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Stepwise Synthesis of Siloxane-Substituted Oligophosphanes $P_n[O(iPr_2Si)_2]_2$ (n = 2, 4)

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The synthesis of siloxane-bridged P_2 and P_4 compounds can be achieved through metalation of primary or cyclic diphosphanylsiloxane compounds and subsequent oxidative coupling using $C_2H_4Br_2$ as reagent. Starting from the cyclic diphosphanylsiloxane $[O(iPr_2Si)_2PH]_2$, the reaction with the silazanides of the earth alkaline metals leads to the metalated compounds $[M(DME)_2\{O(iPr_2Si)_2P\}_2]$ (**1**: M = Ca, **2**: M = Sr, **3**: M = Ba). Subsequent oxidation yields the bicyclic species $P_2[O(iPr_2Si)_2]_2$ (**4**). In an analogous reaction sequence with the primary diphosphanylsiloxane $O(iPr_2Si)_2PH_2$ the cyclic diphosphane $O(iPr_2SiPH)_2$ (**5**) could be obtained and was successfully used for the same reaction pathway, leading to the corresponding metalated compound **6**. Further oxidative coupling resulted in an intermolecular P–P bond formation, yielding the cage compound $P_4[O(iPr_2Si)_2]_2$ (**7**).

Introduction

Phosphanides of the heavy alkaline earth metals have been researched intensively during the last 20 years.[1] They unfold a large variety of structures from solvated monomers to oligomeric molecular species.[2] The reaction of the alkaline earth metal silazanides with primary or secondary phosphanes allows an easy access to this kind of compounds. This approach was recently used yielding multiple and versatile structures from difunctionalized phosphanylsiloxanes.[3] These compounds are useful starting compounds for the formation of different kinds of phosphane species through transmetalation reactions.

Numerous authors reported on reactions of white phosphorus with different kinds of main group element compounds in recent years.[4] From these reactions, fragmentation of the P_4 molecule as well as the formation of larger phosphorus oligomers were observed. In this work we present the stepwise formation of P_2 and P_4 linked siloxane compounds, which were synthesized via metalation and subsequent oxidative coupling starting from primary or secondary cyclic siloxaphosphanes (Scheme 1). In this way, the new metalated coordination compounds **1**–**3** could be obtained from the cyclic diphosphanylsiloxane $[O(iPr_2Si)_2PH]_2$, and from these again, the bicyclic diphosphane $P_2[O(iPr_2Si)_2]_2$ (**4**) could be synthesized. Conveyed to the corresponding primary diphosphanylsiloxane $O(iPr_2Si)_2PH_2$, this reaction pathway led to the cyclic diphosphane $O(iPr_2SiPH)_2$ (**5**) and its reaction products **6** and **7**.

Results and Discussion

The recently described eight-membered ring compound $[O(iPr_2Si)_2PH]_2$ reacts with $Ca[N(SiMe_3)_2]_2$ in DME yielding the colorless complex $[P_2\{O(iPr_2Si)_2\}Ca(DME)_2]$ (**1**). **1** crystallizes from DME in the orthorhombic space group $Pca2_1$ with two independent molecules per unit cell (Table 1). The only difference between these molecules is the alignment of the solvent molecules coordinating the metal center.

The diphosphanylsiloxane ring system is arranged in a bowl-like conformation, different from the free, non-metalated species, which shows a chair-like conformation.[5] The phosphorus atoms at the tips of the bowl are coordinating the Ca atom in a bidentate manner, the remaining free coordination sites of the metal atom are occupied by two DME molecules. Thus, the calcium ion obtains a distorted octahedral coordinitaion sphere. The P–Ca bond lengths are with 291.2–292.8 pm in the expected range of observed values for similar compounds containing bonds between these elements.[6,7] The analogous strontium compound $[P_2\{O(iPr_2Si)_2\}_2Sr(DME)_2]$ (**2**) was obtained from the reaction of $Sr[N(SiMe_3)_2]_2$ with $[O(iPr_2Si)_2PH]_2$ and crystallizes isotype to **1** due to the isotypically molecular assembly (Figure 1).

As expected, the reaction of $Ba[N(SiMe_3)_2]_2$ and $[O(iPr_2Si)_2PH]_2$ in DME yields a similar compound $[P_2\{O(iPr_2Si)_2\}Ba(DME)_2]$ (**3**). In this case, however, a different crystal system and space group are observed. Compound **3** crystallizes in the monoclinic space group $P2_1/n$ with one molecule per unit cell. This difference is sustained in the molecular structure. While in **1** and **2** the bow-shaped siloxane bridges are slightly twisted against each other through the O(1)–O(2) axis, in **3** all silicium atoms are in

