Supersilyl Compounds of Phosphorus, IV[1]
Silicon Compounds, 118[2]

The Triphosphide ($(t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{P}_3\mathrm{Na}$): Formation, X-ray and Ab initio Structure Analyses, Protonation and Oxidation to Triphosphane $(t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{P}_3\mathrm{H}$ and Hexaphosphanes $(t\mathrm{Bu}_3\mathrm{Si})_4\mathrm{P}_6$☆

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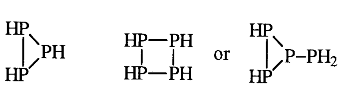
The violet THF adduct $(t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{P}_3\mathrm{Na(THF)}_4$ (**1a**) of the triphosphide $(t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{P}_3\mathrm{Na}$ (**1**) is prepared, (i) by protolysis of the tetraphosphide $(t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{P}_4\mathrm{Na}_2$ (**2**) with an equimolar amount of $\mathrm{CF_3CO_2H}$ in THF (transformation of **2** into **1**), (ii) by the reaction of $t\mathrm{Bu}_3\mathrm{SiNa}$ and the oligophosphane $(t\mathrm{Bu}_3\mathrm{SiP}_3)_n$ in THF (building-down of P_n), and (iii) by the action of $t\mathrm{Bu}_3\mathrm{SiNa}$ on PCl_3 in THF (building-up of P_n). According to X-ray structural analysis, the SiPPPSi skeleton of the anionic part $[t\mathrm{Bu}_3\mathrm{SiPPPSi}t\mathrm{Bu}_3]^-$ of **1a** is W-shaped with two P–P $1^1/_2$ bonds; in addition, **1a** contains a planar deltoid $\mathrm{P_3Na}$ backbone with the 4 THF molecules coordinated to Na. The protolysis of **1a** leads to cyclotriphosphane $(t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{P}_3\mathrm{H}$ (**11**), and the oxidation of **1a** leads to 1,1′-bicyclotriphosphane $(t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{P}_3\text{–}\mathrm{P}_3(\mathrm{Si}t\mathrm{Bu}_3)_2$ (**12**) as the main product and bicyclo[3.1.0]hexaphosphane $(t\mathrm{Bu}_3\mathrm{Si})_4\mathrm{P}_6$ (**13**) as an isomer of **12**. The structures of **11**, **12**, and **13** as well as the structure of **1a** have been unambiguously determined by ^{31}P-NMR studies. Ab initio structure and energy calculations show that the acyclic $\mathrm{P_3H_2}^-$ with allylic conjugation and P–P $1^1/_2$ bonds is thermodynamically more stable than the cyclic isomer whereas, in contrast, the neutral compound $\mathrm{P_3H_3}$ prefers the cyclic form. The exceptional downfield shift of the NMR signal of the central phosphorus in **1a** is in agreement with DFT NMR calculations for a model compound $[\mathrm{H_3SiPPPSiH_3}]\mathrm{Na}$ with P–P $1^1/_2$ bonds.

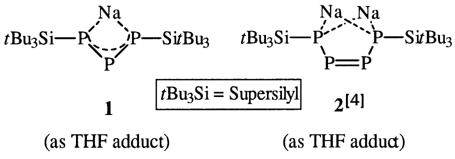
While nitrogen hydrides of the formula $\mathrm{N}_n\mathrm{H}_n$ and their derivatives have an acyclic structure with a double bond, phosphorus hydrides $\mathrm{P}_n\mathrm{H}_n$ and their derivatives show, in accordance with the double-bond rule, cyclic structures without a double bond[3]. This is demonstrated by a comparison of the structures of $\mathrm{N_3H_3}$ and $\mathrm{N_4H_4}$ with those of $\mathrm{P_3H_3}$ and $\mathrm{P_4H_4}$, (see Scheme 1).

Scheme 1



In contrast the tendency of phosphanes $\mathrm{P}_n\mathrm{H}_n$ to form unsaturated acyclic structures increases after deprotonation, because the negative charges of the phosphides obtained may be better stabilized by a π system containing a phosphorus chain. This is suggested by our studies in connection with the triphosphide $(t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{P}_3\mathrm{Na}$ (see Scheme 2) and the tetraphosphide $(t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{P}_4\mathrm{Na}_2$ (cf. refs.[4][5]) which have the structures **1** (disupersilyltriphosphenide) and **2** (disupersilyltetraphosphenediide), respectively.

Scheme 2



The unsaturated cluster anion $\mathrm{R_2P_3}^-$ with substituents R which are sterically constrained (such as supersilyl $t\mathrm{Bu}_3\mathrm{Si}$[5]) is readily formed. Thus, **2** converts into **1** under suitable conditions (see below). The compounds $\mathrm{Mes^*{}_2P_2ELi}$ (Mes* = Supermesityl, E = P, As) and $(t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{E}_3\mathrm{Na}$ (E = N, As) were both synthesized by Jutzi et al.[6] and this

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[+] Simulation of NMR spectra.
[++] X-ray structure analysis.
[+++] Ab initio structure and NMR calculations.

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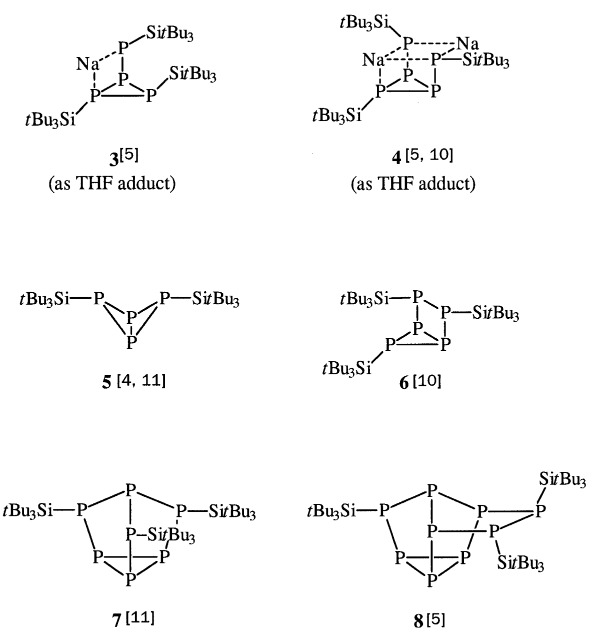
group[7][8]. Finally the anions $[(Me_3Si)_2CPPPC(SiMe_3)_2]^-$[9a] and $[RPPPR]^-$ (RR = $-CH_2CH_2-$ and $-CHPhCHPh-$)[9b] containing a P_3 skeleton with a π system were prepared as alkali metal salts.

In this publication we deal with the syntheses and the structure of **1**, as well as with the protolysis and oxidation of the compound, which proceed by the formation of the triphosphane $(tBu_3Si)_2P_3H$ and two isomers of hexaphosphane $(tBu_3Si)_4P_6$, respectively. In addition, the question concerning the relative stabilities of cyclic and acyclic P_3H_3 and $P_3H_2^-$ is answered by ab initio calculations.

Formation of $(tBu_3Si)_2P_3Na$ (1)

As has already been mentioned, **1** is prepared by transformation of **2**. In addition, **1** may be formed from supersilylphosphanes $(tBu_3Si)_mP_n$ or supersilyldihalogenephosphanes tBu_3SiPX_2 by building-down or building-up the phosphorus framework. In the latter cases, supersilyl sodium tBu_3SiNa in tetrahydrofuran (THF) serves as the reaction partner. Details of the syntheses of **1** are discussed below. In this connection, not only **2**, but also the phosphides **3** and **4** as well as the phosphanes **5**−**8** play a role (see Scheme 3).

