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Open-Chain Polyphosphorus Hydrides (Phosphanes)[†,1]

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Contents

I. Introduction and Scope of the Review

Following the discovery of PH_3 by Gengembre[2] in 1785 and of P_2H_4 by Thénard[3] in 1844, more than 100 years passed before further phosphorus hydrides (phosphanes) of the general composition P_nH_{n+2} were reported.[4,5] These compounds constitute the homologous series of open-chain phosphanes of which, to date, the members with $n = 1–9$ are known.[6] The sum formulae are derived from the formula of the saturated, acyclic hydrocarbons (alkanes) C_nH_{2n+2} where the groups $>CH_2$ and $-CH_3$ are replaced by the corresponding phosphorus-containing structural increments $>PH$ and $-PH_2$, respectively.

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In addition to the open-chain phosphorus hydrides there exist also the monocyclic phosphanes P_nH_n and numerous polycyclic phosphanes of the series P_nH_{n-2},

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

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P_nH_{n-4}, ..., P_nH_{n-18} which were recently the subject of a comprehensive survey.[7] These hydrogen-poorer phosphorus hydrides will only be mentioned in the present review when they are formed in rearrangement or decomposition reactions of open-chain phosphanes.

An excellent review on PH_3, the first member of the series P_nH_{n+2}, has been published.[8] In contrast, the homologous, open-chain *poly*phosphorus hydrides with $n \geq 2$ have not previously been surveyed in depth. Detailed research on these compounds has become possible in the past 25 years as a result of the development of modern laboratory techniques and analytical methods. The present article covers the literature published up to December 1992 and also includes some previously unpublished results from our laboratories in Cologne.

II. General Comments on Open-Chain Phosphanes P_nH_{n+2}

Although open-chain polyphosphorus hydrides have the same simple molecular structures as ethane and higher homologous alkanes, detailed research on these compounds started much later than that of the alkanes. The reason for this can be found in the properties of P_2H_4 as the simplest phosphorus hydride containing a P–P bond in the molecule. Diphosphane(4) is spontaneously inflammable in contact with air and, in contrast to ethane, undergoes rapid decomposition by disproportionation even at room temperature. In light of this instability, it was assumed for a long time that the existence of more phosphorus-rich, open-chain hydrides was unlikely and, thus, the appropriate research did not appear to be fruitful. However, this situation has changed dramatically since the end of the 1950s. Further homologues of the phosphane series P_nH_{n+2} with n = 3–9 were identified among the thermolysis and photolysis products of P_2H_4 first of all in the course of Raman spectroscopic investigations,[4,5] then also by mass spectroscopy,[9-11] and since 1972 above all by NMR spectroscopy.[12]

In order to provide a distinction from the less hydrogen-rich phosphanes with the same number of phosphorus atoms (see above), open-chain phosphanes are named in analogy to borane nomenclature[13] by stating the number of both phosphorus and hydrogen atoms; for example, P_5H_7 is thus designated as pentaphosphane(7). Considering the fact that polycyclic phosphanes with up to 22 phosphorus atoms in the molecule ($P_{22}H_6$, $P_{22}H_4$)[7] are presently known, it becomes apparent that the tendency for the formation of open-chain phosphanes P_nH_{n+2} decreases markedly in favor of cyclic structures with increasing numbers of phosphorus atoms. At first, monocyclic phosphanes P_nH_n are clearly favored over open-chain phosphanes from n = 5 onward while from n = 7 onward the polycyclic compounds P_nH_{n-2m} (m = 1–9) are preferred.

Of the open-chain polyphosphorus hydrides, only triphosphane(5) has been prepared in the pure state in addition to diphosphane(4) (see section V). The more phosphorus-rich homologues were obtained by hydrolysis of calcium phosphide or thermolysis of diphosphane(4) in the form of *phosphane mixtures*—more or less highly enriched—and the structural investigations were performed on these mixtures (see sections VI–IX). The separation of these compounds is extremely difficult because of their very similar properties and their pronounced tendency to undergo disproportionation. In view of their sensitivity to oxidation and their decomposition even in diffuse daylight, all work with open-chain polyphosphorus hydrides must be performed under an inert atmosphere[14] and in weak red light.

The compositions of individual phosphanes and of phosphane mixtures can be determined by chemical analysis. The phosphorus content is preferentially assayed as quinolinium molybdatophosphate according to the method of H. N. Wilson.[15] A volumetric analytical method has been developed for the determination of the hydrogen content.[16] It should be understood that the differences in the hydrogen content between individual homologues of the series P_nH_{n+2} can exceed the difference in the phosphorus content by more than a power of 10. The latter method is based on the thermal decomposition of the phosphane according to eq 1 and reaction of the thus formed monophosphane and other highly volatile polyphosphanes (mainly P_2H_4) with copper according to eqs 2 and 3.

$$3P_nH_{n+2} \xrightarrow{500\ °C} (n+2)PH_3 + (2n-2)P \tag{1}$$

$$6Cu + 2PH_3 \xrightarrow{300\ °C} 2Cu_3P + 3H_2 \tag{2}$$

$$6Cu + P_2H_4 \xrightarrow{300\ °C} 2Cu_3P + 2H_2 \tag{3}$$

The hydrogen formed is transferred to an evacuated gas buret by a Töpler pump while the copper phosphide formed remains in the reaction tube. At the same time, a possible water content resulting from the phosphane preparation (see section III.A) can be determined by absorption on to magnesium perchlorate.

The characterization of a phosphane mixture with regard to the individual compounds present can be achieved by gas chromatography.[17] Silica gel (particle size 0.2–0.3 mm) or, especially, glass balls of the same diameter pretreated with a 10% KOH solution for stabilization of the phosphanes have proved to be suitable packing materials for the separation column. Silicone oil is used as the stationary phase and helium as the carrier gas. A decomposition-free separation of the first members of the series P_nH_{n+2} with n = 1–4 can be achieved at column temperatures between −50 and +200 °C.[17] The separation of higher homologues with $n \geq 4$ as well as their constitutional isomers (see sections VI–IX) and the preparative isolation of individual open-chain polyphosphorus hydrides in the pure state should also be realizable by a shortening of the residence time on the column (increase in heating rate).

Mass spectrometry is particularly suitable for the characterization of phosphane mixtures. In order to avoid disproportionation as much as possible, the substance samples are introduced directly into the ion source of the mass spectrometer at variable evaporation temperatures (−196 to +70 °C) with the aid of a special inlet system.[18] Ionization is by electron impact (10–15 eV) or field ionization. When these conditions are employed, the results will barely be affected by a concomitant disproportionation of the phosphanes in the mass spectrometer. If the sample temperature is increased to above 100 °C or the ionization voltage is set at more than 15 eV, rearrangement and decomposition reactions become predominant.

A further method for determining the composition of phosphane mixtures is provided by ^{31}P NMR spectroscopy. In addition, this method furnishes detailed structural information about the individual components (see sections VI–IX). A major advantage of this technique over mass spectrometry is that the phosphane samples can be investigated at below room temperature and, if necessary, in solution so that disproportionation reactions can be excluded with certainty. The agreement between the compositions of phosphane mixtures determined by mass spectrometry and by ^{31}P NMR spectroscopy is usually satisfactory.

The open-chain polyphosphorus hydrides P_nH_{n+2} with $n = 2$–9 are generally relatively volatile compounds and exhibit no or only very slight intermolecular association. The spontaneous inflammability in air decreases steadily with increasing relative molecular mass (phosphorus content). In contrast to earlier reports in the literature and textbooks, diphosphane(4) and its higher homologues are not explosive but rather burn quietly in atmospheric oxygen with evolution of white fumes of phosphorus pentoxide. Explosions of open-chain phosphanes can, however, occur for two reasons: (i) The product mixture also contains hydrogen, as can be the case when they are prepared by hydrolytic decomposition of metal phosphides—a detonating gas mixture arises in the presence of oxygen and is ignited by the spontaneous inflammation of the phosphane. (ii) PH_3 with bp −88 °C[19] is one of the final products from the disproportionation of phosphanes; thus, even under cooling in dry ice, closed vessels can undergo sudden explosive breakage as a result of the increasing PH_3 pressure. The disproportionation of open-chain polyphosphorus hydrides is generally greatly accelerated by heat and light.

Suitable solvents for diphosphane(4) are given in section III.B. For the more phosphorus-rich, open-chain phosphanes, diphosphane(4), and molten white phosphorus, benzene, cyclooctatetraene, and the hydrocarbon mixtures 1-methylnaphthalene/phenanthrene or toluene/phenanthrene have proved to be useful solvents.[18] The more phosphorus-rich hydrides are markedly stabilized by solution in white phosphorus and aromatic solvents, whereas their solutions in diphosphane(4) are extremely unstable and tend to undergo spontaneous decomposition. In some cases, violent reactions can occur in chlorinated hydrocarbons as solvent.

III. Diphosphane(4), P_2H_4

After the early discovery[3] of the first polyphosphorus hydride P_2H_4, investigations were at first restricted to the preparation of the compound and the determination of its most important properties.[20–22] The formula composition was finally confirmed in the mid-1930s by Royen and Hill[23] through exact determination of the molecular mass, and the knowledge of its physical properties was considerably extended. Until this time, diphosphane(4) was only prepared in very small amounts because of its spontaneous inflammability and ready decomposition. Only when the compound became accessible in amounts of about 10 g 20 years[24–26] later were further investigations started to clarify, above all, the spatial geometry of the molecule (section III.C) and its chemical properties (section III.E).

A. Methods of Preparation

The classical method for the preparation of diphosphane(4),[3,21,22] the decomposition of calcium phosphide with water according to the ideal eq 4, is still the most suitable.[24–27] Further methods for the preparation or formation of P_2H_4 will be discussed below.

$$2CaP + 4H_2O \rightarrow P_2H_4 + 2Ca(OH)_2 \tag{4}$$

For the preparation of larger quantities of P_2H_4, commercial calcium phosphide—technical product containing larger proportions of CaP—is used.[28,29] It was soon discovered in the early work that the quality of the calcium phosphide is of major significance for the yield of P_2H_4.[22] The calcium phosphide should be factory fresh and be in the form of pellets of pea or bean size; finally powdered products are practically worthless.[27] The volatile hydrolysis products contain, in addition to P_2H_4, varying amounts of PH_3 and more phosphorus-rich polyphosphorus hydrides (see sections V–IX); furthermore, hydrogen and possibly some AsH_3 and SiH_4 are also present. In small-scale experiments, high yields of P_2H_4 have been achieved by using calcium phosphide prepared from the reaction of red phosphorus with calcium oxide at 800 °C or with calcium carbide at 810 °C.[28]

The hydrolysis is advantageously performed by addition of oxygen-free water to the solid phosphide at 0 °C under reduced pressure[24,25,27] so that the thermally sensitive diphosphane(4) is rapidly removed from the reaction zone. The yield of P_2H_4 is noticeably lower both on reversed mixing of the components (addition of the phosphide to water) and on reaction under normal pressure.[26] In a procedure that was optimized in comparison to that of ref 27 (hydrolysis of 400 g of phosphide with 400 mL of water at 20 Torr in ca. 3 h, temperature of the reflux condenser −30 to −35 °C, omission of the KOH drying tube),[30] the yield of diphosphane(4) is about 15–25 g. It is collected in about equal amounts by condensation in cold traps at −45 and −78 °C as well as—albeit in a smaller amount together with PH_3—at −196 °C. For the production of larger amounts of P_2H_4, several phosphide hydrolyses are carried out in the same apparatus consecutively by exchanging the reaction flasks; in this way several hundred milliliters of crude diphosphane(4) can be obtained in a semicontinuous process.[30] The product is purified by high vacuum distillation in which the combined condensates are warmed from −78 to −30 °C and highly pure P_2H_4 is recondensed at −78 and −110 °C (main fraction);[27] the distillation residue consists of mostly phosphorus-rich, open-chain phosphanes P_nH_{n+2} (see sections V–IX) and some cyclopentaphosphane, P_5H_5.[6] Small amounts (a few grams) of P_2H_4 can be stored in glass ampules for a few weeks at −78 °C when the ampules are initially sealed under reduced pressure. Larger amounts of the compound are stored in vessels fitted with rubber serum caps[14] (to facilitate the release of PH_3 excess pressure; see section II) cooled with dry ice.[27] Highly pure diphosphane(4) can be stored in the dark under these conditions for several months.[27,30]

Deuteriodiphosphane(4), P_2D_4, can be prepared by the same procedure,[4,24,31] but with the modifications that only 60 mL of D_2O are used for the deuterolysis of 400 g of calcium phosphide and that, after completion of the addition, the portion condensed in the reflux condenser[27] is brought to reaction as far as possible by thawing.[31]

In the preparations of diphosphane(4) and deuteriodiphosphane(4), various amounts of solid, white products are formed which, above all, separate in the upper parts of the cold traps cooled at −45 and −78 °C.[24-26,30] These cannot be removed by treatment with a drying agent (P_4O_{10}, CaH_2) and are often still observed after multiple vacuum distillations of P_2H_4.[25,30] On warming above about −35 °C in contact with diphosphane(4) they increasingly tend to go into solution; the thus obtained solutions are markedly less stable than those of pure P_2H_4. After removal of P_2H_4, separation into a two-phase system occurs in the temperature range between 0 and +20 °C; the lower phase is a CS_2-like liquid and the upper phase a white emulsion which, in contrast to the lower phase, solidifies on cooling to an ice-like mass and contains only traces of P_2H_4 and PH_3 (^{31}P NMR). According to analytical, gas chromatographic, and ^{31}P NMR spectroscopic investigations, the lower, liquid phase consists of almost pure diphosphane(4). Hence, the white, solid products are not, as was believed in earlier work,[11b,25] triphosphane(5) or another, novel phosphorus hydride but are rather clathrate compounds of P_2H_4 in H_2O or P_2D_4 in D_2O, respectively.[30] This result is not surprising since PH_3 also forms a gas hydrate[32] having a decomposition temperature (−6.4 °C, 1 atm) that is considerably higher than the boiling point of PH_3 (−88 °C[19]). The solid products separating at −45 °C also occasionally contain trace amounts of water and polyphosphane oxides (originating from the air trapped in the calcium phosphide; see section III.E).

Diphosphane(4) is also formed in the hydrolyses of other metal phosphides which contain P–P bonds. Thus, the action of water on aluminum phosphide, prepared from the elements using an excess of phosphorus,[8] gives rise to varying amounts of P_2H_4 in addition to PH_3. Other methods for the preparation of P_2H_4 include the disproportionation of white phosphorus with potassium hydroxide solution at +60 °C[23] which, however, proceeds relatively slowly and only gives low yields as well as the action of a silent electrical discharge in a stream of PH_3 at low pressure.[33] But these methods are not suitable for the synthesis of larger amounts of P_2H_4 in the laboratory. In addition, P_2H_4 is also formed in the following reactions: heating of red phosphorus in a stream of hydrogen,[34] the action of atomic hydrogen on red phosphorus,[35] heating of a mixture of red phosphorus and $Ba(OH)_2$ at 225 °C,[36] reaction of H_3PO_2 with acetyl chloride,[37] electrolysis of white phosphorus in an acetic acid medium,[38] and photolysis of PH_3 at 147 nm.[39,40]

B. Physical Properties

Diphosphane(4) is a colorless liquid (melting point −99 °C[23]); it is spontaneously inflammable on contact with air and is thermally unstable above about −30 °C. It decomposes on exposure to daylight and on contact with rough surfaces, as well as in the presence of traces of acid or of mercury. This tendency to decomposition prevents the exact determination of its boiling point; however, a value of 63.5 °C has been extrapolated from experimental vapor pressure data.[25] The heat of evaporation was calculated as 6889 cal mol^{-1}, and the Trouton constant was determined as 20.46. From the heat of decomposition into the elements as determined by calorimetric methods, the enthalpy of formation of P_2H_4 from white phosphorus and hydrogen was calculated[41] as $\Delta H°_f = +5.0 \pm 1.0$ kcal mol^{-1}. Contradictory values for the relative density of diphosphane(4) are given in the literature.[22,24] Recent measurements in the temperature range −78 to +18 °C resulted in the extrapolated value $d_4^{20} = 1.014 \pm 0.002$.[27,30] The refractive index was determined as $n^{20} = 1.66 \pm 0.01$ and the surface tension at 0 °C as $\sigma = 34$ dyn cm^{-1}.[30]

The solubility behavior of diphosphane(4) has been investigated in detail recently.[27,30] The compound is only very slightly soluble in water (0.035 ± 0.003 g of P_2H_4 in 100 g of solution at 0 °C); on the other hand, diphosphane(4) is able to dissolve considerable amounts of water (43.2 ± 1.6 g of H_2O in 100 g of solution at 0 °C). The system diphosphane(4)/methanol also exhibits a mixing anomaly: at 20 °C a saturated solution in methanol contains 23.5 wt % P_2H_4 while pure diphosphane(4) at the same temperature dissolves less than 1 wt % methanol. The following solvents exhibit a very good solubility toward diphosphane(4): benzene, toluene, xylene, *n*-hexane, cyclohexane, tetrahydrofuran, dioxane, 1,2-dimethoxyethane (monoglyme), diethylene glycol monomethyl ether, diethylene glycol dimethyl ether (diglyme), diethyl ether, petroleum ether, carbon disulfide, pyridine, hexamethylphosphoric triamide, tetrachloromethane, and trichloromethane. Diphosphane(4) is only slightly soluble in liquid ammonia.[42] Generally, the purity of the solvent is of decisive importance for the stability of a solution of P_2H_4. The solutions are appreciably more sensitive to light than pure diphosphane(4); on the other hand, the solutions are no longer spontaneously inflammable on contact with atmospheric oxygen at a P_2H_4 content of less than 2–10%. On warming to room temperature increasing decomposition occurs in all cases with evolution of PH_3 and formation of variously colored solid products.

Aqueous solutions of P_2H_4 are neither acidic nor basic. However, in inert solvents diphosphane(4) can be deprotonated by strong bases ($LiBu^n$, $LiPH_2$) and acts as a Lewis base toward strong Lewis acids (B_2H_6, BF_3) (see section III.E).

According to a preliminary X-ray crystallographic investigation of the crystalline powder at −136 °C, solid diphosphane(4) very probably crystallizes in a monoclinic unit cell with the dimensions $a = 3.6$, $b = 6.6$, $c = 5.2$ Å and $\beta = 104°$; however, a related orthorhombic cell cannot yet be definitively discounted. On the assumption of two molecules in the unit cell, as in the case of hydrazine,[43] and in combination with the IR spectrum of the solid (see section III.C), the space groups C_2^1 or C_s^1 are the most probable.[24] A single-crystal X-ray investigation of P_2H_4 has not yet been performed.

