

Diphosphasilanes

Exploration of Novel α, ω -Substituted Diphosphatrisilanes by Combining Experimental Methods and DFT Calculations

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Abstract: The novel diphosphatrisilanes $\{(R_2P-Si(SiMe_3)_2)_2-SiMe_2\}$ [R = Ph, H] and the cyclophosphatrisilabutanes $\{R-PSi_3\}$ [R = H, SiMe_3] have been prepared via salt metathesis reactions between phosphanides and 2,4-dihalogenated pentasilanes and characterized via NMR spectroscopy. The experimental results were supported by DFT calculations. Although P–Si bond formation was observed in all cases, the outcome of the reactions varied depending on the nature of ligands on the phosphanides, forming either linear diphosphatrisilanes or cyclic

phosphatrisilacyclobutanes. DFT studies were performed to get a better understanding of the reactions. The precursor silanes were fully characterized using NMR spectroscopy and singlecrystal X-ray diffraction and offer interesting building blocks. In addition, a modified route for the synthesis of $P(TMS)_3$ was successfully carried out, achieving high yields of up to 73 %, circumventing the use of white phosphorus and phosphine gas during the reaction.

Introduction

 α, ω -phosphorus substituted diphosphanes have been literature known for many years. They are most commonly used as ligands for transition metal complexes such as their monophosphane counterparts.^[1,2] Due to the good electron donating properties of phosphorus, two different types of complexes can be formed. On the one hand ligands **A**, only offering lone pair interactions and on the other hand rare substituents **B** with the ability to form covalent bonds (see Figure 1) with the metal center in complexes.



Figure 1. Types of diphosphane and diphosphanide ligands used for transition metal complexes.

A huge discrepancy can be seen between the amount of known α, ω -diphosphanes with a carbon backbone and those containing a silicon backbone. Even with a very short backbone length of two silicon atoms, only 27 diphosphanes have been

Supporting information and OKCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejic.202000581. characterized, compared to around 70,000 carbon compounds. With an extended backbone length, only one diphosphasilane is known, $\{(PPh_2-SiMe_2)_2SiMe_2\}$,^[3] while there are still over 50,000 complexes for the carbon derivatives. This huge discrepancy can easily be explained by the far lower stability of the silicon compounds to hydrolysis and oxidization, the time-consuming pathway to synthesize useful silicon backbones, and the need for highly reactive phosphanide species to form Si–P bonds.

Nearly all known type **A** silicon ligands feature a [HRP-SiMe₂-]₂ core with R = Me, *i*Pr, Ph.^[4–6] One exception is the [Me₂P-SiMe₂-]₂ core which could be used as a ligand in the synthesis of a molybdenum compound.^[7] There is also one tetraphenylated diphosphasilane known, [Ph₂P-SiMe₂-]₂, synthesized by Hassler.^[3]

The addition of a boron moiety as a substituent on the phosphorus, led to an additional type **A** silicon ligand, $\{[(iPr_2N)_2B]PH-SiMe_2-\}_2,^{[8]}$ which was suitable for coordination as seen in a molybdenum tetracarbonyl complex $\{[(iPr_2N)_2B]PH-SiMe_2-\}_2Mo(CO)_4,^{[9]}$ Coordination of diphosphasilanes **B** is even less explored; cleavage of the hydrogen of [PhPH-SiMe_2-]_2 and subsequent reaction with transition metals led to cyclic compounds of the type $\{-SiMe_2-PPh-M-PPh-SiMe_2-\},^{[10,11]}$

Due to the steric shielding and stabilizing abilities of the trimethylsilyl (SiMe₃, TMS) group, it has been widely applied in main group 4 chemistry.^[12-14] In 2006, Hassler et al.^[15] reported the only diphosphane with the bulky hypersilyl (Si(SiMe₃)₃, Hyp) group on the phosphorus atom. Since then, much research in this field was performed by this working group. Recently, a new diphosphane with the bulky Hyp group could be obtained by Flock et al.,^[16] through coupling of two hypersilylphosphanes (tris(trimethylsilyl)silylphosphine) with tetramethyl-1,2-dichlorosilane (Figure 2).

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Figure 2. Diphosphasilanes synthesized by hypersilylphosphane coupling (R = H, Li, TMS).^[16]

Further expanding on the pathway used by Flock, a novel 2,4-dihydrogenated phosphapentasilane precursor (**7**) and a 2,4-dihalogenated phosphapentasilane precursor (**8**), containing three silicon atoms in the backbone, were synthesized (Figure 3). The usefulness of this precursor used as reaction partner with alkali metal phosphanides to form novel α , ω -phosphorus substituted diphosphanes will be highlighted. These diphosphanes, depending on their phosphorus substituents, may act as either type **A** donating ligand (**12**) or be stepwise transformed into a type **B** substituent with the ability to form covalent bonds to metals (**9**, **11**). The trimethylsilyl (TMS) substituted compound **11** additionally offers the possibility of a direct bond formation with metal halides due to TMS-CI cleavage.^[17]



Figure 3. Synthetic pathway leading to 9,11 and 12.

In addition, we report the optimization of modified synthetic pathways leading to the known 1,1,1,3,3,5,5,5-octamethyl-2,2,4,4-tetrakis-(trimethylsilyl)-pentasilane^[18] and tris-(trimethyl-silyl)phosphine. All the work is supported by DFT calculations to aquire NMR data as well as structural properties of minimum structures. In addition, the spatial arrangement of the calculated minima structures of the compounds will be compared with the single-crystal X-ray structures of the novel 2,4-dihydro-and dichloropentasilanes (**7**, **8**).