Scheme 3



3[5] (as THF adduct)

4[5, 10] (as THF adduct)

5[4, 11]

6[10]

7[11]

8[5]

Transformation of 2

To convert the tetraphosphide **2**, which is easily prepared from P_4 and tBu_3SiNa in THF[4], into the triphosphide **1**, the former is protonated by equimolar amounts of a strong acid (CF_3CO_2H or CF_3SO_3H) in THF at −78 °C. Then, by warming up the reaction mixture to room temp., **1** and tBu_3SiPH_2 are obtained according to Eq. 1.

$$3\ \mathbf{2} \xrightarrow[-4Na^+]{+4H^+} 2\ \mathbf{1} + 2\,tBu_3SiPH_2 \qquad (1)$$

In fact, **1** is produced simultaneously with the pentaphosphide **4** as well as oligophosphanes $(tBu_3SiP_3)_n$ (see below); in addition, the starting material **2** remains unreacted (**1**, **2**, and **4** exist in the molar ratio 2:1:1, increasing amounts of acid lead to a decrease in the amount of **2** and also of **1**[5][10]). As **1** cannot easily be separated from the other products, reaction (1) is less suitable for its preparation.

In the weak acid acetonitrile, **2** quickly transforms according to Eq. 1 ($NaCH_2CN$ may be another product), but the solutions obtained are unstable and after some weeks contain tBu_3SiPH_2 as the one and only soluble phosphorus compound.

Building-Down of Phosphorus Clusters

The reaction of oligophosphanes $(tBu_3SiP_3)_n$ (among others **8**[5]) with *n*-fold molar amounts of tBu_3SiNa is particularly suitable for the synthesis of **1**. In this way, the triphosphide **1** is obtained as the only product according to Eq. 2. The oligophosphanes, on the other hand, are prepared from **2** and a twofold molar amount of a strong acid (CF_3SO_3H) in pentane: **2** + $2H^+ \rightarrow 1/n\,(tBu_3SiP_3)_n + tBu_3SiPH_2$.

$$^1/_n\,(tBu_3SiP_3)_n \text{ (among others } \mathbf{8}) + tBu_3SiNa \rightarrow \mathbf{1} \qquad (2)$$

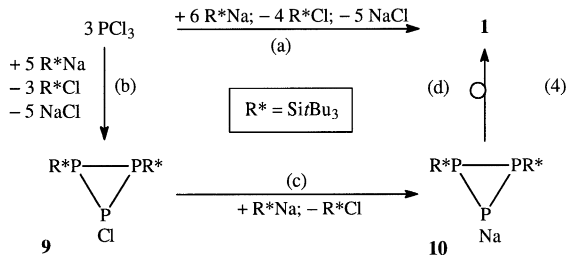
Reaction (2) demonstrates, as does reaction (1), the high tendency for the formation of **1**. The same holds for the reaction shown in (3): a twofold molar amount of tBu_3SiNa degrades the heptaphosphane **7** (which is easily prepared from P_4 and $tBu_3Si{-}SitBu_3$ in THF or toluene at 100 °C together with the tetraphosphane **5**[11]) into the triphosphide **1** and the tetraphosphide **3**. The latter compound is also quantitatively obtained by reaction of the tetraphosphane **5** with equimolar amounts of tBu_3SiNa in THF[5].

$$\mathbf{7} + 2\,tBu_3SiNa \rightarrow \mathbf{1} + \mathbf{3} \qquad (3)$$

In addition, it is worth noting that the pentaphosphane **6** is transformed by tBu_3SiNa into the triphosphide **1** together with other phosphorus containing substances[10].

Building-Up of Phosphorus Clusters

To synthesize **1** by building-up the phosphorus chain, PCl_3 in pentane is slowly added dropwise to a solution of a threefold molar amount of tBu_3SiNa in THF, cooled to −78 °C. While warming up the solution to room temp., the starting materials react according to (4a). In fact, **1** is produced simultaneously with the tetraphosphide **3**, the pentaphosphide **4** as well as some mono- and diphosphides (**1**, **3**, **4**, and the other phosphides are formed in the molar ratio 10:5:3:3).

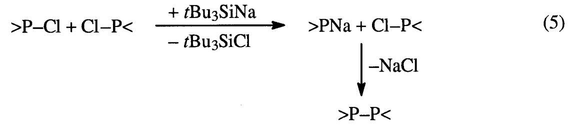


9

10

An insight into the formation pathway of **1** is given by the reaction of PCl_3 with an equimolar amount of tBu$_3$SiNa, the products of which are some chlorine-free and some chlorine-containing supersilylphosphanes[5]; this will be thoroughly discussed elsewhere[12]. Obviously, the chlorine containing compound **9** plays an important role in the building-up of **1**, as it may react with tBu$_3$SiNa with exchange of Cl for Na (Eq. 4c). An isomerization of the phosphide **10** obtained in this way leads to **1** (Eq. 4d).

The formation of **9**, summarized by Eq. 4b, may be interpreted as follows: As a first reaction product, tBu$_3$SiPCl$_2$ is formed from PCl_3 and tBu$_3$SiNa by exchange of Cl^- for tBu$_3$Si$^-$. For steric reasons supersilyldichlorophosphane does not undergo any further supersilanidation[5]. Instead, with the cooperation of PCl_3 and tBu$_3$SiNa, it enters a building-up of phosphorus clusters which proceeds according to the reactions formulated in Eq. 5[5].



$$\begin{tikzcd} {>}P{-}Cl + Cl{-}P{<} \arrow[r, "+\,t\mathrm{Bu_3SiNa}", "-\,t\mathrm{Bu_3SiCl}"'] & {>}PNa + Cl{-}P{<} \arrow[d, "-\mathrm{NaCl}"] \\ & {>}P{-}P{<} \end{tikzcd} \qquad (5)$$

Hereafter, tBu$_3$SiPCl$_2$, PCl_3, and tBu$_3$SiNa first of all may react according to tBu$_3$SiPCl$_2$ + tBu$_3$SiNa $\rightarrow$ tBu$_3$Si-PClNa + tBu$_3$SiCl and 2 tBu$_3$SiPClNa + PCl_3 $\rightarrow$ tBu$_3$Si-PCl−PCl−PClSitBu$_3$ + 2 NaCl under formation of trichlorodisupersilyltriphosphane, which then converts according to Eq. 5 into **9**.

Characterization and Structure of (tBu$_3$Si)$_2$P$_3$Na(THF)$_4$ (1a)

If a solution of 2.8 mmol of **1**, prepared by reaction of (tBu$_3$SiP$_3$)$_n$ with tBu$_3$SiNa in 6 ml of THF (cf. Eq. 2), is concentrated to 2 ml and mixed with 2 ml of pentane, then over several days, deep violet crystals of the THF adduct (tBu$_3$Si)$_2$P$_3$Na(THF)$_4$ (**1a**) of the triphosphide **1** may be obtained. These are extremely sensitive to air and moisture but comparatively stable thermally. However, the tendency of **1** to crystallize from THF is quite low and exchanging THF for another solvent is not advisable, since **1** decomposes when the THF is removed.