C. Spectroscopic and Structural Data

Fehlner and Callen[44] have performed detailed studies on the *mass spectrum* of diphosphane(4) under condi-

Table 1. Mass Spectrum of Diphosphane(4) (50 eV)

m/z	relative abundance	ion	appearance potential, eV	process	ΔH^+_f, kcal mol^{-1}
66	100	$P_2H_4^+$	9.17 ± 0.05	$P_2H_4 \rightarrow P_2H_4^+$	216
65	8	$P_2H_3^+$	12.2 ± 0.2	$P_2H_4 \rightarrow P_2H_3^+ + H$	234
64	52	$P_2H_2^+$	11.1 ± 0.2	$P_2H_4 \rightarrow P_2H_2^+ + H_2$	261
63	46	P_2H^+	14.6 ± 0.3	$P_2H_4 \rightarrow P_2H^+ + H_2 + H$	289
62	60	P_2^+	13.2 ± 0.2	$P_2H_4 \rightarrow P_2^+ + 2H_2$	309
34	≤1[a]	PH_3^+	–		
33	3[a]	PH_2^+	15.3 ± 0.5		
32	8[a]	PH^+	17.4 ± 0.5		
31	8[a]	P^+	19.4 ± 0.5		

[a] Uncorrected for multiplier discrimination.

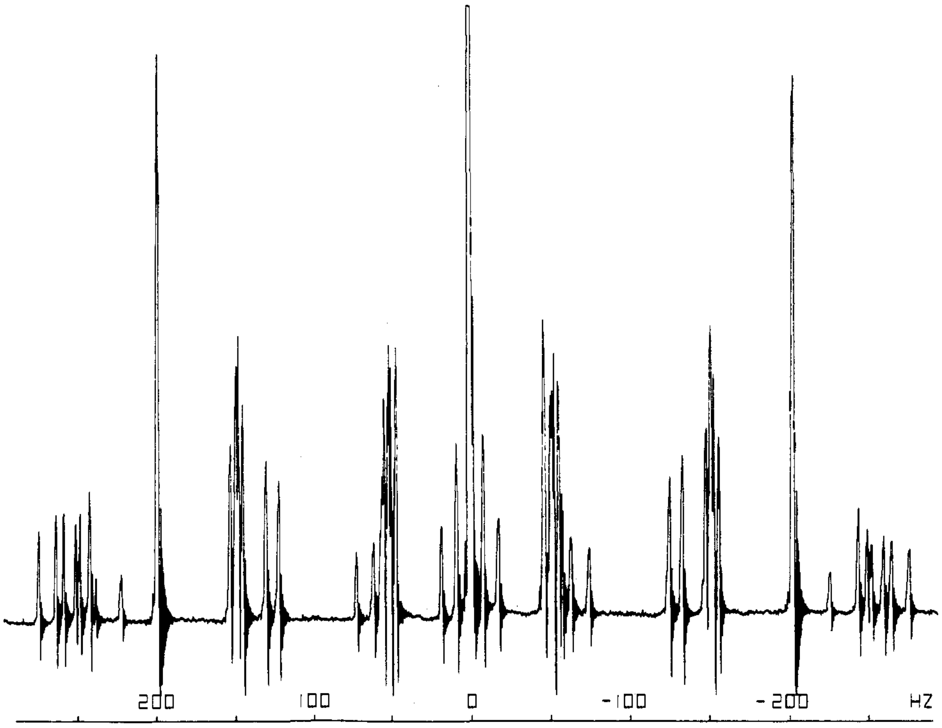


Figure 1. ^{31}P NMR spectrum of P_2H_4 at −80 °C (30.0 MHz).[12]

tions which exclude decomposition of the thermally unstable compound in the ion source of the spectrometer (Table 1). On the basis of these results, earlier literature reports[45,46] which were influenced by decomposition during the measurements need to be corrected. The ionization potential of P_2H_4 was found to be 9.17 ± 0.05 eV; the corresponding ionization potentials of PH_3 and N_2H_4 are of the same order of magnitude (10.05 ± 0.05[44] and 9.00 ± 0.1 eV,[47] respectively). Further details of the mass spectrum of P_2H_4 can be taken from Table 1.

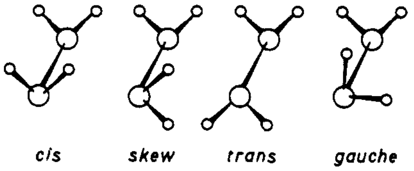
The *^{31}P NMR spectrum* of diphosphane(4) consists of a symmetrical multiplet of 47 lines corresponding to the X part of an $A_2XX'A'_2$ spin system (Figure 1) and collapses to a singlet on decoupling of the ^1H nuclei. The chemical shift of the pure compound at −60 °C amounts to $\delta = -205.0$ (relative to 85% H_3PO_4, negative sign for high field shift) and has a markedly smaller temperature coefficient (0.046 ppm/°C) than PH_3 (0.11 ppm/°C). The chemical shift of a solution of P_2H_4 in carbon disulfide (50.8 mol % P_2H_4, −80 °C) is $\delta = -203.2$ and thus exhibits only a small difference to that of the pure substance at the same temperature ($\delta = -204.0$).[12] These findings indicate that liquid diphosphane(4) is not appreciably associated, in agreement with the value of the Trouton constant (section III.B) and IR spectroscopic results (see below).

The ^{31}P NMR spectrum of pure P_2D_4 consists of a symmetrical multiplet with a chemical shift of $\delta = -206.8$ at −80 °C. The isotope effect on the chemical shift at this temperature in comparison to P_2H_4 amounts to +2.8 ppm. The spectra of samples of P_2D_4 containing PH_3 as an internal standard show additional signals of low intensity which are indicative of an H/D exchange between the two phosphanes.[12]

The *^1H NMR spectrum* of freshly distilled and degassed diphosphane(4) exhibits a practically symmetrical multiplet of 32 lines (the A part of the $A_2XX'A'_2$ spin system) centered at $\delta = 2.51$ (referred to Me_4Si, −60 °C).[12] The contamination of the substance by PH_3 under these conditions is very small, in contrast to earlier measurements at room temperature.[48] The multiplet degenerates to a single sharp line on decoupling the ^{31}P nuclei and this signal does not show any line broadening even at −93 °C. Thus, all protons are equivalent.[12] The following coupling constants were determined from the NMR spectra of P_2H_4 at room temperature:[48] $^1J(P,P) = -108.2$ Hz; $^1J(P,H) = +186.5$ Hz; $^2J(P,H) = +11.9$ Hz; $^2J(H,H_{gem}) = -12$ Hz; $^3J(H,H_{cis}) = +10.5$ Hz; $^3J(H,H_{trans}) = +6.8$ Hz. All NMR spectroscopic results indicate that P_2H_4 in the liquid state very probably undergoes rapid transition between the two mirror image isomeric molecular forms with C_2

symmetry and *gauche* orientation of the free electron pairs at the phosphorus atoms although the existence of a fixed *cis* or *trans* structure is also compatible with the NMR data (see below).[47,48]

The following four, nonplanar molecular structures may be considered for diphosphane(4):



Of these structures, the *cis* form (*syn*, eclipsed, C_{2v}) and the *skew* form (semieclipsed, C_2) are less probable on account of the steric interactions between the hydrogen atoms and since such structures have not been observed for any compound of the type X_2Y_4 (X = N, P, As; Y = H, D, organic group). Thus, either a *trans* structure (*anti*, staggered, C_{2h}) or a *gauche* structure (C_2, two enantiomers) or, in the case of a small barrier to rotation about the P–P bond, a mixture of these two forms is to be expected for diphosphane(4).

First investigations on the *Raman spectrum*[4,26] of liquid P_2H_4 and the *IR spectra*[24] of gaseous and solid P_2H_4 provided strong evidence for the presence of the *gauche* form in all three states of aggregation but could not exclude the *trans* form with certainty. Later investigations of the vibrational spectra of solid P_2H_4, in contrast, led to the prediction of a *trans* structure.[49] These contradictory views remained unclarified in the literature for some time until comprehensive and conscientious reinvestigations of the vibrational spectra of P_2H_4 and P_2D_4 in the solid and gaseous states[50] as well as of P_2H_4 in the liquid state[51] resulted in an irrevocable clarification. Only *one* P–P valency vibration frequency was observed in all IR and Raman spectra and thus only one conformer of P_2H_4 can be present. Since the number of observed Raman bands was greater than six and since, within the limits of experimental accuracy, the frequency values of the IR absorptions and those of the corresponding Raman bands coincided, it was unambiguously demonstrated that the *gauche* form existed,[50,51] which is, therefore, representative for solid, liquid, and gaseous diphosphane(4). On the basis of the equivalence of the protons in the ^{1}H NMR spectra down to low temperatures (see above), the occurrence of a rapid transition between the two enantiomeric *gauche* forms that cannot be differentiated by vibrational spectroscopy must be assumed in liquid P_2H_4. The experimental results indicate that the energy barrier for this process should be relatively small. The irreversibly occurring bands in the Raman spectra recorded at above −60 °C are caused by disproportionation products of P_2H_4, above all PH_3, P_3H_5, and P_4H_6.[4,26,51]

The difference in the position of the P–H valency vibration bands in the IR spectra of gaseous P_2H_4 (2312 cm^{-1})[24,50] and liquid P_2H_4 (2286 cm^{-1})[51] is of the same order of magnitude as that between gaseous PH_3 (2323 cm^{-1} [52]) and solid PH_3 (2305 cm^{-1} [53]). The same is true for the P–D valency vibration bands of gaseous and liquid P_2D_4 (1674 and 1668 cm^{-1}, respectively[24,54]). Even with longer path lengths, no P–H or P–D association bands were detected in the spectra of liquid P_2H_4 and P_2D_4.[30] Hence, in contrast to N_2H_4, intermolecular interactions are very small. This is also substantiated by the IR spectra of P_2H_4 in various solvents such as *n*-hexane, cyclohexane, petroleum ether, tetrachloromethane, carbon disulfide, and hexamethylphosphoric triamide which show no significant deviations from the spectrum of the pure substance. However, an additional, sharp band at 2170 cm^{-1} is observed in the spectrum of a pyridine solution and is attributed to an interaction between the hydrogen atoms of P_2H_4 and the nitrogen atom in pyridine. The spectrum of a solution of P_2H_4 in methanol exhibits a shoulder at ca. 2260 cm^{-1} next to the P–H valency vibration band at 2286 cm^{-1} and in the spectrum of a saturated solution of methanol in P_2H_4 at −78 °C, a shift of the O–H valency vibration band by 62 cm^{-1} in the direction of longer wavelength can be observed. These results are indicative of a weak association between diphosphane(4) and methanol through hydrogen bonds.[30]

The *gauche* structure of P_2H_4 was also confirmed by an investigation of the *microwave spectra* of P_2D_4, P_2D_3H, and P_2H_4.[54] A mathematical analysis gave a torsional angle (as compared to the *cis* conformation) of 74.0 ± 2.2° and a P–P bond length of 2.219 Å. A somewhat earlier *electron diffraction* study[55] of P_2H_4 yielded the following molecular parameters: P–P = 2.218 ± 0.004 Å, P–H = 1.451 ± 0.005 Å, ∠P–P–H = 95.2 ± 0.6°, ∠H–P–H = 91.3 ± 1.4°, torsional angle = 81.8°. Although the refinement of the dihedral angle converged at the value given, free rotation about the P–P bond could not be excluded. From the *PE spectrum*[56] of P_2H_4 it was concluded that the substance existed as a mixture of conformers comprising 90% of the *gauche* form and 10% of the *trans* form.

The *UV absorption spectrum* of diphosphane(4) can only be recorded with difficulty[30] as a consequence of the sensitivity of the compound to UV radiation.[57] In the long-wave region from 2000–3500 Å at room temperature, gaseous P_2H_4 diluted with nitrogen produces a broad absorption band at λ_{max} = 2220 Å together with the absorption for PH_3 at 1910 Å[58] and increasingly stronger bands for more phosphorus-rich hydrides at 2720, 3000, and 3100 Å. The P_2H_4 maximum is shifted slightly in *n*-hexane solution to 2200 Å. The molar extinction coefficient was determined to be $\epsilon \approx 900$ L $mol^{-1}\,cm^{-1}$. After 30 min, the absorption band for P_2H_4 can only be recognized as a shoulder of the band at shorter wavelength for PH_3; in addition, the above-mentioned absorptions at longer wavelengths for the more phosphorus-rich hydrides are present in higher intensities.

D. Theoretical Studies

Numerous semiempirical and *ab initio* calculations have been performed on the molecular structure and, above all, on the relative stabilities of the various conformers of diphosphane(4); in some of the calculations, d functions at phosphorus were also taken into account. The results are summarized in Table 2.

Most of the calculations, especially the most informative,[64,67,71] lead to the conclusion that the *gauche* configuration is the most stable molecular form of diphosphane(4), in analogy to hydrazine.[72] The dihedral angle (as compared with the *cis* configuration) amounts to 76–78°,[64] 76°,[67] or 77.7° [71] (experimental

Table 2. Calculations on the Rotational Conformations of Diphosphane(4)

method	stability order of the conformers	ref(s)
extended MO-LCAO	*cis* > *trans*	59
SCF-IO, EHMO	*gauche* > *cis* > *trans*	60
ab initio SCF	*gauche* > *trans* > *cis*	61,62
ab initio SCF	*trans* ≈ *gauche* > *cis*	63
extended basis set *ab initio* computations	*gauche* > *trans* > *cis*	64
MINDO/3	*gauche* > *trans*	65,66
ab initio SCF	*gauche* > *trans*	67
MNDO	*trans* > *gauche* > *cis*	68
ab initio HF, CI	*gauche* > *trans* > *cis*	69
ab initio HF	*gauche* > *trans* > *cis*	70
ab initio SCF	*gauche* > *trans*	71

value from the microwave spectrum 74 ± 2.2° [54]). In addition, a flat local minimum exists for *trans*-P_2H_4 which is only 0.55 kcal mol^{-1} higher in energy than that for the *gauche*-P_2H_4.[71] The relative stabilities of the *gauche* and *trans* isomers result from a synchronized balance of various effects[71] including, above all, the "*gauche* effect"[73] and the hybridization of the valency orbitals.[64]

Calculations on the dependence of the ^1J(P,P) coupling constant on the dihedral angle gave a satisfactory agreement for the *gauche* configuration of diphosphane(4) with the experimental value (see section III.C) with regard to the sign and the magnitude.[74-76] The significant change in ^1J(P,P) with the spatial structure is mainly determined by the Fermi contact term.[77]

The barrier for pyramidal inversion of phosphorus in diphosphane(4) was determined by a CNDO/2 calculation to be 27.9 kcal mol^{-1}.[78] A somewhat higher value of 30.44 kcal mol^{-1} was obtained from an *ab initio* SCF calculation but was still markedly lower than the energy barrier for PH_3 (33.4 kcal mol^{-1}) calculated by the same method.[67]

Ab initio investigations on the diphosphane(4) radical cation ($P_2H_4^{\cdot+}$)[79,80] have shown that, in contrast to the hydrazine radical cation,[81] both phosphorus centers are pyramidal.

E. Chemical Properties

1. Thermal and Photolytic Decomposition

The predominant chemical property of diphosphane(4) is its transformation under thermal stress or under the influence of light. Since decomposition into the elements is hindered in spite of the positive enthalpy of formation of P_2H_4 (see section III.B), this occurs only upon heating to several hundred degrees Celsius. At lower temperatures, on the other hand, the disproportionation into PH_3 and more phosphorus-rich hydrides is favored both thermodynamically and kinetically.

Numerous investigations have already been performed on the thermal decomposition of diphosphane(4). According to Thénard[3,20] as well as Gattermann and Haussknecht[22] the solid phosphorus hydride P_2H should be formed together with PH_3, whereas Royen and Hill[23,82] postulated the formation of amorphous, yellow phosphorus which contained and/or absorbed varying amounts of PH_3. The composition of the yellow solid depends on the conditions of the decomposition. But no evidence has been obtained for the formation of novel, well-defined phosphorus/hydrogen compounds. According to Evers and Street[25] the thermolysis of P_2H_4 at room temperature in a closed system should give rise to PH_3 and a solid phosphorus hydride with the approximate composition P_9H_4. When this decomposition takes place in the presence of water vapor, the final product is claimed to be $P_{12}H_6$.[83] When these two solids are each heated at 160 °C in a vacuum, PH_3 is evolved to furnish P_9H_3 as the final product; in the light of our current knowledge on the exceptional stability and tendency for formation of nonaphosphane(3), this is highly feasible.[7,10b] On the whole, the authors tend to the conclusion that the thermal decomposition of P_2H_4 leads to nonstoichiometric, solid phosphorus hydrides but not to "absorbates" of PH_3 on yellow phosphorus.

In the course of Raman spectroscopic investigations, Baudler and Schmidt[4,5] found that a disproportionation of P_2H_4 into PH_3 and higher phosphanes (above all P_3H_5) took place on warming or on exposure to light and that the formation of elemental phosphorus could be excluded. Further work in continuation of these investigations led to the isolation or preparative enrichment of a series of novel polyphosphorus hydrides (see sections V–IX).

The phosphorus/hydrogen compounds P_2H_2 and P_3H_5, in addition to PH_3, were identified by Fehlner[11a] during mass spectrometric investigations on the pyrolysis of P_2H_4 under reduced pressure in a flow reactor (see also sections IV and V). The conversion of P_2H_4 into PH_3 and P_2H_2 in the temperature range 297 °C to 377 °C is a zero-order reaction (referred to P_2H_4).[84] In addition, detailed studies of the thermolyses of P_2H_4 and P_2D_4 under reduced pressure in the temperature range 27 to 557 °C were carried out in a static reactor.[85] In this work it was found that P_3H_5 could only be detected below 107 °C and small amounts of P_4 (but no P_2H_2) only at higher temperatures while a labile, solid phosphorus hydride of varying composition was formed over the entire temperatures range and was assumed to participate in the course of the P_2H_4 thermolysis.

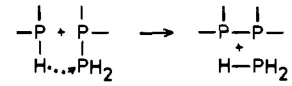
The following results were obtained in an independent study of the thermolysis of diphosphane(4) performed at about the same time in our laboratories in Cologne:[10,31,86-89]

(a) Under mild temperature conditions in both the liquid and gas phases, the first reaction step is a disproportionation into P_3H_5 and PH_3 in which, according to ^{31}P NMR studies, the concentrations of the participating species are in accord with eq 5. On longer

$$2P_2H_4 \rightarrow P_3H_5 + PH_3 \tag{5}$$

heating or at higher temperature, subsequent reactions then give rise to the more phosphorus-rich homologues of the open-chain phosphanes P_nH_{n+2} (see sections VI–IX) until, with increasing phosphorus content in the molecule, the tendency for the formation of open-chain compounds decreases in favor of cyclic products. Beginning with $n = 5$ the monocyclic phosphanes P_nH_n are initially formed while from $n = 7$ onward the polycyclic phosphanes P_nH_{n-2m} (m = 1–9) are clearly preferred (see refs 6 and 7). In general, the thermal decomposition of P_2H_4, depending on the reaction conditions, gives rise to mixtures of various phosphanes in differing proportions, a result which can be explained in terms not only of thermodynamic but also kinetic factors. Finally, at high temperatures, the thermodynamically most stable products of the system, PH_3 and elemental phosphorus, are formed.

