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SUBSTITUTED HEPTAPHOSPHANORTRICYCLENES: DERIVATIVES AND HOMOLOGUES OF $P_7(SiMe_3)_3$ *

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Summary

Homologues and derivatives of $P_7(SiMe_3)_3$ can be synthesized either from $Li_3P_7 \cdot$ 3solv or Na_3P_7, or by cleavage of the P–$SiMe_3$ bond with RX. The reaction of $Li_3P_7 \cdot$ 3DME with the halogen-containing compounds Ph_3SiCl (Ph = C_6H_5), H_3SiI, Me_3SnBr (Me = CH_3), i-C_3H_7Br, $CpFe(CO)_2Br$ yields $P_7(SiPh_3)_3$, $P_7(SiH_3)_3$, $P_7(SnMe_3)_3$, $P_7(i\text{-}C_3H_7)_3$ and $P_7[Fe(CO)_2Cp]_3$. Na_3P_7 reacts with Me_3MCl (M = Si, Ge, Sn) yielding $P_7(MMe_3)_3$. The reaction of $Li_3P_7 \cdot$ 3DME with PMe_2Cl leads to P_2Me_4, but $P_7(PMe_2)_3$ is not formed. Cleavage of the P–Si bond in $P_7(SiMe_3)_3$ by Me_3SnBr or Me_3SnCl gives the compounds $P_7(SiMe_3)_{3-n}(SnMe_3)_n$ with (n = 1, 2 or 3) depending on the molar ratio. The reaction with HI yields mixtures of $H_{3-n}P_7(SiMe_3)_n$, while I_2 converts $P_7(SiMe_3)_3$ into P_2I_4, PI_3 and Me_3SiI. Crystals of the Ge and Sn compounds are less sensitive towards oxidation and hydrolysis than $P_7(SiMe_3)_3$.

The compounds have been identified by ^{31}P NMR and mass spectra. An X-ray structure analysis has shown $P_7(MMe_3)_3$ (M = Si, Ge, Sn, Pb) to be isotypical (space group $P2_1$ (No. 4)). The compounds crystallize as pure enantiomers. Bond lengths and angles vary with their position in the P_7 cage (P–P = 222.2, 218.8, and 218.0 pm) and are almost unaffected by the substitution. The P–M bond lengths are 228.8 (Si); 235.5 (Ge); 253.9 (Sn); 261.7 pm (Pb), showing a small lengthening with respect to calculated values. The cone angle of the bridging P atom decreases with increasing size of M. The P_7 cage vibrations are almost unchanged by the substitution, whereas ν(P–M) and $\nu(M\text{–}C_3)$ change in the usual manner.

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* Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday on 22nd June 1983.

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The discovery of the heptaphosphanortricyclene $P_7(SiMe_3)_3$ ($Me = CH_3$) [1,14] and the alkali-metal phosphides M_3P_7, solvated [2] and unsolvated [3], gave rise to many new reactions not affecting the P_7 skeleton.

In the case of $P_7(SiMe_3)_3$, cleavage of the Si–P bonds [4] yields new compounds, e.g. P_7H_3 [2] (cleavage with MeOH) or $P_7(PbMe_3)_3$ [5] (with Me_3PbCl). In the case of the phosphides M_3P_7 or $M_3P_7 \cdot$ solv., the formation of new compounds is facilitated by the formation of the alkali halides, for example, $Li_3P_7 \cdot 3DME$ and MeBr form P_7Me_3 [2,6], and Na_3P_7 and Me_3SiCl form $P_7(SiMe_3)_3$ [7]. The species (a) $P_7(SiMe_3)_3$, (b) $Li_3P_7 \cdot 3$solv. (solv. = DME, THF) and (c) Na_3P_7 are particularly suitable starting reagents. The most favourable syntheses for these compounds are (a) reaction of white phosphorus with Na/K alloy and subsequent silylation with Me_3SiCl [1], (b) reaction of white phosphorus with MeLi [8], and (c) preparation from red phosphorus and sodium at 500°C [9]. $Li_3P_7 \cdot 3$solv. can also be obtained from P_2H_4 and $LiPH_2$ [2] or P_{white} and $LiPH_2$ [10], and the reaction of $Li_3P_7 \cdot 3$solv. with Me_3SiCl provides another method for the preparation of $P_7(SiMe_3)_3$.

We now report on further reactions of $P_7(SiMe_3)_3$, $Li_3P_7 \cdot 3$solv. and Na_3P_7.

1. Reactions of $Li_3P_7 \cdot 3DME$ with monohalides of various elements

The reactions, which were expected to proceed with formation of solid LiCl, were sometimes quite complex, and the desired compounds were not formed in every case. Reaction of $Li_3P_7 \cdot 3$solv. with Ph_3SiCl ($Ph = C_6H_5$), H_3SiI, Me_3SnBr, i-PrBr ($Pr = C_3H_7$) and $CpFe(CO)_2Br$ ($Cp = C_5H_5$) gave the corresponding derivatives.

1.1. $P_7(SiPh_3)_3$

The formation of $P_7(SiPh_3)_3$ is described by equation 1. A solution of Ph_3SiCl

$$Li_3P_7 \cdot 3DME + 3Ph_3SiCl \xrightarrow[-3\ DME]{toluene} P_7(SiPh_3)_3 + 3LiCl \qquad (1)$$

in toluene is added dropwise to a suspension of $Li_3P_7 \cdot 3DME$ in toluene at -78°C and the mixture stirred at room temperature for 15 h. After separation of LiCl, white crystals of $P_7(SiPh_3)_3$ are precipitated and isolated at -30°C. Carrying out the reaction in THF leads to formation of small amounts of other phosphorus-containing substances in addition to $P_7(SiPh_3)_3$. Analysis: Found: P, 22.66; Si, 8.86. $C_{54}H_{45}P_7Si_3$ calcd.: P, 21.83; Si, 8.45%. The mass spectrum shows the peak for the molecular ion ($m/e = 994.1025$). The ^{31}P NMR spectrum of $P_7(SiPh_3)_3$ displays 3 groups of signals: $\delta(P_a)$ -106.7, $\delta(P_e)$ $+4.1$, $\delta(P_b)$ -156.3 ppm ($P_a = P_{apical}$, $P_e = P_{equatorial}$, $P_b = P_{basal}$; see Fig. 1).

The chemical shifts, the splitting schemes and the intensities of the signals are very similar to those for $P_7(SiMe_3)_3$ [1]. The $SiPh_3$ groups are symmetrically bound to the P_7 skeleton. Because of the steric hindrance an unsymmetrical arrangement is impossible. Furthermore a different orientation or replacement of only one substituent would generate a completely different ^{31}P NMR spectrum, because in such compounds all seven P atoms would be magnetically non-equivalent.

1.2. $P_7(SiH_3)_3$

For the formation of $P_7(SiH_3)_3$ by reactions analogous to that in eq. 1, H_3SiBr and H_3SiI are suitable reagents. A solution of H_3SiI in toluene is added dropwise to

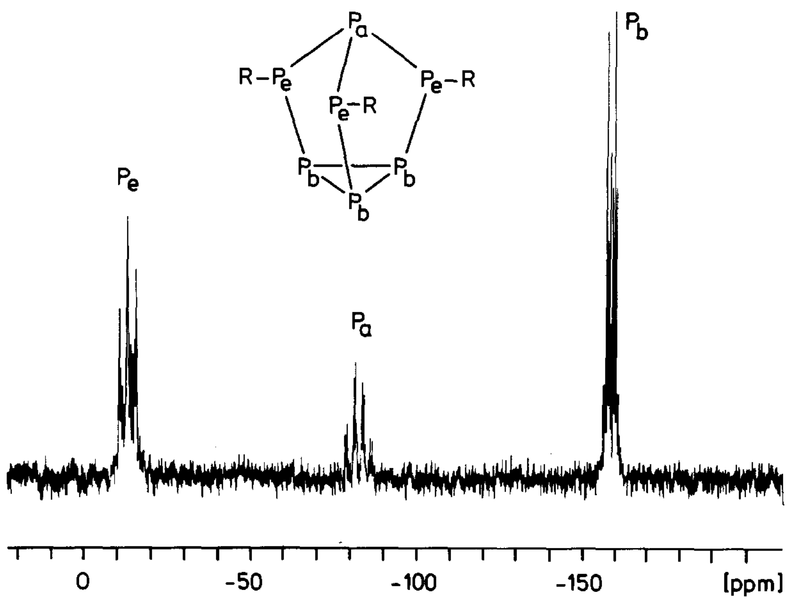

Fig. 1. ^{31}P NMR spectrum of $P_7(SnMe_3)_3$ in C_6D_6, 121.49 MHz (Bruker WH 300), standard: H_3PO_4.

a suspension of $Li_3P_7 \cdot 3DME$ in toluene at $-78°C$ and the mixture warmed to room temperature. After separation of insoluble products the mother liquor contains $P_7(SiH_3)_3$. Similar reactions with H_3SiI in THF or H_3SiBr in toluene gave insoluble polymeric products.