A suitable crystal of the phosphide **1a** selected from many unsuitable crystals was investigated by X-ray structure analysis. The view of the molecule in the crystal (orthorhombic), all atomic positions of which seem to be splitted, is shown in Figure 1. As can be clearly seen, the three P atoms and the Na atom in **1a** occupy the edges of a planar deltoid (P−P−P = 104.2, P−P−Na = 95.2, P−Na−P = 64.3°; sum of the angles of the mean values of the split positions is 358.9°). For each of the outer P atoms a planar surrounding may be outlined, consisting of one P, one Si, and one Na atom, the central P atom has two P atoms as neighbours forming an obtuse angle and the Na atom is coordinated by two P and four O atoms forming a distorted octahedron with a sharp P−Na−P angle. The O atoms are each coordinated to one Na and two C atoms. The P−P distances have a mean value of 2.10 Å, in between those found for P−P single bonds (around 2.20 Å) and those for P−P double bonds (around 2.00 Å)[3]. As can be seen from Table 1, the two P−P distances and the two P−P−Na angles are indeed slightly different [P1−P2 = 2.12, P1−P3 = 2.07 Å; P1−P2−Na = 96.6, P1−P3−Na = 93.7° (mean values); an analogous situation is also observed for the two N−N bonds and the N−N−Na angle of (tBu$_3$Si)$_2$-N$_3$Na(THF)$_2$ in the crystal[13]]. The distance of the sodium atom to the outer phosphorus atom showing the longer P−P bond is shorter than the distance to the outer phosphorus atom showing the shorter −P bond [P2−Na = 3.05, P3−Na = 3.18 Å (mean values)].

As shown by the X-ray structure analysis, the anionic W-shaped part of **1a** with two P−P $1^1/_2$ bonds represents a triphosphaallylic anion, the bonding situation of which can be described by a resonance formula with two limiting structures, as is shown in Eq. 6 (the triphosphenide Mes$_2$*-P$_3$Li was not investigated by means of X-ray diffraction; however according to ^{31}P-NMR it also has an acyclic structure[6]).

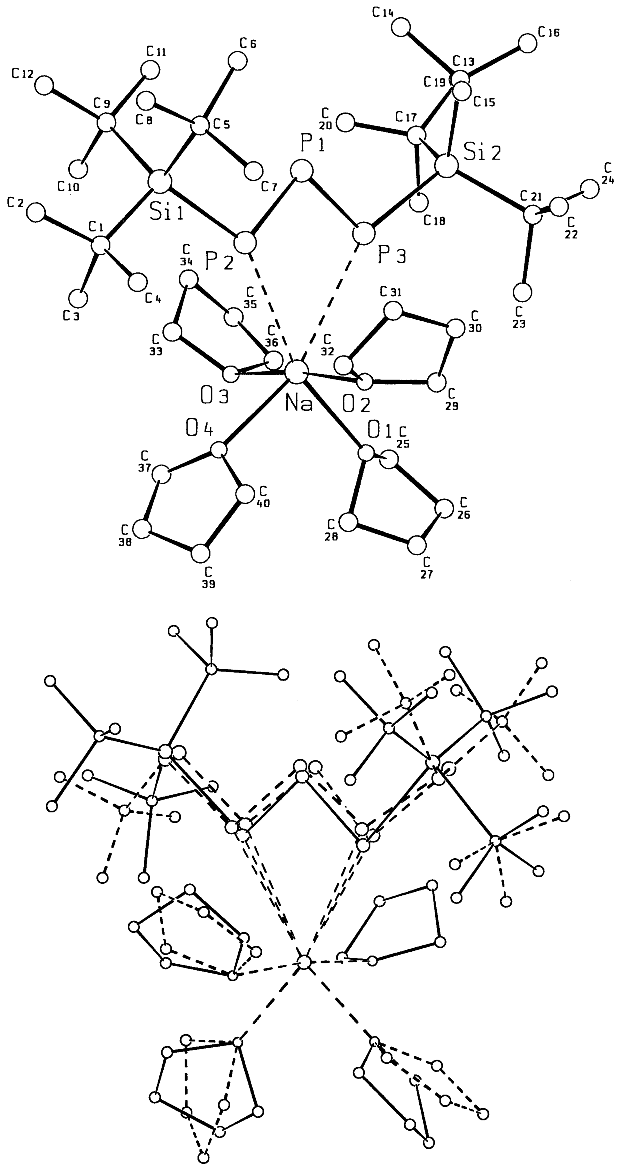
The ^{31}P{^{1}H}-NMR spectrum of the anion in **1a** shows two signals with the splitting pattern of an AX$_2$ spin system in the range typical for the unsaturated twocoordinate phosphorus atom in diphosphenes[14], and in a range which is possible for an unsaturated anionic phosphorus atom[9b] (Figure 2). This is in accord with the *trans-trans* configuration of the anion, as found in the crystal. An isomeric anion with *trans-cis* configuration is, according to the NMR spectra, not present in the C_6D_6 solution, obviously as a consequence of the steric crowding of the supersilyl groups; an isomer with *cis-cis* configuration is not possible for steric reasons and can be definitely ruled out from the signal pattern in the ^{29}Si{^{1}H}-NMR spectrum, which suggests a large $^2J_{PP}$ coupling constant. (In the case of Mes*$_2$P$_3$Li with the less bulky supermesityl substituents, the compound exists as a mixture of the *cis-trans* and the *trans-trans* isomer[6].)

Protolysis and Oxidation of (tBu$_3$Si)$_2$P$_3$Na (1)

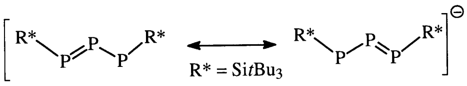
While the protolysis of the tetraphosphide **2** with trifluoroacetic acid in THF, as reported elsewhere[4][5], proceeds nonuniformly with the formation of a number of phosphanes and phosphides containing supersilyl groups, the triphosphide **1** is protolyzed with CF_3CO_2H in THF in a comparatively uniform reaction to form the ring compound **11**. The triphosphene tBu$_3$Si−P=P−PH−SitBu$_3$, which is expected to be the primary product of the protolysis of **1**, is presumably thermodynamically as well as kinetically unstable with respect to the cyclotriphosphane **11**. (In contrast, as product of the protolysis of Mes*$_2$P$_3$Li the unsaturated compound Mes*−P=P−PH−Mes* was obtained[6].)

The oxidation of **2** with tetracyanoethylene in THF proceeds, as reported[4][5], uniformly with the formation of the bicyclotetraphosphane **5**[4], i.e. with retention of the P$_4$ skeleton. On the other hand, the action of TCNE on the triphosphide **1** in THF leads to a doubling of the P$_3$ skeleton: the isomeric hexaphosphanes **12** and **13,** with connected and anellated rings of phosphorus atoms, respectively, are

Figure 1. Molecular structure of $(t\mathrm{Bu_3Si})_2\mathrm{P_3Na(THF)_4}$ (**1a**) in the crystal; top: atom numbering used; bottom: splitting of positions of atoms found (SCHAKAL plot; atoms drawn with arbitrarily chosen atom radii; without H atoms)[a]