(b) The elimination of PH_3 according to eq 5 is an *inter*molecular process, as can be deduced from the mass spectrometric abundancy distribution of the gaseous reaction products (PH_3, PH_2D, PHD_2, PD_3) of the thermolysis of P_2H_4/P_2D_4 mixtures at room temperature. The cleavage of molecular hydrogen occurs



only during the final decomposition into the elements in the high temperature region.

(c) As previously determined by others,[24,25,85] the rate of the thermal decomposition of P_2H_4 at a given temperature decreases with increasing purity of the substrate. On the other hand, the rate of transformation increases markedly on contact with solid surfaces and, above all, in the presence of already formed, yellow solid products. In contrast, the presence of P_3H_5 and P_4H_6 does not exert any autocatalytic influence on the decomposition of P_2H_4. Of course, removal of PH_3 from the reaction system accelerates the decomposition of P_2H_4.

The thermal transformation of P_2H_4 at room temperature is a second-order reaction according to more recent investigations by Blazejowski and Lampe.[90]

The action of a silent electrical discharge on a stream of P_2H_4 under reduced pressure also results in mixtures of more phosphorus-rich phosphanes with three to nine phosphorus atoms in the molecule depending on the reaction conditions. Yellow to vermilion colored, solid polyphosphorus hydrides of unknown composition are formed additionally.[86]

The photolytic decomposition of diphosphane(4) was already observed in early investigations.[3-5,20,22,24,41,58] Fehlner[11b] developed a process for the preparation of P_3H_5 by irradiation of gaseous P_2H_4 at a wavelength of $\lambda = 3500$ Å in a special circulating system (see section V.A). When liquid P_2H_4 under normal pressure at −40 °C is subjected to intense radiation, appreciable quantities of P_3H_5 and P_4H_6 are formed within a short time; on longer irradiation, the molar concentration ratios P_3H_5/P_2H_4 and P_4H_6/P_2H_4 decrease in favor of the formation of a yellow, flaky solid.[89]

2. Reactions with Oxygen and Peroxo Compounds

Diphosphane(4) ignites spontaneously in air and burns with a bright white flame to give phosphorus pentoxide and water which combine to furnish phosphoric acid as the final product.[3,20]

An oxidation product with an intact P–P bond, diphosphane(4) monoxide (1), was identified by mass spectrometry during the fractionation of the volatile hydrolysis products of calcium phosphide.[91] Compound 1 is formed by the reaction of P_2H_4 with the small amount of atmospheric oxygen trapped in the commercial phosphide pellets. The presence of the intact P–P bond in 1 was deduced from the similarities of the mass spectrometric fragmentation patterns between 1 and P_2H_4.

$$P_2H_4 + {}^1/_2O_2 \rightarrow \underset{\mathbf{1}}{H_2PP(O)H_2} \qquad (6)$$

Diphosphane(4) dioxide (2) was also detected by mass spectrometry after longer oxidation of P_2H_4 at −78 °C by an oxygen-containing stream of nitrogen. In addition to 2, the formed solid reaction product also contained water and the monoxide P_2H_2O (3); the latter product was increasingly formed from 2 at above −20 °C.[92]

$$P_2H_4 \xrightarrow{N_2(+O_2)} \underset{\mathbf{2}}{P_2H_4O_2} \xrightarrow{>-20\,^\circ C} \underset{\mathbf{3}}{P_2H_2O} + H_2O \qquad (7)$$

Diphosphane(4) reacts with peroxo compounds such as hydrogen peroxide, tetraline hydroperoxide, trifluoroperoxyacetic acid, and cumene hydroperoxide (which is particularly suited for preparative work) at −30 °C under retention of the P–P bond to furnish phosphinophosphinic acid (4) as the primary product.[93]

$$P_2H_4 + 2H_5C_6C(CH_3)_2OOH \rightarrow \underset{\mathbf{4}}{H_2PPH(O)OH} + 2H_5C_6C(CH_3)_2OH \qquad (8)$$

Compound 4 disproportionates to a major extent *in statu nascendi* to give phosphanes (above all PH_3) and monophosphorus acids of various oxidation states as well as some di(phosphino)phosphinic acid, $(H_2P)_2P(O)OH$ (5). The acids 4 and 5 can be trapped and stabilized as their triethylammonium salts.

3. Reactions with Acids and Hydrogen Halides

Diphosphane(4) generally undergoes disproportionation under the action of acids.[20] The decomposition into PH_3 and more phosphorus-rich solid products of varying composition is also rapid at low temperatures and proceeds autocatalytically in the presence of small amounts of acid. Thus, all glass apparatus used in work with P_2H_4 should be "alkalinized" by treatment with 5% potassium hydroxide solution, half concentrated ammonia solution, or 3% Mucasol solution (Merz & Co., Frankfurt/Main) before use to remove traces of acid.[27,30]

In order to clarify the question of the salt formation of P_2H_4 with hydrogen chloride in analogy to that of hydrazine, Royen and Hill[23] investigated the behavior of the two components over a wide temperature range. The mixture condensate, which is colorless at lower temperatures, acquired a yellow coloration already at −125 °C and rapidly decomposed with liberation of PH_3 at its melting temperature. The already known acid decomposition of P_2H_4 occurred immediately when the components reacted in the gaseous or liquid states.

Diphosphane(4) reacts analogously with liquid hydrogen fluoride.[94] At a molar ratio of 1:1, complete disproportionation with formation of PH_3 and deposition of a yellow solid occurred. With a large excess of HF, difluorophosphorane (6) is formed in a subsequent

$$H_2PPH_2 + HF \rightarrow PH_2F + PH_3 \qquad (9)$$

$$PH_2F + HF \rightarrow \underset{\mathbf{6}}{PH_3F_2} \qquad (10)$$

reaction of PH_2F. Immediately after the start of the reaction weak signals for the primary protonation product $P_2H_5^+$ have been identified in the ^{31}P NMR spectrum.[95]

4. Reactions with Aqueous Sodium Hydroxide and Liquid Ammonia

The reactions of diphosphane(4) with aqueous hydroxide solutions are relatively sluggish.[30] Mixtures of the two components at room temperature appear to be appreciably more stable than the pure phosphane itself. When P_2H_4 is added to an excess of sodium hydroxide solution (d_{20} = 1.17) with gentle stirring, no mutual solution of the two components can be observed at first (see also section III.B). Only after about 15 min does a thin brown film form at the phase boundary with the simultaneous, weak evolution of PH_3. Within 5 h, the proportion of the brown solid encompassing the phosphane which, in turn, slowly turns yellow, increases. After a total of 12 h, the liquid phosphane phase is completely replaced by a solid, yellow product of unknown composition. Over the course of several days, this solid dissolves entirely in the sodium hydroxide solution and, in the process, PH_3, hypophosphorous acid, and some phosphorous acid are formed.

Diphosphane(4) is decomposed by liquid ammonia at −33 °C to furnish a deep-violet colored solution with concomitant evolution of PH_3.[42] After removal of the solvent, a black solid of varying composition containing some solvent in addition to phosphorus and hydrogen remains; this product is soluble in liquid ammonia.

5. Reactions with Metalating Agents

Diphosphane(4) reacts with metalating agents such as *n*-butyllithium or lithium dihydrogen phosphide in tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) again via disproportionation. The final products at −20 °C are trilithium heptaphosphide (7) and PH_3; in the former reaction *n*-butane is also formed.[96]

$$9P_2H_4 + 3LiBu^n \xrightarrow[-20\,°C]{THF} \underset{7}{Li_3P_7} + 11PH_3 + 3Bu^nH \tag{11}$$

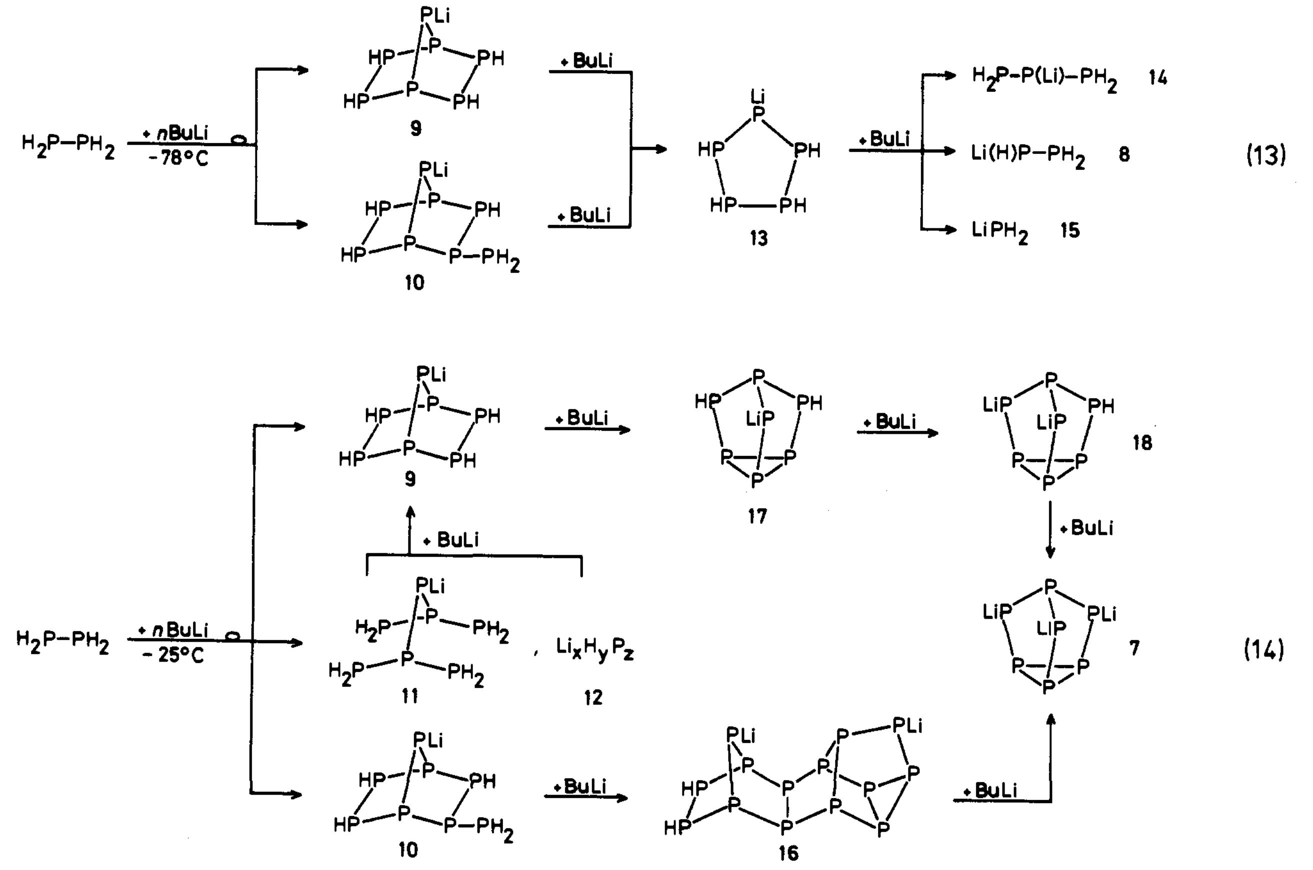
$$9P_2H_4 + 3LiPH_2 \xrightarrow[-20\,°C]{DME} \underset{7}{Li_3P_7} + 14PH_3 \tag{12}$$

Recently, several novel metal hydrogen polyphosphides (partially metalated higher phosphanes) have been detected as intermediates and some of them have been isolated in the pure state at lower temperatures.[6,97-102] In detail, the metalations of P_2H_4 by $LiBu^n$ in THF at −78 or −25 °C proceed as shown in eqs 13 or 14 (Scheme 1).

In each case, the primary step is the formation of lithium trihydrogen diphosphide (8) which, however, is not stable in the presence of diphosphane(4). A rapid cascade of disproportionation and transmetalation reactions of this species furnishes initially the highly reactive monolithiated, more phosphorus-rich, open-chain phosphanes $LiH_{n+1}P_n$ followed by cyclic compounds until metalation products possessing insufficient nucleophilicity for further attack on P_2H_4 are formed. Since the reaction sequence comes to a temporary standstill at this stage, these phosphides are the first products that can be detected.

When the metalation is carried out at −78 °C, the major products are lithium tetrahydrogen heptaphos-

Scheme 1



$$P_2H_4 + LiBu^n \rightarrow \underset{8}{LiH_3P_2} + Bu^nH \qquad (15)$$

phide (9) and lithium pentahydrogen octaphosphide (10), whereas at −25 °C, two potential precursors of 9, namely the open-chain lithium octahydrogen heptaphosphide (11) (see section IX) and a not yet identified phosphide 12, are formed additionally.

Upon further addition of the metalating agent, the reaction at −78 °C proceeds further by way of the lithium tetrahydrogen cyclopentaphosphide (13) to the open-chain phosphides 14, 8, and 15; the tricyclic heptaphosphide 7 is not formed at this temperature. At −25 °C, on the other hand, further 9 is initially formed from the precursors 11 and 12. While compound 9 remains unchanged up to a P_2H_4/$LiBu^n$ ratio of 8:1, 10 reacts to furnish the polycyclic tetradecaphosphide 16. Finally 9 also reacts further by way of the heptaphosphides 17 and 18 to yield the final product 7 which is additionally formed in the last step by degradation of 16. The different courses of the reaction at −25 and −78 °C can be attributed to the increasing solubility of PH_3 in THF with decreasing temperature. Hence, PH_3 can participate to a greater extent in the reaction process at −78 °C. The reader is referred to the recent review article[7] for further information on the structures and additional routes of formation of the polycyclic hydrogen polyphosphides 9, 10, 16, 17, and 18 as well as the heptaphosphide 7 and the monocyclic pentaphosphide 13.

Some of the lithium polyphosphides may also act as metalating agents toward diphosphane(4). Thus, the tetradecaphosphide 16 is accessible from P_2H_4 and the heptaphosphide 7 by a sort of retroreaction and is also the product of the reaction between P_2H_4 and the cyclopentaphosphide 13.[100]

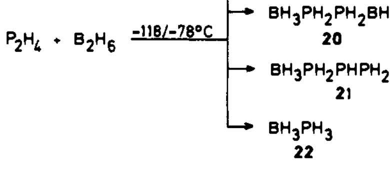
$$P_2H_4 \xrightarrow[-25\,°C]{+Li_3P_7} \underset{16}{Li_2H_2P_{14}} \xleftarrow[-78\,°C]{+LiH_4P_5} P_2H_4 \qquad (16)$$

The monohydrogen heptaphosphide 18 can be prepared analogously by metalation of P_2H_4 with 7 at −25 °C.[99]

$$9P_2H_4 + 2\underset{7}{Li_3P_7} \rightarrow 3\underset{18}{Li_2HP_7} + 11PH_3 \qquad (17)$$

6. Reactions with Boron Compounds

Diphosphane(4) already reacts below its melting point (−99 °C[23]) with diborane(6). According to an earlier publication,[103] the product was assumed to be the 1:1 adduct $P_2H_4{\cdot}B_2H_6$ but a spectroscopic characterization was not reported. More recent investigations[104] have revealed a much more complicated process:



(18)

At −118 °C and B_2H_6/P_2H_4 ratios of 83:1 to 3.3:1, a colorless solid is formed which was shown by ^{31}P, ^{11}B, and ^1H NMR spectroscopy to consist of a mixture of diphosphane–borane 19 and diphosphane–1,2-bis(borane) 20 together with some triphosphane–1,3-bis(borane) 21 and BH_3–PH_3 22.[105,106] The proportion of 20 in the product mixture reaches a maximum of ca. 25% of the total phosphorus even when a large excess of B_2H_6 is used. Apparently the addition of *one* BH_3 group to diphosphane(4) strongly reduces the Lewis basicity of the other PH_2 group. The formation of a 1:1 adduct of the substrates was not observed.[104] The formation of the byproducts 21 and 22 may probably be explained in terms of a partial disproportionation of P_2H_4 under the influence of the Lewis acid B_2H_6. Compounds 19–22 cannot be isolated from the reaction mixture because of their similar properties and the thermal lability of the phosphane–borane adducts.

The reaction of P_2H_4 with $BH_3{\cdot}THF$[107] between −78 and −30 °C leads to similar results.[104] The maximum proportion of 20 in the reaction mixture amounts to ca. 17% of the total phosphorus even with a large excess of $BH_3{\cdot}THF$. On the other hand, when equimolar amounts of the substrates are allowed to react at −78 °C, diphosphane–borane 19 is formed in practically quantitative yield and can be isolated pure from the THF solution.

$$P_2H_4 + BH_3{\cdot}THF \xrightarrow[-THF]{-78\,°C} \underset{19}{BH_3PH_2PH_2} \qquad (19)$$

Compound 19 (mp −69 °C) can be stored at low temperature for several days without decomposition. Above −15 °C, increasing disproportionation with formation of 22, 21, and triphosphane-2-borane, PH_2-$PH(BH_3)PH_2$ (23), occurs until, finally at room temperature, a yellow, insoluble product is formed with vigorous evolution of gases (B_2H_6, PH_3, H_2). Solutions of 19 in THF are considerably more stable than the pure substance. Vigorous, even explosive, reactions occur upon contact with atmospheric oxygen or other oxidizing agents.

Diphosphane(4) also reacts with boron trifluoride even at −118 °C. The unstable product formed is assumed to have the composition $P_2H_4{\cdot}2BF_3$ on the basis of the material balance;[103] however, further investigations on this substance are still needed.

7. Miscellaneous Reactions

As a consequence of its reducing properties, diphosphane(4) reacts with aqueous solutions of silver salts via precipitation of silver and formation of phosphoric acid. A quantitative analysis process for P_2H_4 has been developed on the basis of this reaction.[30]

$$P_2H_4 + 14Ag^+ + 8H_2O \rightarrow 2H_3PO_4 + 14Ag + 14H^+ \qquad (20)$$

Similarly, iodine in aqueous solution also effects a mild oxidation of P_2H_4, generally giving rise to a mixture of monophosphorus acids of varying oxidation states.[31]

In the reaction of P_2H_4 with the triphenylmethyl radical, one P–H bond is cleaved in the primary process to furnish triphenylmethane in quantitative yield. Further reactions of the formed P_2H_3 radical lead to the final products PH_3 and a yellow solid of varying composition.[30]

$$P_2H_4 + (C_6H_5)_3C^{\bullet} \rightarrow (C_6H_5)_3CH + P_2H_3^{\bullet} \tag{21}$$

The action of gaseous diazomethane on diphosphane(4) in the dark or upon photochemical excitation ($\lambda > 3000$ Å) mainly gives rise to the P–P bond insertion product, methylenebis(phosphane) (24) which could be

$$P_2H_4 + CH_2N_2 \xrightarrow{-40/-78\ ^\circ C} \underset{\mathbf{24}}{H_2PCH_2PH_2} + N_2 \tag{22}$$

prepared in the pure state by this route. Byproducts are CH_3PH_2 together with small amounts of $H_2PPHCH_2PH_2$, $CH_3P(H)CH_2PH_2$, $CH_3P(H)PH_2$, and $H_2PCH_2PHCH_2PH_2$.[108]

Tetraphenyldiphosphane reacts with P_2H_4 in the dark at −78 °C in THF or CS_2 with formation of an equilibrium mixture in which 1,1-diphenyldiphosphane can be detected by NMR spectroscopy.[109]

$$H_2PPH_2 + Ph_2PPPh_2 \rightleftharpoons 2Ph_2PPH_2 \tag{23}$$

The reaction with 1,2-diphenyldiphosphane in THF at above +40 °C furnishes monophenyldiphosphane,[109] a product also obtained from P_2H_4 and P_2Ph_4 in the presence of an excess of $PhPH_2$.[110]

$$H_2PPH_2 + H(Ph)PP(Ph)H \rightleftharpoons 2H(Ph)PPH_2 \tag{24}$$

Compounds containing trivalent phosphorus atoms generally function as excellent ligands in coordination chemistry. Accordingly, diphosphane(4) is able to undergo ligand exchange with suitable transition metal complexes. The first mixed carbonyl(diphosphane)-metal complex to be reported was the compound $[P_2H_4\text{-}Mo(CO)_4]_x$ ($x \geq 2$), obtained from tetracarbonyl(norbornadiene)molybdenum(0) and P_2H_4 in pentane at 0 °C;[111] however, further investigations of this product are still necessary.

