Stefan Mueller, MSc

Tetrylenes: An experimental and quantum chemical investigation on low-valent group 14 compounds and their precursors

DOCTORAL THESIS

to achieve the university degree of

Doktor der technischen Wissenschaften

submitted to

Graz University of Technology

Supervisor

Assoc.Prof. Dipl.-Ing. Dr.techn. Michaela Flock

Institute for Inorganic Chemistry

Graz, January 2015

AFFIDAVIT

I declare that I have authored this thesis independently, that I have not used other than the declared sources/resources, and that I have explicitly indicated all material which has been quoted either literally or by content from the sources used. The text document uploaded to TUGRAZonline is identical to the present doctoral thesis.

Date

Signature

You can use facts to prove anything that’s even remotely true. - Homer

Abstract

Tetrylenes are compounds containing a divalent group 14 element in the oxidation state of +II. Stabilization of these else highly reactive species is achieved by steric effects and/or electron donating moieties. While compounds with nitrogen in α,α' position are common in literature, corresponding P,P' derivatives are scarce. All of the diphosphatetrylenes reported so far feature an aromatic moiety in the ligand. With its high sterical demand, supermesitylphosphane (2,4,6-tris(*t*-butyl)phenyl phosphane) is a potential ligand for new tetrylenes. The reaction behavior of supermesitylphosphane (and the trimethylsilyl phosphane derivatives) towards several alkaline metal compounds has been studied extensively in the course of this work. A general preference of desilylation over dehydrogenation could be observed.

Hypersilyl(trimethylsilyl)phosphane, a sterically demanding phosphane ligand, has been used in the synthesis of the first diphosphatetrylene not containing any aromatic groups: bis[hypersilyl(trimethylsilyl)phosphino]stannylene. Accompanied with an in-depth quantum-chemical investigation, attempted synthesis of a cyclic diphosphatetrylene from a hypersilyl substituted diphosphane and tin(II)bromide resulted in a bipyramidal cluster compound. This reaction pathway can be explained with the cleavage of a Si-P bond with $SnBr_2$.

The sterical demand of the molecular environment of the tetrylene is crucial to the overall stability of the compound. A homocyclic silylene, stabilized only by its cyclic structure and geminal trimethylsilyl groups, has been studied quantum-chemically with calculations at the level of density functional theory (DFT). The very accurate method/basis set combination M06L/IGLO-II predicts a ^{29}Si NMR shift of +1133 ppm for this homocyclic silylene, which is in the extreme low field compared to the most down field shift reported to date (+567 ppm). Such silylenes are accessible *via* reductive dehalogenation reaction of a suitable precursor. All of the dihalogenated precursors to this silylene have been synthesized, including a rare cyclopentasilane containing an isolated SiF_2 moiety.

Kurzfassung

Tetrylene sind Verbindungen, die ein divalentes Gruppe-14-Element mit der Oxidationszahl +II enthalten. Sterische Effekte und/oder elektronenspendende Substituenten tragen zur Stabilisierung dieser ansonsten hochreaktiven Spezies bei. Während derartige Verbindungen mit Stickstoff in α,α' Position in der Literatur weit verbreitet sind, ist die Menge an entsprechenden P,P' Derivaten überschaubar. Alle bisher beschriebenen Diphosphatetrylene enthalten einen aromatischen Rest in den Liganden. Der große sterische Anspruch von Supermesitylphosphan (2,4,6-Tris(*t*-butyl)phenylphosphane) macht es zu einem potentiellen Liganden für neue Tetrylene. Das Reaktionsverhalten von Supermesitylphosphan (und den Trimethylsilyl-substituierten Derivaten) gegenüber mehreren Alkalimetallverbindungen wurde im Zuge dieser Arbeit extensiv untersucht. Eine generelle Bevorzugung der Desilylierungsreaktion gegenüber der Dehydrierung konnte beobachtet werden.

Hypersilyl(trimethylsilyl)phosphan, ein sterisch anspruchsvoller Phosphanligand, wurde im Zuge der Synthese des ersten Diphosphatetrylenes, das keinerlei aromatische Gruppen enthält, verwendet: Bis[Hypersilyl(trimethylsilyl)phosphino]stannylen. Begleitet von einer detaillierten quantenchemischen Studie resultierte die versuchte Synthese eines zyklischen Diphosphatetrylens aus einem Hypersilyl-substituierten Diphosphan und Zinn(II)bromid in einer bipyramidalen Clusterverbindung. Dieser Reaktionspfad kann mit der Spaltung einer Si-P Bindung durch $Sn(II)Br_2$ erklärt werden.

Der sterische Anspruch der molekularen Umgebung des Tetrylenes ist ausschlaggebend für die Stabilität der Verbindung. Ein homozyklisches Silylen, welches nur durch die zyklische Struktur und geminale Trimethylsilylgruppen stabilisiert ist, wurde quantenchemisch auf dem Level der Dichtefunktionaltherie (DFT) untersucht. Die Methoden/Basissatz-Kombination M06L/IGLO-II prognostiziert eine ^{29}Si NMR Verschiebung von +1133 ppm für dieses homozyklische Silylen. Solche Silylene sind durch reduktive Dehalogenierung eines geeigneten Edukts zugänglich. Alle dihalogenierten Derivate dieses Silylenes, inklusive eines Zyklopentasilanes, das eine isolierte SiF_2-Gruppe beinhaltet, wurden synthetisiert.

Danksagung

Für die Richtung dieser Arbeit, den Blick fürs Wesentliche, eine allumfassende chemische Ausbildung und alle Freiheiten hat Michi Flock gesorgt. Zusätzlich sind durch finanzielle Unterstützung des Instituts, personifiziert in Frank Uhlig, Konferenzen und Weiterbildungen ermöglicht worden.

Retrospektiv ist es überraschend, fast schon erschreckend, wie viele Leute tatsächlich aktiv am erfolgreichen Abschluss dieser Arbeit beteiligt waren. Ohne Anspruch auf Vollständigkeit: Dank an die Bachelorstudenten Patrick, Nicole, Stefanie, an die serbischen Freunde Nenad und Milena, an die Ideengeber Alk und Roland, und natürlich an meine lieben, geschätzten Bürokameraden und chemischen Wegbegleiter Ana, Eli, Johnny und Modi.

Während diese Arbeit am Blühen und Gedeihen war, war auch das Leben abseits der Chemie ein tolles. Es ist natürlich schwierig, alle Leute namentlich nennen, die ich in in den letzten paar Jahren mit guten Erinnerungen verbinde. Man will ja niemanden auslassen. Versuchen kann man es aber trotzdem: Matthias, Johanna, Wollo, Wolfram, Georg, Bernhard, Gernot, Tici, Mel, Max, Chris, Elsi, Steffi, Martin, Astrid, Monika, Magda, Mike, Gerli, Elli, Sarina, Markus, Jürgen, Uli, Milan, Suri, Meister Shin, alle Nachbarn und wahrscheinlich noch ein paar mehr. Schön, dass ihr da seid.

Mutter, Vater, Schwester, Omi, und der Rest: Ich wünsche jedem so eine Familie, wie ich sie hab. Ihr seids schon klass.

Und Abends steht man dann am Griller, wendet das Fleischlaberl, nimmt einen Schluck gekühltes Bier, winkt durch die Balkontür ins Haus und weiß: Das Leben ist schön.
Es ist mir eine Freude, mit dir durchs Leben zu spazieren.
Danke, meine Liebe, Svenja.

Graz, Januar 2015

Contents

Chapter 1

Introduction

Tetrylenes are uncharged compounds containing group 14 elements in the oxidation state of +II. Such compounds are known for all of the elements from carbon to lead, in varying quantities.

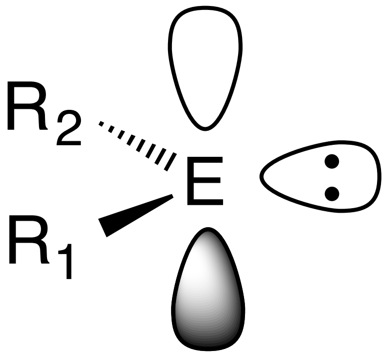


Figure 1.1.: General structure and orbital scheme of tetrylenes.

The higher homologues, e.g. tin and lead, tend to be stable in the oxidation state of +II, taking $SnBr_2$ and $PbCl_2$ as examples. Carbon and silicon clearly favor an oxidation state of +IV. Germanium holds a position in between, with several stable compounds in the oxidation state of +IV. The increasing stability of the oxidation state +II within the group can be shown with compounds like $GeCl_2$·dioxane, where Ge(+II) is only stable through coordination of a solvent. This behavior can easily be explained with the mixing of s and p orbitals. In the higher homologues, the energy gap between these orbitals is too large to be compensated by the hybridization energy, therefore twofold coordination (through oxidation state +II) is preferred. The similarity in energy of s and p orbitals favors hybridization in the lower homologues.

Carbenes, as well as the other tetrylenes, show formal sp^2 hybridization. Two sp^2 orbitals are bonding to the substituents. For singlet tetrylenes, the third in-plane sp^2 orbital is filled with an electron pair and the remaining perpendicular p-orbital does not contain electrons (Fig. 1.1). Some carbenes can be found in the triplet ground state. Here, each of the non-bonding orbitals contains one unpaired electron. However, for the higher tetrylene homologues and N,O,S and halogen substituted carbenes, the singlet ground state is preferred. Consequently, these tetrylenes are Lewis-amphiphilic, they are able to act as electron donor as well as being able to accept electrons *via* the empty p-orbital. The great variety of reaction possibilities of tetrylenes goes hand in hand with high reactivity/instability. Through interaction with Lewis-basic substituents in α, α' position the electrophilicity of the tetrylene can be lowered and therefore the instability decreased. This interaction can be forced by hindered rotation around the tetrylene-substituent bond, which can be achieved through a cyclic backbone. Kinetic stabilization may be reached through spacial protection by a sterically demanding environment. It seems reasonable that the first stable tetrylenes have been carbenes that took advantage of all means of stabilization: electron donating substituents in α position, sterical bulkiness, a cyclic backbone and further intramolecular electronic interactions.

1.1. Arduengo's N-heterocyclic carbenes as foundation stone of tetrylene chemistry.

N-Heterocyclic carbenes (NHCs) are common in chemistry nowadays. This comparatively young compound class has been used extensively in catalysis and as donor ligand, standing in competition with precious metal compounds and common Lewis bases like PMe_3, respectively.[1,2] For long, carbenes have been regarded as elusive intermediates during reactions. Arduengo's synthesis of the first stable carbene, a N-heterocyclic carbene, symbolizes the foundation of a whole new class of compounds, carbenes stable at ambient conditions.[3] The use of an electron rich cyclic backbone and big substituents on the nitrogens in α,α' position enhance the overall stability. The nitrogens themselves provide their electron pair for stabilization. Donation into the empty πp-orbital lowers the carbenes electrophilicity and ultimately leads to the high stability of NHCs. The rigid backbone of the ring hinders rotation around the N-C bonds and subsequently enforces the preferable arrangement of the nitrogen lone pair and the empty πp-orbital seen in Fig. 1.2.

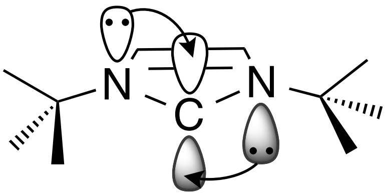


Figure 1.2.: Stabilization of N-heterocyclic carbenes.

Over the course of time, this general theme has been altered and changed countless times, the chemistry around N-heterocyclic carbenes has been and still is a highly dynamic field that is gaining much interest of the scientific community. The next step in the ongoing search for new compounds and for applications of tetrylenes was the substitution of carbon with one of the higher homologues.

1.2. The adaptation of the stabilization patterns in the synthesis of higher carbene homologues.

Inspired by the molecular structure of Arduengo's N-heterocyclic carbene, the first analogous N-heterocyclic silylene has been synthesized by Robert West in 1994[4] (Fig 1.3). The corresponding germylene[5] has even been reported two years earlier, while the Arduengo-type stannylenes have been reported a couple of years later.[6] An Arduengo-type plumbylene, despite lead generally favoring the oxidation state of +II, has not been reported to this day.

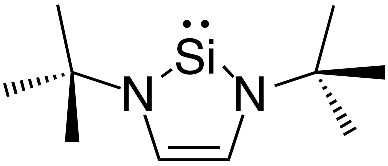
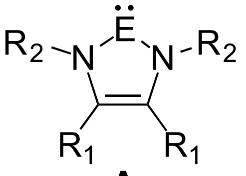


Figure 1.3.: The first stable silylene synthesized by Robert West.

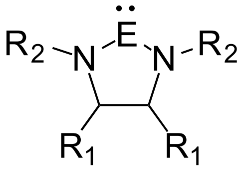
West's silylene, as well as the higher homologues, take advantage of the same means of stabilization as Arduengo's NHC: electron donating nitrogen in α,α' position, sterically demanding *tert*-butyl groups located on the α-nitrogens and an electron rich cyclic allyl backbone that further enhances stabilization through high rigidness and optimal positioning of the nitrogen lone pairs. Over the course of the following years, this system has been modified extensively. First modifications have been undertaken at the backbone of the ring system, compounds of type **B** and **H** (Fig. 1.4) show that unsaturated carbon-carbon bonds are not essential. Intramolecular electronic interactions through delocalization of electrons within the ring seem to have a smaller effect on the stability of the tetrylene compared to the α,α'-substituents and the kinetic stabilization through steric bulkiness.

Figure 1.4 also shows that the backbone, mostly containing aromatic groups in some form, and the sterically demanding groups located on nitrogen were the main targets of modification. Even minor variations in the steric bulkiness of ligands might lead to drastic changes in the stability of the tetrylenes. Taking a zwitterionic ylide-like silylene[37] as an example, a stable silylene is obtained



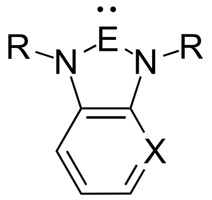
A

E	R_1	R_2
Si	H	*t*Bu
		C(Me_2)-CH_2-*t*Bu
		(2,6-Me)C_6H_3
		(2,6-*i*Pr)C_6H_3
		(2,4,6-Me)C_6H_2
Ge	H	*t*Bu
		CH_2-*t*Bu
	Me	(2,4,6-Me)C_6H_2
Sn	H	(2,4,6-Me)C_6H_2



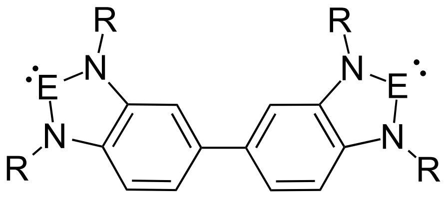
B

E	R_1	R_2
Si	H	*t*Bu
Ge	H	*t*Bu
Sn	H	(2,6-*i*Pr)C_6H_3
	Me	*t*Bu
Pb	H	(2,6-*i*Pr)C_6H_3



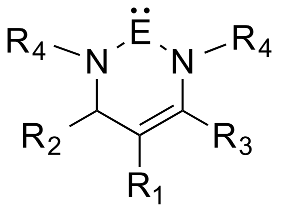
C

E	X	R
Si	CH	CH_2-*t*Bu
Ge	CH	CH_2-*t*Bu
		SiMe_3
		C_6F_5
	N	CH_2-*t*Bu
Sn	CH	Me
		CH(Me)Ph
		CH_2-*t*Bu
		*n*Pr-NMe_2
		Et-OMe
		(2,4,6-Me)C_6H_2
Pb	CH	CH_2-*i*Pr
		CH_2-*t*Bu



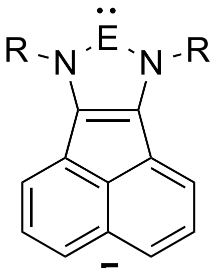
D

E	R
Si	CH_2-*t*Bu
Ge	CH_2-*i*Pr
Pb	CH_2-*i*Pr



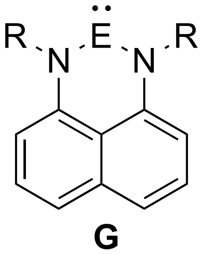
E

E	R_1	R_2	R_3	R_4
Si	H	=CH_2	CH_3	(2,6-*i*Pr)C_6H_3
Ge	H	=CH_2	CH_3	(2,6-*i*Pr)C_6H_3
		*t*Bu	Ph	(2,6-*i*Pr)C_6H_3
				(2,4,6-Me)C_6H_2
	CH_2Ph	=CH_2	CH_3	(2,6-*i*Pr)C_6H_3
	R_2	=CH_2-*n*Pr-	Ph	(2,6-*i*Pr)C_6H_3



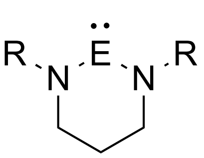
F

E	R
Si	(2,6-Me)C_6H_3
Ge	(2-Ph)C_6H_4
	(2,6-Me)C_6H_3
	(2,5-*t*Bu)C_6H_3
Sn	(2,4,6-Me)C_6H_2



G

E	R
Ge	*i*Pr
Sn	*i*Pr
	SiMe_3
	Si*i*Pr_3

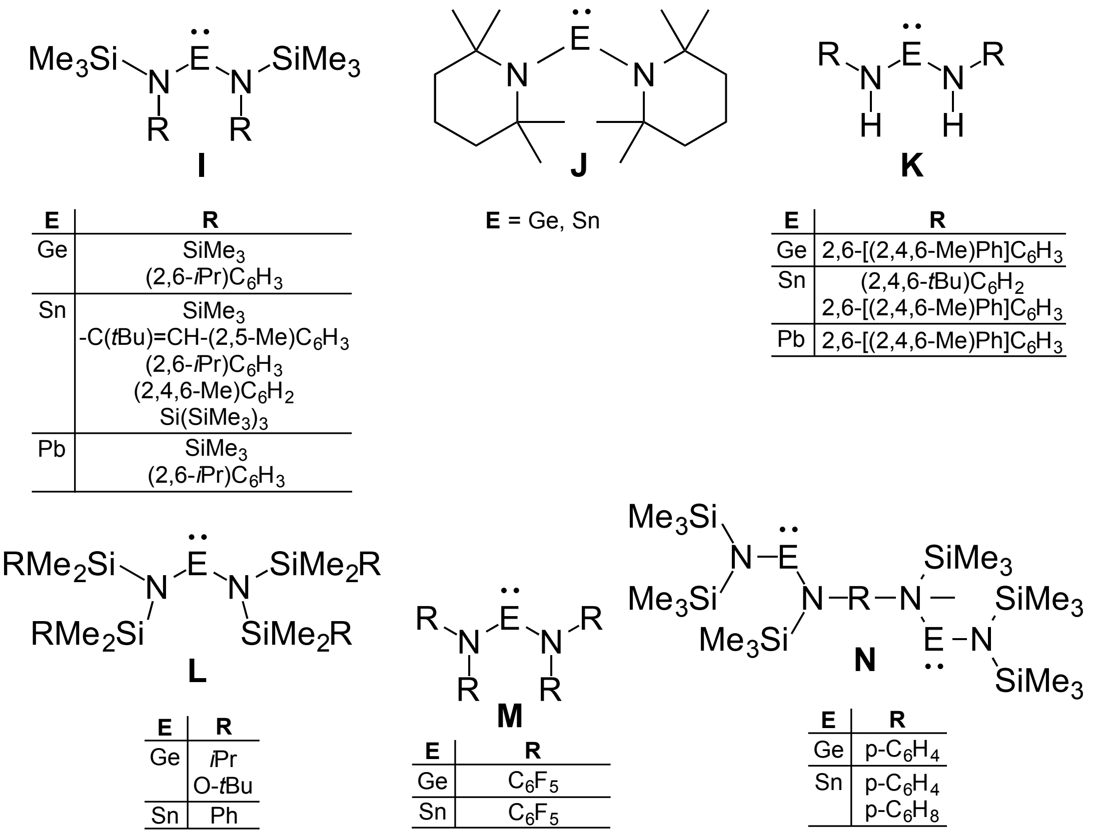


H

E	R
Sn	(2,6-*i*Pr)C_6H_3
Pb	(2,6-*i*Pr)C_6H_3

Figure 1.4.: Various stable N-heterocyclic tetrylenes. **A**[5–11], **B**[5,12–15], **C**[11,16–22], **D**[23,24], **E**[25–30], **F**[31,32], **G**[33–36], and **H**[14,15].

with diisopropyl-phenyl substituents on the α-nitrogens, while the corresponding diethyl-phenyl, dimethyl-phenyl and *t*-butyl derivatives lead to inseparable mixtures or disilenes *via* formal dimerization reaction. These modifications resulted in a respectable amount of N-heterocyclic tetrylenes. It is remarkable that cyclic compounds are dominant, especially for the lower homologues. In fact, no acyclic α,α'-N silylene has been characterized structurally thus far.



E	**R**
Ge	SiMe$_3$ (2,6-*i*Pr)C$_6$H$_3$
Sn	SiMe$_3$ -C(*t*Bu)=CH-(2,5-Me)C$_6$H$_3$ (2,6-*i*Pr)C$_6$H$_3$ (2,4,6-Me)C$_6$H$_2$ Si(SiMe$_3$)$_3$
Pb	SiMe$_3$ (2,6-*i*Pr)C$_6$H$_3$

E = Ge, Sn

E	**R**
Ge	2,6-[(2,4,6-Me)Ph]C$_6$H$_3$
Sn	(2,4,6-*t*Bu)C$_6$H$_2$ 2,6-[(2,4,6-Me)Ph]C$_6$H$_3$
Pb	2,6-[(2,4,6-Me)Ph]C$_6$H$_3$

E	**R**
Ge	*i*Pr O-*t*Bu
Sn	Ph

E	**R**
Ge	C$_6$F$_5$
Sn	C$_6$F$_5$

E	**R**
Ge	p-C$_6$H$_4$
Sn	p-C$_6$H$_4$ p-C$_6$H$_8$

Figure 1.5.: Various stable acyclic α,α'-N-tetrylenes. **I**[38–45], **J**[38,46], **K**[47,48], **L**[42,49,50], **M**[18,51], and **N**[52].

Acyclic α,α'-N-tetrylenes (E = Ge, Sn, Pb) have been reported, although in a smaller number. A closer look at the compounds in Figure 1.5 makes the prevalence of Si-substituents on nitrogen easily recognizable. It is also of note that not both of the substituents on nitrogen have to be sterically demanding. Compounds of type **K** contain secondary amines featuring very bulky aromatic groups as substituents. Given the right (e.g. large enough) N-substituents, the electronic interaction of the nitrogen lone pair with the empty p-type orbital of the tetrylene seems to be a very effective way to stabilize these highly reactive species. In contrast to their nitrogen homologues, α,α'-P-tetrylenes are rare.

1.3. Diphosphatetrylenes

The discussion in section 1.1 has shown that for a lot of N,N'-ligands, silicon and the higher homologues germanium, tin and lead are equally stable. However, the difference between first row element carbon and the higher group 14 elements is significant, as can easily be seen by the vast amount of known N-heterocyclic carbenes. The reaction behavior and sheer accessibility of compounds also changes drastically when the nitrogen in the ligand is exchanged by its higher homologue phosphorus. One of the biggest differences is the decrease in relative electronegativity compared to the group 14 elements (EN (Pauling): N 3.04, P 2.19; Si 1.90, Ge 2.01, Sn 1.96, Pb 1.87). Additionally, effective overlap of the free electron pair of the pnictide with the empty orbital of the tetrylene is facilitated by a certain amount of planarization.[55] Phosphines possess higher inversion energies (and therefore higher planarization energies) which counteracts effective orbital overlap.

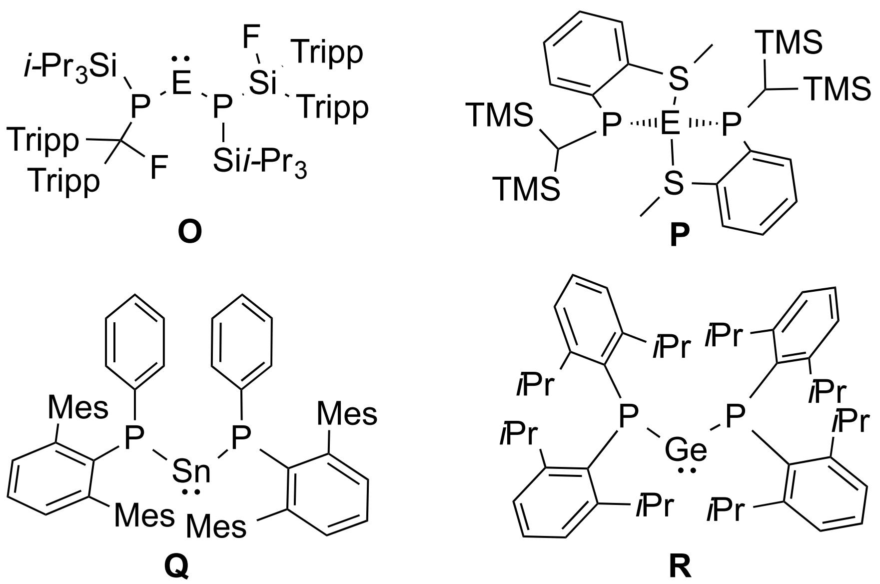
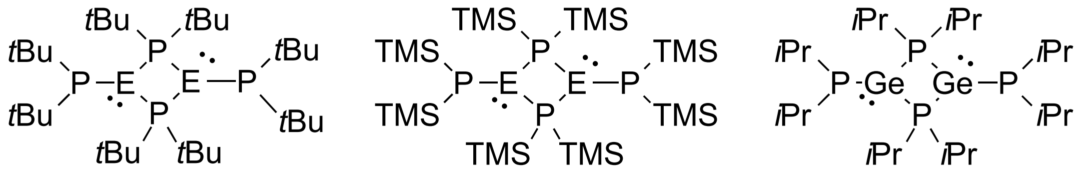


Figure 1.6.: Diphosphatetrylenes can additionally be stabilized by very bulky substituents as well as electron donation from a ligand moiety (type **P**). Compounds by Driess (**O**, E = Ge, Sn, Pb; Tripp = $C_6H_2iPr_3$; 1995)[53], Izod (**P**, E = Ge, Sn, 2012; **R**, 2014)[54,55] and Power (**Q**, Mes = $C_6H_2Me_3$; 2007)[56].

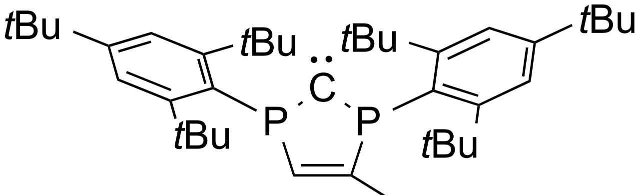
Keeping all these limitations in mind, it comes as no surprise that diphosphatetrylenes are scarce (Fig. 1.6). Generally, larger substituents are required compared to their nitrogen counterparts. Even this steric protection, combined with the electronic interaction with the phosphorus lone pair, is not sufficient for all of the shown compounds. Diphosphatetrylenes of type **P** are for example further stabilized through intramolecular interaction with the sulfur moieties located on the ligand. The use of somewhat smaller and non-interacting substituents on phosphorus leads to dimeric structures. Many of the early diphosphatetrylenes have been characterized as such dimers (Fig. 1.7). The dimerization is caused by instability of the corresponding monomers; a second diphosphatetrylene provides stabilization through head-to-tail cycloaddition.



S **T** **U**

Figure 1.7.: Smaller diphosphastannylenes tend to dimerize, compounds reported by du Mont (**S**, E = Sn, 1977; **U**, 1998)[57], Cowley (**S**, E = Pb, 1988),[58] and Buhro (**T**, E = Sn/Pb, 1993).[59]

Apart from these dimeric structures, the lack of cyclic α,α'-P derivatives is evident. While such compounds containing nitrogen based ligands are common (as seen in Section 1.1) there is in fact only one cyclic low-valent group 14 compound with P-substituents known: the P-heterocyclic carbene depicted in Figure 1.8.



X

Figure 1.8.: The only cyclic diphosphatetrylene to date, a P-heterocyclic carbene.[60]

Intramolecular (like in compounds of type **P**) or intermolecular interactions (like in the dimerization products **S**, **T** and **U**) are certainly helpful in the overall stability, the most crucial contribution however remains the sterical demand of the ligand. Comparison of type **I** N,N'-tetrylenes (R = $SiMe_3$) (Fig. 1.4) and their type **T** congeners shows that the transition from nitrogen to phosphorus can decrease the overall stability enough for dimerization to occur. Compounds of type **Q** show that, given a large enough second substituent like (2,5-Mes)phenyl, even the comparatively small phenyl group is sufficient to obtain stable, monomeric tetrylenes. For acyclic α,α'-N stannylenes of type **K**, the size of the supermesityl group (Mes*, (2,4,6-*t*Bu)Ph-) was sufficient to compensate for the second substituent, plain hydrogen. So naturally, supermesitylphosphane (Mes*PH_2, Mes* = 2,4,6-tris(*t*-butyl)phenyl, Fig. 1.9) caught our attention during the search for ligand systems that would facilitate the synthesis of novel tetrylenes. Mes*PH_2 is stable under ambient conditions, which already proves certain stabilization caused by the steric bulkiness of the Mes*-moiety.

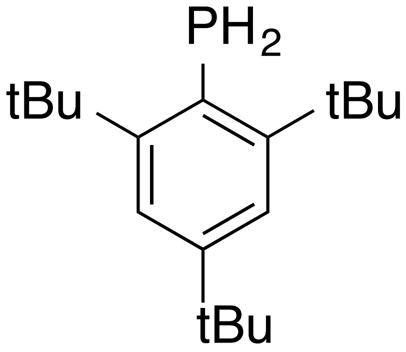


Figure 1.9.: The PH_2 functionality is protected by the steric bulkiness of the supermesityl group.

A thorough investigation of the reaction behavior of a number of derivatives of supermesitylphosphine has been conducted in the course of this work and is reported in Chapter 2.

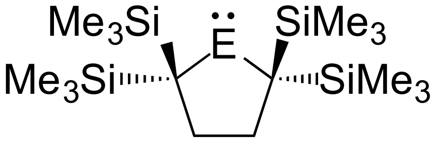
1.4. Non-aromatic phosphine ligands.

All of the previously discussed diphosphatetrylenes feature some kind of aromatic system in the ligand. The question if isolation of diphosphatetrylenes without aromatic substituents is at all possible has not been answered yet. A promising candidate for a sterically demanding non-aromatic ligand is the hypersilyl (-Si(SiMe$_3$)) moiety. During the investigation of diphosphanes by Hassler several years ago^{61} it was used as an integral part of stable phosphines containing a sterically demanding substituent. The hypersilyl group itself possesses no free electron pairs for interaction, so only the lone pair located on phosphorus is able to interact with the tetrylene moiety. This makes donor-acceptor type stabilization from the ligand to the central tetrylene very unlikely, leaving the bulkiness of the ligand as the main source of additional stability. The synthesis of such an highly interesting compound, a hypersilylphosphanyl tetrylene, together with the corresponding precursor, is discussed in chapter 4. As mentioned in the previous chapter, cyclic diphosha derivatives of the higher tetrylenes have been elusive so far. This is even more surprising, as the compounds required as precursors to such cyclic diphosphatetrylenes, diphosphanes, have been used in transition metal chemistry in the past and are well known.

Previously reported diphosphane (or diphosphanide) ligands range from small carbon based systems like (Me$_2$P-CH$_2$-)$_2$ over similar structures featuring a -Me$_2$Si-SiMe$_2$- backbone up to ligands containing boron functionalities within the ligand. The previously mentioned hypersilyl group has not been used in diphosphane ligand chemistry yet. However, the synthesis of the free stannylene described in chapter 4 shows the huge potential of the hypersilyl group in tetrylene chemistry. The experimental and quantum chemical analysis of a diphosphane ligand capped by hypersilyl moieties, that might lead to cyclic diphosphatetrylenes in the future, can be found in chapter 3.

1.5. Silanes and alkanes as ligands for stable tetrylenes

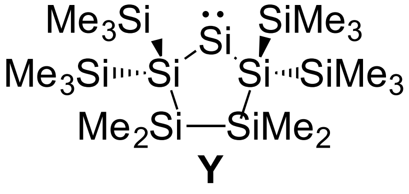
The synthesis of the first stable tetrylenes not containing α-nitrogens by Kira[62–64] symbolizes a giant leap in tetrylene chemistry, proving that for stable compounds of this type a group 15 element in α,α' position is not obligatory (Fig. 1.10). Stabilization is mainly achieved *via* two sterically demanding trimethylsilyl groups on each of the α-carbons and the rigidness of the ring backbone. The most remarkable feature of this series of compounds is the extremely deshielded nature of the silylene derivative: its shift of +567.9 ppm is still the most downfield ^{29}Si NMR shift reported to date.



E = Si, Ge, Sn

Figure 1.10.: Kira's silylene and its germanium and tin homologues.

A compound that has been elusive so far is the Si-homocyclic derivative **Y** of Kira's silylene (Fig. 1.11). First attempts in the synthesis of this highly interesting compound have been performed by Ana Dzambaski under supervision of Karl Hassler at the Institute of Inorganic Chemistry at Graz University of Technology.[65] Later attempts by Xiao, an affiliate of professor Kira, have not yielded the desired silylene, but several decomposition compounds. Isolation of the silylene has also not been successful in the course of this work.



Y

Figure 1.11.: An elusive homocyclic silylene. Attempts of synthesis by Hassler,[61] Xiao,[66] Mueller.

However, the in depth analysis of the dihalogenated precursors (including a compound containing a stable -SiF_2- moiety) is an essential part of this work. Supported by work done by Ana Dzambaski during her PhD. thesis and backed by quantum chemical calculations, the results have been submitted to *Journal of Molecular Structure* and can be found in Chapter 5. Corresponding germylene, stannylene and plumbylene derivatives of **Y** have been successfully synthesized in the past as base-adduct compounds.[67–69] Although the structures feature a Lewis base coordinating to the tetrylene to enhance stability, they prove the general suitability of this homocyclic backbone for stable tetrylenes. There are only few examples of other disilyltetrylenes, most of which feature additional stabilization by a ligand (Fig. 1.12).

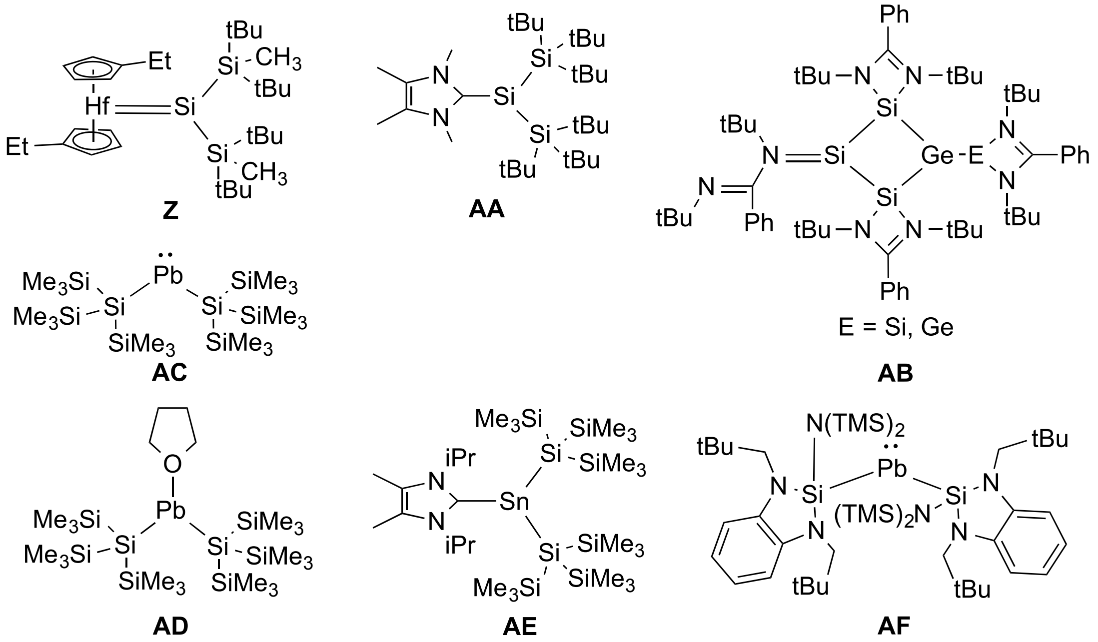


Figure 1.12.: Silyl-substituted tetrylenes reported by Sekiguchi (**Z**,[70] **AA**[71]), So (**AB**[72]), Klinkhammer (**AC**[73]), Hinderberger (**AD**[74]), Escudié (**AE**[75]), and Lappert (**AF**[76]).

Only plumbylene derivatives **AF** and **AC** could be isolated as the free disilyltetrylene. For the latter, the THF-adduct **AD** has also been reported. Compounds with similar interactions with a transition metal as shown for compound **Z** have also been reported for the germylene, stannylene and plumbylene derivatives of **Y**. Compounds **AA** and **AE** show a highly interesting interaction pattern: stabilization has been achieved *via* interaction with a N-heterocyclic carbene. Both are able to act as Lewis acid and base. A free electron pair located on one tetrylene is donated into the empty p-orbital of the other and *vice versa*. Even highly reactive silylenes, like dichlorosilylene $SiCl_2$ can be stabilized by this interaction[77] (Fig. 1.13).

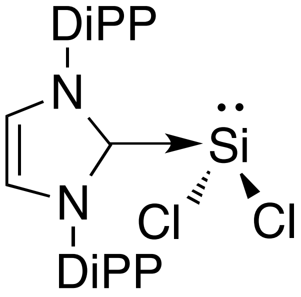


Figure 1.13.: A silylene stabilized by a N-heterocyclic carbene.[77]

All these compounds are great examples for the ever evolving field of tetrylenes. New substituents and means of stabilization lead to a plethora of novel compounds that might lead to future applications as catalytically active species. The necessity of new ligand systems is evident, so beside synthesis of actual tetrylenes, large parts of this work are dedicated to the investigation of tetrylene precursors and sterically demanding ligand systems.

Chapter 2

Reaction behavior of supermesitylphosphane and its silylated derivatives.

Stefan K. Mueller, Elisabeth Schwarz, Gernot Weinberger, Ana Torvisco, Alk Dransfeld and Michaela Flock

Institute for Inorganic Chemistry, Graz University of Technology, Stremayrgasse 9/V, 8010 Graz, Austria

2.1. Abstract

The sterically demanding phophanes Mes*PH_2 **1**, Mes*P(TMS)H **3** and Mes*$P(TMS)_2$ **5** (Mes* = 2,4,6-tris(trimethylsilyl)phenyl) have been investigated in regard to their reaction behavior with *n*-butyl lithium, potassium hydride and potassium *t*-butoxylate. *n*-BuLi leads to deprotonation in **1** and **3** and abstraction of a trimethylsilyl group in **5**. KH and KO*t*Bu show a general preference of desilylation, however previously reported dehydrogantion capabilities are confirmed in the reactions with Mes*PH_2 **1**. Reactions of Mes*PH_2 **1** and Mes*P(TMS)H **3** with the Schwesinger base P_4-*t*-Bu both lead to the free phosphanide Mes*PH^- in the solid state and polar solvents. This separated ion pair Mes*PH^- P_4-*t*-Bu(H^+) **8**, as well as supermesityl(trimethylsilyl)phosphanides **4** (Li^+) and **7** (K^+), have been characterized *via* X-ray diffraction analysis.

2.2. Introduction

Over 3000 compounds can be found in literature containing some variation of supermesityl (Mes*; 2,4,6-tris-(*t*-butyl)-phenyl) substituted by a phosphane moiety. Silyl substituted supermesitylphosphanes are still quite common, with almost a hundred representatives known to date. One of the smaller supermesityl silyl phosphanes, Mes*P(H)$SiMe_3$, and its lithium salt derivative Mes*P(Li)$SiMe_3$ have been used in the formation of diphosphenes[78] and phosphorus-carbon (double) bonds.[79,80] The loss of the trimethylsilyl group under formation of TMS-halide is a common theme in these reactions. Several standard procedures leading to a specific abstraction and therefore functionalization of the phosphorus center are known.

n-Butyl lithium has been used in the past for the cleavage of trimethylsilyl groups of tris(trimethylsilyl)phosphanes.[81,82] However, P-H cleavage is preferred over abstraction of TMS groups from the phosphane.[83] Potassium *t*-butoxylate shows similar reaction behavior with silylphosphanes. Synthesis of potassium phosphanides under formation of the corresponding alcohol as well as the cleavage of a P-$SiMe_3$ with KO*t*Bu has been reported in literature.[61] Latter reaction is comparable to the cleavage of the Si-$SiMe_3$ bond[84] with KO*t*Bu. If both functionalities [$(SiMe_3)_3$Si- and P-H] are present in the same molecule abstraction of hydrogen is preferred over $SiMe_3$ abstraction.

During the search for new ligands to tetrylenes the reaction behavior of Mes*P(H)SiMe$_3$ with the phosphazene base P$_4$-*t*-Bu has been investigated. This Schwesinger base has been used in the past for the synthesis of separated ion pairs *via* hydrogen abstraction and should lead to the free phosphanide with the compounds investigated in the course of this work.

2.3. Experimental

2.3.1. 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.). C_6D_6 has been distilled over sodium and stored under nitrogen atmosphere. *n*-Butyl lithium and potassium *tert*-butylate were bought from Aldrich and used as delivered. 2,4,6-tris(*t*-butyl)phenyl phosphane has been prepared following standard procedures.[85] Trimethylchlorosilane has been distilled prior to use.

2.3.2. NMR

^{1}H (300.2 MHz), ^{13}C (75.5 MHz), ^{29}Si (59.6 MHz) and ^{31}P (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 (δ = 0 ppm) regarding ^{1}H, ^{13}C and ^{29}Si. Coupling constants (J) are reported in Hertz (Hz). All NMR spectra were measured in C_6D_6. Investigations on the formation of ion pair **8** were additionally carried out and measured in THF-d8. Reactions were monitored using a D_2O capillary as external lock signal.

