} ions do not exist for all covalent phosphanes P_nR_m (R = H, alkyl, aryl). Thus, in spite of intensive effort, it has not yet been possible to prepare nonaphosphides of the type $M^I_3P_9$ with a deltacyclane-type constitution.[257]

Investigations on the reactivity of the henicosaphosphide **56** have revealed that smooth substitution reactions with alkyl halides or chloro(trimethyl)silane occur at the phosphidic P atoms of the $P_9(3)$ terminal groups but not at the P^- atom of the $P_7(5)$ middle group. This is presumably a consequence of steric effects. Thus, partially substituted henicosaphosphides of the type $NaP_{21}R_2$ (**58a–d**) are accessible in which the substituents R in the terminal groups are oriented *trans* to each other.[258] On the other hand, protonating agents such as acetylacetone primarily attack the central P^- atom, the position of highest nucleophilicity, so that the hydrogen henicosaphosphide **59** can be obtained by this way.[259] The basicity of the anion HP_{21}^{2-} toward acetylacetone or glacial acetic acid is no longer sufficient for the formation of $P_{21}H_3$ whereas, with stronger acids, decomposition of the $P_{21}(3)$ skeleton takes place. However, the partially organo-substituted henicosaphosphane(3) **59a** can be obtained from **58a** and can, in turn, be metalated quantitatively by $LiBu^n$ to furnish $LiP_{21}Me_2$.[260]



58a: R = Me
58b: R = Et
58c: R = Pr^i
58d: R = SiMe$_3$

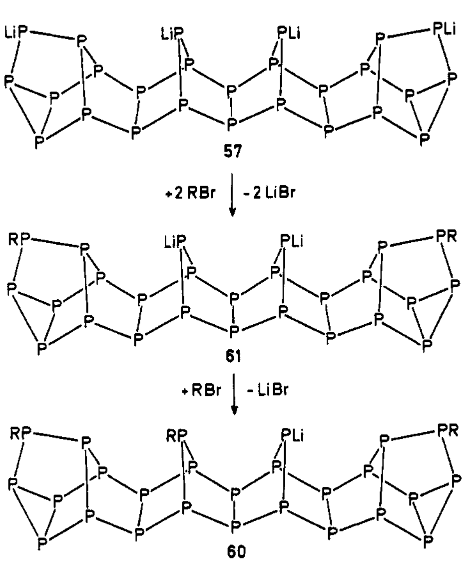


59

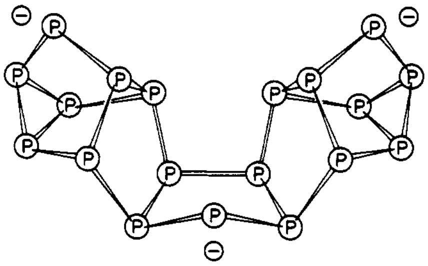
$$\underset{\mathbf{58a}}{NaP_{21}Me_2} \xrightarrow[-Na^+]{+H^+} \underset{\mathbf{59a}}{P_{21}HMe_2} \qquad (52)$$

The triorganohexacosaphosphides $LiP_{26}R_3$ (R = Me, Et) (**60**) are the final products of the alkylation of the hexacosaphosphide **57**.[261] In this case also, the phosphidic P-atoms of the $P_9(3)$ terminal groups are attacked primarily, as demonstrated by the ^{31}P-NMR spectroscopic characterization of the diorganohexacosaphosphides $Li_2P_{26}R_2$ (**61**). Since compound **57** has an additional $P_7(5)$ middle group in comparison to **56**, the steric preconditions for an alkylation in the middle part of the phosphorus skeleton are more favorable; but a substitution at the P^- atom of the second $P_7(5)$ group is still not possible for steric reasons. By contrast, solely a rearrangement of the $P_{26}(4)$ skeleton takes place on reaction of **57** with protonating agents.[260]

In addition to the already-mentioned compounds, the nonadecaphosphides $M^I_3P_{19}$ **62a–c** (**62a**, M^I = Li; **62b**, M^I = Na; **62c**, M^I = K) are also formed in the nucleophilic cleavage of white phosphorus by lithium dihydrogen phosphide or alkali metals.[262] These compounds cannot be isolated in the pure state but rather are only capable of existence in the reaction mixture up to a maximum of 16 P % in equilibrium with other polyphosphides. The compound **62a** is also formed on degradation of the hexadecaphosphide **54** by $LiPH_2$ as well as in the reactions of the heptaphosphide **41** with white phosphorus or iodine or 1,2-dibromoethane. As revealed by two-dimensional ^{31}P-NMR spectroscopy, the P_{19}^{3-} ion has a conjuncto-phosphane skeleton with a five-membered ring middle group. The resultant, relatively "open" total structure is the reason for the high reactivity of this polyphosphide ion.



R = Me, Et



P_{19}^{3-}

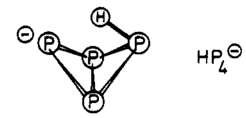
The nonadecaphosphides **62** are further intermediates in the complex sequence of reactions following the nucleophilic cleavage of the P_4 molecule in which the more phosphorus-rich partial structures of Hittorf's phosphorus[263] are constructed. Compounds **62a–c** are formed over a relatively wide range of P_4/M^IPH_2(or M^I) reactant ratios, which is limited on the phosphorus-poor side by the stoichiometry for the formation of $M^I_3P_7$[235] and extends, on the phosphorus-rich side, beyond that for the formation of $M^I_2P_{16}$.[248] It is apparent, also from the other routes of access (see above), that the nonadecaphosphides are an important intermediate in the transformation of the heptaphosphides $M^I_3P_7$ to the hexadecaphosphides $M^I_2P_{16}$. As shown by the compositions of the known polyphosphides with conjuncto-phosphane skeletons (Table IX), the compounds **62** are direct "precursors" of the polyphosphides $M^I_4P_{26}$ and $M^I_3P_{21}$, whose norbornane-

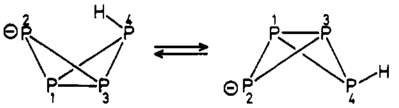
Table IX. Composition of Polyphosphides of the General Formula $M^I_mP_n$ with Conjuncto-Phosphane Skeletons

compound type	M^I:P ratio
$M^I_3P_7$	1:2.3
$M^I_3P_{19}$	1:6.3
$M^I_4P_{26}$	1:6.5
$M^I_3P_{21}$	1:7.0
$M^I_2P_{16}$	1:8.0

type $P_7(5)$ middle groups are apparently built up from the five-membered ring structural element of **62**. Furthermore, it can be seen that the construction of more phosphorus-rich polyphosphides from less phosphorus-rich polyphosphides is astonishingly not accompanied by a regular increase in the size of the phosphorus skeleton. Rather, as shown by the transformation of $M^I_3P_{19}$ to $M^I_2P_{16}$, it appears that, in the case of conjuncto-phosphanes, initially relatively large, "open" skeletal structures are formed; the smaller and "more closed" phosphorus skeletons of the more phosphorus-rich polyphosphides then take shape by successive eliminations of the phosphidic middle groups.[262] The spontaneous formation of the pentaphosphacyclopentadienides M^IP_5 (section III.B) can almost certainly be viewed in this context.[208]

Finally, the nucleophilic cleavage of white phosphorus by alkali metals or lithium dihydrogen phosphide also gives rise to the hydrogen tetraphosphides M^IHP_4 (M^I = Li, Na, K) (**63**).[264] However, prerequisites for this are reaction conditions under which the formation of more phosphorus-rich polyphosphides is suppressed. The reaction of white phosphorus with sodium/potassium naphthalenide solution at low temperature in DME has proved to be particularly suitable. After separation of by products, an approximately 7 × 10^{-2} M solution of (Na/K)HP_4 still containing some phosphorus and naphthalene is obtained. This solution can be stored for about 24 h at −78 °C under exclusion of air without decomposition. At room temperature, transformations into more phosphorus-rich polyphosphides, above all $M^I_2P_{16}$ take place. More stable solutions of (Na/K)HP_4 can be prepared by removal of DME at 0 °C and its replacement by cold dimethylformamide (DMF). Positive-ion FAB mass spectra of such solutions reveal high intensity peaks for the species $NaHP_4^+$ and $[NaHP_4 + DMF + H]^+$. On the other hand, HP_4^- cannot be detected in the negative-ion FAB mass spectrum; apparently $NaHP_4$ exists as a stable ion pair under these measurement conditions. The structure of the anion was elucidated by a complete analysis of the ^{31}P-NMR spectrum of a (Na/K)HP_4 solution (AMN_2X spin system).[264] The HP_4^- ion was found to have a bicyclobutane-type $P_4(2)$ skeleton with, at lower temperatures, the hydrogen atom in an *endo* position. At temperatures above about −25 °C, increasing ring inversion[265] occurs in analogy to bicyclobutane[266] and tetrasilabicyclobutane derivatives.[267] This fluctuating behavior is possibly one of the reasons why the migration of the hydrogen atom to the phosphidic P^- atom cannot be observed by NMR spectroscopy.[264] The energy barrier for ring inversion in the P_4–bicyclobutane system is apparently lower than that in the Si_4–bicyclobutane system (15–18 kcal mol^{-1} [267,268]), and this could be due to the absence of additional substituents on the atoms of the central P^1–P^3 bond. The (Na/K)HP_4 solution reacts with triorganotin chlorides to furnish unsymmetrically substituted bicyclotetraphosphanes of the type $R_3Sn(H)P_4$ (R = Me, Ph, Hex^c, *o*-Tol).[265] These derivatives are markedly more stable than the alkali metal hydrogen tetraphosphides (Na/K)HP_4 and $LiHP_4$,[264] but again are only capable of existence in solution. They probably undergo inversion between all three of the possible configurational isomers (*exo,exo*, *exo,endo*, and *endo,endo* forms) at room temperature.





V. Neutral Polycyclic Phosphanes

A. General Comments

The first polycyclic phosphane, P_4H_2, was reported in 1965 as one of the disproportionation products of diphosphane.[20a] Since then, numerous binary phosphorus/hydrogen compounds of the general composition P_nH_m ($m < n$) have been discovered.[7,9,11,15,20b,159,269] Together with the open-chain phosphanes P_nH_{n+2} and the monocyclic phosphanes P_nH_n, they are found in the distillation residues from preparations of diphosphane and the more phosphorus-rich examples, above all, are found in the thermolysates of diphosphane. The present state of knowledge is summarized in Table X.

As is apparent, the presently known polycyclic phosphorus/hydrogen compounds belong to various series with the compositions P_nH_{n-2} (bicyclic phosphanes) to P_nH_{n-18} (decacyclic phosphanes). In analogy to the nomenclature for boranes,[270] the individual compounds are designated by the numbers of their phosphorus and hydrogen atoms, for example nonaphosphane(5) for P_9H_5. This summary also shows that the tendency for the formation of higher cyclic phosphanes increases markedly with the increasing number of phosphorus atoms.

Up to the present, the only such compound to be isolated in the pure state is heptaphosphane(3) (**52**), which is obtainable by the mild methanolysis of the silyl derivative **53**.[225] Compound **52** is amorphous to

$$\underset{\mathbf{53}}{(Me_3Si)_3P_7} + 3MeOH \xrightarrow{-40\,^{\circ}C} \underset{\mathbf{52}}{P_7H_3} + 3Me_3SiOMe \quad (53)$$

X-rays and insoluble in hydrocarbons, alcohols, ethers, trichloromethane, carbon disulfide, acetonitrile, cyclohexanone, dimethylformamide, dimethyl sulfoxide, hexamethylphosphoric triamide, diphosphane, 1,2-di-*tert*-butyldiphosphane, and molten white phosphorus. However, a sufficient solubility for NMR investigations can be achieved when **52** is prepared directly in a solvent that has proved to be particularly suitable for higher phosphanes of the series P_nH_{n+2} and P_nH_n, namely benzene, 1-methylnaphthalene, or 1-methylnaphthalene/phenanthrene, and the nuclear magnetic resonance

Table X. Polycyclic Phosphorus Hydrogen Compounds (Phosphanes)

phosphanes	P_nH_{n-2}	P_nH_{n-4}	P_nH_{n-6}	P_nH_{n-8}	P_nH_{n-10}	P_nH_{n-12}	P_nH_{n-14}	P_nH_{n-16}	P_nH_{n-18}
tetraphosphanes	P_4H_2								
pentaphosphanes	P_5H_3	P_5H							
hexaphosphanes	P_6H_4	P_6H_2							
heptaphosphanes	P_7H_5	P_7H_3	P_7H						
octaphosphanes	P_8H_6	P_8H_4	P_8H_2						
nonaphosphanes	P_9H_7	P_9H_5	P_9H_3						
decaphosphanes	$P_{10}H_8$	$P_{10}H_6$	$P_{10}H_4$	$P_{10}H_2$					
undecaphosphanes	$P_{11}H_9$	$P_{11}H_7$	$P_{11}H_5$	$P_{11}H_3$					
dodecaphosphanes	$P_{12}H_{10}$	$P_{12}H_8$	$P_{12}H_6$	$P_{12}H_4$	$P_{12}H_2$				
tridecaphosphanes		$P_{13}H_9$	$P_{13}H_7$	$P_{13}H_5$	$P_{13}H_3$	$P_{13}H$			
tetradecaphosphanes			$P_{14}H_8$	$P_{14}H_6$	$P_{14}H_4$	$P_{14}H_2$			
pentadecaphosphanes			$P_{15}H_9$	$P_{15}H_7$	$P_{15}H_5$	$P_{15}H_3$	$P_{15}H$		
hexadecaphosphanes				$P_{16}H_8$	$P_{16}H_6$	$P_{16}H_4$	$P_{16}H_2$		
heptadecaphosphanes				$P_{17}H_9$	$P_{17}H_7$	$P_{17}H_5$	$P_{17}H_3$	$P_{17}H$	
octadecaphosphanes					$P_{18}H_8$	$P_{18}H_6$	$P_{18}H_4$		
nonadecaphosphanes					$P_{19}H_9$	$P_{19}H_7$	$P_{19}H_5$	$P_{19}H_3$	$P_{19}H$
icosaphosphanes					$P_{20}H_{10}$	$P_{20}H_8$	$P_{20}H_6$	$P_{20}H_4$	$P_{20}H_2$
henicosaphosphanes							$P_{21}H_7$	$P_{21}H_5$	$P_{21}H_3$
docosaphosphanes								$P_{22}H_6$	$P_{22}H_4$

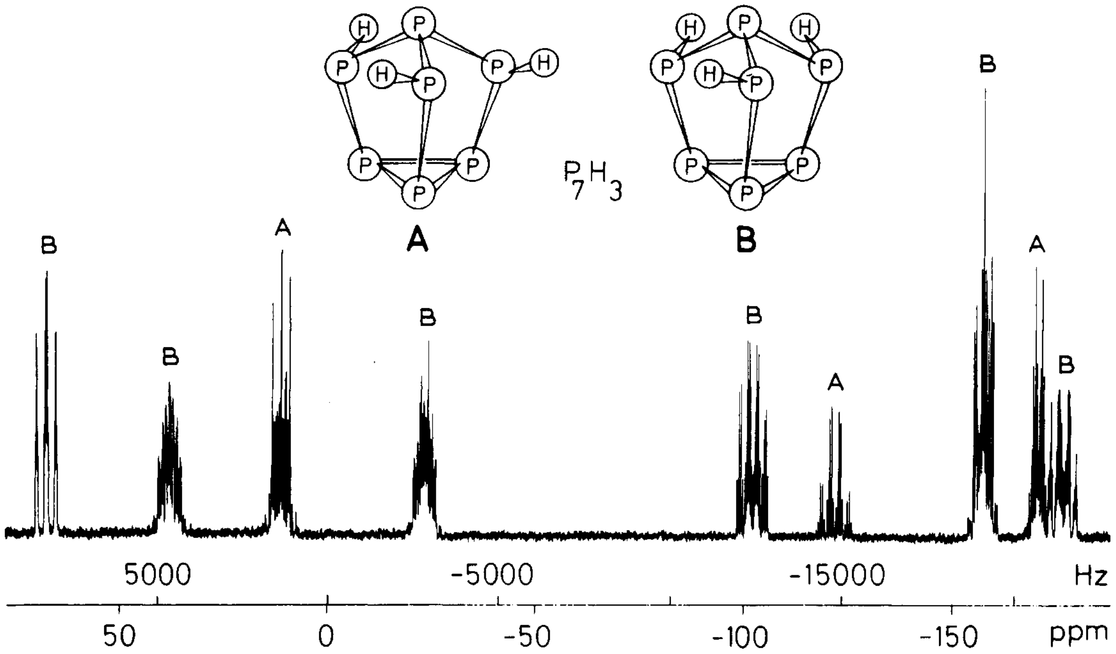


Figure 7. $^{31}P\{^1H\}$ NMR spectrum of P_7H_3, **52** (mixture of isomers), in 1-methylnaphthalene at 27 °C (121.5 MHz).

spectrum recorded as soon as possible.[271] The $^{31}P\{^1H\}$-NMR spectrum of **52** (Figure 7) contains nine complex signal groups which can be assigned to the two configurational isomers **A** and **B** with, respectively, symmetrical and asymmetrical arrangements of the hydrogen atoms on the basis of their intensity ratios and splitting patterns. All observations and, in particular, the complete spectral analysis for the isomer A[271] confirm that **52** has the same nortricyclene-type $P_7(3)$ structure as the starting material **53**; in the case of **53**, however, only the symmetrical isomer could be found on X-ray crystallographic analysis.[239]

The other polycyclic phosphorus hydrides were obtained and investigated as enriched (in some cases highly enriched) mixtures. Because of their similar properties and pronounced tendencies to undergo disproportionation, the separations of these compounds are extremely difficult. And, since the polycyclophosphanes are mostly insoluble and even amorphous to X-rays, most of them are not amenable to direct NMR spectroscopic or X-ray crystallographic studies. Apart from the characterizations of individual compounds by mass spectroscopy,[9] most structural investigations have therefore been carried out on suitable *derivatives* in which the hydrogen atoms have been replaced by organic groups.[9,11] *Organophosphanes* P_nR_m of these types can often be prepared in the pure state and have more favorable properties for structural elucidation than the corresponding parent compounds P_nH_m. Detailed investigations of these compounds have provided decisive contributions to the present state of knowledge on the structure and formation of polycyclic phosphanes.