The first binuclear complexes in which diphosphane(4) serves as a bridging ligand were described somewhat later.[112]

$$2(OC)_5Cr{\cdot}THF + P_2H_4 \xrightarrow[-78\ ^\circ C]{THF} P_2H_4[Cr(CO)_5]_2 + 2\ THF \tag{25}$$

$$C_5H_5Mn(CO)_2{\cdot}THF \xrightarrow[THF,\ -78\ ^\circ C]{+P_2H_4\ (excess)} P_2H_4[C_5H_5Mn(CO)_2]_2,\ \text{byproducts} \tag{26}$$

The structures of both complexes were unambiguously confirmed by IR, mass, and NMR spectroscopy and both compounds are surprisingly stable in the solid state. This stability is probably due to a matrix-like encasement of P_2H_4 in the voluminous metal carbonyl groups as well as back-bonding effects.

IV. Diphosphane(2) or Diphosphene, P_2H_2

The parent compound of the diorganodiphosphenes RP═PR, discovered in 1981,[113] the phosphorus/hydrogen compound P_2H_2, had already been identified by mass spectrometry in 1966 during investigations on the thermolysis products of gaseous P_2H_4.[11a] The pyrolysis was carried out in a flow reactor under reduced pressure and the exiting gases were passed directly into a coupled mass spectrometer. The spectra were investigated under conditions which excluded a decomposition of the phosphorus hydrides in the ion source of the instrument; furthermore, the appearance potentials of selected ions, depending on the reactor temperature, were studied.

The results of these comprehensive investigations[11a,44,85] unequivocally confirm that the unstable phosphorus/hydrogen compound P_2H_2 is formed in the thermolysis of P_2H_4 at above room temperature and under reduced pressure. Its energy of formation was estimated to be 26 ± 8 kcal mol^{-1} and its dissociation energy as 74 kcal mol^{-1}.

$$P_2H_4 \xrightarrow{\Delta} PH_3 + {}^1/_2P_2H_2 \tag{27}$$

Because of its extreme reactivity, P_2H_2 cannot be isolated pure in preparatively useful amounts and so no experimental work on its structural elucidation has been possible to date. According to MNDO calculations,[114] the molecule should be planar and exhibit a P–P bond order of two. A somewhat larger stability is predicted for the *trans* form in comparison to the *cis* form.

Diphosphane(2) monoxide (3) was identified by mass spectrometry as a product of the thermolysis of diphosphane(4) dioxide (2) at above −20 °C (see section III.E.2).[93] Its formation by the cleavage of water from 2 as shown in eq 7 has been confirmed experimentally. However, further work is needed to provide convincing information on the structure of compound 3.

V. Triphosphane(5), P_3H_5

The existence of polyphosphorus hydrides more phosphorus-rich than P_2H_4 was viewed with scepticism for a long time in view of the properties of the latter. In connection with investigations on diphosphane(4) in which they found no evidence for the presence of higher homologues, Royen and Hill[23] in 1936 came to the conclusion that such compounds would hardly ever be accessible because of the extremely high rates of decomposition.

The first indications for the existence of triphosphane(5) were found 20 years later by the presence of an excessive number of lines in the Raman spectrum of diphosphane(4).[4,5] The increase in the intensities of these attendant lines with concomitant evolution of PH_3 on illumination or warming was suggestive of a disproportionation of P_2H_4 with formation of P_3H_5 according to eq 5. The mass spectrometric identification of P_3H_5 was reported in 1964 by Royen et al.[9] in experiments in which they decomposed small amounts of both Mg_3P_2 and Ca_3P_2 in admixture with the corresponding arsenides, nitrides, or germanides with dilute hydrochloric acid directly at the mass spectrometer. A short time later, fractions highly enriched in P_3H_5 could be obtained on a preparative scale either by separation of the products from the reaction of commercial calcium phosphide with pure water or by the distillative workup of aged samples of P_2H_4.[10] At about the same time, Fehlner[11] also reported the mass spectrometric detection of P_3H_5 in the thermolytic and photolytic decomposition of P_2H_4. The chain structure

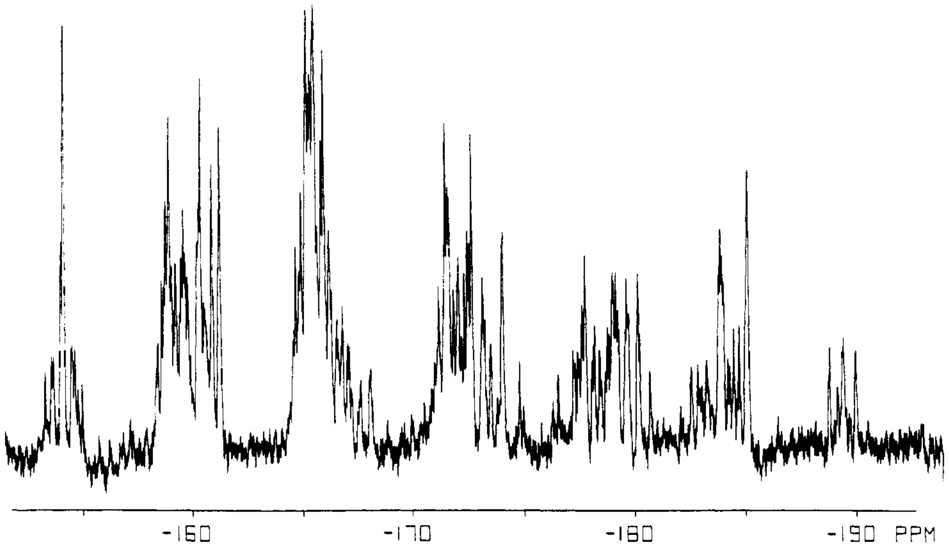


Figure 2. ^{31}P NMR spectrum of P_3H_5 at −60 °C (36.4 MHz).[12]

of P_3H_5 was corroborated in 1972 by means of NMR spectroscopic methods.[12]

A. Preparation and Properties

Triphosphane(5) can be obtained from the volatile hydrolysis products of calcium phosphide[29,86,87] or from the products of the thermolysis or photolysis of diphosphane(4).[11b,89] For preparative purposes, the approach starting from pure diphosphane(4) is more advantageous. Fehlner[11b] obtained mixtures of P_3H_5 with 40% P_2H_4 in a special pyrolysis reactor in this way but could not separate the products without decomposition occurring. Thus, a process for the gas-phase photolysis of P_2H_4 using light with the wavelength λ = 3500 Å in a circulating apparatus was developed. This method enables the preparation of about 10 mg of P_3H_5 in 95% purity in 100 min.

Some time ago, a reproducible process for the preparation of milliliter amounts of practically pure P_3H_5 based on the thermolysis route was developed in our laboratories in Cologne.[6] In a typical run, 81 mL of pure P_2H_4 first gave 63 mL of a clear, yellow thermolysate with a P_3H_5 content of about 20% of the total phosphorus (P-%) after 25 h at +35 °C. The thermolysis was stopped at this stage to prevent a further reaction of P_3H_5 and the formation of solid phosphorus hydrides which would catalyze the decomposition of the liquid phosphanes. The isolation of P_3H_5 was achieved by constant flow distillation in admixture with P_2H_4 (pressure 10^{-4} Torr, bath temperature −40 to +90 °C) and fractional condensation. At −40 °C, 9.1 mL of highly enriched P_3H_5 (86.9 P-%) condensed which contained only small amounts of P_2H_4 and P_4H_6 while 45 mL of P_2H_4 condensed at −196 °C. P_3H_5 was obtained in 96% purity by a repeated distillation. The difficulty of this procedure is comparable with that of the P_2H_4 preparation.[27]

The relatively stable triphosphane derivative **25** (mp 73 °C)[115] also appears to be a suitable substrate for the preparation of P_3H_5: solvolysis under appropriate conditions should lead to the parent compound.

$$\underset{\mathbf{25}}{(Me_3Si)_2PPHP(SiMe_3)_2} + \underset{R = H, \text{ alkyl}}{4ROH} \rightarrow P_3H_5 + 4Me_3SiOR \quad (28)$$

Triphosphane(5) is a colorless liquid that is spontaneously inflammable in the air; it can be stored for several days at −80 °C under exclusion of air and light. A rapid yellow discoloration occurs in diffuse daylight at room temperature followed by decomposition to a yellow solid. The earlier report[11] that P_3H_5 is a solid below −40 °C which upon warming already decomposes with evolution of PH_3 and formation of a yellow solid before or during the melting process could not be confirmed by later investigations.[6] On the basis of plausible assumptions a boiling point of 96[11b] and 97.5 °C,[17] respectively, has been estimated.

B. Spectroscopic Data and Structure

The *mass spectrum* of triphosphane(5)[11,89] confirms the monomolecular structure of this polyphosphorus hydride. Under appropriate measurement conditions in which a decomposition of the compound in the spectrometer is practically excluded, the molecular ion $P_3H_5^+$ exhibits the highest relative abundance. Fragmentation occurs to preferentially form the $P_2H_3^+$ ion, the corresponding other fragment is the electrically neutral PH_2 radical. The appearance potential of the $P_3H_5^+$ ion is 8.7 ± 0.1 eV.[11b]

The *^{31}P NMR spectrum* of triphosphane(5)[6,12] contains a series of complex signal groups in the region from ca. −150 to −190 ppm, thus occurring at lower field than the multiplet of P_2H_4 (Figure 2). No symmetry can be recognized from the appearance of the spectrum. On decoupling of the ^1H nuclei, the $X_1X_2ABX_3AX'_1X'_2$ spin system degenerates to eight sharp signals corresponding to the A_2B spin system of the three-atom chain P_A–P_B–P_A (Figure 3). The ^{31}P NMR parameters of P_3H_5 are compared with those of P_2H_4 and PH_3 in Table 3.

As can be seen from Table 3, the $\delta^{31}P$ chemical shifts are displaced to lower field with increasing chain length; at the same time, the absolute value for the $^1J(P,P)$ coupling constant increases. In the light of contemporary experience,[116] both changes can be attributed to a change in the hybridization: increasing s character of the bonding orbitals at phosphorus with increasing substitution by phosphorus atoms. In the case of P_3H_5,

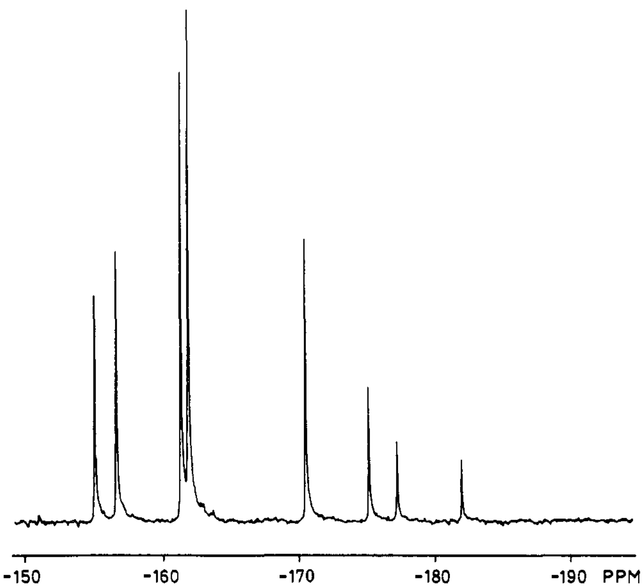


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of P_3H_5 at −20 °C (24.3 MHz).[89]

Table 3. ^{31}P NMR Parameters of P_3H_5 (−60 °C), P_2H_4 (−60 °C), and PH_3 (−90 °C), Solvent-Free

Phosphane	δ	J_{PP}, Hz	ref(s)
P_3H_5	P_A: −156.7 P_B: −173.2	−146.6	6,12
P_2H_4	−205.0	−108.2[a]	12
PH_3	−235.1		12

[a] Determined from the ^1H-undecoupled room-temperature spectrum.[48]

Table 4. Raman Spectrum of P_3H_5, Solvent-Free, −80 °C

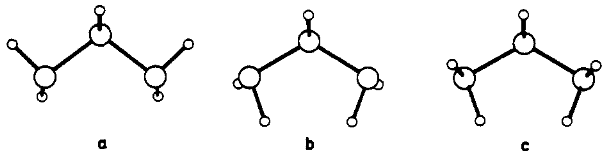
frequency, cm^{-1}	relative intensity	degree of depolarization (state of polarization)	assignment
158	15	0.42 (p)	δ(PPP)
414	63	0.08 (p)	ν_s(PP)
457	14	0.68 (dp)	ν_{as}(PP)
610	1	0.00 (p)	δ(HPP)
655	1	0.00 (p)	δ(HPP)
717	4	0.11 (p)	δ(HPP)
747	1	0.00 (p)	δ(HPP)
835	2	0.00 (p)	δ(HPP)
883	2	0.34 (p)	δ(HPP)
1062	5	0.44 (p)	δ(HPH)
2267	100	0.19 (p)	ν(PH)

the relatively high field position of the signal for the atom P_B is indicative of an increased PH acidity and hence nucleophilicity of the central phosphorus atom.

In the *$^1H\{^{31}P\}$ NMR spectrum*,[12] the center of the signal group for P_3H_5 is shifted to lower field by ca. 0.5 ppm as compared to the singlet of P_2H_4 (section III.C). This further confirms the increased acidity of the longer-chain phosphanes—a situation similar to the sulfanes and silanes. The differences in the chemical shifts between the individual homologues in the ^1H NMR spectra are very much smaller than those in the ^{31}P NMR spectra so that the latter are much more informative for the characterization of phosphane mixtures.

The widening of the angle at the central phosphorus atom of P_3H_5 is also substantiated by the *Raman spectrum*[6] (Table 4). In an approximation treatment of the molecule as a three mass system, the PPP valency angle was found to be 104.5° (<HPH in PH_3, 93.5°;[117] <HPP in P_2H_4, 95.2° [55]). The valency force constant of the P–P bond amounts to 1.77 mdyn/Å and the deformation constant of the PPP valency angle to 0.15 mdyn/Å.

According to *theoretical calculations* (MNDO),[114] three conformers **a**–**c** with symmetry C_s exist for P_3H_5 and of these the conformer **a** exhibits the largest relative stability. The dihedral angles HPPP of the terminal



hydrogen atoms are ±86.2° and ±183.5° so that the free-electron pairs of neighboring phosphorus atoms have almost an *anti* orientation to each other. The somewhat more energy-rich conformer **b** has corresponding dihedral angles of ±4.9° and ±102.3° and is thus characterized by a *gauche* arrangement of neighboring free electron pairs while in the considerably more energy-rich conformer **c** with dihedral angles of ∓1.9° and ∓100.1° the neighboring free-electron pairs are positioned *syn* to each other. The calculated dipole moments of the conformers **a**, **b**, and **c** are 0.72, 2.24, and 3.86 Debye, respectively. In addition to the three C_s conformers, there are also numerous conformers without any symmetry since the two terminal PH_2 groups can rotate independently of each other relative to the P_3 plane. These C_1 conformers are slightly less stable than the isomer **a** but considerably more stable than the isomer **b** while exhibiting rather similar stabilities among themselves. The calculation gave a value of 103.6° for the PPP valency angle which is in very close agreement with the value determined from the Raman spectrum (104.5°).[6] In addition, the structures and energies of the molecular cation and all mass spectrometrically detected fragments of P_3H_5 were calculated.

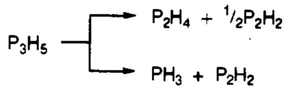
C. Chemical Properties

Like diphosphane(4), triphosphane(5) also undergoes ready disproportionation into more and less phosphorus-rich phosphanes on exposure to light and heat. The formation of tetraphosphane(6) according to eq 29 can already be detected at room temperature after a short time.[6,11b,89] The process is of course favored by removal

$$2P_3H_5 \rightarrow P_4H_6 + P_2H_4 \qquad (29)$$

of the more volatile diphosphane.

Detailed mass spectrometric investigations on the thermolysis of gaseous P_3H_5 in the pressure range 0.2–10 mTorr at temperatures between 180 and 390 °C have revealed that the decomposition of P_3H_5 proceeds by two routes.[118] The transformation to P_2H_4 and P_2H_2



(30)

is a zero-order reaction while that to PH_3 and P_2H_2 is a first-order reaction (with respect to P_3H_5). Heterogeneous mechanisms have been postulated for both reaction paths. The diphosphanes formed decompose further to PH_3 and P_4.

The photolysis of P_3H_5 at 10^{-3} Torr and 30 °C results in appreciably lower proportions of P_4H_6 than the room temperature thermolysis; instead the formation of less phosphorus-rich phosphanes and P_4 predominates.[89]

Whereas triphosphane(5) burns directly to phosphorus pentoxide and water in excess atmospheric oxygen, the corresponding monoxide **26** is formed in the hydrolysis of calcium phosphide by reaction of P_3H_5 with the small amounts of atmospheric oxygen trapped in the phosphide pellets.[91] This product was identified,

$$P_3H_5 + {}^1/_2O_2 \rightarrow \underset{\mathbf{26}}{P_3H_5O} \qquad (31)$$

together with P_2H_4O (see section III.E.2) and other polyphosphane monoxides, by mass spectrometric analysis of the less volatile hydrolysis products. No experimentally substantiated conclusions can yet be drawn about the structure of compound **26**; however, it may reasonably be assumed that the oxygen is bonded to the central phosphorus atom of the P_3 chain since this is the position with the greater nucleophilicity.

Further, structurally confirmed derivatives of triphosphane(5) are lithium tetrahydrogen triphosphide, $H_2PP(Li)PH_2$ (**14**), and triphosphane–1,3-bis(borane), $BH_3PH_2PHPH_2BH_3$ (**21**), which are formed as one of the end products from the reactions of P_2H_4 with LiBu^n and B_2H_6, respectively, as well as triphosphane–2-borane, $H_2PPH(BH_3)PH_2$ (**23**) formed in the disproportionation of diphosphane–borane **19** (see sections III.E.5 and III.E.6).