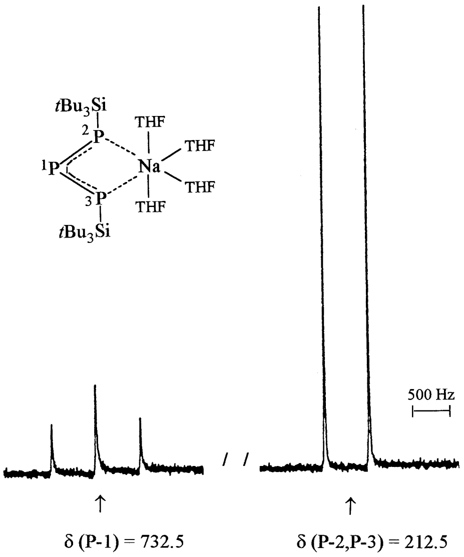


[a] Selected distances [Å] and angles [°] of the molecular structure of **1a** in the crystal with the standard deviations in units of the last significant position in parentheses (all positions of the P and Si atoms seem to be triply split): P(1A)−P(2A) 2.09(2), P(1B)−P(2B) 2.12(2), P(1C)−P(2C) 2.15(2), P(1A)−P(3A) 2.14(3), P(1B)−P(3B) 2.06(2), P(1C)−P(3C) 2.02(2), P(2A)−Si(1A) 2.47(2), P(2B)−Si(1B) 2.26(1), P(2C)−Si(1C) 2.23(2), P(3A)−Si(2A) 2.37(3), P(3B)−Si(2B) 2.26(1), P(3C)−Si(2C) 2.23(2), P(2A)−Na 2.92(2), P(2B)−Na 3.03(1), P(2C)−Na 3.19(2), P(3A)−Na 3.07(2), P(3B)−Na 3.20(1), P(3C)−Na 3.27(2), O(1)−Na 2.349(8), O(2)−Na 2.35(1), O(3)−Na 2.37(1), O(4)−Na 2.359(6); P(2A)−P(1A)−P(3A) 104.6(11), P(2B)−P(1B)−P(3B) 101.3(7), P(2C)−P(1C)−P(3C) 106.6(9), P(1A)−P(2A)−Na 96.2(8), P(1B)−P(2B)−Na 99.7(5), P(1C)−P(2C)−Na 93.9(6), P(1A)−P(3A)−Na 91.0(7), P(1B)−P(3B)−Na 96.1(5), P(1C)−P(3C)−Na 94.1(7), Si(1A)−P(2A)−Na 167.4(7), Si(1B)−P(2B)−Na 150.1(5), Si(1C)−P(2C)−Na 148.9(8), Si(2A)−P(3A)−Na 162.0(12), Si(2B)−P(3B)−Na 155.9(5), Si(2C)−P(3C)−Na 160.3(11), P(2A)−Na−P(3A) 68.0(4), P(2B)−Na−P(3B) 62.5(3), P(2C)−Na−P(3C) 62.4(5), Si(1A)−P(2A)−P(1A) 96.1(10), Si(1B)−P(2B)−P(1B) 104.3(6), Si(1C)−P(2C)−P(1C) 103.0(9), Si(2A)−P(3A)−P(1A) 97.3(11), Si(2B)−P(3B)−P(1B) 105.7(7), Si(2C)−P(3C)−P(1C) 105.5(12).



(6)

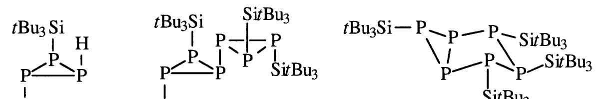
Figure 2. Observed $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR spectrum of **1a** in $\mathrm{C_6D_6}$ at 109.37 MHz (25°C; external 85% $\mathrm{H_3PO_4}$); $^1J_{\mathrm{P1P2}}$ = 552.6 Hz



formed. Presumably, in the first step TCNE oxidizes the triphosphide **1** to form the resonance stabilized triphosphanyl radical $[t\mathrm{Bu_3Si{-}P{=}P{-}P{-}Si}t\mathrm{Bu_3} \rightleftharpoons t\mathrm{Bu_3Si{-}P{-}P{=}P{-}Si}t\mathrm{Bu_3}]^\bullet$, which therefore exists for a longer period of time and changes into the 1,1′-bicyclotriphosphane **12** and the bicyclohexaphosphane **13**.

Unfortunately, the compounds **11**−**13** (see Scheme 4) have not so far been isolated in their pure state; however, their structures, as shown by the formula, can be proved unambiguously from their ^{31}P-NMR spectra (see below). The ^{31}P-NMR data of phosphorus compounds of type **11** ($t\mathrm{Bu_2P_3H}$[15]), **12** ($\mathrm{P_6}t\mathrm{Bu_4}$[16]), and **13** ($\mathrm{P_6}t\mathrm{Bu_4}$[17], $\mathrm{P_6Cp^*_4}$[18]), which were already known, were also quite helpful for this purpose. Other isomers of the cyclophosphanes **11**−**13** could not be spectroscopically detected using NMR. The molecular structures shown for the compounds are obviously the most sterically favorable, and therefore energetically lowest lying.

Scheme 4

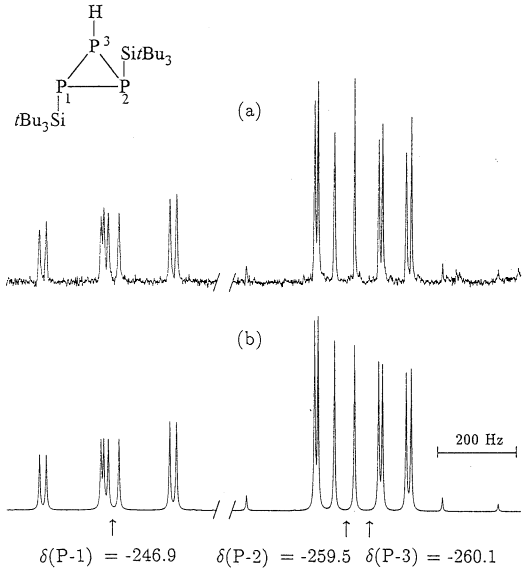


11 **12** **13**

The $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR spectrum of the cyclotriphosphane **11** exhibits the signals of an ABC spin system [δ_A(P-1) = −246.9, δ_B(P-2) = −259.5, δ_C(P-3) = −260.1; $^1J_{\mathrm{P1P2}}$ = −188.0 Hz, $^1J_{\mathrm{P1P3}}$ = −141.3 Hz, $^1J_{\mathrm{P2P3}}$ = −224.2 Hz]. In the proton coupled ^{31}P-NMR spectrum (Figure 3) it extends to an ABCX spin system ($^1J_{\mathrm{P3H}}$ = 137.1 Hz, $^2J_{\mathrm{P1H}}$ = 16.6 Hz, $^2J_{\mathrm{P2H}}$ = 6.9 Hz; regarding the signs of $^1J_{\mathrm{PP}}$ and