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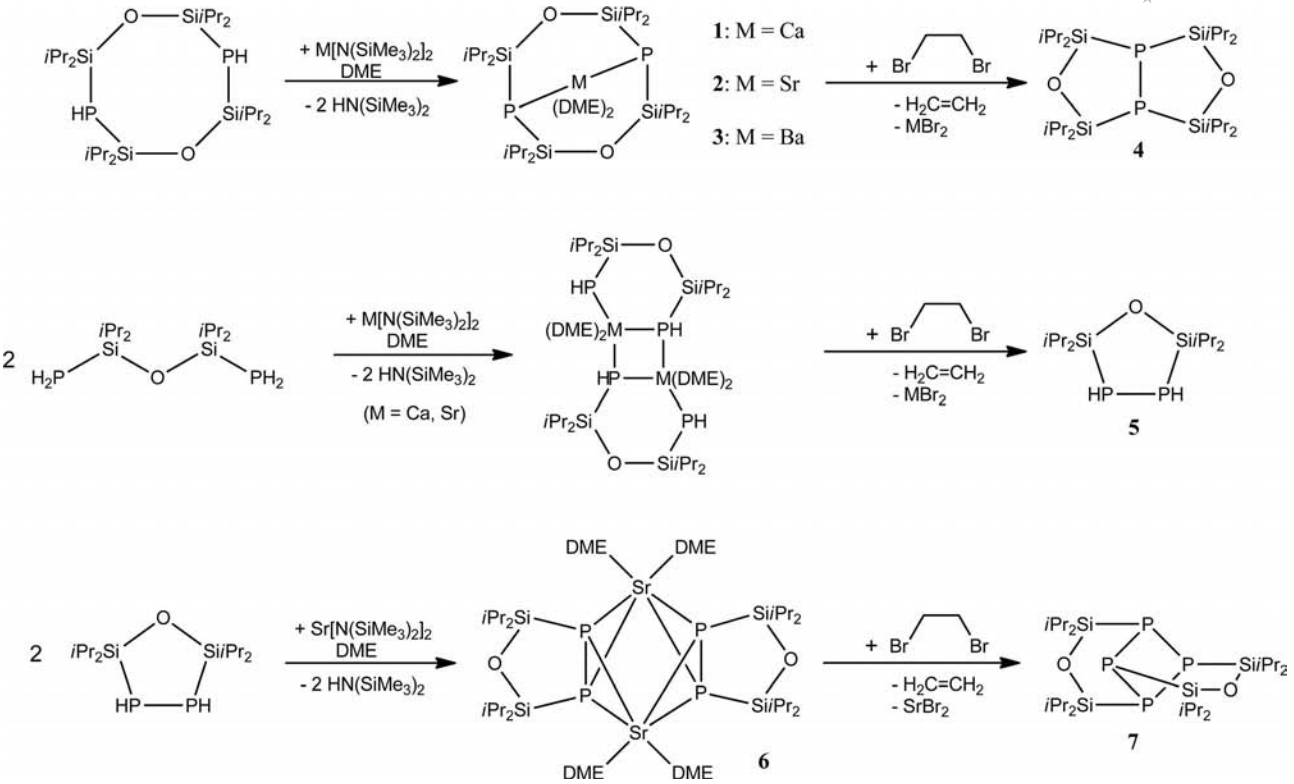

Scheme 1. Synthesis pathway for compounds **1**–**7**.

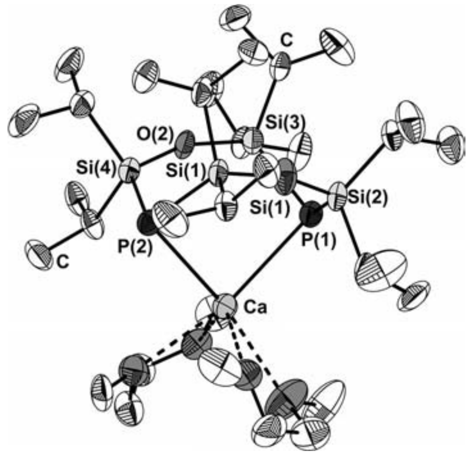

Figure 1. Molecular structure of **1**. Thermal ellipsoids represent a 50% propability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles (°): **1**: Ca–P(1) 292.8(3), Ca–P(2) 291.2(3), P(1)–Si(1) 221.7(3), P(1)–Si(4) 222.3(3), P(2)–Si(2) 221.4(3), P(2)–Si(3), 224.4(3); P(1)–Ca–P(2) 96.21(7), Si(1)–P(1)–Si(4) 104.53(12), Si(2)–P(2)–Si(3) 105.22(12), Si(1)–O(1)–Si(2) 152.9(4), Si(3)–O(2)–Si(4) 154.7(4). Selected bond lengths [pm] and angles [°] of **2** (numbering as for **1**): Sr(1)–P(1) 308.6(2), Sr(1)–P(2) 304.7(3); P(1)–Sr(1)–P(2) 96.64(6).

plane to each other and the Si–O–Si angles are near a linear arrangement [Si–O–Si: 165.06(12) and 176.62(15)°]. This can be attributed to the significantly smaller distance of the siloxane oxygen atoms to the metal center [O(1)–Ba(1) 339.5 pm, O(2)–Ba(1) 315.8 pm] than in compounds **1** and **2** (>380 pm), where the siloxane oxygen atoms are clearly folded away from the metal atom. The sum of the van-der-Waals radii of barium and oxygen amounts to 352 pm, hence, a weak coordinative interaction between barium and the siloxane oxygen atoms is given (Figure 2).