Results and Discussion

In order to synthesize the novel 1,3-difunctionalized diphosphapentasilanes, several precursors were prepared (Figure 3). The reaction pathway from **1** to **5** is literature known.^[18] In this route to **5**, gaseous hydrogen bromide is used to convert the phenylated trisilane **3** to the bromide. This halide was further combined with a second Hyp potassium anion **2** to finally synthesize the pure pentasilane **5** in a salt metathesis reaction. However, we used an alternative approach reacting **3** with triflic acid under mild reaction conditions (0 °C) converting **3** to the triflic adduct, a species first mentioned by Maas et al. in 1989.^[19] The full conversion to **4** could be confirmed with ²⁹Si NMR, which shows a significant change of the signal of the silicon atom connected to the end group from –13.4 ppm for the phenylated up to 56.4 ppm for the triflic species. The reaction of **4** with one equivalent of **2** was performed at –78 °C in toluene with formation of a high amount of potassium triflate precipitate. After aqueous workup and evaporation of the solvent, **5** could be isolated as a colorless waxy substance, which was then further purified by crystallization from ethanol and ethyl acetate, which yielded colorless air stable crystals. Both the crystal structure and the NMR spectra confirm the formation of **5** and correlate to published values.^[18]

Subsequently, the reaction of **5** with two equivalents of KO'Bu was reported by Marschner^[20] using THF as a solvent and reaction temperatures of 60 °C with a reaction time of more than 20 hours. However, by changing the solvent to DME, we found a significant decrease of reaction time (2 h for the mono-anionic species) at room temperature. The formation of the pure dianionic species **6** takes much longer to complete, up to 36 hours for full conversion, which could also be monitored with ²⁹Si NMR spectroscopy.

The conversion of 6 to the yet unknown dihydride 7 was achieved using aqueous degassed sulfuric acid. After extraction of the silane with diethyl ether, the combined organic phases were dried over sodium sulfate. The product remained as a white waxy residue which could be further purified through crystallization from acetone at -30 °C yielding white crystals. Xray and NMR spectroscopy could confirm the formation of the pure dihydride (Figure 4, Table 1). While the bond lengths are in the average range for silanes, the very interesting part of the structure is the orientation of the two hydrogen atoms connected to silicon 1 and 3 with both being on the same side of the silane chain. This behavior is owed to the bulky trimethylsilvl groups on the backbone. To support the experimental data, DFT calculations were performed using mPW1PW91/6-31+G* for the optimization and mPW1PW91/IGLO-II for the calculation of the NMR shifts. Seven different minimum structures were located, with the global minimum matching the crystal structure of 7. The calculated NMR shifts compare well to the experimental values (Table 1).



Figure 4. Crystal structure for 7. All non-hydrogen atoms shown as 30 % shaded ellipsoids.

The chlorination reaction to yield **8** was performed using several chlorination techniques. The first attempt was the standard procedure, using $CCl_4^{[21]}$ as a chlorination agent. After stir-



Table 1. Comparison of experimental and mPW1PW91/IGLO-II// mPW1PW91/ 6-31+G* calculated ²⁹Si NMR shifts and average bond lengths of **7** and **8**.

	δ ²⁹ Si exp.	δ $^{\rm 29}{\rm Si}$ calcd.	Bond ^[a]	Exp. [Å]	Calc. [Å]
7	–11.1 ppm –35.9 ppm –109.4 ppm	–10.9 ppm –29.5 ppm –107.7 ppm	Si-Si Si-C Si-H	2.346(8) 1.876(3) 1.42(2)	2.366(2) 1.897(3) 1.50(1)
8	–8.7 ppm –10.4 ppm –27.2 ppm	4.6 ppm -8.9 ppm -24.2 ppm	Si-Si Si-C Si-Cl	1.40(2) 2.354(5) 1.873(2) 2.119(8) 2.1087(5)	2.377(6) 1.892(2) 2.146(9)

[a] Average bond lengths.

ring the reaction mixture for 24 h at room temperature with excess of CCl_4 , no reaction could be observed. To accelerate the reaction, the mixture was heated to reflux and stirred for another 24 h. A mixture of several short chain silanes and hexachloro ethane were obtained as a consequence of the increased temperature and the radical mechanism of this chlorination route, which induced chain cracking and the coupling of two CCl_3 radicals.

The second approach focused on using TCCA (trichloroisocyanuric acid) as a chlorination agent.^[22] The reaction was performed in THF at -30 °C with 0.66 equivalents of TCCA. The NMR spectra showed formation of the desired dichloride, however no full conversion could be obtained and the separation of the resulting mixture containing cyanuric acid, mono- and di-chloride and some starting product was not possible.

The third approach was based on a strategy published by Dobrovetsky and Chulsky in 2017.^[23] Gaseous hydrogen chloride was used as a chlorination agent and tris(pentafluorophenyl)borane added as a catalyst. The reaction was performed in toluene and at different temperatures from 20 °C down to -80 °C, but no product formation could be observed. This might be explained with the steric shielding of the two TMS groups preventing the formation of the respective transition structure.