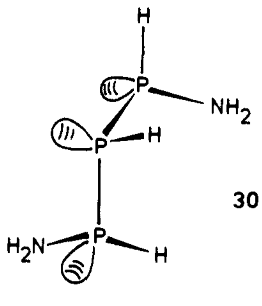
The partially organo-substituted triphosphanes **27a**,[119] **27b**,[120] **28a**,**b**[121] **25**[115,122] (see section V.A), and **29a–d**[122]

$H(R)PP(R)P(R)H$ $Bu^t_2PP(H)PR_2$
27a: R = Ph **28a**: R = $SiMe_3$
b: R = Bu^t **b**: R = Bu^t

$R^1(Me_3Si)PP(H)P(SiMe_3)R^2$
29a: $R^1 = SiMe_3$, $R^2 = Me$
b: $R^1 = SiMe_3$, $R^2 = Bu^t$
c: $R^1 = R^2 = Bu^t$
d: $R^1 = Me$, $R^2 = Bu^t$

are thermally more stable than P_3H_5, especially when the phosphorus chain is shielded against intermolecular disproportionation reactions by the presence of voluminous substituents. In contrast to P_3H_5, the phosphorus atoms of these triphosphane derivatives frequently constitute centers of chirality so that the existence of diastereomers is possible.[119,120,122] The populations of the individual isomers depend on the respective molecular conformations which, in turn, are governed by the tendency for the *gauche* orientation of neighboring free-electron pairs[73] as well as steric interactions between the substituents.

A further "inorganic" derivative of P_3H_5 is the "mixed" nonmetallic hydride 1,3-diaminotriphosphane(5) (**30**).[123] This compound is formed in the reaction of white phosphorus with sodium in liquid ammonia (ratio P/Na = 2:1 or 1.5:1) together with $NaPH_2$, Na_2HP_7, and more phosphorus-rich phosphides. The composition and structure of **30**, which is only stable in liquid ammonia, were confirmed by ^{31}P NMR spectroscopy. Of the three possible diastereomers, only the *erythro,erythro* isomer is formed; probably because it is more favored energetically as a result of the formation of hydrogen bonds between the central phosphorus atom and the *transoid* NH_2 groups. The corresponding simplest mixed hydride $H_2N{-}PH_2$ and its tautomers $HN{=}PH_3$ and $H_3N^+{-}P^-H$ are still unknown.



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VI. Tetraphosphane(6), P_4H_6

A. Formation

Tetraphosphane(6) is an intermediate in the thermal and photochemical decompositions of less phosphorus-rich phosphanes[6,11b] (sections III.E.1 and V.C). Accordingly, thermal reactions of liquid diphosphane(4) and triphosphane(5) generally lead to phosphane mixtures with a variable content of tetraphosphane(6).[10,89,124] The thermolysis products in both cases consist initially of only open-chain phosphorus hydrides which, on continuation of the thermolysis, in part react further to form cyclopentaphosphane, P_5H_5.[7] Phosphane mixtures with a P_4H_6 content of 35–40 P-% together with P_3H_5 (ca. 55 P-%), P_2H_4 (5–10 P-%), and P_5H_5 (<5 P-%) were obtained from the diphosphane(4) thermolysates (see section V.A) by separation of P_2H_4 and PH_3 at −40 °C under high vacuum.[124] In this manner, about 15 mL of a solid-free, yellow phosphane mixture of medium viscosity highly enriched in tetraphosphane(6) could be obtained from 100 mL of P_2H_4. Further enrichment of P_4H_6 by distillative removal of P_3H_5 is not possible since, under these conditions, further disproportionation with formation of P_5H_5 occurs. The highest content of P_4H_6 (48 P-%) was achieved by thermolysis of pure P_3H_5 at +10 °C under high vacuum.[89] Under these conditions, tetraphosphane(6) can be handled without decomposition for short times.

B. Structural Discussion

Starting with tetraphosphane(6), the structural situation of open-chain phosphanes becomes more complex due to the occurrence of isomers. On the basis of an unbranched phosphorus chain, the compound P_4H_6 should be characterized in the $^{31}P\{^1H\}$ NMR spectrum by an AA′BB′ spin system for the two different types of phosphorus atoms. However, the experimentally observed spectrum contains considerably more lines (Figure 4).[6] According to the results of a spectral analysis[6,125] there are two reasons for this: On the one hand, P_4H_6 is always formed as a mixture of the two constitutional isomers with unbranched and branched phosphorus chains ($P_4H_6^n$ and $P_4H_6^i$, respectively) upon

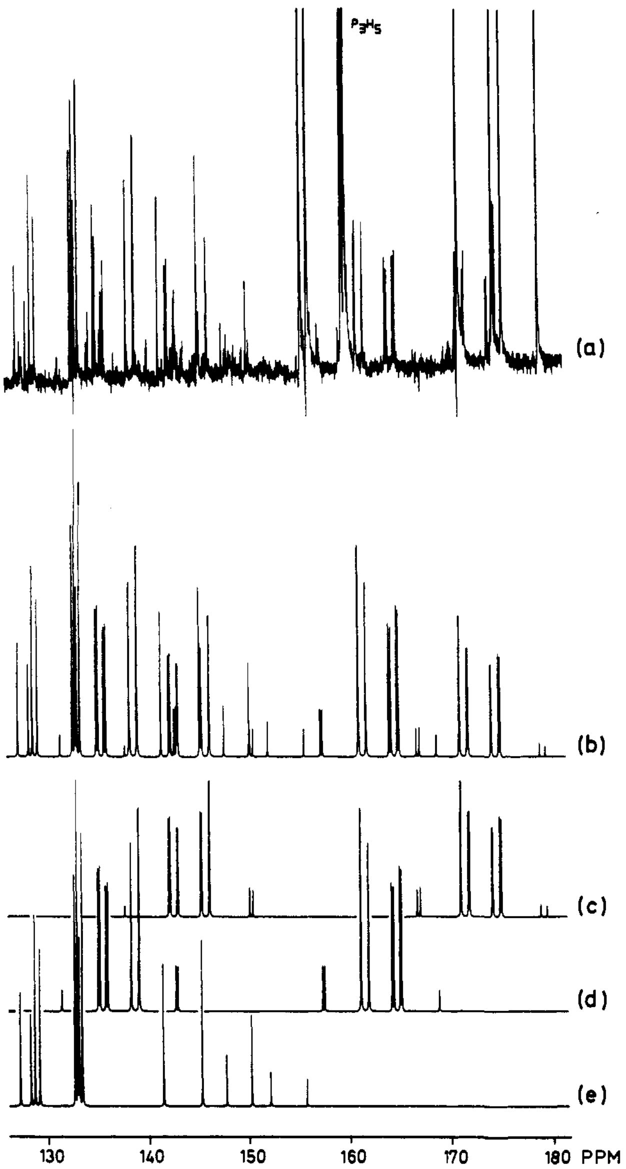
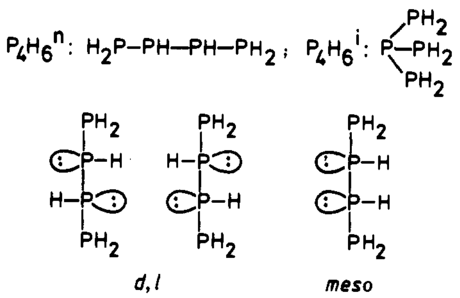


Figure 4. $^{31}P\{^1H\}$ NMR spectrum of a P_3H_5/P_4H_6 mixture at −83 °C (36.4 MHz): (a) observed spectrum (the eight intense signals correspond to the A_2B system of P_3H_5); (b) calculated spectrum of P_4H_6; (c–e) separate simulation of the individual isomers (*meso*-$P_4H_6^n$, *d,l*-$P_4H_6^n$, $P_4H_6^i$).[6]

thermolysis of P_2H_4 or P_3H_5. Isotetraphosphane(6),

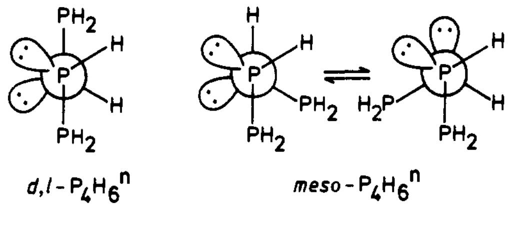

$P_4H_6^n$: $H_2P{-}PH{-}PH{-}PH_2$; $P_4H_6^i$: $P(PH_2)_3$

which may also be considered as triphosphinophosphane or 2-phosphinotriphosphane(5), gives rise to an A_3B spin system (Figure 4e). On the other hand, the two nonterminal phosphorus atoms in *n*-tetraphosphane(6) constitute centers of chirality since they each carry three different substituents and a free-electron pair. On the assumption that the inversion at phosphorus is a slow process in comparison to the NMR time scale, which is valid for open-chain polyphosphorus hydrides below room temperature, two configurational isomers that can be distinguished by NMR spectroscopy exist, namely the *d,l* and the *meso* forms; both diastereomers are characterized by AA′BB′ spin systems (Figure 4, parts d and c, respectively). The superposition of the calculated spectra for the individual isomers (Figure 4b) reproduces the experimentally observed spectrum of P_4H_6 very satisfactorily. Thus the existence of isotetraphosphane(6) and the two configurational isomers of *n*-tetraphosphane(6) has been demonstrated unequivocally. The respective ^{31}P NMR parameters and the relative abundance of the individual isomers are listed in Table 5. In the case of the diastereomers of $P_4H_6^n$ with the *gauche* orientation of the free-electron pairs at P_A and P_B (see below), the AA′BB′ spin system at lower field corresponds to the "stretched" *d,l* isomer and that at higher field to the "angled" *meso* isomer which exists as two degenerate rotamers.[125]

Table 5. ^{31}P NMR Parameters of the Isomers of Tetraphosphane(6) in a P_3H_5–P_4H_6 Mixture at −83 °C[a]

$H_2P_BP_AHP_{A'}HP_{B'}H_2$		$(H_2P_A)_3P_B$
d,l-$P_4H_6^n$ 41.7%	*meso*-$P_4H_6^n$ 28.1%	$P_4H_6^i$ 30.2%
$\delta_A = \delta_{A'} = -137.5$	$\delta_A = \delta_{A'} = -144.6$	$\delta_A = -131.3$
$\delta_B = \delta_{B'} = -163.0$	$\delta_B = \delta_{B'} = -173.0$	$\delta_B = -147.6$
$J_{AB} = J_{A'B'} = -163.8$	$J_{AB} = J_{A'B'} = -168.2$	$J_{AB} = -178.7$
$J_{AA'} = -168.5$	$J_{AA'} = -181.2$	
$J_{A'B} = J_{AB'} = +24.2$	$J_{A'B} = J_{AB'} = +25.7$	
$J_{BB'} = -3.0$	$J_{BB'} = +7.1$	

[a] *J* values are in hertz (Hz).



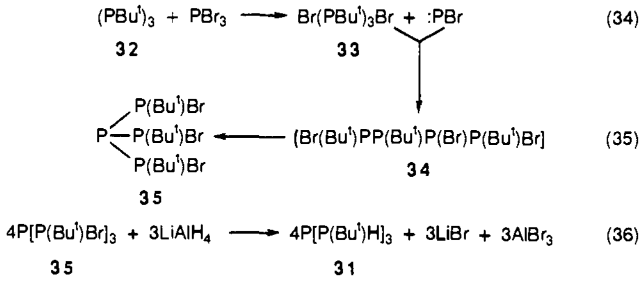
The ratio of the two constitutional isomers of tetraphosphane(6) is influenced by the method of formation of P_4H_6: The proportion of *i*-P_4H_6 is always smaller in thermolysates of P_3H_5 than in those of P_2H_4. It is highly probable that the isomer with the unbranched P_4 chain is preferentially formed according to eq 32 while the isomer with the branched skeleton is preferentially formed according to eq 33.

$$P_3H_5 + P_3H_5 \rightarrow H_2PPHPHPH_2 + P_2H_4 \tag{32}$$

$$P_2H_4 + P_3H_5 \rightarrow H_2PP(PH_2)PH_2 + PH_3 \tag{33}$$

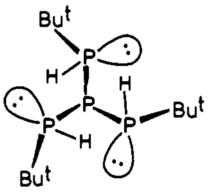
As a consequence of the hyperreactivity of the two species it has not yet been possible to separate *n*-P_4H_6 and *i*-P_4H_6. However, tris(*tert*-butylphosphino)phosphane (31) has been prepared as the first partially substituted derivative of *i*-P_4H_6.[126]

Starting material for this synthesis is the three-membered ring compound **32** which, upon halogenating ring opening with phosphorus(III) bromide, is initially converted to the open-chain triphosphane **33**. Insertion of the intermediarily formed bromophosphanediyl (bromophosphinidene) into the phosphorus chain to furnish the mixed substituted tetraphosphane **34** occurs in a subsequent reaction. As expected, compound **34** is unstable and undergoes spontaneous rearrangement to the constitutional isomer **35**.

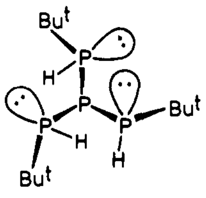


Compound **35** is stable at room temperature and can form two diastereomers of which, however, only the symmetrical isomer with (*R*,*R*,*R*) and (*S*,*S*,*S*) configuration can be detected by ^{31}P NMR spectroscopy. On reaction with lithium aluminum hydride, the bromine atoms are smoothly replaced by hydrogen atoms to furnish **31**.

Compound **31** is not stable at room temperature but can be isolated below −30 °C, in the form of colorless crystals. Immediately after preparation, only the symmetrical isomer **31a** (A_3X spin system) can be detected in the $^{31}P\{^1H\}$ NMR spectrum, indicating that the hydrogenation reaction of **35** proceeds stereoselectively. Subsequently, however—even at −78 °C—the asymmetrical isomer **31b** (ABCX spin system) with the (*R*,*R*,*S*) and (*S*,*S*,*R*) configuration is formed in increasing amounts until the statistical abundancy ratio of **31a**/**31b** = 1:3 is attained at equilibrium [**31a** is drawn as the (*R*,*R*,*R*) enantiomer and **31b** as the (*R*,*R*,*S*) enantiomer]. The rate of the isomerization depends strongly on the solvent: in *n*-pentane at −78 °C equilibrium is reached after about 300 h.[126]



31a



31b

Furthermore, a series of isotetraphosphanes in which all the hydrogen atoms of *i*-P_4H_6 have been replaced by trimethylsilyl or organic groups was prepared recently.[127-130]

From the class of partially organo-substituted *n*-tetraphosphanes, only compounds **36a**,[131] **36b**,[132] and **37**[121] are as yet known. These compounds were prepared by the mild alcoholysis of the corresponding silyl derivatives. A particularly advantageous route for the preparation of **36** is the reaction of the dipotassium salt **38** with *tert*-butyl chloride which proceeds with elimination of isobutene.[132]

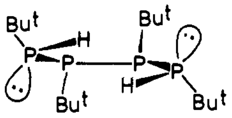
$H(R)P(PR)_2P(R)H$ $Bu^t_2PP(H)P(SiMe_3)PBu^t_2$

36a: R = Ph **37**

b: R = Bu^t

$$K(Bu^t)P(PBu^t)_2P(Bu^t)K + 2Bu^tCl \rightarrow \underset{\mathbf{38}}{} \quad \mathbf{36b} + 2\,H_2C{=}CMe_2 + 2KCl \quad (37)$$

The configurations and conformations of the existing isomers are determined by the tendency for a *gauche* orientation of neighboring free electron pairs as well as by steric factors with increasing spatial requirements of the substituents R. This is clearly apparent in the case of compound **36b** where, of the six possible configurational isomers, only the three diastereomers *threo*/*d*,*l*/*threo*, *erythro*/*threo*/*threo*, and *erythro*/*d*,*l*/*erythro* are formed in solution in the ratio 10:5:1—a deviation from the expected statistical abundancy distribution.[132] Accordingly, only *d*,*l* or *threo* configurations, referred to the central P–P bond, occur in which both an *all-trans* arrangement of the *tert*-butyl substituents and a *gauche* conformation of the free-electron pairs of the phosphorus atoms on the central P–P bond are realized. This situation leads to a spiral-type structure of the P_4 chain, as exemplified for the dominating *threo*/*d*,*l*/*threo* isomer. The relative amounts of the observed isomers are determined by the orientations of the free-electron pairs on the two outer P–P bonds (*gauche*,*gauche*, *trans*,*gauche*, and *trans*,*trans*), respectively.[132]



36b

threo/*d*,*l*/*threo*-isomer

In solution, the three diastereomers of **36b** exist in a mutual dynamic equilibrium at room temperature,[132] whereas the triphosphane **27b** exhibits configurational stability under the same conditions.[120] As to be expected, the barrier to inversion of the phosphorus atoms decreases markedly with increasing length of the phosphorus chain.[134]

Several completely organo- and trimethylsilyl-substituted derivatives of *n*-P_4H_6 are also known.[121]

VII. Pentaphosphane(7), P_5H_7

Mass spectroscopic investigations[10] have shown that phosphane mixtures also containing varying amounts of pentaphosphane(7)[6] are formed by mild thermolysis of diphosphane(4) and triphosphane(5) (sections III.E.1, V.C, and VI.A) as well as in the distillation residues remaining after purification of larger amounts of crude diphosphane.[27] Additional major components of the mixtures are the less phosphorus-rich homologues P_2H_4, P_3H_5, and P_4H_6 as well as smaller amounts of the more phosphorus-rich homologues P_6H_8 and P_7H_9 together with cyclic phosphorus hydrides. Complete characterization of such mixtures under mild conditions with regard to the types and structures of the species present is achieved by ^{31}P NMR spectroscopy. Since the viscosity of the product mixture increases upon enrichment of P_5H_7 by evaporation of the more volatile components under vacuum which, in turn, leads to a broadening of the NMR signals and often also a conversion of P_5H_7 into cyclophosphanes, structural

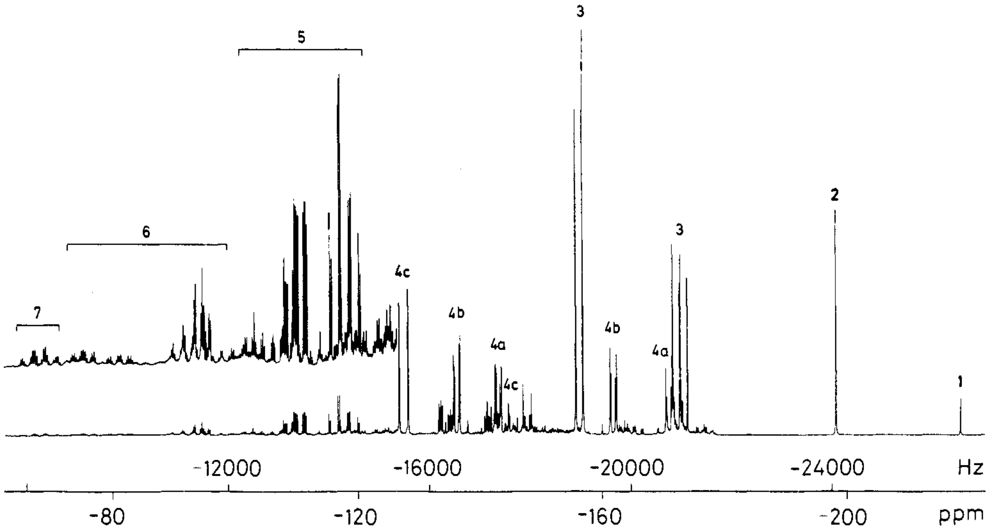
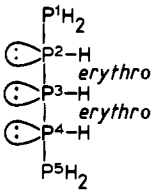