Similar coordination behavior of barium and siloxanes was reported by Drake and Williams et al. several years ago for the compound [$Ba_3\{O(SiPh_2O)_2\}_3$(tetraglyme)$_2$], in which one of the three bridging siloxane oxygen atoms con-

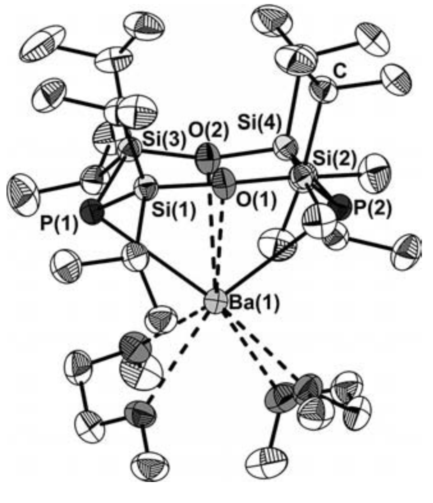

Figure 2. Molecular structure of **3**. Thermal ellipsoids represent a 50% propability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: Ba(1)–P(1) 328.42(8), Ba(1)–P(2) 324.79(9), P(1)–Si(1) 220.04(9), P(1)–Si(3) 220.57(9), P(2)–Si(2) 221.13(9), P(2)–Si(4) 219.86(10), Ba(1)–O(1) 339.56(7), Ba(1)–O(2) 315.82(17); P(1)–Ba(1)–P(2) 105.65(2), Si(1)–P(1)–Si(4) 106.37(3), Si(2)–P(2)–Si(3) 103.03(3), Si(1)–O(1)–Si(2) 176.62(15), Si(3)–O(2)–Si(4) 165.06(12).

tributes to coordinating the central barium atom (Ba···O 314 ppm).[8] In correspondence with our observations, such a coordination does not occur for the corresponding isostructural compounds with strontium as the metal atoms like $[Sr_3\{O(SiPh_2O)_2\}_3(tetraglyme)_2]$ and **2**, respectively.[9] Compounds with metal atoms coordinated by siloxanes are quite scarce due to the low basicity of the oxygen atoms within such an environment. However, a few examples of siloxane complexes are known mostly containing alkali metals.[5,10]

The ^{31}P NMR spectroscopic analysis shows a single singlet at –283.0 ppm for two equivalent phosphorus atoms in **1**, as expected. This is a high-field shift of 14 ppm compared to the non-metalated siloxaphosphane ring system. Due to the similarities of the compounds **1** and **2**, both of them show a almost identical ^{1}H and ^{31}P NMR spectra. For compound **2** a very small low-field shift of the signals compared to **1** can be observed. Noticeable is the clear low-field shift of the singlet in the ^{31}P NMR spectrum (–60.7 ppm) for **3** due to the increasing covalent character of the metal-phosphorus bond with ascending period of the used earth alkaline metal. Apart from that, the NMR spectra show the usual peak pattern like for the compounds **1** and **2** and similar characteristic chemical shifts.

These compounds as representatives of the species of metalated secondary silylphosphanes seemed to be suitable reactants for a possible coupling reaction through metathesis with organic halides. However if $C_2H_4Br_2$ is used for this matter oxidative P–P bond formation occurs.[11] The reaction of compounds **1**–**3** in THF with $C_2H_4Br_2$ yields the bicyclic compound $P_2[O(i\text{Pr}_2Si)_2]_2$ (**4**). This compound crystallises as large rod-shaped crystals (monoclinic, space group *C*2/*c*) from the reaction mixture at –35 °C. **4** can best be described as two isopropyl-substituated P_2Si_2O-five-membered rings which are linked at their shared P–P bond (Figure 3). A similar methyl-substituated compound with nitrogen instead of phosphorus was already obtained in 1971 by Wannagat from the reaction of $O(SiMe_2Cl)_2$ and N_2H_4.[12] Unfortunately no structural data for these compounds is available.

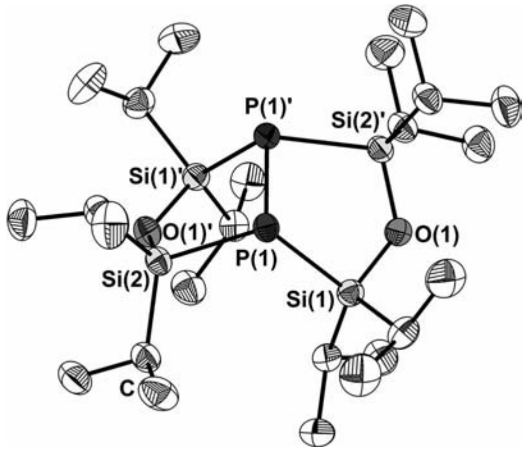

Figure 3. Molecular structure of **4**. Thermal ellipsoids represent a 50% propability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]:P(1)–P(1)′ 224.46(7), P(1)–Si(1) 228.16(5), P(1)–Si(2) 226.69(7), Si(1)–O(1) 165.49(10), Si(2)–O(1)′ 164.79(9); Si(1)–P(1)–Si(2) 106.37(3), Si(1)–O(1)–Si(2)′ 176.62(15).

The two siloxane bridges are folded butterfly-like over their P–P–axis with an Si(1)–P(1)–P(1)′–Si(1)′ angle of torsion of 84.15° and 142.30° for Si(2)–P(1)–P(1)′–Si(2)′ and twisted along the O(1)–O(1′) axis due to the sterically demanding isopropyl groups at the silicon atoms. The Si–O–Si angle with a value of 128.8° is more acute than in **1**–**3** and the corresponding P(H) compound $[O(i\text{Pr}_2Si)_2PH]_2$, while the Si(1)–P(1)–Si(2) angle appears to be enlarged with a value of 112.3°. The bond lengths of P–Si and Si–O are nearly identical with those from the protonated ring compound, in contrast the distance of the two phosphorus atoms (224.5 pm) is slightly longer than the expected value of a typical P–P single bond.