The route that provided the best yields and lowest number of side products was employing phosphorus pentachloride^[24] as a reactant. The starting material was dissolved in DME (1,2dimethoxyethane) and stirred in a 40 °C water bath. Thereafter, two equivalents of phosphorus pentachloride were slowly added. This exothermic reaction induced a color change from colorless to a yellow solution. The reaction mixture was stirred for 24 h to achieve nearly full conversion to the novel dichloride, 8. After removal of the non-dissolved residues by filtration through celite and evaporation of the solvents and phosphorus trichloride, colourless crystals of 8 could be obtained out of DME at -30 °C. (Figure 5, Table 1). The structure is again in accordance with the global minimum calculated by mPW1PW91/6-31+G* (Table 1). In addition, the calculated NMR shifts match the experimental ones, with the largest difference observed at the silicon atoms connected to the chloride, due to the neglect of relativistic effects.^[25,26] Even after substitution of the two hydrogens from 7 with the far larger chloride atoms, the orientation of the two atoms stays quite similar, as can be demonstrated by the comparison of the torsion angles shown in Table 2.



Figure 5. Crystal structure for ${\bf 8}$. All non-hydrogen atoms shown as 30 % shaded ellipsoids.

Table 2. Comparison of experimental and mPW1PW91/6-31+G* calculated torsion angles of $\pmb{7,8,9},$ and $\pmb{12}.$

	Exp. 7 ^[a]	Calc. 7 ^[a]	Exp. 8 ^[b]	Calc. 8 ^[b]	Calc. 9 ^[c]	Calc. 12 ^[d]
R1-Si1-Si2-Si3	65.6 °	71.8 °	54.9 °	79.6 °	28.2 °	45.4 °
R2-Si3-Si2-Si1	55.3 °	43.6 °	50.3 °	50.3 °	38.6 °	48.0 °

[a] R = H. [b] R = CI. [c] $R = PH_2$. [d] $R = PPh_2$.

For the reactions towards the diphosphasilanes 9, 11 and 12, three different phosphanides were added to the dichloride (Figure 6). To get an idea of the influence on the reaction behaviour of the different substituents of the phosphorus (PR₂), the reaction was first performed with a R = H, followed by the reaction with the larger $R = SiMe_3$ and finally the aromatic R =Ph. The reaction yielding 9 was similar to the coupling of Hyp chloride with sodium phosphide, first reported by Hassler et al..^[15] Sodium phosphide and the dichloride 8 were both dissolved in THF. The dichloride solution was then added to the phosphide solution. Immediate gas formation could be observed and a color change of the former yellow solution to orange took place. The solvent was then evaporated, and the remaining orange oil was dissolved in diethyl ether. After 20 h, a white solid (NaCl) dissipated from the light orange solution. The liquid phase was then transferred into a separate vessel via filtration which led to a clear orange solution. The solvent was evaporated, and the product remained as a yellow oil.



Figure 6. Reaction schemes for 9, 11, and 12.

The ³¹P NMR spectra showed that only the desired product **9** formed, but the conversion was not complete. The phosphorus shifts of **9** [-260.1 ppm, t, (¹J_{PH} = 181.2 Hz)] are in the same region as the literature known ones for hypersilyl phosphane [-265.4 ppm, t, (¹J_{PH} = 178.7 Hz)].^[15] The ²⁹Si NMR



showed a doublet at –98.8 ppm with a coupling of 46.4 Hz. This is comparable with the Si shift and coupling of Hyp phosphane [-102.4 ppm, *d*, (${}^{1}J_{PH} = 46.7$ Hz)]..^[15] The structural orientation discussed for **7** and **8** prevails in **9** making it an ideal bidentate ligand for metal complexes. To improve the yield of **9**, the reaction mixture was refluxed for 96 hours. However, during this time, we could see a different reaction taking place, which also explained the high amount of phosphine observed. Instead of an improved yield of **9**, the formerly unknown phosphatrisilacyclobutane **13** formed through cleavage of one Si-P bond followed by an intramolecular ring closure and the generation of one phosphine molecule (Figure 7).



Figure 7. Pathway leading to 13.

There is just one similar compound known published by van Hänisch in 2007^[4] carrying isopropyl substituents on the silicon atoms. The resulting phosphorus shift of **13** [-301.1 ppm, d, (¹J_{PH} = 160.3 Hz)] matches the calculated value for the cyclic phosphasilane, listed in Table 3. Further workup was not possible due to the small amount of product (<0.2 g). Separation should be possible with fractionate sublimation and will be the aim of future work.

Table 3. Comparison of experimental and mPW1PW91/IGLO-II//mPW1PW91/ 6-31+G* calculated ^{29}Si and ^{31}P NMR chemical shifts of 9 and 13.

	δ $^{\rm 29}{\rm Si}$ exp.	δ $^{\rm 29}{\rm Si}$ calcd.	δ ^{31}P exp.	δ ^{31}P calcd.
9	–98.8 ppm –26.9 ppm –9.3 ppm	–96.7 ppm –25.4 ppm –8.7 ppm	–260.1 ppm	–272.6 ppm
13	–63.6 ppm –11.0 ppm –9.8 ppm	–63.8 ppm –8.2 ppm –2.3 ppm	–301.1 ppm	–310.3 ppm

The orientation and capability for steric shielding of compound **9** offers use as a protecting ligand to transition metals, which is poorly investigated due to **9** being only the second reported diphosphatrisilane.