The ^{31}P NMR spectrum of $P_7(SiH_3)_3$ displays 3 groups of signals characteristic of the P_7 skeleton ($\delta(P_a)$ -76, $\delta(P_e)$ -18, $\delta(P_b)$ -139 ppm, expl. of indices see 1.1). After removal of the solvent the mass spectrum shows the M^+ peak ($m/e = 309.8173$) as well as $M^+ - CH_3$ (278.8159), and other fragment ions.

Crystals of $P_7(SiH_3)_3$ were not obtained. When the toluene was removed the remaining yellow residue could not be redissolved, and when THF was added the color changed to brown and decomposition took place.

1.3. $P_7(SnMe_3)_3$

The reaction of $Li_3P_7 \cdot 3DME$ (as suspension in toluene) with Me_3SnBr (molar ratio 1/3, see eq. 1) is almost temperature independent, and can be carried out at 20°C. After separation of LiCl white crystals of P_7 $(SnMe_3)_3$ separated at $-30°C$. Analysis: Found: P, 29.89; Sn, 49.80. $C_9H_{27}P_7Sn_3$ calcd.: P, 30.61; Sn, 50.28%.

The ^{31}P NMR spectrum (in C_6D_6) shows three groups of signals at -157.9, -82.3 and -13.1 ppm (Fig. 1). The shape and the intensity distribution (3/1/3) are characteristic of a compound with a P_7 skeleton and a symmetrical arrangement of the substituents. As can be seen in the ^1H NMR spectrum, the molecule contains only one kind of proton. Because of coupling to a neighbouring P atom, the signal is split into a doublet (δ 0.42 ppm, $^3J(HCSnP)$ 1.5 cps, solvent C_6D_6). The mass spectrum shows the M^+ peak ($m/e = 708$) and all other ions can be accounted for as reasonable fragments. The observed and calculated isotope patterns of the peaks are in good agreement.

1.4. Reactions of alkyl and aryl halides with $Li_3P_7 \cdot 3DME$; $P_7(i\text{-}Pr)_3$

The reactions of $Li_3P_7 \cdot 3DME$ with alkyl and aryl halides would be expected to proceed with precipitation of LiCl and formation of P_7R_3. But, as shown by the preparation of P_7Me_3 [2,6], such syntheses are only successful under certain circumstances. Thus $Li_3P_7 \cdot 3DME$ reacts to give P_7Me_3 only on treatment with MeBr (not with MeCl), only in polar solvents (e.g. THF) and only at low temperatures (−78°C). During the reaction of a suspension of $Li_3P_7 \cdot 3DME$ in DME with $i\text{-}C_3H_7Br$ (molar ratio 1/3) at −78°C the color changes from yellow to red. The mixture is allowed to warm to room temperature, the solvent is removed in vacuo and the residue treated with toluene. After separation of insoluble products and addition of hexane to the solution white $P_7(i\text{-}C_3H_7)_3$ can be precipitated at −30°C.

The ^{31}P NMR spectrum of $P_7(i\text{-}C_3H_7)_3$ (Fig. 2) is quite similar to that of P_7Me_3 [6]. P_7Me_3 and $P_7(i\text{-}C_3H_7)_3$ exist in two isomeric forms corresponding to a symmetrical and an asymmetrical arrangement of the substituents bound to the P_7 skeleton. The mass spectrum of $P_7(i\text{-}Pr)_3$ shows the M^+ peak as well as fragment ions.

Under the conditions described above $Li_3P_7 \cdot 3DME$ and EtBr do not form P_7Et_3. In the ^{31}P NMR spectrum no signal is observed in the region −140 to −160 ppm, typical of the P_3 ring of the P_7 skeleton. The residue remaining after removal of the solvent contains a mixture of higher phosphanes with 9 and 11 P atoms per molecule as shown by mass spectrometry; pure compounds have not yet been isolated. Likewise the reactions of $Li_3P_7 \cdot 3DME$ with t-BuCl and t-BuBr gave no detectable $P_7(t\text{-}Bu)_3$. C_6H_5Br did not react, and C_6F_5Br gave insoluble products (not identified).

1.5. Reactions with transition metal carbonyl halides; $P_7[CpFe(CO)_2]_3$

Transition metal carbonyl halides can react with Li phosphides with formation of new metal to phosphorus bonds. Thus $CpFe(CO)_2[P(SiMe_3)_2]$ [11] can be made

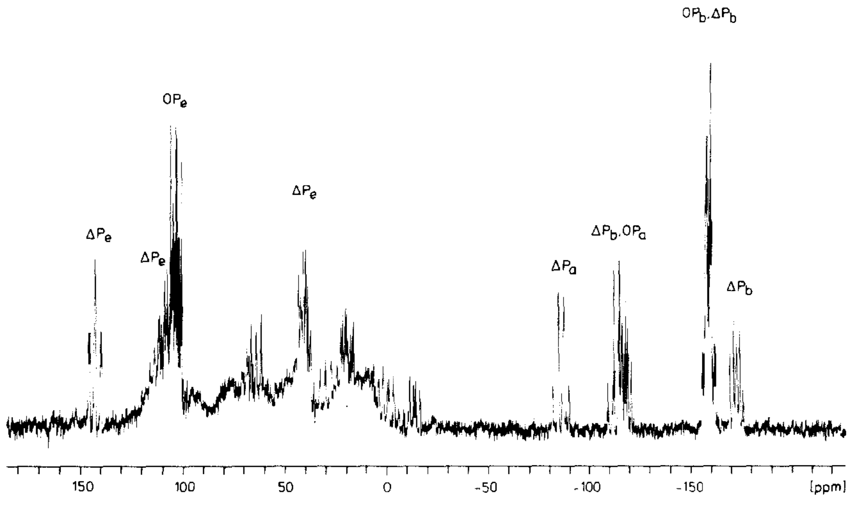

Fig. 2. ^{31}P NMR spectrum of $P_7(i\text{-}C_3H_7)_3$ in toluene; isomers: Δ = asymmetrical, 0 = symmetrical, labelling of P atoms see Fig. 1, 121.49 MHz (Bruker WH 300), standard: H_3PO_4.

from $LiP(SiMe_3)_2$ and $CpFe(CO)_2Br$, and metal halides and $Li_3P_7 \cdot 3DME$ can be assumed to react together in the same way and, in fact, $P_7[CpFe(CO)_2]_3$ is formed by the reaction of $Li_3P_7 \cdot 3DME$ with $CpFe(CO)_2Br$ (molar ratio 1/3) in toluene at room temperature within 17 h. After separation of insoluble substances the product was identified by its ^{31}P NMR spectrum; $\delta(P_a)$ −48.7, $\delta(P_e)$ 47.7, $\delta(P_b)$ −159.3 ppm. The splitting pattern and the intensity distribution (1/3/1) of the sets of signals correspond with those in the ^{31}P NMR spectrum of $P_7(SiMe_3)_3$. The chemical shifts of the three-membered ring P atoms (P_b) are also almost identical. On the other hand the resonance of the equatorial P atoms P_e (connected to the substituents) is, as expected, shifted considerably downfield by the Cp groups at Fe. The resonance of the apical P_a is also shifted downfield. According to the spectrum the P_7 skeleton is symmetrically substituted. The ^{31}P NMR investigation confirms that $P_7[CpFe(CO)_2]_3$ was, in fact, formed in the reaction. It seems this compound is only stable in solvents; removal of the solvent in vacuo causes decomposition with formation of $[CpFe(CO)_2]_2$ (identified by its mass spectrum) and P-containing polymers.