In the ^{29}Si NMR spectrum the triplet at δ = 29.9 ppm results from the "virtual" coupling with both of the phosphorus nuclei and represents the X-part of a AA′X spin system. In this case, it is not possible to resolve the related coupling constants $J_{AA'}$, J_{AX} and $J_{A'X}$ due to the missing combination lines, though the sum of $J_{AX} + J_{A'X}$ can be determined to a value of 59.0 Hz (A = P, X = Si). For the two equivalent phosphorus atoms a singlet at –226.2 ppm is obtained and the ^{1}H NMR shows two signals for the isopropyl groups. Another AA′X pseudo triplet can be found in the ^{13}C NMR for the CH groups. The mass spectrum shows the molecule peak at *m*/*z* 549.9 and a stepwise decay of the compound by loss of one isopropyl group at a time.

Based on the successful oxidative P–P bond formation starting from the compounds **1**–**3**, we investigated whether similar reactions are possible with metalated primary siloxaphosphanes.[3] As described in the literature, the metalation of the diphosphanylsiloxane $O(i\text{Pr}_2SiPH_2)_2$ with $M[N(SiMe_3)_2]_2$ (M = Ca, Sr, Ba) yields the dimeric product $[M\{(P(H)i\text{Pr}_2Si)_2O\}(DME)_2]_2$. The oxidative intramolecular coupling of two phosphorus atoms is realized via elimination of metal bromide through $C_2H_4Br_2$. From this reaction the five-membered P_2Si_2O ring system $(HPi\text{Pr}_2Si)_2O$ (**5**) is obtained. Similar five-membered ring compounds like $HP(SiMe_2PH)_2$ and $HP(SiEt_2PH)_2$ were observed by Fritz[13] as not otherwise characterized by-products from the reactions of lithium phosphides with R_2SiCl_2. The use of alkaline earth metal silazanides as a metalating reagent is crucial for achieving a high degree of conversion. The corresponding lithium compound as a starting material yields considerably less of the target compound **5**. The cause of this seems to be its chain-like structure, which promotes the formation of oligomere by-products through intermolecular bond formation.[14]

Generally, in this synthesis of **5** traces of the reactant $O(i\text{Pr}_2SiPH_2)_2$ and compound **7** are obtained, which can be attributed to a disproportionation reaction. While **5** and $O(i\text{Pr}_2SiPH_2)_2$ can be removed from **7** via distillation in vacuo, the boiling points of $O(i\text{Pr}_2SiPH_2)_2$ and **5** are identical and they cannot be separated this way. So compound **5** always contains small amounts of $O(iPr_2SiPH_2)_2$. The P_2H_2 fragment in **5** represents an AA′XX′ spin system. The AA′ part is to be observed in the ^1H NMR, while the ^{31}P NMR shows the XX′ part. In the $^{29}Si\{H\}$ NMR the complexity is reduced to an AA′X spin system as observed for compound **4**.

Compound **5** still offers two acide P(H) protons, which permit a reaction with an alkaline earth metal silazanide. From the reaction of **5** with $Sr[N(SiMe_3)_2]_2$, the compound $[\{P_2(iPr_2Si)_2O\}_2\{Sr(DME)_2\}_2]$ (**6**) is obtained in form of orange rhombohedral crystals in the monoclinic space group $P2_1/n$. The molecular framework consists of a distorted octahedron, both apical positions are occupied by a strontium atom and the phosphorus atoms are arranged in the four equatorial positions and give rise to an inversion center between the two P–P axis. Due to the coordination of two DME molecules to each of the Sr atoms, they feature a strongly distorted quadratic antiprism as polyhedron of coordination, giving strontium the rare coordination number eight (Figure 4).

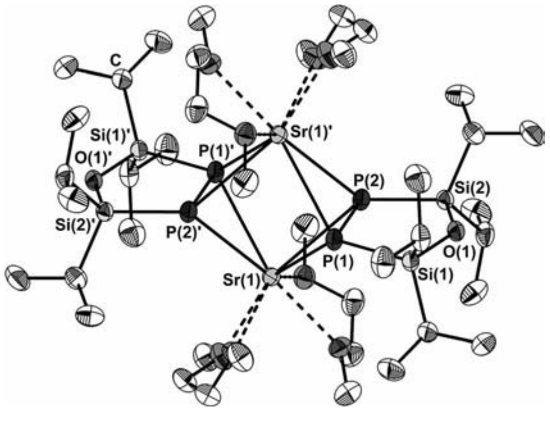

Figure 4. Molecular structure of **6**. Thermal ellipsoids represent a 50% propability level. Hydrogen atoms are omitted for clarity. Thermal ellipsoids represent a 50% propability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: Sr(1)–P(1) 310.86(11), Sr(1)–P(2) 312.71(11), Sr(1)′–P(1) 310.41(10), P(1)–P(2) 229.44(12), P(1)–Si(1) 221.05(11), P(1)–Si(2) 221.41(11), Sr(1)–Sr(1)′ 422.49(8); Sr(1)–P(1)–Sr(1)′ 85.69(2), Sr(1)–P(2)–Sr(1)′ 84.97(2), Si(1)–P(1)–P(2) 98.07(4), Si(2)–P(2)–P(1) 98.29(4), Si(1)–O(1)–Si(2) 124.03(11).