Towards the synthesis of **11**, a necessary challenge was the preparation of tris(trimethylsilyl)phosphine, $P(TMS)_3$, **10**. **10** is highly flammable and pyrophoric (self-igniting), highly problematic to handle and commonly known to be difficult to synthesize. The synthesis of **10** had typically been done with white phosphorus, which is not only toxic and pyrophoric, but also, commercially hard to come by. In combination with the aforementioned disadvantages, the unavoidable formation of hazardous phosphine gas during reactions, renders this method highly unattractive.

Reactions involving phosphorus allotropes as starting materials typically require the presence of an alkali metal reducing agent. First reported by Peterson and Gamble^[26] in 1968, the naphthalene supported reduction of white and red phosphorus was done in the presence of alkali metal alloys to yield M_3P (M = Li, Na, K). Other examples include the formation of (Na/ K)₃P from sodium/potassium alloy and white phosphorus published by Becker,^[27] and the metalation of PH₃ with phenyllithium yielding Li₃P published by Issleib and Tzschach.^[28] Recent results published by Grützmacher^[29] have shown that red phosphorus can also be reacted under mild conditions in the presence of naphthalene with sodium in DME to get good yields of Na₃P. Subsequently, M₃P was treated with trimethylsilyl chloride to afford pure P(TMS)₃.^[26]

Encouraged by the work of Grützmacher, we reduced red phosphorus in the presence of 10 mol-% of naphthalene and sodium in DME, keeping the reaction mixture under reflux for 20 h. This resulted in near full conversion to trisodium phosphanide (Na₃P) as a black suspension. After removal of the naphthalene and further reaction of Na₃P with freshly distilled TMS-CI, followed by another 20 h of reflux, the resulting P(TMS)₃ **10** was isolated in yields of up to 75 %. The purity of the product was determined by ¹H, ³¹P and ²⁹Si NMR spectroscopy, with all shifts matching literature known values.^[30] In sum, this modified route is an effective, safer, high yielding pathway for the synthetically useful and important P(TMS)₃ **10**.

For the attempted synthesis of diphosphatrisilane 11, freshly prepared bis(trimethylsilyl)potassium-phosphanide (P(TMS)₂K) was treated with dichlorotrisilane 8. In this case, the dichloride was dissolved in DME and cooled to -50 °C, thereafter 2.1 equivalents of P(TMS)₂K dissolved in DME were added dropwise with a syringe under vigorous stirring. The solution turned from light yellowish to orange and a white precipitate could be observed. After filtration of the solution and evaporation of the volatiles, a colorless oil remained, which was then investigated with ³¹P and ²⁹Si NMR spectroscopy. This showed a 50:50 mixture of one product species and P(TMS)₃. (remaining P(TMS)₃ was removed under vacuum to afford clean product species) The theoretical calculations for the expected acyclic product **11** did not match the experimental values (Table 4), and the splitting pattern was not indicative for a linear diphosphatrisilane. Instead of the expected triplet signal for the central silicon atom in **11**, four pairs of doublet signals were found in the ²⁹Si spectra. This points to an intramolecular ring formation to 11a (Figure 8, Table 4).

Table 4. Comparison of experimental and mPW1PW91/IGLO-II // mPW1PW91/ $6-31+G^*$ calculated ²⁹Si and ³¹P NMR chemical shifts of **11**, **11a**, and **15**.

	δ $^{\rm 29}{\rm Si}$ exp.	δ $^{\rm 29}\text{Si}$ calcd.	δ ^{31}P exp.	δ ^{31}P calcd.
11		–76.2 ppm –13.8 ppm –8.9 ppm 6.4 ppm		–270.9 ppm
11a	-56.8 ppm -13.7 ppm -10.6 ppm 3.8 ppm	–50.8 ppm –9.3 ppm –6.0 ppm 7.4 ppm	–290.4 ppm	–291.7 ppm
15 ^[4]	–1.7 ppm 9.2 ppm 13.4 ppm	–0.4 ppm 4.1 ppm 10.9 ppm	–237.2 ppm	–236.5 ppm



Figure 8. Pathway leading to 11a.



In contrast to the preparation of **9**, the target acyclic diphosphane **11** is never observed in NMR. This suggests that the acylic, PH_2 -substituted product **9** is more stable than **11**. For a better understanding of the differences between these reactions, the reaction enthalpies for both were calculated. In the case of the reaction from **9** leading to the cyclic compound **13** (Figure 7), the resulting reaction enthalpy ($H_r = H_{products} - H_{educts}$) is +25.3 kJ/mol, indicating the inherent stability of **9**. The proposed reaction path (including transition states) leading to **13** is shown in Figure 9 on a simplified model exchanging the methyl groups at silicon with hydrogen.



Figure 9. Proposed reaction path leading to 13.

Starting from the acyclic diphosphane, a rather high initial energy barrier of 180 kJ/mol has to be overcome for the H transfer in gas phase. From there, an intermediate is reached with a barrier of only 30 kJ/mol for ring closure and evolution of PH_3 gas, which acts as driving force for this reaction.

The reaction enthalpy for the formation of the comparable silane published by van Hänisch,^[4] is -9.8 kJ/mol, which offers an explanation why they cannot detect the disubstituted silane during the experiment. However, the calculated reaction enthalpy from the acyclic silane **11** to **11a** (Figure 8) is -99.2 kJ/mol, explaining why not **11**, but only the direct conversion product **11a** is observed in the NMR spectra.