Reactions of $Li_3P_7 \cdot 3DME$ with $Re(CO)_5Br$, $Re(CO)_5Cl$, $Mn(CO)_5Cl$ and $Mn(CO)_5Br$ in various solvents at several temperatures did not lead to substitution of the P_7 skeleton.

1.6. Reaction of $Li_3P_7 \cdot 3DME$ with Me_2PCl

If the reaction of $Li_3P_7 \cdot 3DME$ with Me_2PCl proceeded simply with the formation of LiCl, the product would be $P_7(PMe_2)_3$. This compound is of special interest for investigations on complexes. The reactions of $Li_3P_7 \cdot 3DME$ with Me_2PCl (molar ratio 1/3) in various solvents (toluene, toluene/THF) at −78 and 20°C in all cases gave P_2Me_4 and Me_2PH as a by-product along with involatile substances, which could not be identified. The reaction seems to involve transmetallation between Li_3P_7 and Me_2PCl to form $LiPMe_2$, which reacts with PMe_2Cl to give P_2Me_4. The simultaneously generated phosphide containing Li and Cl decomposes with formation of LiCl.

2. Reaction of Na_3P_7 with Me_3MCl (M = Ge, Sn)

2.1. $P_7(GeMe_3)_3$ (2)

The preparation of $P_7(GeMe_3)_3$ is analogous to that of $P_7(SiMe_3)_3$ [7] from Na_3P_7 and Me_3SiCl. The equilibrium is influenced by the precipitation of NaCl and the solubility of the product $P_7(GeMe_3)_3$ in the solvent used for the reaction. Because of the sensitivity of the products towards moisture and oxygen, all preparations must be carried out in an inert atmosphere (Ar).

A suspension of Na_3P_7 in toluene is cooled to −33°C. After addition of the stoichiometric amount of Me_3GeCl the solution is stirred and then filtered at room temperature. After some days, the clear yellow filtrate yields light-yellow needle-shaped crystals of $P_7(GeMe_3)_3$.

2.2. $P_7(SnMe_3)_3$ (3)

Compound **3** can be prepared by the cleavage method (cf. 3.3) as well as by reaction of solid Na_3P_7 with Me_3SnCl. The suspension of Na_3P_7 in toluene is cooled to −50°C and Me_3SnCl is added. Colorless crystals of **3** are formed after a few days.

3. The formation of various substituted heptaphosphanortricyclenes by cleavage of the Si–P bonds of $P_7(SiMe_3)_3$

These reactions are complicated because in addition to cleavage of Si–P bonds of $P_7(SiMe_3)_3$, cleavage of P–P bonds is also possible. Thus $P_7(SiMe_3)_3$ reacts with iodine with formation of P_2I_4, PI_3, Me_3SiI and insoluble polymeric products. These compounds are also produced (along with $P_7(SiMe_3)_3$) when iodine is used in a low molar ratio (1/0.5). Me_2PCl and $MePCl_2$ also react with destruction of the P_7 cage. C_6F_5Br gives $P(C_6F_5)_3$ and polymeric substances, neither CH_2Cl_2 nor C_6H_5Br react.

3.1. $P_7(SiMe_3)_{3-n}(SnMe_3)_n$; $n = 1, 2, 3$

The reaction of $P_7(SiMe_3)_3$ with Me_3SnBr leaves the P_7 skeleton unchanged. When the reactants in a molar ratio of 1/2 are brought together in toluene at 20°C, a mixture is formed consisting of $(Me_3Si)_2P_7(SnMe_3)$, $(Me_3Si)P_7(SnMe_3)_2$ and $P_7(SnMe_3)_3$ along with unchanged $P_7(SiMe_3)_3$ and Me_3SiBr. Separation of these different substituted derivatives has not yet been possible. The mass spectrum confirmed the presence of the following compounds: $P_7(SnMe_3)_3$: M^+ 708, $M^+ - CH_3$ 693; $P_7(SnMe_3)_2(SiMe_3)$: M^+ 618, $M^+ - CH_3$ 602.7760; $P_7(SnMe_3)(SiMe_3)_2$: M^+ 527.8791, $M^+ - CH_3$ 512.8531.

The mixture of these compounds is soluble in toluene. The ^{31}P NMR spectrum of this solution shows three sets of signals: (a) −145 to −170 ppm, signals of the P_3ring P atoms (P_b); (b) −80 to −105 ppm, signals of the apical P atoms (P_a); (c) 10 to −20 ppm, signals of the P atoms connected to the $SiMe_3$ and $SnMe_3$ groups (P_e). In mixed substituted P_7 systems all the P atoms are magnetically non-equivalent. In this case, three sets of signals are expected for P_b and for P_e. In addition, there are the signals of the symmetrically substituted compounds (P_b, P_e: a multiplet each). In the mixture the differences between the chemical shifts of the single P_e and P_b atoms are rather small, and so there is superposition of signals. For P_a (in all compounds) an approximate quartet is expected. Four of these are superposed in the set of signals between −80 and −105 ppm. No other resonances were observed. The reaction of $LiP_7(SiMe_3)_2$ with Me_3SnBr (molar ratio 1/1) does not yield pure $P_7(SnMe_3)(SiMe_3)_2$, but instead a mixture of various substituted derivatives. Because the reactivities of the P–$SiMe_3$ or P–$SnMe_3$ bonds are very different ($P_7(SiMe_3)_3$ is split by methanol while $P_7(SnMe_3)_3$ is uneffected), these mixed substituted derivatives are of interest for further investigations.

3.2. $H_nP_7(SiMe_3)_{3-n}$; $n = 1,2,3$

The methanolysis of $P_7(SiMe_3)_3$ yields H_3P_7 as amorphous yellow solid insoluble in organic solvents [2]. The reaction of $P_7(SiMe_3)_3$ with HI is expected to give partly substituted derivatives, according to eq. 2:

$$P_7(SiMe_3)_3 + nHI \rightarrow H_nP_7(SiMe_3)_{3-n} \qquad (2)$$

$(n = 0, 1, 2, 3)$

In fact $P_7(SiMe_3)_3$ and HI (molar ratio 1/1, solvent toluene) gave a mixture of all these compounds. After removal of the solvent in vacuo, an attempt was made to separate the mixture by vacuum sublimation; a yellow solid sublimed at 120°C/10^{-3} Torr, but both this solid and the residue had the same compositions as the mixture before sublimation, as shown by mass spectrometry: $HP_7(SiMe_3)_2$: M^+ 363.9162,

M^+- Me 348.8952; $H_2P_7(SiMe_3)$: M^+ 291.8789, M^+- Me 276.8609; H_3P_7: M^+ 218.8408. As in the case of H_3P_7, the partly hydrated derivatives are insoluble in organic solvents.

3.3. $P_7(SnMe_3)_3$ (3)

Pure samples of **3** can be prepared by the exchange of the ligand $SiMe_3$ with $SnMe_3$ in DME at −50°C. The crude microcrystalline product contains up to 95% of pure **3**. Large rod shaped, colorless crystals, suitable for X-ray investigation, were obtained by recrystallisation in toluene.

The equilibrium of eq. 3

$$P_7(SiMe_3)_3 + 3Me_3SnCl \rightleftharpoons P_7(SnMe_3)_3 + 3Me_3SiCl \qquad (3)$$

is shifted towards the product by precipitation of **3** and by distillation of Me_3SiCl from the mixture.