2.3.3. X-Ray Diffraction

All crystals suitable for single crystal X-ray diffractometry were removed from a Schlenk flask 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 N_2 stream provided by an Oxford Cryosystems cryometer. XRD data collection was performed on a Bruker APEX II diffractometer with use of Mo Kα radiation (λ = 0.71073 Å) and a CCD area detector. Empirical absorption corrections were applied using SADABS[86,87]. The structures were solved with use of either direct methods or the Patterson option in SHELXS and refined by the full-matrix least-squares procedures in SHELXL[88,89]. The space group assignments and structural solutions were evaluated using PLATON[90,91]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in calculated positions corresponding to standard bond lengths and angles. Disorder, as observed for compound **4** and **7** was handled by modeling the occupancies of the individual orientations using free variables to refine the respective occupancy of the affected fragments (PART). Disordered positions for the coordinated ether in compound **4** were refined using 70/30 split positions. Disordered positions for a $SiMe_3$ group, a coordinated DME and a methyl group in a *t*-butyl group in compound **7** were refined using 50/50, 50/50, 55/45 split positions respectively.

2.3.4. Synthesis

2.3.4.1. Synthesis of [2,4,6-tris-(*t*-butyl)-phenyl-trimethylsilyl lithium phosphanide] 4.

2,4,6-tris-(*t*-butyl)-phenyl-trimethylsilyl phosphane (0.40 g, 1.14 mmol) is dissolved in 5 mL of THF. 0.82 mL of 1.6 M *n*-butyl lithium (1.15 eq, 1.31 mmol) in hexanes is added dropwise at RT. The color of the reaction solution changes to yellow and the solution is stirred for additional 2h. After evaporation of all volatile components, the solid residue is redissolved in *n*-hexane. After one week at -30 °C, crystals suitable for X-ray diffraction analysis can be isolated from this solution. Isolated yield: 0.19 g, 42%. ^{1}H NMR (C_6D_6, 293 K) δ: 0.15 ppm (9H, d, $SiMe_3$, $^3J_{HP}$ = 3.9 Hz), 3.04 ppm (18H, o-*t*-Bu) 3.11 ppm (9H, p-*t*-Bu) 7.19 ppm (2H, d, arom., $^4J_{HP}$ = 1.8 Hz). ^{13}C NMR (C_6D_6, 293 K) δ: 4.0 ppm ($SiMe_3$, d, $^2J_{CP}$ = 12.8 Hz), 31.2 ppm (o-C*Me₃*, d, $^3J_{CP}$ = 8.1 Hz), 33.4 ppm (o-*C*Me₃, d, $^4J_{CP}$ = 8.8 Hz), 34.5 ppm (p-C*Me₃*), 38.5 ppm (p-*C*Me₃), 118.5 ppm (arom., d, $^2J_{CP}$ = 3.7 Hz), 118.9 ppm (arom.), 149.5 ppm (arom.), 157.1 ppm (arom.). ^{29}Si NMR (C_6D_6, 293 K) δ: 7.94 ppm (d, $^1J_{\mathrm{SiP}}$ = 21.8 Hz). ^{31}P NMR (C_6D_6, 293 K) δ: -151.4 ppm.

Table 2.1.: Crystallographic data for compounds **4**, **7** and **8**.

Compound	**4**	**7**	**8**
Formula	$C_{46}H_{86}Li_2OP_2Si_2$	$C_{50}H_{96}K_2O_4P_2Si_2$	$C_{22}H_{64}N_{13}P_4 \cdot C_{18}H_{30}P$
Fw (g mol^{-1})	787.14	957.58	912.13
a (Å)	12.0851(8)	20.0706(5)	15.1935(4)
b (Å)	18.6971(14)	16.8422(4)	18.0632(5)
c (Å)	22.1151(16)	18.4115(5)	20.2118(5)
α (°)	90	90	90
β (°)	93.863(5)	109.1550(12)	108.4400(13)
γ (°)	90	90	90
V (Å^3)	4985.7(6)	5879.1(3)	5262.2(2)
Z	4	4	4
Crystal size (mm)	0.10x0.10x0.08	0.22x0.21x0.17	0.15x0.10x0.04
Crystal habit	Block, colorless	Block, yellow	Plate, yellow
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	I2/a	P21/c	P21/c
$d_{\mathrm{calc.}}$ (mg/m^3)	1.049	1.082	1.151
μ (mm^{-1})	0.17	0.29	0.22
T (K)	100(2)	100(2)	100(2)
2Θ range (°)	2.7-27.1	2.3-27.2	2.4-27.1
F(000)	1736	2096	2000
R_{int}	0.058	0.032	0.07
independent reflns	5546	13033	11665
No. of params	296	668	561
R1, wR2 (all data)	R1 = 0.0457	R1 = 0.0727	R1 = 0.0595
	wR2 = 0.0842	wR2 = 0.1352	wR2 = 0.0970
R1, wR2 ($>2\sigma$)	R1 = 0.0326	R1 = 0.0653	R1 = 0.0369
	wR2 = 0.0769	wR2 = 0.1313	wR2 = 0.0869

2.3.4.2. Synthesis of [2,4,6-tris-(*t*-butyl)-phenyl-trimethylsilyl potassium phosphanide]·DME 7.

2,4,6-tris-(*t*-butyl)-phenyl-bis-trimethylsilyl phosphane (0.12 g, 0.28 mmol) is dissolved in 3 mL of DME. A solution of 0.035 g (0.31 mmol) of KO*t*Bu in 2 mL of DME is added dropwise at RT. The colorless solution changes to yellow immediately and is subsequently stirred for 2h. After evaporation of all volatile components, the residue is redissolved in *n*-hexane. After one week at -30 °C, crystals suitable for X-ray diffraction analysis could be isolated from this solution. Isolated Yield: 0.11 g, 82%

^{1}H NMR (C_6D_6, 293 K) δ: 0.16 ppm (9H, d, SiMe$_3$, $^3J_{\mathrm{HP}}$ = 3.4 Hz), 1.46 ppm (9H, p-*t*-Bu) 1.99 ppm (18H, o-*t*-Bu) 2.96 ppm (6H, DME CH_3) 3.00 ppm (4H, DME CH_2) 7.50 ppm (2H, broad s, arom.). ^{13}C NMR (C_6D_6, 293 K) δ: 4.0 ppm ($SiMe_3$, d, $^2J_{CP}$ = 12.8 Hz), 31.2 ppm (o-C*Me₃*, d, $^3J_{CP}$ = 8.1 Hz), 33.4 ppm (o-*C*Me_3, d, $^4J_{CP}$ = 8.8 Hz), 34.5 ppm (p-C*Me₃*), 38.5 ppm (p-*C*Me_3), 58.3 ppm (DME) 71.0 ppm (DME) 118.8 ppm (arom., d, $^2J_{CP}$ = 12.8 Hz), 118.9 ppm (arom.), 143.4 ppm (arom.), 155.9 ppm (arom.). ^{29}Si NMR (C_6D_6, 293 K) δ: -0.70 ppm (d, $^1J_{SiP}$ = 58.4 Hz). ^{31}P NMR (C_6D_6, 293 K) δ: -142.4 ppm.

2.3.4.3. Synthesis of [2,4,6-tris-(*t*-butyl)-phenyl[P_4-*t*-Bu] phosphanide] 8.

2,4,6-tris-(*t*-butyl)-phenyl-trimethylsilyl phosphane (0.035 g, 0.10 mmol) is dissolved in 1 mL of THF and cooled to -70 °C. A 0.8 M solution (0.125 mL, 0.10 mmol) of Schwesinger base P_4-*t*-Bu in hexanes is added dropwise and leads to an immediate color change to dark purple. After evaporation of all volatile components, the residue is dissolved in a mixture of pentane and several drops of THF. Crystals suitable for X-ray diffraction analysis were obtained over the course of 10 days at -30 °C from this solution.

^1H NMR (C_6D_6, 293 K) δ: -0.95 ppm (9H, d, $SiMe_3$, $^3J_{HP}$ = 3.4 Hz), 3.04 ppm (18H, o-*t*-Bu) 3.11 ppm (9H, p-*t*-Bu) 7.27 ppm (2H, d, arom., $^4J_{HP}$ = 4.5 Hz). ^{13}C NMR (C_6D_6, 293 K) δ: 4.0 ppm ($SiMe_3$, d, $^2J_{CP}$ = 12.8 Hz), 31.2 ppm (o-C*Me₃*, d, $^3J_{CP}$ = 8.1 Hz), 33.4 ppm (o-*C*Me_3, d, $^4J_{CP}$ = 8.8 Hz), 34.5 ppm (p-C*Me₃*), 38.5 ppm (p-*C*Me_3), 118.8 ppm (arom., d, $^2J_{CP}$ = 12.8 Hz), 118.9 ppm (arom.), 143.4 ppm (arom.), 155.9 ppm (arom.). ^{29}Si NMR (C_6D_6, 293 K) δ: -0.8 ppm (d, $^1J_{SiP}$ = 57.8 Hz). ^{31}P NMR (C_6D_6, 293 K) δ: -130.6 ppm (broad t, $^1J_{PH}$ = 216.5 Hz). ^{31}P NMR (THF-d8, 293 K) δ: -78.1 ppm (broad d, $^1J_{PH}$ = 180 Hz).

EA.: $C_{16}H_{48}Br_2Si_9$ (529.78 g/mol), Calc. C: 29.42%, H: 7.41%; Found C: 28.04% H: 7.53%.

2.4. Results & Discussion

The reaction of *n*-butyl lithium with Mes*PH_2 **1** (Mes* = 2,4,6 tris(*t*-butyl)phenyl) is well known and yields phosphanide Mes*PHLi **2** (Fig. 2.1). Straightforward salt elimination reaction with trimethylsilyl chloride yields silaphosphane

Mes*P(TMS)H **3**. Similarly, the reaction of **1** with potassium *t*-butoxide yields potassium phosphanide Mes*PHK **6** (Fig. 2.2).

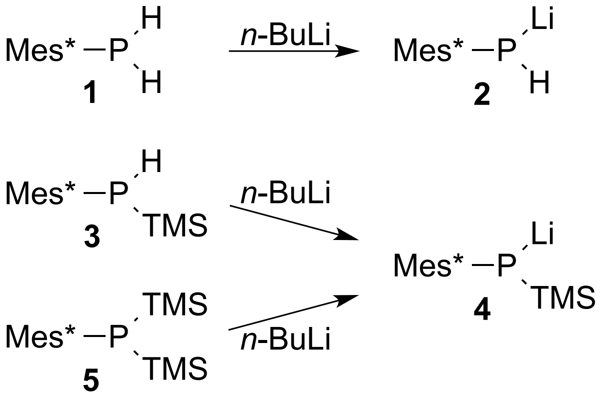


Figure 2.1.: Reactions **1**, **3** and **5** with *n*-butyl lithium.

Mes*P(TMS)H **3** shows the expected reaction behavior. Deprotonation reaction with *n*-butyl lithium yields lithium phosphanide **4**. A subsequent salt elimination reaction with trimethylchlorosilane leads to known Mes*P$(TMS)_2$ **5**. Reaction of **5** with *n*-butyl lithium causes an almost quantitative (>99%) abstraction of one trimethylsilyl group, resulting again in the lithiumphosphanide **4**. Si-P cleavage by *n*-butyl lithium as well as lithiation of primary and secondary phosphanes is well known and expected. However, solid state structure determination of **4** has not been reported to date. Crystallization of **4** in a quality suitable for X-ray diffraction analysis was successful from a mixture of *n*-hexane and toluene (Fig. 2.3).

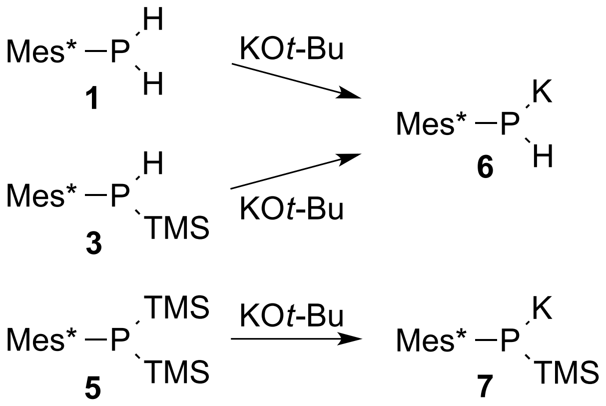


Figure 2.2.: Reactions **1**, **3** and **5** with potassium *t*-butoxide.

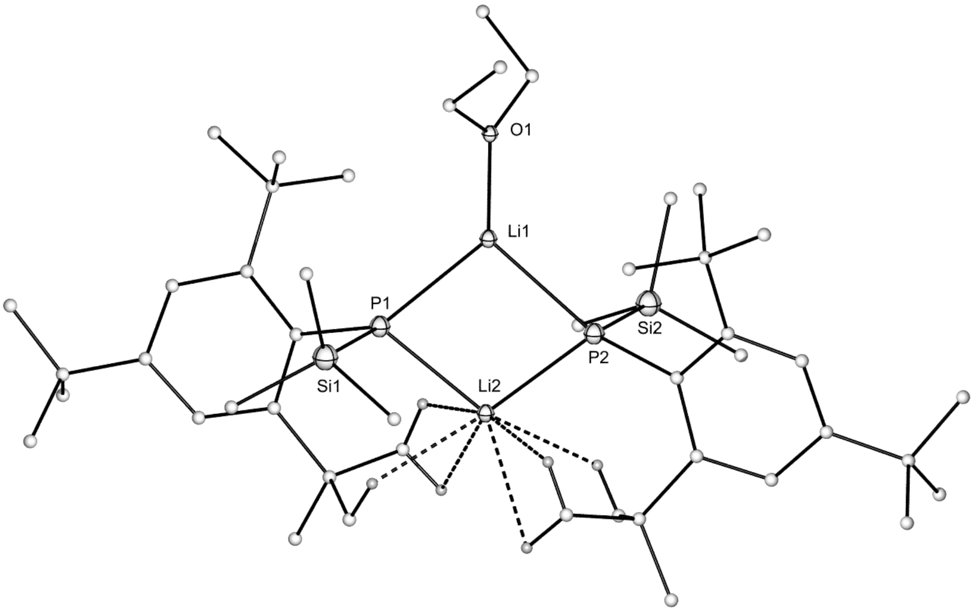


Figure 2.3.: ORTEP plot of compound **4**. Non-interacting hydrogens omitted for clarity.

4 shows asymmetric coordination in the solid state. One of the lithium atoms of the central P-Li-P-Li four membered ring is coordinated by an ether molecule. The second lithium is just stabilized by agostic interactions to *t*-butyl groups of the Mes* ligand and shows a coordination number of 2. It is one of the rare examples of solvent free lithium in organometallic compounds.[92–96] Hydrogen atoms involved in agostic interactions of two of the *t*-butyl groups on the Mes* ligand with lithium in compound **4** were located in the difference map. The values for these Li···H-C contacts are 2.140, 2.365 and 2.745 Å and are, despite the large range of 0.7 Å, within reported values for a Li···H agostic interaction.[97] Potassium *t*-butoxylate shows different reaction preferences (Fig. 2.2). Both Si-P cleavage and deprotonation reactions have been reported in literature with comparable phosphanes bearing a bulky hypersilyl [$(SiMe_3)_3Si-$] moiety.[61] In those compounds, Si-P cleavage and deprotonation of the phosphane are preferred to the abstraction of a hypersilyl $SiMe_3$ group. Reactions with **3** and **5** have shown that generation of the phophanides is achieved *via* formation of trimethylsilyl-*t*-butoxide. Cleavage of the P-Si bond is preferred over P-H cleavage. However, when no trimethylsilyl groups are present in the molecule, quantitative deprotonation under formation of the alcohol takes place. Reaction of **1** with *t*-butoxide yields phosphanide **6** in DME at room temperature.

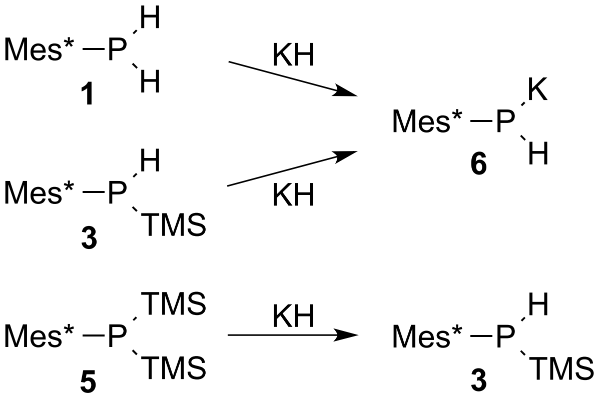


Figure 2.4.: Reactions **1**, **3** and **5** with potassium hydride.

An alternative route to potassium phosphanides is the reaction with potassium hydride. Almost two decades ago, it has been used for the deprotonation of Mes*PH$_2$ (**1**).[98] We investigated the reaction behavior of KH with compounds **3** and **5**. Similar to potassium *t*-butoxylate, potassium hydride leads to a desilylation of **3** and yields phosphanide **6**. Surprisingly, the reaction of KH with Mes*PTMS$_2$ results directly in phosphane Mes*P(TMS)H. The different size of lithium and potassium causes different structural behavior concerning coordination number. Additional to one molecule of DME coordinating to each of the potassium atoms in compound **7**, the potassium centers have agostic interactions with both trimethylsilyl and *t*-butyl ligands. The values for these contacts are within reported values for a K···H-C agostic interaction.[99]

In order to synthesize a separated ion pair a large, very strong base seems to be the right choice. In the past, the Schwesinger base P$_4$-*t*-Bu {[(Me$_2$N)$_3$P=N]$_3$P=N-*t*-Bu} has been used for deprotonation reactions with mesitylphosphane under formation of free phosphanides.[100] The ^{31}P NMR shift of the phosphanide showed an almost linear dependence on the ratio of phosphane to P$_4$-*t*-Bu up to 1:1. At higher ratios, an equilibrium value is reached and no change of NMR shift is observable with further addition of base. The addition of this base to supermesitylphosphane Mes*PH$_2$ in THF-d8 led to different observations in the ^{31}P NMR. As can be seen in Fig. 2.6, the triplet at -131.2 ppm of pure supermesitylphosphane disappears immediately after ad-

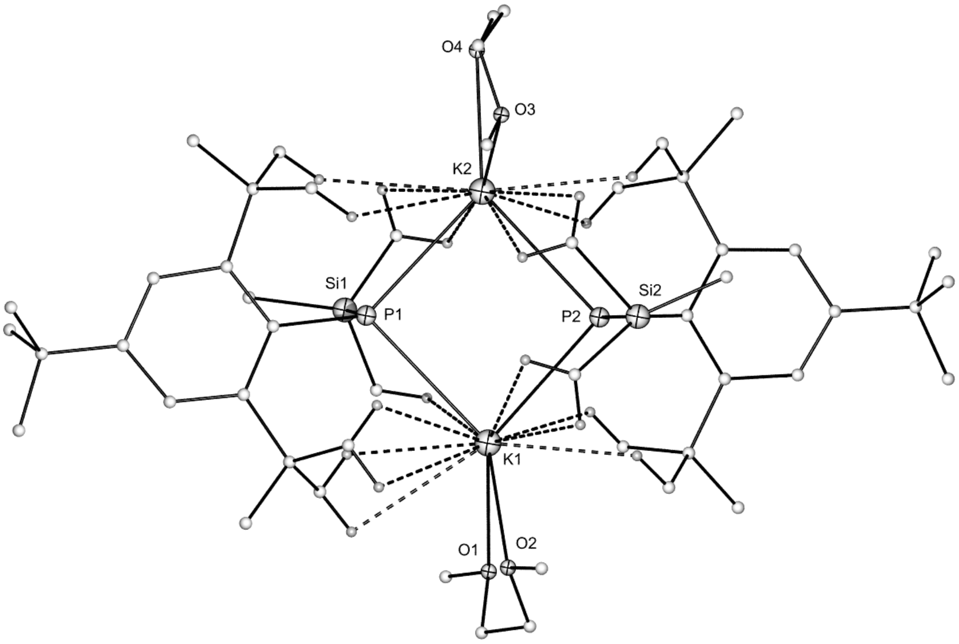


Figure 2.5.: ORTEP plot of compound **7**. Non-interacting hydrogens omitted for clarity.

dition of 0.2 equivalents of Schwesinger base P_4-*t*-Bu. While no signals for any product are visible, signals of the protonated base P_4-*t*-Bu(H^+) are clearly visible. After reaching an equimolar concentration ratio a broad signal at around -78.1 ppm appears. Upon further base addition the broad signal splits into a doublet with a coupling constant of approximately 180 Hz, which is comparable to the coupling constant of educt Mes*PH_2 (205.6 Hz). A dynamic system in which the phosphane is constantly de- and reprotonated by the Schwesinger base seems plausible. THF as Lewis basic solvent might stabilize possible intermediates. Only after an excess of Schwesinger base is present in solution, phosphanide Mes*PH^-, quite possibly stabilized by THF, can be detected by ^{31}P-NMR spectroscopy.

Comparable to the reaction behavior of KH and KO*t*Bu with supermesitylphosphane the reaction of P_4-*t*-Bu with silyl substituted Mes*P(TMS)H **3** in THF does not lead to abstraction of hydrogen but leads to desilylation. ^{31}P NMR spectra recorded from the reaction solution under use of a D_2O capillary resulted in a similar shift as the deprotonation reaction of **1**. After evaporation of the volatile components, crystals of good enough quality for X-ray diffrac-

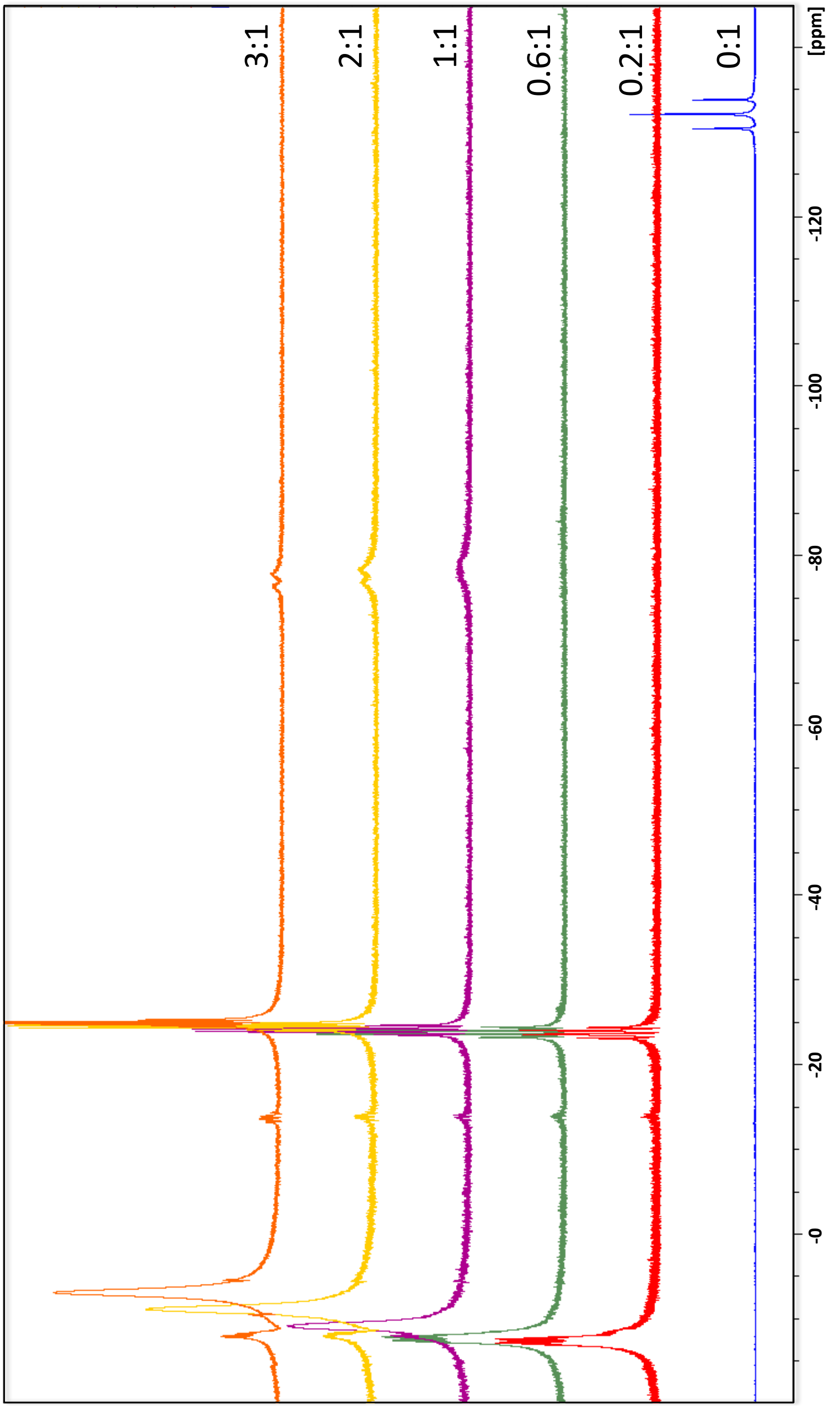


Figure 2.6.: Stepwise addition of Schwesinger base P_4-*t*-Bu to supermesitylphosphane in THF-d8.

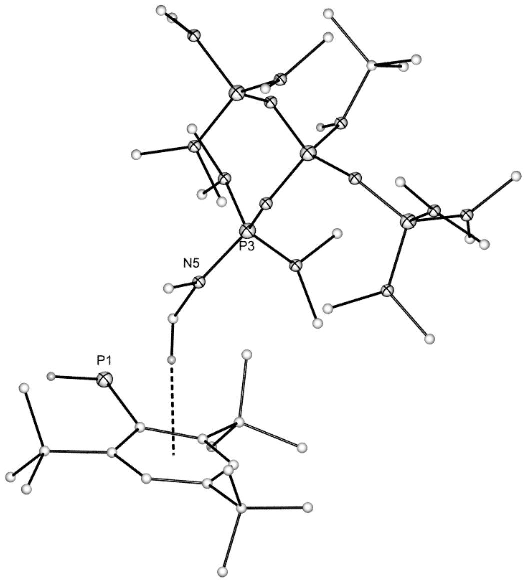


Figure 2.7.: ORTEP plot of compound **8**. Non-interacting hydrogens located on methyl groups omitted for clarity.

tion analysis could be isolated from a mixture of pentane and THF. The yellow crystals were identified as the expected supermesitlyphosphanide **8** (Fig. 2.7). NMR analysis (^{31}P) of these crystals in C_6D_6 however showed a broad triplet at -131 ppm. This strongly suggests that the phosphanide is not stable in apolar solvents and the reaction equilibrium is pushed back to supermesitylphosphane and the non-protonated form of P_4-*t*-Bu. Compound **8** displays a C-H$\cdots\pi$ interaction from one of the methyl groups on the Schwesinger base cation to the phenyl group of the supermesitylphosphanide with a value of 2.595 Å, which is within reported values.[101]

2.5. Conclusion

Derivatization reactions of supermesityl(trimethylsilyl)phosphane led to the isolation of the corresponding phosphanides **4**, **7** and **8**, with lithium, potassium and the protonated Schwesinger base P_4-*t*-Bu(H$^+$) as counter ions, respectively. **7** is only accessible *via* Mes*P(TMS)$_2$, as reactions of Mes*P(TMS)H with KH and KO*t*Bu lead to desilylation. Cleavage of the Si-P bond is also observed as result of the reaction of the supermesityl phosphane with Schwesinger base P_4-*t*-Bu. As suggested by ^{31}P NMR spectroscopy, the ion separation of phosphanide Mes*PH$^-$ P_4-*t*-Bu(H$^+$) in the solid state and polar solvents is revoked when the salt is redissolved in apolar solvents.

The compounds discussed in this chapter further broaden the range of aromatic ligands suitable for diphosphatetrylene synthesis. First attempts in the synthesis of a supermesityl substituted diphosphatetrylene with $SnBr_2$ have not been successful though. An initial change of color to a deep red is in good agreement with DFT calculations, which predict a strong absorption at 502 nm for the disphophastannylene. The color of the reaction solution turns brown soon after the initial addition, which is an indicator for the formation of tin clusters. However, no clean compounds could be isolated from this reaction solution. The sterical demand of the ligands used does not seem to fit the requirements for a stable diphosphastannylene. Their steric bulkiness combined with a functionalization site on the phosphorus should nevertheless be ideal starting points for the synthesis of derivates with different sterical demand, which might lead to ligands suitable for the synthesis of the corresponding diphosphatetrylenes.

The proof that aromaticity in the ligand is not obligatory is shown in the following chapters with the synthesis of aliphatic phosphane- and phosphanide ligands and a free acyclic tetrylene not containing any aromatic moieties.

Chapter 3

Synthesis and Crystal Structures of Novel Silylsubstituted Diphosphanes

Stefan K. Mueller, Gernot Weinberger, Elisabeth Schwarz, Ana Torvisco, Alk Dransfeld, Roland C. Fischer, Karl Hassler and Michaela Flock

Institute for Inorganic Chemistry, Graz University of Technology, Stremayrgasse 9/V, 8010 Graz, Austria

published in *Inorganica Chimica Acta*, 423A, **2014**, 517-523

3.1. Abstract

Reaction of two equivalents of lithium hypersilylphosphanide (hypersilyl, Hyp = tris(trimethylsilyl)silyl) with dichlorotetramethyldisilane at low temperatures gives $[HypPH\text{-}SiMe_2\text{-}]_2$ **10**, a compound with high steric protection on both phosphane functionalities. Dehydrogenation reaction of **10** with *n*-butyl lithium yields the dilithiated [2.1.1] bicyclic phosphanide salt $[HypPLi\text{-}SiMe_2\text{-}]_2$ **11**. The bicyclic structure is confirmed by NMR spectroscopy and X-ray diffraction analysis. As a major byproduct during the synthesis of **10** as well as *via* reaction of **11** with dichlorotetramethyldisilane, 1,4-diphospha-cyclosilahexane $[HypP\text{-}(SiMe_2)_2\text{-}]_2$ **12** is obtained. X-Ray diffraction analysis shows exclusive formation of the *trans*-conformer **12a** in the solid state, which is supported by calculations at the level of density functional theory (DFT).

Keywords: silylphosphanes, diphosphanes, DFT, NMR, X-ray diffraction analysis

3.2. Introduction

Compounds featuring two σ^3-P atoms, e.g. diphosphanes, have been known in literature for many years. Similar to their monophosphane counterparts,[102,103] diphosphanes are frequently used as ligands to transition metals. As a result of the electron donating properties of phosphorus, complexes of the general type $(R_2P\text{-}CH_2\text{-})_2M$ (Fig. 3.1, Type **A**, with R = Me, Ph, and larger substituents; M = Ru, W, Mo) as well as coordination compounds with various group 14 metal halides have been synthesized.[104,105] In all those compounds, the ligands are providing stabilization through interaction of the lone pairs located on the phosphorus atom.[106,107] In contrast to those diphosphane ligands, diphosphanide-based (Type **B**) complexes with a covalent P-M bond are not that common, though known for some 30 years.[108]

All compounds mentioned so far feature a carbon moiety as a backbone (chains or parts of aromatic ring systems) connecting the phosphorus atoms; corresponding silicon derivatives $(R_2P\text{-}SiMe_2\text{-})_2$ (Type **C**) and $(RP\text{-}SiMe_2\text{-})_2M$ (Type **D**) are comparatively unexplored. For effective ligand design and synthesis, small building blocks as precursors are advantageous. $[H_2P\text{-}SiMe_2\text{-}]_2$

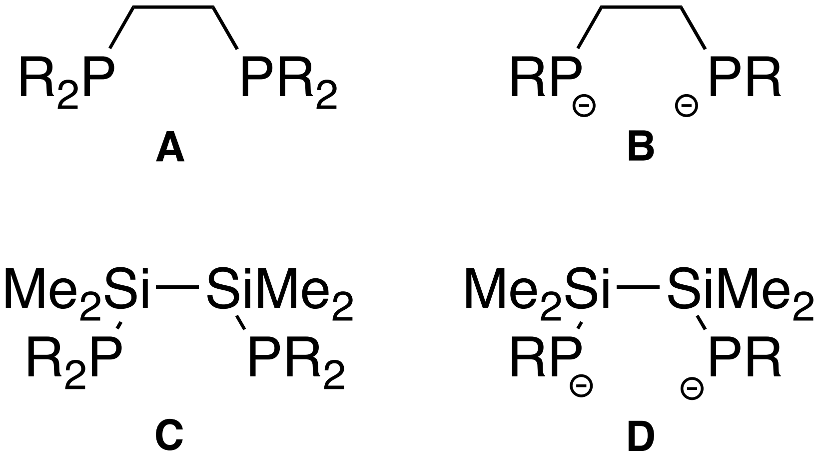


Figure 3.1.: Diphosphane and diphosphanide structure motifs.

and its methyl derivative $[\mathrm{MePH\text{-}SiMe_2\text{-}}]_2$[109] are ideal starting points for synthesis, providing a hydrogen functionality which could easily be used for either introduction of a bulky substituent or formation of a covalent metal-P bond *via* the corresponding lithiated compounds $[\mathrm{HPLi\text{-}SiMe_2\text{-}}]_2$ and $[\mathrm{MePLi\text{-}SiMe_2\text{-}}]_2$, or similar dianionic intermediates. Aside from similar compounds with a larger aliphatic moiety ($[i\mathrm{PrPH\text{-}SiMe_2\text{-}}]_2$[110]) aromatic systems such as the type **D** derivative of $[\mathrm{PhPH\text{-}SiMe_2\text{-}}]_2$ are also known.[111,112] Abstraction of the hydrogen is not obligatory; the molybdenum complex $[\mathrm{PhPHSiMe_2\text{-}}]_2\mathrm{Mo(CO)_4}$[113] shows a donor-acceptor interaction pattern similar to its methyl-substituted derivate $[\mathrm{Me_2P\text{-}SiMe_2\text{-}}]_2\mathrm{Mo(CO)_4}$.[114] Tetraphenylated $[\mathrm{Ph_2P\text{-}SiMe_2\text{-}}]_2$ has been synthesized by Hassler[115] but has not found any application thus far.

Further variations of P-substituents have been achieved through introduction of boron based moieties. $\{[(i\mathrm{Pr_2N})_2\mathrm{B}]\mathrm{PH\text{-}SiMe_2\text{-}}\}_2$[116] has been proven to be a suitable type **C** ligand for the molybdenum tetracarbonyl complex $\{[(i\mathrm{Pr_2N})_2\mathrm{B}]\mathrm{PH\text{-}SiMe_2\text{-}}\}_2\mathrm{Mo(CO)_4}$.[117] The corresponding [2.1.1]bicyclic derivative, $\{[(i\mathrm{Pr_2N})_2\mathrm{B}]\mathrm{PSiMe_2\text{-}}\}_2$, has also shown the ability to form complexes with iron pentacarbonyl.[118]

While all these compounds feature a $(\mathrm{SiMe_2\text{-}})_2$ backbone, corresponding derivatives with a silicon-based terminal P-substituent, that could provide kinetic stabilization, have not been reported to date. In group 14 chemistry, $\mathrm{SiMe_3}$ groups have been used as sterically demanding, stabilizing substituents for several years.[62,67,68] In 2006, Hassler *et al.* reported on several phosphanes and diphosphanes featuring a bulky $\mathrm{\text{-}Si(SiMe_3)_3}$ group, most interestingly simple hypersilylphosphane [$(SiMe_3)_3Si-PH_2$].[61] Linkage of those monophosphane building blocks opens the way to a new type of diphosphane system. In this work we present the synthesis and full characterization of such type **C** and **D** compounds.

3.3. Experimental

3.3.1. General Procedures

All reactions, unless otherwise stated, were carried out using 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.). C_6D_6 was distilled over sodium and stored under nitrogen atmosphere. *n*-Butyl lithium and potassium *t*-butylate were purchased from Aldrich and used as received. Dichlorotetramethyldisilane was prepared following standard procedures.[119] $HypPH_2$, HypPHLi, $HypP(SiMe_3)_2$ $HypP(SiMe_3)K$ were prepared following procedures previously published.[61] After successful synthesis, all compounds were stored under inert conditions at room temperature and were stable for several months.

3.3.2. NMR

^1H (300.2 MHz), ^{13}C (75.5 MHz), ^{29}Si (59.6 MHz) and ^{31}P (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 (δ = 0 ppm) regarding ^1H, ^{13}C and ^{31}Si and relative to 85% H_3PO_4 for ^{31}P. Coupling constants (J) are reported in Hertz (Hz). All NMR spectra were measured in C_6D_6. Reactions were monitored using a D_2O capillary as external lock signal.

3.3.3. X-ray Diffraction

All crystals suitable for single crystal X-ray diffractometry were removed from a Schlenk under inert conditions 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 N_2 stream provided by an Oxford Cryosystems cryometer. Single crystal data collection was performed on a BRUKER APEX II diffractometer with use of Mo Kα radiation (λ = 0.71073 Å) and a CCD area detector. Empirical absorption corrections were applied using SADABS.[86,87] The structures were solved with use of either direct methods or the Patterson option in SHELXS and refined by the full-matrix least-squares procedures in SHELXL.[120,121] The space group assignments and structural solutions were evaluated using PLATON.[90,122] Disorder, as observed for compound **11** was handled by modeling the occupancies of the individual orientations using free variables to refine the respective occupancy of the affected fragments.[121] Disordered positions for the coordinated solvent diethyl ether were refined using 70/30 split positions. Disorder in the terminal $SiMe_3$ groups was refined using 50/50 split positions. Table 3.1 contains crystallographic data and details of measurements and refinements for compounds **10**-**12a**. CCDC 986633, 986634 and 986635 contain the supplementary crystallographic data for compounds **10**-**12**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3.3.4. Computational Details

All calculations have been carried out using the Gaussian09 program package[123] on a computing cluster with blade architecture. For all calculations except calculations of NMR shieldings the mPW1PW91 hybrid functional[124] was used. NMR shieldings were calculated using the M06L[125] pure functional as implemented in Gaussian09. For optimizations and calculation of frequencies the Stuttgart / Dresden basis set denoted by SDD as implemented in Gaussian09 was used, consisting of the D95 basis set[126] for elements up to Argon and Stuttgart / Dresden ECPs for heavier elements.[127,128] For calculation of NMR shieldings the all electron IGLO-II[129] basis set was used.

3.3.5. Synthesis

3.3.5.1. Synthesis of [HypPH-SiMe$_2$-]$_2$ 10

A solution of HypPHLi (1.17 g, 4.10 mmol) in 6 mL of diethyl ether was cooled to -78 °C and slowly added to a cooled (-78 °C) solution of $Me_4Si_2Cl_2$ in 10 mL of toluene *via* cannula under vigorous stirring. The reaction was allowed to warm up to room temperature and was vigorously stirred for 16 hours. After removal of solvents under reduced pressure the residue was dissolved in pentane and filtered from salts. Crystals suitable for X-ray diffraction analysis were obtained from pentane at -30 °C. ^{1}H NMR (C_6D_6, 293 K): δ 0.31 ppm (54H, d, (Me_3Si)$_3$Si, $^4J_{PH}$ = 2.4 Hz), 0.55 ppm (12H, d, Me_2Si, $^3J_{PH}$ = 4.2 Hz), 1.06 ppm (2H, d, P*H*, $^1J_{PH}$ = 193.8 Hz). ^{13}C NMR (C_6D_6, 293 K): δ 1.3 ppm (18C, s, (Me_3Si)$_3$Si), 1.6 ppm (6C, s, Me_3Si). ^{29}Si NMR (C_6D_6, 293 K): δ -99.4 ppm (2Si, dd, $^1J_{SiP}$ = 74.0 Hz, $^4J_{SiP}$ = 2.4 Hz, (Me_3Si)$_3$*Si*), -16.3 ppm (2Si, dd, $^1J_{SiP}$ = 57.9 Hz, $^2J_{SiP}$ = 23.9 Hz), -10.7 ppm (6Si, "t", $^2J_{SiP}$ 5.1 Hz, (Me_3*Si*)$_3$Si). ^{31}P NMR (C_6D_6, 293 K): δ -263.8 ppm (2P, d, $^1J_{PH}$ = 193.8 Hz). Yield: 1.01 g, 73%.

3.3.5.2. Synthesis of [HypPLi-SiMe$_2$-]$_2$ 11

[HypPH-SiMe$_2$-]$_2$ (2.04 g, 3.02 mmol) was dissolved in 10 mL of diethyl ether and cooled to -78 °C. 4.13 mL (6.60 mmol) of 1.6 M *n*-butyl lithium in hexanes were added drop-wise *via* syringe to the solution through a septum. After removal of cooling the reaction was stirred for two hours. Solvents were removed under reduced pressure and replaced with toluene. Crystals suitable for X-ray diffraction analysis were obtained from toluene at -30 °C. ^{1}H NMR (C_6D_6, 293 K): δ 0.40 ppm (54H, s, (Me_3Si)$_3$Si), 0.62 ppm (12H, broad s, Me_2Si). ^{13}C NMR (C_6D_6, 293 K): δ 1.9 ppm (18C, s, (Me_3Si)$_3$Si), 2.0 ppm (6C, s, Me_3Si). ^{29}Si NMR (C_6D_6, 293 K): δ -97.8 ppm (2Si, "t", $^1J_{SiP}$ = 36.9 Hz, (Me_3Si)$_3$*Si*), -25.7 ppm (2Si, "t", $^1J_{SiP}$ = $^3J_{SiP}$ = 21.1 Hz), -15.2 ppm (6Si, "t", $^2J_{SiP}$ = 4.0 Hz, (Me_3*Si*)$_3$Si). ^{31}P NMR (C_6D_6, 293 K): δ -337.9 ppm (2P, sep, $^1J_{PLi}$ = 55.5 Hz). Yield: 1.83 g, 88%.