B. Methods of Preparation

The first polycyclic organophosphane to be reported was trimethylheptaphosphane(3) (**64**), prepared from the heptaphosphide **41** and methyl bromide.[225,272] Other tricycloheptaphosphanes P_7R_3 were obtained analogously (see section V.C.2).

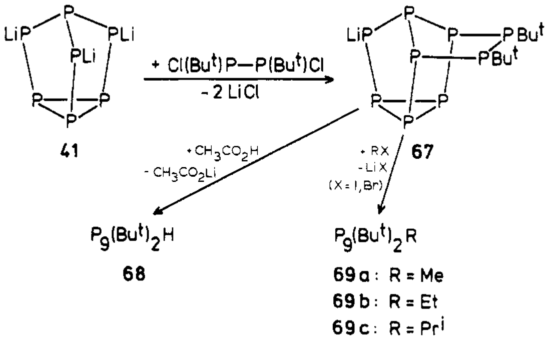
$$\underset{\mathbf{41}}{Li_3P_7} + 3MeBr \rightarrow \underset{\mathbf{64}}{P_7Me_3} + 3LiBr \qquad (54)$$

Furthermore, the octacyclohexadecaphosphanes $P_{16}R_2$ (see section V.B.7) and the partially organo-substituted decacyclohenicosaphosphane $P_{21}HMe_2$ (**59**) (see section IV.B) are similarly accessible by direct alkylation of the corresponding polyphosphides. However, it must be considered that higher phosphanes are readily attacked by nucleophiles with concomitant changes in the phosphorus skeleton. Hence, the reaction of the basic phosphide on already-formed reaction product must be minimized by slow addition of the salt solution to an excess of the alkyl halide. Since, however, corresponding polyphosphides with isolated P_n^{m-} ions do not exist for all polycyclic phosphanes P_nR_m (R = H, alkyl, aryl) (see section IV), this route does not represent a generally applicable synthetic method.

In a few cases, it is possible to construct the $P_n(m)$ skeleton of an organopolycyclophosphane for which a salt-type starting material with the analogous structure is not available by specific reactions. For example, the tricyclohexaphosphane **66** can be obtained by the thermal elimination of two C_5Me_5 groups and simultaneous formation of a new P–P bond from the bicyclohexaphosphane **65**; bis(pentamethylcyclopentadienyl) is formed as a by product by dimerization.[273,274]

$$\underset{\mathbf{65}}{P_6(C_5Me_5)_4} \xrightarrow{\Delta} \underset{\mathbf{66}}{P_6(C_5Me_5)_2} + (C_5Me_5)_2 \qquad (55)$$

Similarly, the partially organo-substituted tetracyclic nonaphosphide **67** can be constructed from the tricyclic heptaphosphide **41** by cyclocondensation with a 1,2-difunctionalized diphosphane. Compound **67** reacts with protonating agents to furnish the diorganononaphosphane(3) **68** and with alkyl halides to furnish the mixed alkylated nonaphosphanes(3) **69a–c**.[275] The



(56)

^{31}P-NMR spectra reveal that **68** and **69** each exist as a mixture of two configurational isomers which differ in the spatial arrangements of the substituents at P^5 (see also section V.C.3).

A special case is the synthesis of the bicyclotetraphosphane **70** which is formed, together with the diphosphene **71** and lithium bromide, in the reaction of (2,4,6-tri-*tert*-butylphenyl)lithium and 1-bromo-2,4,6-tri-*tert*-butylbenzene with white phosphorus.[276,277]

$$4LiR + 4RBr + 3P_4 \rightarrow \underset{\mathbf{70}}{2P_4R_2} + \underset{\mathbf{71}}{2P_2R_2} + 4LiBr \qquad (57)$$

$$R = 2,4,6\text{-}Bu^t{}_3C_6H_2$$

Decomposition of the diphosphene $(Me_3Si)_3CP{=}PSiMe_3$ at −20 °C yields the bicyclotetraphosphane $P_4[C(SiMe_3)_3]_2$ within a few days; steric effects are assumed to be responsible for this process.[278] A similar reaction takes place upon UV irradiation of the diphosphene $(C_5Me_5)P{=}P(C_5Me_5)$.[279]

The above-described preparative routes are each limited to only a few organopolycyclophosphanes, whereas the synthetic methods described below provide general accesses to polycyclic organophosphanes and have thus allowed major contributions to the development of this field to be made in the last 10 years.

Compounds with the general composition $P_{x+y}R_x$ (x,y = number of organo-substituted and number of solely P-substituted phosphorus atoms, respectively) can be prepared by the routes shown in eqs 58–61.[9,11,166,280,281]

$$xRPCl_2 + yPCl_3 + [(2x + 3y)/2]Mg \rightarrow P_{x+y}R_x + [(2x + 3y)/2]MgCl_2 \qquad (58)$$

$$(x/n)(PR)_n + yPCl_3 + (3y/2)Mg \rightarrow P_{x+y}R_x + (3y/2)MgCl_2 \qquad (59)$$

$$xRPCl_2 + (y/4)P_4 + xMg \rightarrow P_{x+y}R_x + xMgCl_2 \qquad (60)$$

$$[(2x + 3y)/2n](PR)_n + yPCl_3 \rightarrow P_{x+y}R_x + (3y/2)RPCl_2 \qquad (61)$$

The reaction according to eq 58 represents the dehalogenation of a mixture of a dichloro(organo)phosphane and phosphorus(III) chloride. As can be seen from the latter two reactions, the organo-substituted phosphorus atoms can also originate from monocyclic compounds $(PR)_n$ and the unsubstituted phosphorus atoms from white phosphorus. Other dehalogenating agents such as alkali metals or lithium hydride may be used in place of magnesium. The route shown in eq 61 represents the ring transformation of a monocyclic organophosphane by phosphorus(III) chloride in the absence of magnesium. In each case, the sum composition of the reaction product, that is the number of organo-substituted phosphorus atoms and the number of phosphorus atoms linked solely to other phosphorus atoms, can be predetermined by the molar ratio of the two phosphorus-containing starting materials. However, whether or not the predetermined stoichiometry leads to a specific organophosphane or only to a mixture of substances with the same sum composition depends on the thermodynamic and kinetic stability of the respective compounds. Furthermore, since the P:R ratios of different organopolycyclophosphanes can be very similar, a mixture of several compounds is always obtained and must then be separated by suitable means (see below). Also decisive for the product palette formed is whether the course of the reaction is controlled by thermodynamic or by kinetic effects. This can be influenced by the detail changes in the performance of the reaction.

Thus, products with more than nine phosphorus atoms can hardly ever be obtained by the routes shown in eqs 58 and 59, even with a large excess of PCl_3, when the reaction is performed rapidly in boiling tetrahydrofuran. The major products are always the organophosphanes P_nR_m with n = 5–9 and m = 3–5, above all the thermodynamically favored compounds of the types P_9R_3 and P_7R_3. On the other hand, the reaction route of eq 60, involving nucleophilic attack on white phosphorus by the carbene or Grignard-type intermediate formed from $RPCl_2$ and magnesium in THF, favors the formation of more phosphorus- and alkyl-rich polycyclophosphanes with n = 9–18 and m = 6–9 under high, stationary concentrations of the starting materials. The degree of substitution is thereby influenced not only by the temperature but also by the steric bulk of the substituent R. Thus, on changing from R = Me to R = Pr^i, the proportion of phosphorus- and alkyl-rich compounds increases noticeably since the corresponding $P_n(m)$ skeletons experience increasing kinetic stabilization. Thus, the formation route for each individual organopolycyclophosphane must be optimized by modification of the reaction conditions in order to maximize the amount of the desired compound in the product mixture and hence facilitate its enrichment or isolation.

A similar situation is valid for a further general route to polycyclic organophosphanes: the thermolysis of less phosphorus-rich compounds. As demonstrated by systematic investigations,[281] open-chain and monocyclic phosphane derivatives only furnish low yields of polycyclic compounds. Bi- and tricyclic *methyl*phosphanes such as P_7Me_5, P_7Me_3, or P_9Me_5 give rise to relatively high proportions of more phosphorus-rich polycyclic products but the thermolysates from the tricyclic compounds are usually insoluble and thus preparatively worthless.

However, the thermolysis reaction can be performed in such a manner that it can be specifically employed for the preparation of more phosphorus-rich polycyclic organophosphanes.[281] The bicyclic heptaphosphanes P_7R_5 with R = Me to R = Bu^t are especially suitable as substrates since they give rise to soluble thermolysis residues. With increasing number of carbon atoms in the substituents, the solubility increases so that the admixture with higher cyclic—above all tricyclic—phosphane derivatives is possible with larger alkyl groups. In the case of R = Pr^i, the product mixture from the primary reaction according to eq 60 has proved to be a particularly good starting material for the thermolysis.[282] In the cases of smaller alkyl groups, the solubility of the thermolysate can be improved by the addition of the corresponding monocyclic compound $(PR)_5$ to the employed heptaphosphane(5).[281] The most suitable thermolysis temperature (in the range 180–230 °C) depends on the alkyl substituent. The thermolysis time increases with increasing size of the substituents and with increasing addition of the respective monocyclic compound $(PR)_5$; it is between 7 and 150 h.

The major products in the thermolysates are the compounds $(PR)_n$ (n = 4, 5; depending on R) and P_9R_3 together with P_7R_5, P_8R_6, P_9R_5, $P_{10}R_4$, $P_{11}R_5$, $P_{12}R_4$, and $P_{13}R_5$—in some cases in considerably enriched amounts. Further products are $(PR)_n$ (n = 3–6, depending on R) as well as smaller amounts of phosphanes of the series P_nR_{n-2} (n = 4–6, 9), P_nR_{n-4} (n = 6–8, 10, 12), P_nR_{n-6} (n = 8, 12, 13), P_nR_{n-8} (n = 10, 11, 14–16), P_nR_{n-10} (n = 13–18), P_nR_{n-12} (n = 15–20), P_nR_{n-14} (n = 16–21), P_nR_{n-16} (n = 19–22), and P_nR_{n-18} (n = 23).[281,282] The quantitative product distribution depends on the respective substituent R, the employed phosphane mixture, and the specific thermolysis conditions used. It is worthy of note in the series P_nR_{n-10} to P_nR_{n-16} that the proportion of even-numbered phosphanes is always larger than that of the odd-numbered phosphanes. In general, more phosphorus-rich, alkyl-poor compounds predominate; hence, this "thermolysis route" is a valuable complement to the preparative procedures described above.

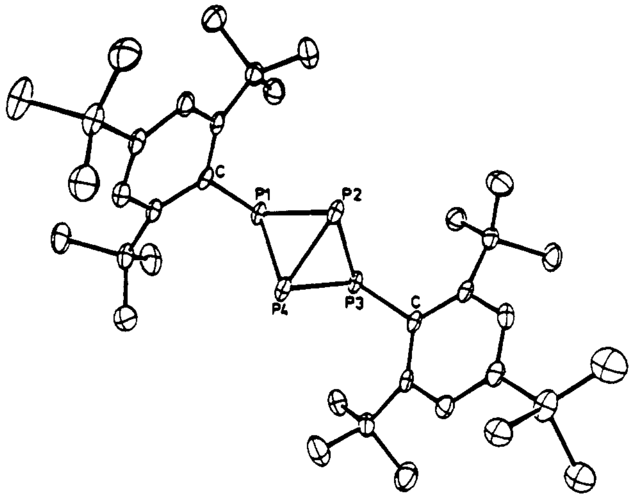


Figure 8. Molecular structure of $P_4(2,4,6\text{-}Bu^t_3C_6H_2)_2$ (**70**) (without hydrogen atoms) in the crystal.[276,277]

For the enrichment or isolation of an organopolycyclophosphane, a strategy involving the combined application of fractional precipitation, column chromatography, high-pressure liquid chromatography, and sublimation has proved to be valuable.[281]

C. Sterically Unhindered Polycyclic Phosphanes

1. Bicyclic Compounds: P_4R_2, P_6R_4, P_7R_5, P_8R_6

The method of preparation of the first organo-substituted bicyclo*tetra*phosphane, $P_4(2,4,6\text{-}Bu^t_3C_6H_2)_2$ (**70**), to be prepared in the pure state and structurally clarified[276,277] has already been described in section V.B, eq 57. Prior to this, only the "inorganic" substituted derivative $P_4[N(SiMe_3)_2]_2$[283] of the phosphorus hydride P_4H_2[20a] was known. The $^{31}P\{^1H\}$-NMR spectrum of **70** shows two multiplets in the high-field region characteristic for three-membered phosphorus rings (see section II.C.2). An X-ray crystal structure analysis (Figure 8) revealed that the compound exists in the solid state as the sterically more favorable *exo,exo* isomer with a folding angle of the P_4 bicyclic system of 95.5°. The central P^2–P^4 bond length is 2.166 Å, i.e. markedly shorter than a normal P–P single bond (2.21 Å[135]). In agreement with quantum mechanical calculations on P_4H_2,[284] this is indicative of an appreciable double-bond character.

A further organobicyclotetraphosphane, $P_4(C_5Me_5)_2$, was detected and characterized by NMR spectroscopy among the products of the reduction of dihalo(pentamethylcyclopentadienyl)phosphanes by alkali metals, lithium naphthalenide, or magnesium.[285]

In contrast to **70**, the unsymmetrically substituted bicyclotetraphosphanes $R_3Sn(H)P_4$ (R = Me, Ph, Hex^c, *o*-Tol) in which the steric shielding of the P_4 bicyclic system is relatively small are only capable of existence in dilute solutions. These compounds are accessible from $(Na/K)HP_4$ solution and R_3SnCl. Their dynamic behavior as detected by NMR spectroscopy is attri-

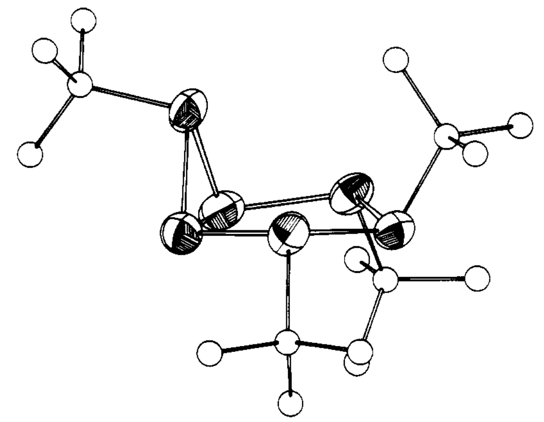


Figure 9. Molecular structure of $P_6Bu^t_4$ (**72b**) (without hydrogen atoms) in the crystal.[287,288]

buted, among other factors, to the ready inversion of the bicyclic ring system (see section IV.B).[265]

The bicyclo*hexa*phosphanes(4) P_6R_4, **72a** (R = Pr^i)[286] and **72b** (R = Bu^t),[287] are formed on dehalogenation of a wide range of mixture ratios of $RPCl_2$ and PCl_3 according to eq 58. By products are, above all, P_8R_6 (see below) and $(PR)_4/(PR)_3$ together with small amounts of more phosphorus-rich polycyclophosphanes. The product distribution depends strongly on the reaction conditions. The best primary yield of **72b** is obtained from a relatively rapid reaction of Bu^tPCl_2 and PCl_3 in a molar ratio of 3:2 (not 2:1!) in boiling THF. Small amounts of **72a** are also formed in the dehalogenation reaction according to eq 60.[281] Compounds **72** are characterized by a considerable tendency for formation. Compatible $^{31}P\{^1H\}$-NMR spectra were obtained, hence, only **72b** has as yet been isolated in the form of colorless crystals. The complete NMR spectral analysis (AA′BB′CD spin system) and the X-ray crystal structure of **72b** (Figure 9) show that the phosphorus skeleton comprises a three-membered ring with an annelated five-membered ring; compounds **72** are thus bicyclo[3.1.0]hexaphosphanes.[287,288] The slightly distorted three-membered ring is arranged practically perpendicular to the relatively planar five-membered ring. In spite of this unusual structure, **72b** is remarkably stable toward heat and atmospheric oxygen. In contrast to other polycyclophosphanes, only *one* configurational isomer is formed due to the presence of the bulky *tert*-butyl groups. Compound **72b** is a constitutional isomer of the 1,1′-bicyclotriphosphane **15** (section II.D.1).

A further bicyclo[3.1.0]hexaphosphane is the compound $P_6(C_5Me_5)_4$ (**65**) (section V.B) obtained by thermolysis of the cyclotriphosphane $(PC_5Me_5)_3$[285] in boiling benzene.[273,274] It crystallizes as yellow needles in the form of a solvent adduct with an equimolar amount of *n*-hexane. The X-ray crystal structure analysis reveals a more pronounced twisting of the five-membered ring in comparison to **72b**; this can be attributed to the larger size of the pentamethylcyclopentadienyl substituent. The remarkably long phosphorus-carbon bonds explain the ready cleavage of C_5Me_5 groups to furnish $P_6(C_5Me_5)_2$ (**66**) (see sections V.B and V.C.2).