Figure 5. $^{31}P\{^1H\}$ NMR spectrum of a mixture of open-chain phosphorus hydrides at −30 °C (121.5 MHz): (1) PH_3; (2) P_2H_4; (3) P_3H_5; (4a) *meso*-$P_4H_6^n$; (4b) *d,l*-$P_4H_6^n$; (4c) $P_4H_6^i$; (5) downfield signals of P_5H_7 isomers; (6) downfield signals of P_6H_8 isomers; (7) downfield signals of P_7H_9 isomers.[135]

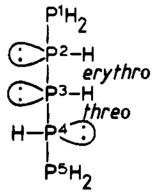
investigations of pentaphosphane(7) have been carried out in phosphane mixtures with a P_5H_7 content of about 10–15 P-%. Figure 5 shows the $^{31}P\{^1H\}$ NMR spectrum of a representative mixture.[135]

The identification of the four possible isomers of P_5H_7 that can be distinguished by NMR spectroscopy [three diastereomers of $P_5H_7^n$ (**39a–c**) as well as $P_5H_7^i$ [or 2-phosphinotetraphosphane(6)] (**40**)] by a direct analysis of the appropriate ^{31}P spin systems (given below the individual formulae) is not possible because the respective partial spectra are in some cases hidden under the strong signals of the isomers of P_4H_6 and P_3H_5. As can be seen from Figures 5 and 6 (see below), however, with increasing chain length or branching the resonance signal of at least one phosphorus atom of the isomers is markedly shifted to a less densely populated region at lower field. This opens the possibility for a "spectroscopic separation" of the spin systems by means of homonuclear ^{31}P selective population transfer experiments (SPT).[136,137]



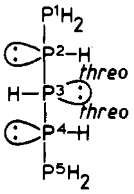
AA'BB'C

39a



ABCDE

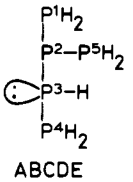
39b



AA'BB'C

39c

$P_5H_7^n$



ABCDE

40

$P_5H_7^i$

The essence of SPT experiments is that the influence of a selective pulse on a specific line of a spin system causes a change in the population difference of the corresponding energy levels and thus a change in the intensities of the lines associated with these levels. This becomes especially clear after subtraction of the "unperturbed" spectrum from the SPT spectrum. Only the perturbed line and the progressively or regressively associated transitions (the latter being characterized by positive or negative line intensities, respectively) can be observed in the resultant difference spectrum. Thus, hidden or low intensity resonances of a spin system can be identified and questions of assignment in connection with the spectral calculation can be answered unambiguously.

The starting parameter sets obtained from a series of SPT experiments for the isomers of P_5H_7 were optimized by systematic variation of the values until an assignment of the calculated lines to those observed experimentally was possible. Since the NMR parameters are by far overdetermined as a result of the large number of lines, it is sufficient to assign only those lines that are not influenced by neighboring signals. The final data sets (Table 6) are then obtained by subsequent iteration; the sign combinations of the coupling constants can be derived unequivocally from the SPT experiments and spectral fitting on the assumption of negative $^1J(P^{III},P^{III})$ couplings.[138] Superposition of the calculated individual spectra provides a highly satisfactory simulation of the experimental $^{31}P\{^1H\}$ NMR spectrum of pentaphosphane(7) (Figure 6).[135]

Accordingly, pentaphosphane(7) exists as a mixture of the three diastereomers of $P_5H_7^n$ (**39a**, *erythro,-erythro*; **39b**, *erythro,threo*; **39c**, *threo,threo*) and the constitutionally isomeric 2-phosphinotetraphosphane(6) ($P_5H_7^i$, **40**). The branched isomer always exhibits the highest relative abundance (Table 6) which is indicative of an increased tendency for its formation in the genesis of pentaphosphane(7). The disproportionation of the less phosphorus-rich homologues apparently proceeds preferentially by way of intermolecular PH_3 elimination from a PH middle group and a PH_2 terminal group which results in the chain branching. The spatial structures of **39a–c** and **40** can be deduced directly from the determined NMR parameters, above all the magnitudes and signs of the coupling constants.[139] The isomer **40** can exist in two

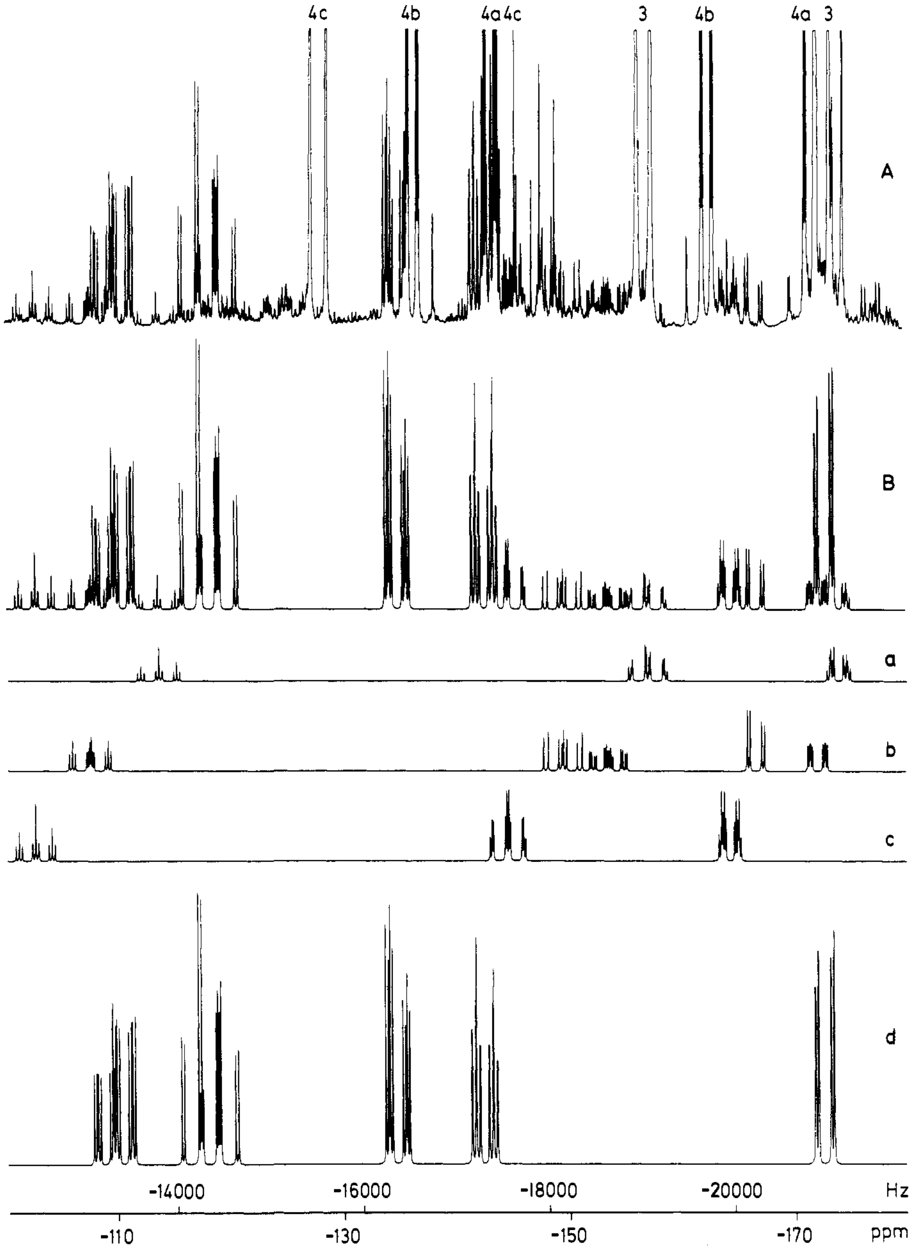
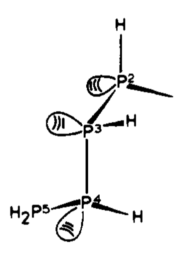
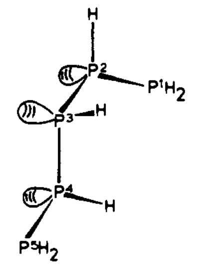


Figure 6. Observed (A) and calculated (B) $^{31}P\{^1H\}$ NMR spectrum of pentaphosphane(7) in a phosphane mixture with 15 P-% P_5H_7 (3, P_3H_5; 4a, *meso*-$P_4H_6{}^n$, 4b, *d,l*-$P_4H_6{}^n$; 4c, $P_4H_6{}^i$) at −30 °C (121.5 MHz). Spectra a–d are simulated spectra of the individual P_5H_7 isomers **39a**, **39b**, **39c**, and **40**, respectively.[135]

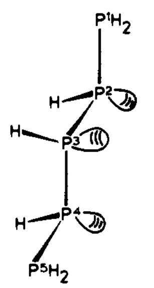
conformations (**A**, **B**) of which **A** should be preferred for steric reasons.



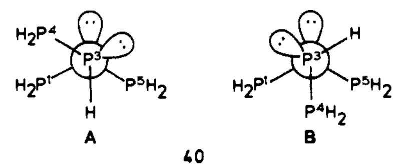
39a



39b



39c



40

Together with the data for the less phosphorus-rich homologues of the series P_nH_{n+2} with n = 1–4, the ^{31}P NMR parameters for the isomers of P_5H_7 render the derivation of general relationships for the dependence of the chemical shifts $\delta^{31}P$ and the coupling constants $^1J(P,P)$ on the structural parameters of open-chain phosphanes possible.[135] At −30 °C, the following relationship is valid for the $\delta^{31}P$ values:

$$\delta^{31}P = -214.9 + 21.7a + 31.8b - 7.3c (\pm 4.4) \quad (38)$$

This relationship describes the dependency of the chemical shift of a phosphorus atom on the numbers a, b, and c of neighboring phosphorus atoms in α-, β-, and γ-positions, respectively, to it. An analogous structural dependency also exists for the $^1J(P,P)$ coupling constants:

$$^1J(P_A,P_B) = -112.5 - 31.7a^* - 15.3b^* (\pm 4.7) \quad (39)$$

where a^* (b^*) is the number of phosphorus atoms in

Table 6. ^{31}P NMR Parameters of $P_5H_7{}^n$ (39a, 39b, 39c) and $P_5H_7{}^i$ (40) in a Mixture of Phosphorus Hydrides with 15 P-% P_5H_7 at −30 °C[a]

	39a 11%	39b 14%	39c 15%	40 60%
δ(1)	−173.1	−171.1	−163.0	−142.1
δ(2)	−156.4	−148.9	−144.1	−117.3
δ(3)	−113.7	−107.5	−102.7	−109.8
δ(4)	−156.4	−153.2	−144.1	−171.3
δ(5)	−173.1	−165.5	−163.0	−134.3
J(1,2)	−160.8	−168.4	−158.9	−191.1
J(1,3)	+34.7	+28.7	+30.9	+43.6
J(1,4)	+27.8	+21.4	+1.1	+8.2
J(1,5)	+1.7	+5.0	±0.0	+45.0
J(2,3)	−191.8	−201.5	−179.8	−206.9
J(2,4)	+27.2	+48.9	+37.9	+32.8
J(2,5)	+27.8	−2.3	+1.1	−191.4
J(3,4)	−191.8	−184.0	−179.8	−175.1
J(3,5)	+34.7	+30.7	+30.9	+31.4
J(4,5)	−160.8	−160.3	−158.9	+1.0

[a] *J* values are in hertz (Hz).

α(β)-position relative to P_A plus the corresponding number of phosphorus atoms relative to P_B after hypothetical cleavage of the P_A–P_B bond. As can be seen from eq 38, α- and β-phosphorus atoms effect a strong low-field shift on the ^{31}P resonances with the β-effect being larger than the α-effect; γ-phosphorus atoms exert a slight shift to high field. The increasing low-field shift of the ^{31}P NMR signals of higher phosphanes in comparison to the spectrum of PH_3 is mainly attributable to a widening of the bonding angle when a hydrogen atom is replaced by a more voluminous PH_2, $P(H)PH_2$, or $P(PH_2)_2$ group (increase of the p component in the hybrid orbital of the free-electron pair). Similarly, the increase in the absolute value of the ^1J(P,P) coupling constant on chain lengthening or branching can be explained in terms of angle widening of the bonding orbitals at phosphorus.

The relationships shown in eqs 38 and 39 make possible the calculation of the ^{31}P NMR parameters of the more phosphorus-rich, open-chain phosphanes and are thus valuable tests in the determination of the constitutions of these compounds (see sections VIII and IX). The calculated δ^{31}P values, however, correspond merely to the averaged resonance positions of the respective diastereomers since their chemical shifts show a "conformation effect" in the sense that molecules with a "stretched" P_n chain (such as **39c**) give rise to signals at lower field than those with one or more "angled" structural units (such as **39b** or **39a**, see Figure 6). An analogous conformational dependency is also observed for the δ^{13}C values of the alkanes.[140] In the case of the ^1J(P,P) coupling constants, a marked difference between the values calculated using eq 39 and the experimentally determined values is indicative of a significant deviation from the *gauche* arrangement of the free-electron pairs at the respective phosphorus atoms. According to the dependence of the ^1J(P,P) coupling constants on the dihedral angle between the free-electron pairs of neighboring phosphorus atoms ($|^1J_{P,P}(cis)| > |^1J_{P,P}(trans)|$[141]), the sign of the observed difference indicates the direction of the twisting.

Furthermore, important information on the configurations and conformations of open-chain phosphanes is provided by the magnitudes and signs of the P,P long-range couplings. Large positive ^2J(P,P) and ^3J(P,P) coupling constants are always observed when the spatial approach of the corresponding phosphorus atoms gives rise to significant lone pair–lone pair or lone pair–proton interactions.[120,126,132]

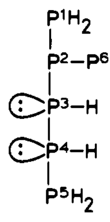
Partially organo-substituted derivatives of the constitutional isomers of pentaphosphane(7) have not yet been reported but two completely organo- or trimethylsilyl-substituted derivatives of isopentaphosphane have been unequivocally characterized together with other polyphosphorus compounds by ^{31}P NMR spectroscopy.[142]

VIII. Hexaphosphane(8), P_6H_8

Small amounts (5–10 P-%) of hexaphosphane(8) exist together with the less phosphorus-rich homologues of the series P_nH_{n+2} with n = 1–5 in liquid phosphane mixtures obtained as mentioned in section VII. This phosphorus hydride was identified and its composition elucidated with certainty by mass spectroscopy as early as the mid-1960s.[10] As a consequence of the developments in apparatus and the methodology of nuclear magnetic resonance spectroscopy, the complete structural elucidation by ^{31}P NMR spectroscopy was realized 20 years later.[143]

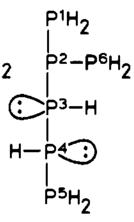
The viscosity increase of the products and the pronounced tendency of higher open-chain phosphanes to undergo disproportionation constitute fundamental difficulties for an enrichment of P_6H_8. Thus the structure determination was made using the same procedure as described for pentaphosphane(7) (see section VII).

Because of the preferred tendency for the formation of branched-chain phosphane skeletons (section VII), to date only isomers with branched P_6 chains, but no diastereomers of $P_6H_8{}^n$ (a total of six), have been identified and structurally clarified by analyses of the respective ^{31}P spin systems. These are the two dia-


erythro

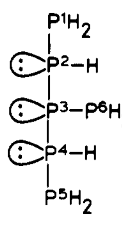
ABCDEF

41a


threo

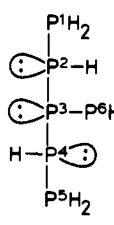
ABCDEF

41b


erythro,
erythro

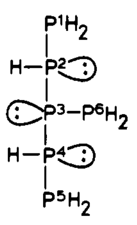
AA'BB'CD

42a


erythro,
threo

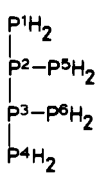
ABCDEF

42b


threo,
threo

AA'BB'CD

42c


sym

AA'A''A'''BB'

43

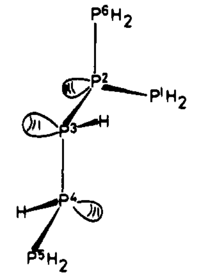
Table 7. ^{31}P NMR Parameters of 2-Phosphinopentaphosphane(7) (41a,b), 3-Phosphinopentaphosphane(7) (42a,b), and 2,3-Diphosphinotetraphosphane(6) (43) in a Phosphane Mixture with 7 P-% P_6H_8 at −30 °C[a]

	41a 17%	41b 13%	42a 16%	42b 26%	43 28%		41a 17%	41b 13%	42a 16%	42b 26%	43 28%
δ(1)	−138.3	−135.3	−176.0	−177.1	−147.4	*J*(2,3)	−211.8	−196.3	−221.1	−232.2	−244.6
δ(2)	−121.9	−127.9	−124.7	−117.9	−94.3	*J*(2,4)	+51.1	+39.6	+44.0	+51.1	+39.2
δ(3)	−75.2	−81.1	−92.1	−92.4	−94.3	*J*(2,5)	+2.3	+41.2	+18.0	+4.5	−203.8
δ(4)	−152.1	−153.5	−124.7	−125.1	−147.4	*J*(2,6)	−189.6	−186.7	+35.7	+35.9	+39.2
δ(5)	−164.5	−171.0	−176.0	−172.7	−147.4	*J*(3,4)	−176.5	−206.1	−221.1	−216.1	−203.8
δ(6)	−133.1	−143.3	−140.9	−146.5	−147.4	*J*(3,5)	+33.2	+32.4	+36.0	+35.0	+39.2
J(1,2)	−189.2	−188.0	−172.8	−174.6	−203.8	*J*(3,6)	+33.2	+54.1	−202.9	−201.3	−203.8
J(1,3)	+45.3	+34.6	+36.0	+35.1	+39.2	*J*(4,5)	−157.0	−159.4	−172.8	−168.9	+4.0
J(1,4)	+19.6	+5.0	+18.0	+10.8	+10.6	*J*(4,6)	+5.2	+13.4	+35.7	+45.2	+67.8
J(1,5)	+3.8	+2.9	±0.0	+3.5	+67.8	*J*(5,6)	+2.9	+2.6	−0.2	+6.3	+10.6
J(1,6)	+42.3	+50.1	−0.2	+6.2	+4.0						

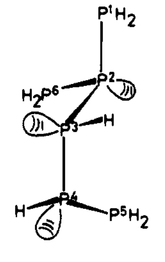
[a] *J* values are in hertz (Hz).

stereomers of 2-phosphinopentaphosphane(7) (**41a**, *erythro*; **41b**, *threo*), two of the three diastereomers of 3-phosphinopentaphosphane(7) (**42a**, *erythro,erythro*; **42b**, *erythro,threo*), and the highly symmetric 2,3-diphosphinotetraphosphane(6) (**43**); the other symmetrical diastereomer of 3-phosphinopentaphosphane(7) (**42c**, *threo,threo*) could not be detected. The ^{31}P NMR parameters determined for the isomers **41a**, **41b**, **42a**, **42b**, and **43** are listed in Table 7. The spectrum calculated using these data is compared with the experimentally observed $^{31}P\{^1H\}$ NMR spectrum of a phosphane mixture containing 7 P-% P_6H_8 in Figure 7. In spite of strong overlapping with the signal groups from P_3H_5, P_4H_6, and P_5H_7, a highly satisfactory agreement can be seen.