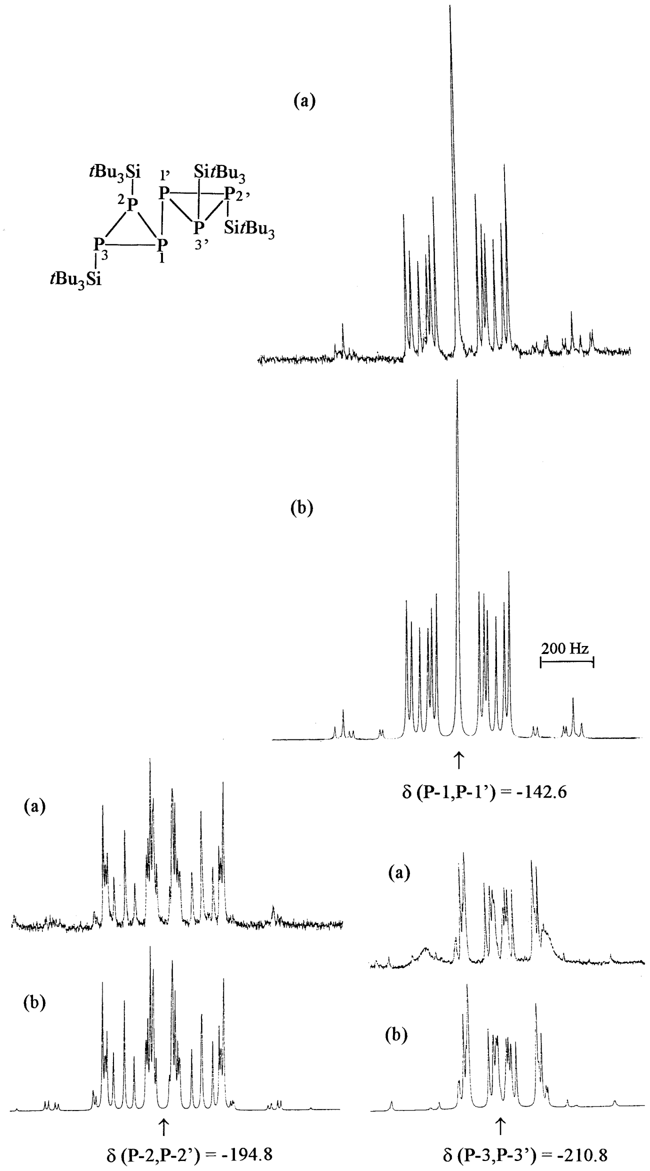
$^1J_{PH}$ see refs.[19][20][21]). Because of the small shift difference between the signals of P-2 and P-3 the spectra deviate strongly from first order. The difference in the PP couplings to P-3 allows an assignment of the signals to P-1 and P-2. The larger coupling constant between P-2 and P-3 indicates a *cis* orientation of the substituents H and Si*t*Bu$_3$ at these phosphorus atoms[22]. For **11** the ^{31}P-NMR chemical shifts, as well as the P−P coupling constants, fall in the range characteristic for cyclotriphosphanes[23][24].

Figure 3. Observed (a) and calculated[20] (b) ^{31}P-NMR spectrum of the cyclotriphosphane **11** at 161.84 MHz in C_6D_6 (0.01 M solution, 25°C, external 85% H_3PO_4); the shift difference between the NMR signals of P-2 and P-3 observed at this frequency is only 102.7 Hz; the relative signs of the coupling constants result from the iterative fitting of the spectrum assuming negative values for $^1J_{PP}$ and positive values for $^1J_{PH}$[19][20][21]: $^1J_{P1P2} = -188.0$, $^1J_{P1P3} = -141.3$, $^1J_{P2P3} = -224.2$, $^1J_{P3H} = 137.1$, $^2J_{P1H} = 16.6$, $^2J_{P2H} = 6.9$ Hz



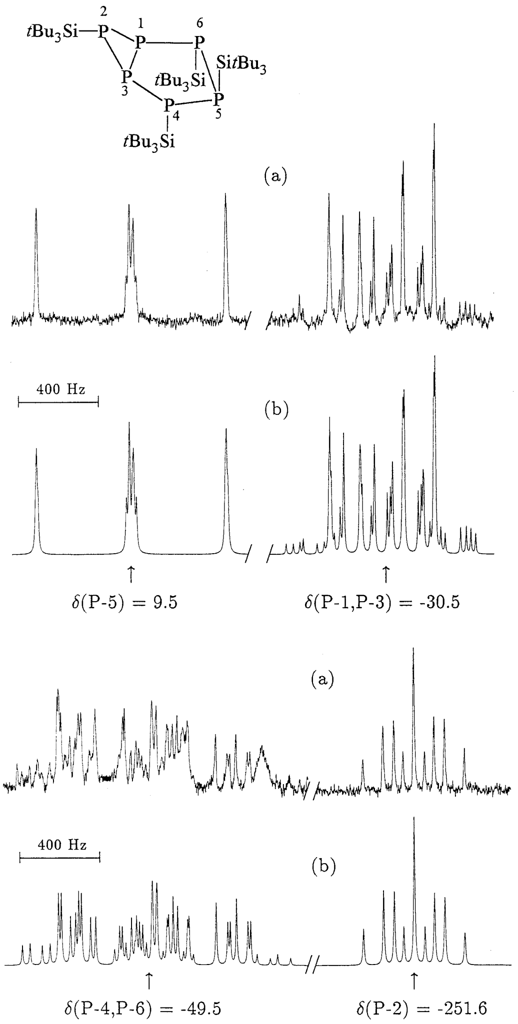
The $^{31}P\{^1H\}$-NMR spectrum of the 1,1′-bicyclotriphosphane **12** shows three multiplets with the classical splitting pattern of an AA′BB′MM′ spectrum. Approximate values for δ_P and J_{PP} can be estimated by simple examination of the experimental spectrum[19]; starting from these values the spectrum can be solved by iterative fitting[20] (Figure 4). The ^{31}P-NMR data of **12** parallel, to a large degree, those of $tBu_2P_3{-}P_3tBu_2$[16]. The chemical shifts of the phosphorus nuclei appear at high field [δ(P-1) = −142.6, δ(P-2) = −194.8, δ(P-3) = −210.8], as is generally found for δ^{31}P in cyclotriphosphanes[23][24]. The direct connection of the two P_3 rings is indicated by the large and negative coupling constant between P-1 and P-1′. The spatial neighbourhood of the lone pairs at P-3 and P-1′ as well as P-1 and P-3′ causes a large and positive coupling constant (57.7 Hz) between these phosphorus atoms, while for $^2J_{P1'P2}$ and $^2J_{P1P2'}$ a much smaller value (1.7 Hz) is observed. This proves the *trans* orientation of the supersilyl substituents at the adjacent phosphorus atoms P-2 and P-3 as well as P-2′ and P-3′. In accord with this is also the sequence of magnitudes of $^1J_{P1P2}$ (−284.7 Hz) and $^1J_{P1P3}$ (−174.9 Hz)[22]. Obviously, like $tBu_2P_3{-}P_3tBu_2$[16], **12** also forms the sterically most favorable all *trans* isomer. In the case of **12**, however, coupling constants $^3J_{P2P2'}$ (7.6 Hz) and $^3J_{P3P3'}$ (0.4 Hz) are found to have the reverse order of magnitude. This difference, as well as the clearly more negative coupling constant $^3J_{P2P3'}$ (−14.1 Hz) observed for **12,** is presumably caused by a larger population of the rotamers with a wider torsion angle P-2,P-1,P-1′,P-2′.

Figure 4. Observed (a) and calculated[20] (b) $^{31}P\{^1H\}$-NMR spectrum of **12** at 109.36 MHz in C_6D_6 (25°C; external 85% H_3PO_4): $^1J_{P1P1'} = -301.1$, $^1J_{P1P2} = {}^1J_{P1'P2'} = -284.7$, $^1J_{P1P3} = {}^1J_{P1'P3'} = -174.9$, $^1J_{P2P3} = {}^1J_{P2'P3'} = -171.8$, $^2J_{P1P2'} = {}^2J_{P1'P2} = 1.7$, $^2J_{P1P3'} = {}^2J_{P1'P3} = 57.7$, $^3J_{P2P2'} = 7.6$, $^3J_{P3P3'} = 0.4$, $^3J_{P2P3'} = {}^3J_{P2'P3} = -14.1$ Hz; the relative signs of the coupling constants result from the iterative fitting of the spectra assuming negative values for $^1J_{PP}$[21]



The structure of the bicyclo[3.1.0]hexaphosphane **13** can be derived from the NMR data after a complete analysis of its $^{31}P\{^1H\}$-NMR spectrum. It shows, as in the case for the analogous hexaphosphanes P_6tBu_4[17] and $P_6Cp^*_4$[18] the four multiplets of an AA′BB′MX spin system (Figure 5). The signal of P-2 (X part) appears at high field (δ =

