Heptaphosphanortricyclenes with Oligosilyl Substituents: Syntheses and Reactions

Pierre Noblet,^[a] Vittorio Cappello,^[a] Günter Tekautz,^[a] Judith Baumgartner,^{[a][‡]} and Karl Hassler^{*[a]}

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Three new nortricyclic P_7R_3 derivatives with R = $(SiMe_3)_2$ -MeSi- $(2)_1$ (SiMe₃)₂PhSi- $(3)_1$ and cyclo-Si₆Me₁₁- (4) were synthesized from red phosphorus, sodium/potassium alloy, and a chlorooligosilane, and their structures were elucidated with X-ray diffraction. Reactions of 2 and 3 and of tri(hypersilvl)heptaphosphane 1 [hypersilv] = $(SiMe_3)_3Si-$] with KOtBu and LiOtBu were performed, which led to different results depending on the size of the substituent. With KOtBu, Si-P bonds were cleaved in 2 and 3, and the mono- and dianions $[P_7R_2]^ [R = (SiMe_3)_2MeSi: 2a; R = (SiMe_3)_2PhSi: 3a]$ and $[P_7R]^{2-}$ [R = (SiMe₃)₂MeSi: **2b**] formed. Crystals of the [K+18-crown-6]+ salt of 2b suitable for X-ray diffraction could be grown successfully. Compound 1 reacted in an unprecedented way with KOtBu at -60 °C. An Si-Si bond was cleaved, and a transient silvl anion formed, which immediately rearranged into a transient heptaphosphanide anion $[Hyp_2P_7]^-$ (1a) under expulsion of bis(trimethylsilyl)silylene.

Introduction

The tricyclic cage of the heptaphosphide anion $[P_7]^{3-}$ is a structural unit that is not only interesting and important for solid-state chemistry, but also for molecular chemistry.^[1] It is present in various Zintl phases, for instance, Li₃P₇.^[2] Its molecular structure has also been determined from the solvate Li₃P₇(tmeda)₃ (tmeda = N,N,N',N'-tetramethylethylenediamine).^[3] Solvated Li₃P₇ is fluxional in solution as well as in the solid state; it undergoes a Cope rearrangement similar to bullvalene.^[4]

The molecular derivatives P_7R_3 feature a nortricyclane structure with either C_3 or $C_{3\nu}$ symmetry of the P_7 unit closely related to the structure of P_4S_3 (see Scheme 1).

A variety of substituents R such as C_nH_m (Me, Et, Bu, *i*Pr, benzyl),^[5] SiMe₃,^[6] SiPh₃,^[7] Si*t*Bu₃,^[8] SnPh₃, GePh₃, or PbPh₃ (Ph = C₆H₅),^[9] as well as phosphanyl groups^[1] have been introduced into the P₇ system over the last thirty years. It is noteworthy that even the formation of P₇Br₃ and P₇I₃ in the reaction of white phosphorus P₄ with Br₂ or I₂ has The silylene immediately inserted into a P-P bond of the basal P_3 ring of **1a**, thereby forming two new isomeric anions $\{Hyp_2P_7[Si(SiMe_3)_2]\}^-$, **1b** and **1c**. The structure of **1c** could be elucidated by X-ray crystallography, whereas 1b was characterized by ³¹P NMR spectroscopy. The proposed reaction mechanism could be further confirmed by performing the reaction between **1** and KO*t*Bu in the presence of a large excess amount of dimethylbutadiene, which trapped the silylene. Just the formation of anion 1a was observed in that case. Anion 1a was also obtained quantitatively when KOtBu was replaced by LiOtBu. Compound 1a reacted with trifluoroacetic acid to give Hyp_2P_7H (1d), which was successfully crystallized and examined by X-ray diffraction. It is the first structural example of a stable and neutral nortricyclic P₇ derivative, R₂P₇H. All compounds were chracterized further by ³¹P and ²⁹Si NMR spectroscopy and elemental analyses.





been reported, albeit without isolation of the cages.^[10] The number of As_7R_3 molecules described in the literature is much smaller, and no neutral molecular derivatives Sb_7R_3 or Bi_7R_3 have been described yet, despite the fact that the anions $[Sb_7]^{3-}$ and $[Bi_7]^{3-}$ are well known as constituents of some Zintl phases.^[11]

There are numerous examples of relatively stable polyphosphorus anions that can be isolated,^[12] which contrasts with a relatively small number of isolable neutral hydrogen polyphosphanes that are inherently unstable.^[1,13] So far, no neutral derivatives R_2P_7H or RP_7H_2 have been isolated and characterized structurally. However, the structures of the anions $[H_2P_7]^-$ and $[HP_7]^{2-}$, which in solution also possess

 [[]a] Institute of Inorganic Chemistry, University of Technology, Stremayrgasse 16, 8010 Graz, Austria E-mail: karl.hassler@tugraz.at

^[‡] X-ray structure analysis

the marked tendency to disproportionate, could be determined in their tetraphenylphosphonium salts.^[14,15] Further studies revealed that alkyl group transfer between anions allowed the preparation of partially alkylated species $[R_2P_7]^-$ and $[RP_7]^{2-}$, and that the reaction of $P_7(SiMe_3)_3$ with *n*BuLi resulted in the formation of $[P_7(SiMe_3)_2]^{-,[16,17]}$ The first crystal structure of an alkylated anion $[R_2P_7]^-$ (R = benzyl) was not reported before 1998.^[18] So far, no dianion $[RP_7]^{2-}$ could be characterized structurally.