3.3.5.3. Synthesis of [HypP-(SiMe$_2$)$_2$-]$_2$ 12a

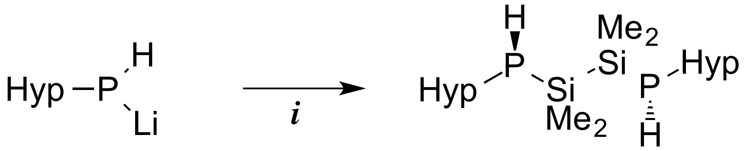
A solution of [HypPLi-SiMe$_2$-]$_2$ (0.80 g, 1.16 mmol) in diethyl ether was added to a cooled (-78 °C), vigourously stirred solution of dichlorotetramethyldisilane *via* cannula. After letting the reaction solution warm up to room temperature, the solvent was removed under reduced pressure und replaced by pentane. Crystals suitable for X-ray diffraction analysis were obtained from pentane at -30 °C. ^{1}H NMR (C_6D_6, 293 K): δ 0.57 ppm (12H, d, $^{3}J_{\mathrm{HP}}$ = 5.4 Hz, Si*Me$_2$*), 0.36 ppm (54H, s, Si*Me$_3$*). ^{13}C NMR (C_6D_6, 293 K): δ 2.84 ppm (4C, "t", $^{2}J_{\mathrm{CP}}$ = 4.3 Hz, Si*Me$_2$*), 3.19 ppm (18C, "t", AMM', $^{3}J_{\mathrm{CP}}$ = 1.0 Hz, Si*Me$_3$*). ^{29}Si NMR (C_6D_6, 293 K): δ -94.3 ppm (2Si, dd, $^{1}J_{\mathrm{PSi}}$ = 106.1 Hz, $^{3}J_{\mathrm{PSi}}$ = 98.6 Hz, *Si*(SiMe$_3$)$_3$), -14.9 ppm (dd, $^{1}J_{\mathrm{SiP}}$ = 83.5 Hz, $^{2}J_{\mathrm{SiP}}$ = 34.5 Hz, *Si*Me$_2$), -10.7 ppm (6Si, "t", $^{2}J_{\mathrm{PSi}}$ = 8.7 Hz, *Si*Me$_3$). ^{31}P NMR (C_6D_6, 293 K): δ -269.4 ppm (2P, s). Yield: 0.84 g, 92%.

Table 3.1.: Crystallographic data for compounds **10**, **11** and **12a**

Compound Number	**10**	**11**	**12a**
Empirical formula	$C_{22}H_{68}P_2Si_{10}$	$C_{30}H_{86}Li_2O_2P_2Si_{10}$	$C_{26}H_{78}P_2Si_{12}$
Formula weight	675.6 g*mol^{-1}	835.70 g*mol^{-1}	789.9 g*mol^{-1}
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073Å	0.71073Å	0.71073Å
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1
Unit cell dimensions	a = 8.3074(3)Å	a = 22.0923(13)Å	a = 8.9696(6)Å
	b = 14.4801(4)Å	b = 20.1910(13)Å	b = 9.6826(6)Å
	c = 18.3740(5)Å	c = 24.5167(16)Å	c = 16.431(1)Å
	α= 90°	α= 90°	α = 98.597(3)°
	β= 98.344(0)°	β= 92.156(3)°	β = 96.722(3)°
	γ = 90°	γ = 90°	γ = 115.982(3)°
Volume	2186.85(12)Å^3	10928.3(12)Å^3	1241.34(14)Å^3
Z	2	8	1
Density (calc.)	1.026 Mg/m^3	1.016 Mg/m^3	1.057 Mg/m^3
Absorption coefficient	0.386 mm^{-1}	0.321 mm^{-1}	0.39 mm^{-1}
F(000)	740	3664	432
Crystal size	0.15 x 0.10 x 0.08 mm	0.36 x 0.25 x 0.18 mm	0.09 x 0.06 x 0.03 mm
Crystal habit	Colorless block	Colorless block	Colorless plate
2θ range	2.24° to 27.13°	2.2° to 28.00°	2.4° to 27.1°
R_{int}	0.040	0.044	0.087
R1, wR2 (all data)	0.0386, 0.0638	0.1029, 0.1800	0.0810, 0.1411
R1, wR2 ($> 2\sigma$)	0.0270, 0.0596	0.0721, 0.1694	0.0537, 0.1269
Index range h	-10<=h<=10	-27<=h<=23	-10<=h<=10
Index range k	-18<=k<=18	-24<=k<=24	-11<=k<=11
Index range l	-23<=l<=23	-30<=l<=30	-19<=l<=19
Reflections collected	40785	21424	4312
Independent reflections	4809	16420	3232
No. of parameters	179	971	194

3.4. Results and Discussion

The reaction of HypPHLi[61] with 1,2-dichlorotetramethyldisilane at -50 °C yielded 1,2-bis(hypersilylphosphanyl)-tetramethyldisilane **10** [HypPH-SiMe$_2$-]$_2$ (Figure 3.2).



10

i: 0.5 Me$_4$Si$_2$Cl$_2$, -50°C, Et$_2$O

Figure 3.2.: Reaction of lithium hypersilylphosphanide with 1,2-dichlorotetramethyldisilane yields *meso*-[HypPH-SiMe$_2$-]$_2$ **10**.

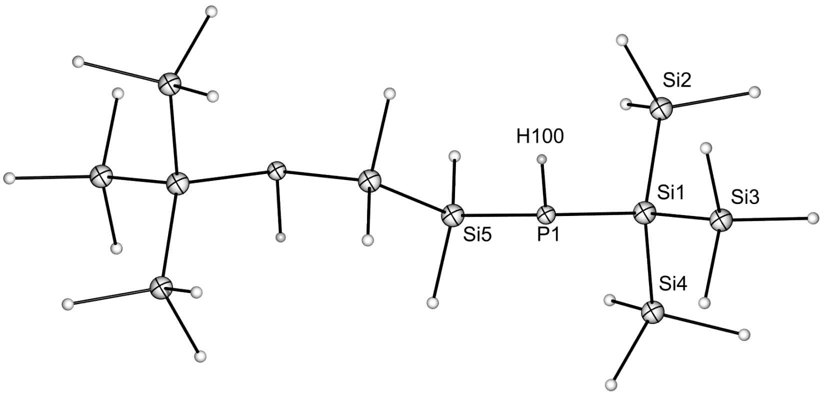


Figure 3.3.: ORTEP-Plot of [HypPH-SiMe$_2$-]$_2$ **10**. Hydrogen atoms on all methyl groups have been omitted for clarity. Non carbon atoms are represented as 30% ellipsoids.

Two stereoisomers regarding the P-atoms should be expected, the *meso*-diastereomers on the one hand and the corresponding (S,S)/(R,R) structures on the other. However, in the obtained ^{31}P-NMR spectra, only one resonance at δ = -263.8 ppm with a $^1J_{PH}$ coupling of 193.8 Hz for both phosphorus atoms can be observed, suggesting either fast conversion of the energetically almost equivalent (see below) diastereomers or exclusivity of one of the diastereomers in solution. While in solution the presence of both diastereomers is plausible, single crystals X-ray diffraction analysis shows a clear stereochemical preference for the solid state. Colorless crystals obtained from pentane could be exclusively identified as **10** in *meso*-conformation (Figure 3.3).

Bond lengths agree well with previously published structures. The Si5-P1 bond between the phosphorus atoms and the $SiMe_2$-backbone is with 224.0(5) pm in the same range as other P-Si bonds in comparable compounds. Hydrogen atoms connected to the phosphorus are on found positions. The P1-H100 bond lies in the normal range of known P-H bonds. With an average distance of 132(2) pm the bond is slightly elongated compared to Westerhausen's $[(i\mathrm{Pr})_3\mathrm{Si}]_2\mathrm{P{-}H}$ (125(3) pm).[130] The Si1-P1 bond to the terminal hypersilyl group is slightly elongated with a length of 227.4(6) pm, but in the expected range for hypersilyl-P bonds. While in the solid state, only one diastereomer is found, however calculations at the level of density functional theory (mPW1PW91/SDD) have shown little difference ($<$ 0.1 kJ/mol) in absolute energy for the diastereomers. Conversion of one of the P-stereocenters would require a transition structure with a planar phosphorus center. With only +48.9 kJ/mol the energy required for inversion of one of the chiral P-atoms is low compared to previously reported inversion energies.[61]

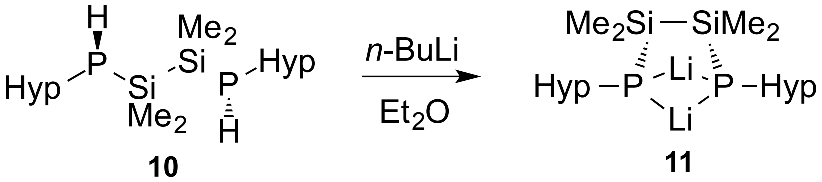


Figure 3.4.: Reaction of **10** with *n*-butyl lithium yields $[\mathrm{HypPLi{-}SiMe_2{-}}]_2$ **11**.

Metalation reaction of **10** in diethyl ether by slow addition of *n*-butyl lithium at -60°C (Figure 3.4) yields a bright yellow solution. Replacement of the solvent with hexane yields colorless crystals of $[\mathrm{HypPLi{-}SiMe_2{-}}]_2$ **11** at -80°C. **11** crystallizes as an ether adduct (Figure 3.5). The hypersilyl-phosphorus bond lengths P1-Si3 and P2-Si7, ranging from 224.1(2) pm to 224.4(1) pm, are slightly shortened compared to **10** and **12a**. The same trend can be observed regarding the bonds (P1-Si1, P2-Si2) to the silicon backbone, with lengths ranging from 221.1(2) pm to 221.9(2) pm. The symmetric [2.1.1] bicyclic structure is also retained in solution. ^{31}P-NMR shows one septet signal at δ -337.8 ppm with $^1J_{\mathrm{PLi}}$ coupling constants of 55.5 Hz (Figure 3.6). Due to

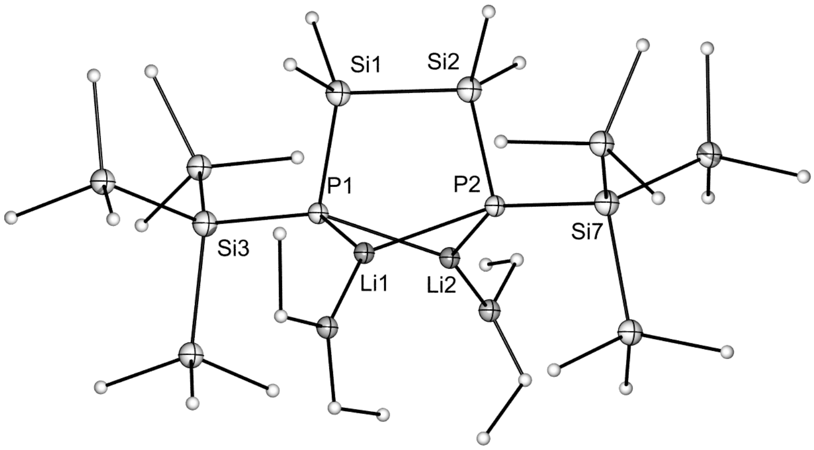


Figure 3.5.: ORTEP-Plot of [HypPLi-SiMe$_2$-]$_2$ **11**. Hydrogen atoms have been omitted for clarity. Non carbon atoms are represented as 30% ellipsoids.

the absence of further signals and the characteristic coupling pattern of two Li-atoms a preservation of the structural features of the solid state structure is confirmed.

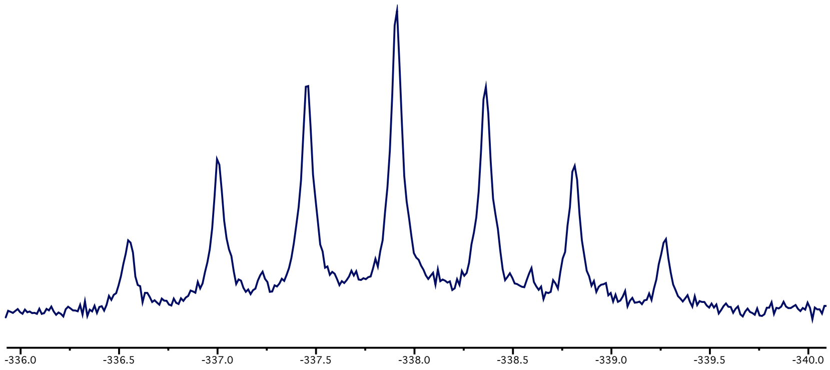


Figure 3.6.: $^{1}J_{\mathrm{LiP}}$-coupling in the high-field region of the ^{31}P-spectrum of **11**

There are a couple of related structures known in literature,[116, 131–134] the most similar being [MePLi-SiMe$_2$-]$_2$.[109] Compared to this methyl derivative, average P-Li bond lengths are slightly shortened (255.5(5) pm and 249.9(9) pm, respectively). All of the literature-known structures show a two-fold solvent coordination for each lithium atom, in contrast to the coordination of one single diethyl ether molecule per lithium cation in **11**. However, there are some acyclic compounds known with a solvent to lithium ratio of 1:1[110, 135, 136] and one solvent-free structure[92] stabilized by intramolecular π-interaction. Its molecular structure makes **11** an ideal starting point for ring-closure reactions.

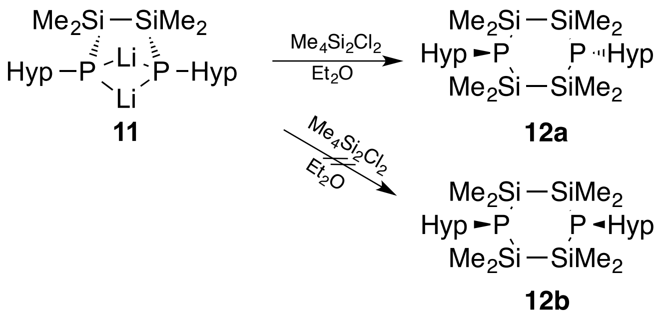


Figure 3.7.: Reaction of **11** with 1,2-dichlorotetramethyldisilane yields *trans*-[HypP-$(SiMe_2)_2$-$]_2$ **12a** after recrystallization.

Reaction of **11** with 1,2-dichlorotetramethyldisilane yields 1,4-diphosphacyclohexasilane [HypP-$(SiMe_2)_2$-$]_2$ **12a** (Figure 3.7). It is also formed as a major byproduct during the synthesis of **10**, especially with usage of a slight excess (1.2 eq.) of *n*-butyl lithium during the preceeding lithiation of the educt $HypPH_2$. Similarly to **10**, only one signal (δ -269.4 ppm) can be observed for both of the phosphorus atoms in ^{31}P-NMR spectroscopy. This can either be caused by a dynamic equilibrium of the stereoisomers or the exclusivity of the thermodynamically favored stereoisomer in solution.

Theoretical investigation of conformations and thermodynamic stability of **12a** gave interesting results. Compared to **10** and the systems investigated by Hassler,[61] the inversion barrier for the phosphorus atoms is even lower with a relative energy of only 36.4 kJ/mol and does not rule out the presence of more than one stereoisomer in solution. In contrast to the isoenergetic stereoisomers of **10**, the *trans*-stereoisomer in chair conformation **12a** is clearly energetically favored. Compared to the chair *cis*-configuration **12b**, **12a** is more stable by -29.8 kJ/mol (Figure 3.8). Even after a possible initial formation of the *cis*-isomer, the energetic barrier between **12a** and **12c** (6.6 kJ/mol) can quite easily be overcome and result in formation of *trans*-isomer **12a**. The relative thermodynamic energies are a good explanation for the preference of the *trans*-isomer in the solid state and at low temperatures.

The ring itself is most stable in a chair conformation. Further minima can be found in twist conformation, including a *cis*-twist **12d** (+6.6 kJ/mol) and a *trans*-twist **12e** (+20 kJ/mol) configuration. As can be seen in Figure 3.9, the main difference between **12a** and **12b** (as well as between **12d** and **12e**) is

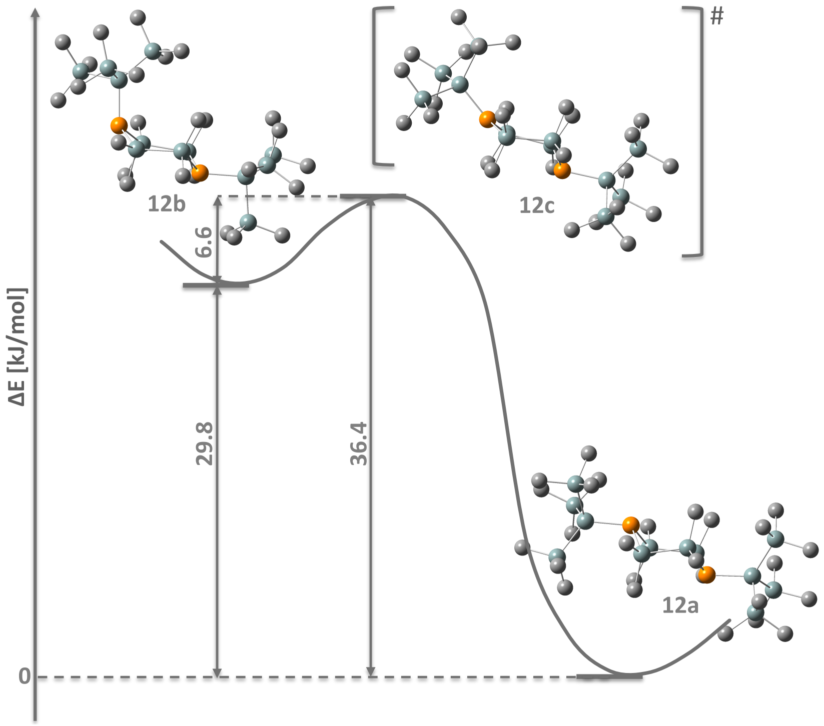
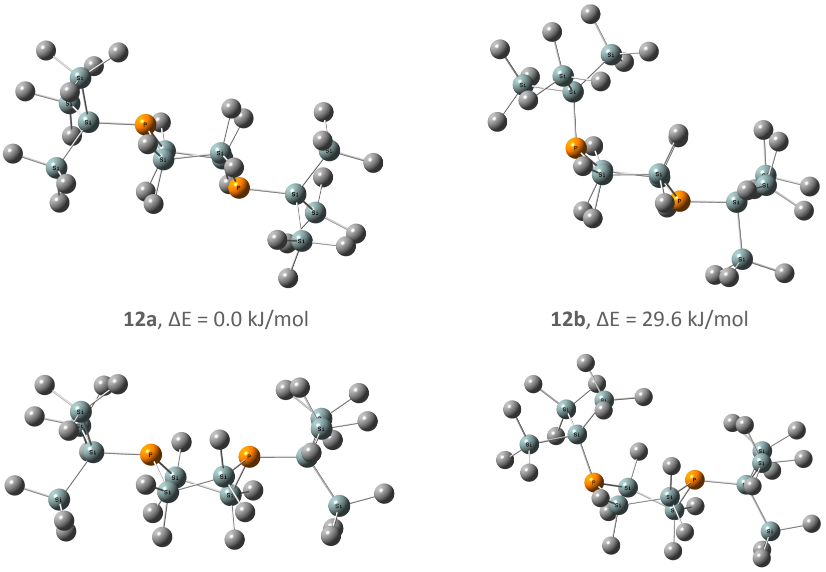


Figure 3.8.: Relative energies of **12a**, **12b** and their transition structure **12c** at the mPW1PW91/SDD level.



12a, ΔE = 0.0 kJ/mol

12b, ΔE = 29.6 kJ/mol

12d, ΔE = 6.6 kJ/mol

12e, ΔE = 20.0 kJ/mol

Figure 3.9.: Comparison of different minimum structures of **12** and their relative energy in kJ/-mol.

the relative positioning of the hypersilyl moieties. While **12a** and **12d** keep the bulky substituents on phosphorus comparatively unaffected by each other, their steric repulsion easily explains the higher relative energy of **12b** and **12e**. All configurations except **12a** show a distinct dipole moment in the magnitude of water (1.62, 2.16 and 2.79 Debye for **12e**, **12d** and **12b**, respectively). The calculations for **12a** show virtually no dipole moment (0.21 Debye), resulting in additional stabilization of that configuration in apolar solvents, next to its highest thermodynamic stability.

Computational results correlate well with experimentally obtained data; also in the solid state **12** can be exclusively found in chair conformation **12a** as suggested by the theoretical results (Figure 3.10). A bond length of 230.3(1) pm (P1-Si2) between the phosphorus atoms and the hypersilyl groups fits well in the range of previously reported hypersilyl-P bond lengths.[61] The bond length is increased compared to educt **10** (+2.9 pm). This can be attributed to the two sterically demanding $SiMe_2$ moieties on P besides the hypersilyl group. In **10** only one $SiMe_2$ next to the hydrogen atom results in less steric repulsion.

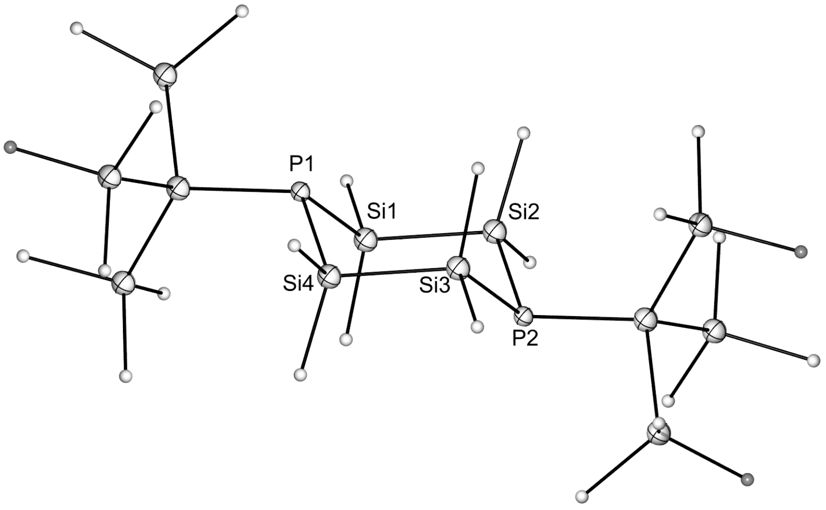


Figure 3.10.: ORTEP-Plot of $[HypP\text{-}(SiMe_2)_2\text{-}]_2$ **12a**. Hydrogen atoms have been omitted for clarity. Non carbon atoms are represented as 30% ellipsoids.

Compounds **10**, **11** and **12** show interesting NMR properties. The bridging silicon atoms connecting both phosphorus atoms (Figure 3.11, Si_b, Si'_b) as well as the central silicon atoms of the hypersilyl moiety (Si_c, Si'_c) show the expected doublet of a doublet in ^{29}Si NMR. The corresponding $^1J_{Si_bP}$ and $^1J_{Si_cP}$ coupling constants are substantially larger than the $^2J_{Si_bP'}$ and $^4J_{Si_cP'}$ (additionally $^3J_{Si_cP'}$ for **11**) couplings constants, respectively.

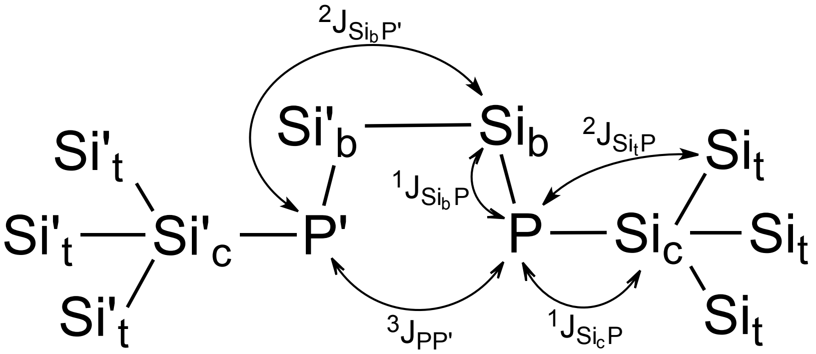
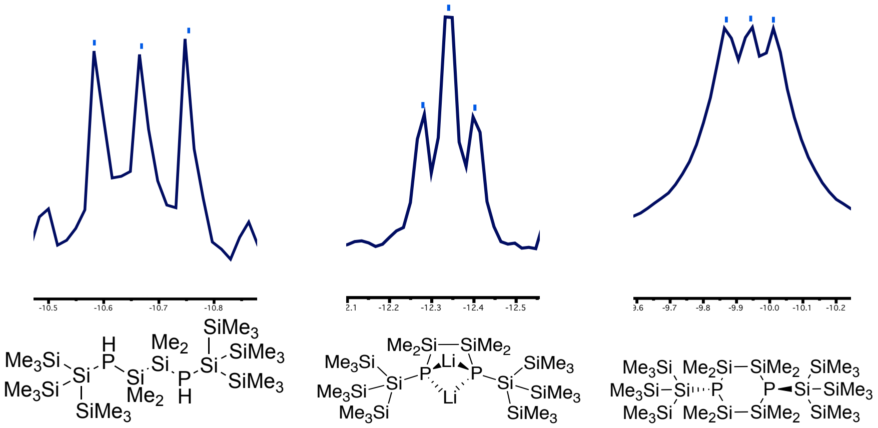


Figure 3.11.: Labeling scheme for discussion of coupling constants.

The terminal $SiMe_3$ groups on the hypersilyl moiety (Si_t, Si'_t) show different behavior. With the assumption of fast rotability around the phosphorus silicon bond Si_c-P on the NMR time scale, a doublet with a $^2J_{Si_tP}$ coupling constant comparable to $^2J_{Si_bP'}$ should be expected. However, the coupling pattern shown in Figure 3.12 shows three peaks for the hypersilyl moiety for all three discussed compounds. A possible explanation for this coupling pattern is the presence of a AA'X spin system regarding the silicon in the $SiMe_3$ moieties, with A,A' being the phosphorus atoms. The relative height of the central peak compared to the outer peaks varies with the ratio of the $^3J_{PP'}$ to the $^2J_{Si_tP}$ coupling constant, leading to different line shapes for different relative environments of the corresponding phosphorus atoms, as seen in Figure 3.12 for **10** (left), **11** (middle) and **12a** (right). Temperature dependent NMR-measurements which were carried out for **10** did not have significant influence on the coupling pattern. Calculations at the level of DFT (M06L/IGLO-II) showed that this Si-P coupling is strongly dependent on the spatial arrangement of the $SiMe_3$ groups relative to the adjacent phosphorus atom. $SiMe_3$ groups in *syn*-conformation relative to the lone pair show a much higher coupling than in *anti*-conformation. Taking compound **12** as an example, the calculated minimum structures, as well as the solid state geometry, show two $SiMe_3$ in *syn*- and one $SiMe_3$ group in *anti*-configuration. With a barrier of only 16 kJ/mol, the rotation of the hypersilyl group in solution is too fast compared to the NMR time scale for a possible signal separation of the $SiMe_3$ groups, though.



10 **11** **12a**

Figure 3.12.: ^{29}Si NMR coupling patterns of the terminal SiMe$_3$ moieties in **10** (left), **11** (middle) and **12a** (right)

3.5. Conclusion & Outlook

The reaction of diphosphane [HypPH-SiMe$_2$-]$_2$ **10** with *n*-butyl lithium leads to a selective abstraction of a hydrogen atom, while similar reactions have been used for Si-P cleavage in the past.[137] The resulting [2.1.1] bicylic diphosphanide [HypPLi-SiMe$_2$-]$_2$ **11** provides an ideal starting point for further reactions, with its hypersilyl moieties causing steric bulkiness. The comparatively low inversion barrier also contributes to the overall flexibility of the ligand system. Reactions investigating applications of this diphosphane system are currently in progress.

Chapter 4

A stable diphosphastannylene and attempted synthesis of a cyclic diphosphastannylene

Stefan K. Mueller, Elisabeth Schwarz, Gernot Weinberger, Ana Torvisco, Alk Dransfeld, Karl Hassler, Michaela Flock

Institute for Inorganic Chemistry, Graz University of Technology, Stremayrgasse 9/V, 8010 Graz, Austria

4.1. Abstract

Reaction of $HypP(SiMe_3)_2$ **13** (Hyp = $(SiMe_3)_3Si$-) with potassium *t*-butoxide in dimethoxy ethane gives dimeric $[HypP(SiMe_3)K]\cdot DME$ **14**, a sterically protected potassium phosphanide. The novel free diphosphastannylene $[HypP(SiMe_3)]_2Sn$ **15** is accessible *via* reaction of **14** with tin(II)bromide in THF at low temperatures. In the solid state, **15** shows neither coordination of a solvent nor inter/intramolecular interactions. The attempted synthesis of the analogous cyclic stannylene $[HypP\text{-}SiMe_2\text{-}]_2Sn$ **16** led to the formation of a bipyramidal tin cluster capped by two hypersilyl-P moieties.

4.2. Introduction

Compounds containing group 14 elements in the oxidation state of +II bearing diamino based ligands have been well established over the last decades.[2,138,139] Interaction of the nitrogen lone pair with the vacant orbital on the tetrylene, the comparably low energy barrier to planar nitrogen and the distinct difference in electronegativity, especially compared to higher homologues in the group, are the main stabilizing factors in those compounds. The stability of α,α'-diphospha-tetrylenes is mainly dependent on the sterical demand of the substituents on phosphorus. The first diphosphatetrylene, $\{[(t\text{-Bu})_2P]_2Sn\}_2$[57], was found as a dimer in the solid state as well as in solution. It comes as no surprise that tetrylenes with comparable ligand size ($\{[(i\text{Pr})_2P]_2Ge\}_2$[56], $[(t\text{Bu})_2P]_2Pb\}_2$[58] and $\{[(SiMe_3)_2P]_2Sn\}_2$[59]) also undergo dimerization.

For the isolation of monomeric structures larger substituents containing aromatic moieties have been used. Compounds like $\{[(Tripp)_2FSi](i\text{Pr}_3Si)P\}_2E$ (E = Ge, Sn, Pb and Tripp = 2,4,6-$i\text{Pr}_3C_6H_2$) reported by Driess in 1995[53] as well as $\{[2,5\text{-}(Mes)_2Ph](Ph)P\}_2Sn$ reported by Power in 2007[56] could be clearly characterized as monomers in solution via NMR-experiment and yielded crystals suitable for X-Ray diffraction spectroscopy in the first case. Further monomeric tetrylenes include diphospholide stannylenes by Westerhausen[140,141] and stannylenes stabilized by η-5 interaction *via* formation of phosphastannenocenes.[142] In 2012, Izod and coworkers succeeded in the synthesis of comparatively small diphosphatetrylenes $\{[(Me_3Si)_2CH]P(C_6H_4$-

-2-SMe)}$_2$E (E = Ge, Sn).[54] Additional stabilization of discrete momomers is reached by intramolecular stabilization *via* coordination of a sulfur lone pair.

The difference between nitrogen and phosphorus as tetrylene ligands is even more severe regarding cyclic systems. In fact, only one cyclic P,P' tetrylene, P-heteroyclic carbene, is known to date.[60] Compounds like α,α'-dialkyl-[62] and α,α'-disilyl-tetrylenes[67,68] however have shown that cyclic tetrylenes are indeed stable given the right steric conditions. Those tetrylenes (or their corresponding cyclic precursors) are accessible via 1:1 reaction of a ligand backbone with the corresponding group-14 halide and, in the case of silylenes, subsequent reductive dehalogenation with alkali metals. For the synthesis of α,α'-diphosphorus tetrylenes, adaptation of the general structure of those ring systems seems appropriate. The hypersilyl moiety [(SiMe$_3$)$_3$Si-] provides great steric protection to neighboring groups while generally not being reactive itself, if not specifically targeted.[84]

Recent work[143] has shown that backbone systems featuring a hypersilyl moiety can be functionalized to ideal precursors to such ring systems. Their corresponding monomeric precursors[61] have been used in the synthesis of stable diphosphanes and are a promising starting point for novel open chain α,α'-P-tetrylenes. Unlike the ligands of all previously reported monomeric diphosphatetrylenes, these ligands feature neither aromatic nor any additional electron donating moieties. The present work describes the synthesis of cyclic and acyclic diphospha-tetrylenes using such hypersilyl based ligands as the main source of stabilization.

4.3. Experimental

4.3.1. 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.). C_6D_6 has been destilled over sodium and stored under nitrogen atmosphere. *n*-Butyl lithium and potassium *tert*-butylate were bought from Aldrich and used as delivered. Dichlorotetramethyldisilane has been prepared following standard procedures.[119] HypP($SiMe_3$)K **14** and (HypPLi-$SiMe_2$-)$_2$ **11** were prepared following procedures previously published.[61,143]

Table 4.1.: Crystallographic data for compounds **14** and **15**

Compound	[HypP($SiMe_3$)K]·DME **14**	[HypP($SiMe_3$)]$_2$Sn **15**
Formula	$C_{16}H_{46}KO_2PSi_5$	$C_{24}H_{72}P_2Si_{10}Sn$
Fw (g*mol^{-1})	481.05	822.34
a (Å)	14.0472(17)	15.0762(5)
b (Å)	13.0421(16)	17.9321(6)
c (Å)	17.176(2)	17.7455(6)
α (°)	90	90
β (°)	104.743(5)	103.3230(16)
γ (°)	90	90
V (Å3)	3043.1(6)	4668.3(3)
Z	4	4
Crystal size (mm)	0.15x0.12x0.09	0.35x0.20x0.09
Crystal habit	Block, orange	Block, orange
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
d_{calc} (mg/m^3)	1.05	1.17
μ (mm^{-1})	0.43	0.89
T (K)	100(2)	100(2)
2Θ range (°)	2.0-27.2	2.3-27.1
F(000)	1048	1744
R_{int}	0.511	0.054
independent reflns	6694	10321
No. of params	415	358
R1, wR2 (all data)	R1 = 0.3808 wR2 = 0.3078	R1 = 0.0313 wR2 = 0.0460
R1, wR2 ($>2\sigma$)	R1 = 0.0952 wR2 = 0.1890	R1 = 0.0209 wR2 = 0.0427

4.3.2. NMR

^{1}H (300.2 MHz), ^{13}C (75.5 MHz), ^{29}Si (59.6 MHz), ^{31}P (121.5 MHz) and ^{119}Sn (111.9 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 (δ = 0 ppm) regarding ^{1}H, ^{13}C and ^{29}Si, relative to 85% H_3PO_4 for ^{31}P and relative to $SnMe_4$ in the case of ^{119}Sn. Coupling constants (*J*) are reported in Hertz (Hz). All NMRs were taken in C_6D_6. Reactions were monitored using a D_2O capillary as external lock signal.

4.3.3. X-Ray Diffraction

All crystals suitable for single crystal X-ray diffractometry were removed from a vial 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 N_2 stream provided by an Oxford Cryosystems cryometer or Kryoflex low temperature cooling unit. XRD data collection was performed on a Bruker APEX II diffractometer with use of Mo Kα radiation (λ = 0.71073 Å) and a CCD area detector. Empirical absorption corrections were applied using SADABS.[87,122] The structures were solved with use of either direct methods or the Patterson option in SHELXS and refined by the full-matrix least-squares procedures in SHELXL.[88,89] The space group assignments and structural solutions were evaluated using PLATON.[90,91] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in calculated positions corresponding to standard bond lengths and angles.

4.3.4. Computational Details

All calculations have been carried out using the Gaussian09 program package[123] on a computing cluster with blade architecture. For all calculations except calculations of magnetic shieldings the mPW1PW91 hybrid functional[124] was used. Magnetic shieldings were calculated using the M06L[125] pure functional as implemented in Gaussian09. For optimizations and calculation of frequencies the basis set combination denoted by SDD as implemented in Gaussian09[126–128] was used. For calculation of NMR shieldings and UV/VIS absorptions the all electron IGLO-II[129] basis set was used.

4.3.5. Synthesis

4.3.5.1. Synthesis of [HypP($SiMe_3$)K·DME] 14

1.00 g (2.4 mmol) HypP($SiMe_3$)$_2$ **13** and 0.28 g (2.5 mmol) of potassium *tert*-butoxylate are brought into a Schlenk flask under inert atmosphere. Dissolution of the solid, colorless educts in 6 mL of dimethoxy ethane (DME) at 0 °C led to an immediate change of color to intense yellow. After vigorous stirring for 24 h all volatile components were removed under reduced pressure. The residue was redissolved in a mixture of pentane and toluene. Crystals suitable for X-Ray diffraction analysis were obtained from this solution at -30 °C. Yield: 0.98 g, 87%. ^{1}H NMR (C_6D_6, 293K): δ 0.09 ppm (27H, s, (*Me3*Si)$_3$Si) 0.17 (9H, broad s, *Me3*Si). ^{13}C NMR (C_6D_6, 293K): δ 2.0 ppm (9C, d, $^{3}J_{CP}$ = 12.2 Hz, (*Me3*Si)$_3$Si), 8.5 ppm (3C, d, $^{2}J_{CP}$ = 11.6 Hz, *Me3*Si). ^{29}Si NMR (C_6D_6, 293K): δ -94.9 ppm (Si, d, $^{1}J_{SiP}$ = 118.2 Hz, (Me$_3$Si)$_3$*Si*), -14.8 ppm (3Si, d, $^{2}J_{SiP}$ = 11.4 Hz (Me$_3$*Si*)$_3$Si), -0.53 ppm (1Si, d, $^{1}J_{SiP}$ = 78.9 Hz, Me$_3$*Si*). ^{31}P NMR (C_6D_6, 293 K): δ -355.6 ppm.

4.3.5.2. Synthesis of [HypP(SiMe$_3$)]$_2$Sn 15

A solution of HypP(SiMe$_3$)K·DME (0.92 g, 1.91 mmol) in 6 mL of DME was cooled to -50 °C and slowly added to a cooled (-50 °C) suspension of SnBr$_2$ in 10 mL of THF in a 100 mL Schlenk flask via cannula under vigorous stirring. Upon addition the reaction solution turned to dark green. The reaction was allowed to warm up to room temperature and was vigorously stirred for 16 hours. After removal of solvents under reduced pressure the residue was dissolved in pentane and filtered from salts. Crystals suitable for X-Ray diffraction analysis were obtained from pentane at -30 °C. Yield: 0.72 g, 92%. ^{1}H NMR (C_6D_6, 293 K): δ 0.35 ppm (27H, broad s, (*Me3*Si)$_3$Si), 0.50 ppm (9H, d, $^{3}J_{HP}$ = 3.6 Hz, *Me3*Si). ^{13}C NMR (C_6D_6, 293 K): δ 2.7 ppm (18C, broad s, (*Me3*Si)$_3$Si), 6.5 ppm (6C, dd, $^{2}J_{CP}$ = 7.2 Hz, $^{4}J_{CP}$ = 6.0 Hz, *Me3*Si). ^{29}Si NMR (C_6D_6, 293 K): δ -91.5 ppm (2Si, dd, $^{1}J_{SiP}$ = 79.6 Hz, $^{3}J_{SiP}$ = 10.8 Hz, (Me$_3$Si)$_3$*Si*), -9.9 ppm (6Si, dd, $^{2}J_{SiP}$ = 5.0 Hz, $^{4}J_{SiP}$ = 3.8 Hz, (Me$_3$*Si*)$_3$Si), 6.1 ppm (2Si, dd, $^{1}J_{SiP}$ = 51.5 Hz, $^{3}J_{SiP}$ = 5.0 Hz, Me$_3$*Si*). ^{31}P NMR (C_6D_6, 293 K): δ -104.9 ppm ($^{1}J_{^{117}SnP}$ = 1423 Hz, $^{1}J_{^{119}SnP}$ = 1486 Hz). ^{119}Sn NMR (C_6D_6, 293 K): δ 1466.7 ppm (t, $^{1}J_{SnP}$ = 1486 Hz).

4.4. Results and discussion

The synthesis of [HypPK-SiMe$_3$] **14** has been described before,[61] but was modified for this work. The replacement of toluene with monoglyme results in similarly high yields (>85%) as the published routine, but makes the addition of 18-crown-6 obsolete and the reaction can be handled at room temperature.

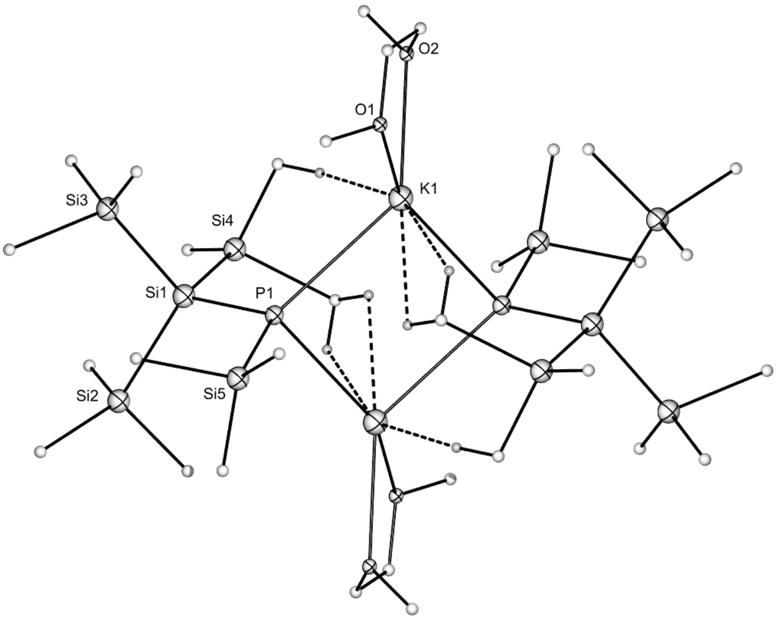
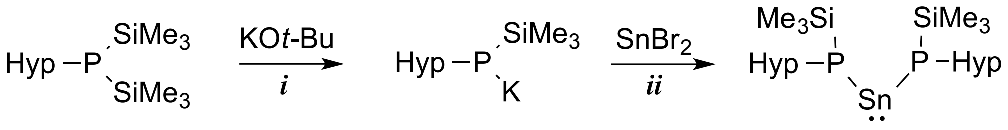


Figure 4.1.: Solid state structure of dipotassium salt **14** obtained by X-ray diffraction analysis. Hydrogen atoms have been omitted for clarity. Intramolecular agnostic interaction between the hypersilyl moieties and potassium are depicted as dashed lines.

Crystals suitable for X-Ray diffraction analysis are obtained after removal of the solvent and recrystallization from toluene with slow evaporation of the solvent at room temperature. The compound crystallizes in a dimeric structural pattern, with a four membered P-K-P-K ring as central element (see Figure 4.1). Each of the potassium ions is further stabilized by one dimethoxyethane molecule and agostic interactions to the methyl groups on the hypersilyl moiety. Under inert conditions, the compound is stable for an extended period of time.



13 **14** **15**

i: DME, 0°C → RT, 24h
ii: DME/THF, -50°C → RT
Hyp = $(SiMe_3)_3Si$

Figure 4.2.: Reaction of **13** with potassium *t*-butoxylate yields phosphanide **14**. Further reaction with tin(II)bromide yields free diphosphastannylene **15**.

The reaction of [HypPK-SiMe$_3$] **14** in diethyl ether with tin(II)bromide in THF (Fig. 4.2) leads to an immediate change of color to a rich emerald green. After replacement of the solvents with toluene and filtration, dark green needles can be obtained at low temperatures (-30 °C). Analysis *via* X-Ray diffraction gave the molecular structure of [HypP-(SiMe$_3$)]$_2$Sn **15** (Figure 4.3).