Under suitable conditions (stoichiometry, temperature, and reaction time), the dehalogenation reactions according to eqs 58 and 59 give rise to the bicyclo*hepta*phosphanes(5) P_7R_5 (**73a**, R = Me; **73b**, R = Et; **73c**, R = Pr^i) which can be isolated as oily liquids (**73a,b**) or as a colorless solid (**73c**).[166,286] At room temperature, **73a** undergoes rearrangement within a few weeks to $(PMe)_5$ and P_9Me_5 (section V.C.2). The structures of **73a–c** were elucidated by complete analyses of their $^{31}P\{^1H\}$-NMR spectra (ABCDEFG spin system).[289] As shown exemplarily for **73a** in Figure 10, each of the seven phosphorus atoms gives rise to an isolated, intense signal group. The calculated NMR parameters,[289] which allow highly satisfactory simulations of the experimentally recorded spectra of **73a–c** to be obtained, prove unequivocally the existence of a norbornane-type structure; hence compounds **73** are 2,3,5,6,7-pentaorganobicyclo[2.2.1]heptaphosphanes. In addition to the predominant configurational isomer with the maximal *trans* arrangement of the substituents, each compound also exists as other isomers in lower relative abundancies. This can be deduced from the occurrence of additional, weaker signals with similar δ values and splitting patterns (Figure 10). The formation of several configurational isomers also explains the poor tendency of compounds **73** to crystallize, just like many other organopolycyclophosphanes.

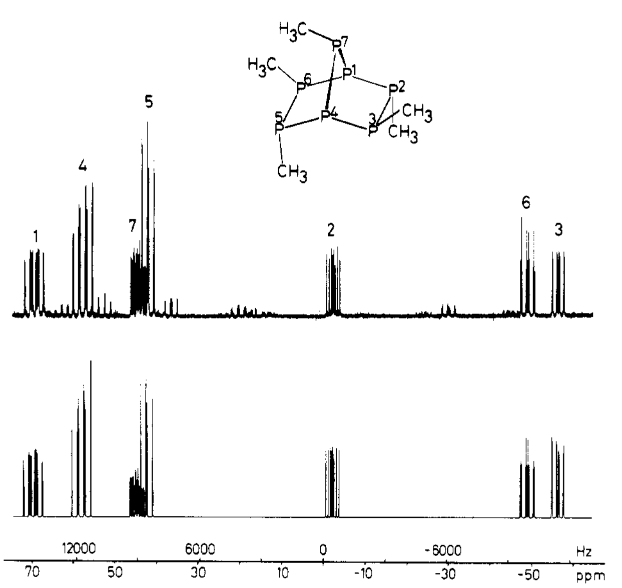
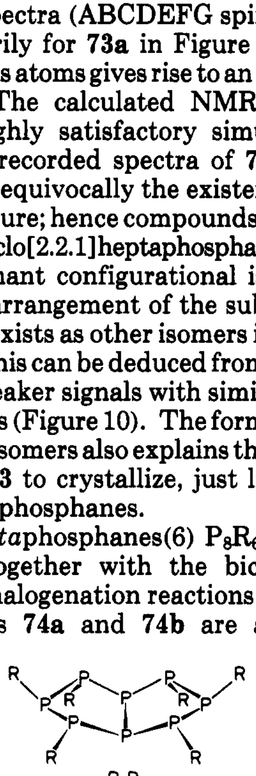


Figure 10. Observed (upper) and calculated (lower) $^{31}P\{^1H\}$ NMR spectrum of P_7Me_5 (**73a**), in benzene-d_6 at 30 °C (202.46 MHz).

The bicyclo*octa*phosphanes(6) P_8R_6, **74a–c**, are always formed together with the bicycloheptaphosphanes(5) in dehalogenation reactions according to eq 58. Compounds **74a** and **74b** are also formed in reactions according to eq 59.[9,290] Compounds **74b** and **74c** were isolated in the pure state as viscous oils whereas compound **74a** was enriched to about 50 mol % in the product mixture. According to NMR spectroscopic studies, especially a complete analysis of the $^{31}P\{^1H\}$-



P_8R_6

74a : R = Me
74b : R = Et
74c : R = Pr^i

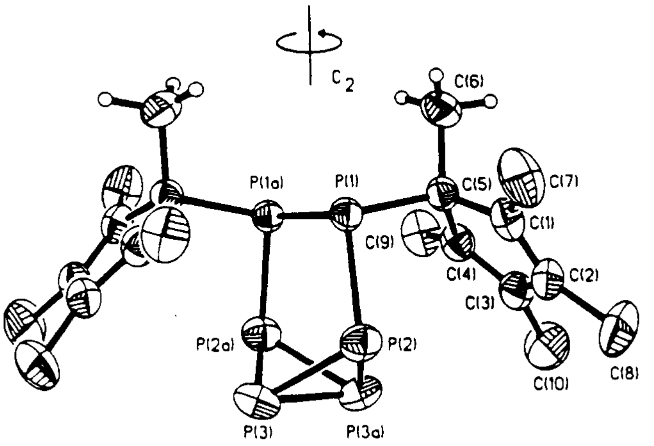


Figure 11. Molecular structure of $P_6(C_5Me_5)_2$ (**66**) in the crystal.[274]

NMR spectrum of **74b**,[291] compounds **74** exist as 2,3,4,6,7,8-hexaorganobicyclo[3.3.0]octaphosphanes with a pentalane-type P_8 skeleton. The electron pairs occupy axial and the organic groups equatorial positions. With increasing spatial requirements of the substituents, steric interactions between the *cis*-oriented organic groups lead to an increasing folding of the bicyclic system. This can be recognized by the high-field shifts of the ^{31}P-NMR signals of the atoms P^1 and P^5. This also explains why the pentalane-type framework is no longer capable of existence in the corresponding *tert*-butyl compound (see section V.D).

The concomitant formation of compounds **74** and **73**—even when the appropriate stoichiometries are used—is most probably attributable to the fact that both the octaphosphanes(6) and the heptaphosphanes(5) contain a bicyclic molecular framework comprised of two five-membered phosphorus rings. From the observed product distributions, it can be deduced that the P_7 skeleton with a one-atom bridge has a considerably larger tendency for formation than the P_8 skeleton with a zero-atom bridge in the case of smaller substituents (Me, H). However, the stability difference between the two bicyclophosphane frameworks changes with increasing spatial requirements of the substituents (Et, Pr^i) since the steric interactions between the substituents at P^6 and P^7 in **73** are appreciably larger than those of the *cis*-oriented substituents in **74**; accordingly, the ratio **74**:**73** increases.

2. Tricyclic Compounds: P_6R_2, P_7R_3, P_8R_4, P_9R_5, $P_{10}R_6$

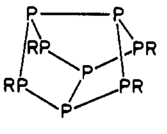
The preparation of the tricyclo*hexa*phosphane $P_6(C_5Me_5)_2$ (**66**) by thermolysis of the bicyclophosphane $P_6(C_5Me_5)_4$ (**65**) in boiling xylene[273,274] has already been described in section V.B, equation (55). The compound is only slightly sensitive to oxidation and is stable up to 180 °C. Its structure has been elucidated by NMR spectroscopy and an X-ray crystal structure analysis (Figure 11). The $P_6(2)$ skeleton thus consists of a P_4 tetrahedron in which one edge is bridged by a C_5Me_5-substituted P_2 moiety; compound **66** is thus 3,4-bis(pentamethylcyclopentadienyl)tricyclo[3.1.0.0^{2,6}]-hexaphosphane. The bond length in the P_2 bridge (2.164 Å) is markedly shorter than the other P–P bonds in **66**, the folding angle between the planes of the three-membered phosphorus rings of the bicyclobutane unit is 115.5°, an increase of 20° in comparison to the bicyclotetraphosphane **70** (section V.C.1).

The parent compound of the tricyclo*hepta*phosphanes(3) is the phosphorus/hydrogen compound P_7H_3 which can be obtained in the pure state (see section V.A). Its derivatives P_7R_3 constitute the most thoroughly investigated, neutral, polycyclic phosphanes since they are particularly easy to prepare. In analogy to the preparation of P_7Me_3 (**64**) by alkylation of Li_3P_7 (**41**) (section V.B),[225,272] the following homologous alkyl compounds $P_7Pr^i{}_3$,[292,293] P_7Et_3, $P_7Bu^n{}_3$, and $P_7Bu^i{}_3$,[293] as well as the silyl and stannyl derivatives $P_7(SiMe_3)_3$,[225] $P_7(SiH_3)_3$,[292,293] $P_7(SiPh_3)_3$, and $P_7(SnMe_3)_3$[292] have been prepared in the pure state. Furthermore, the heptaphosphanes $P_7[Fe(CO)_2Cp]_3$,[292] $P_7(SiH_2Me)_3$, $P_7(SiMe_2PEt_2)_3$,[293] and $P_7(SbBu^t{}_2)_3$[294] have been detected and characterized by NMR spectroscopy. The phosphino-substituted compound $P_7(PBu^t{}_2)_3$ was isolated in the form of yellow crystals from the reaction of **41** with $Bu^t{}_2PF$.[294] Similarly, reactions of Na_3P_7[295] with Me_3MCl (M = Si, Ge, Sn) furnished the heptaphosphanes $P_7(MMe_3)_3$.[292] The readily accessible silyl derivative $(Me_3Si)_3P_7$ (**53**)[236] is also a suitable starting material; its reactions with R_3MCl (R = Me, Ph; M = Si, Ge, Sn, Pb) give rise to the heptaphosphanes $P_7(SiPh_3)_3$, $P_7(GePh_3)_3$,[296] $P_7(SnR_3)_3$ (R = Me,[292] Ph[296]), and $P_7(PbMe_3)_3$.[297] Reactions of **53** with Me_3SnX (X = Cl, Br) in a molar ratio of 1:2 furnish a mixture of the compounds $P_7(SiMe_3)_{3-n}(SnMe_3)_n$ (n = 1–3), the reaction with HI in a ratio of 1:1 in toluene yields a mixture of the partially H-substituted heptaphosphanes $P_7(SiMe_3)_{3-n}H_n$ (n = 0–3).[292] Large amounts of the alkyl-substituted compounds P_7R_3 with R = Me, Et, Pr^i are also produced by dehalogenation reactions according to eq 59 under optimized conditions and can be isolated in the pure state.[298] The mixed-substituted heptaphosphanes $P_7(SiMe_3)_2Me$, $P_7(SiMe_3)_2Bu^t$, and $P_7(SiMe_3)Bu^t{}_2$ were formed in the reactions of white phosphorus with LiMe or $LiBu^t$ and subsequent treatment with Me_3SiCl and were characterized by NMR spectroscopy.[66]

The structures of compounds P_7R_3 as 3,5,7-trisubstituted tricyclo[2.2.1.0^{2,6}]heptaphosphanes were confirmed by ^{31}P-NMR spectroscopy and, above all, the complete analysis of the $^{31}P\{^1H\}$-NMR spectrum of P_7Me_3 (**64**).[299] Moreover, single-crystal X-ray analyses of the compounds $P_7(MMe_3)_3$ (M = Si,[239] Ge, Sn,[292] Pb[297]), $P_7(MPh_3)_3$ (M = Si, Ge, Sn),[296] and $P_7(PBu^t{}_2)_3$[294] have been performed. The organo-substituted heptaphosphanes(3) always occur—like the parent compound P_7H_3 (**52**) (section V.A)—as a mixture of the two configurational isomers **A** and **B** with the substituents in a symmetrical or asymmetrical orientation, respectively, with regard to the C_3 axis of the nortricyclene-type skeleton. In the case of **52**, the isomer ratio as determined by the signal intensities in the $^{31}P\{^1H\}$-NMR spectrum more or less corresponds to the statistical value of **A**/**B** = 1:3,[271] whereas for P_7Me_3 it is clearly shifted in favor of the symmetrical isomer, **A**/**B** = 1:1.8.[272,299] This is probably due to steric interactions between the substituents arranged asymmetrically to the C_3 axis in isomer **B**. This tendency is more pronounced with larger alkyl groups (R = Et, Pr^i, Bu^n, Bu^i)[293] and the symmetrical isomer **A** is formed exclusively in the cases of the sterically demanding substituents R_3M (R = Me, Ph; M = Si, Ge, Sn, Pb) and $Fe(CO)_2Cp$.[236,292,296,297]

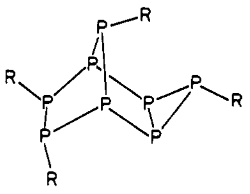
The crystal structure analyses reveal that the bond lengths and angles in the P_7 cage change only slightly upon variation of the substituents. A slight twisting of the P_7 framework about the 3-fold axis is observed in each case; this is caused by steric interactions between the substituents and the free electron pairs of the bridging atoms and decreases on going from M = Si to M = Pb.[292,296,297] Molecular vibrational spectra of the compounds $P_7(MR_3)_3$ (R = Me, Ph; M = Si, Ge, Sn, Pb) have also been investigated.[292,296,297]

The parent compound of the tricyclo*octa*phosphanes(4), the phosphorus hydride P_8H_4, has been detected in relatively small amounts among the hydrolysis products of calcium phosphide.[20b] Attempts to prepare the organic derivatives **75a,b** according to the reactions of eqs 58–60 have shown that these compounds have a low tendency for formation; thus as yet only **75b** has been enriched up to about 30 mol % together with other cyclophosphanes.[281,300] The constitution of **75** as 2,4,6,8-tetraorganotricyclo[3.3.-0.0^{3,7}]octaphosphanes with a bisnoradamantane-type P_8 skeleton (*a*-P_8R_4) was deduced from the characteristic ^{31}P-NMR signals of **75b**.



a-P_8R_4

75a: R = Et
75b: R = Pr^i

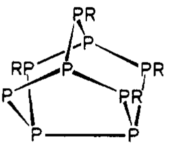


b-P_8R_4

76: R = Pr^i

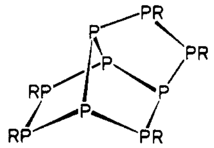
In attempts to increase the amount of **75b** by thermolysis of the crude reaction product at 230 °C, an increase in the yield was indeed detected by mass spectroscopy. However, separation and complete analysis of the $^{31}P\{^1H\}$-NMR spectrum of the compound thus obtained in 95% purity revealed that the constitutional isomer **76** was formed by this "thermolysis" route.[301] This isomer has a homonorbornene-type phosphorus skeleton (*b*-P_8R_4) and is, therefore, a 3,6,7,8-tetraorganotricyclo[3.2.1.0^{2,4}]octaphosphane. On the basis of MNDO calculations for P_8Me_4, the *exo*-homonorbornene isomer is somewhat more stable (ΔH°_f = −120.1 kcal mol^{-1}) than the bisnoradamantane isomer (ΔH°_f = −115.8 kcal mol^{-1}). Accordingly, **75b** rearranges to **76** with concomitant partial disproportionation even on gentle warming. However, the $P_8(4)$ structural unit of **75** is apparently stabilized by incorporation into larger P_n frameworks like those of the tetracyclodecaphosphanes $P_{10}R_4$ (section V.C.3), the pentacyclododecaphosphanes $P_{12}R_4$ (section V.C.4), or Hittorf's phosphorus.[263]

The tricyclo*nona*phosphanes(5) **77a** and **77b** are formed as major products and can be isolated as yellow oils from the reactions according to eq 58 or 59 under suitable conditions of stoichiometry, temperature, and time.[166,302] Their constitutions as 2,4,6,8,9-pentaorganotricyclo[3.3.1.0^{3,7}]nonaphosphanes with a noradamantane-type P_9 framework (*a*-P_9R_5) were deduced from the $^{31}P\{^1H\}$-NMR spectra. Since the >PR ring components in these molecules are separated from each other by unsubstituted phosphorus atoms, a deviation from the maximal *trans* arrangement of the substituents does not lead to a drastic destabilization. Hence, both compounds were obtained as mixtures of configurational isomers in comparable amounts (e.g., **77a**, three isomers in the ratio of approximately 40:40:20) and this accounts for their poor crystallization properties.



a-P_9R_5

77a: R = Me
77b: R = Et



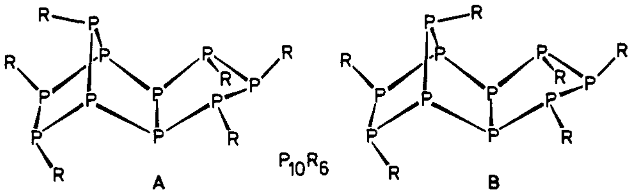
b-P_9R_5

78a: R = Me
78b: R = Et
78c: R = Pr^i

If the syntheses of the nonaphosphanes(5) are performed from white phosphorus according to eq 60, mixtures of **77** and a further constitutional isomer **78** in lower relative abundancy (*b*-P_9R_5) are obtained. In the case of R = Et, **78b** could be isolated as a pale-yellow, oily liquid while **78a** and **78c** could be highly enriched.[11,281,303] As substantiated by a complete analysis of the $^{31}P\{^1H\}$-NMR spectrum of **78b**,[303] these compounds have a constitution analogous to that of the hydrocarbon brexane; **78a–c** are thus 2,4,5,8,9-pentaorganotricyclo[4.3.0.0^{3,7}]nonaphosphanes. According to an MNDO calculation of the ΔH°_f values of *a*-P_9H_5 and *b*-P_9H_5 (−54.5 and 58.7 kcal mol^{-1}, respectively),[304] the *b* isomer has the larger relative stability, in contrast to the carbocyclic analogues.[305] This is substantiated by the fact that, on stirring **77b** with aluminum chloride in THF at room temperature, evidence for a rearrangement to **78b** was obtained. Compounds **78a–c** are also each formed as a mixture of several configurational isomers. In the case of **78b**, the configurations and thus the assignments of the spin systems in the $^{31}P\{^1H\}$-NMR spectrum could be unambiguously deduced for the two major isomers of comparable abundance on the basis of the P,P long-range couplings.[303]

As shown by the results for the compound pairs **75**/**76** and **77**/**78**, the formation of constitutional isomers among the polycyclophosphanes resembles that among the polycycloalkanes. Unlike the changes of the skeletal structure within a single class of compounds with increasing spatial requirements of the substituents (see section V.D), constitutional isomers always occur when several frameworks with comparable stabilities are possible for one and the same compound.