The reaction of $P_7(SiMe_3)_3$ with Me_3GeCl under analogous conditions is not satisfactory because of the high solubility of $P_7(GeMe_3)_3$ in DME. In this case use of Na_3P_7 as the starting compound is more suitable.

The cleavage of the P–Si bond by the halide Me_3MCl can be interpreted in terms of nucleophilic attack by the Cl atom at the $SiMe_3$ ligands as the first step, and the reaction at this Si atom is a typical S_N2 process. This initial attack is followed by departure of the Me_3SiCl molecule, and reaction of the P bridge atom with excess Me_3SnCl.

$P_7(SnMe_3)_3$ is slightly soluble in DME and THF, but soluble in toluene and benzene. It decomposes in a closed system at 182°C without melting because of the thermal lability of the P–Sn bond. Daylight also decomposes the compound. Attempts to sublime **3** at 130°C and 10^{-3} bar gave a lot of decomposed sublimate along with small amounts of $P_7(SnMe_3)_3$, which was identified from its X-ray powder pattern. In contrast to the very air and moisture sensitive $P_7(SiMe_3)_3$ [14], the crystals of $P_7(SnMe_3)_3$ are stable under ambient conditions for several days, but in solution the compound shows a sensitivity comparable to that of the silicon compound. The unreactivity can be explained in terms of coating of the crystal surface by non volatile hydrolysis products, e.g. Me_3SnOH and $(Me_3Sn)_2O$.

4. Infrared spectra of $P_7(MMe_3)_3$; M = Si, Ge, Sn, Pb

The infrared spectra of $P_7(MMe_3)_3$ (M = Si (**1**), Ge (**2**), Sn(**3**), Pb (**4**)) were recorded on a Perkin–Elmer 283 infrared spectrometer, with the results shown in Table 1. The FIR spectra were recorded on a Bruker FIR spectrometer at the Max Planck Institut für Festkörperforschung, Stuttgart. Table 1 and Fig. 3 show the frequencies (cm^{-1}) in the region 1000–100 cm^{-1}. The main feature of all four spectra is almost constant, i.e. the valence vibrations of the P_7 skeleton are ligand independent. The ν(P–M) and $\nu(M-C_3)$ bonds shift to lower frequencies with increasing atomic weights of M. The rocking and wagging vibrations shift only slightly with this increase in the mass of M. The two bands, which are well separated in the silicon compound, are almost coincident in the lead compound.

The spectrum of the silicon compound is similar to that of [1]. The $\nu(P_7$ skeleton) vibrations agree well with the Raman spectra of Ba_3P_{14} [12] and Na_3P_7 [13]. This good agreement confirms our assignment.

TABLE 1

INFRARED SPECTRA [a] OF $P_7(MMe_3)_3$ (M = Si, Ge, Sn, Pb) IN THE REGION 1000–100 cm^{-1}. Si: NUJOL MULL, KBr-WINDOWS; Ge: NUJOL MULL, CsI WINDOWS; Sn: KBr PELLET; Pb: KBr PELLET; FIR: PE PELLET

M = Si (**1**)	M: Ge (**2**)	M: Sn (**3**)	M = Pb (**4**)	Assignment
835 (vvs, broad)	820 (vvs, broad)	772 (vvs, broad)	765 (vvs, broad)	$\tau(CH_3)$
750 (vs)	755 (sh)	715 (sh)		
690 (s)	599 (vs)	530 (vs)	472 (vs)	$\nu(MC_3)$
622 (vs)	565 (vs)	511 (vs)	455 (vs)	
468 (s)	{467 (sh) 462 (s)}	455 (s)	445 (s)	$\nu(P_7$ skeleton)
450 (m)	441 (s)	438 (s)	433 (s)	
422 (w)	413 (s)	410 (m)	403 (m)	
350 (w)	350 (s)	356 (m)	350 (m)	
	275 (vw)	276 (w) FIR	265 (vw)	
	270 (w)	271 (m) FIR		
405 (s)	370 (vs)	337 (s)	310 (s)	ν(P-M)
		150 (vs)——FIR	——115 (vs)	

[a] Abbreviations: vvs, very very strong; vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

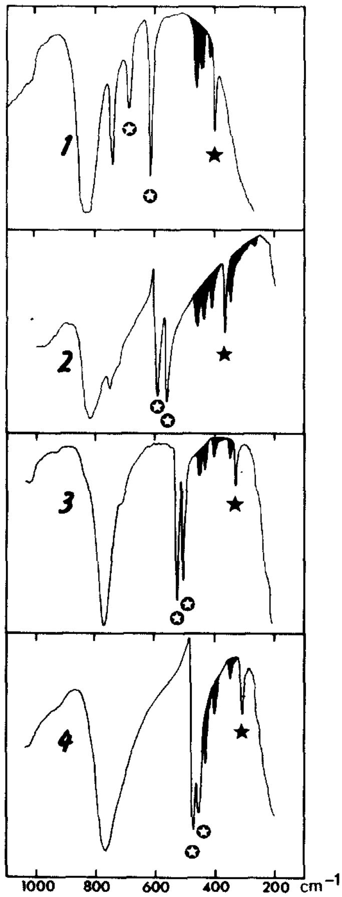

Fig. 3. Infrared spectra of **1–4** in the region 1000–200 cm^{-1}. The fundamental vibrations of the P_7 skeleton are marked black; the black star indicates γ(P–M); the white star indicates $\gamma(M–C_3)$; the non marked strong bands are $\gamma(CH_3)$.

5. X-ray structure analysis

5.1. Experimental

Due to their lower sensitivity towards moisture and air, the single crystals of $P_7(GeMe_3)_3$ (**2**) were obtained by the procedure described earlier [14]. Single crystals of $P_7(SnMe_3)_3$ (**3**) can be handled for a short time in air, and so they were fixed in a sealed capillary with silicone grease. The quality of the single crystals was tested by film methods, which also confirmed the expected isotypism to the silicon compound [14]. Lattice constants are determined by the refined 2θ values of 12 (**2**) and 15 (**3**) selected reflexions in the range $15° \leq 2\theta \leq 25°$. The intensities of 1690 (2693) reflexions *hkl* (Mo-K_α; $3° \leq 2\theta \leq 55°$ for **2**, **3**) were collected on an automated four circle diffractometer P3 (SYNTEX). ψ scan data of 7(14) reflexions were used as input for the empirical absorption correction. After conventional data reduction, the intensities of 1352 (2249) reflexions *hkl* with $I \leq 3\sigma(I)$ were used for the refinement starting with the positional parameters of the silicon compound. The isotropic reliability factors were $R(\text{iso}) = 0.12$ (0.07). The refinement with anisotropic temperature factors and introduction of an extinction correction yields $R(\text{aniso}) = 0.075$ (0.037) and $R_w = 0.063$ (0.037). The test for the enantiomers ($x' = x$; $y' = -y$; $z' = z$) in both cases yields the same reliability factors, but strongly different P–M distances. In the case **2** the conformation of the crystal investigated, is equivalent to the former described **1** [14], whereas the conformation of the crystal investigated of **3** agrees to that of **4** [5].

5.2. Result *

Tris(trimethylgermyl)heptaphosphanortricyclene $P_7(GeMe_3)_3$ (**2**) and tris(trimethylstannyl)heptaphosphanortricyclene $P_7(SnMe_3)_3$ (**3**) crystallize monoclinically in the space group $P2_1$ (No. 14) (*a* 973.5(6); *b* 1760.2(9); *c* 690.9(4) pm; β 99.36(5)°; d_x 1.620 g cm^{-3} and *a* 988.6(5); *b* 1808.7(6); *c* 693.9(2) pm; $\beta = 99.43(3)°$; d_x 1.922 g cm^{-3}) with $Z = 2$ formula units in the unit cell.

Positional and thermal parameters are given in Table 2, bond distances and bond angles in Table 3. All calculations were carried out with the SHELXTL-System [15] on the computer ECLIPSE S 250 of the Max Planck Institute Stuttgart. The bond distances and angles were calculated by use of the program ORFFEE [16].