The P–P distance with a value of 229.4 pm is slightly widened by the ionic character of the P–Sr bond as a result of the two very close negative charges at the phosphorus atoms. The length of the P–Sr bond with 311.5 pm on average is longer than in other known strontium phosphanides due to the high coordination number of the strontium.[3,15] Compared to the structure of $[Sr(HPiPr_2Si)_2O(DME)_2]_2$ (see Scheme 1) with a central Sr_2P_2 ring, the distance between the two metal atoms shrunk from 502.0 pm to 422.4 pm in **6**. Changing the structure from a planar Sr_2P_2 four-membered ring to an octahedral type (Figure 4) therefore is associated with a significant approach of the metal atoms. This peculiar difference in the structure of the strontium compounds formed with the very similar anions $[O(iPr_2SiP)_2]^{2-}$ and $[O(iPr_2SiPH)_2]^{2-}$ can be attributed to the higher degree of compensation of the two negative charges at the P atoms by the metal cation for the octahedral topology.

This metalated compound **6** can again be used for an oxidative coupling via elimination of $SrBr_2$ with $C_2H_4Br_2$ and yields the compound $P_4[O(iPr_2Si)_2]_2$ (**7**) as colorless rod shaped crystals. Compound **7** consists of a slightly folded P_4 ring with an angle of torsion (P(2)–P(4) axis) of 162.6° wherein alternate phosphorus atoms are connected via $(iPr_2Si)_2O$ units, resulting in an all-*trans* configuration (Figure 5).

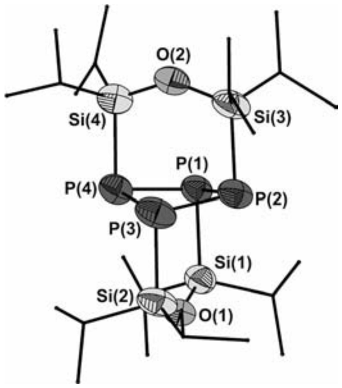

Figure 5. Molecular structure of **7**. Thermal ellipsoids represent a 50% propability level. Hydrogen atoms are omitted for clarity and the isopropyl groups are displayed as stick models due to their heavy disorder. Selected bond lengths [pm] and angles [°]: P(1)–P(2) 223.2(2), P(2)–P(3) 223.4(3), P(3)–P(4) 225.1(3), P(4)–P(1) 224.6(3), P(1)–Si(1) 227.3(2), P(2)–Si(3) 226.8(3), P(3)–Si(2) 228.2(3), P(4)–Si(4) 228.4(3); P(1)–P(2)–P(3) 89.81(9), P(2)–P(3)–P(4) 89.18(9), P(3)–P(4)–P(1) 89.01(10), P(4)–P(1)–P(2) 89.34(9), Si(1)–O(1)–Si(2) 140.5(3), Si(3)–O(2)–Si(4) 141.3(3).

The folding of the P_4 ring is low compared to other P_4 ring compounds such as P_4tBu_4, were the folding angle amounts to 155.5°.[16] A comparable double-bridged P_4 ring system was synthesized by Driess et al. with the compound $[\{HC(CMeNiPr_2C_6H_3)(C(CH_2)NiPr_2C_6H_3)\}Si]_2P_4$ obtained from the reaction of the silylene $[\{HC(CMeNiPr_2C_6H_3)(C(CH_2)NiPr_2C_6H_3)\}Si]$ and white phosphorus. It contains a strongly folded phosphorus four-membered ring system with an angle of torsion of 120°, caused by the very short staggered Si bridges.[17]

This arrangement, which consists of two formally condensed five-membered ring-systems of **5**, is unexpected, since the formation of a ladder-like structure would be more likely considering the structure of the precursor molecules. The formation of **7** is obviously a result of a rearrangement of P–P or P–Si bonds by a so far unknown mechanism. Compound **7** can also be obtained directly via reaction of the primary diphosphanylsiloxane $O(iPr_2SiPH_2)_2$ with the silazanides of the alkaline earth metals and subsequent elimination of the metal salt through dibromoethane in highly concentrated solution ($c > 0.75$ mol/ L). Small amounts of the precursor $O(iPr_2SiPH_2)_2$ are always traced as a by-product in the second step of this synthesis. This leads to the assumption that intermolecular hydrogen exchange is favored due to the high concentration and is only occurring in insignificantly amounts for the synthesis of **5** in sufficient diluted solution.

Conclusions

Based on the known dimeric metalated compounds available from the primary diphosphanylsiloxane $O(iPr_2SiPH_2)_2$ with the alkaline earth metals, it was possible to metalate the cyclic compound $[O(iPr_2Si)_2PH]_2$, which leads to monomeric species sharing the same structural assembly. These metalated compounds and their primary analogues were successfully used as precursors for an oxidative coupling reaction for intramolecular P–P bond formation. Hence, we were able to construct siloxane-linked P_2 and P_4 fragments by means of recurring metalation and oxidative coupling. This reaction pathway promises a comprehensive use for further investigations.

Experimental Section

General: All working procedures were performed under rigorous exclusion of oxygen and moisture using a Schlenk line and nitrogen atmosphere. Solvents were dried and freshly distilled before use. NMR spectra were recorded on a Bruker DPX Avance 300 and Avance III. The structural analyses were carried out with appropriate single crystals on an automatic diffractometer. The structures were solved and refined with SHELXTL and Xstep32 (Table 1). The vibrational spectra were gathered with a Perkin–Elmer GX spectrometer and the microanalyses were made with the model "elementar vario MICRO CUBE". The starting compounds $[M\{N(SiMe_3)_2\}_2(THF)_2]$ (M = Ca, Sr, Ba)[18,19] and $[O(iPr_2SiPH)_2]_2$[5] were prepared by reported methods.