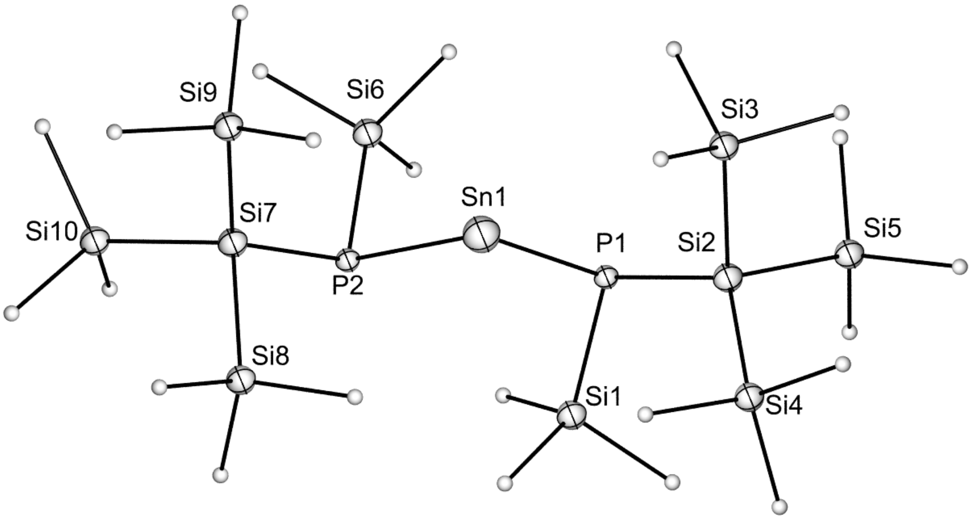


Figure 4.3.: Solid state structure of stannylene **15** obtained by X-ray diffraction analysis. Hydrogen atoms have been omitted for clarity.

There are neither solvent molecules coordinating the stannylene nor can any agostic intramolecular or intermolecular interaction be observed. The strongly deshielded character is also manifested in the ^{119}Sn-NMR spectrum of **15** with a low field shift of 1466.7 ppm (Figure 4.4). As expected for a tin atom substituted by two equivalent phosphorus moieties, the signal is a triplet with a $^{1}J_{^{119}\mathrm{SnP}}$ coupling constant of 1486 Hz. This coupling, as well as the slightly smaller $^{1}J_{^{117}\mathrm{SnP}}$ (1423 Hz) coupling can also clearly be observed *via* ^{31}P NMR spectroscopy (Figure 4.5). This coupling constants are somewhat smaller compared to the ^{119}Sn-^{31}P couplings observed for the free stannylene reported by Driess (~1620-1690 Hz)[53] and generally larger than the coupling constants found for terminal ligands in dimeric stannylenes (~1000-1200 Hz).[57,59]

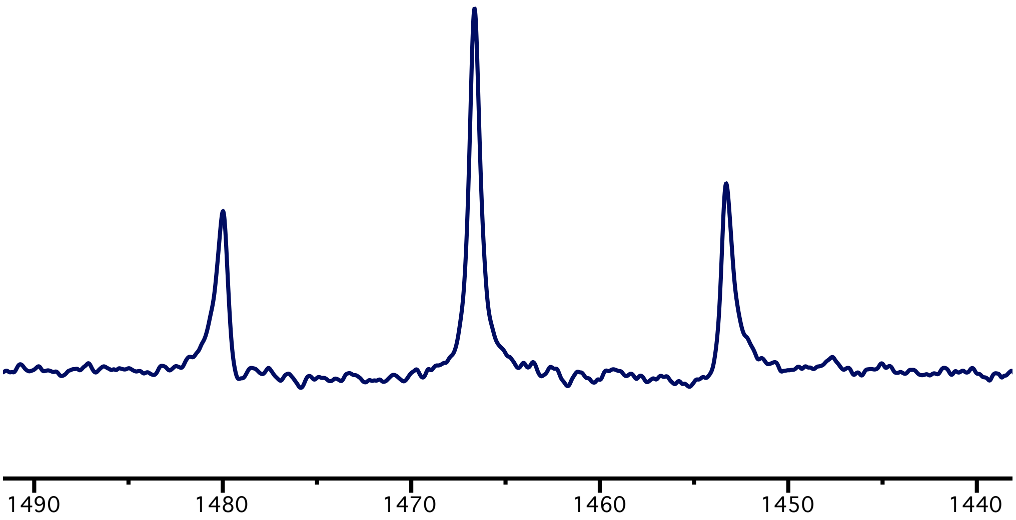


Figure 4.4.: ^{119}Sn NMR resonance of **15** in the low field region.

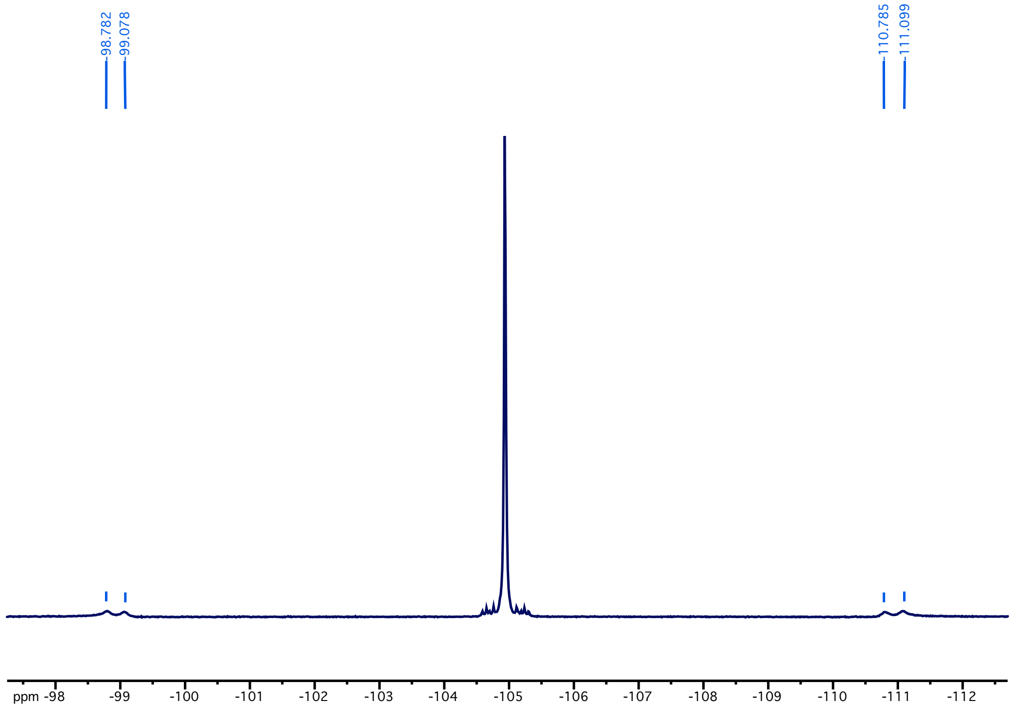
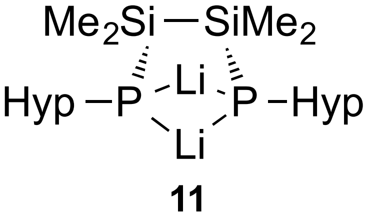
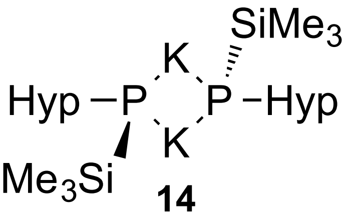


Figure 4.5.: ^{31}P NMR resonance of **15**.

Calculations at the level of density functional theory (M06L/IGLO-II//mPW1PW91/SDD) predict an absorption at 676 nm for the free stannylene, resulting in a green color. As coordination of a solvent would have direct influence on the HOMO-LUMO gap (resulting in a absorption at 495 nm) the color of the solution hardens the evidence of the persistence of the non-coordinated structure in solution. Recently[143] we reported on the synthesis of several diphosphanes, which can be seen as the bidentate derivatives of the monophosphane used for the synthesis of **15**. The bicyclic structure of $[HypPLi\text{-}SiMe_2\text{-}]_2$ **11** shows strong similarities to the dimeric structure of $[HypPK\text{-}SiMe_3]$ **14** (Fig. 4.6). Given the success during the synthesis of **15** a similar approach for a possible cyclic stannylene $[HypP\text{-}(SiMe_2)\text{-}]_2Sn$ **16** was chosen.



11

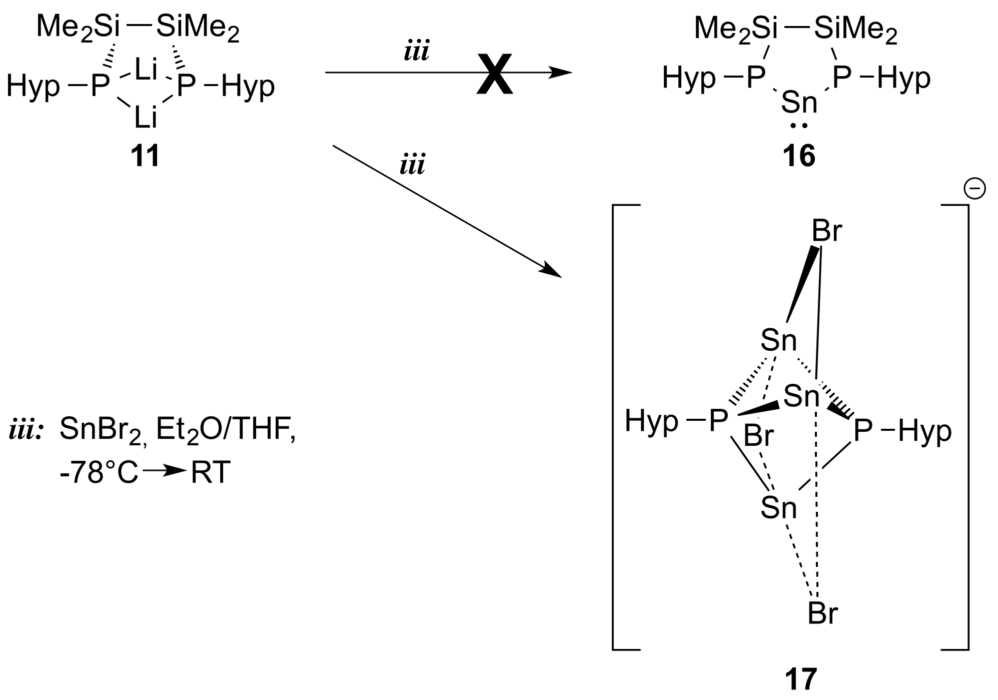


14

Figure 4.6.: Comparision of the solid state structures of **11** and **14**.

The addition of tin(II)bromide in THF to a cooled (-70 °C) solution of **11** led to a change of color of the solution, from pale yellow to a deep red, which continued to darken to a brownish-red solution. A new product could be observed at -465.8 ppm in ^{31}P-NMR, a singlet signal showing satellites, possibly from ($^1J_{^{117}SnP}/^1J_{^{119}SnP}$) coupling. ^{119}Sn NMR did not show any resonances in the expected region, moreover the quality of spectra was too bad for a clear identification of any peaks. Removal of the solvents and dissolution of the solid residue in toluene led to the isolation of a low quality crystal.

The preliminary structure obtained from the available data strongly suggests formation of product **17** (Fig. 4.7). **17** features a trigonal bipyramide as central element, with a plane of three Sn ions topped by one P-hypersilyl moiety on each side. The three bromide ions are also located in the central plane. Two of the bromide ions act as connecting points to the next molecular units.



iii: SnBr$_2$, Et$_2$O/THF, -78°C → RT

Figure 4.7.: Reaction of **11** does not lead to the isolation of cyclic stannylene **16** but a trigonal bipyramidal structure **17**, capped by hypersilyl moieties. In the solid state, molecules are connected *via* the coordinated bromide ions.

As the formation of this product requires the cleavage of the P-SiMe$_2$ bond, we investigated the reaction of tin(II)bromide with previously synthesized [HypP-(SiMe$_2$)$_2$-]$_2$ **12**, which has proven to be stable over extended periods of time and inert to *n*-butyl lithium. Reactions in THF in the magnitude of milligrams have shown quantitative cleavage of the P-SiMe$_2$ bonds, resulting in the formation of dibromotetramethyldisilane and various other unidentified products. Given the facts that SnBr$_2$ can lead to Si-P cleavage and that calculations on the desired tetrylene **16** showed the HOMO→LUMO transition at 498 nm, the deep red color immediately after the reaction indicates a possible formation of the cyclic stannylene in the first step, followed by subsequent decomposition to cluster compound **17** *via* cleavage of the P-SiMe$_2$ bond. The difference in the HOMO→LUMO transition energy between the cyclic and non-cyclic structure is not exclusive to the stannylene derivatives of these compounds. Calculations run on the equivalent germylenes (Fig. 4.8) did also show a difference in the HOMO→LUMO excitations between the cyclic and acyclic structure, although less pronounced. Absorptions at 475 nm for the cyclic germylene and 576 nm for the acyclic structure should result in yellow-orange and purple products, respectively. Comparable to the stannylene, formation of the desired tetrylenes

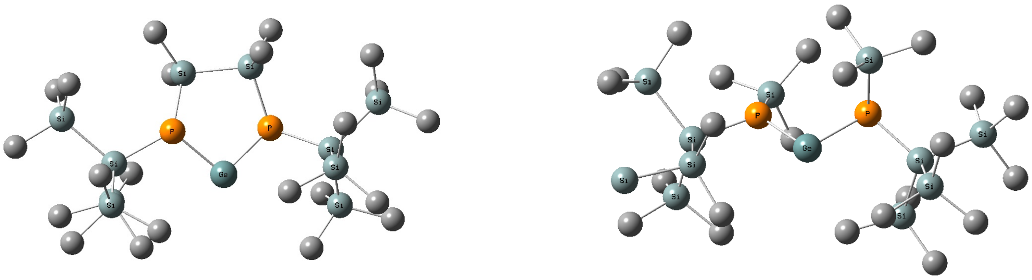


Figure 4.8.: Calculated structures of cyclic and acyclic germylene homologues to **16** and **15**, hydrogen atoms are omitted for clarity.

should be easily observable by change of color. This fact should facilitate the identification (and subsequent isolation) of the germanium derivatives in future reactions.

4.5. Conclusion and outlook

The synthesis of $[HypP(SiMe_3)]_2Sn$ resulted in the first free stannylene without aromatic moieties in the ligand. Its precursor, [HypPK-$SiMe_3$] has been accessible without use of a crown ether and can be found in the solid state in a dimeric structure, each potassium being further stabilized by a dimethoxy ethane molecule. The synthesis of the equivalent cyclic stannylene has not been successful due to cleavage of the P-$SiMe_2$ by tin (II) bromide. Variations of the reaction conditions might lead to the isolation of the cyclic stannylene in the future. The color of the corresponding germylenes should give clear indications on the reaction progress in future attempts.

While N,N' substituted tetrylenes are ubiquitous in modern chemistry and diphosphatetrylenes are rare but known for all group 14 elements, tetrylenes with silicon moieties in α positions are only known for the higher homologues (Ge, Sn, Pb). Just like the stable diphosphastannylene not containing any aromatic moieties reported in this chapter, a homocyclic silylene has not been reported up to this point. The next chapters contain an in-depth discussion about the precursors to such an homocyclic silylene, reports on the attempted synthesis as well as a quantum chemical investigation of the spectroscopic properties of the silylene itself and some of the most promising trapping products.

Chapter 5

Synthesis and Characterization of 1,1-dihalogenated cyclopentasilanes

Stefan K. Mueller, Ana Dzambaski, Nicola Altenhuber, Ana Torvisco, Karl Hassler and Michaela Flock

Institute for Inorganic Chemistry, Graz University of Technology, Stremayrgasse 9/V, 8010 Graz, Austria

submitted to Journal of Molecular Structure

Compounds **18**, **19** and **21**-**23** are part of Ana Dzambaski's PhD. thesis[65]

5.1. Abstract

Ring closure reaction of 2,5-dipotassium-2,5-bis(trimethylsilyl)-decamethylhexasilane with trichlorosilane yields the sterically protected halogenated cyclopentasilane **18**. Reaction of **18** with lithium aluminum hydride leads to the dihydrogenated cyclosilane **19**. The corresponding difluoro-, dichloro-, dibromo- and diiodo-derivatives **20**, **21**, **22**, and **23** are accessible *via* derivatization reactions from **18** (**21**) or **19** (**20**, **22**, **23**). All compounds have been structurally characterized by X-Ray diffraction analysis. Comparison of experimental NMR-shifts with data obtained from density functional theory (DFT) calculations showed outstanding performance of the M06L functional in the calculation of NMR shieldings.

5.2. Introduction

Cyclopentasilanes have been well established in literature. Derivatives such as Si_5H_{10}[144] and the perhalogenated species Si_5F_{10}, Si_5Cl_{10}, Si_5Br_{10}, and Si_5I_{10}[145–148] have been prepared several decades ago. In addition to these per-substituted cyclopentasilanes and compounds with mixed substitution patterns including pentaphenylcyclopentasilane,[149] there are also some monohalogenated derivatives reported in literature. Compounds of type Si_5R_9X (R = Me, Ph; X = F, Cl, Br, I),[150–153] 1-chloro-1-methyl octaphenylcyclopentasilane[154] and novel chlorocyclopentasilane Si_5H_9Cl[155] all possess monofunctionality on one specific site in the molecule.

In contrast to the monohalogenated compounds, 1,1'-dichloro-octaphenylcyclopentasilane is a rare cyclopentasilane with one doubly halogenated silicon site[156] and no other halogenated positions within the ring system. The phenyl groups provide some steric protection to the difunctionalized silicon atom. Attempted reactions to a cyclopentasilane containing a SiF_2 moiety have been unsuccessful, though. The concept of steric protection of the halogenated site in the molecule opened up the way to a new class of compounds. Reductive dehalogenation of such dihalogenes can lead to the formation of silylenoids and silylenes, which can subsequently react to disilenes. Several acyclic and cyclic disilenes have been synthesized *via* this reductive coupling pathway.[157–171] To accomplish formation of a disilene, the above mentioned reductive halogenation step is crucial. The design of the molecular environment of the halogenated site in terms of sterical demand is essential. With the synthesis of the first stable dialkyl silylene[62] Kira has shown that even the intermediate silylene can be stabilized just by sterical protection. The stability of Kira's silylene is caused by sterically demanding trimethylsilyl-groups on the carbons in α,α'-position. Analogous germylenes, stannylenes and plumbylenes with only silicon atoms in the ring backbone[67,68] have shown that inductive effects caused by the difference in electronegativity is not essential for stability. These and other tetrylenes[172,173] have been synthesized by reductive dehalogenation. Other examples have shown that the kind of halogen (Cl vs. Br) can lead to a different outcome of the dehalogenation reaction, resulting in either silylenoids or rearrangement products of silylenes.[66] In this work we investigate a series of sterically protected dihalogenated cyclopentasilanes (Fig. 5.1), which could be of interest in future reductive dehalogenation reactions opening the door to new highly interesting compounds.

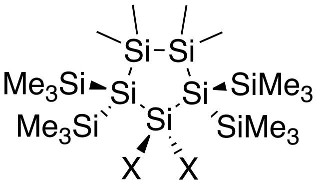


Figure 5.1.: General structure of the discussed compounds, X = H, F, Cl, Br, I.

5.3. Experimental

5.3.1. General Procedures

All reactions, unless otherwise stated, were carried out using 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.). C_6D_6 has been distilled over sodium and stored under nitrogen atmosphere. 2,5-dipotassium-2,5-bis(trimethylsilyl)-decamethylhexasilane[84] has been prepared following standard procedures. Trichlorosilane has been distilled prior to use. Potassium *t*-butoxide, tetrachloromethane, tetrabromomethane, iodoform and lithium aluminum hydride have been used as purchased without further purification. Elemental analysis was performed with an Elementar Vario EL III.

5.3.2. NMR

^{1}H (300.2 MHz), ^{13}C (75.5 MHz) and ^{29}Si (59.6 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 (δ = 0 ppm) regarding ^{1}H, ^{13}C and ^{29}Si. Coupling constants (*J*) are reported in Hertz (Hz). All NMR spectra were measured in C_6D_6. Reactions were monitored using a D_2O capillary as external lock signal.

5.3.3. X-Ray Diffraction

All crystals suitable for single crystal X-ray diffractometry were removed from a Schlenk flask 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 N_2 stream provided by an Oxford Cryosystems cryometer or Kryoflex low temperature cooling unit. XRD data collection was performed on either a Bruker APEX II (**18**, **20**) or a SMART APEX (**19**, **23**) diffractometer with use of Mo Kα radiation (λ = 0.71073 Å) and a CCD area detector. Empirical absorption corrections were applied using SADABS.[87,122] The structures were solved with use of either direct methods or the Patterson option in SHELXS and refined by the full-matrix least-squares procedures in SHELXL.[88,89] The space group assignments and structural solutions were evaluated using PLATON.[90,91] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in calculated positions corresponding to standard bond lengths and angles. Hydrogen atoms located on silicon Si1 on compounds **18** and **19** were found in the difference map. Disorder, as observed for compound **18**, was handled by modeling the occupancies of the individual orientations using free variables to refine the respective occupancy of the affected fragments. Compound **18** also displays intermolecular halide interactions (Si-H$\cdots$Cl) with neighboring molecules with values of 2.93 and 2.81 Å. These values fall within expected ranges.[174]

CCDC 685035-685036, 685039, 998872 contain the supplementary crystallographic data for compounds **18**-**20**, **23** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 5.1.: Crystallographic data for compounds **18**-**20**, and **23**

Compound	**18**	**19**	**20**	**23**
Empirical formula	$C_{16}H_{49}ClSi_9$	$C_{16}H_{50}Si_9$	$C_{16}H_{48}F_2Si_9$	$C_{16}H_{48}I_2Si_9$
Formula weight	529.78 g*mol^{-1}	495.37 g*mol^{-1}	531.35 g*mol^{-1}	747.15 g*mol^{-1}
Temperature	100(2) K	100(2) K	100(2) K	100(2) K
Wavelength	0.71073Å	0.71073Å	0.71073Å	0.71073Å
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	P2/n	C2/c
Unit cell dims.	a = 12.822(3)Å	a = 12.686(3)Å	a = 13.1574(4)Å	a = 16.212(3)Å
	b = 9.0780(18)Å	b = 8.5821(17)Å	b = 8.7354(3)Å	b = 9.453(4)Å
	c = 14.759(3)Å	c = 15.438(3)Å	c = 14.5320(5)Å	c = 22.514(4)Å
	α= 90°	α= 90°	α = 90.00°	α = 90.00°
	β= 106.07(3)°	β= 107.21(3)°	β = 105.7070°	β = 94.62(2)°
	γ = 90°	γ = 90°	γ = 90.00°	γ = 90.00°
Volume	1650.8(6) Å^3	1605.6(6) Å^3	1607.87(9)Å^3	3439.1(17) Å^3
Z	2	2	2	4
Density (calc.)	1.066 Mg/m^3	1.025 Mg/m^3	1.098 Mg/m^3	1.443 Mg/m^3
Abs. coeff.	0.446 mm^{-1}	0.374 mm^{-1}	0.386 mm^{-1}	2.148 mm^{-1}
F(000)	576	544	576	1504
Crystal size (mm)	0.44x0.34x0.30	0.50x0.35x0.15	0.20x0.15x0.10	0.36x0.32x0.24
2θ range	1.87° to 24.99°	1.83° to 25.00°	2.75° to 27.40°	1.91° to 25.00°
R1, wR2 (all data)	0.1118, 0.2211	0.0843, 0.1437	0.0238, 0.0526	0.0663, 0.1367
R1, wR2 ($> 2\sigma$)	0.0777, 0.1862	0.0732, 0.1393	0.0204, 0.0511	0.0451, 0.1059
Index range h	-7<=h<=15	-15<=h<=15	-16<=h<=17	-19<=h<=19
Index range k	-10<=k<=7	-9<=h<=10	-11<=h<=11	-11<=k<=11
Index range l	-17<=l<=13	-13<=h<=18	-18<=h<=18	-26<=l<=26
Reflns collected	2660	2821	3657	2770
Independent reflns	1917	2524	3339	2234
No. of parameters	136	126	131	131

5.3.4. Computational Details

All calculations have been carried out using the Gaussian09 program package[123] on a computing cluster with blade architecture. The mPW1PW91 hybrid functional[124] was used for all calculations excluding calculations of NMR shieldings. Magnetic shieldings were calculated using the M06L[125] pure functional as implemented in Gaussian09. For optimizations and calculation of frequencies the basis set combination denoted as SDD was used, consisting of the D95 basis set[126] for elements up to Argon and Stuttgart / Dresden ECPs for heavier elements.[127,128] For calculation of NMR shieldings the all electron IGLO-II[129] basis set was used (6-311G* for iodine[175]).

5.3.5. Synthesis

5.3.5.1. Synthesis of 1-chloro-3,3,4,4-tetramethyl-2,2,5,5-tetrakis(trimethylsilyl)cyclopentasilane 18

A solution of trichlorosilane (1.24 g; 9.12 mol) in DME (dimethoxyethane, 15 mL) is added dropwise to a cooled (-60 °C) solution of 2,5-dipotassium-2,5--bis(trimethylsilyl)-decamethylhexasilane (4.96 g; 9.12 mol) in 20 mL of DME. The reaction mixture is slowly warmed to room temperature over a period of 2 hours and stirred for 16 hours. After removal of all volatile compounds the brown residue is dissolved in pentane. After filtration colorless crystals suitable for X-ray structure analysis are obtained at -30 °C. Yield: 4.01 g, 83%.

^{1}H NMR (C_6D_6, 293 K) δ: 0.30 ppm (6H, s, $SiMe_2$), 0.31 ppm (18H, s, $SiMe_3$), 0.40 ppm (18H, s, $SiMe_3$), 0.42 ppm (6H, s, $SiMe_2$), 5.88 ppm (1H, t, SiHCl, $^1J_{Si,H}$ = 191 Hz). ^{13}C NMR (C_6D_6, 293 K) δ: -1.64 ppm ($SiMe_2$), -1.62 ppm ($SiMe_2$), 2.7 ppm ($SiMe_3$), 3.6 ppm ($SiMe_3$). ^{29}Si NMR (C_6D_6, 293 K) δ: -126.3 ppm ($Si(SiMe_3)_2$), -25.4 ppm ($SiMe_2$), -7.6 ppm ($SiMe_3$), -5.9 ppm ($SiMe_3$), 9.1 ppm (d, SiHCl, $^1J_{Si,H}$ = 191 Hz). EA.: $C_{16}H_{49}ClSi_9$ (529.78 g/mol), Calc. C: 36.27%, H: 9.32%; Found C: 36.76% H: 9.64%.

5.3.5.2. Synthesis of 3,3,4,4-tetramethyl-2,2,5,5-tetrakis(trimethylsilyl)cyclopentasilane 19

0.31 mL of a 1 M solution of lithium aluminium hydride in diethyl ether is added dropwise to a solution of **18** (0.15 g; 0.28 mmol) in 5 mL of diethyl ether at 0 °C. The reaction solution is slowly warmed up to room temperature. After removal of all volatile components the colorless residue is dissolved in pentane and salts removed by filtration. Colorless crystals suitable for X-ray structure analysis are obtained from *n*-heptane. Yield: 0.14 g, 100%.

^{1}H NMR (C_6D_6, 293 K) δ: 0.30 ppm (36H, s, $SiMe_3$), 0.38 ppm (12H, s, $SiMe_2$), 3.57 ppm (t, 18H, SiH_2, $^1J_{Si,H}$ = 177 Hz). ^{13}C NMR (C_6D_6, 293 K) δ: -1.7 ppm ($SiMe_2$), 2.8 ppm ($SiMe_3$). ^{29}Si NMR (C_6D_6, 293 K) δ: -136.6 ppm (*Si*($SiMe_3$)$_2$), -97.6 ppm (t, SiH_2, $^1J_{Si,H}$ = 177 Hz), -23.2 ppm ($SiMe_2$), -7.8 ppm ($SiMe_3$).

EA.: $C_{16}H_{50}Si_9$ (495.35 g/mol), Calc. C: 38.80%, H: 10.17%; Found C: 36.14% H: 10.07%.

5.3.5.3. Synthesis of 1,1-difluoro-3,3,4,4-tetramethyl-2,2,5,5-tetrakis(trimethylsilyl)cyclopentasilane 20

A suspension of zinc fluoride (0.30 g; 2.90 mmol) in 5 mL of diethyl ether is added dropwise to a solution of **19** (0.47 g; 0,95 mmol) in 5 mL of diethyl ether and kept under reflux for 48 hours. After removal of all volatile components the colorless residue is dissolved in pentane and salts removed by filtration. Colorless crystals suitable for X-ray structure analysis are obtained from *n*-pentane at -30 °C. Yield: 0.50 g, 99%.

^{1}H NMR (C_6D_6, 293 K) δ: 0.30 (36H, d, $SiMe_3$, $^5J_{HF}$ = 1.89 Hz), 0.35 (12H, d, $SiMe_2$, $^5J_{HF}$ = 1.80 Hz). ^{13}C NMR (C_6D_6, 293 K) δ: -2.6 ppm ($SiMe_2$), 2.6 ppm ($SiMe_3$). ^{29}Si NMR (C_6D_6, 293 K) δ: -132.9 ppm (*Si*($SiMe_3$)$_2$, $^2J_{SiF}$ = 11.7 Hz), -30.1 ppm ($SiMe_2$, $^3J_{SiF}$ = 7.3 Hz), -7.0 ppm ($SiMe_3$, t, $^3J_{SiF}$ = 3.0 Hz), 64.6 ppm (SiF_2, $^1J_{SiF}$ = 248.6 Hz).

5.3.5.4. Synthesis of 1,1-dichloro-3,3,4,4-tetramethyl-2,2,5,5-tetrakis(trimethylsilyl)cyclopentasilane 21

18 (1.08 g; 2.0 mmol) is dissolved in carbon tetrachloride (30 mL) and refluxed for 48 hours at 80 °C under nitrogen atmosphere. Colorless crystals suitable for X-ray structure analysis are obtained directly from the reaction solution. Yield: 0.86 g, 81%.

^{1}H NMR (C_6D_6, 293 K) δ: 0.37 ppm (36H, s, $SiMe_3$), 0.38 ppm (12H, s, $SiMe_2$). ^{13}C NMR (C_6D_6, 293 K) δ: -1.7 ppm ($SiMe_2$), 3.5 ppm ($SiMe_3$). ^{29}Si NMR (C_6D_6, 293 K) δ: -113.3 ppm ($\mathit{Si}(SiMe_3)_2$), -27.5 ppm ($SiMe_2$), -5.8 ppm ($SiMe_3$), 63.0 ppm ($SiCl_2$).

EA.: $C_{16}H_{48}Cl_2Si_9$ (564.23 g/mol), Calc. C: 34.06%, H: 8.57%; Found C: 34.54% H: 8.78%.

5.3.5.5. Synthesis of 1,1-dibromo-3,3,4,4-tetramethyl-2,2,5,5-tetrakis(trimethylsilyl)cyclopentasilane 22

Tetrabromomethane (6.36 g; 19.2 mmol) and **19** (0.95 g; 1.92 mmol) are dissolved in *n*-heptane and stirred at 50 °C for three days. All volatile components including excess tetrabromomethane are removed under reduced pressure. The pure product in form of colorless crystals suitable for X-ray diffraction analysis is obtained *via* recrystallization from *n*-pentane -30 °C. Yield: 0.40 g, 32%.

^{1}H NMR (C_6D_6, 293 K) δ: 0.37 ppm (36H, s, $SiMe_3$), 0.40 ppm (12H, s, $SiMe_2$). ^{13}C NMR (C_6D_6, 293 K) δ: -1.6 ppm ($SiMe_2$), 3.6 ppm ($SiMe_3$). ^{29}Si NMR (C_6D_6, 293 K) δ: -109.3 ppm ($\mathit{Si}(SiMe_3)_2$), -27.0 ppm ($SiMe_2$), -4.9 ppm ($SiMe_3$), 41.0 ppm ($SiBr_2$).

EA.: $C_{16}H_{48}Br_2Si_9$ (529.78 g/mol), Calc. C: 29.42%, H: 7.41%; Found C: 28.04% H: 7.53%.

5.3.5.6. Synthesis of 1,1-diiodo-3,3,4,4-tetramethyl-2,2,5,5-tetrakis(trimethylsilyl)cyclopentasilane 23

Iodoform (7.95 g; 20.0 mmol) and **19** (1.00 g; 2.0 mmol) are dissolved in *n*-heptane and stirred at 50 °C for fourteen days. Rigorous reaction control (*via* ^{29}Si-NMR) is obligatory since after conversion of the starting material decomposition of the product can be observed. All volatile components including excess iodoform are removed under reduced pressure. The pure product in form of colorless crystals suitable for X-ray diffraction analysis is obtained *via* recrystallization from *n*-pentane -30 °C. Yield: 0.77 g, 52%.

^{1}H NMR (C_6D_6, 293 K) δ: 0.38 ppm (36H, s, $SiMe_3$), 0.43 ppm (12H, s, $SiMe_2$). ^{13}C NMR (C_6D_6, 293 K) δ: -1.5 ppm ($SiMe_2$), 3.7 ppm ($SiMe_3$). ^{29}Si NMR (C_6D_6, 293 K) δ: -106.0 ppm (*Si*($SiMe_3)_2$), -39.0 ppm (SiI_2), -25.8 ppm ($SiMe_2$), -2.3 ppm ($SiMe_3$).

EA.: $C_{16}H_{48}I_2Si_9$ (529.78 g/mol), Calc. C: 36.27%, H: 9.32%; Found C: 36.76 % H: 9.64%.

5.4. Results & Discussion

The ring closure reaction of 2,5-dipotassium-2,5-bis(trimethylsilyl)-decamethylhexasilane with trichlorosilane gives cyclopentasilane **18** in moderate yields. The halogenated silicon is kinetically protected by the sterical demand of the vicinal trimethylsilyl groups. While this environment has a stabilizing effect on the molecule,[67,68] it also makes derivatization reactions more difficult. However, it was possible to synthesize the dihydro- as well as difluoro-, dichloro-, dibromo-, and diiodo-derivates *via* one or two step reaction procedures (Figure 5.2).

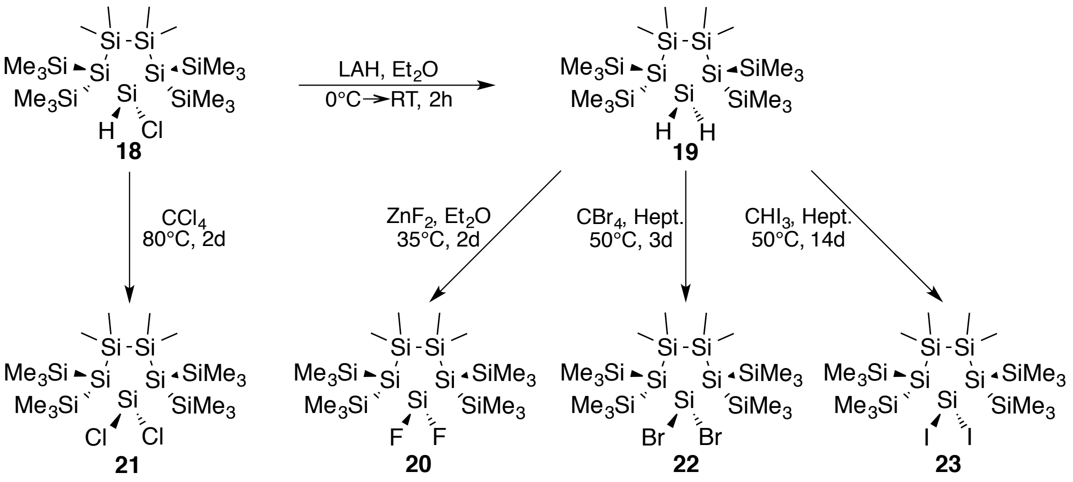


Figure 5.2.: Reaction pathway for the synthesis of compounds **19**, **20**, **21**, **22**, and **23**.

Compared to the synthesis of the halogenated compounds, dihydrogenated derivative **19** is quite easily accessible. The hydrogenation reaction of **18** with lithium aluminum hydride in diethyl ether at 0 °C gives **19** in quantitative yields in less than an hour. Next to **19**, **21** is the only derivative available in one reaction step from **18**. Substitution of the second hydrogen on the central silicon atom of **18** is achieved through a chlorination reaction in neat tetrachloromethane. However, the reaction conditions have to be altered significantly; reaction times of 48 hours at reflux temperatures are necessary to obtain good yields. Reaction of **21** with zinc fluoride yields a mixture of products consisting of **20**, **21** and their mixed halogen intermediate, the corresponding 1-chloro-1-fluoro-cyclopentasilane, which could be observed via NMR spectroscopy but not be isolated.

19 is the starting point for the synthesis of the difluoro-(**20**), dibromo-(**22**) and diiodo-(**23**) derivatives. Quantitative ($> 99\%$) synthesis of **20** from **19** with zinc fluoride requires similar reaction times but lower temperatures (48 h, diethyl ether reflux) compared to the synthesis of **21**. It is of some note that this is the first cyclopentasilane, with the exception of the elusive perfluorinated Si_5F_{10},[145] containing a SiF_2 group. Synthesis of the dibromo derivative is more time consuming. After stirring **19** with tetrabromomethane in heptane for several days only medium yields can be achieved. Yields can be further increased by elongation of the reaction time. Long reaction times ($\sim$2 weeks) are also required in the synthesis of the diiodo-derivative **23** which can be prepared *via* the reaction of **19** with iodoform at elevated temperatures. A proposed alternative route in the synthesis of **21** and **22**[66] could not be reproduced with satisfying yields, even after multiple attempts.

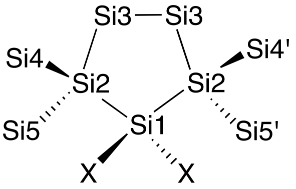


Figure 5.3.: Labeling scheme of the Si-backbone. All methyl groups have been omitted for clarity, X = H(**19**), F(**20**), Cl(**21**), Br(**22**), I(**23**).

Compounds **18**-**23** could be crystallized at low temperatures from apolar solvents. All bond lengths and angles fall within expected ranges (Table 5.2). As expected, halogen-silicon bond lengths increase with the size of the halogen, the Si1-Cl bond length increases from 1.98 Å to 2.10 Å with the exchange of hydrogen (**18**) with chlorine (**21**) on Si1. Bond lengths within the silicon backbone (Si1-Si2, Si2-Si3, Si3-Si3') vary less than three picometers within a range of 2.34 Å (Si1-Si2, **18**) to 2.37 Å (Si3-Si3', **23**), but follow no strict trends. The angle Si2-Si1-Si2' increases with the size of the halogen from 110.02° (**19**) to 113.80° (**23**). An opposite trend can be observed for the angle within the backbone (Si1-Si2-Si3), decreasing with halogen size from 105.06° (**19**) to 101.19° (**23**). The torsion of the ring backbone Si2-Si3-Si3'-Si2' is substantially influenced by the substituent (hydrogen or halide) on Si1; torsion angles range from 24.09° in **20** to 32.90° in **23**. **18**, **19**, and **20** show a smaller torsion angle of around 25°, while in the heavier derivatives **21**-**23** the angle enlarges to 30-32°.

Table 5.2.: Selected bond lengths and angles of compounds **18**-**23** obtained from X-Ray diffraction analysis.

	18	**19**	**20**	**21**	**22**	**23**
Si1-H (Å, avg.)	1.388(1)	1.420(1)	-	-	-	-
Si1-X (Å, avg.)	1.98(2)	-	1.610(2)	2.096(2)	2.266(2)	2.493(2)
Si1-Si2 (Å, avg.)	2.341(2)	2.352(2)	2.344(2)	2.349(2)	2.357(2)	2.367(2)
X-Si1-X (°)	103.32(2)	106.52(2)	101.54(2)	102.47(2)	102.35(2)	101.65(2)
Si1-Si2-Si3 (°)	103.95(8)	105.06(2)	102.93(2)	102.39(2)	101.73(2)	101.19(2)
Si2-Si1-Si2' (°)	112.07(11)	110.02(9)	113.36(2)	113.14(8)	113.51(4)	113.78(13)
Si2-Si3-Si3'-Si2' (°)*	25.0	25.3	24.1	29.4	31.8	32.9

*Angles calculated from symmetry-generated structures

The same divide amongst the compounds can be found regarding the unit cell dimensions. Compounds **18**-**20** share similar size and volume, as well as **21**-**23**. All the compounds are found in the monoclinic crystal system, though. Interestingly, derivative **18** is the only compound showing intermolecular interactions in the extended structures, even though all of the compounds except **19** would generally be able to form this interaction pattern in the solid state. The distances from the chlorine atom to the backbone methyl groups of the neighboring molecule of **18** are 2.81 Å and 2.93 Å and are falling within expected ranges[174] (Figure 5.4).

Analysis *via* ^{29}Si-NMR spectroscopy has shown the expected shift dependence on the substituent type on Si1 (Table 5.3). While the transition from fluorine to chlorine only causes a small change in the ^{29}Si NMR shift (-1.6 ppm) on Si1, an upfield shift to 41.0 ppm can be observed in dibrominated compound **22**; an effect, that is even more drastic in diiodo compound **23** (-39 ppm). Similar trends, although less pronounced, have been observed for the series Me$_3$Si-X (X = F, Cl, Br, I) with 31.1 ppm, 29.0 ppm, 26.4 ppm, and 8.6 ppm, respec-

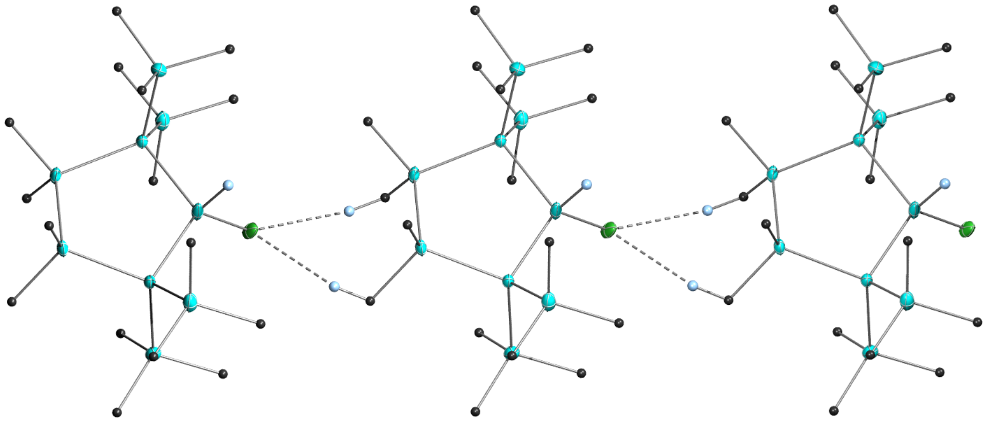


Figure 5.4.: Intermolecular interactions in the extended solid state structure of compound **18**.

tively.[176]

Table 5.3.: Comparison of DFT calculated and measured ^{29}Si NMR data.