In 1963, a tricyclo*deca*phosphane, $P_{10}Ph_6$, with an adamantane-type structure was reported[306] but this could not be confirmed in later work.[135,307] This is no longer surprising since the outstanding significance of five-membered ring structural units in the construction of polycyclophosphanes—in contrast to the polycycloalkanes—has now been recognized.[9] Thus, the compounds $P_{10}H_6$[15] and $P_{10}Pr^i_6$,[166] already identified by mass spectroscopy, would be expected to have a different structure. This assumption was fully confirmed by investigations on the decaphosphanes(6) **79a–c** which were obtained in amounts of about 3 mol % according to eq 60. Compounds **79b** and **79c** were, respectively, enriched to 38% or isolated in the pure state and unequivocally characterized as 3,4,5,8,9,10-hexaorganotricyclo[5.2.1.0^{2,6}]decaphosphanes by ^{31}P-NMR spectroscopy.[281,308] The P_{10}(6) framework is thus



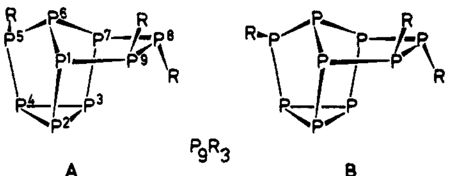
$P_{10}R_6$

79a : R = Me
79b : R = Et
79c : R = Pr^i

a conjuncto-phosphane made up of a norbornane-type P_7 unit with an annelated five-membered ring. A polycycloalkane, $C_{10}H_{16}$, with an analogous constitution[309,310] has been known for a long time; it can be transformed into the thermodynamically more stable adamantane by heating with aluminum bromide.[311] The reversed stability order in the case of the decaphosphane(6) is assumed to be due to the smaller bond angle at phosphorus in comparison to carbon. According to detailed NMR investigations on **79c**, in particular a homoscalar-correlated 2D-^{31}P{^{1}H}-NMR spectrum, the two configurational isomers **A** and **B** coexist in a ratio of 3:1 and differ solely in the spatial arrangement of the isopropyl group at P^{10}.

3. Tetracyclic Compounds: P_9R_3, $P_{10}R_4$, $P_{11}R_5$

The tetracyclo*nona*phosphanes(3) **80** represent an especially interesting class of compounds. Like the parent compound P_9H_3,[20b] the organo-substituted derivatives of P_9R_3 (**80a**, R = Me; **80b**, R = Et; **80c**, R = Pr^i; **80d**, R = Bu^t) also exhibit an excellent thermal stability and pronounced tendency for formation; thus,



P_9R_3

80a: R = Me
80b: R = Et
80c: R = Pr^i
80d: R = Bu^t

they are always formed in the thermolysis of open-chain or cyclic phosphane derivatives.[54,60,166,272,287] The compound **80b** is most conveniently prepared by the thermolysis of $(PEt)_5$ and P_4 in a molar ratio of 1:2 at 240 °C.[312] On the other hand, **80c** and **80d** are obtained by dehalogenation reactions according to eqs 59 and 58, respectively; in the case of **80d**, a short thermolysis at 300 °C suffices to further enrich the compound in the product mixture.[280,312] A preparatively more efficient access to **80d** is the cleavage of P_4 by Na/K alloy and subsequent reaction of the phosphide mixture with Bu^tPCl_2.[313] The stepwise construction of mixed alkyl-substituted nonaphosphanes(3) of the type $P_9(Bu^t)_2R$ (**69**) has been described in section V.B.

Compounds **80b** and **80c** are lemon-yellow, highly viscous oils, whereas **80d** forms pale yellow crystals that are only slightly sensitive toward oxidation. As shown by their ^{31}P{^{1}H}-NMR spectra, all compounds investigated have the same structural framework. Spectral interpretations[280] and, above all, complete analyses of the ^{31}P{^{1}H}-NMR spectra of **80b** and **80d**,[312] reveal that the nonaphosphanes(3) possess a phosphorus skeleton analogous to that of the hydrocarbon deltacyclane, i.e. they are 5,8,9-triorganotetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonaphosphanes. This constitution was confirmed by an single-crystal X-ray structure analysis of **80d** (Figure 12).[312,314] The same deltacyclane-type framework also exists as a partial structure in the polyphosphide ions $H_2P_{14}^{2-}$, P_{16}^{2-}, P_{19}^{3-}, P_{21}^{3-}, and P_{26}^{4-} (see section IV).

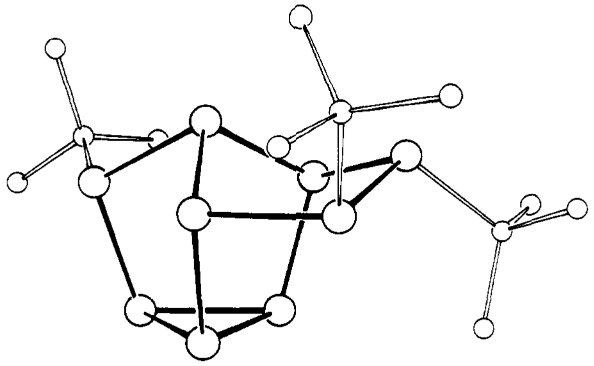


Figure 12. Molecular structure of $P_9Bu^t_3$ (**80d**) (without hydrogen atoms) in the crystal.[312,314]

The structural results demonstrate further that, for each compound, two configurational isomers **A** and **B** exist in solution in varying amounts and that they differ in the spatial orientation of the substituents to each other. The isomer ratio **A**:**B** increases with increasing size of the organic group R (**80b**, **A**/**B** = 66:34; **80d**, **A**/**B** = 80:20; both at 22 °C). As shown by the results of the X-ray structural analysis of **80d** and confirmed for the whole solid substance by cold dissolution (−40 °C) of a large number of crystals under NMR spectroscopic monitoring, the major isomer **A** separates exclusively under suitable conditions. If the solution of pure isomer **A** prepared at −40 °C is allowed to stand at 25 °C for about 30 min, the characteristic isomer population for **80d** (see above) can then again be observed in the ^{31}P{^{1}H}-NMR spectrum.[212] This finding proves that the conversion of isomer **A** into isomer **B**—which can only proceed through inversion—already occurs at an appreciable rate at room temperature.

The various inversion processes that can occur during the interconversions of the four different molecules of the enantiomer pairs **A**, **A′** and **B**, **B′** are summarized in Figure 13. The signal groups A–I (for the molecules **A** and **A′**) and a–i (for the molecules **B** and **B′**) and their assignments to the respective phosphorus nuclei 1–9 are listed under each of the configurational isomers. As can be seen, the observed transformation of the isomer **A** into the isomer **B** can result from an inversion at P^5 or by simultaneous inversions at P^8 and P^9. The latter process, however, leads to the enantiomer **B′** which cannot be differentiated in the 1D-^{31}P-NMR spectrum. Simultaneous inversions at all three organic substituted P atoms (P^5, P^8, P^9) convert each molecule into its corresponding enantiomer. A differentiation between all possible processes can be achieved with the help of a two-dimensional ^{31}P{^{1}H}-NMR exchange spectrum;[315] here the magnetization transfers associated

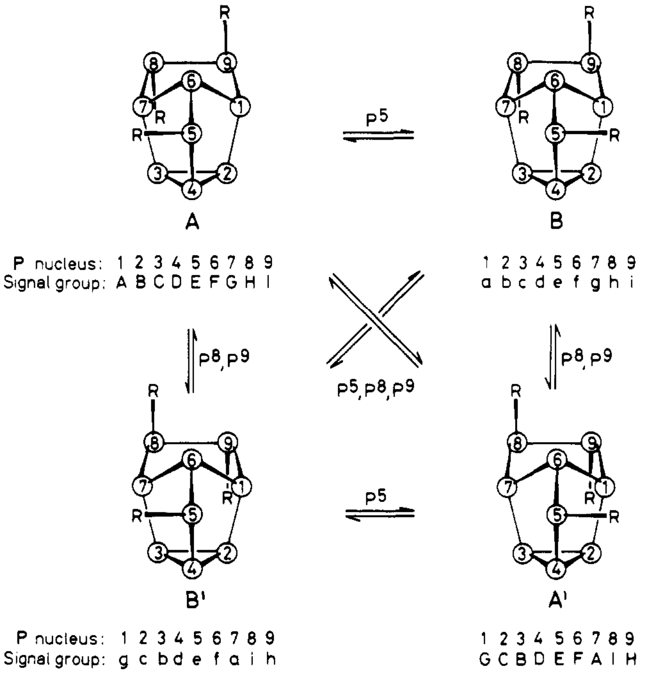


Figure 13. Possible inversion processes for the configurational isomers of P_9R_3 (**80**).

with the resonance shifts of the individual P nuclei are each visible as two cross peaks between the involved signal groups. As can be seen from the corresponding exchange spectrum of **80d**,[312] the dominating process is the configuration inversion at P^5, followed by quasi-synchronous inversions at P^8 and P^9, and also possibly at P^5, P^8, and P^9.[316] The activation parameters for the first two processes were determined from a line-shape analysis of the ^1H-NMR spectra of **80d**; the third process could not be considered for methodological reasons.[317]

inversion at P^5:

$$\Delta H^{\ddagger} = 18.5 \pm 2 \text{ kcal mol}^{-1}$$

$$\Delta S^{\ddagger} = -9.3 \pm 0.5 \text{ kcal mol}^{-1}$$

inversion at P^8 and P^9:

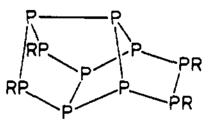
$$\Delta H^{\ddagger} = 30.1 \pm 2 \text{ kcal mol}^{-1}$$

As expected, the enthalpy of activation for the second process is considerably larger than that for the first since inversion at adjacent nuclei will inevitably lead to steric interactions between the two *tert*-butyl groups.[318] The value for the first process is about half the size of that for PH_3[319] and lies in the range of the inversion barriers for open-chain organophosphanes with P–P bonds in their molecular skeletons.[320]

The observation that the ethyl compound **80b**—irrespective of its method of formation—always exhibits the same isomer ratio in solution at room temperature (see above) is a first indication for a thermodynamic equilibrium between the two isomers. Indeed, the same inversion processes as for **80d** could also be demonstrated for **80b** by 1D- and 2D-NMR investigations.[312] However, they proceed at lower rates than those of **80d** under identical conditions; this is in accord with the general rule that bulky substituents lower the barrier to inversion.[320]

Following this first evidence for inversion at phosphorus in polycyclophosphanes of the series P_9R_3,[312] corresponding configurational changes were also observed under mild conditions for other polycyclic organophosphanes such as $P_{11}Pr^i_3$, $P_{12}Pr^i_4$, $P_{13}Pr^i_5$, and $P_{14}Pr^i_4$ (see sections V.C.4 and V.C.5). Thus it is apparent that these highly compact cage molecules exhibit a remarkable dynamic behavior.

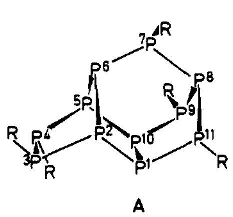
Together with the tricyclooctaphosphanes *a*-P_8R_4 (section V.C.2), small amounts of the corresponding tetracyclo*deca*phosphanes(4) **81a–c** are always formed in dehalogenation reactions according to eqs 58–60. Of these, **81c** has been enriched to the extent of about 15%.[281] Its structure as 4,5,9,10-tetraisopropyltetracyclo[5.2.1.0^{2,6}.0^{3,8}]decaphosphane was confirmed by ^{31}P-NMR spectroscopy and can be derived from that of the bisnoradamantane-type *a*-$P_8Pr^i_4$ isomer by the addition of a two-atom bridge with formation of a new five-membered ring. The compounds **81a** and **81b** should have the same structure since small substituents favor the five-membered ring unit and the organic groups (in a maximal *trans* orientation) do not experience any steric hindrance.



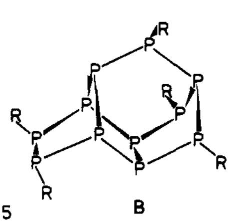
$P_{10}R_4$

81a: R = Me
81b: R = Et
81c: R = Pr^i

The tetracyclo*undeca*phosphanes(5) $P_{11}R_5$ (**82a**, R = Me; **82b**, R = Et; **82c**, R = Pr^i) are usually formed together with the tricyclononaphosphanes *a*-P_9R_5 (section V.C.2) and have been enriched to 60, 85, and 35%, respectively.[281] Just recently, the preparation of **82c** as a pale yellow, highly viscous oil in 91% purity and its complete structural characterization were reported.[321] This enabled the constitution as a 3,4,7,9,11-pentaorganotetracyclo[6.2.1.0^{2,6}.0^{5,10}]undecaphosphane with a P_{11}(5) skeleton analogous to that of the hydrocarbon 2,8-ethanonoradamantane[322]—as previously deduced from qualitative interpretations of the $^{31}P\{^1H\}$-NMR spectra of **82a–c**[281]—to be confirmed. Furthermore, the existence of two configurational isomers of **82c** in a ratio of **A**:**B** $\simeq$ 3:1 was demonstrated by 2D ^{31}P- and ^{13}C-NMR spectroscopy. These isomers differ in the spatial arrangement of the isopropyl groups on the two-atom bridge atoms (P^3, P^4). The "propeller-like" arrangement of the substituents around P^8 is characteristic for the noradamantane-type P_9 partial structure (see also section V.C.7).



A



$P_{11}R_5$

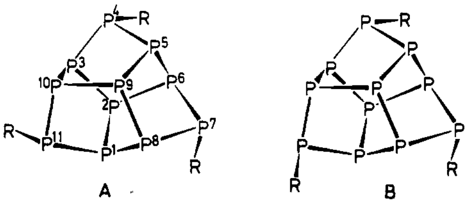
B

82c: R = Pr^i

4. Pentacyclic Compounds: $P_{11}R_3$, $P_{12}R_4$, $P_{13}R_5$, $P_{14}R_6$

The isopropyl derivatives are especially suitable for investigations of phosphorus-rich organopolycyclophosphanes. On the one hand, they have the typical skeletal structures of the sterically unhindered members of the individual classes of compounds (see section V.D); on the other hand, they are more soluble than the corresponding methyl and ethyl compounds and, accordingly, more easily isolated and characterized by spectroscopic methods. In addition, the larger isopropyl groups exert a kinetic stabilization on the phosphorus-rich $P_n(m)$ skeletons. The higher-cyclic, alkyl-poor isopropylphosphanes described in sections V.C.4–7 were all prepared by dehalogenation reactions according to eq 60 and subsequent thermolysis of the primarily formed product mixtures (section V.B).

The pentacyclic triisopropyl*undeca*phosphane(3) (**83**) is present in the thermolysate of the crude product only to the extent of about 1 mol % but can be isolated in the pure state as bright yellow crystalline needles.[323] Analysis of the 2D-^{31}P{^{1}H}-NMR spectrum revealed that the compound is 4,7,11-triisopropylpentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecaphosphane which exists in solution as the two isomers **A** and **B** in the statistically expected ratio of 1:3 with symmetrical and unsymmetrical, respectively, arrangements of the isopropyl substituents. According to the X-ray structural analysis, only the major isomer **B** is present in the crystal state and which, upon redissolution, reverts to the characteristic isomeric mixture of **A** and **B** by inversion (see section V.C.3). As can be seen from a comparison of the isomerization conditions (temperature and time) with those for $P_9Bu^t_3$ (**80d**), the barrier to inversion is noticeably higher for **83**. Some of the observed bond lengths and angles in **83** show considerable deviations from the normal values.[135] This is indicative of a considerable strain in the $P_{11}(3)$ skeleton made up of six five-membered ring units; this fact could also account for the low tendency for formation. The undecaphosphane(3) $P_{11}(SiMe_3)_3$, prepared from Na_3P_{11}[325] and Me_3SiCl, has the same constitution and also exists in the solid state only as the asymmetrical isomer, as shown by an X-ray structural analysis.[326]



$P_{11}R_3$; R = Pr^i
83

The pentacyclo*dodeca*phosphanes(4) **84a–d** are formed in larger amounts than **83** and **84c** can be isolated as light-yellow, crystal platelets.[327,328] As shown by a single-crystal analysis (Figure 14), the $P_{12}(4)$ skeleton is made up of two annelated norbornane-type $P_7(5)$ partial structures linked by a zero-atom bridge. Accordingly, compound **84c** is 3,4,9,10-tetraisopropylpentacyclo[6.4.0.0^{2,6}.0^{5,12}.0^{7,11}]dodecaphosphane. The bond lengths and angles of the phosphorus skeleton show appreciable differences; in particular, the zero-atom bridging bonds of the central $P_8(4)$ unit are lengthened considerably. This is indicative of the significant strain in this structural element, a fact that is also reflected in the low tendency for formation of the compounds α-P_8R_4 (section V.C.2) and $P_{10}R_4$ (section V.C.3). According to NMR spectroscopic studies, a further isomer **B** with C_s symmetry exists in solution in addition to the isomer **A** with C_2 symmetry present in the crystal state (ratio **A**/**B** = 3:2). Upon dissolution of the pure isomer **A**, a partial transformation to the isomer **B** takes at a remarkable rate place even below room temperature.