$[P_2\{O(iPr_2Si)_2\}_2Ca(DME)_2]$ (1): 0.200 g (0.40 mmol) $Ca[N(SiMe_3)_2]_2$ are dissolved together with 0.220 g (0.40 mmol) $[O(iPr_2Si)_2PH]_2$ in 10 mL DME and stirred for 5 min at room temperature. After 16 h colorless square plates of **1** are crystallizing; yield 0.208 g (0.27 mmol, 67.6%). Elemental analysis [%] found (calcd.): C 49.86 (49.83), H 9.38 (9.93). ^1H NMR ([D$_8$]THF): δ = 0.74 [m, 4 H, $C\boldsymbol{H}(CH_3)_2$], 1.06 (m, 52 H, *i*Pr), 3.20 (s, 12 H, DME), 3.35 (s, 8 H, DME) ppm. $^{13}C\{^1H\}$ NMR ([D$_8$]THF): δ = 18.7 (s, $\boldsymbol{C}H_3$), 19.0 (d, $^3J_{PC}$ = 5.7 Hz, $\boldsymbol{C}H_3$), 19.2 (d, $^3J_{PC}$ = 2.8 Hz, $\boldsymbol{C}H_3$), 20.1 (d, $^3J_{PC}$ = 9.0 Hz, $\boldsymbol{C}H_3$), 20.3 (s, $\boldsymbol{C}H$), 21.99 (d, $^2J_{PC}$ = 26.2 Hz, $\boldsymbol{C}H$), 57.9 (s, DME), 71.8 (s, DME) ppm. $^{29}Si\{^1H\}$ NMR ([D$_8$]THF): δ = 18.3 (d, $^1J_{PSi}$ = 73.5 Hz) ppm. ^{31}P NMR ([D$_8$]THF): δ = –283.0 (s) ppm.

$[P_2\{O(iPr_2Si)_2\}_2Sr(DME)_2]$ (2): 0.200 g (0.36 mmol) $Sr[N(SiMe_3)_2]_2$ are dissolved together with 0.200g (0.36 mmol) $[O(iPr_2Si)_2PH]_2$ in 10 mL DME and stirred for 5 min at room temperature. After 16 h colorless square plates of **2** are crystallizing; yield 0.215 g (0.26 mmol, 72.2%). Elemental analysis [%] found (calcd.): C 45.32 (46.94), H 9.84 (9.35). ^1H NMR ([D$_8$]THF): δ = 0.81 [m, 4 H, $C\boldsymbol{H}(CH_3)_2$], 1.19 (m, 52 H, *i*Pr), 3.31 (s, 12 H, DME), 3.46 (s, 8 H, DME) ppm. $^{13}C\{^1H\}$ NMR ([D$_8$]THF): δ = 16.9 (s, $\boldsymbol{C}H_3$), 17.3 (d, $^3J_{PC}$ = 6.1 Hz, $\boldsymbol{C}H_3$), 17.5 (d, $^3J_{PC}$ = 3.2 Hz, $\boldsymbol{C}H_3$), 18.4 (d, $^3J_{PC}$ = 8.8 Hz, $\boldsymbol{C}H_3$), 18.7 (s, $\boldsymbol{C}H$), 20.2 (d, $^2J_{PC}$ = 26.3 Hz, $\boldsymbol{C}H$), 56.2 (s, DME), 69.9 (s, DME) ppm. $^{29}Si\{^1H\}$ NMR ([D$_8$]THF): δ = 18.2 (d, $^1J_{PSi}$ = 74.6 Hz) ppm. ^{31}P NMR ([D$_8$]THF): δ = –280.7 (s) ppm.

$[P_2\{O(iPr_2Si)_2\}_2Ba(DME)_2]$ (3): 0.240 g (0.40 mmol) $Ba[N(SiMe_3)_2]_2$ are dissolved together with 0.220 g (0.40 mmol) $[O(iPr_2Si)_2PH]_2$ in 10 mL DME and stirred for 5 min at room temperature. After 16 h colorless square plates of **3** are crystallizing; yield 0.243 g (0.28 mmol, 71.3%). Elemental analysis [%] found (calcd.): C. 43.54 (44.25), H 7.95 (8.82). ^1H NMR ([D$_8$]THF): δ = 0.83 [m, 4 H, $C\boldsymbol{H}(CH_3)_2$], 1.19 (m, 52 H, *i*Pr), 3.31 (s, 12 H, DME), 3.47 (s, 8 H, DME) ppm. $^{13}C\{^1H\}$ NMR ([D$_8$]THF): δ = 18.8 [s, $CH(\boldsymbol{C}H_3)_2$], 19.2 [d, $^3J_{PC}$ = 5.9 Hz, $CH(\boldsymbol{C}H_3)_2$], 19.5 [d, $^3J_{PC}$ = 3.4 Hz, $CH(\boldsymbol{C}H_3)_2$], 20.4 [d, $^3J_{PC}$ = 8.8 Hz, $CH(\boldsymbol{C}H_3)_2$], 20.9 [s, $\boldsymbol{C}H$-

Table 1. X-ray structure data of **1**, **2**, **3**, **4**, **6** and **7**.[20]