Comp.		Si1	Si2	Si3	Si4	Si5
18	exp	9.1	-126.3	-25.4	-5.9	-7.9
	calc	13.8	-125.9	-20.4	-2.6	-5.5
	Δ	4.7	0.4	5.0	3.3	2.4
19	exp	-97.6	-136.6	-23.2	-7.8	*
	calc	-87.2	-126.0	-12.7	-0.3	*
	Δ	10.4	10.6	10.5	7.5	*
20	exp	64.6	-132.9	-30.1	-7.0	*
	calc	63.0	-135.7	-24.6	-3.1	*
	Δ	-1.6	-2.7	5.4	3.9	*
21	exp	63.0	-113.3	-27.5	-5.8	*
	calc	72.8	-113.2	-22.5	-2.9	*
	Δ	9.8	0.1	5.0	2.9	*
22	exp	41.0	-109.3	-27.0	-4.9	*
	calc	67.3	-111.5	-20.7	-2.6	*
	Δ	26.3	-2.2	6.3	2.3	*
23	exp	-39.0	-106.0	-25.8	-2.3	*
	calc	60.3	-98.2	-20.4	-4.1	*
	Δ	99.3	7.8	5.4	-1.8	*

*identical to Si4

The silicon atoms Si2, Si2' still exhibit remarkable dependence on the Si1 substituents, with a range of -136.6 ppm for X = H (**19**) to -106.0 ppm for X = I (**23**). For backbone silicon atoms Si3 and Si3' the effect is similar but somewhat smaller in the halogenated compounds **20**-**23** (-30.1 ppm to -25.8 ppm). However, hydrogen substitution on Si1 leads to a low field shift (-25.4 ppm for **18** and -23.2 ppm for **19**). The ^{29}Si NMR shift of the trimethylsilyl groups (Si4, Si4', Si5, Si5') is akin to the trend of Si2 and Si2' in a range from -7.8 ppm

(**19**) to -2.3 ppm (**23**). During the synthesis of **20**, **22**, and **23** the trimethylsilyl groups function as a reliable reaction monitor. An asymmetric substitution pattern on Si1 can be easily observed, as the signal for Si4, Si4', Si5, Si5' splits into a pair of signals (similar to the shift pattern of **18**).

These trends are corroborated by calculations at the level of density functional theory (DFT). Simulated NMR shifts fit well for the compounds including no heavier elements than chlorine (compounds **18**, **19**, **20** and **21**). Naturally, errors on Si1 increase drastically with introduction of heavy elements bromine (Δ = 26.3 ppm) and iodine (Δ = 99.3 ppm); calculated NMR shifts for Si2('), Si3('), Si4(') stay in a reasonable range (Figure 5.3, Table 5.3).

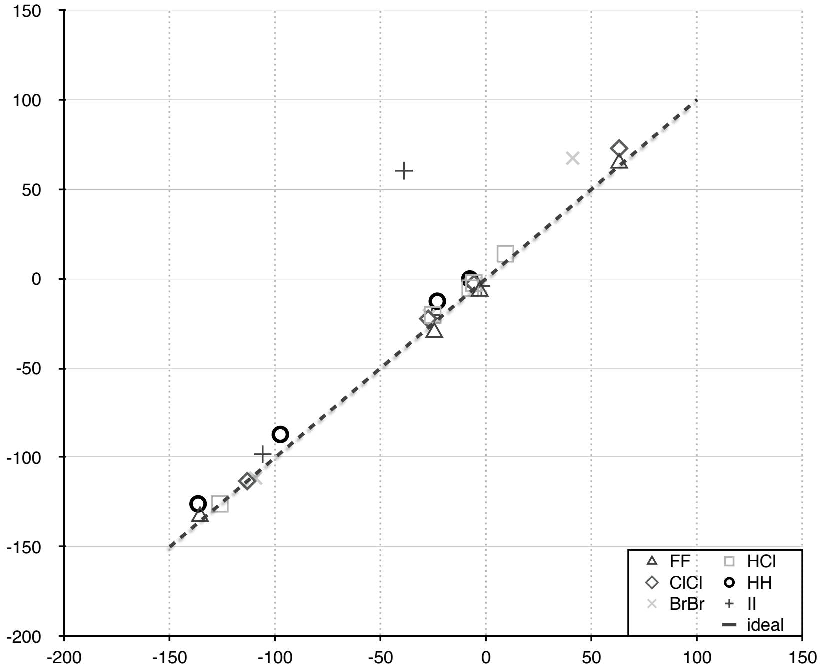


Figure 5.5.: Comparison of calculated and experimental ^{29}Si NMR shifts of compounds **18**-**23**.

NMR shieldings calculated at our level (M06L/IGLO-II) show errors of a small enough magnitude and give a good estimation of experimental values. Not only does this hold true for halogenated silanes but also for silylenes. To further prove the reliability of the method/basis set combination, calculations were run with a test set containing halogenated silanes and silylenes.[177] A RMSE (root mean standard error) of 14.7 ppm with a maximum deviation of around 40 ppm for brominated silanes was found (see Figure 5.6). Our calculation on Kira's dialkyl silylene shows only a slight underestimation in the calculated shift (+544 ppm) compared to the experimental value of +567 ppm,[62] which is still the most downfield ^{29}Si NMR shift reported to date. As these small errors allow a quite reliable prediction of the NMR shieldings, it is even more remarkable, that the calculated shift for the silylene that would result from reductive dehalogenation reaction of the investigated compounds lies in the extreme downfield at +1133 ppm. Besides the formation of the peak in the very downfield, a possible silylene formation could also be observed by the disappearance of the high field shift caused by Si2, Si2' between -133 ppm (compound **20**) and -106 ppm (compound **23**). The new electronic environment would lead to a downfield shift to around -25 ppm. So observation of the formation of a stable silylene in solution should be straightforward *via* ^{29}Si NMR monitoring.

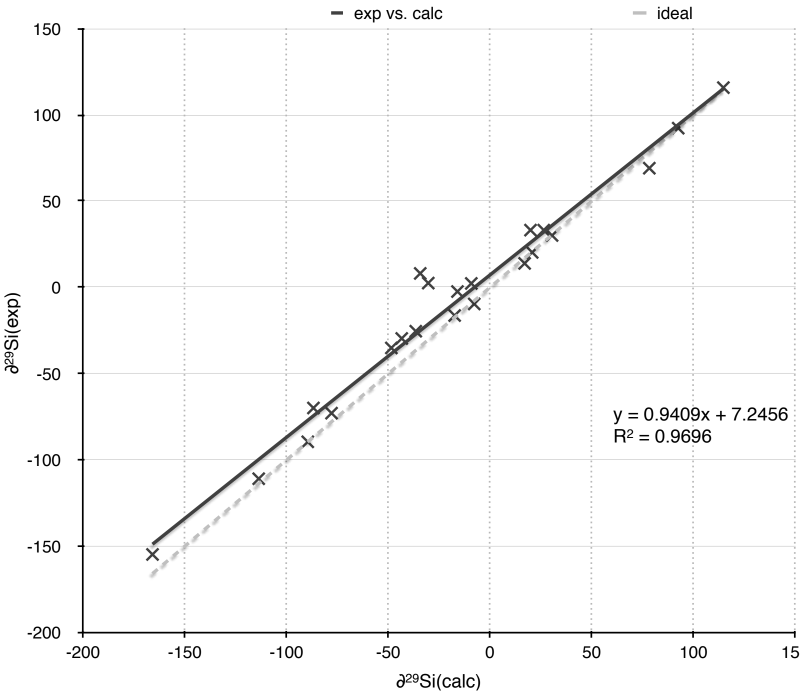


Figure 5.6.: Comparison of calculated and experimental NMR shifts of a test set containing halogenated silanes.

It seems, however, that although the silylene is sterically encumbered its high reactivity is maintained. Our own attempts in isolating the desired silylene have not been successful so far, one of the main problems being silyl group rearrangement. An up to date literature search reveals only two previous attempts to synthesize this homocyclic silylene. Recent work of Xiao *et. al.* led to the isolation of some decomposition compounds[66] that indicate a possible silylene intermediate, however, no NMR data was acquired during the reaction. During an attempted synthesis of the silylene in 2008 by reductive dehalogenation reaction of **22**, Hassler reported on a ^{29}Si NMR shift of +735 ppm[178] but was not successful in isolating the compound or one of its decomposition products. Although the observed value differs drastically from the calculated shift of +1133 ppm it still lies in the expected extreme low field range of the ^{29}Si NMR shifts for this silylene. This suggests that the compound observed by Hassler is not the free silylene but some adduct or other intermediate. An in-depth theoretical investigation of possible adducts and rearrangements products will be discussed in a forthcoming publication.

5.5. Conclusion

A series of cyclopentasilanes has been investigated in view of their structural features and NMR-spectroscopic properties, including the first cyclopentasilane containing only one SiF_2 moiety. Only derivative **18** shows intermolecular halogen-hydrogen interaction in the solid state. The M06L/IGLO-II method gives a satisfying approximation of NMR-shifts of the investigated compounds. Calculations at this level predict a ^{29}Si NMR shift in the extreme low field at 1133 ppm for the free silylene. Reaction control *via* ^{29}Si NMR spectroscopy during a reductive dehalogenation reaction of one of the precursors would enable direct observation of the formation and possible subsequent decomposition of the desired silylene.

5.6. Acknowledgement

We thank Dr. Judith Baumgartner for preliminary X-ray diffraction analysis.

Chapter 6

Reductive dehalogenation of 1,1-dihalogenated cyclopentasilanes

Stefan K. Mueller and Michaela Flock

Institute for Inorganic Chemistry, Graz University of Technology, Stremayrgasse 9/V, 8010 Graz, Austria

6.1. Introduction

An essential part of this work is the reduction of the dihalogenated cyclopentasilanes discussed in the previous chapter. During her PhD. thesis, Ana Dzambaski has already worked on this topic.[65] The most impressive attribute was the low field ^{29}Si NMR shift reported by Dzambaski and Hassler in a publication in 2008 in *Silicon Chemistry*:[178] a shift of +735 ppm. This would be the most downfield ^{29}Si NMR shift to date, however no single crystal of this compound or any trapping or decomposition products could be isolated from the reaction solution, so complete characterization was not possible. In the following years, corresponding germylenes, stannylenes and plumbylenes have been reported as base adducts. These compounds have been synthesized either from reductive dehalogenation of a dihalogenated precursor (Ge) or reaction with the divalent higher homologue (Sn, Pb).[67–69] The target of this part of the current work was the quantum chemical investigation of the free silylene **24** (Fig. 6.1) and its trapping products. The results of this theoretical work are compared with experimentally obtained data.

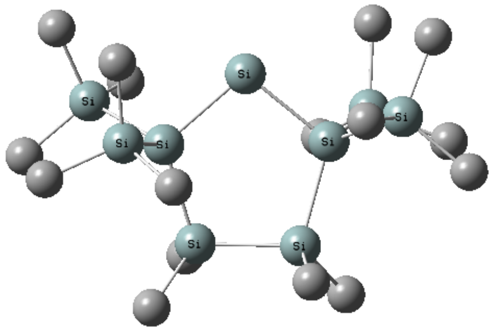


Figure 6.1.: Optimized structure of the desired homocyclic silylene **24**. All hydrogen atoms are omitted for clarity.

6.2. Quantum chemical results

As the desired silylene has not been accessible experimentally so far, several compounds have been investigated quantum chemically at the level of density functional theory (DFT). Calculations were run on the silylene itself (Fig. 6.1) and products **25**-**30** resulting from stabilization with triethyl silane, isoprene, trimethylphosphane, triethylphosphane, water, and methanol, respectively. Optimized structures are shown in Fig. 6.3. Structures have been optimized using the mPW1PW91[124] method with the basis set combination denoted as SDD[126–128] as implemented in Gaussian09.[123] The same method/basis set combination has been applied for the calculation of vibrational spectra, which have also been used to determine if the optimized structures are indeed minimum structures. The analysis of the precursors in the previous chapter showed that the M06L[125] functional in combination with the IGLO-II basis[129] performs exceptionally well in the calculation of NMR shieldings. This combination has also been used for the simulation of UV/VIS spectra *via* calculation of the electronic excitations.

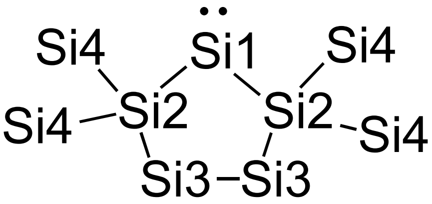
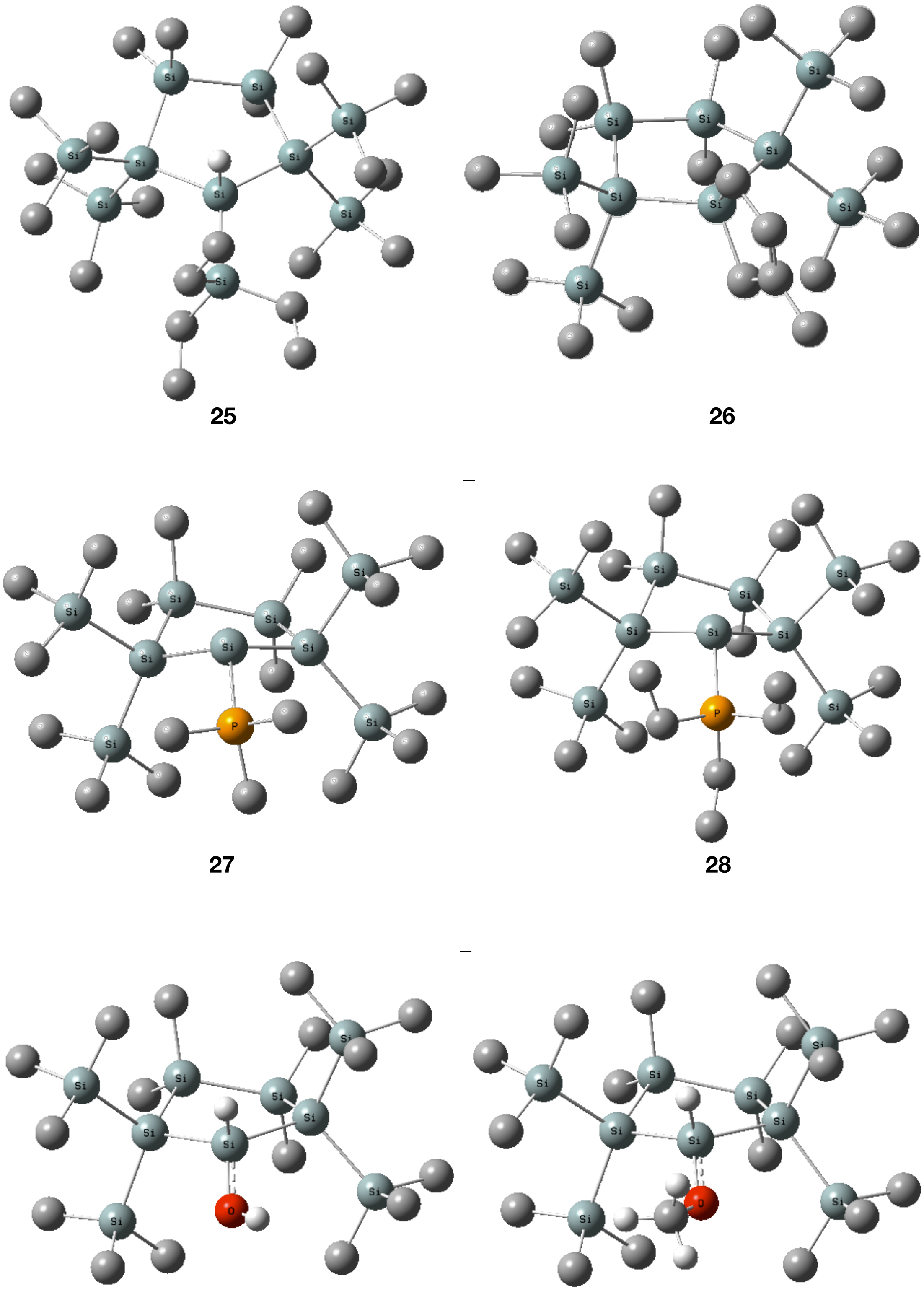


Figure 6.2.: Labeling scheme of the desired silylene.

^{29}Si NMR spectroscopy is the primary tool of characterization for the silylene and its trapping products. The shift difference for silylene Si1 compared to the value reported in 2008 (calc.: +1133.8 ppm, exp: 735 ppm[178]) could be explained with the formation of some kind of adduct in solution. The influence of the main components of the reaction solution, K^+, Br^- and THF are shown in table 6.1. The Lewis acid K^+ only has minor influence on the NMR shift, coordination with a potassium ion leads to an even more downfield shift of almost 1200 ppm for Si1. Electron donation by THF leads to shifts in the area of 230 ppm, a slight upfield deviation is observed with additional potassium ion



25 **26**

27 **28**

29 **30**

Figure 6.3.: Calculated molecular structures of the trapping products of silylene **24** with triethylsilane (**25**), isoprene (**26**), trimethylphosphine (**27**), triethylsilane (**28**), water (**29**), and methanol (**30**).

coordination. Coordination of a bromide ion has the biggest influence on the Si1, resulting in shift ranges which are also observed for conventional bromosilanes. The shifts for Si2 are strongly dependent on the coordination of Si1 as well. Apart from K⁺ coordination, where a downfield shift can also be observed for Si2, coordination with all of the Lewis bases lead to shifts in the high field, comparable to the quaternary silicons discussed in the previous chapter.

Table 6.1.: ^{29}Si NMR shifts of Si1 and Si2 of adduct derivatives of silylene **24** and the disilene structure resulting from trimethylsilyl migration. Shifts for the uncoordinated silylene given as reference. All values are referenced to tetramethylsilane (σ = 372.7 ppm).

Adduct type	δ Si1 [ppm]	δ Si2 [ppm]	δ Si2' [ppm]
K^+	1194.3	-17.1	*
THF	230.8	-121.5	*
Br^-	15.7	-115.6	*
K^+ / THF	210.8	-112.9	*
K^+ / Br^-	63.4	-113.5	-107.0
Disilene	152.4	147.8	-108.4
Silylene	1133.8	-25.0	*

*identical to Si2

The shifts calculated for the decomposition product obtained from trimethylsilyl migration, a disilene, also fall in the expected ranges. Values of around 150 ppm are obtained for Si1 and Si2, now part of a Si=Si double bond, the other, quaternary Si2 is shifted to -108 ppm. In summary, the rather accurate performance of the used method does not predict a shift in a range that would fit to the experimental value of 735 ppm. No further NMR data has been reported in the publication mentioned above. Calculations state that all other shifts (Si2-Si4) should be found in the range of -30 to +5 ppm.

To facilitate their identification in future reactions, NMR shifts for the trapping products have also been calculated. Visualized in Fig. 6.4, stabilization has several recognizable effects on the ^{29}Si NMR shifts of the silylene. The biggest influence can naturally be observed for Si1. Its extraordinary low field shift vanishes due to stabilization.

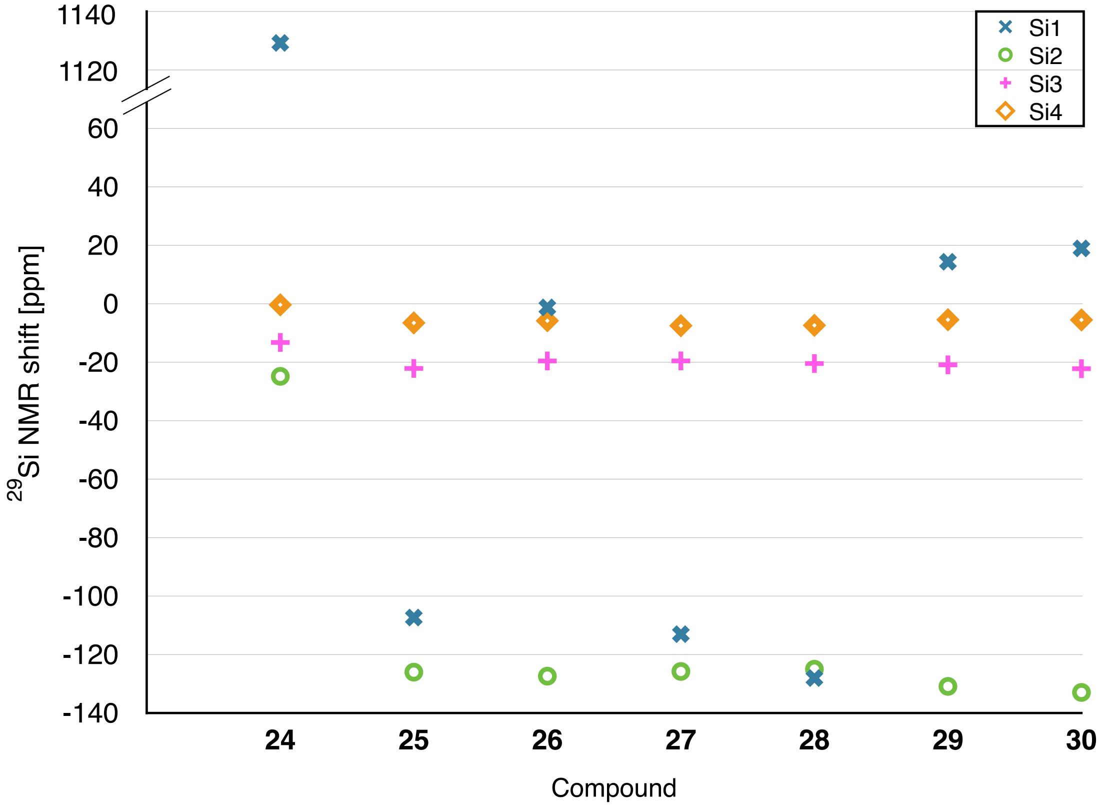


Figure 6.4.: Comparison of calculated NMR-shifts for silylene **24** and stabilized products **25** (Et_3SiH), **26** (Isoprene), **27** (PMe_3), **28** (PEt_3), **29** (H_2O), and **30** (MeOH).

Depending on the type of trapping reagent, the Si1 shift is found at either -130 to -100 ppm (Et_3SiH, PMe_3, PEt_3; **25**, **27**, **28**) or 0-20 ppm (isoprene, water, methanol; **26**, **29**, **30**). The results for the phosphane adducts **27** and **28** are remarkable, as even coordination with a bromide ion does not effect a shift in this high field region. Si2 is experiencing a distinct up field shift with stabilization from -25 ppm to around -125 ppm for all stabilized compounds **25**-**30**. This value is comparable to the values measured for the halogenated cyclopentasilanes in the previous chapter. Shifts for Si3 and Si4 change only marginally within a range of around 10 ppm throughout all investigated compounds. In contrast to Si1 and Si2 they are no useful indicators for the progress of the trapping reaction.

Investigation of the reaction energies, enthalpies and free energies obtained from frequency calculations gave interesting, but somewhat expected results (Table 6.2). The reactions of the silylene with all of the trapping reagents are energetically favored. The insertion into the O-H bond of water (**29**) or methanol (**30**) is strongly exothermic with energies of around -200 to -250 kJ/mol. Stabilization energies of similar magnitude (around -270 kJ/mol) can be observed for the cycloaddition of isoprene to the silylene. Caused by its comparatively high sterical demand, the reaction with triethyl silane is not as favored. The repulsion of the ethyl groups from the silylenes TMS moieties leads to smaller stabilization energies.

Table 6.2.: Reaction energies ($E_{\text{ZPE,products}}$-$E_{\text{ZPE,educts}}$), enthalpies (H_{products}-H_{educts}) and free energies (G_{products}-G_{educts}) for the synthesis of trapping products **25**, **26**, **27**, **28**, **29**, and **30** in kJ/mol.

Comp.	ΔE_{ZPE}	ΔH	ΔG
25 (Et_3SiH)	-159.91	-161.47	-92.11
26 (Isoprene)	-269.46	-273.66	-205.06
27 (PMe_3)	-98.09	-96.62	-35.66
28 (PEt_3)	-90.58	-87.47	-24.95
29 (H_2O)	-246.62	-251.08	-205.43
30 (MeOH)	-248.78	-251.29	-197.63

Comparable effects of the sterical demand of the trapping reagents on stabilization energies can be observed for phosphine adducts **27** and **28**; trapping with trimethylphosphine is slightly more favored. Nevertheless, especially the calculated free energies show that this kind of donor-acceptor interaction is less favored (-35 kJ/mol for **27** and -25 kJ/mol for **28**) compared to the formation of chemical bonds with all other trapping reagents. The phosphines have been used for the trapping of the corresponding germylene and stannylene, where larger bond lengths and therefore more space between the geminal trimethylsilyl groups lead to less steric repulsion. The energies should however still be high enough to trap the desired silylene.

The results of time-dependent DFT (TD-DFT) calculations suggest that reaction control should be quite straightforward just by visual inspection (Figs. 6.7 - 6.13). With an energy difference of only 1.55 eV, the HOMO→LUMO excitation of the silylene can already be found in the near infrared. As expected, this corresponds to the excitation of an electron located in the n-orbital of the silylene into its empty $p\pi$-orbital. However, there are a couple of transitions (HOMO-1→LUMO at 546 nm, HOMO-2→LUMO at 522 nm) into this $p\pi$-orbital in the visible region of the electromagnetic spectrum (Fig. 6.5). These transitions should result in a deep red to purple coloring of the reaction solution.

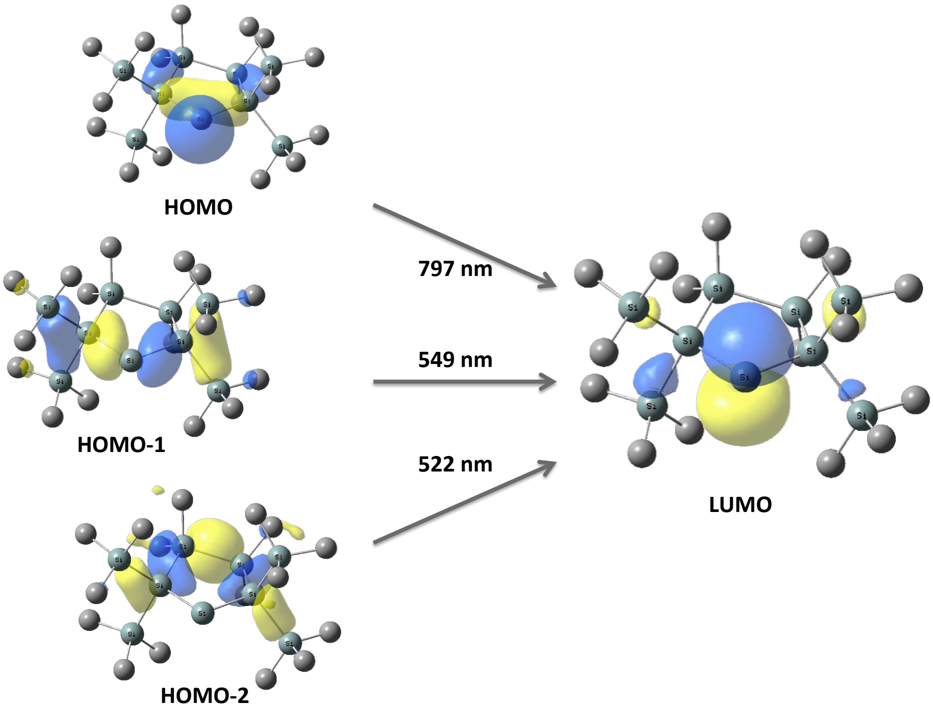


Figure 6.5.: Electronic transitions of silylene **24** from HOMO-2, HOMO-1 and HOMO into the LUMO.

Stabilization by any of the trapping reagents should lead to a change of color. Compounds **25**, **26**, **29**, and **30** do not possess any electronic transitions in the visible region of the electromagnetic spectrum. Only compounds **27** and **28** (379 nm and 374 nm, respectively) feature barely visible excitations, which should result in a yellowish coloration of the reaction solution. In both cases, these HOMO→LUMO transitions originate from the π-like Si-P bond into the corresponding anti-bonding orbital and the backbone Si-ring (Fig. 6.6). Using all this data, the characterization of the silylene or one of its trapping products should be strongly facilitated.

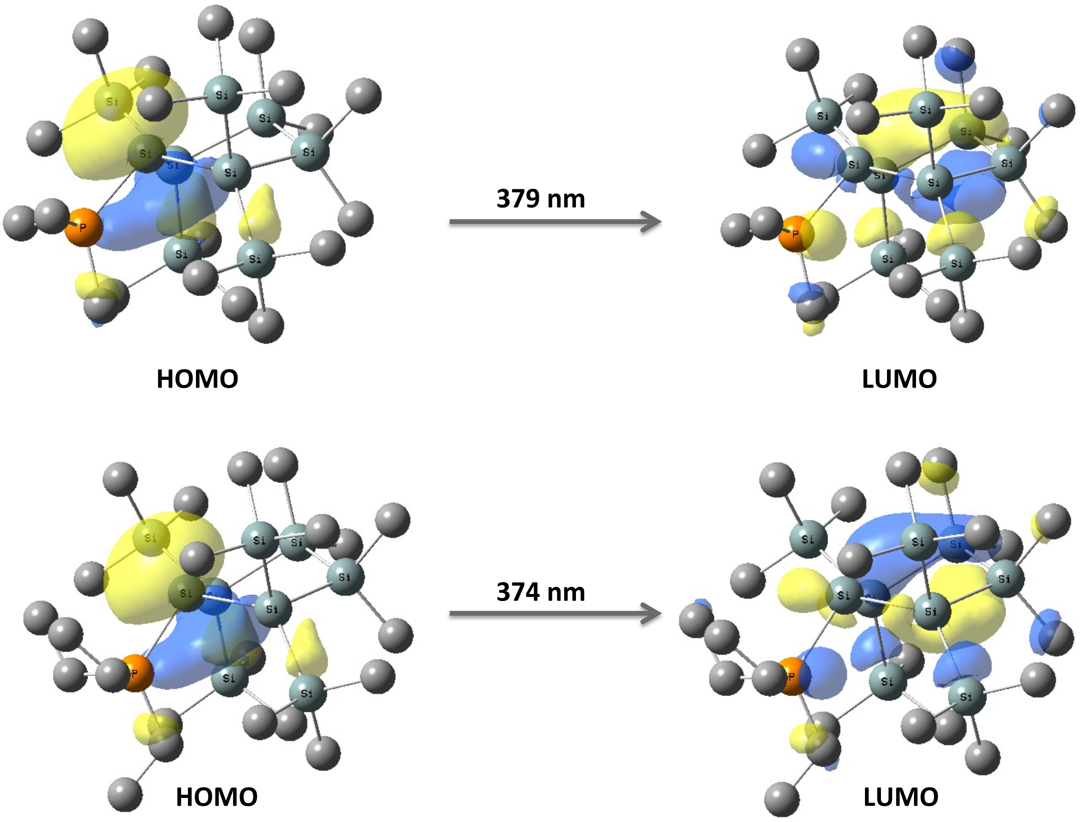


Figure 6.6.: HOMO-LUMO transitions of stabilized silylenes **27** and **28**.

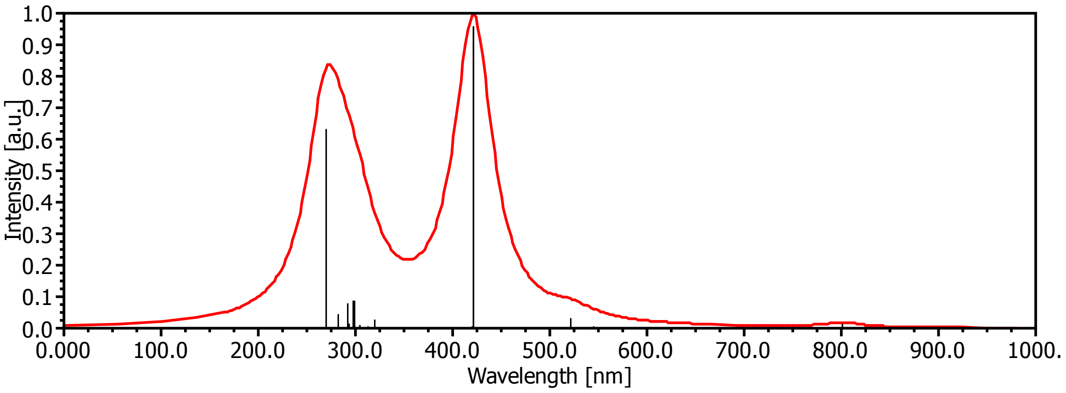


Figure 6.7.: Calculated UV/VIS spectrum of compound **24**.

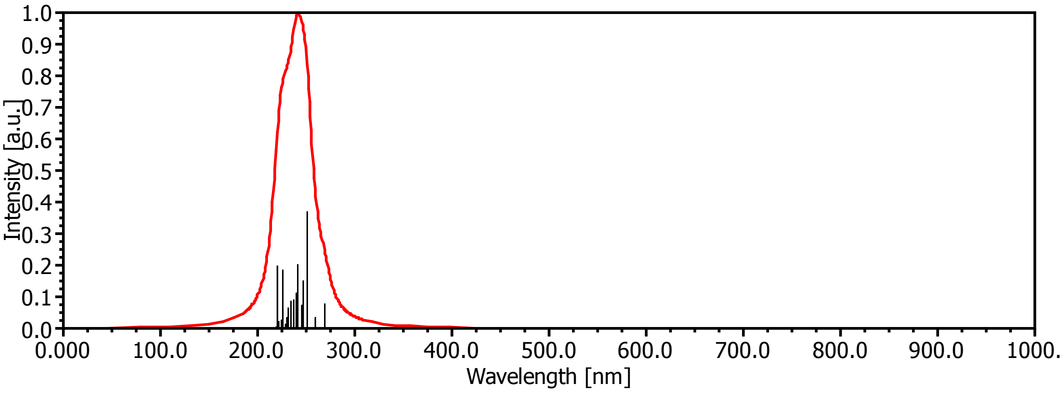


Figure 6.8.: Calculated UV/VIS spectrum of compound **25**.

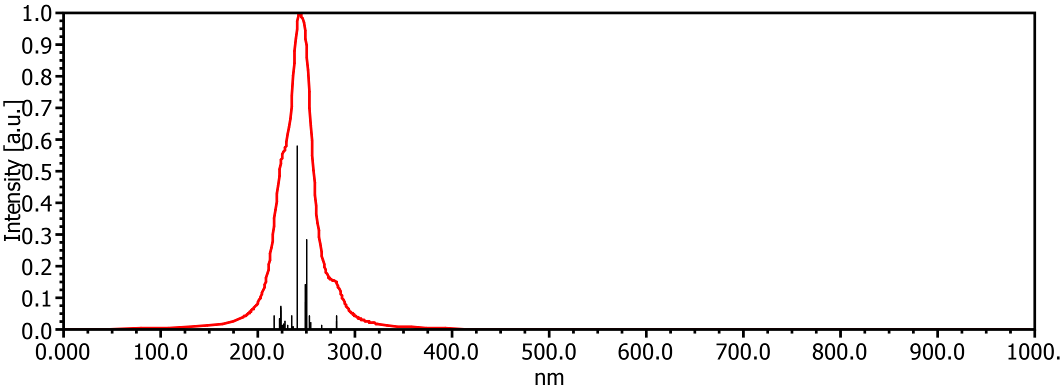


Figure 6.9.: Calculated UV/VIS spectrum of compound **26**.

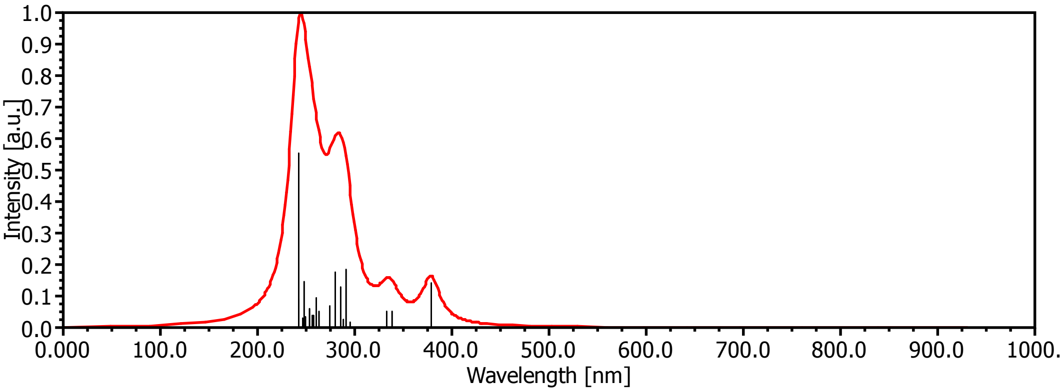


Figure 6.10.: Calculated UV/VIS spectrum of compound **27**.

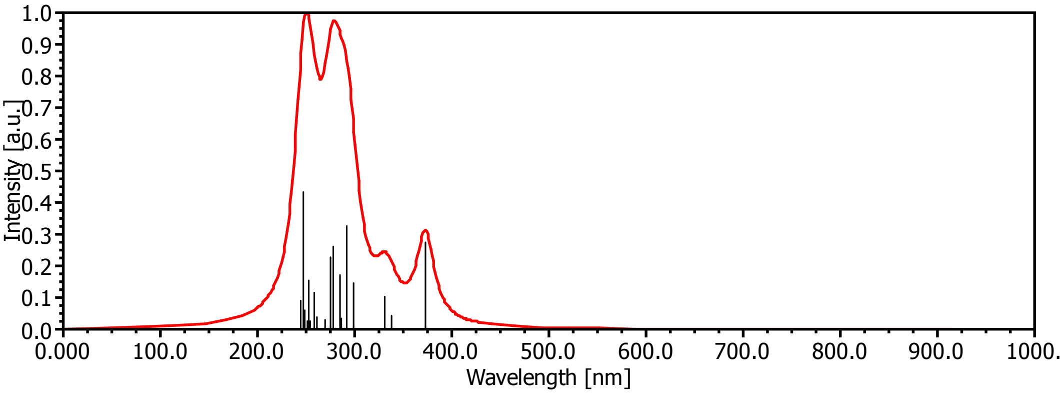


Figure 6.11.: Calculated UV/VIS spectrum of compound **28**.

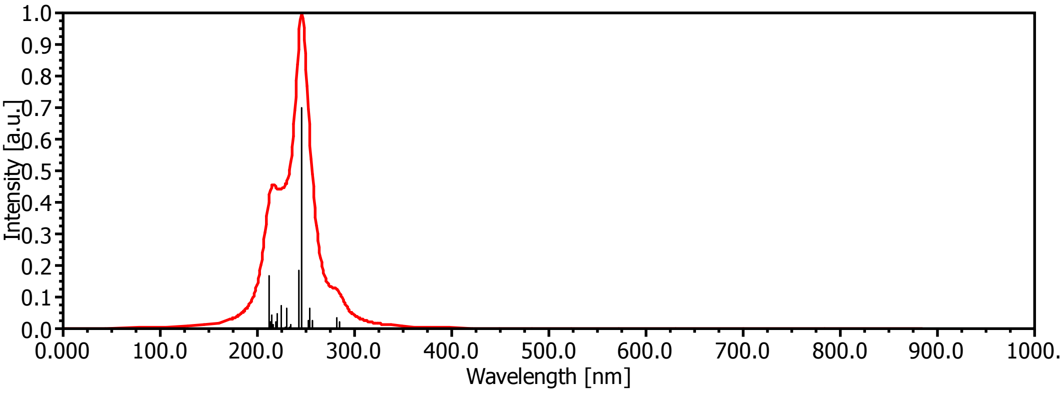


Figure 6.12.: Calculated UV/VIS spectrum of compound **29**.

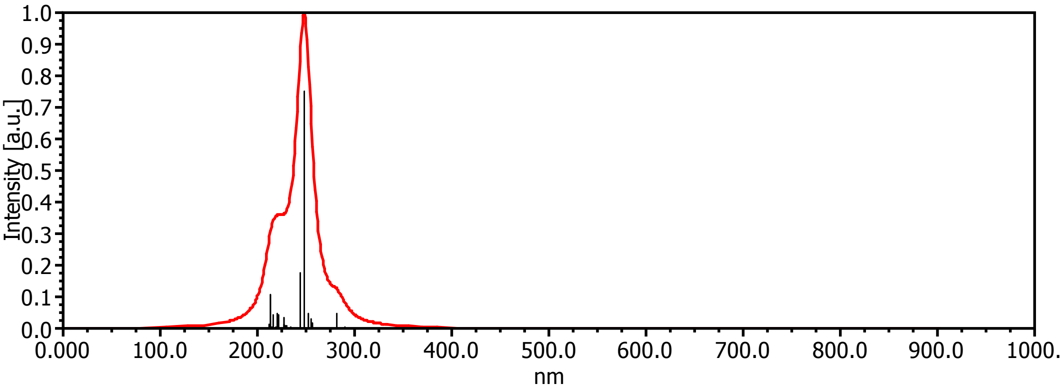


Figure 6.13.: Calculated UV/VIS spectrum of compound **30**.