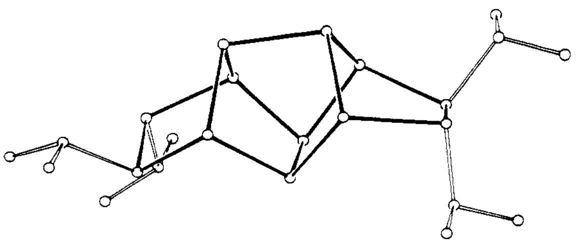
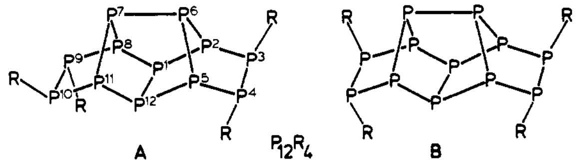


Figure 14. Molecular structure of $P_{12}Pr^i_4$ (**84c**) (without hydrogen atoms) in the crystal.[327,329]



84a: R = Me
84b: R = Et
84c: R = Pr^i
84d: R = Bu^t

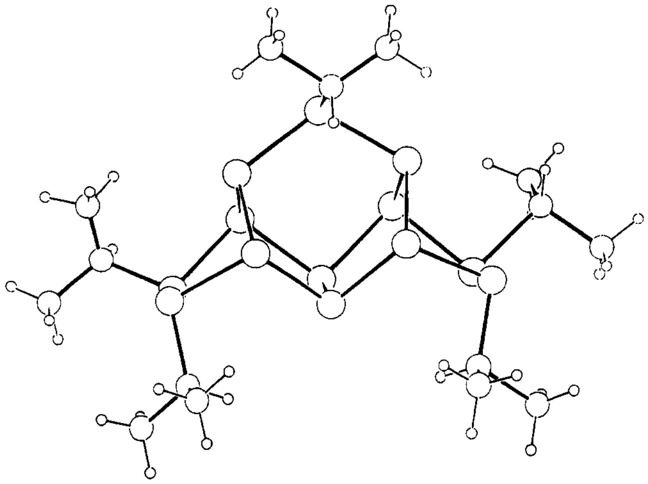


Figure 15. Molecular structure of $P_{13}Pr^i_5$ (**85c**) in the crystal.[330]

The pentacyclo*trideca*phosphanes(5) **85a–d** are always formed together with the pentacyclododecaphosphanes(4); compound **85c** has been isolated in the form of colorless, crystalline needles.[327,330] An X-ray structural analysis (Figure 15) has shown that the $P_{13}(5)$ skeleton has a structure derived from the noradamantane-type α-$P_9(5)$ skeleton by condensation of two P_2 bridges with concomitant formation of two new five-membered rings. The constitution can also be described either as the annelation of two heptaphosphanorbornane units which are also linked by an additional one-atom bridge or as the insertion of a phosphorus atom into the P^6–P^7 zero-atom bridge of the $P_{12}(4)$ skeleton.

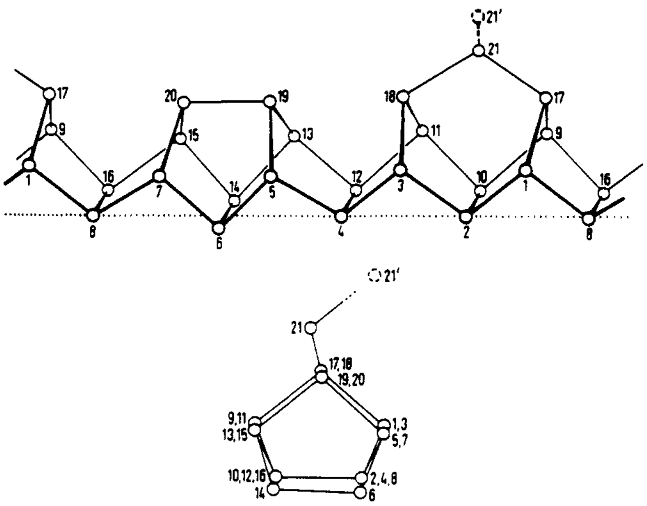
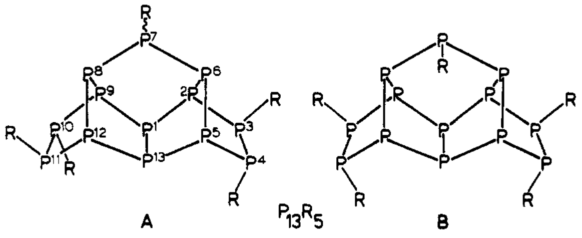


Figure 16. Part of a tube of Hittorf's phosphorus: (above) perspective view; (below) view in the direction of the tube's axis.[263]

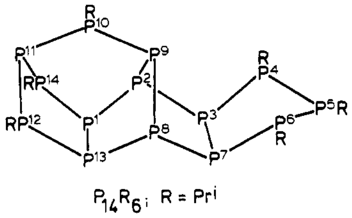
Hence, **85c** is 3,4,7,10,11-pentaisopropylpentacyclo-[7.4.0.0^{2,6}.0^{5,13}.0^{8,12}]tridecaphosphane. The $P_{12}(4)$ and $P_{13}(5)$ skeletons are essential structural units of Hittorf's phosphorus (Figure 16);[263] this accounts for the appreciable tendencies for formation and the high thermal stabilities of the compounds **84** and **85**. The tridecaphosphanes(5) **85** contain the most phosphorus-rich, unchanged partial structure of the element phosphorus in the form of a discrete molecule known to date. Detailed NMR studies of **85c** have shown that it exists in solution as two configurational isomers **A** and **B** with the symmetries C_1 and C_s, respectively, in a ratio of approximately 2:1. Isomer **B** corresponds to the form existing in the crystal state (Figure 15) which, in solution at room temperature, is transformed to a large extent into the isomer **A**. A further symmetrical isomer was not detected, hence the barrier to inversion at the atom P^7 in the isomer **B** must be considerably higher than those at the atoms P^3 and P^4 or P^{10} and P^{11}, respectively.



$P_{13}R_5$

85a: R = Me
85b: R = Et
85c: R = Pr^i
85d: R = Bu^t

A further pentacyclic organophosphane, hexaisopropyl*tetradeca*phosphane(6) (**86**), has been enriched to approximately 30%[331] and its structure elucidated as 3,4,5,9,11,14-hexaisopropylpentacyclo[9.2.1.0^{2,9}.0^{3,7}.0^{8,13}]tetradecaphosphane by ^{31}P-NMR spectroscopy. This structure can be derived from that of the undecaphosphane **82c** by the addition of an isopropyl-substituted P_3 bridge which completes the formation of a new five-membered ring. No experimentally substantiated information on the configuration is as yet available.



$P_{14}R_6$; R = Pr^i
86

5. Hexacyclic Compounds: $P_{14}R_4$

The hexacyclo*tetradeca*phosphane(4) **87** is present in the thermolysate of the crude product obtained according to eq 60 to the extent of approximately 3 mol % and has been isolated in the form of yellow, crystalline needles.[282,332] As revealed by an X-ray crystal structure analysis (Figure 17), the chiral $P_{14}(4)$ skeleton is built up of two norbornane-type $P_7(5)$ units linked by three zero-atom bridges (P^1–P^8, P^6–P^7, P^{13}–P^{14}) in such a manner that a central six-membered ring (P^5,P^6,P^7,P^{12},P^{13},P^{14}) is formed. Compound **87** is thus 3,4,10,11-tetraisopropylhexacyclo[6.6.0.0^{2,6}.0^{5,14}.0^{7,12}.0^{9,13}]tetradecaphosphane. The lengths of the P–P bonds vary between 2.186 (P^1–P^8, P^8–P^9) and 2.269 Å (P^1–P^{14}). Channels are formed on packing the molecules into crystals and these can take up varying amounts of the solvent (THF), which is given off on heating above 90 °C or under high vacuum to leave an insoluble solid.

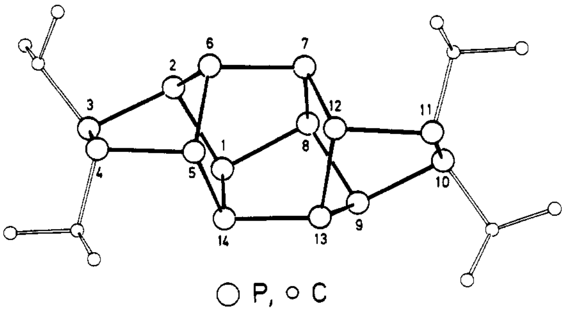
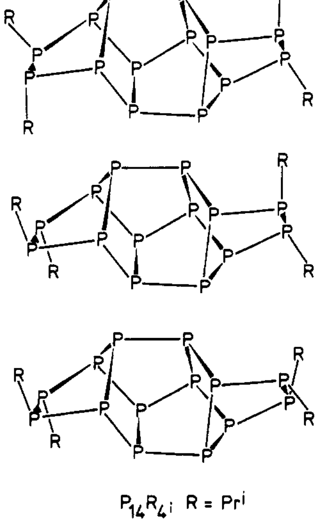


Figure 17. Molecular structure of $P_{14}Pr^i_4$ (**87**) (without hydrogen atoms) in the crystal.[332]



$P_{14}R_4$; R = Pr^i
87

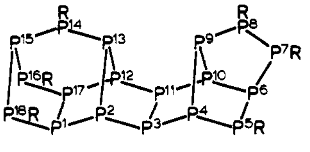
When the THF-containing crystals are dissolved in the same solvent in the cold and the solution is warmed to

+10 °C, two further isomers **B** and **C** can be detected in the $^1H\{^{31}P\}$-NMR and $^{13}C\{^1H,^{31}P\}$-DEPT NMR spectra in addition to the isomer **A** present in the crystal state. Isomer **B** differs from isomer **A** by inversion at P^3 and P^4 or P^{10} and P^{11}, respectively, while **C** differs through configuration reversals at all isopropyl-substituted phosphorus atoms. And after about 15 min, the typical isomer population of **A**/**B**/**C** ≈ 4:4:1 for **87** is reached. As can be seen from a comparison of the isomerization conditions, the barrier to inversion for **87** is lower than that for $P_{11}Pr^i_3$ (**83**), higher than that for $P_9Bu^t_3$ (**80d**), and similar to that for $P_{12}Pr^i_4$ (**84c**).

A further tetradecaphosphane(4), $P_{14}(SiMe_3)_4$, was obtained as a byproduct in the synthesis of $P_7(SiMe_3)_3$ (**53**) but was not further characterized structurally.[236] The molecule is assumed to be made up of two nortricyclene-type $P_7Pr^i_2$ units linked together through a σ-bond.

6. Heptacyclic Compounds: $P_{18}R_6$

Although the heptacyclo*octadeca*phosphane(6) **88** is only present to about 0.6 mol % in the thermolysate of the crude product, it can be enriched in the fractions of the higher-cyclic isopropylphosphanes by chromatographic workup and has been isolated in the pure state as a bright yellow solid.[333] NMR spectroscopic investigations reveal that **88** has a conjuncto-phosphane skeleton made up of a $P_{11}(5)$ and a brexane-type *b*-$P_9(5)$ element annelated at their P_2 bridges, thus forming a central, pentalane-type $P_8(6)$ partial structure as is also present in Hittorf's phosphorus. Hence, compound **88** is 5,7,8,14,16,18-hexaisopropylheptacyclo[13.2.1.$0^{2,13}$.$0^{3,11}$.$0^{4,9}$.$0^{6,10}$.$0^{12,17}$]octadecaphosphane. A $C_{18}H_{24}$ polycycloalkane with a constitution analogous to that of **88** has not yet been reported. The $^{13}C\{^1H,^{31}P\}$-DEPT NMR spectrum and HPLC chromatogram of **88** indicate that two isomers with C_1 symmetry exist in solution in a ratio of approximately 2:1. However, no experimentally substantiated conclusions can yet be made about the configurations. Even so, it may be assumed that in both molecules the isopropyl groups at P^{14}, P^{16}, and P^{18}—like in $P_{11}Pr^i_5$ (section V.C.3)—are arranged in a "propeller-like" manner around P^{15} and those at P^7 and P^8—as in *b*-P_9R_5 (section V.C.2)—have a *trans* orientation. The two isomers presumably differ through configuration reversals at the $(PR)_2$ bridge of the brexane-type $P_9(5)$ partial structure.



$P_{18}R_6$; R = Pr^i

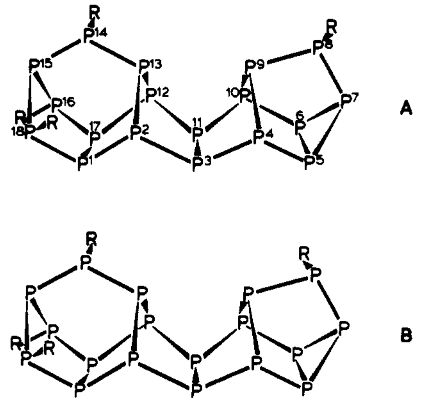
88

7. Octacyclic Compounds: $P_{16}R_2$, $P_{18}R_4$, $P_{20}R_6$

The octacyclo*hexadeca*phosphanes(2) **89a** and **89b** were obtained in high yield by direct alkylation of the corresponding polyphosphide **54** (section IV.B) under suitable conditions.[252] Their constitutions were confirmed by the similarities of their molecular vibrational spectra with those of **54** and by their mass spectral fragmentation patterns. Accordingly, compounds **89** contain the same conjuncto-phosphane skeleton made up of two annelated $P_9(3)$ elements as the phosphide **54** and, hence, are 4,12-dialkyloctacyclo[7.7.0.$0^{2,6}$.$0^{3,8}$.$0^{5,7}$.$0^{10,14}$.$0^{11,16}$.$0^{13,15}$]hexadecaphosphanes. ^{31}P-NMR spectroscopic investigations have not yet been possible because of their limited solubilities and thus experimentally confirmed conclusions on their configuration are not available. However, the two organic groups probably have a *trans* orientation to each other in analogy to the structurally related henicosaphosphide $NaP_{21}Et_2$ (**58b**).

$$\begin{array}{llll} \underset{\mathbf{54}}{Li_2P_{16}} + 2RBr \rightarrow & P_{16}R_2 & + 2LiBr & (62) \\ & \mathbf{89a}\text{: } R = Me & & \\ & \mathbf{b}\text{: } R = Et & & \end{array}$$

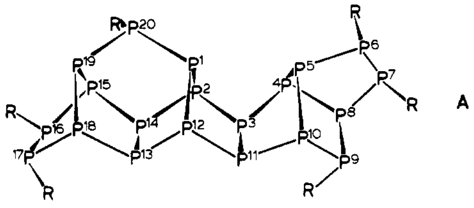
The octacyclo*octadeca*phosphane(4) **90** was obtained in 95% purity by the "standard procedure" (dehalogenation according to eq 60, subsequent thermolysis, and separation of the thermolysate).[334] The bright yellow solid has properties very similar to those of $P_{18}Pr^i_6$ (**88**) (section V.C.6) and $P_{20}Pr^i_6$ (**91**) (see below) but, in contrast to these compounds, exhibits three signal groups in the ^{31}P-NMR spectrum at $\delta = -94, -141$, and -154 in the high-field region typical for three-membered phosphorus rings. A complete structure elucidation on the basis of a 2D-$^{31}P\{^1H\}$-NMR spectrum revealed that the $P_{18}(4)$ skeleton of **90** consists—like the $P_{18}(6)$ skeleton of **88**—of a $P_{11}(5)$ structural element which, in the case of **90**, is annelated to a deltacyclane-type $P_9(3)$ unit. Hence, compound **90** is 8,14,16,18-tetraisopropyloctacyclo[13.2.1.$0^{2,13}$.$0^{3,11}$.$0^{4,9}$.$0^{5,7}$.$0^{6,10}$.$0^{12,17}$]octadecaphosphane. A $C_{18}H_{22}$ polycycloalkane with an analogous constitution is still unknown. The more alkyl-rich octadecaphosphane **88** can be formally converted into the less alkyl-rich octadecaphosphane **90** by formation of a P–P bond between the atoms P^5 and P^7 with concomitant removal of the alkyl groups and formation of the three-membered ring in the $P_9(3)$ partial skeleton. Compound **90** exists in solution as a mixture of the isomer **A** and a further isomer **B** of considerably lower abundance. Isomer **B** differs from isomer **A** by a configuration reversal at P^8. An analogous isomerism also occurs with the nonaphosphadeltacyclanes P_9R_3 (**80**) (section V.C.3).