5.3. Discussion

Figure 4 shows the heptaphosphanortricyclene molecules $P_7(MMe_3)_3$ with M = Si (**1**), Ge (**2**), Sn (**3**), Pb (**4**). These isotopical compounds crystallize in the space group $P2_1$ (No. 4) as pure enantiomeres. Three different types of P–P bonds are present in the P_7 cage, namely A (base–base), B (base–bridge), and C (bridge–bridgehead). In the molecules P_7R_3 and As_7R_3, the sequence of the bond lengths is A > B > C, whereas the corresponding anions P_7^{3-} [17] and As_7^{3-} [18] and Sb_7^{3-} [19] show the sequence A > C > B. In the series $P_7(MMe_3)_3$ with varying M no drastic variation of the P–P bond type A, B and C (Table 3) is observed, but a slight decrease can be

(Continued on p. 76)

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* Supplementary material can be ordered from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG with reference to no. CSD50364, and the names of the authors and the title of this paper.

TABLE 2

ATOMIC COORDINATES AND $U_{eq.}$ (pm^2), WITH STANDARD DEVIATIONS IN PARENTHESES

Atom	$P_7(GeMe_3)_3$				Atom	$P_7(SnMe_3)_3$			
	x	y	z	$U_{eq.}$		x	y	z	$U_{eq.}$
Ge(1)	0.3117(4)	0.1665(2)	0.1341(5)	73(1)	Sn(1)	0.30589(9)	0.16325(6)	0.12250(14)	51(1)
Ge(2)	0.7154(3)	0.3573(2)	0.6764(4)	66(1)	Sn(2)	0.70770(9)	0.35636(6)	0.68513(13)	47(1)
Ge(3)	0.7976(4)	0	0.6460(5)	66(1)	Sn(3)	0.80497(9)	0	0.64656(13)	46(1)
P(21)	0.4986(8)	0.2372(4)	0.3071(11)	63(3)	P(21)	0.4996(3)	0.2385(2)	0.3131(5)	46(1)
P(22)	0.7750(8)	0.2289(4)	0.6461(10)	60.3)	P(22)	0.7735(3)	0.2219(2)	0.6510(5)	42(1)
P(23)	0.6398(8)	0.0701(4)	0.4214(11)	64(3)	P(23)	0.6308(3)	0.0734(2)	0.4116(5)	45(1)
P(30)	0.5745(8)	0.1715(4)	0.5682(10)	60(3)	P(30)	0.5737(3)	0.1699(2)	0.5676(5)	43(1)
P(31)	0.6652(10)	0.2231(5)	0.1297(10)	72(3)	P(31)	0.6619(4)	0.2263(2)	0.1378(5)	53(1)
P(32)	0.8528(9)	0.2303(5)	0.3653(12)	71(3)	P(32)	0.8471(3)	0.2267(2)	0.3691(5)	51(1)
P(33)	0.7823(9)	0.1181(5)	0.2390(11)	75(3)	P(33)	0.7694(4)	0.1209(2)	0.2285(5)	54(1)
C(11)	0.366(3)	0.083(2)	−0.027(4)	79(12)	C(11)	0.3721(16)	0.0766(10)	−0.0491(23)	71(6)
C(12)	0.202(4)	0.235(2)	−0.045(6)	135(18)	C(12)	0.1869(20)	0.2404(10)	−0.0601(31)	104(8)
C(13)	0.207(4)	0.130(2)	0.329(5)	105(16)	C(13)	0.194(2)	0.120(1)	0.337(3)	98(9)
C(21)	0.721(4)	0.412(2)	0.439(5)	100(15)	C(21)	0.7096(20)	0.4184(9)	0.4274(25)	81(7)
C(22)	0.536(3)	0.367(2)	0.781(4)	80(12)	C(22)	0.5104(15)	0.3653(9)	0.7753(24)	69(6)
C(23)	0.862(3)	0.395(2)	0.888(4)	79(12)	C(23)	0.8673(18)	0.3945(10)	0.9086(22)	76(6)
C(31)	0.963(3)	0.055(2)	0.758(6)	104(16)	C(31)	0.9836(14)	0.0582(8)	0.7747(22)	61(5)
C(32)	0.848(5)	−0.084(2)	0.497(7)	146(22)	C(32)	0.870(2)	−0.086(1)	0.469(3)	105(9)
C(33)	0.692(4)	−0.034(2)	0.848(5)	97(15)	C(33)	0.697(2)	−0.046(1)	0.855(2)	79(7)

H(11A)	0.363	0.037	0.043	93	H(11A)	0.387	0.032	0.028	93
H(11B)	0.458	0.093	−0.053	93	H(11B)	0.303	0.068	−0.161	93
H(11C)	0.301	0.081	−0.148	93	H(11C)	0.456	0.091	−0.091	93
H(12A)	0.137	0.206	−0.134	108	H(12A)	0.119	0.215	−0.150	108
H(12B)	0.262	0.262	−0.116	108	H(12B)	0.143	0.273	0.018	108
H(12C)	0.154	0.269	0.028	108	H(12C)	0.245	0.268	−0.132	108
H(13A)	0.203	0.076	0.324	109	H(13A)	0.197	0.066	0.336	109
H(13B)	0.115	0.151	0.303	109	H(13B)	0.234	0.137	0.465	109
H(13C)	0.253	0.147	0.456	109	H(13C)	0.100	0.135	0.309	109
H(21A)	0.709	0.378	0.333	89	H(21A)	0.704	0.385	0.318	89
H(21B)	0.810	0.437	0.450	89	H(21B)	0.633	0.451	0.408	89
H(21C)	0.648	0.449	0.424	89	H(21C)	0.793	0.446	0.440	89
H(22A)	0.494	0.319	0.783	83	H(22A)	0.477	0.317	0.800	83
H(22B)	0.477	0.402	0.700	83	H(22B)	0.519	0.394	0.893	83
H(22C)	0.557	0.387	0.913	83	H(22C)	0.447	0.389	0.674	83
H(23A)	0.905	0.353	0.961	83	H(23A)	0.911	0.353	0.979	83
H(23B)	0.820	0.428	0.972	83	H(23B)	0.933	0.422	0.850	83
H(23C)	0.930	0.422	0.830	83	H(23C)	0.829	0.426	0.997	83
H(31A)	1.029	0.019	0.825	73	H(31A)	1.045	0.025	0.854	73
H(31B)	0.939	0.092	0.847	73	H(31B)	1.028	0.078	0.674	73
H(31C)	1.002	0.079	0.654	73	H(31C)	0.958	0.098	0.854	73
H(32A)	0.887	−0.066	0.389	109	H(32A)	0.881	−0.066	0.344	109
H(32B)	0.766	−0.114	0.454	109	H(32B)	0.956	−0.105	0.532	109
H(32C)	0.915	−0.114	0.581	109	H(32C)	0.803	−0.124	0.450	109
H(33A)	0.675	0.008	0.928	83	H(33A)	0.668	−0.007	0.933	83
H(33B)	0.743	−0.073	0.926	83	H(33B)	0.618	−0.072	0.789	83
H(33C)	0.604	−0.055	0.785	83	H(33C)	0.756	−0.079	0.937	83

TABLE 3

BOND DISTANCES (pm) AND BOND ANGLES (°) FOR $P_7(GeMe_3)_3$ (**2**) AND $P_7(SnMe_3)_3$ (**3**), WITH STANDARD DEVIATIONS IN PARENTHESES