Two methods are commonly used for the preparation of these species. First, melts of the composition K_3P_7 and K_3As_7 can be used by fusing the elements at approximately 1000 °C in sealed tubes, a procedure for which special equipment is needed. Moreover, it is extremely dangerous because polypnictides are known to spontaneously detonate even under anaerobic conditions, thus making this method unattractive for preparative purposes. However, the use of the pure Zintl phases allowed the preparation and structural characterization not only of derivatives P_7R_3 , but also of $[H_2P_7]^-$, $[(C_6H_5CH_2)_2P_7]^-$, and $[(C_6H_5CH_2)_2-As_7]^{-,[18,19]}$

The second method starts from elemental phosphorus, preferably (but not necessarily) from the red modification due to safety reasons. In a solvent such as dimethoxyethane, red or white phosphorus reacts with sodium/potassium alloy to form a nonstoichiometric phosphide $Na_x P/K_x P$, which gives excellent yields of (SiMe₃)₃P₇ (78%) when treated with ClSiMe₃.^[20] With this method, we were able to prepare the first oligosilyl-substituted heptaphosphane P_7R_3 with R = Si(SiMe_3)_3 (1).^[21] In the present work, we describe the synthesis of the cages with $R = SiMe(SiMe_3)_2$ (2), SiPh(SiMe₃)₂ (3), and cyclo-Si₆Me₁₁ (4), as well as some reactions of 1, 2, and 3. Preliminary results of these studies have already been reported elsewhere.[22,23] It is worth mentioning that substituted P7 systems such as [HypP7(PHyp)]²⁻ are formed in the treatment of white phosphorus with KSi(SiMe₃)₃.^[24]

accumulate a negative charge. Consequently, derivatives such as $[RP_7]^{2-}$, $[R_2P_7]^-$, and P_7R_3 are expected to possess exceptional electronic stability for substituents R that are capable of supporting sufficient positive charge. A further kinetic stabilization of these species can be achieved if in addition R is a sterically demanding group. As both these properties can be found in oligosilyl groups, we have set out to develop a method for the synthesis of oligosilylheptaphosphanes and to investigate their reactivities. The introduction of oligosilyl groups offers two further advantages that are not found in organoheptaphosphanes. First, Si–P bonds can be cleaved at low temperatures with various reagents such as BuLi, *t*BuOK, or C₂Cl₆, and second, Si–Si bonds also can be cleaved at temperatures as low as -70 °C, for instance, with *t*BuOK.^[25]

All cages P_7R_3 with $R = SiMe(SiMe_3)_2$ (2), SiPh- $(SiMe_3)_2$ (3), and Si_6Me_{11} (4), were prepared from red phosphorus, sodium/potassium alloy and a halosilane RX. For $R = cyclo-Si_6Me_{11}$, iodoundecamethylcyclohexasilane was used due to its increased reactivity; chlorosilanes were used in all other cases. A general procedure is presented in the Experimental Section.

X-ray structures of the cages 2, 3, and 4, which crystallize racemically as mixtures of enantiomers, are shown in Figure 1 with hydrogen atoms omitted for clarity. Details of the structures can be found in the Experimental Section.

As all bond lengths and bond angles are in a normal range, we will not discuss them here, but focus briefly on the distance h from the apical phosphorus atom to the center of the basal triangular plane, which depends on the type of substituents (Scheme 2).



Results and Discussion

Syntheses and X-ray Structures of P7R3

The stability of the heptaphosphanide $[P_7]^{3-}$ is well known and certainly reflects the tendency of phosphorus to





Scheme 2.

Figure 1. ORTEP drawings (30% probabilities, top views) of the molecular structures of $P_7[SiMe(SiMe_3)_2]_3$ (2, left), $P_7[SiPh(SiMe_3)_2]_3$ (3, center), and $P_7[Si_6Me_{11}]_3$ (4, right). Hydrogen atoms are omitted for clarity.



 $(316 \text{ pm}^{[8]})$, and Si(SiMe₃)₃ (318 pm^[21]). The values for the cages 2, 3, and 4 prepared in this work are (315 ± 1) pm, close to that for SiMe₃. From group-electronegativity considerations, the partial negative charge on the equatorial phosphorus atoms is expected to decrease in the series Si- $(SiMe_3)_3 > Si_6Me_{11} > SiMe(SiMe_3)_2 > SiPh(SiMe_3)_2 >$ SiMe₃. Accordingly, the cages should become more elongated, which is not observed. On the contrary, tri(hypersilyl)heptaphosphane 1 [hypersilyl = $Hyp = Si(SiMe_3)_3$] possesses the largest h value, which we attribute to nonbonded van der Waals interactions between the hypersilvl groups.^[21] The smallest H···H nonbonded distances in 1 are close to the twofold value of the van der Waals radius for hydrogen, given in the literature as 120-145 pm.^[27] The three hypersilyl groups therefore act like a belt that compresses and elongates the cage. Quite obviously, these interactions are somewhat smaller for the other oligosilyl groups.