Compound	**1**	**2**	**3**	**4**	**6**	**7**
Empirical formula	$C_{32}H_{76}O_6P_2Si_4Ca$	$C_{32}H_{76}O_6P_2Si_4Sr$	$C_{32}H_{76}O_6P_2Si_4Ba$	$C_{24}H_{56}O_2P_2Si_2$	$C_{40}H_{96}O_{10}P_4Si_4Sr_2$	$C_{24}H_{56}O_2P_4Si_4$
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$Pca2_1$	$Pca2_1$	$P2_1/n$	$C2/c$	$P2_1/n$	$P2_1/n$
Formula units	8	8	4	4	2	4
Temperature [K]	190	180	190	190	190	100
Unit cell dimensions [units: pm, °]	a = 2596.0(5) b = 1483.2(3) c = 2349.7(5) α = 90 β = 90 γ = 90	a = 2600.4(5) b = 1487.1(3) c = 2361.6(5) α = 90 β = 90 γ = 90	a = 1172.5(2) b = 2031.1(4) c = 1868.4(4) α = 90 β = 92.14(3) γ = 90	a = 2083.0(4) b = 815.78(16) c = 1983.4(8) α = 90 β = 104.20(3) γ = 90	a = 1285.2(3) b = 1383.8(3) c = 1722.6(3) α = 90 β = 101.62(3) γ = 90	a = 1189.3(2) b = 1389.0(3) c = 2197.8(4) α = 90 β = 103.93(3) γ = 90
Cell volume [10^6 pm^3]	9047(3)	9133(3)	4446.3(15)	3267.4(11)	3000.6(10)	3516.3(12)
Density [g/cm^3]	1.131	1.191	1.298	1.120	1.271	1.078
Absorption coefficient [mm^{-1}]	0.350	1.390	1.108	0.298	2.008	0.367
2Θ range [°]	2.74–45.4	2.74–49.16	2.96–51.32	4.24–51.18	3.62–51.34	3.50–43.98
Reflections measured	29947	17434	30406	9454	20614	19889
Independent reflections	11840 (R_{int} = 0.0996)	11234 (R_{int} = 0.0597)	8223 (R_{int} = 0.0269)	3038 (R_{int} = 0.0331)	5618 (R_{int} = 0.0632)	4314 (R_{int} = 0.0551)
Parameters	811	811	406	257	271	292
R_1 [$F_o \geq 4\sigma(F_o)$]	0.0614	0.0530	0.0251	0.0276	0.0383	0.0868
wR_2 (all data)	0.1401	0.1213	0.0960	0.0978	0.0629	0.2711
GOOF	1.002	0.980	0.822	0.893	1.739	1.034
Residual electron density	0.303/–0.303	0.396/–0.333	0.492/–0.419	0.255/–0.210	0.550/–0.502	0.886/–0.315

$(CH_3)_2]$, 21.9 [d, $^2J_{PC}$ = 26.2 Hz, $\boldsymbol{C}H(CH_3)_2$], 58.0 (s, DME), 71.7 (s, DME) ppm. $^{29}Si\{^1H\}$ NMR ([D$_8$]THF): δ = 17.9 (d, $^1J_{PSi}$ = 76.5 Hz) ppm. ^{31}P NMR ([D$_8$]THF): δ = –260.7 (s) ppm.

$P_2[O(iPr_2Si)_2]_2$ (4): In 10 mL of DME 0.350 g (0.63 mmol) $Sr[N(SiMe_3)_2]_2$ and 0.314 g (0.63 mmol) $[O(iPr_2Si)_2PH]_2$ are dissolved and stirred for 10 h at room temperature. This leads to a colorless powder of **2**. Subsequently, 1.5 equiv. $C_2H_4Br_2$ (0.95 mmol, 0.08 mL) are added at 0 °C and the mixture is stirred for another 12 h. The solvent is removed in vacuo and the residue is extracted with 10 mL *n*-pentane. After concentration of the solution, colorless rods of **4** are obtained at –35 °C; yield 0.288 g (0.52 mmol, 82.2 %). Elemental analysis [%] found (calcd.): C 52.58 (52.32), H 9.54 (10.24). ^1H NMR (C_6D_6): δ = 1.21 (m, 24 H, *i*Pr), 1.28 (m, 32 H, *i*Pr) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 17.9 [t, $^2J_{PC}$ = 5.4 Hz, $\boldsymbol{C}H(CH_3)_2$], 18.1 [s, $CH(\boldsymbol{C}H_3)_2$], 18.6 [s, $CH(\boldsymbol{C}H_3)_2$] ppm. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ = 29.9 (pseudo-t, $^1J_{PSi}$ = 29.5 Hz) ppm. ^{31}P NMR (C_6D_6): δ = –226.2 (s) ppm. MS (EI, 70 eV): *m*/*z* (%) = 549.9 (100) $[M]^+$, 506.8 (87) $[M - iPr]^+$, 464.8 (70) $[M - 2\ iPr]^+$, 422.8 (56) $[M - 3\ iPr]^+$, 380.8 (40) $[M - 4\ iPr]^+$.