Figure 5. Observed (a) and calculated[20] (b) $^{31}P\{^{1}H\}$-NMR spectrum of **13** at 109.37 MHz in C_6D_6 (25°C; external 85% H_3PO_4): $^{1}J_{P1P2} = {}^{1}J_{P2P3} = -159.5$, $^{1}J_{P1P3} = -245.9$, $^{1}J_{P1P6} = {}^{1}J_{P3P4} = -397.1$, $^{1}J_{P4P5} = {}^{1}J_{P5P6} = -487.7$, $^{2}J_{P1P4} = {}^{2}J_{P3P6} = 23.2$, $^{2}J_{P1P5} = {}^{2}J_{P3P5} = 11.7$, $^{2}J_{P2P4} = {}^{2}J_{P2P6} = 105.4$, $^{2}J_{P4P6} = 34.7$, $^{3}J_{P2P5} < 1.0$ Hz; the relative signs of the coupling constants result from the iterative fitting of the spectrum assuming negative values for $^{1}J_{PP}$[21]



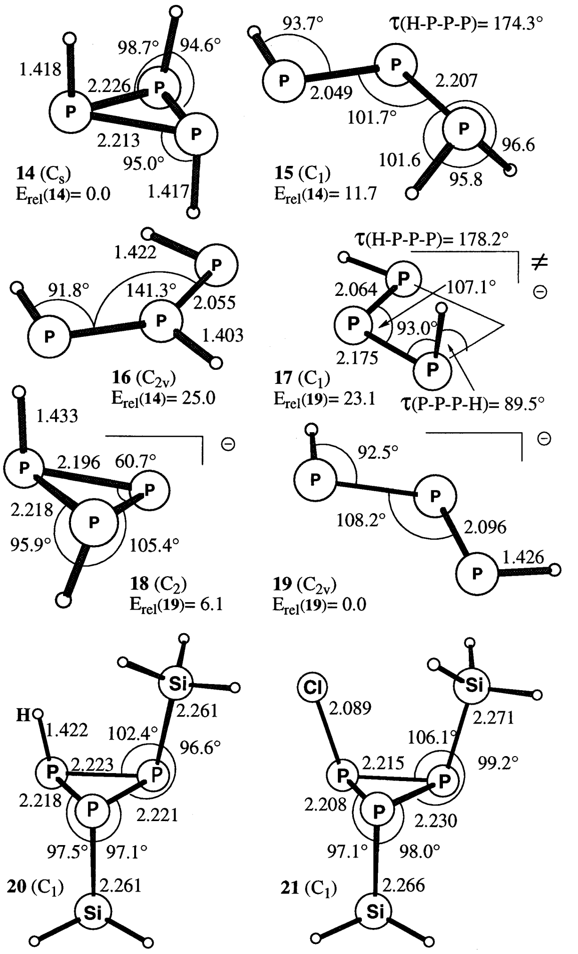
−251.6) as a triplet of triplets and can be understood, practically, according to a first order interpretation. On the other hand the signal of P-5 (M part, δ = 9.5) deviates considerably from the first order $(J_{P\text{-}4P\text{-}5})/\nu_0[\delta(P\text{-}4) - \delta(P\text{-}5)] = 0.08$ at 109.37 MHz). For the phosphorus atoms P-1 and P-3 at the bridgehead positions δ = −30.5, and for the adjacent phosphorus atoms P-4 and P-6 in the pentaphospholane ring δ = −49.5; the characteristic splitting pattern for the A and the B part of an AA′BB′M spin system[19] is observed, each doubled by coupling with P-2. The presence of a cyclotriphosphane ring in **13** is indicated by the chemical shift at high field for P-2 as well as by the large and negative coupling constant $^{1}J_{P1P3} = -245.9$ Hz (regarding the sign see ref.[21]). As in the case of $P_6t\text{Bu}_4$[17] $^{1}J_{P1P6}$ and $^{1}J_{P5P6}$ are clearly larger than $^{1}J_{PP}$ in the cyclotriphosphane ring, and here have values of −397.1 Hz and −487.7 Hz, respectively, which are remarkably large values. The large and positive coupling constant between P-2, P-4 and P-6 (+105.4 Hz) indicates that the lone pairs at these phosphorus atoms are facing each other. The $t\text{Bu}_3\text{Si}$ substituents at P-2 as well as at P-4 and P-6 must therefore occupy in the first case the axial position and in the last two cases the equatorial positions, as shown by the X-ray structure analyses for $P_6t\text{Bu}_4$[17] and $P_6\text{Cp}^*{}_4$[18] in the crystal.

Cyclic versus Acyclic $P_3H_2^-$, P_3H_3 and Derivatives: Ab initio Structure, Energy and NMR Calculations

Figure 6 comprises the results of ab initio calculations concerning structure and relative energies of cyclic P_3H_3 (**14**) and $P_3H_2^-$ (**18**) as well as of their acyclic isomers (**15**, **16**, **17**, **19**) and two derivatives of *cyclo*-P_3H_3 (**20**, **21**). Our RMP2/6-31+G* calculations of the parent $P_3H_2^-$ anion show that the acyclic planar *trans-trans* form **19** with allylic conjugation[25], $[HP{\overset{...}{-}}P{\overset{...}{-}}PH]^-$, and P−P $1^1/_2$ bonds[25] is thermodynamically 6.1 kcal/mol more stable than the cyclic isomer **18** (isomerization of **19** via **17** to a *trans-cis* isomer has a barrier of 23.1 kcal/mol, see Figure 6). With silyl substituents the allyl preference increases slightly [E_{rel} for cyclic $(H_3Si)_2P_3^-$ is 7.6 kcal/mol]. In contrast, neutral compounds with a P_3 framework like P_3H_3 (**14**)[26], $(H_3Si)_2P_3H$ (**20**), $(H_3Si)_2P_3Cl$ (**21**) prefer the cyclic form. Structural alternatives with a terminal PH_2 group are less stable than the global minimum for the neutral *cyclo*-P_3H_3 [E_{rel} (H_2PPPH, **15**) with respect to **14** is 11.7 kcal/mol, Figure 6] as well as for the anionic *acyclo*-$P_3H_2^-$ [E_{rel} (H_2PPP^-) with respect to **19** is 12.7 kcal/mol)]. Therefore, cyclization of the "protonated anion" **1** to **11** and ring opening of the "reduced halogenide" **9** to **1** is in agreement with our ab initio results for the simple models R_2P_3X and $R_2P_3^-$ with R = H or SiH_3 and X = H or Cl.

Both the acyclic anion $R_2P_3^-$ (in **1** with R = $\text{Si}t\text{Bu}_3$; calcd. for R = H, SiH_3) and the cyclic isomer could have two ^{31}P-NMR signals. The question is which R_2P_3Na model structure provides computed NMR data which are in agreement with the experiment? Unfortunately, ab initio NMR calculations which neglect electron correlation give $\delta^{31}P$ values for the model complexes, $(RP{\overset{...}{-}}P{\overset{...}{-}}PR,Na)$ (R = H or SiH_3), with unusually large deviations of several hundred ppm. However, density functional NMR calculations (SOS-DFPT[27]), which include correlation are in good agreement with GIAO-MP2[28] (explicit consideration of correlation) and should only deviate by the order of 37 ppm from the experiment[29]. Our SOS-DFPT/Perdew-Wang functional '91/B3///RMP2/6-31G*, NMR values for an appropriate model of **1** (modeling the silyl substituent by SiH_3 and the solvated sodium by bare Na^+) are in reasonable agreement with the experiment for the W-shaped, C_S-symmetric acyclic form with a folded deltoid P_3Na moiety ($\delta DPB3^{31}P$ = 720 and 176, corresponding to 733 and 213) and exclude any cyclic form[30]. The $\delta DPB3^{31}P$ values for the strictly planar Si_2P_3Na framework indicate that this transition structure of the molecule, in solution or in the crystalline framework, occurs only intermittently during the permanent internal motion of the molecule.