Reaction of 1 with tBuOK and tBuOLi

As reported earlier, *t*BuOK can be used for cleaving Si–P bonds to give a potassium phosphanide and a silyl ether. For instance, $P(SiMe_3)_3$ reacts with *t*BuOK to form $KP(SiMe_3)_2$ and *t*BuOSiMe_3,^[28] and experiments with $(SiMe_3)_3SiP(SiMe_3)_2$ have shown that it is the *P*-trimethyl-silyl group that is cleaved exclusively with concomitant formation of $(SiMe_3)_3SiP(SiMe_3)K$.^[29] Unshielded Si–P bonds react much more quickly with *t*BuOK than Si–Si bonds do, which is easily understood from bond polarities.

Due to the effective shielding of the Si–P bonds by the hypersilyl groups, the treatment of tri(hypersilyl)heptaphosphane with 1 equiv. of *t*BuOK in thf proceeds by means of Si–Si bond cleavage (Scheme 3). The resulting silyl anion immediately rearranges into a heptaphosphanide anion $[Hyp_2P_7]^-$ (1a) and bis(trimethylsilyl)silylene, which is in-



Scheme 3. Reaction of tri(hypersilyl)heptaphosphane 1 with tBuOK and tBuOLi.



Figure 2. ORTEP plots (30% probabilities, hydrogen atoms not shown) of the molecular structure of the K+18-crown-6 salt of 1c shown without (left) and with SiMe₃ groups (right). Selected distances [pm] and angles [°]: P(1)–P(2) 223.2(3), P(1)–P(3) 222.3(3), P(1)–P(4) 230.0(11), P(2)–P(5) 224.8(12), P(3)–P(6) 226.3(7), P(4)–P(6) 229.3(17), P(7)–P(5) 214.8(14), P(5)–Si(3) 230.7(12), P(6)–Si(3) 233.5(7), P(4)–K 364.5(12), P(7)–K 366.3(11), P(2)–Si(2) 229.6(3), P(3)–Si(1) 227.5(2); P(2)–P(1)–P(3) 96.07(10), P(2)–P(1)–P(4) 101.0(3), P(3)–P(1)–P(4) 90.5(3), P(1)–P(2)–P(5) 104.3(3), P(1)–P(3)–P(6) 90.6(3), P(1)–P(4)–P(7) 107.7(5), P(1)–P(4)–P(6) 87.9(4), P(5)–P(7)–P(4) 66.6(5), P(6)–P(4)–P(7) 109.6(6), P(5)–Si(3)–P(6) 105.9(3), P(1)–P(2)–Si(2) 103.73(11), P(1)–P(3)–Si(1) 100.13(10).

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serted into the P–P bond of the basal P_3 ring that lies opposite to the P atom, which formally bears the negative charge. A novel phosphanide anion $[Hyp_2P_7Si(SiMe_3)_2]^-$ (**1b**) is formed, which then rearranges into anion **1c** through P–P bond shift. The four-membered SiP₃ ring present in **1b** is

transformed into a five-membered SiP_4 ring with concomitant formation of a P₄ ring. Scheme 1 summarizes the reaction sequence, which occurs at a temperature as low as -70 °C. To the best of our knowledge, this is the first example of a silylene insertion into a P–P bond of the P₇ nor-



Scheme 4. Isomers of $[R_2P_7]^-$, top views. C is chiral.



Scheme 5. Numbering of the P atoms in 1, 1a, 1b, and 1c; $R = SiMe_3$.



Figure 3. ³¹P{¹H} NMR spectra (δ [ppm]) of 1, of the potassium salt 1a, of 1b, and of an approximately 20:80 mixture between 1b and 1c. From top to bottom.

tricyclane system. With regard to previously reported reactions between P_4 and silylenes R_2Si , it is not surprising that the insertion occurs into a P–P bond of the P_3 ring.^[30]

When the reaction between 1 and tBuOK is carried out in the presence of 18-crown-6, 1c crystallizes from toluene as the [K·18-crown-6]⁺ salt. Figure 2 presents two views of the molecular structure of the anion and shows that the orientation of a hypersilyl group has changed due to inversion at a P atom. So far, we have been unable to obtain crystals of 1a or 1b, because only 1c crystallized from the reaction mixture. By employing low-temperature ³¹P NMR spectroscopy, we were, however, able to record spectra of pure 1b prior to the isomerization to 1c. When crystals of the $[K\cdot 18$ -crown-6]⁺ salt of 1c are dissolved in toluene or thf, the equilibrium between 1b and 1c is reestablished immediately; all attempts to obtain ³¹P NMR spectra of pure 1c failed. It is also noteworthy that neither 1b nor 1c do react with a further equivalent of KOtBu at temperatures below 30 °C.

To corroborate the hypothesis that bis(trimethylsilyl)silylene is an intermediate, the reaction between 1 and KOtBu was repeated in the presence of an excess amount of dimethylbutadiene, with the expectation that the silylene would be trapped and that anion **1a** would be formed, which it did. Though we were unsuccessful in growing crystals of 1a, the ³¹P NMR spectra are unambiguous. Moreover, treatment of 1 with CsF in thf also resulted in the formation of 1a through Si-P bond cleavage, thereby giving an identical ³¹P NMR spectrum. As six signals in the intensity ratio 1:1:1:1:1:2 are observed for 1a, the asymmetric isomer C formed, as shown below. This can be deduced from the presence of two signals with triplet structures in the range for the equatorial, Si-substituted P atoms at δ = -10 and -50 ppm. Formation of 1a through Si-P bond cleavage thus involves no inversion at a P atom. Formation

of isomer **B** is unlikely due to steric interaction of the two hypersilyl groups.