Removal of P(TMS)₃ under vacuum and heat resulted in formation of small amounts (\approx 10 %) of **13** (see Supporting information). Attempts to isolate **11a** and **13** were unsuccessful. Table 4 shows the comparison of the calculated and experimental NMR chemical shift values of **11a** and the silane reported by van Hänisch (**15**; (*i*Pr₂Si)₃PSiMe₃; Figure 10).^[4] The calculated and experimental ³¹P and ²⁹Si NMR chemical shifts for **11a** compare nicely.

A difference of \approx 50 ppm is observed in the experimental and calculated ³¹P NMR between **11a** and (*i*Pr₂Si)₃PSiMe₃ (Figure 10), caused by the substituents on the silyl backbone.



Figure 10. Structure of ((*i*Pr₂Si)₃PSiMe₃).^[4]

For the reaction yielding the third stable diphosphatrisilane 12, diphenyl-lithium phosphanide was treated with dichloride 8. In this case, the phosphanide was dissolved in DME and cooled to -50 °C. A solution of the dichlorosilane 8 in DME was then added dropwise, which resulted in an immediate color change of the former light yellowish solution to a dark red. After stirring the resulting mixture for at least 20 hours, the solution turned nearly colorless. The resulting trisilane 12 could be confirmed with ³¹P and ²⁹Si NMR and compared to the so far only stable diphosphatrisilane (14) reported by Hassler in 1988^[3] (see Figure 11). Due to hydrolysis of the phosphanide and the very small amount of reactants used, only 40 % of the dichloride 8 could be converted to 12. Further improvement of the reaction conditions is ongoing. After evaporation of the volatile components, a nearly colorless waxy substance remained.



Figure 11. Comparison of 14 and 12.

While in both cases the signal of the central silicon appears as a triplet in the ²⁹Si NMR spectra, the range of the shifts differs substantially due to the different silicon substitution pattern. The full list of observed and calculated NMR shifts can be found in Table 5. Another interesting point is the comparison of the torsion angles with the other trisilane species (Table 2). Even with the large phenyl substituents, the orientation of the two phosphorus groups indicates a good possibility to act as a protecting type **A** ligand towards transition metals. First test reactions are encouraging and the use of these diphosphanes in transition metal and main group metal chemistry are part of our ongoing research.

Table 5. Comparison of experimental and mPW1PW91/IGLO-II calculated $^{29}{\rm Si}$ and $^{31}{\rm P}$ NMR chemical shifts of 12 and 14.

	δ ²⁹ Si exp.	δ ²⁹ Si calcd.	δ ³¹ P exp.	δ ^{31}P calcd.
12	–79.4 ppm –24.9 ppm	–74.5 ppm –18.1 ppm	–49.2 ppm	–37.2 ppm
14	–8.5 ppm –39.8 ppm –16.6 ppm	–8.1 ppm –41.0 ppm –19.4 ppm	–54.6 ppm	–55.4 ppm

Conclusion

The presented modified routes leading to the protected pentasilane (**5**) and $P(TMS)_3$ (**10**) offer simple, high yielding pathways for needed precursor molecules. Especially, the pathway to $P(TMS)_3$ has several advantages compared to most known routes, such as high yield and no use of either white phos-



phorus or phosphine gas. The novel 2,4-dihydrido- and dichloropentasilanes (**7**, **8**) are new powerful synthetic building blocks not only for the synthesis of the protected 2,4-diphosphapentasilanes, but also opening pathways to polycondensation and further functionalization reactions. The rare 2,4-diphosphapentasilanes themselves offer similar use as transition metals ligands as their carbon analogues and could offer a large variety of interesting properties for metalorganic chemistry. Their application as ligands in transition metal and main group metal chemistry is currently tested.

All ³¹P and ²⁹Si experimental NMR shifts, as well as the structural parameters of the single crystal X-ray characterized compounds, perfectly match the DFT calculated data.

A demonstrative example where DFT calculations proved invaluable was the elucidation of the reaction pathways and conditions leading to **9,11a** and **13**, as no comparable NMR data was known so far. With the help of the calculations we were able to confirm the unexpected ring closure reactions, by comparison of the calculated NMR shifts and enthalpies of formation.

This demonstrates the advantages of combining experimental characterization techniques and theoretical DFT calculations when performing novel synthetic chemistry in order to provide the best information regarding reaction pathways, synthetic conditions, product formation and characterization.

Experimental Section

General Procedures

All reactions, unless otherwise stated, were carried out using either standard Schlenk line techniques or in a glovebox under nitrogen atmosphere. All dried and deoxygenated solvents were obtained from a solvent drying system (Innovative Technology, Inc.). C₆D₆ was distilled from sodium and stored under nitrogen atmosphere. nButyllithium and potassium tert-butylate were purchased from Aldrich and used as delivered. Alkaline compounds, such as the reported phosphanides, were already described before to be extremely reactive, and immediate decomposition at room temperature is very likely.^[31] Compounds 1-3 were prepared using the reported pathway.^[18] Bis(trimethylsilyl)potassium phosphanide and diphenyl-lithium phosphanide were prepared according to literature known routes.[31,32] The purity of all reported compounds was established by the absence of impurities, detected by NMR measurement for all nuclei (1H, 13C, 29Si, and 31P NMR). Melting point measurements were carried out by threefold determination with a Stuart Scientific SMP 50 (up to 400 °C).