6.3. Synthesis and Calculations

In order to synthesize the desired silylene, the reaction of dibrominated cyclopentasilane **22** with potassium graphite has been conducted several times. Upon addition of the cyclopentasilane in THF onto two equivalents of C_8K at -75 °C the color changed to yellow immediately. Some of the reaction attempts also resulted in a deeply red colored solution. This color fits well to the results obtained by time dependent DFT calculations. However, comparable colors have been observed for anionic silicon species during the synthesis of the precursors. So despite the agreement with calculations, observation of the color of the solution does not give definitive information about the species present in the reaction. Filtration from excess graphite and attempted crystallization did not lead to the isolation of the silylene. Educt **22** was obtained in some of the reaction attempts, i.e. no reduction reaction did occur. Reaction times and temperatures were changed in ranges of 0.5 - 4 h and -80 - 0 °C respectively. The outcome of the reactions did not improve with alteration of reaction conditions. In most cases, no signals could be detected at all in ^{29}Si NMR and isolation of a crystalline compound was not successful. The assumed highly reactive nature of the silylene, together with the outcome of the dehalogenation reactions, led to the conclusion that additional stabilization might be obligatory. Mechanisms for stabilization used in the past include complexation with an electron donating species and insertion into Si-H or O-H bonds. All the trapping reagents investigated quantum chemically (triethylsilane **25**, isoprene **26**, trimethyl phosphine **27**, triethyl phosphine **28**, water **29**, and methanol **30**) have also been used in the attempted trapping of the silylene. Reduction reactions have been conducted in presence of the phosphines, while the other reagents have been added to the corresponding reaction solutions five minutes after the beginning of the reaction. Disappointingly, these reactions did not result in the isolation of a clean product either.

Each reaction solution was analyzed by ^{29}Si NMR spectroscopy after filtration of excess graphite. For this, the reaction was either run in deuterated THF-d8 or a D_2O capillary was used as external lock when non-deuterated solvents were used. In most attempts, either no signal oder only signals caused by the educt **22** could be observed. NMR analysis of the compounds discussed in

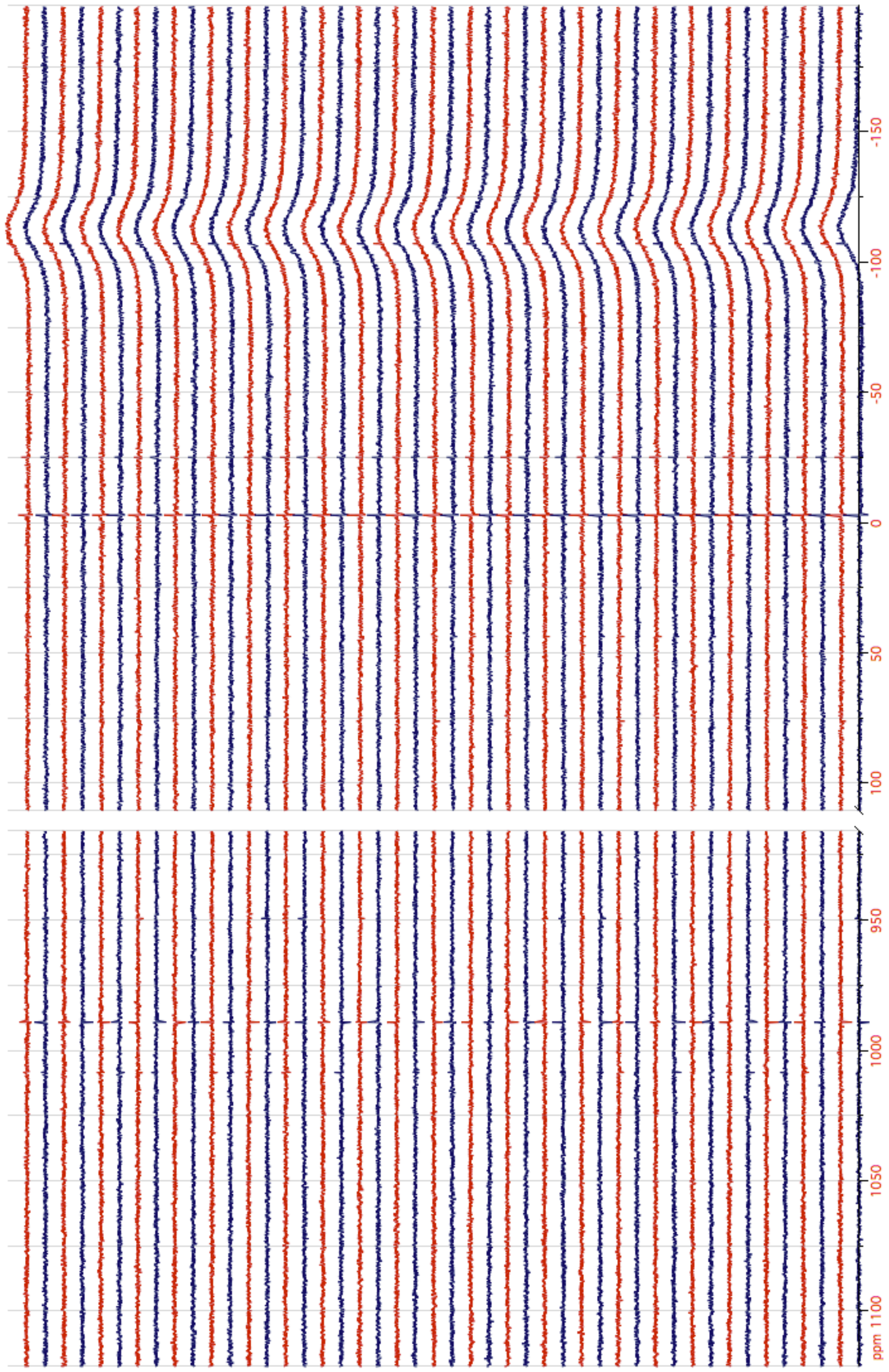


Figure 6.14.: Arrayed ^{29}Si NMR spectra of the reductive dehalogenation of **22**.

the previous chapter has shown that the signal for Si1 is not detectable with the ^{29}Si-DEPT sequence used at our institute. This made data acquisition with a regular ^{29}Si NMR experiment necessary. The major drawback of this method are the required relaxation times of over a minute, which prolonges the acquisition of spectra drastically. Despite the fact that no single crystal of the product could be isolated in any of the reaction attempts, one of the reductive dehalogenation reactions without trapping reagent was analyzed *via* arrayed ^{29}Si spectroscopy over the course of several days (Fig. 6.14).

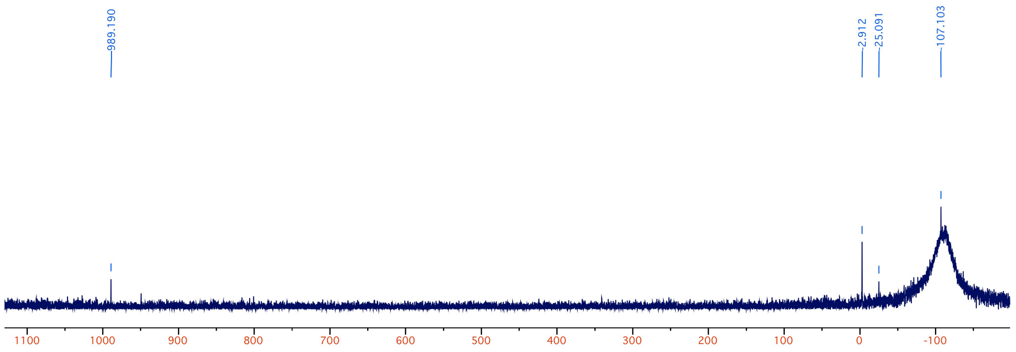


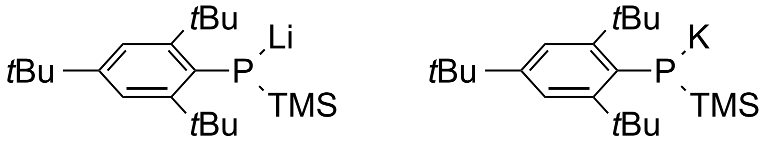
Figure 6.15.: Extract of the arrayed spectra in Fig. 6.14.

Taking a closer look (Fig. 6.15) at those arrayed spectra, four peaks can be identified. A high field shift of -107.9 ppm (Si2), an intense signal at -2.9 ppm (Si4), a smaller signal at -22 ppm, and a resonance in the extreme low field at +989.2 ppm (Si1). Compared to the most downfield ^{29}Si NMR resonance reported to date, Kiras silylene at +567.2 ppm, this value is outstanding. The signals are persistent for extended periods of time, as the shown NMR spectra have been recorded over the course of 5 days. At first sight, the number of shifts observed fit well to the expected silylene structure. Compared to the calculated shifts discussed above, some discrepancies can be detected. The most crucial factor is the shift for Si2 at -107.9 ppm. Calculations predict a shift of -25 ppm for quaternary silicon Si2, comparable to the shift of backbone Si3. The slightly differing signals for Si3 and Si4 can be explained with the expected deviation of calculated and empirical values. The low field shift of 989.2 ppm clearly suggests the presence of a silylene in solution, but the calculations predict an even higher value of around 1133 ppm. This high field shift can be explained with adduct formation in the solution. Next to coordinating THF, also some interactions with potassium and bromide present in solution is easily imaginable. Such coordination could also lead to the upfield shift of Si1 and is an explanation for the high field shift of -107.9 ppm, as coordination clearly has influence on the Si2 shift. Decomposition of the silylene to a disilene or any other product involving migration of a trimethylsilyl group can be ruled out due to the number of shifts observed. As none of the investigated compounds fit the experimental shift exactly, the unambiguous determination of the exact structure present in solution is open for future work, which should have a heavy emphasis on isolation of the products and subsequent X-ray diffraction analysis.

Chapter 7

Conclusion and Outlook

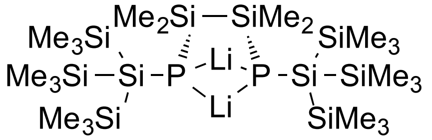
The main targets of this work have been the experimental and quantum chemical investigation of novel tetrylenes, their precursors and appropriate ligand systems. A broad range of potential ligands to diphosphatetrylenes has been synthesized in the course of this PhD. thesis and discussed in Chapters 2 and 3. The compounds shown in Figs. 7.1 and 7.2 show a variety of highly interesting ligands. Like all ligands in diphosphatetrylenes reported so far, compounds **4** and **7** feature an aromatic moiety with bulky substituents. Through substitution with a trimethylsilyl group, which is providing significant steric stabilization itself, both compounds can be functionalized and fine-tuned to specific steric requirements. Such functionalization reactions should be facilitated by the data obtained from this reaction behavior study. Compound **8**, obtained by reaction of the silylated supermesitylphosphine with Schwesinger base P_4-*t*-Bu, shows great dependence of the ^{31}P-NMR shift on the solvent used. A downfield shift of +52.5 ppm can be observed with solvent change from C_6D_6 to THF-d8, an effect caused by separation and reassociation of the ion pair in the respective solutions.



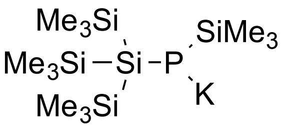
4 **7**

Figure 7.1.: Supermesitylphosphane ligands **4** and **7** described in Chapter 2.

Interesting NMR properties have also been observed for sterically demanding diphosphanes **10** and **12** and diphosphanide **11**. The formation of an AA'X spin system with regard to the hypersilyl $SiMe_3$ moieties (A,A' = P,P') leads to the observation of highly interesting coupling patterns in ^{29}Si NMR that are dependent on the $^3J_{PP'}$ and $^2J_{PSi}$ coupling constants.



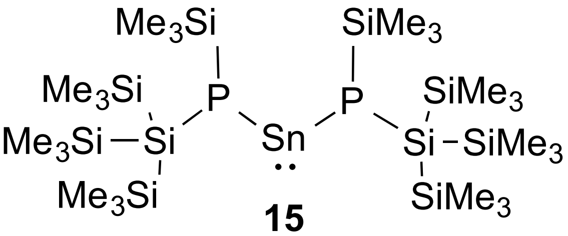
11



14

Figure 7.2.: Hypersilylphopshane ligands **11** and **14** described in Chapter 3 and 4.

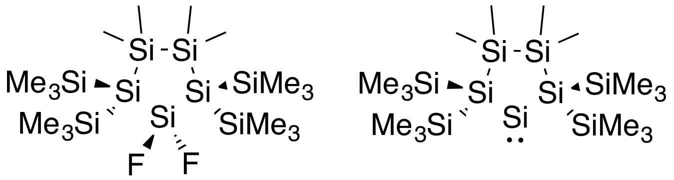
The general suitability of the hypersilyl group as sterically demanding group on phosphorus has been shown with the synthesis of the first stable diphosphastannylene **15** not containing any aromatic moieties (Chapter 4, Fig.7.3). The steric bulkiness of the hypersilyl(trimethylsilyl)phosphane ligand is the main cause for stabilization, aside from the interaction of phosphorus with the stannylene. The stannylene is stable as a monomer in solution and the solid state. This is the potential starting point to a whole new class of non-aromatic, phosphasilane based ligands for tetrylenes. Past reports on diphosphatetrylenes have shown that very specific ligand systems could be suitable just for one of the group 14 elements. Slight variations of the ligand could be required for isolation of the higher and lower homologues (i.e. the germylene and plumbylene), but should be easily accessible through substitution of the trimethylsilyl group.



15

Figure 7.3.: Acyclic diphosphastannylene **15** descriped in Chapter 4.

The high dependence of the stability of the tetrylene on the ligand was also shown in the attempted synthesis of the cyclic diphosphastannylene **16**. Ligand **10** is the diphosphane equivalent of the ligand used for the synthesis of stannylene **15**, with two hypersilyl phosphane moieties linked by a disilane backbone. The overall sterical demand comparable to two of the hypersilyl(trimethylsilyl)phosphane ligands used for the synthesis of **15**. The bicyclic structure of diphosphanide **11** also shows the preference of cyclic geometries in solution and the solid state. Regarding its size and chemical properties, the ligand is a highly promising starting point for tetrylene synthesis. However, the forced geometry of cyclic tetrylenes that greatly enhances overall stability for N,N'-heterocyclic systems does not have the same effects with P,P'-tetrylenes. Compared to equivalent nitrogen based ligands, the donation of the free electron pair into to the empty pπ-orbital of the tetrylene is not as effective, which is caused by higher planarization energies for phosphorus and a non-ideal geometric environment. Cyclic diphosphatetrylene **16** decomposes rapidly after initial formation, as indicated by the color change of the reaction solution. Fine tuning of the ligand can be one of the way to achieve higher stability of this compound. Furthermore, the use of stabilizing agent, e.g. a Lewis base, during the reaction might lead to the isolation of the first cyclic non-carbon P,P'-tetrylene.



21 **24**

Figure 7.4.: Silanes **20**, **21**, **22**, and **23** and silylene **24** described in Chapters 5 and 6.

Chemistry of equally great novelty has been conducted with the attempted synthesis of homocyclic silylene **24**. As precursors to this highly desired species, all of the halogenated precursors have been synthesized in the course of this work (Chapters 5 and 6, Fig. 7.4). Difluoride **20** is one of the rare examples of an isolated -SiF_2- in a homocyclic silane, which shows that the molecular environment is generally suitable to stabilize else highly reactive species. Reductive dehalogenation of the dibromide precursor did not lead to the isolation of the desired silylene, although signals of a stable compound could be detected in ^{29}Si NMR over several days. However the nature of this species is doubtful, as observed resonances and shifts calculated by density functional theory show distinct discrepancies. The method/basis set combination M06L/IGLO-II has shown great performance in the calculation of magnetic shieldings of halogenated silanes and silylenes. Using these calculated spectroscopic properties of the silylene and some of its trapping products the identification of products resulting from future attempts of silylene synthesis should be facilitated. All of the investigated trapping reagents (Et_3SiH, Isoprene, PMe_3, PEt_3, H_2O and MeOH) are suitable for the stabilization of the silylene, with the most negative reaction energies and enthalpies for water and methanol. The most interesting property remains the ^{29}Si NMR shift of the silylene itself. The calculated shift of around 1130 ppm is impressive compared to the current most downfield shift reported (567 ppm).

List of Figures

List of Tables

Bibliography

[1] Herrmann, W. A.; Koecher, C. *Chem. Rev.*, **1997**, *36*, 2162.

[2] Cazin, C. S. J. *Dalton Trans.*, **2013**, *42*, 7254.

[3] Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.*, **1991**, *113*(1), 361.

[4] Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.*, **1994**, *116*, 2691.

[5] Herrmann, W. A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F.-R.; Bock, H.; Solouki, B.; Wagner, M. *Angew. Chem. Int. Ed. Engl.*, **1992**, *31*(11), 1485.

[6] Gans-Eichler, T.; Gudat, D.; Nieger, M. *Angew. Chem. Int. Ed.*, **2002**, *41*(11), 1888.

[7] Moser, D. F.; Guzei, I. A.; West, R. *Main Group Met. Chem.*, **2001**, *24*, 811.

[8] Mitra, A.; Brodovitch, J.-C.; Kremper, C.; Percival, P. W.; Vyas, P.; West, R. *Angew. Chem. Int. Ed.*, **2010**, *49*, 2893.

[9] Zark, P.; Schafer, A.; Mitra, A.; Haase, D.; Saak, W.; West, R.; Mueller, T. *J. Organomet. Chem.*, **2010**, *695*, 398.

[10] Kong, L.; Zhan, J.; Song, H.; Cui, C. *Dalton Trans.*, **2009**, 5444.

[11] Kuhl, O.; Lonnecke, P.; Heinecke, J. *Polyhedron*, **2001**, *20*, 2215.

[12] Hill, N. J.; Moser, D. F.; Guzei, I. A.; West, R. *Organometallics*, **2005**, *24*, 3346.

[13] Mansell, S. M.; Herber, R. H.; Nowik, I.; Ross, D.; Russel, C. A.; Wass, D. F. *Inorg. Chem.*, **2011**, *50*, 2252.

[14] Charmant, J. P. H.; Haddow, M. P.; Hahn, F. E.; Heitmann, D.; Frohlich, R.; Mansell, S. M.; Russel, C. A.; Wass, D. F. *Dalton Trans.*, **2008**, 6055.

[15] Mansell, S. M.; Russel, C. A.; Wass, D. F. *Inorg. Chem.*, **2008**, *47*, 11367.

[16] Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Blaser, D. *J. Organomet. Chem.*, **1996**, *521*, 211.

[17] Pfeiffer, J.; Maringgele, W.; Noltemeyer, M.; Meller, A. *Chem. Ber.*, **1989**, *122*, 245.

[18] Huang, M.; Kireenko, M. M.; Zaitsev, K. V.; Oprunenko, Y. F.; Churakov, A. V.; Howard, J. A. K.; Lermontova, E. K.; Sorokin, D.; Linder, T.; Sundermeyer, J.; Karlov, S. S.; Zaitseva, G. S. *Eur. J. Inorg. Chem.*, **2012**, 3712.

[19] Hahn, F. E.; WIttenbacher, L.; Le Van, D.; Zabula, A. V. *Inorg. Chem.*, **2007**, *46*, 7662.

[20] Dickschat, J.; Urban, S.; Pape, T.; F., G.; Hahn, F. E. *Dalton Trans.*, **2010**, *39*, 11519.

[21] Braunschweig, H.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *Z. Anorg. Allg. Chem.*, **1995**, *621*, 1922.

[22] Hahn, F. E.; Heitmann, D.; Pape, T. *Eur. J. Inorg. Chem.*, **2008**, 1039.

[23] Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *Z. Anorg. Allg. Chem.*, **2005**, *631*, 1383.

[24] Dickschat, J.; Heitmann, D.; Pape, T.; Hahn, F. E. *J. Organomet. Chem.*, **2013**, *744*, 160.

[25] Driess, M.; Yao, S.; Brym, M.; van Wullen, C.; Lentz, D. *J. Am. Chem. Soc.*, **2006**, *128*, 9628.

[26] Driess, M.; Shenglai, Y.; Brym, M.; van Wullen, C. *Angew. Chem. Int. Ed.*, **2006**, *45*, 4349.

[27] Woodul, W. D.; Carter, E.; Muller, R.; Richard, A. F.; Stasch, A.; Kaupp, M.; Murphy, D. M.; Driess, M. *J. Am. Chem. Soc.*, **2011**, *133*, 10074.

[28] Choong, S. L.; Woodul, W. D.; Schenk, C.; Stasch, A.; Richard, A. F.; Jones, C. *Organometallics*, **2011**, *30*, 5543.

[29] Xiong, Y.; Shenglai, Y.; Driess, M. *Chem. Asian J.*, **2012**, *7*, 2145.

[30] Wang, W.; Inoue, S.; Yao, S.; Driess, M. *Organometallics*, **2011**, *30*, 6490.

[31] Fedushkin, I. L.; Lukoyanov, A. N.; Khvoinova, N. M.; Cherkasov, A. V. *Izv. Akad. Nauk SSSR.Ser.Khim.(Russ.)(Russ.Chem.Bull.)*, **2013**, 2454.

[32] Fedushkin, I. L.; Skatova, A. A.; Chudakova, V. A.; Khvoinova, N. M.; Baurin, A. Y.; Dechert, S.; Hummert, M.; Schumann, H. *Organometallics*, **2004**, *23*, 3714.

[33] Bazinet, P.; Yap, G. P. A.; Richeson, D. S. *J. Am. Chem. Soc.*, **2001**, *123*, 11162.

[34] Bazinet, P.; Yap, G. P. A.; DiLabio, G. A.; Richeson, D. S. *Inorg. Chem.*, **2005**, *44*, 4616.

[35] Avent, A. G.; Drost, C.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *Z. Anorg. Allg. Chem.*, **2004**, *630*, 2090.

[36] Jimenez-Perez, V. M.; Manoz-Flores, B. M.; Roesky, H. W.; T., S.; Pal, A.; Beck, T.; Yang, Z.; Stalke, D.; Santillan, R.; Witt, M. *Eur. J. Inorg. Chem.*, **2008**, 2238.

[37] Yao, S.; Xiong, Y.; Driess, M. *Organometallics*, **2011**, *30*(7), 1748.

[38] Chorley, R. W.; Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P.; Power, P. P.; Olmstead, M. M. *Inorg. Chim. Acta*, **1992**, *198*, 203.

[39] Meller, A.; Ossig, G.; Maringgele, W.; Stalke, D.; Herbst-Irmer, R.; Freitag, S.; Sheldrick, G. M. *Z.Naturforsch.,B: Chem.Sci.*, **1992**, *47*, 162.

[40] Fjeldberg, T.; Hope, H.; Lappert, M. F.; Power, P. P.; Thorne, A. J. *Chem. Commun.*, **1983**, 639.

[41] Hitchcock, P. B.; Hu, J.; Lappert, M. F.; Layh, M.; Severn, J. *Chem. Commun.*, **1997**, 1189.

[42] Babcock, J. R.; Liable-Sands, L.; Rheingold, A. L.; Sita, L. R. *Organometallicsga*, **1999**, *18*, 4437.

[43] Tang, Y.; Felix, A. M.; Zakharov, L. N.; Rheingold, A. L.; Kemp, R. A. *Inorg. Chem.*, **2004**, *43*, 7239.

[44] Westerhausen, M.; Greul, J.; Hausen, H.-D.; Schwarz, W. *Z. Anorg. Allg. Chem.*, **1996**, *622*(8), 1295–1305.

[45] Bares, J.; Sourek, V.; Padelkova, Z.; Meunier, P.; Pirlo, N.; Cisarova, I.; Ruzicka, A.; Holecek, J. *Collect.Czech.Chem.Commun.*, **2010**, *75*, 121.

[46] Lappert, M. F.; Slade, M. J.; Atwood, J. L.; Zaworotko, M. J. *Chem. Commun.*, **1980**, 621.

[47] Merrill, W. A.; Wright, R. J.; Stanciu, C. S.; Olmstead, M. M.; Fettinger, J. C.; Power, P. P. *Inorg. Chem.*, **2010**, *49*, 7097.

[48] Hitchcock, P. B.; Lappert, M. F.; Thorne, A. J. *Chem. Commun.*, **1990**, 1587.

[49] Schnepf, A. *Z. Anorg. Allg. Chem.*, **2006**, *632*, 935.

[50] Veith, M.; Rammo, A. *Z. Anorg. Allg. Chem.*, **2001**, *627*, 662.

[51] Huang, M.; Kireenko, M. M.; Lermontova, E. K.; Churakov, A. V.; Oprunenko, Y. F.; Zaitsev, K. V.; Sorokin, D.; Harms, K.; Sundermeyer, J.; Zaitseva, G. S.; Karlov, S. S. *Z. Anorg. Allg. Chem.*, **2013**, *639*, 592.

[52] Braunschweig, H.; Hitchcock, P. B.; Lappert, M. F.; Pierssens, L. J.-M. *Angew. Chem. Int. Ed.*, **1994**, *33*, 1156.

[53] Driess, M.; Janoschek, R.; Pritzkow, H.; Rell, S.; Winkler, U. *Angew. Chem. Int. Ed. Engl.*, **1995**, *34*(15), 1614.

[54] Izod, K.; Clark, E. R.; Clegg, W.; Harrington, R. W. *Organometallics*, **2012**, *31*(1), 246.

[55] Izod, K.; Rayner, D.; El-Hamruni, S.; Harrington, R. W.; Baisch, U. *Angew. Chem. Int. Ed.*, **2014**, *53*, 3636.

[56] Druckenbrodt, C.; du Mont, W.-W.; Ruthe, F.; Jones, P. G. *Z. anorg. allg. Chem.*, **1998**, *624*(4), 590.

[57] du Mont, W.-W.; Kroth, H.-J. *Angew. Chem. Int. Ed. Engl.*, **1977**, *16*(11), 792.

[58] Cowley, A. H.; Giolando, D. M.; Jones, R. A.; Nunn, C. M.; Power, J. M. *Polyhedron*, **1988**, *7*(19–20), 1909.

[59] Goel, S. C.; Chiang, M. Y.; Rauscher, D. J.; Buhro, W. E. *J. Am. Chem. Soc.*, **1993**, *115*(1), 160.

[60] Martin, D.; Baceiredo, A.; Gornitzka, H.; Schoeller, W. W.; Bertrand, G. *Angew. Chem. Int. Ed. Engl.*, **2005**, *44*(11), 1700.

[61] Cappello, V.; Baumgartner, J.; Dransfeld, A.; Hassler, K. *Eur. J. Inorg. Chem.*, **2006**, 4589.

[62] Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.*, **1999**, *121*, 9722.

[63] Kira, M.; Ishida, S.; Iwamoto, T.; Ichinohe, M.; Kabuto, C.; Ignatovich, L.; Sakurai, H. *Chem. Lett.*, **1999**, *28*(3), 263.

[64] Kira, M.; Yauchibara, R.; Hirano, R.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.*, **1991**, *113*(20), 7785.

[65] Džambaski, A. *New Acyclic and Cyclic Oligosilanes: Precursors for Phosphasilenes, Cyclotrisilanes, and Silylenes*. PhD thesis, Graz University of Technology, **2007**.

[66] Xiao, X.-Q.; Zhao, H.; Xu, Z.; Lai, G.; Xiao-Lin, H.; Li, Z. *Chem. Commun.*, **2013**, *49*, 2706.

[67] Arp, H.; Baumgartner, J.; Marschner, C.; Müller, T. *J. Am. Chem. Soc.*, **2011**, *133*, 5632.

[68] Hlina, J.; Baumgartner, J.; Marschner, C.; Albers, L.; Müller, T. *Organometallics*, **2013**, *32*(11), 3404.

[69] Arp, H.; Baumgartner, J.; Marschner, C.; Zark, P.; Müller, T. *J. Am. Chem. Soc.*, **2012**, *134*(14), 6409. PMID: 22455750.

[70] Nakata, N.; Fujita, T.; Sekiguchi, A. *J. Am. Chem. Soc.*, **2006**, *128*, 16024.

[71] Tanaka, H.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.*, **2012**, *134*, 5540.

[72] Yeong, H.-X.; Zhang, S.-H.; Xi, H.-W.; Guo, J.-D.; Lim, K. H.; Nagase, S.; So, C.-W. *Chem.–Eur. J.*, **2012**, *18*, 2685.

[73] Klinkhammer, K. W.; Schwarz, W. *Angew. Chem. Int. Ed.*, **1995**, *34*, 1334.

[74] Becker, M.; Forster, C.; Franzen, C.; Hartrath, J.; Kirsten, E.; Knuth, J.; Klinkhammer, K. W.; Sharma, A.; Hinderberger, D. *Inorg. Chem.*, **2008**, *47*, 9965.

[75] Katir, N.; Matioszek, D.; Ladeira, S.; Escudie, J.; Castel, A. *Angew. Chem. Int. Ed.*, **2011**, *50*, 5352.

[76] Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *Angew. Chem. Int. Ed.*, **1997**, *36*, 2514.

[77] Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D. *Angew. Chem. Int. Ed.*, **2009**, *48*(31), 5683.

[78] Niecke, E.; Altmeyer, O.; Nieger, M. *Angew. Chem.*, **1991**, *103*(9), 1158.

[79] Song, M.; Donnadieu, B.; Soleilhavoup, M.; Bertrand, G. *Chem.–Asian J.*, **2007**, *2*(7), 904.

[80] Yasunami, M.; Ueno, T.; Yoshifuji, M.; Okamoto, A.; Hirotsu, K. *Chem. Lett.*, **1992**, *21*(10), 1971.

[81] Schäfer, H.; Leske, W. *Z. anorg. allg. Chem.*, **1987**, *550*(7), 57.

[82] Domańska-Babul, W.; Baranowska, K.; Grubba, R.; Matern, E.; Pikies, J. *Polyhedron*, **2007**, *26*(18), 5491.

[83] Tam, E. C. Y.; Maynard, N. A.; Apperley, D. C.; Smith, J. D.; Coles, M. P.; Fulton, J. R. *Inorg. Chem.*, **2012**, *51*(17), 9403. PMID: 22900884.

[84] Kayser, C.; Kickelbick, G.; Marschner, C. *Angew. Chem. Int. Ed.*, **2002**, *41*(6), 989.

[85] Yoshifuji, M.; Shibayama, K.; Inamoto, N. *J. Am. Chem. Soc.*, **1983**, *105*, 2495.

[86] Bruker. *APEX2 and SAINT*. Bruker AXS Inc., Madison, WI, USA, 2012.

[87] Blessing, R. *Acta Crystallogr. A*, **1995**, *51*, 33.

[88] Sheldrick, G. M. *Acta Crystallogr. Sect. A*, **1990**, *46*(6), 467.

[89] Sheldrick, G. M. *Acta Crystallogr. Sect. A*, **2008**, *64*(1), 112.

[90] Spek, A. L. *J. Appl. Crystallogr.*, **2003**, *36*, 7.

[91] Spek, A. L. *Acta Crystallogr. Sect. D*, **2009**, *65*(2), 148.

[92] Driess, M.; Pritzkow, H. *Z. Anorg. Allg. Chem.*, **1996**, *622*(9), 1524.

[93] Karsch, H. H.; Appelt, A.; Deubelly, B.; Muller, G. *J. Chem. Soc., Chem. Commun.*, **1987**, 1033.

[94] Hitchcock, P. B.; Lappert, M. F.; Power, P. P.; Smith, S. J. *J. Chem. Soc., Chem. Commun.*, **1984**, 1669.

[95] Ellison, J. J.; Power, P. P. *Inorg. Chem.*, **1994**, *33*, 4231.

[96] Eichhorn, B.; Noeth, H.; Seifert, T. *Eur. J. Inorg. Chem.*, **1999**, 2355.

[97] Scherer, W.; Sirsch, P.; Shorokhov, D.; McGrady, G. S.; Mason, S. A.; Gardiner, M. G. *Chem.–Eur. J.*, **2002**, *8*, 2324.

[98] Rabe, G. W.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.*, **1997**, *36*(10), 1990. PMID: 11669811.

[99] Torvisco, A.; Decker, K.; Uhlig, F.; Ruhlandt-Senge, K. *Inorg. Chem.*, **2009**, *48*, 11459.

[100] Uhlig, F.; Uhlig, W. *Phosphorus, Sulfur Silicon Relat. Elem.*, **1993**, *84*, 181.

[101] Janiak, C. J. *Chem. Soc., Dalton Trans.*, **2000**, 3885.

[102] Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Phosphorus Ligand Effects in Homogeneous Catalysis and Rational Catalyst Design*. John Wiley and Sons Ltd., **2012**.

[103] Lühr, S.; Holz, J.; Börner, A. *ChemCatChem*, **2011**, *3*(11), 1708.

[104] Cheng, F.; Hector, A. L.; Levason, W.; Reid, G.; Webster, M.; Zhang, W. *Inorg. Chem.*, **2010**, *49*(2), 752. PMID: 20017559.

[105] Davis, M. F.; Levason, W.; Reid, G.; Webster, M. *Dalton Trans.*, **2008**, 2261.

[106] Goudriaan, P. E.; van Leeuwen, P. W. N. M.; Birkholz, M.-N.; Reek, J. N. H. *Eur. J. Inorg. Chem.*, **2008**, *2008*(19), 2939.

[107] Lu, D.; Salem, G. *Coord. Chem. Rev.*, **2013**, *257*(5–6), 1026.

[108] Andriamizaka, J. D.; Couret, C.; Escudie, J.; Satge, J. *Phosphorus, Sulfur Silicon Relat. Elem.*, **1982**, *12*(3), 265.

[109] von Hänisch, C.; Matern, E. *Z. anorg. allg. Chem.*, **2005**, *631*(9), 1655.

[110] von Hänisch, C.; Traut, S.; Stahl, S. *Z. anorg. allg. Chem.*, **2007**, *633*(13-14), 2199.

[111] Thiele, S. K.-H.; Monroy, V. M.; Wilson, D. R.; Stoye, H. Metal complex compositions and their use as catalysts to produce polydienes. Patent WO 2003033545 A2 20030424, 2003.

[112] Thiele, S. K.-H.; Monroy, V. M.; Wilson, D. R. Random or block copolymers produced using metal complex catalysts. Patent WO 2002090394 A1 20021114, 2002.

[113] Sheldrick, W. S.; Borkenstein, A. *Acta Cryst. B*, **1977**, *B33*(9), 2916–18.

[114] Stelzer, O.; Unger, E.; Wray, V. *Chem. Ber.*, **1977**, *110*(10), 3430.

[115] Hassler, K.; Seidl, S. *Monatsh. Chem.*, **1988**, *119*(11), 1241.

[116] Chen, T.; Duesler, E. N.; Paine, R. T.; Nöth, H. *Inorg. Chem.*, **1999**, *38*(22), 4993.

[117] Chen, T.; Jackson, J.; Jasper, S. A.; Duesler, E.; Nöth, H.; Paine, R. T. *J. Organomet. Chem.*, **1999**, *582*(1), 25.

[118] Dou, D.; Kaufmann, B.; Duesler, E. N.; Chen, T.; Paine, R. T.; Noeth, H. *Inorg. Chem.*, **1993**, *32*(14), 3056.

[119] Hengge, E.; Pletka, H. D.; Hoefler, F. *Monatsh. Chem.*, **1970**, *101*(2), 325.

[120] Sheldrick, G. M. *SADABS, Version 2.10, Siemens Area Detector Correction*. University of Göttingen, Göttingen, Germany, 2002.

[121] Sheldrick, G. M. *SHELXS2013*. University of Göttingen, Göttingen, Germany, 2013.

[122] Van der Sluis, P.; Spek, A. L. *Acta Crystallogr. Sect. A*, **1990**, *46*, 194.

[123] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision A.1*. Gaussian, Inc., Wallingford CT, 2009.

[124] Adamo, C.; Barone, V. *J. Chem. Phys.*, **1998**, *108*, 664.

[125] Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.*, **2006**, *125*, 1.

[126] Dunning, T. H.; Hay, P. J. *Modern Theoretical Chemistry*, volume 3. Plenum, New York, **1976**.

[127] Igel-Mann, G.; Stoll, H.; Preuss, H. *Mol. Phys.*, **1988**, *65*(6), 1321.

[128] Bergner, A.; Dolg, M.; Küchle, W.; Stoll, H.; Preuß, H. *Mol. Phys.*, **1993**, *80*(6), 1431.

[129] Kutzelnigg, W.; Fleischer, U.; Schindler, M. in *Deuterium and Shift Calculation*, volume 23 of *NMR Basic Principles and Progress*, 165. Springer Berlin Heidelberg, Heidelberg, 1990.

[130] Westerhausen, M.; Low, R.; Schwarz, W. *J. Organomet. Chem.*, **1996**, *513*, 213.

[131] Anderson, D. M.; Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P.; Zora, J. A. *J. Organomet. Chem.*, **1987**, *333*(2), C13.

[132] Hitchcock, P. B.; Lappert, M. F.; Leungt, W.-P.; Yin, P. *J. Chem. Soc., Dalton Trans.*, **1995**, 3925.

[133] Stein, D.; Dransfeld, A.; Flock, M.; Rüegger, H.; Grützmacher, H. *Eur. J. Inorg. Chem.*, **2006**, *2006*(20), 4157.

[134] Edge, R.; Less, R. J.; Naseri, V.; McInnes, E. J. L.; Mulvey, R. E.; Wright, D. S. *Dalton Trans.*, **2008**, 6454.

[135] Bartlett, R. A.; Olmstead, M. M.; Power, P. P.; Sigel, G. A. *Inorg. Chem.*, **1987**, *26*(12), 1941.

[136] Westerhausen, M.; Rotter, T.; Görls, H.; Birg, C.; Warchhold, M.; Nöth, H. *Z.Naturforsch.,B: Chem.Sci.*, **2005**, *60*, 766.

[137] May, E.; Hitchcock, P. B.; Lappert, M. F.; Rai, A. K. *J. Organomet. Chem.*, **1987**, *325*(1), 1.

[138] Haaf, M.; Schmedake, T. A.; West, R. *Acc. Chem. Res.*, **2000**, *33*(10), 704.

[139] Asay, M.; Jones, C.; Driess, M. *Chem. Rev.*, **2011**, *111*, 354.

[140] Westerhausen, M.; Oßberger, M. W.; Keilbach, A.; Gückel, C.; Piotrowski, H.; Suter, M.; Nöth, H. *Z. Anorg. Allg. Chem.*, **2003**, *629*(12-13), 2398.

[141] Westerhausen, M.; Digeser, M. H.; Nöth, H.; Ponikwar, W.; Seifert, T.; Polborn, K. *Inorg. Chem.*, **1999**, *38*(13), 3207.

[142] Brym, M.; Francis, M. D.; Jin, G.; Jones, C.; Mills, D. P.; Stasch, A. *Organometallics*, **2006**, *25*(20), 4799.

[143] Mueller, S. K.; Weinberger, G.; Schwarz, E.; Torvisco, A.; Dransfeld, A.; Fischer, R. C.; Hassler, K.; Flock, M. *Inorg. Chim. Acta*, **2014**, *423*, 517.

[144] Hengge, E.; Bauer, G. *Angew. Chem.*, **1973**, *85*(7), 304.

[145] Pai, Y.-M.; Chen, C.-K.; Liu, C.-S. *J. Organomet. Chem.*, **1982**, *226*(1), 21.

[146] Hengge, E.; Kovar, D. *J. Organomet. Chem.*, **1977**, *125*(2), C29.

[147] Hengge, E.; Bauer, G. *Monatsh. Chem.*, **1975**, *106*(2), 503.

[148] Hengge, E.; Kovar, D. *Angew. Chem.*, **1981**, *93*(8), 698.

[149] Hengge, E.; Marketz, H. *Monatsh. Chem.*, **1970**, *101*(2), 528.

[150] Ishikawa, M.; Kumada, M. *J. Chem. Soc. D, Chem. Commun.*, **1969**, *10*, 567b–8.

[151] Ishikawa, M.; Kumada, M. *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, **1971**, *1*(4), 229–234.

[152] Jenkner, P. K.; Spielberger, A.; Hengge, E. *Heteroat. Chem.*, **1992**, *3*(4), 443.

[153] Oeschl, U.; Siegl, H.; Hassler, K. *J. Organomet. Chem.*, **1996**, *506*(1), 93.

[154] Hengge, E.; Sommer, R. *Monatsh. Chem.*, **1977**, *108*(6), 1413.

[155] Stueger, H.; Mitterfellner, T.; Fischer, R.; Walkner, C.; Patz, M.; Wieber, S. *Inorg. Chem.*, **2012**, *51*(11), 6173.

[156] Hengge, E. F.; Hassler, K.; Schrank, F. *Heteroat. Chem.*, **1990**, *1*(6), 455.

[157] Masamune, S.; Eriyama, Y.; Kawase, T. *Angew. Chem. Int. Ed. Engl.*, **1987**, *26*, 583.

[158] Watanabe, H.; Takeuchi, K.; Fukawa, N.; Kato, M.; Goto, M.; Nagai, Y. *Chem. Lett.*, **1987**, 1341.

[159] Weidenbruch, M.; Pellmann, A.; Pan, Y.; Pohl, S.; Saak, W.; Marsmann, H. *J. Organomet. Chem.*, **1993**, *450*, 67.

[160] Tokitoh, N.; Suzuki, H.; Okazaki, R. *J. Am. Chem. Soc.*, **1993**, *115*, 10428.

[161] Kira, M.; Murayama, T.; Kabuto, C.; Ebata, K.; Sakurai, H. *Angew. Chem. Int. Ed. Engl.*, **1994**, *33*, 1489.

[162] Schmedake, T. A.; Haaf, M.; Apeloig, Y.; Mueller, T.; Bukalov, S.; West, R. *J. Am. Chem. Soc.*, **1999**, *121*, 10231.

[163] Ichinohe, M.; Kinjo, R.; Sekiguchi, A. *Organometallics*, **2003**, *22*, 4621.

[164] Iwamoto, T.; Okita, J.; Kabuto, C.; Kira, M. *Organomet. Chem.*, **2003**, *686*, 105.

[165] Tsutsui, S.; Kwon, E.; Tanaka, H.; Matsumoto, S.; Sakamoto, K. *Organometallics*, **2005**, *24*, 4629.

[166] Sekiguchi, A.; Ichinohe, M.; Yamaguchi, S. *J. Am. Chem. Soc.*, **1999**, *121*, 10231.

[167] Kira, M.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.*, **1996**, *118*, 10303.

[168] Iwamoto, T.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.*, **1999**, *121*, 886.

[169] Ichinohe, M.; Matsuno, T.; Sekiguchi, A. *Angew. Chem. Int. Ed.*, **1999**, *38*, 2194.

[170] Matsumoto, S.; Tsutsui, S.; Kwon, E.; Sakamoto, K. *Angew. Chem. Int. Ed.*, **2004**, *43*, 4610.