The lithium salt of 1a can be easily obtained by replacing tBuOK by tBuOLi, which possesses much less tendency to cleave Si–Si bonds. Again, isomer C is formed (Scheme 4).

Due to magnetic inequivalence of the P atoms, all signals in the proton-decoupled ³¹P NMR spectra of cages 1-1care second-order multiplets. Scheme 5 presents the numbering of the P atoms used in the assignment of the resonances, and Figure 3 displays the spectra of pure 1, 1a, and 1b and of a mixture between 1b and 1c, which contained about 80% of 1c.

The peak assignments correspond to the atom numbering used in Scheme 5 and are supported by connectivities obtained from COSY spectra.

Formation of Hyp₂P₇H (1d)

By treatment of **1a** with CF_3COOH , colorless single crystals of the neutral heteroleptic cage Hyp₂P₇H could be obtained from *n*-hexane, which we were able to characterize by X-ray diffraction. It is the first known structure of a neutral heptaphosphane that bears a hydrogen atom, and at the same time of a neutral heteroleptically substituted heptaphosphane. An ORTEP drawing is presented in Figure 4. The compound is stable at room temperature and shows no tendency to undergo hydrogen/silyl exchange reactions.

Treatment of 1c + 1d with Chlorosilanes

When we treated a mixture of the anions 1c and 1d with ClSiMe₂SiMe₂Cl, two heptaphosphane cages connected with an SiMe₂SiMe₂ bridge formed, which was corrobo-

Figure 4. ORTEP drawing (30% probabilities, hydrogen atoms not shown) of the molecular structure of Hyp_2P_7H (1d). Selected distances [pm] and angles [°]: P(1)–P(2) 215.8(2), P(1)–P(3) 216.7(2), P(1)–P(4) 216.9(2), P(2)–P(5) 219.3(2), P(3)–P(7) 218.9(2), P(4)–P(6) 218.3(2), P(5)–P(6) 228.0(2), P(5)–P(7) 220.3(2), P(6)–P(7) 219.9(2), P(2)–H(99) 115(4), P(3)–Si(1) 226.6(2), P(4)–Si(5) 228.0(2); P(3)–P(1)–P(2) 99.60(9), P(3)–P(1)–P(4) 98.12(8), P(2)–P(1)–P(4) 95.67(8), P(1)–P(2)–P(5) 103.32(9), P(1)–P(3)–P(7) 102.28(8), P(1)–P(4)–P(6) 103.03(8), P(2)–P(5)–P(6) 105.94(9), P(2)–P(5)–P(7) 100.27(8), P(3)–P(7)–P(5) 108.22(9), P(3)–P(7)–P(6) 100.69(8), P(4)–P(6)–P(5) 100.10(8), P(4)–P(6)–P(7) 107.73(8), P(5)–P(7)–P(6) 60.06(7), P(5)–P(7) 60.07(8), P(6)–P(7) 59.87(7), P(1)–P(3)–Si(1) 111.16(8), P(1)–P(4)–Si(5) 110.54(8).

Figure 5. ORTEP plots (30% probabilities, hydrogen atoms omitted for clarity) showing the molecular structure of [(SiMe₃)₂-MeSiP₇]²⁻²[K⁺·18-crown-6] (**2b**). Left: top view; right: side view. Selected distances [pm] and angles [°]: P(1)–P(2) 217.4(1), P(1)–P(3) 217.0(1), P(1)–P(4) 221.6(1), P(2)–P(5) 215.4(1), P(3)–P(6) 213.4(1), P(4)–P(7) 218.7(1), P(5)–P(6) 225.7(1), P(5)–P(7) 226.2(1), P(6)–P(7) 226.5(1), P(4)–Si(1) 227.0(1), P(2)–K(1) 336.5(1), P(3)–K(1) 359.5(1), P(5)–K(1) 367.9(1), P(6)–K(1) 383.3(1), P(2)–K(2) 334.3(1), P(5)–K(2) 356.2(2), P(4)–K(2) 367.6(2); P(3)–P(1)–P(2) 105.02(6), P(3)–P(1)–P(4) 103.03(5), P(2)–P(1)–P(4) 93.47(6), P(1)–P(2)–P(5) 99.11(5), P(1)–P(3)–P(6) 99.07(5), P(1)–P(4)–P(7) 101.88(5), P(5)–P(7)–P(6) 60.04(4), P(6)–P(7)–P(5) 59.80(4), P(7)–P(5)–P(6) 60.16(4), P(2)–P(5)–P(7) 106.80(5), P(3)–P(6)–P(5) 106.42(5), P(4)–P(7)–P(6) 103.19(5).