Computational Details

All calculations have been carried out using the Gaussian09 program package^[33] on a computing cluster with blade architecture. For all calculations, the mPW1PW91 hybrid functional^[34] was used. For geometry optimizations and the subsequent calculation of vibrational frequencies, the 6-31+G* basis set^[33] was used. For the calculation of all magnetic shieldings the IGLO-^[35]II basis set was applied. PH₃ and tetramethylsilane, both optimized at the same level of theory, were used as references for NMR chemical shifts with a magnetic shielding o³¹P 581.7 (correction factor to H₃PO₄ -266.1)^[36] and 352.2 for ²⁹Si.

NMR

¹H (300.2 MHz), ¹³C (75.5 MHz), ²⁹Si (59.6 MHz) and ³¹P (121.5 MHz) NMR spectra were recorded on a Mercury 300 MHz spectrometer from Varian at 25 °C. Chemical shifts are given in parts per million (ppm) relative to TMS ($\delta = 0$ ppm) regarding ¹H, ¹³C, and ²⁹Si and relative to 85 % H₃PO₄ in the case of ³¹P. Coupling constants (*J*) are reported in Hertz (Hz).

Single Crystal X-ray Crystallography

All crystals suitable for single-crystal X-ray diffractometry were removed from a vial or a Schlenk and immediately covered with a layer of silicone oil. A single crystal was selected, mounted on a glass rod on a copper pin, and placed in the cold N₂ stream provided by an Oxford Cryosystems cryostream. XRD data collection was performed for compounds 7 and 8, on a Bruker APEX II diffractometer with use of an Incoatec microfocus sealed tube of Mo- K_{α} radiation (λ = 0.71073 Å) and a CCD area detector. Empirical absorption corrections were applied using SADABS or TWINABS.^[37,38] The structures were solved with use of the intrinsic phasing option in SHELXT and refined by the full-matrix least-squares procedures in SHELXL.^[39–41] The space group assignments and structural solutions were evaluated using PLATON.^[42,43] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in calculated positions corresponding to standard bond lengths and angles. Disorder was handled by modeling the occupancies of the individual orientations using free variables to refine the respective occupancy of the affected fragments (PART).^[44] Disordered positions for the carbon positions in a terminal -SiMe₃ moiety in compound 8 were refined using 60/40 split positions. All crystal structures representations were made with the program Diamond^[45] with all nonhydrogen atoms displayed as 30 % ellipsoids, see Table 1.

Supporting Information contains crystallographic data and details of measurements and refinement for compounds **7** and **8**.

Deposition Numbers 2004732 (for **7**) and 2004733 (for **8**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Synthesis

Synthesis of 1,1,1,3,3-Pentamethyl-2,2-bis(trimethylsilyl)-trisilyl-trifluoromethanesulfonate (4): 7.5 g (19.6 mmol) of **3** were dissolved in 30 mL of toluene and cooled to 0 °C with an ice bath. Under vigorous stirring, 1.8 mL (20.4 mmol) of triflic acid were added dropwise with a syringe. The former colorless clear solution turned turbid yellowish. After evaporation of the volatile compounds, 8.9 g (19.5 mmol 99 %) of a white waxy solid remained. ¹H NMR (300 MHz, [C₆D₆]): δ = 0.18 (s, 27H; TMS), 0.59 (s, 6H; Ch₃); ¹⁹F NMR (300 MHz, [C₆D₆]): δ = -77.60 (s; CF₃); ¹³C NMR (75 MHz, C₆D₆): δ = 1.82 (s; TMS), 4.81 (s; CH₃), 118.56 ppm (q, ¹J_{C,F} = 317.1 Hz; CF₃); ²⁹Si NMR (59.6 MHz, C₆D₆): δ = 56.6 (s; Si-OTrif), -10.4 (s; TMS), -133.5 ppm (s; Si(SiR)₄).

Synthesis of 1,1,1,3,3,5,5-Octamethyl-2,2,4,4-tetrakis(trimethylsilyl)-pentasilane (5): 8.9 g (19.6 mmol) of **4** were dissolved in 10 mL of toluene and cooled to -78 °C. Then 6.2 g (21.56 mmol) of freshly prepared hypersilyl potassium **2** were dissolved in 10 mL of toluene and added dropwise to **4**. Immediately, a white solid crashed out of the colorless solution. After stirring at room temperature for 20 h, the solution was poured onto 100 mL of an ice cooled 1 M H₂SO₄ solution and extracted 3 times with Et₂O. After drying over Na₂SO₄, filtration, and evaporation of the volatile compounds, a white waxy substance remained, which could further be purified



by recrystallization from EtOH/EtAc at -30 °C to yield 6.5 g (11.8 mmol 60 %) of colorless crystals. (mp: 171–172 °C) ¹H NMR (300 MHz, $[C_6D_6]$): $\delta = 0.36$ (s, 54H; TMS), 0.63 (s, 6H; Ch₃); ¹³C NMR (75 MHz, C_6D_6): $\delta = 4.2$ (s; TMS), 6.1 (s; CH₃); ²⁹Si NMR (59.6 MHz, C_6D_6): $\delta = -9.7$ (s; TMS), -26.3 (s; -Si(Me₂)-TMS), -119.0 ppm (s; Si(SiR)₄).