2		**3**		**2**		**3**	
Ge(1)–C(12)	192.2(37)	Sn(1)–C(12)	210.9(19)	C(12)–Ge(1)–C(13)	110.9(17)	C(12)–Sn(1)–C(11)	110.0(7)
Ge(1)–C(13)	192.6(39)	Sn(1)–C(11)	213.5(18)	C(12)–Ge(1)–C(11)	106.1(15)	C(12)–Sn(1)–C(13)	111.0 (8)
Ge(1)–C(11)	196.7(33)	Sn(1)–C(13)	214.3(22)	C(12)–Ge(1)–P(21)	107.3(11)	C(12)–Sn(1)–P(21)	104.9 (5)
Ge(1)–P(21)	236.2(8)	Sn(1)–P(21)	253.8(3)	C(13)–Ge(1)–C(11)	111.6(14)	C(11)–Sn(1)–C(13)	111.1(7)
				C(13)–Ge(1)–P(21)	105.9(10)	C(11)–Sn(1)–P(21)	114.2(4)
Ge(2)–C(21)	191.0(35)	Sn(2)–C(21)	211.4(17)	C(11)–Ge(1)–P(21)	115.1(9)	C(13)–Sn(1)–P(21)	105.4(5)
Ge(2)–C(23)	198.4(27)	Sn(2)–C(23)	213.7(16)				
Ge(2)–C(22)	200.3(31)	Sn(2)–C(22)	215.0(16)	C(21)–Ge(2)–C(23)	110.3(14)	C(21)–Sn(2)–C(23)	109.5(7)
Ge(2)–P(22)	235.1(8)	Sn(2)–P(22)	253.9(4)	C(21)–Ge(2)–C(22)	114.5(15)	C(21)–Sn(2)–C(22)	109.9(7)
				C(21)–Ge(2)–P(22)	111.5(11)	C(21)–Sn(2)–P(22)	113.1(5)
Ge(3)–C(32)	191.1(43)	Sn(3)–C(33)	210.5(18)	C(23)–Ge(2)–C(22)	105.7(12)	C(23)–Sn(2)–C(22)	111.2(6)
Ge(3)–C(31)	193.0(31)	Sn(3)–C(31)	212.2(14)	C(23)–Ge(2)–P(22)	103.2(10)	C(23)–Sn(2)–P(22)	101.9(5)
Ge(3)–C(33)	195.7(39)	Sn(3)–C(32)	214.7(20)	C(22)–Ge(2)–P(22)	110.9(10)	C(22)–Sn(2)–P(22)	111.0(4)
Ge(3)–P(23)	234.8(8)	Sn(3)–P(23)	254.3(3)				
				C(32)–Ge(3)–C(31)	109.5(18)	C(33)–Sn(3)–C(31)	112.9(6)
P(21)–P(30)	216.9(10)	P(21)–P(31)	217.8(5)	C(32)–Ge(3)–C(33)	111.0(17)	C(33)–Sn(3)–C(32)	110.0(7)
P(21)–P(31)	220.0(13)	P(21)–P(30)	218.4(5)	C(32)–Ge(3)–P(23)	104.4(13)	C(33)–Sn(3)–P(23)	106.3(5)
P(21)–Ge(1)	236.2(8)	P(21)–Sn(1)	253.8(3)	C(31)–Ge(3)–C(33)	111.6(16)	C(31)–Sn(3)–C(32)	107.0(7)
				C(31)–Ge(3)–P(23)	114.5(11)	C(31)–Sn(3)–P(23)	116.1(4)
P(22)–P(30)	218.6(11)	P(22)–P(30)	217.9(4)	C(33)–Ge(3)–P(23)	105.6(11)	C(32)–Sn(3)–P(23)	104.2(5)
P(22)–P(32)	219.5(12)	P(22)–P(32)	219.8(5)				
P(22)–Ge(2)	235.1(8)	P(22)–Sn(2)	253.9(4)	P(30)–P(21)–P(31)	102.8(4)	P(31)–P(21)–P(30)	102.3(2)
				P(30)–P(21)–Ge(1)	105.7(4)	P(31)–P(21)–Sn(1)	102.5(2)
P(23)–P(33)	219.0(12)	P(23)–P(30)	217.6(5)	P(31)–P(21)–Ge(1)	103.6(4)	P(30)–P(21)–Sn(1)	104.0(2)

P(23)–P(30)	219.7(10)	P(23)–P(33)	219.1(5)				
P(23)–Ge(3)	234.8(8)	P(23)–Sn(3)	254.3(3)	P(30)–P(22)–P(32)	102.1(4)	P(30)–P(22)–P(32)	101.5(2)
				P(30)–P(22)–Ge(2)	104.1(4)	P(30)–P(22)–Sn(2)	101.7(2)
P(30)–P(21)	216.9(10)	P(30)–P(23)	217.6(5)	P(32)–P(22)–Ge(2)	101.2(3)	P(32)–P(22)–Sn(2)	99.9(2)
P(30)–P(22)	218.6(11)	P(30)–P(22)	217.9(4)				
P(30)–P(23)	219.7(10)	P(30)–P(21)	218.4(5)	P(33)–P(23)–P(30)	102.1(4)	P(30)–P(23)–P(33)	102.2(2)
				P(33)–P(23)–Ge(3)	100.1(4)	P(30)–P(23)–Sn(3)	107.7(2)
P(31)–P(21)	220.0(13)	P(31)–P(21)	217.8(5)	P(30)–P(23)–Ge(3)	109.2(4)	P(33)–P(23)–Sn(3)	98.9(1)
P(31)–P(33)	223.7(12)	P(31)–P(33)	222.3(5)				
P(31)–P(32)	224.4(11)	P(31)–P(32)	222.8(5)	P(21)–P(30)–P(22)	97.4(4)	P(23)–P(30)–P(22)	100.4(2)
				P(21)–P(30)–P(23)	97.7(4)	P(23)–P(30)–P(21)	97.7(2)
P(32)–P(22)	219.5(12)	P(32)–P(22)	219.8(5)	P(22)–P(30)–P(23)	100.1(4)	P(22)–P(30)–P(21)	98.0(2)
P(32)–P(33)	222.2(11)	P(32)–P(33)	222.7(5)				
P(32)–P(31)	224.4(11)	P(32)–P(31)	222.8(5)	P(21)–P(31)–P(33)	106.6(4)	P(21)–P(31)–P(33)	106.9(2)
				P(21)–P(31)–P(32)	100.2(4)	P(21)–P(31)–P(32)	101.0(2)
P(33)–P(23)	219.0(12)	P(33)–P(23)	219.1(5)	P(33)–P(31)–P(32)	59.5(3)	P(33)–P(31)–P(32)	60.0(2)
P(33)–P(32)	222.2(11)	P(33)–P(31)	222.3(5)				
P(33)–P(31)	223.7(12)	P(33)–P(32)	222.7(5)	P(22)–P(32)–P(33)	102.0(4)	P(22)–P(32)–P(33)	102.4(2)
				P(22)–P(32)–P(31)	106.5(5)	P(22)–P(32)–P(31)	106.7(2)
C(11)–Ge(1)	196.7(33)	C(11)–Sn(1)	213.5(18)	P(33)–P(32)–P(31)	60.1(3)	P(33)–P(32)–P(31)	59.9(2)
C(12)–Ge(1)	192.2(37)	C(12)–Sn(1)	210.9(19)				
C(13)–Ge(1)	192.6(39)	C(13)–Sn(1)	214.3(22)	P(23)–P(33)–P(32)	107.5(5)	P(23)–P(33)–P(31)	100.7(2)
				P(23)–P(33)–P(31)	100.2(5)	P(23)–P(33)–P(32)	106.7(2)
C(21)–Ge(2)	191.0(35)	C(21)–Sn(2)	211.4(17)	P(32)–P(33)–P(31)	60.4(4)	P(31)–P(33)–P(32)	60.1(2)
C(22)–Ge(2)	200.3(31)	C(22)–Sn(2)	215.0(16)				
C(23)–Ge(2)	198.4(27)	C(23)–Sn(2)	213.7(16)				
C(31)–Ge(3)	193.0(31)	C(31)–Sn(3)	212.2(14)				
C(32)–Ge(3)	191.1(43)	C(32)–Sn(3)	214.7(20)				
C(33)–Ge(3)	195.7(39)	C(33)–Sn(3)	210.5(18)				