rated by the ³¹P NMR spectra. No crystals could be obtained yet. Hyp₂P₇-SiMe₂SiMe₂-P₇Hyp₂ could also be obtained by treating sodium/potassium phosphide first with 1 equiv. of ClSiMe₂SiMe₂Cl and in a second step with 4 equiv. of (SiMe₃)₃SiCl. A mixture between R₂P₇SiMe₂Si- $Me_2P_7R_2$ and 1 formed, from which 1 could not be separated quantitatively through fractional crystallization from toluene. With $(SiMe_3)_3SiCl$, 1c + 1d give back cage 1 exclusively. Quite obviously, bis(trimethylsilyl)silylene is expelled under the reaction conditions, and the cyclotriphosphane ring is reformed. This is not surprising, as reactions of silylenes are known to be reversible.^[31] Most noteworthy, the treatment of 1c + 1d with chlorotrimethylsilane proceeds without extrusion of (SiMe₃)₂Si, as several second-order signals between $\delta = +120$ and 0 ppm prove. So far, we have been unable to separate silvlated 1c from silvlated 1d by fractional crystallization. Therefore, detailed results of these ongoing investigations will be reported elsewhere.

Treatment of 2 and 3 with tBuOK

As the Si–P bonds in 2 and 3 are less shielded than in 1 due to the smaller size of the oligosilyl groups, the treatments with *t*BuOK proceed by means of Si–P cleavage. With 1 equiv. of *t*BuOK, the monoanions $[R_2P_7]^-$ form quantitatively $[R = SiMe(SiMe_3)_2: 2a; R = SiPh(SiMe_3)_2: 3a]$. From the ³¹P NMR spectra we deduce that the asymmetric isomers C are formed in both cases, despite the fact that only five resonances with intensities 1:1:2:1:2 are observed in each case because of overlapping signals. Two signals with a triplet structure are observed in the region between $\delta = 0$ and -30 ppm, which is typical for the equatorial P atoms that bear silyl substituents (see the Experimental Section). Due to substituent interactions, formation of isomers **B** can safely be excluded.

It is of some note that in the reaction of $P_7(SiMe_3)_3$ with *t*BuLi or LiP(SiMe_3)_2, the symmetric isomer **A** of $[P_7(SiMe_3)_2]^-$ is initially formed, which decomposes quickly

with formation of Li₃P₇, LiP(SiMe₃)₂, P(SiMe₃)₃.^[17] Interestingly, isomer C is obtained when *t*BuOK is used for the Si–P bond cleavage, but isomer A with *t*BuOLi. At room temperature, both the lithium and potassium salts are stable in solution for days.^[32]

As the ³¹P NMR spectra are very similar to those of 1a, no pictures are presented here. In the presence of 18-crown-6, needle-like crystals of 2a could be grown from toluene. Unfortunately, they were too thin for X-ray diffraction.

Treatment of **2** with 2 equiv. of *t*BuOK afforded the dianion $[RP_7]^{2-}$ (**2b**), which in the presence of 18-crown-6 gave crystals suitable for a structure determination by employing X-ray diffraction. Results are presented in Figure 5.

As can be deduced from the NMR spectra, **2b** is fluxional in solution and undergoes a Cope-like rearrangement. At room temperature, just broad signals are observed, which split into seven second-order resonances at low temperatures (-60 °C). An analogous degenerate Cope rearrangement between two identical valence tautomers was also observed for [HP₇]²⁻ by employing temperature-dependent ³¹P NMR spectroscopy.^[33]

Conclusion

Heptaphosphanes P_7R_3 functionalized with various oligosilyl groups R can be synthesized from red phosphorus, sodium/potassium alloy, and a suitable halooligosilane. They show unusual thermal stability and can be used for further derivatizations, either by Si–P or Si–Si bond cleavage.

When R is a trisilaryl group, one or two Si–P bonds can be cleaved by KOtBu with concomitant formation of the heptaphosphanides $[P_7R_2]^-$ or $[P_7R]^{2-}$ and a silyl ether tBuOR. Contrary to lithium heptaphosphanide $[P_{7^-}(SiMe_3)_2]^-Li^+$, which decomposes quickly, the potassium salts are stable, crystallize readily in the presence of 18crown-6, and can be used for further reactions.

These results open up doors for further investigations, which are in progress.

Experimental Section

Spectroscopy: NMR spectra were recorded with a Bruker MSL 300 or a Varian Unity Inova 300 spectrometer. The ²⁹Si{¹H} and ³¹P{¹H} spectra were measured in solutions in thf or toluene in 10 mm tubes with capillaries containing D₂O that served as external lock, except when C₆D₆ was used. The insensitive nuclei enhanced by polarization transfer (INEPT) pulse sequence was used for the ²⁹Si spectra. Due to coupling over two and three bonds, which causes line broadening, the accuracy of ¹J_{Si,P} values is not better than an estimated ±5 Hz.