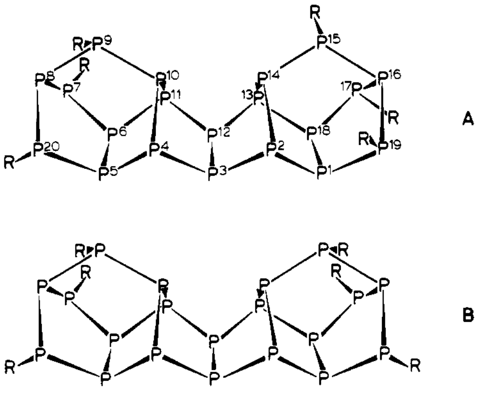
$P_{18}R_4$; R = Pr^i

90

Presently, the most phosphorus-rich, polycyclic organophosphane to be obtained in a practically pure state and completely characterized structurally is the octacyclo*icosa*phosphane(6).[335] This compound does not occur in the primary products of reaction 60 but is present in the thermolysate to the extent of about 0.9 mol %. It is formed as a 1:1 mixture of the two constitutional isomers *a*-$P_{20}Pr^i_6$ (**91**) and *b*-$P_{20}Pr^i_6$ (**92**)



a-$P_{20}R_6$; R = Pr^i
91



b-$P_{20}R_6$; R = Pr^i
92

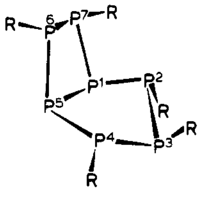
which each exist in solution as two configurational isomers **A** and **B**. Compound **91** was obtained as a mixture of the diastereomers (ratio **A**/**B** ≈ 4:1) in 98% purity; compound **92** was isolated in the form of the separated configurational isomers (ratio **A**/**B** = 2.5:1) in 85% and 90% purity, respectively. According to detailed NMR studies, in particular 2D-$^{31}P\{^1H\}$-spectroscopy, the $P_{20}(6)$ skeleton of **91** consists of a $P_{13}(5)$ unit and a brexane-type *b*-$P_9(5)$ group annelated at the P_2 bridges. In the case of **92**, the skeleton is made up of two $P_{11}(5)$ elements—such as those occurring also in the octadecaphosphanes **88** and **90**. Hence, **91** is 6,7,9,16,17,20-hexaisopropyloctacyclo[$10.8.0.0^{2,14}.0^{3,11}.0^{4,8}.0^{5,10}.0^{13,18}.0^{15,19}$]icosaphosphane and **92** is 7,9,15,17,19,20-hexaisopropyloctacyclo[$14.2.1.1^{5,8}.0^{2,14}.0^{3,12}.0^{4,10}.0^{6,11}.0^{13,18}$]icosaphosphane. $C_{20}H_{26}$ polycyclic hydrocarbons with constitutions analogous to those of **91** and **92** are still unknown. The constitutional isomer **91** differs from $P_{18}Pr^i_6$ (**88**) by the presence of an additional, isopropyl-substituted P_2 bridge which completes the formation of a new five-membered ring annelated over three phosphorus atoms. The noradamantane-type *a*-$P_9(5)$ and the pentalane-type $P_8(6)$ structural units are characteristic for **91** and **92** as well as for the octadecaphosphanes **88** and **90**. These units are also structural elements of Hittorf's phosphorus and apparently have a pronounced tendency for formation. The configuration of the minor isomer **B** of **91** has not yet been determined with certainty but probably differs from that of the major isomer **A** by configuration reversals at P^6 and P^7 or at P^{16}, P^{17}, and P^{20}. In both cases, the isopropyl groups at P^6 and P^{20} would be on the "same side of the molecule"—in contrast to the isomer **A**—and this would account for the lower relative abundance of the isomer **B**. In the case of **92**, the major isomer **A** has C_2 symmetry and an *all-trans* arrangement of the organic groups, whereas the isomer **B** has C_s symmetry as a consequence of configuration reversals at the three isopropyl-substituted phosphorus atoms of one $P_{11}(5)$ structural element.

D. *tert*-Butyl-Substituted Polycyclophosphanes

The already clarified structures of polycyclic organophosphanes P_nR_m have demonstrated that the typical skeletal structures of the individual classes of compounds remain unchanged upon variation of the substituents within the range of relatively small alkyl groups (R = Me to R = Pr^i). However, this is no longer valid on going from R = Pr^i to R = Bu^t. As a consequence of steric interactions between the substituents, especially in the case of bi- and tricyclic *tert*-butylphosphanes, significant changes often occur in the phosphorus skeletal structures. Furthermore, the steric shielding of the $P_n(m)$ framework by the bulky *tert*-butyl groups effects a kinetic stabilization of those phosphorus skeletons which could otherwise not exist on account of their high reactivities. For these reasons, unexpected structures are frequently encountered among the alkyl-rich, *tert*-butyl-substituted polycyclophosphanes. The preparations of *tert*-butylpolycyclophosphanes discussed in the following sections V.D.1 to V.D.3 were carried out in the same manner as the syntheses of compounds bearing smaller alkyl groups (section V.B).

1. Bicyclic Compounds: $P_7Bu^t_5$, $P_8Bu^t_6$, $P_9Bu^t_7$, $P_{10}Bu^t_8$

On the basis of detailed NMR studies and in contrast to the pentaorganobicyclo[2.2.1]heptaphosphanes **73a–c** (section V.C.1), penta-*tert*-butyl*hepta*phosphane(5) (**93**) has a novel $P_7(5)$ skeleton composed of a five-membered ring and an annelated four-membered ring. Thus, compound **93** is 2,3,4,6,7-penta-*tert*-butylbicyclo[3.2.0]heptaphosphane.[336] The large, positive $^2J(P^4,P^6)$ coupling constant indicates that the four-membered ring is considerably angled toward the five-membered ring and that the Bu^t group at P^6 has an *exo* orientation. As a result of steric interactions between the substituents in the 3- and 7-positions, the four-membered ring and the five-membered ring are twisted relative to each other at the zero-atom bridge P^1–P^5 and this results in a folding of the four-membered ring. In contrast to the polycyclophosphanes with smaller organic groups, **93** exists in solution as a *single* configurational isomer.



P_7R_5; R = Bu^t
93

Hexa-*tert*-butyl*octa*phosphane(6) (**94**), prepared by dehalogenation according to eq 58 or by cyclocondensation of 1,2,3-tri-*tert*-butyltriphosphane with diphosphorus tetraiodide according to eq 13,[56] exhibits

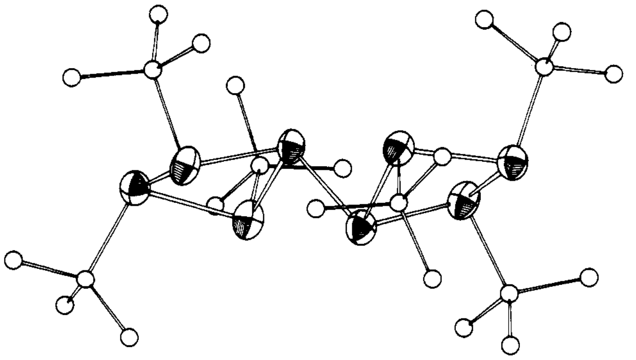
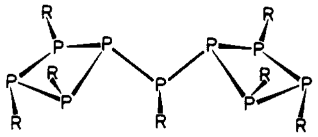


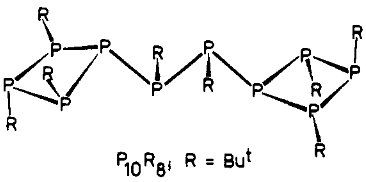
Figure 18. Molecular structure of $P_8Bu^t{}_6$ (**94**) (without hydrogen atoms) in the crystal.[56]

remarkable structural differences in comparison to the hexaorganobicyclo[3.3.0]octaphosphanes **74a–c** (section V.C.1). As confirmed by spectroscopic results and a single-crystal X-ray analysis (Figure 18), **94** has the structure of a 2,2′,3,3′,4,4′-hexa-*tert*-butyl-1,1′-bicyclotetraphosphane in which two four-membered phosphorus rings are linked together by a σ-bond. All P–P bond lengths in the nonplanar four-membered rings and in the bridge are almost identical. On the other hand, the arsenic analogue $As_8Bu^t{}_6$ [56] has the same pentalane-type structure as the sterically unperturbed octaphosphanes(6).

The same structural principle as for **94** is also realized in the next higher homologues of the compound class $P_nBu^t{}_{n-2}$ with 9 and 10 phosphorus atoms in the molecule. The NMR spectra of the *nona*phosphane **95** and the *deca*phosphane **96** indicate that, in the former case, one $>PBu^t$ group and, in the latter case, a diphosphane chain consisting of two $>PBu^t$ groups has been inserted between the two *tert*-butyl-substituted P_4 rings.[337] Compound **95** is thus bis(2,3,4-tri-*tert*-butylcyclotetraphosphanyl)-*tert*-butylphosphane and **96** is 1,2-bis(2,3,4-tri-*tert*-butylcyclotetraphosphanyl)-1,2-di-*tert*-butyldiphosphane; the latter exists exclusively in the *meso* form.



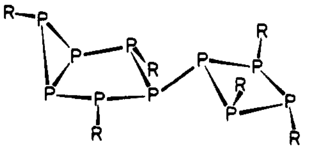
P_9R_7; R = Bu^t
95



$P_{10}R_8$; R = Bu^t
96

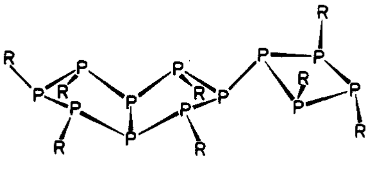
2. Tricyclic Compounds: $P_{10}Bu^t{}_6$, $P_{12}Bu^t{}_8$, $P_{13}Bu^t{}_9$

According to detailed NMR spectroscopic investigations, hexa-*tert*-butyl*deca*phosphane(6) (**97**), obtained in the pure state according to eq 58,[338] has a different constitution to the compound **17** with the same composition (section II.D.1) obtained from $(PBu^t)_2$-$PSnMe_3$ (**14**) and PCl_3. The $P_{10}(6)$ skeleton of **97** also differs from that of the decaphosphanes(6) **79a–c** (section V.C.2) bearing smaller alkyl groups. It is built up of a bicyclic $P_6(4)$ and a monocyclic $P_4(4)$ partial structure joined together through a σ-bond. The unusual constitution of **97** as 2,4,6-tri-*tert*-butyl-3-(2,3,4-tri-*tert*-butylcyclotetraphosphanyl)bicyclo[3.1.0]-hexaphosphane is understandable in the light of the fact that the *tert*-butylphosphanes $P_6Bu^t{}_4$ (**72b**) and $(PBu^t)_4$ are among the main products of reaction 58. The existence of three different $P_{10}(6)$ skeletons demonstrates that the structures of polycyclic organophosphanes P_nR_m are determined both by the synthetic route and by the spatial requirements of the substituents.

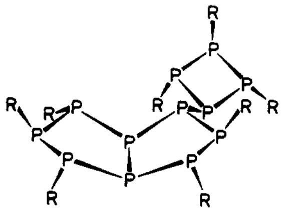


$P_{10}R_6$; R = Bu^t
97

The octa-*tert*-butyl*dodeca*phosphane(8), which is preferentially formed on thermolysis of the bicyclohexaphosphane **72b**, also consists of a bicyclic partial skeleton with a σ-bonded P_4 ring. It is formed as a mixture of the constitutional isomers *a*-$P_{12}Bu^t{}_8$ (**98**) and *b*-$P_{12}Bu^t{}_8$ (**99**) in almost equal amounts; the isomers differ in the type of linkage of the two structural elements and can be separated by chromatography.[339] 2D-$^{31}P\{^1H\}$-NMR spectroscopy reveals that **98** is 2,4,6,7,8-penta-*tert*-butyl-3-(2,3,4-tri-*tert*-butylcyclotetraphosphanyl)bicyclo[3.3.0]octaphosphane, whereas the isomer **99**, with approximately the same stability, has the $P_4Bu^t{}_3$ substituent in the 2-position. The cyclotetraphosphanyl substituent apparently exerts a lower steric stress on the pentalane-type $P_8(6)$ skeleton than does a further *tert*-butyl group (see section V.D.1); this may be attributable to the different lengths of P–P and P–C bonds.

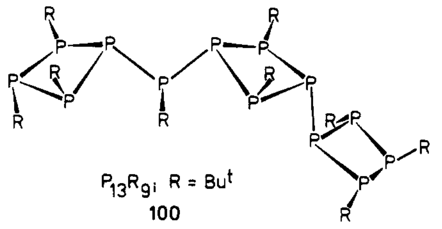


a-$P_{12}R_8$; R = Bu^t
98



b-$P_{12}R_8$; R = Bu^t
99

The structure deduced for nona-*tert*-butyl*trideca*phosphane(9) (**100**), the next higher homologue in the compound class $P_nBu^t{}_{n-4}$, by NMR spectroscopy is surprising.[340] The molecule is constructed from the bicyclic compounds $P_9Bu^t{}_7$ (**95**) and $P_8Bu^t{}_6$ (**94**) in such a way that the middle ring is shared by both partial structures. Compound **100** is thus 3-[*tert*-butyl(2,3,4-tri-*tert*-butylcyclotetraphosphanyl)phosphino]-



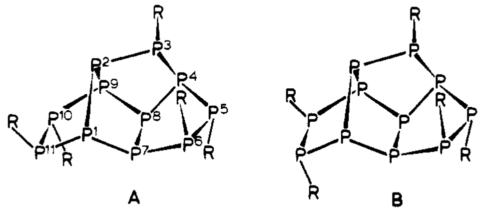
$P_{13}R_9$; R = Bu^t

100

2,2′,3′,4,4′-penta-*tert*-butyl-1,1′-bicyclotetraphosphane, i.e. the first organophosphane to contain three P_4 rings linked together by σ-bonds either directly or through an exocyclic phosphino group. The configuration of **100** was deduced from its 2D-$^{31}P\{^1H\}$-NMR spectrum.

3. Tetracyclic Compounds: $P_{11}Bu^t_5$

Of the tetracyclic *tert*-butylphosphanes investigated to date, tri-*tert*-butyl*nona*phosphane(3) (**80d**) possesses the same deltacyclane-type structure as the nonaphosphanes P_9R_3 **80a–c** with smaller alkyl groups (section V.C.3). In contrast, penta-*tert*-butyl*undeca*phosphane(5) (**101**) differs significantly from the previously known undecaphosphanes $P_{11}R_5$ **82a–c** (section V.C.3), as revealed by NMR spectroscopic studies. Thus, the $P_{11}(5)$ skeleton in **101** is not derived from the nonaphosphane with the noradamantane-type structure (*a*-P_9R_5, **77**) but rather from the constitutionally isomeric nonaphosphane with the brexane-type structure (*b*-P_9R_5, **78**).[341] The construction principle, however, is the same in both cases, namely the condensation of a two-atom bridge with formation of a new five-membered ring. Hence, compound **101** is 3,5,6,10,11-penta-*tert*-butyltetracyclo[5.4.0.0^{2,9}.0^{4,8}]undecaphosphane. It exists in solution as a mixture of the configurational isomers **A** and **B** in a ratio of approximately 1.25:1; the isomers differ in the spatial arrangement of the *tert*-butyl groups at P^{10} and P^{11}.



$P_{11}R_5$; R = Bu^t

101

4. Conclusions

The structures of alkyl-rich, polycyclic *tert*-butylphosphanes cannot be classified in a general construction plan similar to that for the sterically unperturbed polycyclophosphanes with smaller alkyl substituents (see section V.F). The formation of molecules in which the partial structural units are joined together through σ-bonds is typical for bi- and tricyclic *tert*-butylphosphanes. In spite of the unfavorable endocyclic bonding angles in comparison to P_5 rings, P_4 rings are formed with particular frequency. The sterically favored *all-trans* orientation of the substituents to each other and to the "σ-linked" molecular components can be achieved in this way. P_5 rings are only found within annelated ring systems such as those in $P_6Bu^t_4$ (**72b**), $P_7Bu^t_5$ (**93**), $P_{10}Bu^t_6$ (**97**), $P_{12}Bu^t_8$ (**98**, **99**), or $P_{11}Bu^t_5$ (**101**) since, in these cases, a *trans* arrangement of the remaining *tert*-butyl groups on the five-membered ring is possible.

In the alkyl-poor, tetracyclic compound $P_{11}Bu^t_5$ (**101**), naturally no σ-linked four-membered ring units like those in the bi- and tricyclic *tert*-butylphosphanes with eight or more phosphorus atoms are possible. As a necessary alternative, a somewhat modified $P_{11}(5)$ skeleton in comparison to that of the other $P_{11}R_5$ compounds **82a–c** is formed. This framework contains a P_7 ring as a structural element of a polycyclophosphane for the first time. On the other hand, all tetracyclic nonaphosphanes P_9R_3 **80a–d** have the same deltacyclane-type structure since steric interactions between the substituents are relatively small even in the case of the *tert*-butyl compound **80d**. As these steric interactions become less important in the classes of higher-cyclic compounds, the structural differences between analogous compounds with small and bulky organic groups also disappear.