Figure 6. RMP2/6-31G* (and 6-31+G* for anions) geometries (bond length in [A], angles in [°] and relative energies (in [kcal/mol]) for P_3H_3, $P_3H_2^-$ and $(H_3Si)_2P_3X$ (X = H, Cl)



We would like to thank the *Deutsche Forschungsgemeinschaft* for supporting our research and the *Computer-Chemie-Centrum Erlangen* for computer time on an HP735 platform.

Experimental Section

All experiments were carried out under dry argon with strict exclusion of air and moisture. CF_3SO_3H, CF_3CO_2H, TCNE, CD_3CN, and PCl_3 were commercially available. $(t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{P}_4\mathrm{Na}_2$ (**2**) in THF[4], $t\mathrm{Bu}_3\mathrm{SiNa}$ in THF[31], and $(t\mathrm{Bu}_3\mathrm{Si})_3\mathrm{P}_7$ (**7**)[11] were prepared according to literature procedures. The solvents (pentane, benzene, tetrahydrofuran) were distilled from sodium/benzophenone immediately before use.

The NMR spectra were recorded with a JEOL FX-90-Q (^{1}H/^{13}C/^{29}Si: 89.55/22.52/17.79 MHz), a JEOL GXS-270 (^{1}H/^{13}C/^{29}Si/^{31}P: 270.17/67.94/53.67/109.37 MHz), and a JEOL EX-400 (^{1}H/^{13}C/^{31}P: 399.78/100.53/161.84 MHz) spectrometer. The ^{29}Si-NMR spectra were recorded with the INEPT pulse sequence using empirically optimized parameters for polarization transfer from the *t*Bu substituents. The mass spectra (electron impact) were recorded with a Varian CH7 instrument.

Conversion of **2** *into* **1**: a) 5.22 mmol (0.4 ml) of CF_3CO_2H in 2 ml of pentane was added dropwise with stirring to a cooled (−78 °C) solution of 5.22 mmol of **2** in 50 ml of THF and the resulting deep red reaction mixture was warmed up after 1 h to ambient temp. While warming, the solution changed colour to red-violet. According to the ^{31}P-NMR spectrum (C_6D_6) the reaction solution contained, in addition to $t\mathrm{Bu}_3\mathrm{SiPH}_2$ and small amounts of $t\mathrm{Bu}_3\mathrm{SiPHNa}$ (identified by comparison with authentical samples[32]), the phosphorus compounds **1** (see below), **2** (unreacted starting material) and **4** (identified by comparison with an authentic sample[10]) in a molar ratio of 2:1:1, as well as the oligophosphane $(t\mathrm{Bu}_3\mathrm{SiP}_3)_n$ (see below).

b) From a solution of 0.138 mmol of **2** in 2 ml of THF the solvent was removed in vacuo and 1 ml of CD_3CN added to the remaining deep red solid to yield a violet solution. According to the ^{31}P-NMR spectrum of this solution, **1** (identified by comparison with an authentic sample, see below) and $t\mathrm{Bu}_3\mathrm{SiPD}_2$ (identified by comparison with an authentic sample[32]) were formed as the only phosphorus-containing products in a molar ratio of 1:1. After removing the CD_3CN in vacuo, $t\mathrm{Bu}_3\mathrm{SiPD}_2$ was separated from the residue by sublimation (100 °C/10^{-3} mbar) and isolated as colourless needles. – ^{1}H NMR (CD_3CN, internal TMS): δ = 1.14 (d; $^4J_{PH}$ = 0.46 Hz; 3 *t*Bu). – ^{13}C{^{1}H} NMR (CD_3CN, internal TMS): δ = 22.8:30.9 (d/d; $^2J_{CP}/^3J_{CP}$ = 6.1/3.0 Hz; 3 *t*Bu). – ^{29}Si NMR (CD_3CN, external TMS): δ = 24.0 (d; $^1J_{SiP}$ = 30.7 Hz; Si*t*Bu$_3$). – ^{31}P{^{1}H} NMR (CD_3CN, external 85% H_3PO_4): δ = −268.9 (quint; $^1J_{PD}$ = 29.4 Hz; PD_2).

Note: In the course of a few weeks the violet colour of the reaction solution vanished and it then contained, according to the ^{31}P-NMR spectrum, $t\mathrm{Bu}_3\mathrm{SiPD}_2$ as the only phosphorus compound. According to the ^{29}Si-NMR spectrum $t\mathrm{Bu}_3\mathrm{SiCN}$ also formed (identified by comparison with an authentic sample[33]).

c) **2**, dissolved in a pentamethyldiethyltriamine (PMDTA)/benzene mixture, converted in the course of several months at ambient temp. into **1** and $t\mathrm{Bu}_3\mathrm{SiPHNa}$ (as PMDTA adducts); at the same time additional, and as yet unidentified, phosphorus-containing products were formed.

Formation of **1** *from Supersilylpolyphosphanes:* a) 3.45 mmol of **2** in 50 ml of THF was added dropwise to a solution of 6.94 mmol (0.61 ml) of CF_3SO_3H in 5 ml of pentane at ambient temp. The deep red colour of the solution of **2** changed to yellow on contact with the acid. According to the ^{31}P-NMR spectrum (C_6D_6) polyphosphanes together with $t\mathrm{Bu}_3\mathrm{SiPH}_2$ were formed (molar ratio of the polyphosphane phosphorus to the monophosphane phosphorus in accord with Eq. 2 is 3:1). The solvent and all volatile materials were removed in vacuo, the residue dissolved in 10 ml of pentane and all insoluble material (CF_3SO_3Na) separated by filtration. After several days at −25 °C, a yellow solid precipitated from the filtrate, which was separated, dissolved in heptane and precipitated again at −25 °C. Repetition of this procedure several times afforded 0.820 g of a yellow and very air-sensitive solid polyphosphane product. According to the ^{31}P-NMR spectrum, this product was free of $t\mathrm{Bu}_3\mathrm{SiPH}_2$, and according to elemental analysis had the composition $t\mathrm{Bu}_3\mathrm{SiP}_3$[34]. After removal of the pentane and heptane in vacuo from the respective filtrates, solid $t\mathrm{Bu}_3\mathrm{SiPH}_2$ was obtained from the remaining residue by sublimation at 100 °C/10^{-3} mbar (identified by comparison with an authentic sample[32]).