X-ray Structure Analysis: For X-ray structure analyses, the crystals were mounted onto the tip of glass fibers, and data collection was performed with a Bruker-AXS SMART APEX CCD dif-

fractometer by using graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å). The data were reduced to F_o^2 and corrected for absorption effects with SAINT^[34] and SADABS,^[35] respectively. The structures were solved by direct methods and refined by full-matrix least-squares method (SHELXL97).^[36] If not noted otherwise, all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles, except for H(99) in **1d**. All diagrams were drawn with 30% probability thermal ellipsoids, and all hydrogen atoms were omitted for clarity. Crystallographic data (excluding structure factors) for the structures of compounds **1c**, **1d**, **2**, **2b**, **3**, and **4** reported in this paper are summarized in Table 1. CCDC-612400 (**1c**), -612415 (**1d**),

Synthesis: All syntheses and manipulations were carried out under either N₂ or Ar by using standard Schlenk techniques. Solvents were first dried with Al₂O₃ by using a column purification system from Innovative Technology and then distilled from sodium, potassium, sodium/potassium alloy, or LiAlH₄ to remove traces of moisture and oxygen. 18-crown-6 and KO/Bu were subjected to vacuum sublimation prior to use. Chloro- and iodosilanes such as (Me₃Si)₃SiCl, (Me₃Si)₂SiMeCl, (Me₃Si)₂SiPhCl, and (Me₂Si)₅Si-MeI, were prepared and purified according to procedures described in the literature. Elemental analyses were performed with a Heraeus Vario Elementar.

-612402 (2), -612401 (2b), -612399 (3), and -612403 (4) contain the

supplementary crystallographic data for this paper. These data can

be obtained free of charge from The Cambridge Crystallographic

Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for the Synthesis of P_7R_3 : Typically, red phosphorus (8.06 g, 260.00 mmol) was suspended in dimethoxyethane (dme; 150 mL). Then sodium/potassium alloy (3.40 g) prepared

Table 1. Crystallographic data for compounds 1c, 1d, 2, 2b, 3, and 4.

| | 1d | 2b | 2 | 1c | 3 | 4 |
|---|--|--------------------------------|--------------------------------|---|--|--------------------------------|
| Empirical formula | C ₁₈ H ₅₅ P ₇ Si ₈ | C45H85K2O12P7Si3 | $C_{21}H_{63}P_7Si_9$ | C ₃₆ H ₈₇ KO ₆ P ₇ Si ₁₁ | C ₃₆ H ₆₉ P ₇ Si ₉ | C33H99P7Si18 |
| M _r | 713.13 | 1197.39 | 785.31 | 1180.94 | 971.51 | 1218.53 |
| T[K] | 100(2) | 100(2) | 100(2) | 223(2) | 223(2) | 100(2) |
| Size [mm] | $0.38 \times 0.28 \times 0.20$ | $0.42 \times 0.38 \times 0.28$ | $0.36 \times 0.28 \times 0.16$ | $0.38 \times 0.26 \times 0.15$ | $0.45 \times 0.32 \times 0.01$ | $0.44 \times 0.32 \times 0.20$ |
| Crystal system | monoclinic | monoclinic | triclinic | triclinic | monoclinic | trigonal |
| Space group | P2/c | $P2_1/n$ | ΡĪ | PĪ | $P2_1/c$ | R3c |
| a [Å] | 15.712(3) | 17.570(4) | 9.689(2) | 13.297(6) | 21.069(4) | 15.639(3) |
| b [Å] | 9.605(2) | 20.443(4) | 15.325(3) | 15.036(7) | 10.880(2) | 15.639(3) |
| c [Å] | 26.969(5) | 18.726(4) | 15.900(3) | 20.819(10) | 26.624(5) | 53.22(2) |
| a [°] | 90 | 90 | 99.90(3) | 69.65(2) | 90 | 90 |
| β ^[°] | 101.67(3) | 105.37(3) | 91.02(3) | 79.46(2) | 109.74(3) | 90 |
| γ [°] | 90 | 90 | 97.63(3) | 64.14(2) | 90 | 120 |
| $V[Å^3]$ | 3986(2) | 6485(2) | 2303(2) | 3509(3)(2) | 5744(2) | 11273(5) |
| Z | 4 | 4 | 2 | 2 | 4 | 6 |
| $\rho_{\rm calcd.}$ [g cm ⁻³] | 1.188 | 1.226 | 1.132 | 1.118 | 1.123 | 1.077 |
| $\mu \text{ [mm^{-1}]}$ | 0.561 | 0.423 | 0.516 | 0.456 | 0.426 | 0.473 |
| F(000) | 1520 | 2544 | 840 | 1258 | 2064 | 3924 |
| θ range [°] | 1.32-24.72 | 1.50-24.71 | 1.71-25.00 | 1.78-24.71 | 1.03-23.25 | 1.69-26.36 |
| Reflections collected/ | | | | | | |
| unique | 27335/6820 | 44643/11042 | 10106/7401 | 23930/11625 | 34503/8243 | 28347/5117 |
| Completeness to θ [%] | 99.9 | 99.9 | 91.1 | 97.1 | 99.9 | 99.9 |
| Data/restraints/ | | | | | | |
| parameters | 6820/0/320 | 11042/0/631 | 7401/0/355 | 11625/909/934 | 8243/0/445 | 5117/1/187 |
| Goodness of fit on F^2 | 0.99 | 1.10 | 1.04 | 1.13 | 1.04 | 1.13 |
| Final R indices | $R_1 = 0.063,$ | $R_1 = 0.059,$ | $R_1 = 0.043,$ | $R_1 = 0.103,$ | $R_1 = 0.078,$ | $R_1 = 0.064,$ |
| $[I > 2\sigma(I)]$ | $wR_2 = 0.145$ | $wR_2 = 0.113$ | $wR_2 = 0.116$ | $wR_2 = 0.257$ | $wR_2 = 0.201$ | $wR_2 = 0.124$ |
| R indices | $R_1 = 0.116$, | $R_1 = 0.081,$ | $R_1 = 0.050,$ | $R_1 = 0.125$, | $R_1 = 0.118$, | $R_1 = 0.073$, |
| (all data) | $wR_2 = 0.167$ | $wR_2 = 0.122$ | $wR_2 = 0.122$ | $wR_2 = 0.270$ | $wR_2 = 0.222$ | $wR_2 = 0.128$ |
| Largest difference | - | - | - | - | - | - |
| peak/hole [eÅ ³] | 0.69/0.45 | 0.48/0.31 | 0.73/-0.35 | 1.08/0.58 | 0.98/0.44 | 0.51/0.44 |