In the course of investigations on *tert*-butyl-substituted polycyclophosphanes, the further *tert*-butylpolycyclophosphanes listed below have been detected by mass spectrometry among the primary products of the dehalogenation reactions and in the thermolysis residues but further work is still needed with respect to their structural elucidations:[342] $P_{10}Bu^t_2$, $P_{11}Bu^t_9$, $P_{11}Bu^t_7$, $P_{11}Bu^t_3$, $P_{12}Bu^t_{10}$, $P_{12}Bu^t_6$, $P_{13}Bu^t_7$, $P_{13}Bu^t_3$, $P_{14}Bu^t_8$, $P_{14}Bu^t_6$, $P_{14}Bu^t_4$, $P_{15}Bu^t_9$, $P_{15}Bu^t_7$, $P_{15}Bu^t_5$, $P_{15}Bu^t_3$, $P_{16}Bu^t_{10}$, $P_{16}Bu^t_8$, $P_{16}Bu^t_6$, $P_{16}Bu^t_4$, $P_{17}Bu^t_9$, $P_{17}Bu^t_5$, $P_{17}Bu^t_3$, $P_{18}Bu^t_8$, $P_{18}Bu^t_6$, $P_{18}Bu^t_2$, $P_{19}Bu^t_9$, $P_{19}Bu^t_7$, $P_{19}Bu^t_3$, $P_{20}Bu^t_6$, $P_{21}Bu^t_7$, and $P_{21}Bu^t_3$.

E. Properties and Reactions of Polycyclic Phosphanes

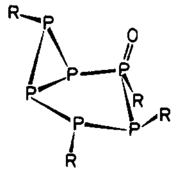
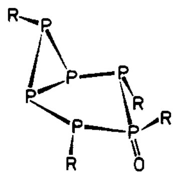
1. General Properties of Organopolycyclophosphanes

The polycyclic organophosphanes prepared in the pure state on a preparative scale are all colorless to yellow liquids or solids but only rarely crystalline. Their solubility in common solvents decreases with increasing number of phosphorus atoms and decreasing number of alkyl groups; within a particular class of compounds the solubility increases with increasing number of carbon atoms in the substituents. In the case of compounds with small organic groups, a marked decrease in solubility often occurs when the solutions are allowed to stand for some time or after complete removal of the solvent. This physical aggregation process which has not yet been clarified in detail is also the reason for the extremely poor solubility of the parent polycyclic phosphorus hydrides. The stability of organopolycyclophosphanes toward atmospheric oxygen increases with increasing number of phosphorus atoms and increasing spatial requirements of the substituents.

2. Polycyclophosphane Oxides

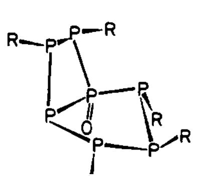
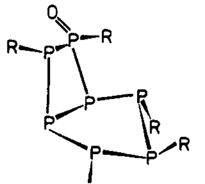
Like all other compounds of trivalent phosphorus, polycyclic phosphanes are oxidatively attacked by atmospheric oxygen. Although no visible changes can be observed when solid, phosphorus-rich compounds such as P_7H_3 (**52**) are exposed to the atmosphere, the formation of, e.g., P_7H_3O[343] can subsequently be demonstrated by mass spectrometry. Rapid oxidation of organopolycyclophosphanes generally occurs in solution, as can be seen from the appearance and increasing intensities of additional signals in the ^{31}P-NMR spectra.

It has been found that the bicyclophosphanes $P_6Bu^t_4$ (**72b**) and $P_7Bu^t_5$ (**93**) in solution react with less than a stoichiometric amount of dry air at room temperature to form the monoxides **102**/**103** or **104**/**105**, respectively.[344] When the stoichiometric amount of atmospheric oxygen is employed, the corresponding dioxides and other subsequent products are also formed. Both monoxides are produced as mixtures of two constitutional isomers (ratios **102**/**103** = 4.5:1; **104**/**105** ≈ 1:1); **102** and **103** can be separately isolated, whereas **104** and **105** cannot be separated even by high-pressure liquid chromatography. The structures have been confirmed by complete analyses of the $^{31}P\{^1H\}$-NMR spectra in addition to IR and ^{1}H-NMR data. Accordingly, in each case, the oxygen atom is bonded exocyclically to the P_n skeleton of the parent compound. The product formation is apparently controlled by steric factors. Thus, the observed isomer ratio in the case of $P_6Bu^t_4O$ is indicative that, in the starting material **72b**, the five-membered ring atom P^3 is more strongly shielded by the *tert*-butyl groups than the neighboring atoms P^2 and P^4 (statistical isomer ratio 2:1). In the case of **93**, exocyclic bonding of oxygen at P^1 and P^7 is apparently equally favored while that at P^2 or P^4 is hindered by the *endo*-orientation of the substituent at P^7. The fact that no isomers of $P_6Bu^t_4O$ are formed with oxygen on the three-membered ring may be attributed to the predominant s character of the free electron pairs of the respective atoms in **72b**.



P_6R_4O; R = Bu^t

102

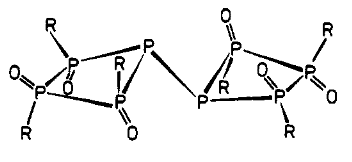
103



P_7R_5O; R = Bu^t

104

105

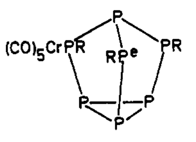
The 1,1′-bicyclotetraphosphane **94** is more resistant to oxidation and only reacts in solution with pure oxygen at higher temperatures and then with P–P bond cleavage and formation of 1,2-di-*tert*-butyldiphosphane dioxide. In contrast, **94** can be smoothly converted to the hexaoxide **106** at room temperature by treatment with hydrogen peroxide, peracetic acid, or cumene hydroperoxide (high selectivity),[345] whereas at above 30 °C decomposition into P_2 units also takes place. Compound **106** is characterized by an extremely high tendency for formation and can even be detected by ^{31}P-NMR spectroscopy along with oxygen-poorer oxides when the reaction is carried out at a molar ratio of 1:1. The structure was deduced from its $^{31}P\{^1H\}$-NMR spectrum which exhibited three multiplets of an $AA'B_2B'_2CC'$ spin system; the resonance positions, intensity ratios, and coupling patterns can only be accommodated by an exocyclic bonding of oxygen to the organo-substituted phosphorus atoms. Furthermore, the IR spectrum contains an absorption band in the region typical for P═O valency vibrations. Therefore, compound **106** is 2,2′,3,3′,4,4′-hexa-*tert*-butyl-1,1′-bicyclotetraphosphane 2,2′,3,3′,4,4′-hexaoxide.


$P_8R_6O_6$; R = Bu^t

106

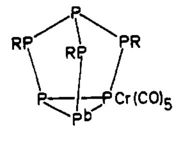
3. Transition Metal Complexes of Polycyclophosphanes

As a consequence of the different types of phosphorus atom present, polycyclophosphanes represent interesting ligands for complex chemistry. In the past few years, the coordination ability of some tricycloheptaphosphanes P_7R_3 and the tetracyclononaphosphane $P_9Bu^t_3$ toward metal carbonyl fragments of chromium and iron has been investigated. The products thus obtained were characterized structurally by their $^{31}P\{^1H\}$-NMR spectra and single-crystal X-ray analyses.

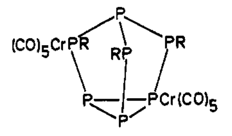

107a: R = Et

107b: R = Pr^i

107c: R = SiMe$_3$

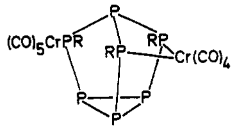

R = PBu$^t_2$

108


109a: R = Et

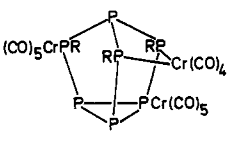
109b: R = Pr^i

109c: R = SiMe$_3$


110a: R = Et

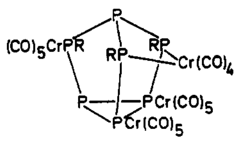
110b: R = Pr^i

110c: R = SiMe$_3$


111a: R = Et

111b: R = Pr^i

111c: R = SiMe$_3$


113a: R = Et

113b: R = SiMe$_3$

The heptaphosphanes(3) P_7R_3 (R = Et, Pr^i, SiMe$_3$) reacted with $Cr(CO)_5THF$ in a molar ratio of 1:1 to furnish the complexes **107a–c** in which the $Cr(CO)_5$ fragment is bonded to an equatorial bridging phosphorus atom (P^e).[346–348] When R = PBu^t_2, the compound **108** with an analogous composition but with the metal carbonyl fragment coordinated to a basal phosphorus atom of the three-membered ring (P^b) is formed.[349] In the reactions of P_7R_3 (R = Et, Pr^i, $SiMe_3$) with 2 mol of $Cr(CO)_5THF$ or of **107a–c** with a further mol of $Cr(CO)_5THF$, the complexes **109a–c** are formed in which the second $Cr(CO)_5$ group is bonded in each case to a P^b atom. Upon standing in solution, the compounds **109a** and **109b** undergo rearrangement with elimination of carbon monoxide to furnish the complexes **110a** and **110b** in which the $Cr(CO)_5$ fragment is bonded to a P^e atom while the $Cr(CO)_4$ fragment forms a bridge between the two other P^e atoms of the $P_7(3)$ skeleton.[346,347] The products **110a** and **110b** can also be obtained from **107a** and **107b** by reaction with $Cr(CO)_4(nbd)$ (nbd = 2,5-norbornadiene)[346] while the silyl-substituted complex **110c** is only obtainable from **107c** by this latter route.[348] The reaction of **109a** with a further mole of $Cr(CO)_5THF$ gives rise to a mixture of the compounds **109a**, **110a**, **111a**, and $P_7Et_3[Cr(CO)_5]_3$ (**112a**, only detectable by spectroscopy). Of these products, **109a** and **112a** undergo rearrangement in solution to furnish **110a** and **111a**, respectively. In the complex **111a**, the $Cr(CO)_4$ unit forms a bridge between two P^e atoms, while one $Cr(CO)_5$ group is bonded to the remaining P^e atom and the other to one of the two P^b atoms directly linked to the P^e atoms bearing the $Cr(CO)_4$ bridge.[346] The analogous compounds **111b** and **111c** were prepared by reactions of **109b** and **109c** with $Cr(CO)_4(nbd)$.[346,348] The reaction of P_7Et_3 with $Cr(CO)_5THF$ in a molar ratio of 1:5 gave rise to the complexes **111a** and **113a**. Compound **113a** can be derived from **111a** by the introduction of a further $Cr(CO)_5$ group at the second P^b atom directly linked to the P^e atoms bearing the $Cr(CO)_4$ bridge.[346,347] The corresponding silyl-substituted complex **113b** is formed in the reaction of **109c** with 3 equiv of $Cr(CO)_5THF$ whereas the 1:1 reaction gives rise to the isolable compound $P_7(SiMe_3)_3[Cr(CO)_5]_3$ (**112b**). The ^{31}P-NMR spectrum of **112b** indicates that two $Cr(CO)_5$ groups are bonded to P^b atoms and that the third is bonded either to the apical (P^a) atom or to a P^e atom.[348]

When $P_7(PBu^t_2)_3$ is allowed to react with more than one mole of $Cr(CO)_5THF$, coordination also occurs on the exocyclic phosphino groups and compounds with five-membered metallacyclic rings of the type $P^a–P^e–P^{exo}–Cr(CO)_4–P^e$ are formed preferentially. The simplest complex containing this structural element is $P_7(PBu^t_2)_3[Cr(CO)_4]$, prepared directly by the 1:1 reaction of $P_7(PBu^t_2)_3$ with $Cr(CO)_4(nbd)$.[349]

Reactions of $Fe_2(CO)_9$ with the heptaphosphanes(3) P_7R_3 (R = Et, PBu^t_2) in the molar ratio of 1:1 lead to the complexes $P_7R_3[Fe(CO)_4]$ in which the metal carbonyl fragment is bonded to the same phosphorus atoms as in the corresponding chromium complexes (P^e or P^b, respectively).[350]

The nonaphosphane(3) $P_9Bu^t_3$ (**80d**) reacts with $Cr(CO)_5THF$ and $Fe_2(CO)_9$ to give, depending on the molar ratio employed, the complexes $P_9Bu^t_3[Cr(CO)_5]$ and $P_9Bu^t_3[Fe(CO)_4]$ or $P_9Bu^t_3[Cr(CO)_5]_2$ and $P_9Bu^t_3[Fe(CO)_4]_2$, respectively. In the mononuclear complexes, the $M(CO)_n$ groups are coordinated to the *tert*-butyl-substituted P^5 atom in each case while, in the dinuclear complexes, the P^2 atom of the three-membered ring is additionally complexed (see structural formula of **80d**, section V.C.3).[350,351] As in the case of **80d**, the respective complexes are formed as diastereomeric mixtures.

Taken as a whole, the presently available results on the coordination ability of polycyclophosphanes indicate that the compositions and structures of the so-formed complexes are controlled by steric and electronic factors.[346–351]

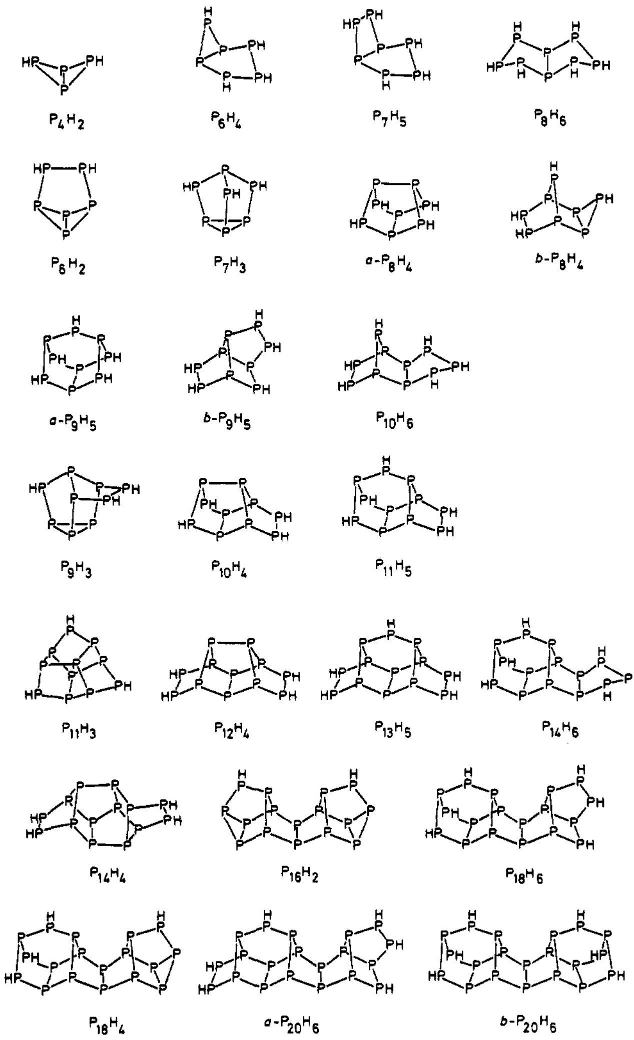
F. On the Structures of Polycyclic Phosphorus Hydrides and the Formation of Sterically Unperturbed $P_n(m)$ Skeletons

The organopolycyclophosphanes described in section V.C provide the key to an understanding of the structures of the polycyclic phosphorus hydrides of which, to date, only P_7H_3 (**52**) has been available for a direct nuclear magnetic resonance investigation of its structure (see section V.A). As has been demonstrated, the typical skeletal structures of the individual classes of compounds P_nR_m are retained in all cases upon variation of the substituents within the range of relatively small alkyl groups (R = Me to Pr^i); thus, changes in the structures upon replacing the organic groups by hydrogen atoms can also be excluded. Hence, the molecular structures determined for the sterically unperturbed organopolycyclophosphanes are also representative for the corresponding phosphorus hydrides. Our present state of knowledge on polycyclic phosphorus hydrides can be summarized as in Chart I.

With regard to their structures, the various polycyclic $P_n(m)$ skeletons exhibit close mutual relationships. Thus, for example, the bicyclic $P_6(4)$ skeleton can be derived formally from the tricyclic $P_7(3)$ cage by removal of one of the three one-atom bridges. The norbornane-type $P_7(5)$ skeleton and the tetracyclic $P_9(3)$ skeleton differ from the $P_7(3)$ cage only by the opening of one bond in the three-membered ring or by the linkage of two equatorial P atoms through a two-atom bridge, respectively. The pentacyclic $P_{14}(6)$ framework can be built up from the tetracyclic $P_{11}(5)$ skeleton by the addition of a three-atom bridge. Furthermore, the $P_7(5)$, $P_8(6)$, and $P_9(5)$ skeletons are all essential structural unit groups of Hittorf's phosphorus.[263] It is these structural relationships that are responsible for the ready mutual interconversions and the common genesis of the various polycyclophosphanes.