Synthesis of 1,1,1,3,3,5,5,5-Octamethyl-2,4-bis(trimethylsilyl)penta-2,4-dipotassium-disilanide (6): 5.0 g (9.0 mmol) of 5 were combined with 2.2 g of KO^tBu in a Schlenk vessel and 20 mL of DME were added. The color of the solution turned yellow and was kept stirring for another 40 hours at room temperature during which the color changed to dark green. After removal of the volatile compounds, 4.4 g (9.0 mmol 99 %) of a dark green waxy substance remained. ¹H NMR (300 MHz, [C₆D₆]): δ = 0.62 (s, 36H; TMS), 0.97 (s, 6H; Ch₃); ¹³C NMR (75 MHz, C₆D₆): δ = 8.1 (s; TMS), 10.5 (s; CH₃); ²⁹Si NMR (59.6 MHz, C₆D₆): δ = -5.8 (s; TMS), -17.9 (s; -Si(Me₂)-TMS), -168.9 ppm (s; Si(SiR)₄).

Synthesis of 1,1,1,3,3,5,5,5-Octamethyl-2,4-bis(trimethylsilyl)pentasilyl-2,4-dihydride (7): 4.4 g (9.0 mmol) of 6 were dissolved in 20 mL of toluene and transferred with a cannula onto 100 mL of a 1 m solution of degassed ice cooled H₂SO₄. The color of the solution changed from green to grey and was extracted three times with Et₂O. After drying over Na₂SO₄, filtration, and evaporation of the volatile compounds, a colorless oil remained, which could further be purified by recrystallization from acetone at -30 °C to yield 2.2 g (5.4 mmol 60 %) of colorless air sensitive crystals. ¹H NMR (300 MHz, [C₆D₆]): δ = 0.26 (s, 36H; TMS), 0.45 (s, 6H; Ch₃), 2.67 (s, 2H; Si-H); ¹³C NMR (75 MHz, C₆D₆): δ = -11.2 (s; TMS), -36.0 (s; -Si(Me₂)-TMS), -109.4 ppm (s; Si(SiR)₄).

Synthesis of 1,1,1,3,3,5,5,5-Octamethyl-2,4-bis(trimethylsilyl)pentasilyl-2,4-dichloride (8): 2.2 g (5.0 mmol) of 7 were dissolved in 15 mL of DME and stirred in a 40 °C water bath. Subsequent addition of 2.2 g (10.0 mmol) of PCl₅ led to a gas formation and an immediate color change from colorless to yellow. After further stirring for 20 h at room temperature, the volatile compounds were evaporated, yielding 2.35 g (4.9 mmol 97.6 %) of a yellowish oil, which could further be purified by recrystallization from DME at -30 °C to yield colorless air sensitive crystals. ¹H NMR (300 MHz, $[C_6D_6]$): $\delta = -2.1$ (s; CH₃), -0.26 (s; TMS); ²⁹Si NMR (59.6 MHz, C_6D_6): $\delta = -8.83$ (s; Si-Cl), -10.4 (s; TMS), -27.3 ppm (s; -Si(Me₂)-).

Synthesis of 1,1,1,3,3,5,5,5-Octamethyl-2,4-bis(trimethylsilyl)pentasilyl-2,4-diphosphine (9): 0.44 g (0.92 mmol) of 8 were dissolved in 5 mL of THF and transferred into a nitrogen drybox. Thereafter, 0.21 g (2.02 mmol) of DME complexed NaPH₂ were dissolved in 5 mL of THF and added dropwise to the dichloride. An immediate color change from yellow to orange and a rise of temperature could be observed. After removal of the volatile compounds, a yellowish solid remained, which was further purified through addition of Et₂O and filtration of salts. The product remains combined with unreacted 8 as a yellowish oil. ¹H NMR (300 MHz, [C₆D₆]): $\delta = 0.30$ (s, 36H; TMS), 0.47 (s, 6H; Ch₃) , 1.35 (s, 4H; PH₂); ¹³C NMR (75 MHz, C₆D₆): $\delta = -0.04$ (s; TMS), 1.25 (s; CH₃); ²⁹Si NMR (59.6 MHz, C₆D₆): $\delta = -9.3$ ppm (d, ²J_{SIP} = 7.8 Hz; TMS-Si), -26.9 ppm (t, ²J_{SIP} = 13.6 Hz; P-Si-Si-Si-P), -98.8 ppm (d, ¹J_{SIP} = 48.2 Hz; -Si-Si-P); ³¹P NMR (121.5 MHz, C₆D₆): $\delta = -260.1$ (t; ¹J_{PH} = 181.6 Hz; PH₂).

Synthesis of Tris(trimethylsilyl)phosphine (10): 18.98 g (1.8 mol) of red phosphorus was brought into a 2 L three-necked flask connected to a mechanical stirrer and a reflux condenser and a bubbler.

1 L of dry DME were transferred to the phosphorus and 7.69 g (0.06 mol) of naphthalene were added. Under vigorous stirring, 41.36 g (1.8 mol) of sodium were added to the red reaction mixture and the mixture was kept under reflux for 20 h during which the suspension turned black. After separation of the solution and the black solid, the Na₃P was dried and afterwards dispersed in 500 mL of DME. 254 mL (2 mol) of freshly distilled TMS-Cl was brought into a dropping funnel and mixed with 300 mL of DME. This solution was added under vigorous stirring to the Na₃P dispersion. The reaction mixture got viscous and the color changed to light grey. The reaction mixture was then kept under reflux for 20 h. Then, solvent and P(TMS)₃ were separated from the salt with a filter cannula and the remaining salts were washed with 400 mL of pentane to extract all of the product. After removal of the volatile components, a dark yellow to brown viscous mass remained, which could be purified through vacuum distillation yielding 128 mL (0.44 mol) of a colorless liquid (73 %). ¹H NMR (300 MHz, $[C_6D_6]$): $\delta = 0.23$ (s, 27H; CH₃); ²⁹Si NMR (59.6 MHz, C₆D₆): $\delta = -2.78$ (d, ¹J_{SiP} = 27.5 Hz; TMS); ³¹P NMR (121.5 MHz, C_6D_6): $\delta = -252.4$ (s).