from Na (1.47 g, 64.00 mmol) and K (1.86 g, 47.5 mmol) was added, and the reaction mixture was heated to reflux for 20 h. The dme was then removed by evaporation in vacuo and replaced by toluene (ca. 200 mL). Then a solution of the required oligosilane (111.5 mmol) in toluene (50 mL) was added dropwise at room temperature [for 1: $(SiMe_3)_3SiCl$ (31.57 g); for 2: $(SiMe_3)_2MeSiCl$ (25.08 g); for 3: $(SiMe_3)_2PhSiCl$ (32.00 g); for 4: $Si_6Me_{11}I$ (51.38 g)]. Subsequently, the mixture was again heated to reflux for 3 h to complete the reaction, and the salts were then separated by filtration. From the toluene solutions, colorless crystals of the heptaphosphanes with a quality suitable for X-ray analysis could be grown at -80 °C. Yields ranged from 50 to 75%.

Compound 2: ³¹P NMR (toluene): $\delta = 0$ (m, 3 P), -85 (m, 1 P), -167 (m, 3 P) ppm. ²⁹Si NMR (toluene): $\delta = -15.5$ (SiMe₃), -51.7 [¹J_{Si,P} = (83.5 ± 5) Hz, SiMe] ppm. C₂₁H₆₃Si₉P₇ (785.30): calcd. C 33.02, H 8.81; found C 32.25, H 7.97.

Compound 3: ³¹P NMR (toluene): $\delta = 0$ (m, 3 P), -98 (m, 1 P), -165 (m, 3 P) ppm. ²⁹Si NMR (toluene): $\delta = -13.9$ (SiMe₃), -51.0 [¹ $J_{Si,P} = (95.4 \pm 5)$ Hz, SiPh)] ppm. C₃₆H₆₉Si₉P₇ (971.51): calcd. C 44.51, H 7.16; found C 44.19, H 7.47.

Compound 4: ³¹P NMR (toluene): $\delta = 0$ (m, 3 P), -84 (m, 1 P), -169 (m, 3 P) ppm. ²⁹Si NMR (toluene): $\delta = -36.6, -38.2, -41.0$ (SiMe₂), -42.0 [¹ $J_{Si,P} = (110.0 \pm 5)$ Hz, SiMe] ppm. C₃₃H₉₉Si₁₈P₇, (1218.49): calcd. C 32.53, H 8.19; found C 33.77, H 7.96.

Treatment of Hyp₃P₇ (1) with KOtBu. Synthesis of 1b and 1c: KOtBu (0.06 g, 0.53 mmol) and 18-crown-6 (0.23 g, 0.53 mmol) were added to a solution of 1 (0.50 g, 0.52 mmol) in toluene (ca. 20 mL) at a temperature of -60 °C. The solution slowly turned orange and then red. After 3 h, no more starting material 1 could be detected by ³¹P NMR spectroscopy. The solution that contained a mixture of 1b and 1c was then cooled to -80 °C. After several days, red crystals of the [K·18-crown-6]⁺ salt of 1c suitable for X-ray diffraction were obtained. The reaction could also be performed in thf solution in the absence of 18-crown-6 with identical results. ³¹P NMR (toluene): $\delta = 130$, 117, 48, 23, -27, -62, -74, -170 ppm. ²⁹Si NMR (toluene): $\delta = 13.0$ (SiP₂), -8.6 (SiMe₃), -19.6 (SiMe₃), -86 (SiSi₃) ppm.

Treatment of Hyp₃P₇ (1) with KOtBu in the Presence of Dimethylbutadiene. Formation of 1a: A solution of KOtBu (0.03 g, 0.26 mmol) and 2,3-dimethylbutadiene (DMB; 0.28 g, 3.43 mmol, 13-fold excess amount) in thf (10 mL) was cooled to -70 °C. Then, a solution of 1 (0.25 g, 0.26 mmol) in thf (10 mL) was added dropwise. The reaction mixture turned orange and was stirred at that temperature for another 3 h. According to the ³¹P NMR spectrum, 1a formed almost quantitatively. Minor byproducts were 1b and 1c. ³¹P NMR (thf): $\delta = -10$ (m, 1 P), -50 (m, 1 P), -67 (m, 1 P), -76 (m, 1 P), -95 (m, 1 P), -188 (m, 2 P) ppm. ²⁹Si NMR (thf): δ = -11.9 (SiMe₃), -99.9 [d, ¹J_{Si,P} = (101 ± 5) Hz] ppm.