[171] Kobayashi, H.; Iwamoto, T.; Kira, M. *J. Am. Chem. Soc.*, **2005**, *127*, 15376.

[172] Protchenko, A. V.; Birjkumar, K. H.; Dange, D.; Schwarz, A. D.; Vidovic, D.; Jones, C.; Kaltsoyannis, N.; Mountford, P.; Aldridge, S. *J. Am. Chem. Soc.*, **2012**, *134*(15), 6500.

[173] Asay, M.; Inoue, S.; Driess, M. *Angew. Chem.*, **2011**, *123*, 9763.

[174] Alvarez, S. *Dalton Trans.*, **2013**, *42*(24), 8617.

[175] Glukhovstev, M.; Pross, A.; McGrath, M.; Radom, L. *J. Chem. Phys.*, **1995**, *193*, 1878.

[176] Lauterbur, P. *Determination of Organic Substances by Physical Methods, Vol. 2.* Academic Press, **1962**.

[177] Flock, M.; Dransfeld, A. *Chem. Eur. J.*, **2003**, *9*, 3320.

[178] Hassler, K.; Dzambaski, A.; Baumgartner, J. *Silicon Chem*, **2008**, *3*, 271.

Appendix A

Optimized structures of investigated compounds

A.1. Compounds 1-7: Reaction behavior of supermesitylphosphane and its silylated derivatives.

2,4,6-tris(*t*-butyl)-phenylphosphane 1

```
Energy = -1045.6295116

 C        1.67835100    0.24169100   -0.01221000
 C        0.80199300    1.32517500   -0.01021600
 C       -0.60014200    1.18406300   -0.00266400
 C       -1.15211800   -0.13839300   -0.00950300
 C       -0.27497700   -1.27605000   -0.01123300
 C        1.11023200   -1.03656400   -0.00908800
 H        1.22030300    2.31760000   -0.01218900
 H        1.78191100   -1.88137700   -0.01036000
 C       -1.42736900    2.50962900    0.01937100
 C       -2.36620900    2.62340300   -1.21005700
 C       -2.22245600    2.64555900    1.34425400
 C       -0.52176600    3.76637700   -0.04788500
 H       -1.80686300    2.46177300   -2.13835200
 H       -3.19830300    1.91902300   -1.17736100
 H       -2.80086000    3.62938000   -1.24588500
 H       -1.53729500    2.62486400    2.19925800
 H       -2.75283500    3.60561600    1.35651100
 H       -2.96119900    1.85386300    1.47235100
 H       -1.16474900    4.65254600   -0.03399900
 H        0.15131200    3.84275700    0.81243100
 H        0.07138200    3.80514400   -0.96822000
 C       -0.70685600   -2.77805600    0.01684000
 C       -1.32829800   -3.14049500    1.39204000
 C       -1.63824300   -3.15678000   -1.16466100
 C        0.50260000   -3.74014000   -0.13358400
 H       -0.58377800   -2.99975400    2.18335000
 H       -2.20050600   -2.54110900    1.65652500
 H       -1.63472900   -4.19337800    1.39545900
 H       -1.17638600   -2.86756300   -2.11529300
 H       -1.78266300   -4.24340700   -1.17777700
 H       -2.62556400   -2.70176400   -1.12101700
 H        0.12534500   -4.76819500   -0.13104700
 H        1.03793100   -3.58708500   -1.07677900
 H        1.21285900   -3.65849900    0.69538300
```

C	3.20726500	0.40335600	-0.01556700
C	3.64338400	1.88079600	-0.02086800
C	3.79897900	-0.26758800	1.24810000
C	3.79536200	-0.27571200	-1.27652100
H	3.28067800	2.40858000	-0.90978500
H	3.28578200	2.41346000	0.86719800
H	4.73732900	1.93911600	-0.02408100
H	3.56631200	-1.33636500	1.28608500
H	4.89014200	-0.16121600	1.25709700
H	3.40094500	0.19586500	2.15716700
H	4.88652800	-0.16966500	-1.28892600
H	3.56235500	-1.34463200	-1.30729400
H	3.39522200	0.18222600	-2.18746200
P	-3.04794500	-0.25473600	-0.00616900
H	-3.24416200	-0.61697400	-1.38783200
H	-3.21567400	-1.58141000	0.48808300

2,4,6-tris(*t*-butyl)-phenyl lithium phosphanide[·THF] 2

Energy = -1284.97399554

C	-3.12950500	-0.66827500	-0.07976400
C	-2.95618700	0.71480500	-0.01517100
C	-1.69916900	1.34923700	0.02962200
C	-0.50399400	0.54340800	0.01615600
C	-0.67474600	-0.89369500	0.01476400
C	-1.96455800	-1.44195100	-0.05137600
H	-3.83920400	1.33365900	-0.01157500
H	-2.07318300	-2.51776700	-0.07336200
C	-1.72141400	2.90474600	0.10543200
C	-1.14232400	3.38235000	1.46542600
C	-1.00833000	3.54364400	-1.11549000
C	-3.15455800	3.49598200	0.06921500
H	-1.82166600	3.08722000	2.27406000
H	-0.16289900	2.96089800	1.69216100
H	-1.05531800	4.47629100	1.47551300
H	-1.59800300	3.35275700	-2.02010300
H	-0.93763800	4.63052400	-0.97887900
H	-0.00772300	3.14863300	-1.28898400
H	-3.07371700	4.58780800	0.12169900
H	-3.68227300	3.25028400	-0.85875300
H	-3.76463700	3.17183100	0.91962600
C	0.49785400	-1.91398500	0.13223200
C	1.46953300	-1.82063700	-1.07826500
C	1.20411300	-1.72002200	1.50766000
C	0.03638200	-3.39289500	0.13646800
H	0.96507300	-2.20373100	-1.97149800
H	1.77519300	-0.79901000	-1.32718200
H	2.35761700	-2.45066000	-0.91225600
H	0.58651800	-2.15531000	2.29876500
H	2.17218300	-2.24993900	1.54246400
H	1.31445200	-0.65804200	1.76590600
H	0.91877400	-4.03557800	0.24719400
H	-0.63834000	-3.61423000	0.96934600
H	-0.45808100	-3.67159100	-0.79966800
C	-4.50719400	-1.34507400	-0.16568900
C	-5.66312800	-0.32605000	-0.18085000
C	-4.59166800	-2.18321900	-1.46466000
C	-4.70949400	-2.27783000	1.05330400
H	-5.68081100	0.27959400	0.73199800
H	-5.59592700	0.34933000	-1.04083100
H	-6.62010300	-0.85644200	-0.24733200
H	-3.81421000	-2.95342500	-1.49649900
H	-5.56583500	-2.68276400	-1.53657600
H	-4.46493100	-1.54398200	-2.34504900
H	-5.68741000	-2.77222700	0.99949500
H	-3.94115300	-3.05672500	1.09591700

```
 H       -4.66150100   -1.70799800    1.98764300
 P        1.23546800    1.25414800   -0.13640000
 H        1.10706200    2.53080800    0.47855300
 Li       2.88627800   -0.25950300    0.56880500
 O        4.72588400   -0.23291800    0.35137300
 C        5.28346800    1.04583700   -0.15449100
 H        4.52122000    1.50195500   -0.78854300
 H        5.48320500    1.69068600    0.70687300
 C        6.56395400    0.64226800   -0.88376000
 H        7.28888100    1.45805400   -0.91836800
 H        6.34110800    0.33776700   -1.91077600
 C        7.06157800   -0.55750200   -0.05416400
 H        7.74161200   -1.20326600   -0.61341400
 H        7.58193700   -0.21001100    0.84350500
 C        5.76321400   -1.28154900    0.32112500
 H        5.47234900   -2.01891800   -0.43368400
 H        5.79648300   -1.75441500    1.30487100
```

2,4,6-tris(*t*-butyl)-phenyltrimethylsilylphosphane 3

```
Energy = -1454.2510224
```

```
 C        2.39605300   -0.06929600    0.30868000
 C        1.71230600   -1.24160800   -0.01317200
 C        0.40752500   -1.25298700   -0.54728600
 C       -0.27923200   -0.00221000   -0.69591400
 C        0.46678000    1.21767900   -0.54872000
 C        1.76903400    1.13625800   -0.02772700
 H        2.21126700   -2.18362900    0.14775400
 H        2.32230600    2.05226600    0.12131100
 C       -0.14098800   -2.63784500   -1.01521000
 C       -1.35283600   -3.12553300   -0.18672300
 C       -0.50884800   -2.57073400   -2.52027600
 C        0.92322200   -3.75723100   -0.89469400
 H       -1.13376200   -3.07661600    0.88628200
 H       -2.25415400   -2.54760600   -0.39181300
 H       -1.57235000   -4.17029500   -0.43764500
 H        0.37285400   -2.30674600   -3.11482400
 H       -0.86748900   -3.55140700   -2.85626400
 H       -1.29345200   -1.83929300   -2.72101100
 H        0.50415700   -4.67526400   -1.32024400
 H        1.83609100   -3.52381400   -1.45224600
 H        1.18882400   -3.97372400    0.14623600
 C       -0.00745500    2.63235700   -1.00272100
 C       -0.44997500    2.59376800   -2.49015200
 C       -1.10091200    3.22335900   -0.07932000
 C        1.14051300    3.67557100   -0.97044000
 H        0.40972200    2.34286800   -3.12138500
 H       -1.23258800    1.86688900   -2.70633100
 H       -0.81794800    3.58122700   -2.79369300
 H       -0.71142600    3.33051100    0.93944400
 H       -1.38853000    4.21929600   -0.43709100
 H       -2.00247300    2.61545000   -0.03160800
 H        0.76584200    4.61275300   -1.39657600
 H        1.47992300    3.89758900    0.04699700
 H        2.00083000    3.36024300   -1.56948800
 C        3.79551100   -0.06086500    0.94401700
 C        4.31138300   -1.48029800    1.24738200
 C        4.80080200    0.62111900   -0.01568100
 C        3.74579700    0.72766700    2.27525100
 H        3.64429100   -2.01532900    1.93224500
 H        4.42158200   -2.07721300    0.33524500
 H        5.29679800   -1.41873100    1.72210400
 H        4.51613800    1.65533800   -0.23305200
 H        5.80179300    0.63595000    0.43156800
 H        4.85710400    0.08088000   -0.96683800
 H        4.73942000    0.75480900    2.73791100
```

H	3.41879500	1.76072000	2.12040000
H	3.05076300	0.25789700	2.97955400
P	-2.15316000	-0.09210700	-1.00404900
H	-2.42992200	1.27259000	-1.30755100
Si	-3.07019700	0.04340200	1.19116600
C	-3.99866200	-1.57224900	1.58050000
H	-3.31960900	-2.39802600	1.80658700
H	-4.64456800	-1.41648800	2.45358100
H	-4.63417600	-1.87437700	0.74153600
C	-1.73604100	0.36449200	2.50257200
H	-1.24884200	1.33080900	2.34716600
H	-2.17945200	0.35686300	3.50596500
H	-0.95953000	-0.40627600	2.46385700
C	-4.37749100	1.43133900	1.14263800
H	-4.94878200	1.43532200	2.07911500
H	-3.93308300	2.42280000	1.01713900
H	-5.08511900	1.26921200	0.32205700

2,4,6-tris(*t*-butyl)-phenyltrimethylsilyl lithium phosphanide 4

Energy = -3156.0387289

C	4.46953600	0.68448200	0.67560800
C	3.57894600	-0.30495700	0.11104900
C	4.04019500	-1.65952300	0.08180100
C	5.41695100	-1.91388900	0.30381100
C	6.33306000	-0.93445800	0.66701400
C	5.80723600	0.34164400	0.91601600
H	5.77314100	-2.92851700	0.18606800
H	6.47605500	1.09989800	1.29908700
C	4.05173400	2.12793500	1.07796500
C	3.23654200	-2.99128000	-0.09035300
C	7.83353200	-1.20461000	0.85582600
C	8.21445800	-2.66103500	0.52966000
H	9.29468900	-2.79441300	0.65476300
H	7.71425100	-3.37107700	1.19779500
H	7.96407200	-2.92242200	-0.50448100
C	8.23296300	-0.92027500	2.32421300
H	9.30411100	-1.10484100	2.46940800
H	8.03076400	0.11832000	2.60448900
H	7.67560500	-1.56759100	3.00994000
C	8.64199600	-0.27464100	-0.08117500
H	8.39149200	-0.46761400	-1.12991900
H	8.43555300	0.78058100	0.12347900
H	9.71776600	-0.44041800	0.05324400
C	3.90105700	3.03364300	-0.16604200
H	3.14397200	2.63242000	-0.84074400
H	3.61692700	4.04996300	0.13925800
H	4.85444100	3.09509500	-0.70406000
C	5.10074900	2.81764100	1.98759300
H	5.34052800	2.21526300	2.87052500
H	6.03004300	3.05137300	1.45723500
H	4.68361500	3.76973300	2.33562300
C	2.75414500	2.08975700	1.91776800
H	2.44588700	3.10993200	2.17902600
H	1.94118600	1.60470100	1.37422700
H	2.92315400	1.53525800	2.84809300
C	3.52422500	-3.87720700	1.15924200
H	4.58344900	-4.10997700	1.28111900
H	3.18850400	-3.37057800	2.07077600
H	2.98325900	-4.82741400	1.07321200
C	3.69551400	-3.74798600	-1.36169500
H	3.15118400	-4.69602300	-1.45466600
H	3.50244700	-3.15289700	-2.25912000
H	4.76395300	-3.97911000	-1.33836600
C	1.70214500	-2.90429100	-0.14540200
H	1.37476700	-2.46949800	-1.09344300

H	1.28907400	-3.91712100	-0.06584300
H	1.32845800	-2.32155200	0.70795100
C	-3.65519100	-0.32511900	-0.12317100
C	-4.06569900	-1.67299200	-0.37229400
C	-4.68116000	0.69475700	-0.13683600
C	-5.44988300	-1.97970400	-0.34376300
C	-6.02846200	0.30865200	-0.14004300
C	-6.44814200	-1.02861000	-0.17614700
H	-5.74500600	-3.01410800	-0.45702400
H	-6.78818800	1.07666300	-0.10371200
C	-3.22099000	-2.93341400	-0.75867200
C	-1.70362100	-2.77090300	-0.95384900
H	-1.48586800	-1.92859000	-1.62325600
H	-1.21718700	-2.64255900	0.01703200
H	-1.31225200	-3.68579200	-1.41574900
C	-3.40507800	-4.05093500	0.30069600
H	-2.81926800	-4.93575600	0.02152100
H	-3.06428200	-3.70863800	1.28331600
H	-4.44791400	-4.36213600	0.40023900
C	-3.74031500	-3.43915900	-2.13726800
H	-4.80610900	-3.67419700	-2.12838600
H	-3.57534300	-2.67797500	-2.90796600
H	-3.19957900	-4.34803900	-2.42807100
C	-4.41266200	2.22697600	-0.19581700
C	-3.89956000	2.77397800	1.15665600
H	-2.93998200	2.32445300	1.41435600
H	-3.78877300	3.86479100	1.10178300
H	-4.61984900	2.54974300	1.95227300
C	-3.42733600	2.53762200	-1.34639100
H	-3.20849700	3.61193700	-1.37602500
H	-2.48720900	1.99800800	-1.22236500
H	-3.87019500	2.24947600	-2.30727700
C	-5.69108000	3.04094100	-0.52414200
H	-6.17518700	2.69539700	-1.44386500
H	-6.42388000	3.02206100	0.29004100
H	-5.40325800	4.08815900	-0.67216700
C	-7.94232300	-1.37419900	-0.08600100
C	-8.70220800	-0.71202400	-1.26096100
H	-9.77214700	-0.94499700	-1.20179300
H	-8.59492300	0.37713900	-1.24835300
H	-8.32288300	-1.07553900	-2.22214400
C	-8.19992800	-2.89191500	-0.14307700
H	-7.86810500	-3.32497200	-1.09349900
H	-7.69352000	-3.41836100	0.67359100
H	-9.27414200	-3.08610000	-0.04907500
C	-8.50814400	-0.84016900	1.25239200
H	-7.99773200	-1.30582800	2.10235800
H	-8.38102800	0.24349500	1.33897500
H	-9.57940500	-1.06167000	1.32888200
O	-0.01936600	3.71160100	-0.22018300
C	-0.26508400	4.47334400	1.00586000
H	-0.73785000	3.75707100	1.68160900
H	0.70505200	4.76399000	1.43006500
C	0.66853000	4.42248100	-1.30503300
H	1.40377600	3.71530600	-1.69384000
H	1.21224000	5.27469200	-0.87961600
C	-0.29047000	4.85675100	-2.40595600
H	-1.00675600	5.60405100	-2.05665300
H	0.27919200	5.28557500	-3.23808900
H	-0.85101000	3.99847800	-2.78586400
C	-1.15868400	5.69209700	0.81172300
H	-0.68247900	6.45690600	0.19117800
H	-2.10915100	5.40772400	0.35472000
H	-1.36859400	6.14155900	1.78848200
Li	-0.04359700	1.79745100	-0.17797500
Li	0.02147100	-1.10511000	-0.36911900
P	-1.88149300	0.12075700	0.45172200
Si	-1.98845500	-0.37860200	2.71555000
P	1.97516200	0.25222000	-0.78621100
Si	2.59320500	0.12569900	-3.01521800
C	1.66189000	-1.24946400	-3.96937700

H	1.92981900	−1.22518800	−5.03362400
H	1.89293700	−2.24885100	−3.58705200
H	0.57740700	−1.10105000	−3.89558100
C	2.09884800	1.75915200	−3.88030300
H	1.03361400	1.97804100	−3.73979300
H	2.68129200	2.59829500	−3.48451300
H	2.28714100	1.69300000	−4.95937500
C	4.47272600	−0.10484600	−3.20745200
H	5.00816100	0.70303200	−2.69836600
H	4.81356700	−1.04795400	−2.77097400
H	4.75037000	−0.09207800	−4.26899900
C	−0.96325000	−1.92647100	3.18338700
H	0.09613200	−1.77957100	2.94045900
H	−1.03300900	−2.11951200	4.26181800
H	−1.31428300	−2.82098100	2.65787300
C	−3.78954200	−0.63775100	3.27304900
H	−4.26684700	−1.44271600	2.70557500
H	−3.82483900	−0.89361000	4.33950700
H	−4.37890600	0.27027600	3.11358300
C	−1.22278400	1.06653300	3.70789000
H	−0.18803700	1.25524600	3.39835100
H	−1.79998400	1.98689600	3.56853800
H	−1.21212600	0.83064700	4.77970700

2,4,6-tris(*t*-butyl)-phenyl–bis(trimethylsilyl)phosphane 5

Energy = −1862.8601966

C	−3.13103400	−0.26568300	−0.04105300
C	−2.26470700	−1.35730800	−0.10622400
C	−0.87477500	−1.23104000	−0.29812600
C	−0.30840600	0.08327200	−0.37639000
C	−1.20232100	1.20812900	−0.51312200
C	−2.57665400	0.99025600	−0.30545200
H	−2.68055100	−2.34640500	0.00041500
H	−3.24471600	1.83786500	−0.35403400
C	−0.09338100	−2.55457000	−0.52520400
C	0.56079900	−2.47752400	−1.92432500
C	0.95302200	−2.83067700	0.57147900
C	−1.00897400	−3.80273600	−0.55768100
H	−0.21311500	−2.40264700	−2.69630700
H	1.20404900	−1.60329400	−2.02010000
H	1.15672000	−3.37650100	−2.12242400
H	0.46594100	−2.90929900	1.55017500
H	1.46511300	−3.77969700	0.37181500
H	1.70264400	−2.04369100	0.61928800
H	−0.39046700	−4.67528800	−0.79593800
H	−1.48543400	−3.99738200	0.40938400
H	−1.78520300	−3.72996900	−1.32629500
C	−0.80031600	2.65950100	−0.93506800
C	−0.12520600	3.45059500	0.21238700
C	0.11165200	2.62763300	−2.18635200
C	−2.03691000	3.49749300	−1.35608400
H	−0.74757000	3.42640100	1.11515600
H	0.85654500	3.03963700	0.44710600
H	−0.00255400	4.49943600	−0.08580400
H	−0.39841000	2.13001200	−3.01928900
H	0.34996100	3.65321300	−2.49360200
H	1.04940800	2.10877800	−1.98782800
H	−1.68043800	4.44539000	−1.77298800
H	−2.63267500	2.99736000	−2.12713900
H	−2.68723900	3.74641300	−0.51031600
C	−4.63407500	−0.40263400	0.24682100
C	−5.05117700	−1.86028700	0.52017000
C	−4.99108800	0.44146800	1.49460700
C	−5.44734500	0.11182200	−0.96588600
H	−4.87424200	−2.50454300	−0.34827100

H	-4.51436400	-2.28064600	1.37773900
H	-6.12243900	-1.89804600	0.74635500
H	-4.74516200	1.49818500	1.35080400
H	-6.06470400	0.37110100	1.70559600
H	-4.44318100	0.08582700	2.37393500
H	-6.52178600	0.01759900	-0.76853100
H	-5.23671200	1.16474900	-1.17725500
H	-5.21112300	-0.46582400	-1.86606000
P	1.50457000	0.57991400	-0.04408900
Si	3.39569600	-0.23056900	-1.14429600
C	4.01699400	-2.01916000	-0.91873900
H	3.34007600	-2.75680900	-1.35430400
H	4.99009300	-2.11172500	-1.41891000
H	4.15667200	-2.26487100	0.13825400
C	3.21679900	0.16259900	-2.99876700
H	3.06336700	1.23589200	-3.14752300
H	4.13529300	-0.12648000	-3.52472800
H	2.38104100	-0.36564100	-3.46623500
C	4.71867100	0.92888500	-0.40878000
H	5.66965900	0.78696900	-0.93696800
H	4.41704000	1.97500600	-0.51639500
H	4.89481900	0.73097900	0.65364200
Si	1.80185900	0.38216700	2.27491700
C	3.03044800	-0.95953900	2.85300600
H	3.99628300	-0.86923800	2.34501500
H	3.21036600	-0.83239300	3.92829900
H	2.65050700	-1.97114600	2.69201200
C	0.09576100	0.10512900	3.06047000
H	0.18014600	0.11222400	4.15430800
H	-0.60148000	0.89474900	2.76385600
H	-0.33754200	-0.85038300	2.75174000
C	2.50789600	2.05820200	2.84053800
H	2.71024800	2.03856200	3.91884400
H	3.44416600	2.29174600	2.32316200
H	1.80259000	2.86979000	2.63964100

2,4,6-tris(*t*-butyl)-phenyl potassium phosphanide[·DME] 6

Energy = -1382.15186213

C	-3.78647300	-0.80160900	-0.04550900
C	-3.72871700	0.58864300	0.05736700
C	-2.53055400	1.32775700	0.06209700
C	-1.26461000	0.63783800	-0.04198300
C	-1.31792500	-0.80865300	-0.15350400
C	-2.55794900	-1.46355800	-0.15160800
H	-4.65904200	1.12886400	0.13808200
H	-2.57420000	-2.54180900	-0.23619800
C	-2.68160900	2.87153800	0.18371000
C	-2.03599300	3.37886300	1.50350600
C	-2.13779400	3.57454100	-1.09149700
C	-4.15755300	3.34048500	0.27653200
H	-2.67156100	3.08657300	2.34838800
H	-1.04295000	2.96696900	1.68368300
H	-1.96308800	4.47436800	1.49647400
H	-2.83900200	3.40946300	-1.91872100
H	-2.05706200	4.65680100	-0.92541500
H	-1.16462100	3.20007000	-1.40890800
H	-4.16382700	4.43421500	0.35826400
H	-4.73711200	3.07428000	-0.61439900
H	-4.66757600	2.94262700	1.16082800
C	-0.06257200	-1.72521200	-0.28073500
C	0.70819700	-1.39998400	-1.58758200
C	0.82531300	-1.60330200	0.98608100
C	-0.40250500	-3.23277800	-0.38292200
H	0.12045900	-1.73222100	-2.45057200
H	0.87145800	-0.32312700	-1.70560000

H	1.66787900	-1.94327700	-1.61473400
H	0.30697000	-2.05805100	1.83793300
H	1.77372000	-2.14744400	0.84502900
H	1.01842000	-0.55713200	1.24793800
H	0.53563200	-3.79590800	-0.46892400
H	-0.92697700	-3.59956600	0.50583000
H	-1.00686400	-3.46274800	-1.26678000
C	-5.10078400	-1.59827300	-0.04751700
C	-6.33810600	-0.69054100	0.08975900
C	-5.23253400	-2.38784000	-1.37299700
C	-5.10902200	-2.59633300	1.13648900
H	-6.31891300	-0.12288100	1.02666400
H	-6.41056600	0.02038800	-0.74075100
H	-7.24791700	-1.30230400	0.08680700
H	-4.39470900	-3.07886400	-1.51228200
H	-6.16018600	-2.97442500	-1.38195100
H	-5.24685300	-1.70360300	-2.22836900
H	-6.04077100	-3.17645200	1.14525900
H	-4.27387000	-3.30159900	1.07294300
H	-5.02382600	-2.06275000	2.08943800
P	0.40955600	1.48334500	-0.03562500
H	0.05191100	2.85519500	0.06951800
K	3.24783100	0.39875500	-0.30002300
C	6.27075600	0.53507800	-2.48355300
H	6.23634000	-0.44066200	-2.98520300
H	5.57190500	1.21806600	-2.96716600
H	7.28478700	0.94624500	-2.55593200
O	5.86033800	0.42374300	-1.09509300
C	6.71496400	-0.45148400	-0.31223500
H	6.54725300	-1.49612100	-0.60853700
H	7.76978100	-0.19718600	-0.48851500
C	6.40820500	-0.26862900	1.15864900
H	7.10109700	-0.89104600	1.74286500
H	6.54671600	0.78182300	1.45074900
O	5.04102600	-0.67672300	1.41158300
C	4.72317000	-0.81430400	2.82326800
H	3.67885700	-1.11991600	2.88136700
H	5.35463800	-1.58149800	3.28726400
H	4.85518500	0.13850400	3.35163800

2,4,6-tris(*t*-butyl)-phenyl potassium phosphanide 7

Energy = -3581.58231107

C	-4.86895000	0.90527700	-0.86559000
C	-4.29159300	-0.26393400	-0.23586500
C	-5.15589600	-1.39424700	-0.06529800
C	-6.55494400	-1.21693100	-0.21362500
C	-7.14048400	-0.03586700	-0.65286800
C	-6.25699900	0.98253500	-1.04163700
H	-7.20184700	-2.05156800	0.02269800
H	-6.67720900	1.87843200	-1.47826300
C	-4.04709800	2.12076800	-1.38183100
C	-4.79151700	-2.89115900	0.20686700
C	-8.65892100	0.16629200	-0.77386800
C	-9.45574000	-1.05864400	-0.28538400
H	-10.52972500	-0.85556700	-0.36618500
H	-9.24076400	-1.94897000	-0.88701300
H	-9.23644400	-1.28915500	0.76305800
C	-9.03515000	0.42698800	-2.25284100
H	-10.11721300	0.57802300	-2.35147300
H	-8.53411100	1.31783700	-2.64489600
H	-8.74680100	-0.42301000	-2.88084100
C	-9.08298100	1.38558800	0.08059400
H	-8.84066800	1.22054400	1.13596600
H	-8.57090300	2.29795200	-0.24125500
H	-10.16331700	1.55592800	-0.00418000

C	-3.58409600	3.00132600	-0.19597100
H	-3.05015500	2.39083600	0.53719200
H	-2.93513400	3.81415800	-0.55261200
H	-4.45336600	3.45181500	0.29766600
C	-4.86709500	3.04583900	-2.31618100
H	-5.30945000	2.49333300	-3.15229800
H	-5.66305900	3.58216300	-1.78861700
H	-4.19250600	3.80274100	-2.73530600
C	-2.85767700	1.63581900	-2.24539600
H	-2.25753600	2.49457700	-2.57795900
H	-2.21649600	0.94039100	-1.69905200
H	-3.23078800	1.12193500	-3.13917100
C	-5.42777300	-3.74515600	-0.93135500
H	-6.51547900	-3.65757500	-0.97618400
H	-5.02926500	-3.43649600	-1.90445300
H	-5.18634500	-4.80471000	-0.77754900
C	-5.38098500	-3.35553900	1.56207900
H	-5.14152100	-4.41232500	1.73737900
H	-4.96819200	-2.76913900	2.38720300
H	-6.46970500	-3.25146300	1.59207000
C	-3.30234600	-3.27607700	0.18508800
H	-2.74559600	-2.82710000	1.00573800
H	-3.23328700	-4.37214600	0.25509300
H	-2.83649500	-2.95088700	-0.75122000
C	4.18367800	-0.16672800	-0.14173000
C	5.05800100	-1.18266600	-0.65204900
C	4.76446700	0.78680700	0.78178300
C	6.45830500	-1.02685300	-0.49024800
C	6.15610100	0.83858800	0.93928700
C	7.04093200	-0.00944000	0.25576800
H	7.10893000	-1.74470400	-0.97254100
H	6.57753400	1.58284700	1.60154100
C	4.70518500	-2.54126100	-1.34538800
C	3.22440900	-2.95384900	-1.38019100
H	2.80110000	-2.94567500	-0.37082100
H	2.62219800	-2.28388100	-1.99187300
H	3.15287200	-3.97578200	-1.77811400
C	5.24070400	-2.56445400	-2.79827100
H	5.02411500	-3.53346600	-3.26573700
H	4.76882200	-1.78295700	-3.39895600
H	6.32300800	-2.40740100	-2.83866400
C	5.40494800	-3.68012400	-0.54338800
H	6.49325200	-3.59086900	-0.52800200
H	5.05844200	-3.68042000	0.49695200
H	5.15821400	-4.65079100	-0.99142700
C	3.94450100	1.79130900	1.64228400
C	3.43562800	2.96475400	0.77107600
H	2.86517500	2.57972400	-0.07787000
H	2.80809500	3.64126000	1.36894200
H	4.28491600	3.54083700	0.38471400
C	2.78380900	1.06118300	2.35940900
H	2.18355600	1.77888100	2.93519200
H	2.13555000	0.54448100	1.64719900
H	3.18766600	0.32167400	3.06189000
C	4.78143400	2.42820700	2.78084500
H	5.25724200	1.67082000	3.41350000
H	5.55398900	3.10829500	2.40677400
H	4.11096700	3.02143700	3.41503000
C	8.55936400	0.18340200	0.39120500
C	8.97477800	0.04367800	1.87591800
H	10.05740000	0.18295900	1.98463000
H	8.47572700	0.78663100	2.50598400
H	8.71451900	-0.94956100	2.25791200
C	9.35897200	-0.84836300	-0.42695000
H	9.17029600	-1.87184600	-0.08369100
H	9.11723500	-0.79166300	-1.49396400
H	10.43190500	-0.65376500	-0.31655400
C	8.94204800	1.59614600	-0.11314700
H	8.67887900	1.71356200	-1.16986800
H	8.42069900	2.37718300	0.44922600
H	10.02096300	1.76241900	-0.00405200

C	-0.54948100	5.87209200	0.07641200
H	-1.62030400	5.79187500	0.30780300
H	-0.34701900	6.87541500	-0.32704400
C	0.36330600	4.34899400	3.34158900
H	-0.11133300	5.14036400	3.93611600
H	0.04702900	3.37742200	3.71802700
H	1.45450000	4.44004700	3.42003100
C	0.12014100	-5.60240800	0.68379200
H	0.29537200	-6.67307700	0.50309500
H	-0.82972400	-5.48250600	1.22174300
C	1.96695700	-3.12006400	2.77716900
H	2.96547700	-3.10157300	2.32325300
H	1.65049500	-2.09872200	2.98535400
H	1.99525600	-3.69174200	3.71366700
P	2.38032100	0.08010900	-0.75747600
Si	2.70276600	0.73363400	-2.94304800
P	-2.51033500	-0.18300300	0.47703700
Si	-2.88714900	-0.19411100	2.75034400
C	-2.41905400	-1.80279100	3.69634600
H	-2.46469200	-1.62739200	4.77975700
H	-3.08662600	-2.63756900	3.46194800
H	-1.39721700	-2.11379400	3.44560000
C	-1.69175300	1.11866800	3.48680200
H	-0.65021800	0.88924100	3.22317800
H	-1.94502900	2.11305600	3.10159900
H	-1.76272900	1.14173000	4.58234200
C	-4.66239400	0.30655900	3.23802400
H	-4.88062500	1.31643600	2.87480800
H	-5.40241200	-0.36658600	2.79488900
H	-4.78567700	0.29264100	4.32855000
C	2.19781700	-0.53304500	-4.29866700
H	1.14089500	-0.80434000	-4.18000700
H	2.31957900	-0.09051000	-5.29640000
H	2.78625900	-1.45442300	-4.26250600
C	4.46922300	1.36721000	-3.29059500
H	5.22253000	0.60242100	-3.08014500
H	4.57160600	1.68004000	-4.33765600
H	4.68805700	2.22628400	-2.64713100
C	1.50003900	2.20083400	-3.24933000
H	0.46176400	1.89682700	-3.05992800
H	1.75330800	3.04313400	-2.59519900
H	1.56126200	2.54071600	-4.29170600
K	0.02736400	-2.14511800	-0.19364300
K	-0.10705900	2.25176600	0.15550400
C	-0.71058800	-5.58279600	-1.59585900
H	-1.75572500	-5.70351500	-1.28574300
H	-0.66878400	-4.96765300	-2.49516400
H	-0.27537500	-6.56700600	-1.81197300
O	0.98948400	-3.68389300	1.86421900
O	0.06249500	-4.89363300	-0.58164300
C	0.27242100	5.68734700	1.33208200
H	0.04652800	6.51562100	2.02007700
H	1.34398500	5.70753800	1.09127200
C	-0.61333500	5.20342100	-2.24524300
H	-0.27387000	4.39910700	-2.89597900
H	-1.70670300	5.28645100	-2.29800900
H	-0.16022500	6.14900100	-2.57003800
O	-0.06879800	4.42499300	1.95835700
O	-0.17922700	4.86809700	-0.90136900
C	1.26603800	-5.06028600	1.51047400
H	2.20373500	-5.12082400	0.94135900
H	1.36276000	-5.66734300	2.42310100

A.2. Compounds 10-12e: Synthesis and Crystal Structures of Novel Silylsubstituted Diphosphanes

[HypPH-SiMe$_2$-]$_2$ 10

```
Energy = -4456.7129528

 Si      4.79241000   -0.00291800   -0.01689200
 Si      5.05784400   -1.41079600    1.91489800
 C       4.81598900   -0.47368100    3.56058000
 H       4.93346900   -1.17039200    4.40013900
 H       3.82241400   -0.02294600    3.63413700
 H       5.56238500    0.31949500    3.67826700
 C       3.81938600   -2.85828500    1.82533100
 H       3.98757800   -3.55021700    2.65987400
 H       3.93033000   -3.41898600    0.89128600
 H       2.78510400   -2.50429000    1.88194200
 C       6.82825700   -2.13302500    1.93473600
 H       7.58675600   -1.34305200    1.92964900
 H       7.00917100   -2.78428100    1.07318800
 H       6.97107700   -2.73149300    2.84330700
 Si      6.08361300   -0.89312100   -1.84684100
 C       5.55989100   -2.71227900   -2.10237100
 H       4.48758800   -2.78309600   -2.31313700
 H       5.77556900   -3.32346300   -1.21942400
 H       6.10057100   -3.14552300   -2.95306000
 C       7.96740900   -0.82898300   -1.53716000
 H       8.49255300   -1.31363200   -2.36998000
 H       8.25012900   -1.34365900   -0.61442500
 H       8.32673500    0.20330900   -1.47339500
 C       5.69218300    0.08344800   -3.43640600
 H       6.10386100   -0.43555200   -4.31107200
 H       6.12732900    1.08773600   -3.40521200
 H       4.61072900    0.18512900   -3.57083000
 Si      5.34050000    2.30052200    0.35166200
 C       7.20023800    2.41147300    0.77250000
 H       7.48033900    3.45458400    0.96466100
 H       7.82148600    2.04071100   -0.04843000
 H       7.44183100    1.82797300    1.66758400
 C       4.98247200    3.32129100   -1.21860800
 H       5.15238100    4.38743300   -1.02349900
 H       3.94642300    3.19524000   -1.54879200
 H       5.63236400    3.02003600   -2.04578000
 Si      0.95080700    0.65448000    0.31855400
 C       0.70539600    2.46339500   -0.23033200
 H      -0.15657500    2.90895900    0.27888200
 H       0.53149200    2.51382700   -1.30964300
 H       1.58491000    3.07555400   -0.00396700
 C       1.22203600    0.54423600    2.19920300
 H       2.08722600    1.13979100    2.50622200
 H       1.38608800   -0.49044600    2.51408600
 H       0.33684200    0.91855300    2.72671100
 P      -2.66913000    0.18498700    1.04045100
 H      -2.46537200    1.57919200    0.72901400
 Si     -4.79246100    0.00295400    0.01680900
 Si     -5.05758300    1.41085700   -1.91498300
 C      -4.81519300    0.47357800   -3.56049600
 H      -4.93220500    1.17016400   -4.40021600
 H      -3.82166600    0.02264500   -3.63356400
 H      -5.56169800   -0.31947800   -3.67835900
 C      -3.81930100    2.85847100   -1.82512700
 H      -3.98741000    3.55043100   -2.65966400
 H      -3.93049900    3.41910400   -0.89106800
 H      -2.78497100    2.50459500   -1.88155000
 C      -6.82804900    2.13294300   -1.93538300
```

H	-7.58649300	1.34290900	-1.93059000
H	-7.00933800	2.78417500	-1.07389700
H	-6.97057800	2.73140300	-2.84401000
Si	-6.08413200	0.89297800	1.84646200
C	-5.56044500	2.71214400	2.10208100
H	-4.48813500	2.78291900	2.31283200
H	-5.77614900	3.32340500	1.21919800
H	-6.10109300	3.14531300	2.95283500
C	-7.96787700	0.82880700	1.53651500
H	-8.49305200	1.31421200	2.36887700
H	-8.25043400	1.34274400	0.61332200
H	-8.32731900	-0.20350000	1.47357800
C	-5.69296500	-0.08357600	3.43610800
H	-6.10486100	0.43536700	4.31070000
H	-6.12803900	-1.08790000	3.40479100
H	-4.61152800	-0.18517700	3.57074800
Si	-5.34024100	-2.30053500	-0.35184400
C	-7.19986600	-2.41140900	-0.77321600
H	-7.48019200	-3.45455000	-0.96485800
H	-7.82129700	-2.03995400	0.04726200
H	-7.44097300	-1.82837300	-1.66874400
C	-4.98264500	-3.32116500	1.21861500
H	-5.15250600	-4.38732100	1.02353300
H	-3.94668700	-3.19510200	1.54907100
H	-5.63276100	-3.01984700	2.04558900
C	-4.37276900	-3.06399600	-1.81029800
H	-4.54874600	-2.51673100	-2.74147000
H	-3.29488900	-3.07882800	-1.62372100
H	-4.69947400	-4.10067700	-1.96117900
Si	-0.95080100	-0.65438900	-0.31776100
C	-0.70545300	-2.46327500	0.23124900
H	0.15697900	-2.90867200	-0.27732300
H	-0.53238200	-2.51374200	1.31069100
H	-1.58469900	-3.07555500	0.00414500
C	-1.22161100	-0.54429100	-2.19849500
H	-2.08613900	-1.14067100	-2.50578800
H	-1.38660300	0.49026100	-2.51334500
H	-0.33591000	-0.91770000	-2.72579600
P	2.66884700	-0.18479400	-1.04023600
H	2.46517400	-1.57901800	-0.72883700
C	4.37345300	3.06381400	1.81050000
H	4.55071900	2.51711100	2.74176400
H	4.69928900	4.10086900	1.96067200
H	3.29541000	3.07753000	1.62480700

[HypPLi-SiMe$_2$-]$_2$ 11

Energy = -4470.9981983

Si	-1.20481400	-2.38528900	-0.06340400
Si	1.18677600	-2.38042000	0.13976100
P	1.79228200	-0.23124500	-0.10731800
Si	3.97729600	0.33732500	-0.01222700
Si	4.70093600	0.62829500	2.22789000
Si	3.96664100	2.46529000	-1.06219200
Si	5.47721900	-1.06986200	-1.19082600
P	-1.80090200	-0.22229800	-0.01793500
Si	-3.98857300	0.34158200	0.00344000
Si	-4.91683400	0.23098700	2.18397600
Si	-3.87658200	2.62790700	-0.62988500
Si	-5.34338800	-0.82006500	-1.55684900
Li	0.02148500	0.51705100	1.32801300
Li	-0.03082700	0.27060500	-1.56937200
C	4.34047100	-0.89362100	3.29273400
C	3.80390800	2.10141700	3.02118800
C	6.56688700	0.96264300	2.32437700
C	2.48466500	3.49538200	-0.47625700