$(HPiPr_2Si)_2O$ (5): 7.17 g (12.97 mmol) $Sr[N(SiMe_3)_2]_2$ are dissolved in 150 mL THF and 4.48 mL (12.97 mmol) $O(iPr_2SiPH_2)_2$ are added. After stirring for 16 h at room temperature, 1.68 mL (19.46 mmol, 1.5 equiv.) $C_2H_4Br_2$ are added dropwise at 0 °C and stirred for another 10 h. The solvent is removed in vacuo and the remaining residue extracted with 2 × 50 mL *n*-pentane. The solvent of the combined extracts is removed via distillation and the remaining yellow oil is purified by means of distillation at 1×10^{-3} mbar and 70 °C; yield 2.455 g (7.96 mmol, 61.34 %). ^1H NMR (C_6D_6): δ = 1.03 (m, 28 H, *i*Pr), 1.26 (m, J_A = 175.7, J_X = 17.0, J = 191.1, J' = 21.0 Hz, 2 H, $P\boldsymbol{H}$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 15.3 (pseudo-t, J = 9.9 Hz, $\boldsymbol{C}H$), 15.5 (s, CH), 17.5 (pseudo-t, J = 2.8 Hz, $\boldsymbol{C}H_3$), 17.6 (pseudo-t, J = 1.9 Hz, $\boldsymbol{C}H_3$), 17.7 (s, $\boldsymbol{C}H_3$), 18.0 (s, $\boldsymbol{C}H_3$) ppm. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ = 36.9 (pseudo-t, $^1J_{PSi}$ = 22.3 Hz) ppm. ^{31}P NMR (C_6D_6): δ = –228.3 (m, J_A = 175.7, J_X = 17.0, J = 191.1, J' = 21.0 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2947 (vs), 2892 (s), 2869 (vs), 2756 (w), 2725 (m), 2290 (s), 2098 (w), 1463 (vs), 1385 (s), 1365 (m), 1242 (m), 1162 (w), 1066 (vs), 1052 (vs), 992 (vs), 960 (vs), 919 (s), 883 (vs), 805 (w), 742 (s), 719 (s), 663 (s), 628 (vs), 574 (s), 513 (m), 497 (w), 464 (m), 417 (w) cm^{-1}.

$[\{P_2(iPr_2Si)_2O\}_2\{Sr(DME)_2\}_2]$ (6): 0.280 g (0.51 mmol) $Sr[N(SiMe_3)_2]_2$ are dissolved in 5 mL DME and 0.16 mL (0.51 mmol) $[O(iPr_2Si)_2PH]_2$ are added. The solution is concentrated and after three days at 0 °C orange colored rhombic crystals of **6** are obtained; yield 0.169 g (0.15 mmol, 57.7 %). Elemental analysis [%] found (calcd.): C 40.95 (41.38), H 8.12 (8.42). ^1H NMR (C_6D_6): δ = 1.18 (m, 56 H, *i*Pr), 2.98 (s, 24 H, DME), 3.26 (s, 16 H, DME) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 17.9 (s, $\boldsymbol{C}H$), 20.1 (d, $^3J_{PC}$ = 3.5 Hz, $\boldsymbol{C}H_3$), 58.5 (s, DME), 72.1 (s, DME) ppm. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ = 36.7 (m) ppm. ^{31}P NMR (C_6D_6): δ = –289.4 (s) ppm.

$P_4[O(iPr_2Si)_2]_2$ (7): 0.400 g (0.67 mmol) $Sr[N(SiMe_3)_2]_2$ are dissolved in 10 mL THF at 0 °C 0.200 g (0.67 mmol) $(HPiPr_2Si)_2O$ are added and stirred for 12 h at room temperature. Then 1.5 equiv. (0.06 mL, 1.00 mmol) $C_2H_4Br_2$ are added at 0 °C and stirred for another 10 h at room temperature. The solvent is removed in vacuo, and the precipitated $SrBr_2$ is extracted with 10 mL *n*-pentane. After reducing the volume to a few milliliters and cooling to –35 °C for 10 d, colorless crystals of **7** can be isolated; yield 0.081 g (0.13 mmol, 39.4 %). Elemental analysis [%] found (calcd.): C 46.59 (47.03), H 9.21 (9.21). ^1H NMR (C_6D_6): δ = 1.34 [d, J_{HH} = 7.5 Hz, 12 H, $CH(C\boldsymbol{H}_3)_2$], 1.42 [d, $^3J_{HH}$ = 7.5 Hz, 12 H, $CH(C\boldsymbol{H}_3)_2$], 1.96 [sept, $^3J_{HH}$ = 7.5 Hz, 4 H, $C\boldsymbol{H}(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 15.4 [m, 8 C, $\boldsymbol{C}H(CH_3)_2$], 18.1 [s, $CH(\boldsymbol{C}H_3)_2$], 18.5 [s, $CH(\boldsymbol{C}H_3)_2$] ppm. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ = 14.9 (m) ppm. ^{31}P NMR (C_6D_6): δ = –116.7 (s) ppm. MS (EI, 70 eV): *m*/*z* (%) = 612.3 (100) $[M]^+$, 569.2 (38) $[M - iPr]^+$.

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[20] STOE-IPDS 2 (Mo-K_α radiation, λ = 0.71073 A). The structure was resolved by direct methods and refined against F^2 by the full-matrix least-squares technique (Ba, Sr, Ca, P, Si, O and C were refined anisotropically, H atoms were calculated at ideal

positions). The isopropyl groups of compound **7** are heavily disordered, so these C atoms were refined isotropically with split sites and without determining H atoms. CCDC-819141 (for **1**), -819142 (for **2**), -819143 (for **3**), -819144 (for **4**), -819145 (for **6**), -819146 (for **7**) 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.

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