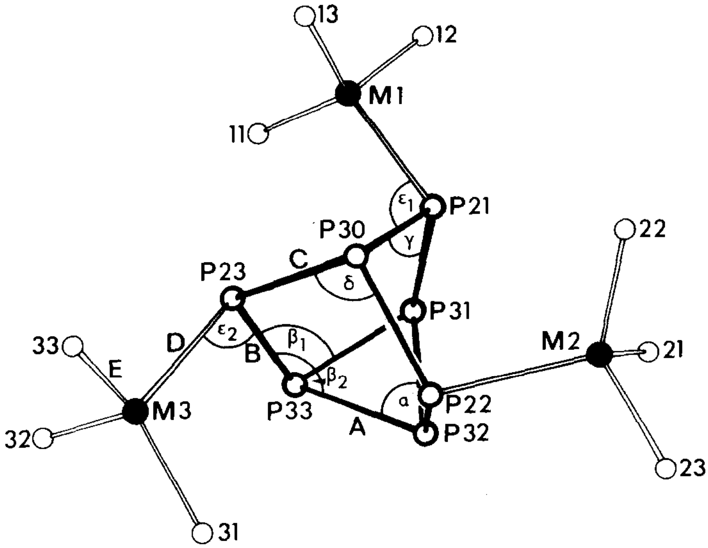

Fig. 4. $P_7(MMe_3)_3$; M = Si (**1**); Ge (**2**); Sn (**3**); Pb (**4**). The atom and mean distances and angles labelling is given (cf. Table 3). The numbers refer to the carbon atom labelling.

recognized for type B. The mean bond lengths in the P_7 cage (219.5; 220.4; 219.8; and 218.9 pm) decrease from Ge → Pb, which corresponds to the decreasing height *h* (Table 4). This sequence is not continued by the silicon compound; the Allred–Rochow electronegativities are in the order Ge > Si > Sn > Pb and this may account for the apparent anomaly. Variation of the bond lengths and the height *h* does not change the topology of the cage, which is not influenced by the substitu-

TABLE 4

COMPARISON OF MEAN DISTANCES (pm) AND ANGLES (°) IN COMPOUNDS $P_7(MMe_3)_3$, M = Si (**1**), Ge (**2**), Sn (**3**), Pb (**4**). THE TYPES REFER TO THE LABELLING IN Fig. 4. α IS BY DEFINITION 60°. *h* REFERS TO THE ELEVATION OF P 30 WITH RESPECT TO THE THREE-MEMBERED P BASE

Type	**1**	**2**	**3**	**4**
A	221.4(4)	223.4(11)	222.6(5)	221.2(10)
B	219.2(4)	219.5(11)	218.9(5)	217.6(11)
C	218.0(4)	218.4(11)	218.0(5)	217.8(9)
D	228.8(4)	235.5(8)	253.9(3)	261.7(7)
E	188(1)	194(4)	213(3)	219(3)
β_1	101.0(2)	100.8(4)	101.4(2)	101.7(4)
β_2	107.1(2)	106.9(5)	106.8(2)	107.0(4)
γ	102.2(2)	102.4(4)	102.0(2)	101.6(4)
δ	98.3(2)	98.4(4)	98.7(2)	98.8(4)
ϵ_1	107.6(4)	106.3(4)	104.5(2)	103.8(4)
ϵ_2	102.2(4)	101.6(4)	100.4(2)	100.2(4)
h (pm)	315.4	315.8	314.3	312.2

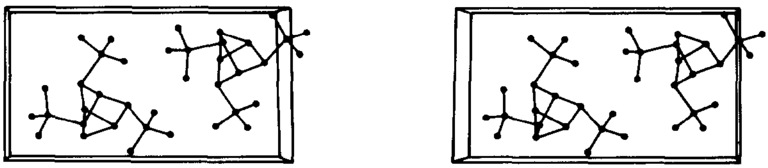

Fig. 5. Stereoplot of the unit cell of $P_7(MMe_3)_3$. Origin is in the left upper corner. (a down, b right, c perpendicular to the paper).

tion. This is clearly revealed by the practically unchanged internal angles α, β, γ and δ (Table 4).

The twisting of the P_7 cage, which can be measured by the difference between β_1 and β_2, is not changed at all. One would expect, that the increasing P–M distances as M is varied from Si to Pb lower the steric hindrance and therefore allow the P_7 cage to relax, and we must assume that the twisting of the cage is at a maximum in all four compounds. The distances of type D (P–M) are somewhat larger than the sum of covalent radii (P: 111 pm; Si 117 pm; Ge: 122 pm; Sn: 141 pm; Pb: 147 pm). Even if a small correction for the change of electronegativity [17] is introduced, the discrepancies between observed and calculated bond lengths do not disappear. This can be attributed to a general steric hindrance by the bulky MMe_3 substituents. The distances E (Me–C_{ij}) are within the known ranges and show no abnormal behavior. The exocyclic angles ϵ_1 and ϵ_2 reflect the influence of the ligand MMe_3 in a clear manner. Both angles are lowered as M becomes larger. The lowering of the angles ϵ together with the increase of the P–M distance result in nearly constant intramolecular Van der Waals' distances 360 pm between the CH_3 groups and the neighboring bridging P atoms. For an undistorted ψ-tetrahedral P atom one would expect bond angles in the range 101 to 102°. The limiting condition of the minimal Van der Waals' distance $P \cdots CH_3$, however, means that only increase of the P–M bond length could enable approximation to the ideal ψ tetrahedral configuration at the bridging P atom. This is almost reached in the lead compound. Fig. 5 shows the packing of the enantiomeric molecules in the unit cell.

6. Experimental details

Because of the sensitivity of the reagents and products to hydrolysis and oxidation all reactions were carried out in close equipment under an inert gas.

6.1. Reactions of $Li_3P_7 \cdot 3DME$ with monohalides of various elements

6.1.1. Preparation of $P_7(SiPh_3)_3$. A solution of 4.9 g (16.6 mmol) Ph_3SiCl in 20 ml toluene was added dropwise at 20°C to a suspension of 2.8 g (5.5 mmol) $Li_3P_7 \cdot 3DME$ (preparation see [8]) in 50 ml toluene, and the mixture was stirred for 1 h. After separation of insoluble products white crystalline $P_7(SiPh_3)_3$ was precipitated at −30°C, filtered off, and dried in vacuo; yield (isolated): 0.8 g (14.5%).

6.1.2. Preparation of $P_7(SnMe_3)_3$. A solution of 2.3 g (9.43 mmol) Me_3SnBr in 10 ml toluene was added dropwise at 20°C to a suspension of 1.4 g (2.76 mmol) $Li_3P_7 \cdot 3DME$ in 30 ml toluene, and the mixture was stirred for some hours, during which some products separated out. Subsequently $P_7(SnMe_3)_3$ was precipitated at

$-30°C$ and the small white crystals (analytically pure) were filtered off and dried in vacuo; yield (isolated) 0.6 g (30.7%).

6.1.3. Reactions of $Li_3P_7 \cdot 3DME$ with H_3SiX (X = Br, I). A solution of 2.88 g (18.2 mmol) H_3SiI in 15 ml toluene was added dropwise at $-80°C$ to a suspension of 2.65 g (5.2 mmol) $Li_3P_7 \cdot 3DME$ in 50 ml toluene. The mixture was slowly warmed to room temperature and insoluble products are filtered off. The LiI still in solution was crystallized as LiI · 1DME and separated. The remaining solution contained $P_7(SiH_3)_3$ (^{31}P NMR spectrum). Toluene was removed in vacuo; the residue was only slightly soluble in toluene and immediately decomposed by THF. Neither the same reaction in THF at $-78°C$ nor the reaction of $Li_3P_7 \cdot 3DME$ with H_3SiBr yielded $P_7(SiH_3)_3$.

6.1.4. Reactions of $Li_3P_7 \cdot 3DME$ with alkyl and aryl halides. The same procedure was used in all cases. The pure halide was added dropwise to a solution (or suspension) of $Li_3P_7 \cdot 3DME$ in a solvent (for exact conditions see Table 5). After 2h the insoluble product was removed and investigated by mass spectrometry, and the ^{31}P NMR-spectrum of the filtrate was recorded. Soluble P-containing compounds were detected only from the reactions involving EtBr and i-PrBr. Yellow P_7(i-Pr)$_3$ was precipitated at $-30°C$, filtered off, and dried in vacuo; yield: 10%.