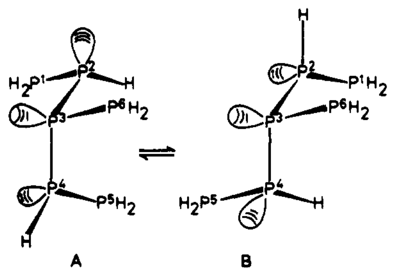
The assignments of the diastereomers to the observed spin systems are based on the preferred *gauche* orientations of neighboring free-electron pairs, the dependency of the $^1J(P,P)$ coupling constants on the dihedral angles, and the $^3J(P,P)$ and $^4J(P,P)$ long-range couplings (see section VII). On a time average, the following conformations are present:[139]



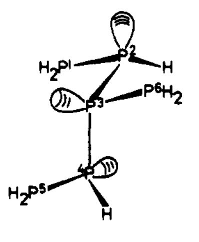
41a



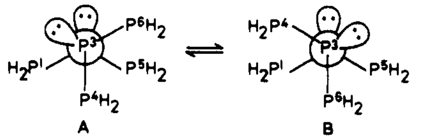
41b



42a



42b



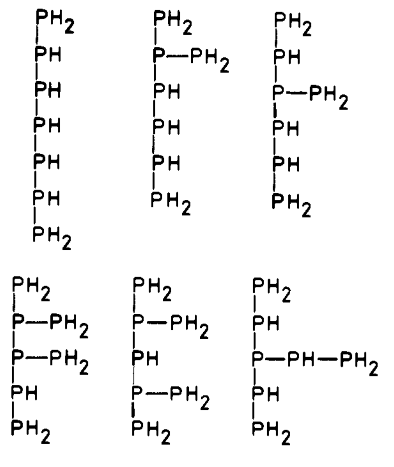
43

In the cases of **42a** and **43**, two degenerated conformers (**A**, **B**) exist in a rapid, dynamic equilibrium.

The identified isomers of P_6H_8 are configurationally stable in comparison to the NMR time scale at −30 °C. Rapid decomposition of hexaphosphane(8) occurs upon warming to room temperature.

IX. Heptaphosphane(9), P_7H_9

Although heptaphosphane(9) is only present to an extent of 3–5 P-% in thermolysates from P_2H_4 or P_3H_5, it can be irrevocably identified alongside other, less phosphorus-rich homologues by mass[6,144,145] and ^{31}P NMR spectroscopy.[135] The presence of P_7H_9 in the mixture is demonstrated by a characteristic low-field "quartet" at δ = −68 in the $^{31}P\{^1H\}$ NMR spectrum (see Figure 5). This signal group provides a suitable key for the ^{31}P NMR spectroscopic structure elucidation based on SPT experiments (see section VII). Of particular interest was the question of whether the tendency for the formation of branched phosphorus skeletons is continued in the case of heptaphosphane(9) for which six constitutional isomers are feasible.



Two spin systems have been identified by irradiation of the different lines of the "quartet" which, according to the results of the spectral analysis correspond to the diastereomers of one of the two constitutional isomers with maximal chain branching, namely 2,3-diphosphinopentaphosphane(7) (**44a**, *erythro*; **44b**, *threo*).[146] The calculation of the ^{31}P NMR parameters (Table 8) still reveals some uncertainties with regard to a few long-range couplings because most of the multiplets of

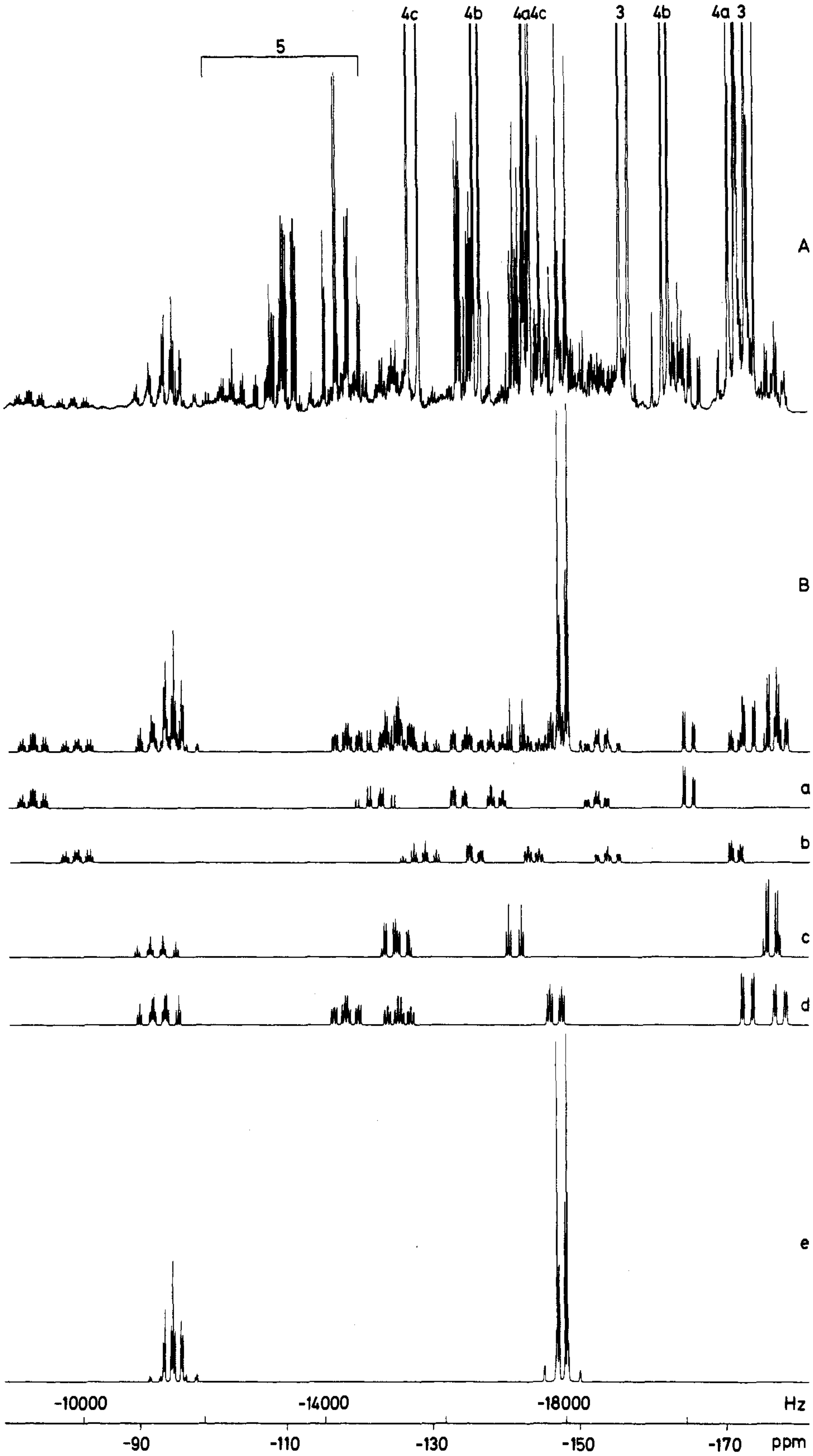


Figure 7. Observed (A) and calculated (B) $^{31}P\{^1H\}$ NMR spectrum of hexaphosphane(8) in a phosphane mixture with 7 P-% P_6H_8 (3, P_3H_5; 4a, *meso*-$P_4H_6^n$; 4b, *d,l*-$P_4H_6^n$; 4c, $P_4H_6^i$; 5, downfield signals of P_5H_7 isomers) at −30 °C (121.5 MHz). Spectra a–e are simulated spectra of the individual P_6H_8 isomers **41a**, **41b**, **42a**, **42b**, and **43**, respectively.[143]

44a and **44b** are almost completely hidden by signal groups of the less phosphorus-rich homologues. In spite of this provisional nature of the data sets, superposition of the calculated individual spectra provides a fairly satisfactory simulation of the experimentally observed $^{31}P\{^1H\}$ NMR spectrum of heptaphosphane(9) (Figure 8).[146]

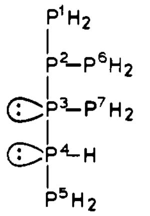
In addition to the constitution, the assignments of the observed spin systems to the two configurational isomers and the spatial structures of **44a** and **44b** can

Table 8. ^{31}P NMR Parameters of 2,3-Diphosphinopentaphosphane(7) (Diastereomers 44a and 44b) in a Phosphane Mixture with 4 P-% P_7H_9 at −30 °C[a]

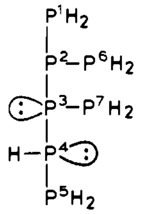
	44a 60%	44b 40%
δ(1)	−145.6	−148.4
δ(2)	−100.0	−102.6
δ(3)	−68.2	−68.0
δ(4)	−129.7	−124.8
δ(5)	−172.8	−177.0
δ(6)	−149.1	−145.9
δ(7)	−157.6	−150.2
J(1,2)	−202.2	−201
J(1,3)	+37.5	+37
J(1,4)	+16.2	+6
J(1,5)	±0.0[b]	?
J(1,6)	+43.3	+49
J(1,7)	+6.1	+11
J(2,3)	−252.6	−234
J(2,4)	+48.0	+44
J(2,5)	+7.5	+24
J(2,6)	−204.0	−198
J(2,7)	+40.8	+38
J(3,4)	−203.8	−241
J(3,5)	+35.0[b]	+35
J(3,6)	+37.8	+43
J(3,7)	−213.3	−213
J(4,5)	−166.4	−173
J(4,6)	+6.0	+13
J(4,7)	+51.3	+35
J(5,6)	±0.0[b]	?
J(5,7)	+8.2	?
J(6,7)	+18.4	?

[a] *J* values are in hertz (Hz). [b] The value was estimated and not included in the iteration.

be derived from the ^{31}P NMR parameters (see sections VI–VIII). In the case of 44a, the conformer A should,

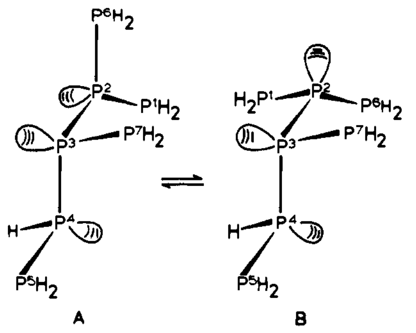


erythro
ABCDEFG
44a

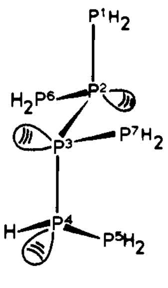


threo
ABCDEFG
44b

on a time average, exhibit a slightly higher population on the basis of the magnitude ratios of significant $^{3}J(P,P)$ couplings.



44a



44b

The inversion of the phosphorus atoms of 2,3-diphosphinopentaphosphane(7) at −30 °C is slow in comparison to the NMR time scale while rapid decomposition takes place on warming to room temperature.

The fact that, of the six possible constitutional isomers, only one of the two P_7H_9 isomers with maximal chain branching has as yet been detected further substantiates the outstanding tendency for the formation of tertiary phosphorus atoms in the construction of longer chain phosphanes (see section VII). Hence, of the remaining five isomers of P_7H_9, at least the 2,4-diphosphinopentaphosphane(7) should also be capable of existence and thus be detectable. A monometalated derivative of this isomer, the heptaphosphide LiH_8P_7 (11; see Scheme 1) is formed in addition to other polyphosphides by the reactions of P_2H_4 with $LiBu^n$ or Li_3P_7 (7) at −25 °C (see section III.E.5).[97,98,101]

X. Conclusion and Perspectives

The investigations performed on open-chain polyphosphorus hydrides (phosphanes) over the last 25 years have shown that the long-known compounds PH_3 and P_2H_4 are indeed merely the first members of a homologous series with the general formula P_nH_{n+2}. Through the use of modern preparative techniques for the handling of air-sensitive substances and the methodological developments in spectroscopy, it has been possible to detect further homologues with n = 3–9 and to elucidate the structures of those members with n = 3–7. These compounds display close relationships in their structural features with the saturated acyclic hydrocarbons. The reason for this can be found in the identical numbers of valency electrons of the groups $>CH_2$ and $>\dot{P}H$ as well as $\geqslant CH$ and $\geqslant P$: which are thus able to form analogous skeletal frameworks. In the case of the open-chain polyphosphorus hydrides, the tendency for the formation of branched molecular skeletons is definitely favored with increasing number of chain atoms. Certain differences to the alkanes result from the following special features of phosphorus:

(i) The P–P bonds are subject to ready *inter*molecular attack via the free electron pairs; thus disproportionation reactions of the phosphanes take place under appreciably milder conditions than in the cases of the alkanes or silanes.

(ii) The conformational flexibility of the P_n chains also leads, with increasing number of phosphorus atoms, to *intra*molecular interactions of the P–P bonds and subsequent cyclization reactions; thus from n = 5 onward the stability of the open-chain phosphanes P_nH_{n+2} decreases significantly in favor of the monocyclic and polycyclic phosphorus hydrides P_nH_n and P_nH_{n-2m} (m = 1–9), respectively.

(iii) As a result of the trivalence of phosphorus, centers of chirality occur considerably more frequently in open-chain phosphanes than in the corresponding hydrocarbons.

Is an extension of our knowledge on open-chain polyphosphorus hydrides to be expected in the future? In spite of the increasing instability of these compounds with increasing phosphorus content, the use of more sophisticated preparative techniques and methods of structure analysis should lead to the detection of a few

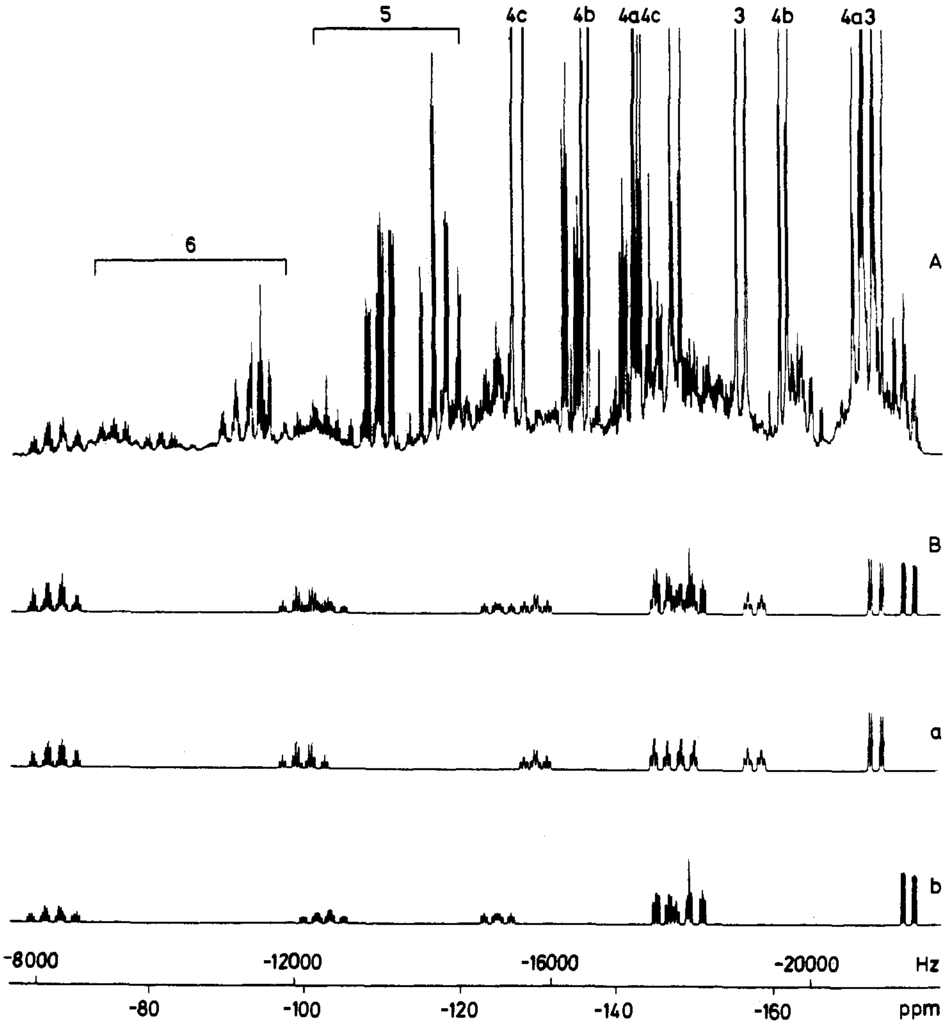


Figure 8. Observed (A) and calculated (B) $^{31}P\{^1H\}$ NMR spectrum of heptaphosphane(9) in a phosphane mixture with 4 P-% P_7H_9 (3, P_3H_5, 4a, *meso*-$P_4H_6{}^n$, 4b, *d*,*l*-$P_4H_6{}^n$, 4c, $P_4H_6{}^i$, 5, downfield signals of P_5H_7 isomers; 6, downfield signals of P_6H_8 isomers) at −30 °C (121.5 MHz). Spectra a and b are simulated spectra of the individual P_7H_9 isomers **44a** and **44b**, respectively (in the case of **44b**, the long-range couplings indicated in Table 8 with question marks were each taken as 0 Hz).[146]

further homologues of the series P_nH_{n+2} with $n > 9$. Also, the complete structural characterization of the already known compounds P_7H_9, P_8H_{10}, and P_9H_{11} will most certainly be realized. Above all, however, research on the reaction behavior of open-chain phosphanes, which can now be extended from diphosphane(4) also to triphosphane(5) and tetraphosphane(6), promises to provide a wealth of interesting preparative and structural results.