Synthesis of 3,3-Dimethyl-1,2,2,4,4-pentakis(trimethylsilyl)phosphatrisilacyclobutane (11a): 0.39 g (0.81 mmol) of 8 were dissolved in 5 mL of DME and cooled to -50 °C. Then 0.35 g (1.62 mmol) of freshly prepared bis(trimethylsilyl)potassium phosphanide dissolved in 3 mL of DME were added dropwise to the dichloride. An immediate color change from orange to a cloudy yellow solution occurred and the solution was stirred for another 20 hours at room temperature. After removal of the salts though Celite filtration and removal of the volatile compounds, 0.33 g (0.65 mmol 80 %) of a yellowish oil remained. ¹H NMR (300 MHz, $[C_6D_6]$: $\delta = 0.33$ (s, 45H; TMS), 0.49 (s, 6H; Ch₃); ¹³C NMR (75 MHz, C_6D_6): $\delta = 1.84$ (s; TMS-Si), 2.04 (s; TMS-P), 3.33 (s; CH₃); ²⁹Si NMR (59.6 MHz, C_6D_6): δ = 3.83 (d, ${}^{1}J_{SiP}$ = 45.4 Hz; TMS-P), -10.66 (d, ${}^{2}J_{SiP}$ = 15 Hz; TMS-Si), -13.7 ppm (d, ${}^{2}J_{SiP}$ = 18.0 Hz; -Si(Me₂)-), -56.8 ppm (d, ${}^{1}J_{SiP}$ = 51.8 Hz; Si(Si₃)-P; ${}^{31}P$ NMR (121.5 MHz, C_6D_6): $\delta = -290.46$ (s; PSi₃).

Synthesis of 1,1,1,3,3,5,5,5-Octamethyl-2,4-bis(trimethylsilyl)pentasilyl-2,4-diphenyl-diphosphine (12): 0.13 g (0.465 mmol) of diphenyl-lithium phosphanide were dissolved in 5 mL of DME and cooled to -50 °C. Then 0.11 g (0.232 mmol) of 8 dissolved in 1 mL of DME were added dropwise to the dichloride. An immediate color change from red to a yellowish solution occurred and the solution was stirred for another 20 hours at room temperature, thereafter the solution was nearly colorless. After removal of the volatile compounds, 0.25 g (0.32 mmol 30 %) of a colorless oil remained. ¹H NMR (300 MHz, $[C_6D_6]$): $\delta = 0.20$ (s, 36H; TMS), 0.62 (s, 6H; Ch₃), 7.60 (m, 20H; Ph); ¹³C NMR (75 MHz, C_6D_6): δ = 0.01 (s; TMS-Si), 2.48 (s; CH₃), 128.15 (d, ${}^{1}J_{CH}$ = 25.2 Hz; =CH-), 135.70 (d, ${}^{1}J_{CH}$ = 19.66 Hz; = CH-), 137.82 (d, ¹J_{CH} = 21.09 Hz; =CH-); ²⁹Si NMR (59.6 MHz, C_6D_6): $\delta = -8.6$ (d, ${}^2J_{SiP} = 2.8$ Hz; TMS-Si), -24.9 (t, ${}^2J_{SiP} = 37.4$ Hz; -Si(Me₂)-), -79.4 ppm (d, ¹J_{SiP} = 83.6 Hz Si(Si₃)-P; ³¹P NMR (121.5 MHz, C_6D_6): $\delta = -49.2$ (s; PPh₂Si).

Synthesis of 3,3-Dimethyl-2,2,4,4-tetrakis(trimethylsilyl)-phosphatrisilacyclobutane (13): 0.48 g (0.81 mmol) of a mixture of **8** and **9** were dissolved in 3 mL of benzene and kept under reflux for 72 hours. After removal of the salts though Celite filtration and removal of the volatile compounds, 0.05 g (0.11 mmol 14 %) of a yellowish oil remained. ¹H NMR (300 MHz, [C₆D₆]): δ = 0.32 (s, 36H; TMS), 0.51 (s, 6H; Ch₃), 0.91 (s, 1H; PH); ¹³C NMR (75 MHz, C₆D₆): δ = 1.19 (s; TMS-Si), 2.47 (s; CH₃); ²⁹Si NMR (59.6 MHz, C₆D₆): δ = -9.8 (d, ²J_{SIP} = 4.0 Hz; **TMS**-Si), -11.0 (d, ²J_{SIP} = 4.1 Hz; Si-Si-Si), -63.6 (d, ¹J_{SIP} = 35.7 Hz; P-Si); ³¹P NMR (121.5 MHz, C₆D₆): δ = -301.0 (d; ¹J_{PH} = 160.4 Hz; PH).



Keywords: Phosphorus · Silanes · Structure elucidation · Synthesis design · Ab initio calculations

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