A solution of 2.80 mmol of $t\mathrm{Bu}_3\mathrm{SiNa}$ in 6 ml of THF was slowly added dropwise to a solution of 0.820 g (2.80 mmol with respect to the formula $t\mathrm{Bu}_3\mathrm{SiP}_3$) of the solid yellow polyphosphane (see above) in 10 ml of THF. The colour of the reaction solution changed from yellow to deep violet. According to the ^{31}P-NMR spectrum, **1** was quantitatively formed, which proved the identity of the polyphosphane to be $(t\mathrm{Bu}_3\mathrm{SiP}_3)_n$. The reaction solution was concentrated to 5 ml and mixed with 2 ml of pentane. In the course of 10 d violet, and very air- and moisture-sensitive crystals of sodium 2,3-bis(tri-*tert*-butylsilyl)triphosphenide−tetrahydrofuran(1/4) (**1a**) separated. − ^{1}H NMR (C_6D_6/THF, internal TMS): δ = 1.38 (br.; 2 Si*t*Bu$_3$). − ^{13}C{^{1}H} NMR (C_6D_6/THF, internal TMS): δ = 25.3 (br.; 6 *C*Me$_3$), 32.3 (br.; 6 C*Me*$_3$). − ^{29}Si NMR (C_6D_6/THF, external TMS): δ = 18.3 (td; $^1J_{SiP} + {}^3J_{SiP}$ = 47.1 Hz; $^2J_{SiP}$ = 7.1 Hz; 2 Si*t*Bu$_3$). − ^{31}P{^{1}H} NMR (C_6D_6/THF, external 85% H_3PO_4): cf. Figure 1. − X-ray structure investigation [cf. section on characterization and structure of $(t\mathrm{Bu_3Si})_2\mathrm{P_3Na(THF)_4}$ (**1a**)].

b) A solution of 0.445 mmol *t*Bu$_3$SiNa in 1 ml of THF was added dropwise to 0.181 g (0.222 mmol) of **7** at ambient temp. The reaction mixture immediately adopted a red-violet colour. According to the ^{31}P-NMR spectrum **1** (identified by comparison with an authentic sample, see above) and **3** formed in a molar ratio of 1:1. After a longer period of time dark red crystals of highly air- and moisture-sensitive 1-[tri-*tert*-butylsilyl(sodio)phosphanidyl]-2,3-*trans*-bis(tri-*tert*-butylsilyl)cyclotriphosphane−tetrahydrofuran-(1/*n*) (**3**) were formed from the red-violet reaction solution (identified by comparison with an authentic sample[12]).

Note: The phosphide **3** was also formed quantitatively from the reaction of **5** with an equimolar amount of *t*Bu$_3$SiNa in THF.

Formation of **1** *from Phosphorus Trichloride:* A solution of 0.184 g (1.35 mmol) of PCl_3 in 0.5 ml of heptane was added dropwise to a cooled (−78 °C) solution of 4.6 mmol *t*Bu$_3$SiNa in 10 ml of THF (procedure A); alternatively a solution of 11.5 mmol *t*Bu$_3$SiNa in 25 ml of THF was added dropwise to a cooled (−78 °C) solution of 0.623 g (4.98 mmol) of PCl_3 in 20 ml of THF (procedure B). The resulting reaction mixtures were then warmed up to ambient temp. According to the ^{31}P-NMR spectrum the triphosphide **1** (see above), the tetraphosphide **3**[5], the pentaphosphide **4**[5][10], monophosphides (see below), and diphosphides (see below) were formed in a molar ratio of about 10:5:3:1:2 for procedure A, and of about 7:4:3:1:4 for procedure B [the compounds were identified by comparison of the ^{31}P-NMR data with those of authentical samples; cf. references given with the numbers of the compounds; the mono- and diphosphides were formed in only small amounts (giving one and two ^{31}P-NMR signals, respectively) and are not yet identified.

Note: After the insoluble materials from the reaction solution, obtained according to procedure B, were separated by filtration, and the solution was concentrated to 15 ml and cooled to −25 °C, a microcrystalline precipitate of a mixture of the compounds mentioned above was obtained. The filtrate ("mother liquor"), which contains **1**, **3**, **4**, and other phosphides in a molar ratio of 8:5:3:3, was further treated with CF_3CO_2H and with TCNE (see below).

Reaction of **1** *with Trifluoracetic Acid:* A solution of 0.060 g (0.53 mmol) of CF_3CO_2H in 0.5 ml of heptane was added dropwise at ambient temp. to 2 ml of the "mother liquor" (described above and obtained from PCl_3 and *t*Bu$_3$SiNa in THF) which contained, as shown from titration, 0.56 mmol/ml of anionic phosphorus. The solvents and all volatile materials were removed in vacuo, the residue was dissolved in pentane, the insoluble material (CF_3CO_2Na) separated by filtration, and the pentane then removed in vacuo and the residue dissolved in 1 ml of C_6D_6. According to the ^{31}P-NMR spectrum, protonated **1** (≡ **11**), protonated **3**[5] and protonated **5**[5][10] were formed in a molar ratio of about 3:5:3, together with monophosphanes, diphosphanes, and other phosphanes. The structure of *trans*-bis(supersilyl)cyclotriphosphane (**11**), which could not be isolated from the reaction mixture, was unambiguously proved from the ^{31}P-NMR spectra [cf. section on the protolysis and oxidation of $(t\mathrm{Bu_3Si})_2\mathrm{P_3Na}$ (**1**)]. The ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra revealed no additional information for **11** because of superposition of its signals with the signals of other compounds present in the mixture.

Reaction of **1** *with Tetracyanethylene:* 2 ml of the "mother liquor" described above (obtained from PCl_3 and *t*Bu$_3$SiNa in THF, and which contained, as shown from a titration, 0.56 mmol/ml anionic phosphorus) was added dropwise to 0.059 g (0.46 mmol) of TCNE at ambient temp. The solvent and all volatile materials were removed in vacuo, the residue was dissolved in pentane, unsoluble materials were removed by filtration, and finally the pentane was evaporated in vacuo and the residue dissolved in 0.8 ml of C_6D_6. According to the ^{31}P-NMR spectrum, **5**[4][11], **6**[10], **12**, and **13** are formed in a molar ratio of 2:7:8:1 together with other phosphanes. Assuming, that **4** was oxidized uniformly to **6** and **1** was oxidized only to **12** and **13**, the compounds **1** and **4**, present in the "mother liquor" in a molar ratio of 8:3, must be found in the reaction solution, after the oxidation, in a molar ratio of 4:3 (experimentally observed 9:7 ≡ 4:3.1). The structures of 2,2′,3,3′-tetrasupersilyl-1,1′-bicyclotriphosphane (**12**) and 2,4,5,6-tetrasupersilylbicyclo[3.1.0]hexaphosphane (**13**), which could not be isolated from the reaction mixture, were unambiguously derived from the ^{31}P-NMR spectra [cf. section on the protolysis and oxidation of $(t\mathrm{Bu_3Si})_2\mathrm{P_3Na}$ (**1**)]. The ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra revealed no additional information for **12** and **13**, due to the superposition of their NMR signals with the signals of other compounds present in the mixture.

X-ray Structure Determination of $(t\mathrm{Bu_3Si})_2\mathrm{P_3Na(THF)_4}$ (**1a**): Diffractometer STOE IPDS, Mo-K_α radiation, λ = 0.71069 Å. A small violet crystal was fixed in perfluoroether and analyzed in a Mark-tube at T = 200(2) K. Crystallographic data: $C_{40}H_{86}NaO_4P_3Si_2$, M_f = 803.17, orthorhombic, space group $Pna2_1$ (No. 33), a = 24.433(6), b = 17.439(7), c = 12.005(6) Å, V = 5115(4) Å^3, Z = 4, $d_{\mathrm{calcd.}}$ = 1.043 g cm^{-3}, μ = 0.204 mm^{-1}, F(000) = 1768. − Data collection: ω scans, 2Θ = 2.38−21.00° in $-32 \le h \le 32$, $-22 \le k \le 8$, $-15 \le l \le 15$. 10985 measured reflections, of which 4866 symmetry independent. − Solution of the structure: Restraints, 390 parameters optimized, $R1[I > 2\sigma(I)]$ = 0.0787, $wR2$ = 0.1802, GOF = 2.128; residual electron density = 0.389 and −0.388 e Å^{-3}. For further details of the crystal structure investigation (for example splitting of the positions of the atoms) see ref.[35].

☆ Dedicated to Professor Dr. *Heinrich Nöth* on the occasion of his 70th birthday.

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[35] Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-101056. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) code + 44(0)1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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