XI. Acknowledgments

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XII. References

(1) Contributions to the Chemistry of Phosphorus, Part 229. For Part 228, see: Baudler, M.; Tschäbunin, H.; Hasenbach, J. *Z. Naturforsch.*, in press.
(2) Gengembre, P. *Hist. Mém. Acad. Roy. Sci.* 1785, *10*, 651.
(3) Thénard, P. *C. R. Acad. Sci. Paris* 1844, *18*, 652.
(4) Baudler, M.; Schmidt, L. *Naturwissenschaften* 1957, *44*, 488.
(5) Baudler, M.; Schmidt, L. *Naturwissenschaften* 1959, *46*, 577.
(6) Baudler, M. *Angew. Chem.* 1982, *94*, 520; *Angew. Chem., Int. Ed. Engl.* 1982, *21*, 492.
(7) Baudler, M.; Glinka, K. *Chem. Rev.* 1993, *93*, 1623.
(8) Fluck, E. *Top. Curr. Chem.* 1973, *35*, 1.
(9) (a) Royen, P.; Rocktäschel, C.; Mosch, W. *Angew. Chem.* 1964, *76*, 860; *Angew. Chem., Int. Ed. Engl.* 1964, *3*, 703. (b) Royen, P.; Rocktäschel, C. *Z. Anorg. Allg. Chem.* 1966, *346*, 290.
(10) (a) Baudler, M.; Ständeke, H.; Borgardt, M.; Strabel, H. *Naturwissenschaften* 1965, *52*, 345. (b) Baudler, M.; Ständeke, H.; Borgardt, M.; Strabel, H.; Dobbers, J. *Naturwissenschaften* 1966, *53*, 106.
(11) (a) Fehlner, T. P. *J. Am. Chem. Soc.* 1966, *88*, 1819, 2613. (b) Fehlner, T. P. *J. Am. Chem. Soc.* 1968, *90*, 6062.
(12) Junkes, P.; Baudler, M.; Dobbers, J.; Rackwitz, D. *Z. Naturforsch.* 1972, *27b*, 1451.
(13) IUPAC Commission on Nomenclature of Inorganic Chemistry *Pure Appl. Chem.* 1972, *30*, 683. Leigh, G. J., Ed. *Recommendations 1990*; Blackwell Scientific Publ.: Oxford, 1990; pp 23 and 217.
(14) Fehér, F.; Kuhlbörsch, G.; Luhleich, H. *Z. Naturforsch.* 1959, *14b*, 466; *Z. Anorg. Allg. Chem.* 1960, *303*, 294.
(15) Wilson, H. N. *Analyst* 1951, *76*, 65; 1954, *79*, 535.
(16) Baudler, M.; Ständeke, H.; Kemper, M.; Krause, U. M. To be published.
(17) Baudler, M.; Ständeke, H.; Kemper, M. *Z. Anorg. Allg. Chem.* 1972, *388*, 125.

(18) Baudler, M.; Krause, U. M.; Kronenberg, W. Unpublished results (1977/78).
(19) Rossim, F. D.; Wagman, D. D.; Evans, W. H.; Levine, S.; Jaffé, I. *Natl. Bur. Std. Circ.* (*U.S.*) **1952**, *Circ. No. 500*, 571.
(20) Thénard, P. *C. R. Acad. Sci. Paris* **1844**, *19*, 313; *Ann. Chim. Phys.* [*3*] **1845**, *14*, 5; *Liebigs Ann. Chem.* **1845**, *55*, 27.
(21) Hofmann, A. W. *Ber. Dtsch. Chem. Ges.* **1874**, *7*, 530.
(22) Gattermann, L.; Haussknecht, W. *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 1174.
(23) Royen, P.; Hill, K. *Z. Anorg. Allg. Chem.* **1936**, *229*, 97.
(24) Nixon, E. R. *J. Phys. Chem.* **1956**, *60*, 1054.
(25) Evers, E. C.; Street, E. H. *J. Am. Chem. Soc.* **1956**, *78*, 5726.
(26) Baudler, M.; Schmidt, L. *Z. Anorg. Allg. Chem.* **1957**, *289*, 219.
(27) Baudler, M.; Ständeke, H.; Borgardt, M.; Strabel, H.; Dobbers, J.; Schultes, A.; Rackwitz, D. In *Handbook of Preparative Inorganic Chemistry*, 3rd ed. (*Handbuch der Präparativen Anorganischen Chemie, Bd. 1*); Brauer, G., Ed.; Enke Verlag: Stuttgart, 1975; Vol. 1, p 514.
(28) Pytlewski, L. L. Ph.D. Thesis, University of Pennsylvania, 1960.
(29) Strabel, H. Dissertation, Köln University, 1967.
(30) Baudler, M.; Ständeke, H.; Borgardt, M.; Strabel, H.; Dobbers, J.; Kemper, M.; Schöner, Ch. P.; Skrodzki, H. D.; Krause, U. M.; Faber, W. To be published.
(31) Schmidt, L. Dissertation, Köln University, 1959.
(32) (a) von Stackelberg, M. *Naturwissenschaften* **1949**, *36*, 327, 359. (b) von Stackelberg, M.; Müller, H. R. *Z. Elektrochem.* **1954**, *58*, 25.
(33) Albrand, J. P.; Anderson, S. P.; Goldwhite, H.; Huff, L. *Inorg. Chem.* **1975**, *14*, 570.
(34) Retgers, J. W. *Naturwiss. Rundsch.* **1895**, *10*, 384.
(35) Wiles, D. M.; Winkler, C. A. *J. Phys. Chem.* **1957**, *61*, 620.
(36) Datta, J. *J. Indian Chem. Soc.* **1952**, *29*, 101.
(37) Michaelis, A.; Pitsch, M. *Liebigs Ann. Chem.* **1900**, *310*, 45.
(38) Tomilov, A. P.; Osadchenko, I. M. *Zh. Vses. Khim. Ova. im. D.I. Mendeleeva* **1972**, *17*, 691; *Chem. Abstr.* **1973**, *78*, 91748z.
(39) Ferris, J. P.; Benson, R. *J. Am. Chem. Soc.* **1981**, *103*, 1922.
(40) Blazejowski, J.; Lampe, F. W. *J. Phys. Chem.* **1981**, *85*, 1856.
(41) Gunn, S. R.; Green, L. G. *J. Phys. Chem.* **1961**, *65*, 779.
(42) Street, E. H.; Gardner, D. M.; Evers, E. C. *J. Am. Chem. Soc.* **1958**, *80*, 1819.
(43) Collin, R. L.; Lipscomb, W. N. *Acta Crystallogr.* **1951**, *4*, 10.
(44) Fehlner, T. P.; Callen, R. B. *Adv. Chem. Ser.* **1968**, *72*, 181.
(45) Saalfeld, F. E.; Svec, H. J. *Inorg. Chem.* **1963**, *2*, 50.
(46) Wada, Y.; Kiser, R. W. *Inorg. Chem.* **1964**, *3*, 174.
(47) Dibeler, V. H.; Franklin, J. L.; Reese, R. M. *J. Am. Chem. Soc.* **1959**, *81*, 68.
(48) Lynden-Bell, R. M. *Trans. Faraday Soc.* **1961**, *57*, 888; *Mol. Phys.* **1963**, *6*, 601.
(49) Frankiss, St. G. *Inorg. Chem.* **1968**, *7*, 1931.
(50) Odom, J. D.; Wurrey, C. J.; Carreira, L. A.; Durig, J. R. *Inorg. Chem.* **1975**, *14*, 2849.
(51) Baudler, M.; Vogel-Raudschus, M.; Dobbers, J. *Z. Anorg. Allg. Chem.* **1977**, *437*, 78.
(52) McConaghie, V. M.; Nielson, H. H. *J. Chem. Phys.* **1953**, *21*, 1836.
(53) Hardin, A. H.; Harvey, K. B. *Can. J. Chem.* **1964**, *42*, 84.
(54) Durig, J. R.; Carreira, L. A.; Odom, J. D. *J. Am. Chem. Soc.* **1974**, *96*, 2688.
(55) Beagley, B.; Conrad, A. R.; Freeman, J. M.; Monaghan, J. J.; Norton, B. G.; Holywell, G. C. *J. Mol. Struct.* **1972**, *11*, 371.
(56) Elbel, S.; Tom Dieck, H.; Becker, G.; Ensslin, W. *Inorg. Chem.* **1976**, *15*, 1235.
(57) Berthelot, D.; Gaudechon, H. *C.R. Hebd. Seances Acad. Sci.* **1913**, *156*, 1243.
(58) Halman, M. *J. Chem. Soc.* **1963**, 2853.
(59) Issleib, K.; Gründler, W. *Theor. Chim. Acta* **1968**, *11*, 107.
(60) Cowley, A. H.; White, W. D.; Damasco, M. C. *J. Am. Chem. Soc.* **1969**, *91*, 1922.
(61) Robert, J. B.; Marsmann, H.; Van Wazer, J. R. *J. Chem. Soc., Chem. Commun.* **1970**, 356.
(62) Absar, I.; Robert, J. B.; Van Wazer, J. R. *J. Chem. Soc., Faraday Trans. 2* **1972**, 799.
(63) Wagner, E. L. *Theor. Chim. Acta* **1971**, *23*, 127.
(64) Ahlrichs, R.; Heinzmann, R.; Zirz, C. *Theor. Chim. Acta* **1976**, *43*, 29.
(65) Goetz, H.; Frenking, G.; Marschner, F. *Phosphorus Sulfur* **1978**, *4*, 309.
(66) Frenking, G.; Goetz, H.; Marschner, F. *Phosphorus Sulfur* **1979**, *7*, 295.
(67) Cowley, A. H.; Mitchell, D. J.; Whangbo, M.-H.; Wolfe, S. *J. Am. Chem. Soc.* **1979**, *101*, 5224.
(68) Bews, J. R.; Glidewell, C. *J. Mol. Struct.* (*THEOCHEM*) **1983**, *94*, 305.
(69) Sen, K. D.; Ohta, K.; Morokuma, K. *J. Mol. Struct.* (*THEOCHEM*) **1984**, *109*, 287.
(70) Magnusson, E. *Aust. J. Chem.* **1986**, *39*, 735.
(71) Schiffer, H.; Ahlrichs, R.; Häser, M. *Theor. Chim. Acta* **1989**, *75*, 1.
(72) Veillard, A. *Theor. Chim. Acta* **1966**, *5*, 413.
(73) Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102.
(74) Albrand, J. P.; Faucher, H.; Gagnaire, D.; Robert, J. B. *Chem. Phys. Lett.* **1976**, *38*, 521.
(75) Galasso, V. *J. Magn. Reson.* **1979**, *36*, 181.
(76) Duangthai, S.; Webb, G. A. *Org. Magn. Reson.* **1983**, *21*, 199.
(77) Ramsey, N. F. *Phys. Rev.* **1953**, *91*, 303.
(78) Rauk, A.; Andose, J. D.; Frick, W. G.; Tang, R.; Mislow, K. *J. Am. Chem. Soc.* **1971**, *93*, 6507.
(79) Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1985**, *107*, 2596.
(80) Clark, T. *J. Am. Chem. Soc.* **1985**, *107*, 2597.
(81) Clark, T. *J. Comput. Chem.* **1983**, *4*, 404.
(82) Royen, P.; Hill, K. *Z. Anorg. Allg. Chem.* **1936**, *229*, 112.
(83) Stock, A.; Böttcher, W.; Lenger, W. *Ber. Dtsch. Chem. Ges.* **1909**, *42*, 2839.
(84) Fehlner, T. P. *J. Am. Chem. Soc.* **1967**, *89*, 6477.
(85) Callen, R. B.; Fehlner, T. P. *J. Am. Chem. Soc.* **1969**, *91*, 4122.
(86) Borgardt, M. Dissertation, Köln University, 1968.
(87) Dobbers, J. Dissertation, Köln University, 1968.
(88) Rackwitz, D. Dissertation, Köln University, 1975.
(89) Baudler, M.; Krause, U. M. Unpublished results, 1977.
(90) Blazejowski, J.; Lampe, F. W. *J. Phys. Chem.* **1981**, *85*, 1856.
(91) Baudler, M.; Ständeke, H.; Dobbers, J.; Borgardt, M.; Strabel, H. *Naturwissenschaften* **1966**, *53*, 251.
(92) Baudler, M.; Kemper, M. *Naturwissenschaften* **1971**, *58*, 624.
(93) Baudler, M.; Heumüller, H. To be published.
(94) Seel, F.; Velleman, K. *Z. Anorg. Allg. Chem.* **1971**, *385*, 123.
(95) Minkwitz, R.; Liedtke, A. *Inorg. Chem.* **1989**, *28*, 4238.
(96) Baudler, M.; Ternberger, H.; Faber, W.; Hahn, J. *Z. Naturforsch.* **1979**, *34b*, 1690.
(97) Baudler, M. *Angew. Chem.* **1987**, *99*, 429; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 419.
(98) Baudler, M.; Heumüller, R. *Z. Naturforsch.* **1984**, *39b*, 1306.
(99) Baudler, M.; Heumüller, R.; Langerbeins, K. *Z. Anorg. Allg. Chem.* **1984**, *514*, 7.
(100) Baudler, M.; Heumüller, R.; Germeshausen, J.; Hahn, J. *Z. Anorg. Allg. Chem.* **1985**, *526*, 7.
(101) Baudler, M.; Heumüller, R. *Z. Anorg. Allg. Chem.* **1988**, *559*, 49.
(102) Baudler, M.; Heumüller, R.; Düster, D. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1007.
(103) Beichl, G. J.; Evers, E. C. *J. Am. Chem. Soc.* **1958**, *80*, 5344.
(104) Baudler, M.; Block, Ch. To be published.
(105) Gamble, E. L.; Gilmont, P. *J. Am. Chem. Soc.* **1940**, *62*, 717.
(106) Rudolph, R. W.; Parry, R. W.; Farran, C. F. *Inorg. Chem.* **1966**, *5*, 723.
(107) Rice, B.; Livasy, J. A.; Schaeffer, G. W. *J. Am. Chem. Soc.* **1955**, *77*, 2750.
(108) Baudler, M.; Dockhorn, A. Unpublished results, 1976–1977.
(109) Baudler, M.; Heumüller, H. *Z. Anorg. Allg. Chem.* **1977**, *437*, 73.
(110) Baudler, M.; Carlsohn, B.; Koch, D.; Böhm, W.; Schröter, I. Unpublished results, 1975–1976.
(111) Barlow, C. G.; Ebsworth, E. A. V.; Holywell, G. C. *Angew. Chem.* **1969**, *81*, 330; *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 372.
(112) Sellmann, D. *Angew. Chem.* **1973**, *85*, 1123; *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 1020.
(113) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587.
(114) Bews, J. R.; Glidewell, Ch. *J. Mol. Struct.* (*THEOCHEM*) **1983**, *94*, 305.
(115) Fritz, G.; Härer, J. *Z. Anorg. Allg. Chem.* **1981**, *481*, 185.
(116) (a) Hahn, J.; Baudler, M.; Krüger, C.; Tsay, Y.-H. *Z. Naturforsch.* **1982**, *37b*, 797. (b) Aime, S.; Harris, R. K.; McVicker, E. M.; Fild, M. *J. Chem. Soc., Dalton Trans.* **1976**, 2144. (c) McFarlane, H. C. E.; McFarlane, W. *J. Chem. Soc., Chem. Commun.* **1975**, 582.
(117) de Alti, G.; Costa, G.; Galasso, V. *Spectrochim. Acta* **1964**, *20*, 965.
(118) Fehlner, T. P. *J. Am. Chem. Soc.* **1968**, *90*, 4817.
(119) (a) Baudler, M.; Koch, D.; Carlsohn, B. *Chem. Ber.* **1978**, *111*, 1217. (b) Baudler, M.; Reuschenbach, G. *Phosphorus Sulfur* **1980**, *9*, 81.
(120) Baudler, M.; Hellmann, J.; Reuschenbach, G. *Z. Anorg. Allg. Chem.* **1984**, *509*, 38.
(121) Fritz, G.; Vaahs, T. *Z. Anorg. Allg. Chem.* **1987**, *552*, 18.
(122) Fritz, G.; Stoll, K. *Z. Anorg. Allg. Chem.* **1986**, *538*, 78.
(123) Baudler, M.; Düster, D. *Z. Naturforsch.* **1987**, *42b*, 330.
(124) Baudler, M.; Kronenberg, W. Unpublished results, 1980–1981.
(125) Baudler, M.; Riekehof-Böhmer, R.; Krause, U. M. *Z. Anorg. Allg. Chem.* **1986**, *543*, 45.
(126) Baudler, M.; Hellmann, J.; Schmidt, Th. *Z. Naturforsch.* **1983**, *38b*, 537.
(127) Fritz, G.; Stoll, K.; Hönle, W.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1986**, *544*, 127.
(128) Fritz, G.; Jarmer, M.; Matern, E. *Z. Anorg. Allg. Chem.* **1990**, *586*, 37.
(129) Fritz, G.; Jarmer, M.; Matern, E. *Z. Anorg. Allg. Chem.* **1990**, *586*, 47.
(130) Fritz, G.; Vaahs, T.; Jarmer, M. *Z. Anorg. Allg. Chem.* **1990**, *589*, 12.
(131) Baudler, M.; Reuschenbach, G.; Hahn, J. *Z. Anorg. Allg. Chem.* **1981**, *482*, 27.
(132) Baudler, M.; Reuschenbach, G.; Hellmann, J.; Hahn, J. *Z. Anorg. Allg. Chem.* **1983**, *499*, 89.

(133) Issleib, K.; Hoffmann, W. *Chem. Ber.* **1966**, *99*, 1320.

(134) (a) Rauk, A.; Allen, L. C.; Mislow, K. *Angew. Chem.* **1970**, *82*, 453; *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 400. (b) Baechler, R. D.; Mislow, K. *J. Am. Chem. Soc.* **1971**, *93*, 773.

(135) Baudler, M.; Krause, U. M.; Hahn, J.; Riekehof-Böhmer, R. *Z. Anorg. Allg. Chem.* **1986**, *543*, 35.

(136) Pachler, K. G. R.; Wessels, P. L. *J. Chem. Soc., Chem. Commun.* **1974**, 1038.

(137) Hahn, J. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: Deerfield Beach, 1986; p 331.

(138) Finer, E. G.; Harris, R. K. *Mol. Phys.* **1967**, *13*, 65.

(139) For the sake of clarity, the sawhorse representations are based on models with tetrahedral angles; the somewhat smaller bonding angles at phosphorus do not cause any significant changes in the steric situation.

(140) Seidman, K.; Maciel, G. E. *J. Am. Chem. Soc.* **1977**, *99*, 659.

(141) Albrand, J. P.; Faucher, H.; Gagnaire, D.; Robert, J. B. *Chem. Phys. Lett.* **1976**, *38*, 521.

(142) Fritz, G.; Vaahs, T.; Jarmer, M. *Z. Anorg. Allg. Chem.* **1990**, *586*, 61.

(143) Hahn, J.; Riekehof-Böhmer, R.; Baudler, M. *Z. Anorg. Allg. Chem.* **1987**, *546*, 7.

(144) Baudler, M. *Pure Appl. Chem.* **1980**, *52*, 755.

(145) Baudler, M. *ACS Symp. Ser.* **1981**, *171*, 261.

(146) Baudler, M.; Riekehof-Böhmer, R.; Hahn, J. *Z. Anorg. Allg. Chem.* **1987**, *547*, 149.