The formation of five-membered ring structural elements is of extreme significance in the construction of polycyclic phosphane skeletons. This is also an important distinction to carbon chemistry and explains, among others, why the decaphosphanes(6), $P_{10}R_6$, do not have an adamantane-type structure (section V.C.2). However, with the increasing annelation of five-membered rings, increasing strain energies are generated which can be seen, for example, from the stability order *a*-P_8Me_4 < *b*-P_8Me_4.[301] In addition to five-membered ring units, partial skeletons of three- and six-membered rings are also formed, whereas structural elements containing four-membered rings or rings with more than six phosphorus atoms do not occur in sterically unperturbed polycyclic phosphanes. The reason for the nonexistence of four-membered ring partial structures can almost certainly be seen in the fact that the parallel σ-bonds separated by a single-bond distance would cause a general destabilization of the framework.[127,134] The compound $P_7Bu^t_5$ (**93**) is the first example of a molecular, polycyclic phosphane containing an annelated four-membered ring as a

Chart I



From left to right:

tetraphosphane(2), P_4H_2, is bicyclo[1.1.0]tetraphosphane;
hexaphosphane(4), P_6H_4, is bicyclo[3.1.0]hexaphosphane;
heptaphosphane(5), P_7H_5, is bicyclo[2.2.1]heptaphosphane;
octaphosphane(6), P_8H_6, is bicyclo[3.3.0]octaphosphane;
hexaphosphane(2), P_6H_2, is tricyclo[3.1.0.0^{2,6}]hexaphosphane;
heptaphosphane(3), P_7H_3, is tricyclo[2.2.1.0^{2,6}]heptaphosphane;
octaphosphane(4), P_8H_4, exists as the two constitutional isomers tricyclo[3.3.0.0^{3,7}]octaphosphane (a-P_8H_4) and tricyclo[3.2.1.0^{2,4}]octaphosphane (b-P_8H_4);
nonaphosphane(5), P_9H_5, also exists as the two constitutional isomers tricyclo[3.3.1.0^{3,7}]nonaphosphane (a-P_9H_5) and tricyclo[4.3.0.0^{3,7}]nonaphosphane (b-P_9H_5);
decaphosphane(6), $P_{10}H_6$, is tricyclo[5.2.1.0^{2,6}]decaphosphane;
nonaphosphane(3), P_9H_3, is tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonaphosphane;
decaphosphane(4), $P_{10}H_4$, is tetracyclo[5.2.1.0^{2,6}.0^{3,8}]decaphosphane;
undecaphosphane(5), $P_{11}H_5$, is tetracyclo[6.2.1.0^{2,6}.0^{5,10}]undecaphosphane;
undecaphosphane(3), $P_{11}H_3$, is pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecaphosphane;
dodecaphosphane(4), $P_{12}H_4$, is pentacyclo[6.4.0.0^{2,6}.0^{5,12}.0^{7,11}]dodecaphosphane;
tridecaphosphane(5), $P_{13}H_5$, is pentacyclo[7.4.0.0^{2,6}.0^{5,13}.0^{8,12}]tridecaphosphane;
tetradecaphosphane(6), $P_{14}H_6$, is pentacyclo[9.2.1.0^{2,9}.0^{3,7}.0^{8,13}]tetradecaphosphane;
tetradecaphosphane(4), $P_{14}H_4$, is hexacyclo[6.6.0.0^{2,6}.0^{5,14}.0^{7,12}.0^{9,13}]tetradecaphosphane;
octadecaphosphane(6), $P_{18}H_6$, is heptacyclo[13.2.1.0^{2,13}.0^{3,11}.0^{4,9}.0^{6,10}.0^{12,17}]-octadecaphosphane;
hexadecaphosphane(2), $P_{16}H_2$, is octacyclo[7.7.0.0^{2,6}.0^{3,8}.0^{5,7}.0^{10,14}.0^{11,16}.0^{13,15}]-hexadecaphosphane;
octadecaphosphane(4), $P_{18}H_4$, is octacyclo[13.2.1.0^{2,13}.0^{3,11}.0^{4,9}.0^{5,7}.0^{6,10}.0^{12,17}]-octadecaphosphane; and
icosaphosphane(6), $P_{20}H_6$, exists as the two constitutional isomers octacyclo[10.8.0.0^{2,14}.0^{3,11}.0^{4,8}.0^{5,10}.0^{13,18}.0^{15,19}]icosaphosphane (a-$P_{20}H_6$) and octacyclo[14.2.1.1^{5,8}.0^{2,14}.0^{3,12}.0^{4,10}.0^{6,11}.0^{13,18}]icosaphosphane (b-$P_{20}H_6$).

structural element and this is a result of the special steric demands.

In summary, the structures of polycyclic phosphanes and their sterically unperturbed derivatives, according to contemporary knowledge, are determined by the following rules.[9,11]

(1) In accord with the sum formula of a compound, the same, formally deducable polycyclic structures as those for hydrocarbons with analogous compositions are possible, whereby a P atom substituted by a monofunctional group is equivalent to a CH_2 unit and a P atom bonded only to other phosphorus atoms is equivalent to a CH unit.

(2) Of the constitutional isomers possible according to rule 1, those containing the maximum number of five-membered ring units will be formed. When several skeletons with similar structures and stabilities are possible, constitutional isomers may be formed.

(3) If the composition according to the formula requires the presence of other structural elements in addition to five-membered rings, three- and six-membered rings but not four- or seven-membered rings will be incorporated into the phosphane structure. Phosphane skeletons containing three-membered rings are thermally more stable than those containing six-membered rings.

(4) The $P_n(m)$ skeletons of higher-condensed phosphanes are often formally constructed from those of lower-condensed phosphanes by one of the following basic operations:

(a) Coupling of two H- or R-substituted phosphorus atoms by a two-atom bridge to form a new five-membered ring with elimination of the substituents generates the next-higher condensed phosphane containing two phosphorus atoms more:

$$P_n(m) \rightarrow P_{n+2}(m)$$

Respective examples are the transformations $P_4(2) \rightarrow P_6(2)$, $P_6(4) \rightarrow b\text{-}P_8(4)$, $P_7(3) \rightarrow P_9(3)$, $P_7(5) \rightarrow b\text{-}P_9(5)$, $a\text{-}P_8(4) \rightarrow P_{10}(4) \rightarrow P_{12}(4)$, $P_8(6) \rightarrow P_{10}(6)$, $a\text{-}P_9(5) \rightarrow P_{11}(5) \rightarrow P_{13}(5)$, $P_{18}(6) \rightarrow a\text{-}P_{20}(6)$.

(b) Coupling of two H- or R-substituted phosphorus atoms by a one-atom bridge increases the number of phosphorus atoms by one and concomitantly reduces the number of substituents by one; this leads to a change from an even-numbered to an odd-numbered phosphane and vice versa:

$$P_n(m) \rightarrow P_{n+1}(m-1)$$

Respective examples are the transformations $P_6(4) \rightarrow P_7(3)$, $P_7(5) \rightarrow a\text{-}P_8(4)$, $b\text{-}P_8(4) \rightarrow P_9(3)$, $P_8(6) \rightarrow a\text{-}P_9(5)$, $P_8(6) \rightarrow b\text{-}P_9(5) \rightarrow P_{10}(4)$, $P_{10}(6) \rightarrow P_{11}(5)$.

(c) Coupling of two adjacent, H- or R-substituted phosphorus atoms by a three-atom bridge leads to the next-higher condensed phosphane containing three phosphorus atoms and one substituent more:

$$P_n(m) \rightarrow P_{n+3}(m+1)$$

Respective examples are the transformations $P_7(5) \rightarrow P_{10}(6)$, $P_{11}(5) \rightarrow P_{14}(6)$.

(d) Intramolecular formation of a zero-atom bridge between two H- or R-substituted phosphorus atoms with elimination of the substituents generates the next-higher condensed phosphane with the same number of phosphorus atoms but with two substituents less:

$$P_n(m) \rightarrow P_n(m-2)$$

Respective examples are the transformations $P_6(4) \rightarrow P_6(2)$, $P_7(5) \rightarrow P_7(3)$, $P_8(6) \rightarrow$ *a*-$P_8(4)$, *b*-$P_9(5) \rightarrow P_9(3)$, $P_{10}(6) \rightarrow P_{10}(4)$, $P_{18}(6) \rightarrow P_{18}(4)$.

The fact that the construction principles according to a–d are not merely of a formal nature is demonstrated by, among others, the synthesis of $P_6(C_5Me_5)_2$ (**66**) from $P_6(C_5Me_5)_4$ (**65**) (section V.B).

(5) Phosphanes with highly condensed $P_n(m)$ skeletons can form particular, compact structures which are energetically favored; for example $P_{11}(3)$, $P_{14}(4)$.

(6) The construction of particularly phosphorus-rich structures occurs by way of annelation of two identical or different phosphane skeletons [$P_7(5)$, *b*-$P_9(5)$, $P_9(3)$, $P_{11}(5)$, $P_{12}(4)$, $P_{13}(5)$] to furnish a conjuncto-phosphane with a pentalane-type $P_8(6)$ partial structure. With increasing numbers of phosphorus atoms, increasing larger components of Hittorf's phosphorus (see Figure 16) in which the free valencies are saturated by hydrogen atoms or organic groups are formed.

(7) Of the possible configurational isomers, the one with the maximal *trans* arrangement of the substituents is formed preferentially. The occurrence of further isomers depends on the steric interactions between the substituents in deviations from the *all-trans* orientation.

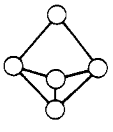
On the whole, the wide range of structures that Nature is able to compose by combination of just a few building blocks and coupling patterns is surprising and fascinating. The structural variety of the polycyclic phosphanes is exceeded only by those of the cyclic boranes and cycloalkanes. Since the structural principles mentioned above have proved to be generally applicable to date, they form the basis for the deduction of the most probable structures for those polycyclophosphanes included in Table X for which the corresponding organic derivatives have not yet been investigated structurally.

VI. Structural Relationships between Polycyclic Phosphanes and Unsubstituted P_n Clusters

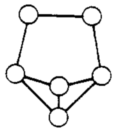
The structures of polycyclic phosphanes have attained particular interest in recent years on account of theoretical calculations on unsubstituted P_n clusters.[352–354] Close structural relationships between the two classes of compounds exist and polycyclophosphanes and P_n clusters with the same number of phosphorus atoms can often formally be interconverted.

The tetrahedral structure of the P_4 molecule has been confirmed for a long time.[355] Opening of one P–P bond and saturation of the free valencies thus produced by monofunctional substituents gives rise to the bicyclotetraphosphanes P_4R_2 (R = H, organic group).

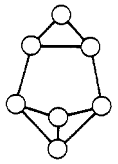
Ab initio calculations for P_n clusters with n = 5–10 have given the following ground state geometries: P_5 has a tetracyclic structure which is derived from the P_4 tetrahedron by insertion of a two-coordinate phosphorus atom into one of the P–P bonds.[352] Analogously, the benzvalene-type structure of P_6 can be interpreted as the insertion of a P_2 bridge into the P_4 molecule.[352,354] P_7 differs from P_6 by the annelation of a three-membered ring onto the two-atom bridge.[352] In the ground state, the P_8 cluster does not have a cubane-type but rather a cuneane-type structure.[352,354] Two energetically similar forms which can be derived from the P_8 cuneane-type structure are predicted for P_9: in the more stable isomer one of the three-membered rings is enlarged to a four-membered ring, whereas the other isomer, with about 0.14 eV more energy and a distorted C_{2v} structure, is derived by the insertion of a phosphorus atom into the zero-atom bridge between the two four-membered rings of the P_8 cuneane.[253] Differing structural prognoses have been obtained for P_{10}. According to Jones et al.,[353] the most stable isomer has C_s symmetry while Ahlrichs et al.[354] calculated that the isomer with C_{2v} symmetry should have somewhat lower energy. Both forms show close structural relationships with the P_8 cuneane-type structure.



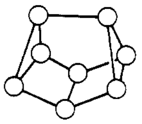
P_5 (C_{2v})



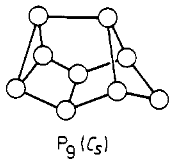
P_6 (C_{2v})



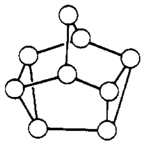
P_7 (C_s)



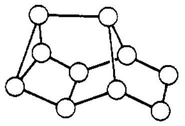
P_8 (C_{2v})



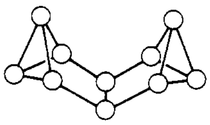
P_9 (C_s)



P_9 (C_s)



P_{10} (C_s)



P_{10} (C_{2v})

The prediction of the most stable isomer of P_n clusters becomes more and more difficult with increasing numbers of phosphorus atoms on account of the numerous minima with, in cases, similar energies on the potential hypersurface. However, a clear tendency for the formation of tube-type P_n structures is apparent;[353] such structures result from the coupling of smaller P_n clusters through two σ-bonds or from annelation onto unsaturated P_2 bridges.[354] Examples of the latter are the P_{10} isomer with C_{2v} symmetry, which is made up of two annelated P_6 clusters, and the particularly stable P_{18} isomer with C_{2v} symmetry (not shown),[354] which analogously comprises two P_{10} clusters with C_s symmetry.

The predicted structural variety in the unsubstituted P_n clusters reflects the observed wide range of structures for the $P_n(m)$ skeletons of polycyclic phosphanes; and the same structural principles can be recognized. As can be seen from the molecular structures of the polycyclophosphanes, polyhedral, "compact" structures are formed, depending on the formula composition, in the cases of smaller numbers of phosphorus atoms. The formation of tube-like $P_n(m)$ skeletons commences, similar to the P_n clusters, with the decaphosphanes $P_{10}R_6$ and $P_{10}R_4$ (R = H, organic group) and the dodecaphosphanes $P_{12}R_4$. In the cases of the neutral polycyclophosphanes and the isolated polycyclic anions, the linkage of smaller structural elements by annelation to furnish a pentalane-type $P_8(6)$ partial structure dominates.

Polycyclophosphanes frequently possess the same or a similar skeletal structure as that calculated for the most stable isomer of the unsubstituted P_n cluster with the same number of phosphorus atoms. Thus, the constitution of the tricyclohexaphosphanes(2), P_6R_2, can be interpreted as a saturation of the double bond of the benzvalene-type P_6 cluster. Similarly, the a-$P_8(4)$ skeleton of the tricyclooctaphosphanes(4) with a bisnoradamantane-type structure can be derived from the cuneane-type P_8 cluster by opening of the two three-membered rings and saturation of the free valencies by monofunctional substituents. The analogous relationship between the tricyclononaphosphanes(5) with the a-$P_9(5)$ skeleton and the somewhat more energy-rich P_9 cluster exemplarily demonstrates that a structural relationship may also exist between polycyclophosphanes and other, less-stable isomers of P_n clusters.

The results of theoretical investigations on unsubstituted P_n clusters provide valuable help for the prediction of the most likely skeletal structures for some polycyclophosphanes whose structures have not yet been clarified. Thus, the pentaphosphanes(1) and pentaphosphanes(3) should be derived from the P_5 cluster by introduction of a monofunctional substituent at the phosphorus atom with the coordination number two or by the additional opening of one of the three-membered rings and saturation of the thus formed free valencies, respectively. The resultant structures for P_5R and P_5R_3 (R = H, organic group) are in complete harmony with the predictions of the construction rule 4b (section V.F). The constitution of P_5R_3 (P_4 ring with orthogonally annelated P_3 ring) corresponds furthermore with the skeletal structure of the homologous bicyclic system P_6R_4 (P_5 ring with annelated P_3 ring; section V.C.1).

Similar to the case of the pentaphosphanes(1) and the P_5 cluster, the heptaphosphanes(1) should differ from the P_7 cluster by the presence of a monofunctional substituent on the two-coordinated phosphorus atom of the latter. The thus prophesized structure for P_7R is also in harmony with the result starting from P_6R_2 according to construction principle 4b.

The structure of the octaphosphanes(2) can simply be derived from the cuneane-type P_8 cluster by opening of one of the three-membered rings to a five-membered ring and saturation of the thus formed free valencies. The same constitution for P_8R_2 is also predicted by rule 4d starting from P_8R_4.

In the case of the decaphosphanes(2), the addition of two monovalent substituents to the double bond of the P_{10} cluster with C_s symmetry is to be expected. The thus resultant structure for $P_{10}R_2$ is identical to that deduced starting from $P_{10}R_4$ according to rule 4d.

With larger numbers of phosphorus atoms, the structural relationships between the polycyclic phosphanes and the unsubstituted P_n clusters are, at present, not so clear since isomers with similar stabilities can occur with increasing frequency in both classes of compounds.

VII. Conclusions and Perspectives

Investigations on homocyclic polyphosphorus compounds over the past 25 years have opened a fascinating new chapter on "element-near" compounds in the book about phosphorus chemistry. The use of generally applicable synthetic routes and modern NMR methods for structure elucidation has uncovered and characterized a surprising palette of new compounds with, in part, unexpected structures. Simultaneously, the close relationships between phosphorus and carbon chemistry[9] have become apparent to an astonishing extent. For example, who would have dared suggest that, during the construction of phosphorus-rich polyphosphides from phosphorus-poorer examples, a mesomerism-stabilized pentaphosphacyclopentadienide ion containing unsubstituted phosphorus atoms with the coordination number two would be formed spontaneously? The low barriers to inversion at phosphorus in some cage-like organopolycyclophosphanes are similarly surprising.

What perspectives can be recognized for future research in this field? The structures of numerous polycyclic phosphorus hydrides and the corresponding, sterically unperturbed organopolycyclophosphanes still remain to be elucidated. Even though the structure of the most probable skeleton can frequently be deduced with the help of the general principles given above, the examples of constitutionally isomeric polycyclophosphanes clearly emphasize that the structure of a specific compound can only be finally clarified by experimental methods. Furthermore, there is still a large number of identified but not yet structurally characterized *tert*-butylpolycyclophosphanes which may provide further surprises on closer investigation.

In addition, all classes of compounds—the neutral *monocyclophosphanes* as well as the *polyphosphides* with isolated anions and also the neutral *polycyclophosphanes*—hold the promise of a rich chemistry on which research has only just been started. Through reactions at the free electron pairs of the phosphorus atoms, novel derivatives with retention of the P_n skeleton may be obtained; alternatively insertion reactions may give rise to the formation of novel heterocyclic systems.

Thus, many opportunities for the discovery of new reactions and molecular structures still exist in the field of monocyclic and polycyclic phosphanes and the intuition, experimental expertise, and patience of the synthetic chemist will be in demand for many more years. The authors hope that this review article will help prepare the ground for further developments in this fertile field of phosphorus chemistry.

VIII. Acknowledgments

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