6.1.5. $P_7[CpFe(CO)_2]_3$. A mixture of 0.84 g (1.65 mmol) $Li_3P_7 \cdot 3DME$ and 1.28 g (4.98 mmol) $CpFe(CO)_2Br$, and 70 ml toluene was stirred at 20°C for 16 h. The insoluble material (only a small amount) was separated. A ^{31}P NMR spectrum of the solution confirmed the presence of $P_7[CpFe(CO)_2]_3$. After removal of toluene in vacuo the residue was investigated by mass spectrometry; only the peaks from $[CpFe(CO)_2]_2$ (M^+ and corresponding fragments) were observed. Reactions in THF ($-50°C$) or DME ($-78°C$) gave no detectable $P_7[CpFe(CO)_2]_3$.

6.1.6. Reactions of $Li_3P_7 \cdot 3DME$ with Me_2PCl. Reaction in toluene: A solution of 0.85 ml (9.07 mmol) Me_2PCl in 25 ml toluene was added dropwise at $-78°C$ to a suspension of 1.49 g (2.93 mmol) $Li_3P_7 \cdot 3DME$ in 50 ml toluene. The mixture was warmed to room temperature and the insoluble products were removed. Neither the ^{31}P NMR spectrum of the filtrate nor the mass spectrum of the residue gave any

TABLE 5

REACTIONS OF $Li_3P_7 \cdot 3DME$ WITH ALKYL AND ARYL HALIDES; REACTION CONDITIONS

Li_3P_7 (mmol)	RCl		Solvents	T (°C)	Products [a]
	Formula	Amount (mmol)			
5.91	C_2H_5Br	17.77	DME	−78	A
7.09	i-C_3H_7Br	21.13	DME	−78	(i-$C_3H_7)_3P_7$
2.56	Me_3CBr	7.66	DME	RT	B
0.98	Me_3CBr	2.99	Toluene	RT	B
2.36	Me_3CBr	7.08	Toluene	RT [b]	B
2.95	Me_3CCl	11.68	DME	RT	B
4.1	C_6H_5Br	12.4	THF	−78, RT	no reaction
2.4	C_6F_5Br	7.22	Toluene	RT	B

[a] A: Mixture of higher phosphanes with 9 and 11 P atoms per molecule. B: No soluble P containing compounds; no P_7 system in the residue. [b] Reaction with exclusion of light.

evidence for the formation of $P_7(PMe_2)_3$. Only P_2Me_4, Me_2PCl and a little Me_2PH were detected.

Reaction in toluene/THF: A solution of $Li_3P_7 \cdot 3DME$ in THF was added dropwise at $-78°C$ to a solution of Me_2PCl in toluene (molar ratio 1/3). The subsequent procedure and the results were the same as for the reaction in pure toluene.

6.2. Reactions of Na_3P_7 with Me_3MCl (M = Ge, Sn)

6.2.1. $P_7(GeMe_3)_3$ (2). Approximately 2.85 g (9.97 mmol) Na_3P_7 [9] were suspended in 250 ml toluene (purified by distillation with Na/K-benzophenone) and cooled to $-33°C$ (cryostat) and 3.7 ml (29.92 mmol) of Me_3GeCl was added in one portion. After stirring two days at $-33°C$ the solution was filtered at room temperature. After some days in the refrigerator, the clear yellow filtrate gave light-yellow needle-shaped crystals of $P_7(GeMe_3)_3$. Polycrystalline material was obtained by evaporation of the solvent (total yield, non optimized ~ 40%).

6.2.2. $P_7(SnMe_3)_3$. A suspension of 0.95 g (3.3 mmol) Na_3P_7 in 500 ml toluene in a 1 liter flask was cooled to $-50°C$ and 2.0 g (10 mmol) Me_3SnCl were added. The mixture was stirred vigorously for 10 h, then filtered at room temperature. Colorless crystals separated from the light yellow filtrate (yield 80%). The crystals were identified by X-ray powder and single crystal methods as $P_7(SnMe_3)_3$.

6.3. Reactions including cleavage of Si–P bonds in $P_7(SiMe_3)_3$

6.3.1. $P_7(SiMe_3)_{3-n}(SnMe_3)_n$; n = 1, 2, 3. Cleavage with Me_3SnBr: At room temperature a solution of 2.08 g (8.54 mmol) Me_3SnBr in 20 ml toluene was added dropwise to a solution of 1.86 g (4.27 mmol) $P_7(SiMe_3)_3$ in 60 ml toluene. The reaction mixture was stirred overnight and volatile substances were evaporated. The residue contained $P_7(SiMe_3)_3$, $P_7(SiMe_3)_2(SnMe_3)$, $P_7(SiMe_3)(SnMe_3)_2$ and $P_7(SnMe_3)_3$ as was shown by mass spectrometry. From a solution of this residue in 80 ml toluene slightly yellow (almost white) crystals (0.9 g) were obtained at $-30°C$. Crystals and mother solution consisted of the same mixture of compounds as described above (confirmed by MS and ^{31}P NMR).

Cleavage with $LiP(SiMe_3)_2$ and subsequent reaction with Me_3SnBr: At $-78°C$ a solution of 1.01 g (5.5 mmol) $LiP(SiMe_3)_2$ in 20 ml DME was dropped to a solution of 2.4 g (5.5 mmol) $P_7(SiMe_3)_3$ in 70 ml DME. The reaction mixture was allowed to warm up slowly to room temperature, then cooled again to $-78°C$; 0.85 ml (5.5 mmol) Me_3SnBr were added dropwise. Heating the mixture to room temperature was followed by evaporation of all volatile substances. The subsequent procedure as well as the products were the same as described above (cleavage with Me_3SnBr).

6.3.2. Reactions of $P_7(SiMe_3)_3$ with HI. The molar ratio of $P_7(SiMe_3)_3$ and HI was 1/1, temperatures were -78 and $0°C$.

Reaction at 0°C: A solution of HI in toluene was added dropwise to a solution of $P_7(SiMe_3)_3$ in toluene (both solutions: 0°C). The reaction mixture was warmed to room temperature and volatile products were removed in vacuo. The residue was investigated by mass spectrometry. A subsequent vacuum sublimation (120°C, 10^{-3} Torr) yielded a yellow solid, but this solid as well as the residue consisted of the same mixture of compounds as before the sublimation (shown by mass spectrometry). The following compounds were detected: $P_7(SiMe_3)_3$, $HP_7(SiMe_3)_2$, $H_2P_7SiMe_3$ and (little) H_3P_7. Only $P_7(SiMe_3)_3$ was soluble in organic solvents.

Reaction at $-78°C$: A solution of $P_7(SiMe_3)_3$ in toluene was frozen with liquid nitrogen. After condensation of the necessary amount of HI the reaction temperature was fixed with a dry ice/methanol bath. The subsequent procedure and the products were the same as above.

6.3.3. $P_7(SnMe_3)_3$. $P_7(SiMe_3)_3$ was prepared as described by Fritz and Hölderich [1]. However it is not necessary to evaporate all the DME, $P(SiMe_3)_3$ and $P_2(SiMe_3)_4$. $P_7(SiMe_3)_3$ crystallizes well from the partly (1/3) evaporated filtrate obtained from the reaction mixture.

A mixture of 3.8 g (8.7 mmol) $P_7(SiMe_3)_3$ (**1**) and 5.7 g (28.7 mmol) Me_3SnCl in 100 ml DME was stirred at $-50°C$ for about 30 h. $P_7(SnMe_3)_3$ (**3**) separated as a white solid soon after the reaction began. Me_3SiCl was distilled into a trap ($-78°C$) under reduced pressure at 3 h intervals. The precipitate was filtered off, washed with DME and recrystallized from toluene, to give colorless, rod shaped crystals (yield 95%, decomposition at 182°C in a sealed tube (DTA)).

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