Treatment of Hyp₃P₇ (1) with LiOtBu. Synthesis of 1a: A solution of LiOtBu (0.021 g, 0.26 mmol) in thf (10 mL) was added to a solution of **1** (0.25 g, 0.26 mmol) in thf (10 mL). The reaction mixture was stirred at 25 °C for 10 d, and the progress of the reaction was monitored by ³¹P NMR spectroscopy. Compound **1** was quantitatively converted into the lithium salt of **1a**. Even at room temperature, $[Hyp_2P_7]$ -Li⁺ showed no tendency to decompose noticeably over a period of two weeks. ³¹P NMR (thf): $\delta = -10$ (m, 1 P), -48 (m, 1 P), -70 (m, 1 P), -75 (m, 1 P), -95 (m, 1 P), -190 (m, 2 P) ppm. ²⁹Si NMR (thf): $\delta = -9.8$ (SiMe₃), -99.8 [d, ¹J_{Si,P} = (100 ± 5) Hz] ppm.

Treatment of 1a with CF₃COOH. Synthesis of 1d: A solution of CF₃COOH (0.12 g, 1.05 mmol) in toluene (10 mL) was added

dropwise to a solution of **1a** (1.05 mmol) in toluene [10 mL, prepared from **1** and KO/Bu (1.00 g)] at -70 °C. The reaction mixture was then allowed to come to room temperature. After decantation from the salts, the toluene was removed in vacuo and replaced by *n*-hexane. At -30 °C, colorless crystals of **1d** formed. Yield ca. 0.2 g (27%). ³¹P NMR (C₆D₆): $\delta = +17$ (t, 1 P), -5 (m, 2 P), -109 (m, 1 P), -155 (m, 2 P), -171 (m, 1 P) ppm. ²⁹Si NMR (C₆D₆): $\delta = -8.8$ (SiMe₃), -93.9 [d, ¹J_{Si,P} = (82±5) Hz], -95.1 [d, ¹J_{Si,P} = (90±5) Hz] ppm. ¹H NMR (C₆D₆): $\delta = 0.42$ (9H, SiMe₃), 0.39 (9H, SiMe₃), 3.1 [¹J_{P,H} = (191±5) Hz, 1H] ppm. C₁₈H₅₅Si₈P₇ (713.13): calcd. C 30.32, H 7.77; found C: 30.72, H 7.24.

Treatment of 2 and 3 with KO/Bu. Synthesis of 2a, 2b, and 3a: For 2a, KO/Bu (0.166 g, 1.48 mmol) and 18-crown-6 (0.385 g, 1.48 mmol) were added with a spatula to a solution of 2 (1.16 g, 1.48 mmol) in toluene (20 mL) at room temperature. The solution immediately turned orange and was stirred for an additional 1 h to complete the reaction. At -80 °C, crystals of the [K·18-crown-6]⁺ salt of 2a were obtained, which unfortunately were not suitable for X-ray structure determination due to their small size. From the ³¹P NMR spectra, a nearly 100% conversion of 2 into 2a could be deduced. The reaction could also be carried out in thf without the addition of 18-crown-6. ³¹P NMR (toluene): δ = -18 (m, 1 P), -32 (m, 1 P), -58 (m, 2 P), -92 (m, 1 P), -188 (m, 2 P) ppm. ²⁹Si NMR (toluene): δ = -8.5 (SiMe₃), δ = -49.0 [¹J_{P,Si} = (89 ± 5) Hz, SiMe] ppm.

Compound 2b: KO*t*Bu (0.33 g, 2.96 mmol) and 18-crown-6 (0.77 g, 2.96 mmol) were added to a solution of **2** (1.16 g, 1.48 mmol) in toluene (20 mL) at room temperature. The solution, which turned orange immediately, was stirred for another 1 h to complete the reaction and then stored at -80 °C. After several days, yellow-orange crystals of the [K·18-crown-6]⁺ salt of **2b** were obtained, which were suitable for X-ray diffraction experiments. Again, the reaction was quantitative. ³¹P NMR (-60 °C, toluene): $\delta = -38$ (m, 1 P), -60 (m, 1 P), -77 (m, 1 P), -83 (m, 1 P), -122 (m, 1 P), -125 (m, 1 P), -224 (m, 1 P) ppm.

Compound 3a: KO*t*Bu (0.046 g, 0.41 mmol) and 18-crown-6 (0.11 g, 0.41 mmol) were added with a spatula to a solution of **3** (0.40 g, 0.41 mmol) in toluene (20 mL) at room temperature. The solution immediately turned orange and was stirred for another 1 h to complete the reaction. The solution was concentrated by evaporation of the toluene in vacuo and stored at -80 °C for two weeks. However, no crystallization could be observed. As deduced from the ³¹P NMR spectra, the reaction proceeded quantitatively. ³¹P NMR (toluene): $\delta = -7$ (m, 1 P), -30 (m, 1 P), -68 (m, 2 P), -88 (m, 1 P), -193 (m, 2 P) ppm. ²⁹Si NMR (toluene): $\delta = -12.0$ (SiMe₃), -50.6 [¹J_{P,Si} = (95 ± 5) Hz, SiPh] ppm.

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