C	5.53451700	3.46904100	-0.69509000
C	3.82429400	2.28571200	-2.94574000
C	5.90003100	-2.62374900	-0.18772700
C	7.10713900	-0.15252300	-1.51704100
C	4.77347300	-1.58912900	-2.86949000
C	-1.91635600	-3.46385400	1.32944000
C	-1.64366200	-3.28138400	-1.68633200
C	1.64650600	-3.14742900	1.81769900
C	1.87107400	-3.57215200	-1.17578900
C	-4.68094800	-1.46732600	2.98314700
C	-4.08176500	1.50735600	3.31237700
C	-6.77816400	0.59799800	2.15038700
C	-5.45269100	3.59015200	-0.19458200
C	-2.42322500	3.48233400	0.24034300
C	-3.59887300	2.80048800	-2.49905800
C	-5.77241300	-2.55905700	-0.93281700
C	-4.47742200	-0.96550200	-3.23490400
C	-6.98162100	0.09648600	-1.83855900
H	3.26799100	-1.10376500	3.33848500
H	4.69663800	-0.73032100	4.31725600
H	4.83754500	-1.78891600	2.90568100
H	2.71618700	1.99772200	2.93997700
H	4.08364000	3.05123700	2.55395200
H	4.05292800	2.16991000	4.08712200
H	7.14941100	0.09105200	2.00704900
H	6.85203200	1.18755200	3.35953400
H	6.87093500	1.81157700	1.70426800
H	2.52559000	3.69234700	0.59973400
H	1.53740800	2.98627700	-0.68373100
H	2.46564000	4.46287200	-0.99270200
H	5.61608700	3.72146300	0.36735700
H	5.51371100	4.41190100	-1.25538900
H	6.44541900	2.93394400	-0.98151100
H	2.97483600	1.65511800	-3.22936800
H	4.72606900	1.83937000	-3.37775000
H	3.68536300	3.26845500	-3.41279500
H	6.43928900	-2.36773100	0.73058100
H	6.54632400	-3.28760900	-0.77500300
H	5.01060400	-3.19387200	0.09795500
H	7.55562400	0.24047600	-0.59928000
H	6.96876300	0.68631000	-2.20740600
H	7.83252000	-0.83692200	-1.97414200
H	3.80854400	-2.09257800	-2.76844900
H	5.46354400	-2.27804200	-3.37188200
H	4.62935200	-0.72435600	-3.52501700
H	-1.62522100	-3.09650200	2.31804600
H	-1.55545700	-4.49507100	1.23492000
H	-3.01016200	-3.48855600	1.28974500
H	-1.23298200	-2.76887100	-2.56293000
H	-2.72719700	-3.35778600	-1.82400900
H	-1.23825300	-4.30021300	-1.68046300
H	1.22075000	-2.58546600	2.65529300
H	2.73264300	-3.17523100	1.95353300
H	1.27390400	-4.17658500	1.88389600
H	1.63918500	-3.23309200	-2.19018100
H	1.43211600	-4.56907600	-1.04803800
H	2.95758700	-3.67979800	-1.09553700
H	-3.62009600	-1.71269700	3.08604100
H	-5.15198500	-2.26521600	2.40029000
H	-5.12850800	-1.47668900	3.98457100
H	-2.99517500	1.36919000	3.32765800
H	-4.44562000	1.40192500	4.34165200
H	-4.28539500	2.53433600	2.99223000
H	-7.32942200	-0.18323300	1.61636200
H	-7.00527500	1.55488200	1.67041000
H	-7.17136700	0.63589900	3.17373700
H	-5.60437500	3.65437400	0.88790900
H	-6.34788400	3.13470000	-0.63002700
H	-5.38200700	4.61542800	-0.57816400
H	-2.52817300	3.45418600	1.32970200
H	-2.35877500	4.53426700	-0.06332200

```
H       -1.47378300    3.00111500   -0.01838400
H       -4.47923500    2.48532900   -3.06885000
H       -2.75079800    2.19679000   -2.83950600
H       -3.39371700    3.84631500   -2.75842400
H       -4.88177100   -3.14950200   -0.69708000
H       -6.34133400   -3.10494200   -1.69542300
H       -6.38995400   -2.51614800   -0.02929500
H       -3.48379600   -1.41226800   -3.14121200
H       -4.35938700    0.01564700   -3.70573400
H       -5.06814300   -1.59265500   -3.91370700
H       -7.54159800    0.24184300   -0.90953600
H       -7.61649400   -0.48112000   -2.52183300
H       -6.82395600    1.08101200   -2.29140100
```

$[HypP\text{-}(SiMe_2)_2\text{-}]_2$ 12a [chair, trans]

```
Energy = -5194.135886

Si       4.57074800   -0.05786700    0.00953200
Si       5.21422300   -0.75923600    2.22803000
Si       5.57842000    2.09348600   -0.44028000
Si       5.48093400   -1.59145900   -1.64405200
C        4.61816400   -2.51030300    2.69775700
H        4.99049200   -3.25940700    1.99262100
H        5.00536800   -2.76356500    3.69298400
H        3.52871000   -2.58533500    2.73431700
C        7.12598700   -0.80490900    2.25605900
H        7.47040800   -1.20004000    3.22009000
H        7.52652900   -1.44935300    1.46633800
H        7.55649000    0.19225300    2.12721600
C        5.70615900   -3.36517600   -0.96755700
H        6.38804500   -3.38685100   -0.11069500
H        4.75800000   -3.81666100   -0.66433000
H        6.14080300   -3.99411100   -1.75506000
C        7.21137100   -1.04437600   -2.24599600
H        7.57417400   -1.77191800   -2.98330200
H        7.18287700   -0.06378400   -2.73113300
H        7.93776100   -1.00467700   -1.42794000
C        4.33021500   -1.64373300   -3.16100000
H        4.27889700   -0.66333800   -3.64529700
H        4.70295100   -2.37343300   -3.89100600
H        3.30893400   -1.91512100   -2.87882600
C        7.48625300    2.05675900   -0.31449700
H        7.94123300    1.30747700   -0.96512700
H        7.87164700    3.04124300   -0.61088500
H        7.81970200    1.86694300    0.71025500
C        5.12578100    2.60639500   -2.22354700
H        5.36282000    3.66369800   -2.39475400
H        5.70160200    2.01241200   -2.94209700
H        4.06554200    2.45010700   -2.43866200
C        5.05052900    3.42788200    0.82551500
H        3.97893800    3.44455900    1.03188100
H        5.57089200    3.26222500    1.77547600
H        5.34173700    4.41980400    0.45716600
C        4.63204900    0.46215200    3.57340100
H        3.54073600    0.51783400    3.62843000
H        5.00274100    0.13661600    4.55349700
H        5.01148100    1.47202900    3.38756200
Si       1.17391500    1.93892500    0.14228700
C        1.73255500    3.44113600   -0.90517700
H        1.57184900    3.23628300   -1.96812900
H        1.14647800    4.32751000   -0.63367000
H        2.78782900    3.68466100   -0.76462600
C        1.39005200    2.30770300    2.00166700
H        0.85139600    1.57295600    2.60638300
H        2.44408900    2.28272600    2.29406400
H        0.99248800    3.30168700    2.23963100
```

Si	-4.55400300	-0.08941000	0.04039900
Si	-1.19257000	1.89465900	-0.34085600
Si	-5.43581000	-1.52984400	1.77501100
Si	-5.57977600	2.04605800	0.52659300
Si	-5.29297500	-0.79914800	-2.14481200
C	-1.47481900	2.19197700	-2.20221600
H	-2.54279000	2.16760500	-2.43894400
H	-1.08394500	3.17707400	-2.48411700
H	-0.97350100	1.43923100	-2.81463500
C	-1.78540200	3.45128500	0.59971300
H	-2.83880800	3.67133900	0.41131000
H	-1.64999000	3.33524500	1.67862100
H	-1.19999200	4.31904100	0.27173800
C	-5.39711300	3.25921600	-0.94072800
H	-5.77094900	4.25001300	-0.65334400
H	-4.36190500	3.37142300	-1.27450900
H	-5.98933100	2.91525600	-1.79604000
C	-4.87621600	2.81016700	2.13258800
H	-3.85368800	2.48326100	2.33387000
H	-4.88235600	3.90516100	2.07566500
H	-5.49400200	2.51394700	2.98649900
C	-7.45742000	1.81086100	0.80271200
H	-7.92000000	2.79257400	0.96755300
H	-7.95099400	1.34504900	-0.05473400
H	-7.65740300	1.19728900	1.68681900
C	-7.24054400	-2.02505100	1.38020700
H	-7.28868500	-2.67085300	0.49640900
H	-7.65676100	-2.58717500	2.22594300
H	-7.88307000	-1.15767200	1.20328200
C	-4.45573700	-3.14193800	2.03702600
H	-3.41592200	-2.92815900	2.30016500
H	-4.90852100	-3.70007800	2.86655900
H	-4.46328800	-3.78519000	1.15263000
C	-4.90147300	-2.63930500	-2.46550500
H	-5.29830300	-3.27926500	-1.67006800
H	-5.36067100	-2.95415800	-3.41096100
H	-3.82479400	-2.81703400	-2.54111500
C	-7.19018100	-0.58333600	-2.24479200
H	-7.71116300	-1.10589000	-1.43743900
H	-7.47068700	0.47429200	-2.20555800
H	-7.55035200	-0.98818800	-3.19917200
C	-4.54722800	0.24365500	-3.55747100
H	-4.81424000	1.30005100	-3.45151000
H	-3.45692900	0.17512600	-3.59505800
H	-4.94203600	-0.10854500	-4.51889700
C	-5.39172000	-0.59048200	3.43589700
H	-4.38793000	-0.20019400	3.63222300
H	-6.09375800	0.24835000	3.45307000
H	-5.66006100	-1.27175100	4.25311700
P	-2.24063700	0.00057900	0.55956500
P	2.29239300	0.05300100	-0.65824200
Si	1.11011300	-1.63044500	0.43783600
Si	-1.05300400	-1.66552300	-0.58751100
C	-1.77409300	-3.39466100	-0.22346400
H	-1.72394500	-3.63743700	0.84082100
H	-2.81566500	-3.48117900	-0.54291600
H	-1.18754100	-4.14113200	-0.77321400
C	-0.87097100	-1.48103400	-2.47712300
H	-1.82726900	-1.28682400	-2.97172800
H	-0.17281300	-0.67754600	-2.72780700
H	-0.46025200	-2.41271300	-2.88659900
C	0.90432200	-1.43836400	2.32521100
H	1.81235000	-1.05718400	2.80082400
H	0.08003700	-0.75260900	2.54597500
H	0.66092300	-2.40860800	2.77613000
C	1.93301900	-3.30360300	0.02638200
H	2.08725400	-3.40717300	-1.05215900
H	2.89937100	-3.40794700	0.52671200
H	1.29015200	-4.12619800	0.36149500

[HypP-(SiMe$_2$)$_2$-]$_2$ 12b [chair, cis]

Energy = -5194.1189027

Si	-4.11930000	-0.02150000	-0.35459300
Si	-4.77471700	2.26145000	-0.77524300
Si	-6.06121000	-1.13031100	0.58349800
Si	-3.63734300	-1.02922100	-2.50068300
C	-3.29994300	3.25805200	-1.48013300
H	-3.24320900	3.11033400	-2.56434600
H	-3.43353300	4.33150800	-1.29740300
H	-2.34085200	2.95155800	-1.05597500
C	-6.16110300	2.42035200	-2.08163200
H	-6.51149700	3.46074800	-2.09445400
H	-5.79315300	2.18468900	-3.08528000
H	-7.01973600	1.77901900	-1.86983400
C	-2.35838400	-0.02965700	-3.50336100
H	-2.68459900	1.00272000	-3.66172700
H	-1.38787300	-0.00164400	-2.99870400
H	-2.21247100	-0.49446700	-4.48641100
C	-5.29694400	-1.02678800	-3.45380900
H	-5.13168200	-1.41979700	-4.46523700
H	-6.03344400	-1.67210100	-2.96283000
H	-5.73126600	-0.02817700	-3.54573600
C	-3.06621700	-2.84823700	-2.46088700
H	-3.75283000	-3.47708100	-1.88651100
H	-3.04322000	-3.22913000	-3.49009700
H	-2.06249000	-2.95670000	-2.04402900
C	-7.67726900	-0.43694200	-0.16897500
H	-7.70904700	-0.55077600	-1.25730900
H	-8.53032000	-0.98476000	0.25145500
H	-7.81142700	0.62275100	0.07108400
C	-6.05424800	-3.00675400	0.22073500
H	-6.91323400	-3.47750000	0.71543300
H	-6.13835700	-3.20609200	-0.85312800
H	-5.14568600	-3.49279000	0.58662600
C	-6.12817900	-0.85800900	2.46638700
H	-5.23756800	-1.25990700	2.95766700
H	-6.17441800	0.20868400	2.70684100
H	-7.01620600	-1.34870200	2.88489700
C	-5.43199500	3.01565000	0.85005300
H	-4.78479100	2.78305100	1.69914200
H	-5.51524000	4.10604500	0.76449200
H	-6.42902500	2.61823300	1.07089000
Si	-1.32431200	-1.76348300	1.81790400
C	-2.25173800	-3.32413900	1.22398900
H	-2.57083900	-3.25474400	0.18288500
H	-1.61116800	-4.20776900	1.33078600
H	-3.13738200	-3.47672000	1.85091800
C	-1.09284800	-2.00016900	3.69938900
H	-0.42868200	-1.25768900	4.14527700
H	-2.06395200	-1.93660900	4.20201200
H	-0.67024800	-2.99444600	3.88882400
Si	4.17012900	-0.03057900	-0.20385100
Si	0.83721500	-1.81974800	0.75031800
Si	5.66261200	-0.18154000	1.68831800
Si	4.54600400	-1.87789300	-1.73509100
Si	4.87258700	1.87955800	-1.54702900
C	0.57354200	-2.35039700	-1.05965400
H	1.52395700	-2.52352000	-1.56814000
H	-0.00440400	-3.28161300	-1.09431800
H	0.02653800	-1.58301200	-1.61554600
C	1.75492100	-3.20033700	1.70437600
H	2.80155400	-3.27535000	1.39943200
H	1.73814000	-2.98890600	2.77770700
H	1.27599300	-4.17272900	1.53623000
C	3.42316700	-1.82633100	-3.28911600
H	3.98521400	-1.42801600	-4.14057200
H	3.09130600	-2.83777100	-3.55205800

H	2.53548100	-1.20273500	-3.15745700
C	4.40279000	-3.59847500	-0.91911000
H	3.36877500	-3.86753600	-0.68953100
H	4.79915400	-4.35079000	-1.61306900
H	4.98482400	-3.65782500	0.00656400
C	6.34982700	-1.73937400	-2.35758900
H	6.57487300	-2.61163000	-2.98481700
H	6.49891900	-0.84374800	-2.96793800
H	7.07195600	-1.71794900	-1.53645200
C	7.46139100	-0.64042400	1.23218800
H	7.89977700	0.04996600	0.50641000
H	8.08025200	-0.61648100	2.13824900
H	7.51842600	-1.65361300	0.81954800
C	5.64567100	1.51664700	2.55847900
H	4.61856700	1.79737700	2.81432800
H	6.23022500	1.47664400	3.48600100
H	6.07108100	2.30268400	1.92486300
C	4.35443500	3.63051900	-0.99608000
H	4.66870100	3.84803800	0.02892100
H	4.85894900	4.34704900	-1.65754600
H	3.27893200	3.80497000	-1.07279600
C	6.78521600	1.91040300	-1.51685900
H	7.15230900	2.19216600	-0.52430300
H	7.23520000	0.95231100	-1.78707500
H	7.13902100	2.66585100	-2.23035000
C	4.31380400	1.67623600	-3.36357900
H	4.80609200	0.82348800	-3.84026900
H	3.23290400	1.52957500	-3.45036500
H	4.58056200	2.57832100	-3.92851600
C	5.02705200	-1.49662600	2.91256400
H	3.98829500	-1.29140700	3.18806300
H	5.07803300	-2.50512300	2.48800400
H	5.63709100	-1.48272000	3.82466300
P	2.14001100	0.08897300	1.05502700
P	-2.72535200	0.08714600	1.55515100
Si	-1.15333600	1.79576400	1.81718000
Si	0.84493500	1.93702600	0.49607000
C	1.73493300	3.40777400	1.33830600
H	1.58977600	3.35305500	2.42169100
H	2.81001100	3.39028800	1.15206700
H	1.33771000	4.36621500	0.98357500
C	0.61319600	2.23429200	-1.37017300
H	1.58281000	2.25914200	-1.87739900
H	0.01850200	1.43496100	-1.82057200
H	0.10433200	3.18684400	-1.55852200
C	-0.50662900	1.50252700	3.59670700
H	-1.30978200	1.13292400	4.24223300
H	0.33023100	0.79945700	3.62487000
H	-0.15473500	2.45759700	4.00526500
C	-1.98967700	3.51153000	1.90176100
H	-2.51689200	3.80236900	0.99356000
H	-2.70278100	3.52116200	2.73345400
H	-1.22063700	4.26524100	2.11000200

[HypP-(SiMe$_2$)$_2$-]$_2$ 12c [transition cis-trans]

Energy = -5194.1343359

Si	-4.68852300	0.01928500	0.20677800
Si	-6.08068700	-1.42568400	-1.12688000
Si	-5.59441500	2.24145600	0.01358700
Si	-4.59865000	-0.63474900	2.51794600
C	-5.29723100	-3.13149900	-1.44707400
H	-5.09486300	-3.66627400	-0.51411400
H	-5.98640400	-3.74156700	-2.04437200
H	-4.36129400	-3.03604400	-2.00557900
C	-7.73447700	-1.71150400	-0.20978300

H	-8.37582700	-2.37569000	-0.80284400
H	-7.57353700	-2.18743100	0.76404000
H	-8.27898000	-0.77745200	-0.04345000
C	-4.49324200	-2.53206300	2.69113800
H	-5.40553600	-3.01701600	2.32722400
H	-3.64683700	-2.93894300	2.13079600
H	-4.36504300	-2.80550900	3.74591000
C	-6.17384600	-0.05607200	3.43579300
H	-6.13283000	-0.38871900	4.48070000
H	-6.26702500	1.03504300	3.43772100
H	-7.08005800	-0.47561100	2.98621500
C	-3.07318400	0.15795300	3.33635300
H	-3.00553300	1.22729000	3.11473000
H	-3.11703900	0.03285700	4.42561500
H	-2.15548400	-0.31724600	2.97515400
C	-7.45965400	2.11937100	0.42025600
H	-7.64605200	1.61769100	1.37428300
H	-7.88347900	3.12988900	0.48188600
H	-8.00093900	1.57884600	-0.36307800
C	-4.81815500	3.41718800	1.29936600
H	-5.24213500	4.42336000	1.19318200
H	-5.03365400	3.06712500	2.31470900
H	-3.73369100	3.49145000	1.19269900
C	-5.44495400	2.91929100	-1.76634300
H	-4.60362300	2.47701000	-2.30564500
H	-6.35494500	2.68476700	-2.32869700
H	-5.32301200	4.00865400	-1.76170400
C	-6.41661800	-0.60830900	-2.81661400
H	-5.47409200	-0.34614800	-3.30840600
H	-6.96232500	-1.30083400	-3.46944000
H	-7.01414900	0.30368100	-2.71882600
Si	-1.03360800	1.63241700	-1.29285700
C	-1.82795000	3.36234200	-1.13021100
H	-2.02429100	3.62690700	-0.08800500
H	-1.13120700	4.10255500	-1.54111500
H	-2.76225900	3.43842400	-1.69035800
C	-0.53767600	1.39111800	-3.11976000
H	0.19019300	0.58176500	-3.22796700
H	-1.41588800	1.16835500	-3.73396000
H	-0.06769100	2.30840200	-3.49655200
Si	4.53167700	-0.00113300	0.08712200
Si	0.99011200	1.79564500	-0.00948500
Si	5.77898900	-0.68825300	-1.86816800
Si	5.36711000	2.19594200	0.64838000
Si	5.09287400	-1.41949700	1.96928300
C	0.65719800	1.77101600	1.86602400
H	1.57141600	1.58413300	2.43794800
H	0.23754300	2.73084600	2.19153200
H	-0.06680800	0.98797500	2.10723000
C	1.69240400	3.48604500	-0.56422700
H	2.67283600	3.70308900	-0.13576800
H	1.78737900	3.51512000	-1.65468800
H	1.00818500	4.28636100	-0.25836400
C	4.39214100	3.05125900	2.05275000
H	4.79747800	4.05851700	2.21328200
H	3.32405400	3.14615200	1.84838300
H	4.50336300	2.49319900	2.98830500
C	5.41478000	3.29632900	-0.91348200
H	4.49888700	3.22521300	-1.50535400
H	5.56364600	4.34664500	-0.63359000
H	6.25231800	2.99963200	-1.55472300
C	7.16418500	2.07279600	1.29328800
H	7.58813900	3.08373800	1.35147500
H	7.19963300	1.64136600	2.29904400
H	7.80591900	1.47594200	0.63978200
C	7.64643200	-0.31658900	-1.69113500
H	8.07815400	-0.78318500	-0.80053900
H	8.17697900	-0.70852900	-2.56828500
H	7.83891900	0.76020800	-1.64222700
C	5.59036900	-2.56363500	-2.17446400
H	4.54969900	-2.82520100	-2.38691800

H	6.19685600	-2.85979700	-3.03961500
H	5.92315700	-3.15325900	-1.31323600
C	6.99630200	-1.61081800	1.99481600
H	7.52076400	-0.65517000	1.92479500
H	7.29657700	-2.09658000	2.93222400
H	7.33285000	-2.24648400	1.16853700
C	4.55040500	-0.59700000	3.60667000
H	5.14044300	0.30448000	3.80344500
H	3.49376500	-0.31142800	3.59355300
H	4.70390600	-1.28900200	4.44396200
C	4.41351500	-3.20166500	1.92253900
H	3.32314900	-3.24328200	1.94913200
H	4.75683500	-3.73514400	1.03040700
H	4.79433100	-3.74049400	2.79986500
C	5.11797100	0.24361800	-3.39246500
H	4.03328200	0.12228000	-3.47182300
H	5.33101900	1.31543500	-3.32943400
H	5.58450000	-0.14509500	-4.30640300
P	2.34400300	0.09850500	-0.85702600
P	-2.47862200	-0.09074600	-0.67305900
Si	-1.09272100	-1.92700700	-1.06007400
Si	1.12229600	-1.74748600	-0.13459600
C	1.99908600	-3.29057900	-0.84618600
H	1.97358500	-3.26735900	-1.94012500
H	3.04521400	-3.33770400	-0.53423500
H	1.50228700	-4.20751500	-0.50844000
C	0.92674000	-1.90961200	1.76118900
H	1.76105900	-1.44163600	2.29143200
H	0.00131100	-1.44634800	2.11977900
H	0.89332000	-2.96962500	2.04248400
C	-1.04875100	-2.33484700	-2.92208300
H	-2.05888500	-2.57015100	-3.27452600
H	-0.67453800	-1.49568400	-3.51275200
H	-0.40580500	-3.20387300	-3.10858500
C	-1.74146600	-3.47284500	-0.13614500
H	-1.66412700	-3.34640500	0.94744100
H	-2.78466100	-3.67853500	-0.38762500
H	-1.14746400	-4.34965800	-0.42198400

[HypP-(SiMe$_2$)$_2$-]$_2$ 12d [twist, cis]

Energy = -5194.133756

Si	4.38791500	0.00422200	0.27205000
Si	4.85587000	1.76469700	1.87910600
Si	5.73137700	0.31150400	-1.70603000
Si	5.04205300	-2.04260600	1.38678100
C	3.35704300	1.97923500	3.03355900
H	3.14140000	1.05305300	3.57502800
H	3.55584700	2.77271100	3.76507400
H	2.45586500	2.23750700	2.46987600
C	6.38243700	1.34797100	2.95326700
H	6.55168200	2.17066400	3.65982000
H	6.24041100	0.43252300	3.53511500
H	7.28819100	1.23554400	2.34812800
C	4.11369400	-2.14518100	3.05189200
H	4.51662200	-1.41810300	3.76530400
H	3.04590300	-1.93833100	2.93432200
H	4.22689600	-3.14447600	3.49036500
C	6.92319300	-2.08141300	1.73245100
H	7.13060300	-2.87190700	2.46537800
H	7.47941800	-2.32316200	0.82077200
H	7.31093100	-1.14180900	2.13042400
C	4.71981300	-3.62351200	0.36299100
H	5.23493900	-3.57446600	-0.60230000
H	5.12074400	-4.48607300	0.91083800
H	3.66120000	-3.80979400	0.17314500

C	7.56596200	0.31907900	-1.16383700
H	7.85458900	-0.61370900	-0.67188800
H	8.20622600	0.44960500	-2.04562600
H	7.77684700	1.14322200	-0.47362000
C	5.47985100	-1.09416100	-2.97190200
H	6.10892900	-0.91718000	-3.85331100
H	5.75440500	-2.06824200	-2.55372600
H	4.43883200	-1.15052400	-3.30428500
C	5.43163700	1.97186800	-2.60172600
H	4.43870000	2.02770400	-3.05612600
H	5.54654400	2.82368600	-1.92479400
H	6.17151100	2.07918100	-3.40532400
C	5.25815500	3.44213300	1.05611200
H	4.44087300	3.80444600	0.42797000
H	5.43713000	4.18912200	1.84008600
H	6.16389300	3.38154600	0.44285000
Si	1.21122100	1.56644900	-1.33225000
C	1.43791400	1.07969900	-3.16476700
H	1.13116800	0.04960400	-3.35694700
H	0.85278500	1.73876700	-3.81807400
H	2.49139800	1.17293100	-3.44855000
C	2.05478000	3.26060700	-1.08328100
H	1.97080600	3.59779600	-0.04690100
H	3.11467800	3.20551600	-1.34762000
H	1.58542900	4.01378800	-1.72777900
Si	-4.38795700	-0.00426700	0.27205800
Si	-1.07755400	1.92488200	-0.65303300
Si	-4.85583000	-1.76448400	1.87939300
Si	-5.04227600	2.04267200	1.38653300
Si	-5.73120200	-0.31167700	-1.70613400
C	-2.01311300	2.73814000	-2.10811700
H	-3.07603600	2.85921800	-1.88411200
H	-1.59331400	3.72956300	-2.31984100
H	-1.92924200	2.13276000	-3.01610500
C	-0.92121200	3.11796800	0.82893800
H	-1.88244100	3.30657200	1.31355500
H	-0.25302100	2.67486800	1.57464200
H	-0.50232900	4.08013000	0.51241800
C	-4.72000800	3.62354800	0.36271600
H	-5.12113100	4.48608600	0.91045900
H	-3.66137200	3.80991500	0.17308700
H	-5.23494000	3.57443600	-0.60267600
C	-4.11405100	2.14544600	3.05171200
H	-3.04625200	1.93856300	2.93425800
H	-4.22726600	3.14480800	3.49003000
H	-4.51705000	1.41848100	3.76519700
C	-6.92345100	2.08133400	1.73205200
H	-7.13094800	2.87148400	2.46532400
H	-7.47959100	2.32349000	0.82043100
H	-7.31123000	1.14154200	2.12954600
C	-6.38253300	-1.34772700	2.95334100
H	-7.28827300	-1.23560400	2.34812200
H	-6.55168600	-2.17026100	3.66010100
H	-6.24068700	-0.43210600	3.53495800
C	-5.25772400	-3.44217800	1.05675200
H	-4.44031100	-3.80442700	0.42874400
H	-5.43653800	-4.18902400	1.84090000
H	-6.16344500	-3.38197400	0.44342700
C	-7.56589100	-0.31867300	-1.16431700
H	-7.85450700	0.61449400	-0.67308100
H	-8.20598800	-0.44974300	-2.04614600
H	-7.77700700	-1.14230000	-0.47356000
C	-5.47905200	1.09360300	-2.97229900
H	-5.75317300	2.06791400	-2.55438100
H	-4.43799400	1.14942400	-3.30464600
H	-6.10817800	0.91666900	-3.85368300
C	-5.43170400	-1.97231600	-2.60141500
H	-4.43878400	-2.02838100	-3.05582400
H	-5.54669000	-2.82397500	-1.92429500
H	-6.17161400	-2.07971600	-3.40496800
C	-3.35707200	-1.97860400	3.03401300

H	-2.45597000	-2.23752800	2.47050900
H	-3.14116100	-1.05213600	3.57487400
H	-3.55612600	-2.77154300	3.76604500
P	-2.01780400	-0.03346600	0.21986200
P	2.01779000	0.03340300	0.21988600
Si	1.07751800	-1.92495000	-0.65305900
Si	-1.21130600	-1.56651100	-1.33225800
C	-2.05476400	-3.26073400	-1.08341300
H	-1.97027900	-3.59830400	-0.04719800
H	-3.11479100	-3.20561000	-1.34722200
H	-1.58567000	-4.01365000	-1.72841100
C	-1.43798900	-1.07977600	-3.16479200
H	-2.49142200	-1.17334000	-3.44867000
H	-1.13156100	-0.04957500	-3.35692600
H	-0.85260300	-1.73863200	-3.81808200
C	0.92109200	-3.11803300	0.82891900
H	1.88224900	-3.30649300	1.31373200
H	0.25270600	-2.67499200	1.57448600
H	0.50239700	-4.08026600	0.51236200
C	2.01323100	-2.73810900	-2.10809500
H	1.92940300	-2.13268400	-3.01605700
H	3.07613900	-2.85911500	-1.88397000
H	1.59353600	-3.72955500	-2.31991200

[HypP-(SiMe$_2$)$_2$-]$_2$ 12e [twist, trans]

Energy = -5194.6706267

Si	4.04419000	0.01251600	-0.39534700
Si	4.28339500	-1.78207700	-2.01764000
Si	5.70971900	-0.23765600	1.33226300
Si	4.46961700	2.05990600	-1.61581600
C	2.60573000	-2.13381700	-2.84819800
H	2.21579900	-1.23790600	-3.34145000
H	2.72000000	-2.92441400	-3.60077200
H	1.85507000	-2.45106200	-2.11855800
C	5.53136000	-1.32064400	-3.38967000
H	5.61246100	-2.16052500	-4.09134700
H	5.21000300	-0.44113200	-3.95600500
H	6.52893600	-1.12494000	-2.98333500
C	3.22324000	2.17354500	-3.05826100
H	3.44203000	1.41389000	-3.81685900
H	2.19515500	2.01682800	-2.71922700
H	3.28334400	3.15742600	-3.54003700
C	6.23829600	2.10637300	-2.34319900
H	6.31327500	2.97009700	-3.01681900
H	6.98621100	2.23863400	-1.55469900
H	6.49724000	1.21209200	-2.91296300
C	4.37724600	3.63252700	-0.53281600
H	5.13055200	3.59802600	0.26155000
H	4.59498300	4.50707200	-1.15936900
H	3.40352300	3.78913400	-0.06568300
C	7.41382900	-0.26786700	0.46504000
H	7.62081400	0.66842000	-0.06063500
H	8.20418300	-0.41945000	1.21104200
H	7.47942000	-1.08379200	-0.26282900
C	5.69107900	1.20781500	2.57746400
H	6.47566300	1.05813700	3.32976100
H	5.87803200	2.16688200	2.08365300
H	4.73170800	1.27915000	3.09877300
C	5.56262900	-1.87014100	2.30837400
H	4.62807800	-1.93121400	2.87146300
H	5.62020200	-2.73902500	1.64634000
H	6.39056300	-1.93655700	3.02550400
C	4.95137700	-3.39210100	-1.23394400
H	4.29711200	-3.77755900	-0.44778100
H	5.03462100	-4.16236400	-2.01128000

H	5.94909600	−3.24120400	−0.80767900
Si	1.20741000	−1.61402200	1.71727500
C	1.68353800	−1.15747100	3.50742700
H	1.35274900	−0.15452600	3.78170000
H	1.23052200	−1.86792200	4.21004900
H	2.76957000	−1.20341300	3.63693800
C	2.04943000	−3.28245500	1.31943200
H	1.90028200	−3.56977500	0.27541800
H	3.12473800	−3.22850400	1.51329200
H	1.63329000	−4.07343700	1.95508600
Si	−4.02501700	0.04235800	−0.38338100
Si	−1.12878400	−2.06905400	1.34956000
Si	−5.98693000	1.01248000	0.64562400
Si	−3.27087700	1.32917100	−2.27082500
Si	−4.86038500	−2.05711000	−1.26957600
C	−1.68098300	−3.29143500	2.71257800
H	−2.72079800	−3.59981200	2.56093100
H	−1.05035400	−4.18887300	2.71638600
H	−1.62025300	−2.81954700	3.69858700
C	−1.13524000	−2.94341500	−0.34170100
H	−2.12177900	−3.34043500	−0.58810100
H	−0.82097600	−2.25234800	−1.12914800
H	−0.43386600	−3.78573000	−0.32332100
C	−1.59726800	0.68105200	−2.91335600
H	−1.19077900	1.36165900	−3.67211100
H	−0.85663400	0.57865100	−2.11353600
H	−1.71970800	−0.30336300	−3.37742000
C	−3.14750200	3.19546700	−1.88631000
H	−2.32676800	3.42399800	−1.20210600
H	−2.96917900	3.74846500	−2.81719000
H	−4.07669300	3.57190700	−1.44513500
C	−4.57247800	1.15603700	−3.66171900
H	−4.25555000	1.74341000	−4.53293800
H	−4.69174100	0.11781000	−3.98561500
H	−5.55070000	1.52906400	−3.34226800
C	−5.60628300	2.45089400	1.83520800
H	−5.09766500	3.28209700	1.33906600
H	−6.54964300	2.82785300	2.25061600
H	−4.98317300	2.10761900	2.66651400
C	−7.18490100	1.68864400	−0.68232400
H	−7.48454100	0.92553600	−1.40560100
H	−8.09239200	2.06780200	−0.19543800
H	−6.73106200	2.52074400	−1.23237000
C	−6.63004700	−1.79581300	−1.94950900
H	−6.65867500	−1.02748400	−2.72840100
H	−6.97468700	−2.73765600	−2.39589800
H	−7.34074400	−1.51840000	−1.16614200
C	−3.85059500	−2.69007400	−2.76646900
H	−4.06326600	−2.07999300	−3.65103800
H	−2.77193700	−2.67737700	−2.60099400
H	−4.14738900	−3.72134900	−2.99648600
C	−4.97700700	−3.40351700	0.07816100
H	−4.01119500	−3.62164000	0.54019800
H	−5.66046500	−3.09234900	0.87392600
H	−5.36270000	−4.33290400	−0.35952000
C	−6.86002000	−0.32620800	1.69123900
H	−7.22540300	−1.16013000	1.08467200
H	−6.16950500	−0.72558800	2.44187900
H	−7.71870100	0.11172700	2.21569400
P	−2.66107800	−0.29757000	1.50987900
P	1.72046900	−0.06313000	0.06408100
Si	0.87594100	1.86334100	1.07046700
Si	−1.27330000	1.48182700	2.12400800
C	−2.13914500	3.17961800	1.99271600
H	−2.50805200	3.38843100	0.98663000
H	−2.98384800	3.22731600	2.68457400
H	−1.43241000	3.97188200	2.26939900
C	−1.07747700	1.14794800	3.99704700
H	−2.03977900	1.34899100	4.48127800
H	−0.81736900	0.10798400	4.20794900
H	−0.31962000	1.79895900	4.44817700

C	0.55904500	3.11466000	-0.33684900
H	1.48629800	3.41753900	-0.82930900
H	-0.08933300	2.66990400	-1.09610200
H	0.07143600	4.01596800	0.05134000
C	2.00013900	2.66073800	2.39555000
H	2.10014400	2.01236000	3.27072100
H	3.00311600	2.84619000	1.99998700
H	1.58060400	3.61888000	2.72699300
C	-13.95664255	0.24290451	4.37818038
H	-13.59998813	-0.76590549	4.37818038
H	-13.59996971	0.74730270	5.25183189
H	-13.59996971	0.74730270	3.50452888
H	-15.02664255	0.24291769	4.37818038

A.3. Compounds 14-16: A stable diphosphastannylene and attempted reaction of a stable cyclic diphosphastannylene

[HypP(SiMe$_3$)K·DME] 14

Energy = -5209.63563

Si	-4.41680500	-0.09765700	-0.17762100
Si	-3.81050300	0.04348900	-2.50039400
Si	-5.62372700	1.92025200	0.32266600
Si	-5.92128100	-1.98167100	-0.04270200
C	-3.19576100	-1.65498900	-3.13503400
H	-4.01874800	-2.36996900	-3.23741900
H	-2.71266000	-1.54600700	-4.11444700
H	-2.47072500	-2.07676000	-2.43010500
C	-5.21512700	0.64778200	-3.65074500
H	-4.88590700	0.60193900	-4.69685300
H	-6.11728400	0.03683800	-3.55187500
H	-5.48373100	1.68677400	-3.42875700
C	-4.90249700	-3.57527400	0.22565400
H	-4.31867700	-3.81294300	-0.67077200
H	-4.19567400	-3.44271500	1.05161100
H	-5.55589500	-4.42769200	0.45003700
C	-6.92169600	-2.17173300	-1.66682200
H	-7.59032200	-3.03894300	-1.59042500
H	-7.53927600	-1.28588000	-1.85274100
H	-6.27317600	-2.32247300	-2.53567300
C	-7.24314200	-1.83872000	1.33427100
H	-7.87540700	-0.95692300	1.18024600
H	-7.89266700	-2.72336300	1.30966700
H	-6.80177300	-1.76939200	2.33134700
C	-7.29990300	1.97364000	-0.60362800
H	-7.96101800	1.16758600	-0.26593500
H	-7.80911400	2.92675300	-0.41078900
H	-7.17083200	1.86987900	-1.68539700
C	-6.01094700	2.11661800	2.18426900
H	-6.52814800	3.06886500	2.35898700
H	-6.65902900	1.31026300	2.54397400
H	-5.09528300	2.11224000	2.78435600
C	-4.60777500	3.45582500	-0.20479000
H	-3.62527500	3.45097000	0.28029200
H	-4.46084100	3.48122100	-1.29069400
H	-5.13161100	4.37482500	0.08848200
C	-2.35303100	1.26424700	-2.72269600
H	-1.44368200	0.82328600	-2.30100000
H	-2.17426700	1.45889300	-3.78782800
H	-2.55525100	2.21669600	-2.22177200
Si	-2.63712400	-0.61258700	3.07885300

C	-1.42417400	-1.97831500	3.66317600
H	-0.38768500	-1.71117700	3.42797500
H	-1.49678400	-2.12206900	4.74921300
H	-1.66679100	-2.92845000	3.17326600
C	-4.37048700	-1.16020500	3.65439900
H	-5.13493900	-0.43303000	3.36817400
H	-4.63576300	-2.12915700	3.21947300
H	-4.38565300	-1.26029800	4.74741500
C	-2.17457200	0.96277600	4.06950100
H	-2.29799900	0.80489400	5.14891500
H	-1.12764400	1.22896700	3.88041500
H	-2.80604500	1.80550500	3.76725500
K	-0.17039000	2.08628900	0.00433200
P	-2.33998600	-0.31547100	0.81539400
K	0.11286400	-2.29047200	-0.08682600
P	2.30851000	0.03319500	-0.88851300
Si	2.80516000	0.11219300	-3.13602400
Si	4.28344700	0.18103800	0.31747900
Si	3.56351000	0.87491300	2.50414900
Si	5.88965100	1.83531300	-0.36475500
Si	5.40364200	-1.92327400	0.68334500
C	3.32496300	1.82683000	-3.81523200
H	3.28659800	1.82497200	-4.91275700
H	2.65207300	2.60759100	-3.44462600
H	4.34216300	2.09420900	-3.51383300
C	1.16898700	-0.31183900	-4.04148000
H	0.79892600	-1.30102900	-3.75162400
H	0.38644700	0.41989900	-3.81592000
H	1.33018800	-0.31308000	-5.12735500
C	4.10651800	-1.13759900	-3.76924300
H	5.06604600	-1.01325900	-3.25889200
H	3.77137600	-2.16631800	-3.59797500
H	4.26988700	-1.00168300	-4.84655300
C	5.01468800	3.47604400	-0.80613700
H	4.64670800	3.96825200	0.10054200
H	5.70929600	4.16112000	-1.30860500
H	4.15869500	3.30331700	-1.46362000
C	6.92467500	1.24690200	-1.86238800
H	7.65486300	2.01624000	-2.14397400
H	7.47616100	0.33168200	-1.61950500
H	6.29785300	1.03866900	-2.73449300
C	7.12822800	2.22157500	1.04465500
H	7.87513100	2.94612700	0.69500000
H	6.62066100	2.65731100	1.91232300
H	7.65787700	1.32364300	1.37762100
C	1.99231200	-0.08748200	3.01500100
H	1.61766000	0.26043400	3.98595500
H	1.19643400	0.04079000	2.27232100
H	2.20631100	-1.15842100	3.09777800
C	3.12247800	2.74031700	2.52564700
H	2.51250400	3.01275000	1.65729800
H	2.56959400	2.98933700	3.44073400
H	4.02887500	3.35521800	2.50109200
C	4.87812300	0.59025100	3.86585800
H	5.08030900	-0.47702100	4.00714900
H	5.82471100	1.08152100	3.61944400
H	4.52353800	0.99399100	4.82294000
C	7.14844700	-1.69405300	1.44011600
H	7.81401100	-1.15920100	0.75343400
H	7.10852100	-1.13153100	2.37868300
H	7.59927400	-2.67292200	1.64886300
C	4.40004000	-3.01460700	1.89606800
H	4.92509300	-3.96472900	2.06095400
H	4.27445300	-2.52567100	2.86788400
H	3.40749000	-3.24011900	1.49163900
C	5.58871700	-2.93816400	-0.92270000
H	5.97677600	-3.93976200	-0.69698300
H	4.61702100	-3.03961000	-1.41667400
H	6.27352700	-2.45849800	-1.62935900
C	1.19345200	-5.47387400	-1.20711100
H	1.19261100	-6.39084500	-1.81464700

H	2.19953400	−5.03289600	−1.23361300
C	0.81397800	−5.83465800	0.21193800
H	1.49288400	−6.62263700	0.57011200
H	−0.21766100	−6.21189000	0.24269400
O	0.22448700	−4.53299600	−1.73516100
O	0.93513800	−4.66355500	1.05652300
C	0.84101900	−4.97268000	2.47104800
H	1.65090700	−5.64897500	2.77205100
H	0.93680100	−4.03115900	3.00984000
H	−0.12812400	−5.42939600	2.70973500
C	0.29471100	−4.38673500	−3.17712300
H	0.11821700	−5.35040800	−3.67180300
H	−0.49236900	−3.68859200	−3.46116200
H	1.26946500	−3.98953500	−3.48774300
C	−0.21126000	5.63851700	0.66006000
H	−0.63276300	6.54090700	1.12699700
H	0.88493600	5.68785100	0.71686900
C	−0.66009700	5.58645700	−0.78382300
H	−1.75401100	5.50033400	−0.83953500
H	−0.34986000	6.51671100	−1.28252900
O	−0.04158700	4.44858800	−1.43321600
O	−0.68808800	4.45735600	1.35131100
C	−0.13744400	4.49062600	−2.87972600
H	0.38109300	5.37312500	−3.27552100
H	0.34685300	3.58940000	−3.25367900
H	−1.18538100	4.50328500	−3.20575300
C	−0.62906900	4.57387800	2.79642000
H	−1.24431600	5.41503900	3.14056400
H	−1.02912100	3.64609900	3.20336300
H	0.40465900	4.71243200	3.13838600

[HypP-(SiMe$_2$)-]$_2$Sn 15

Energy = −4538.7604156

Si	−3.63415700	0.21506900	−0.37511100
Si	−3.06434500	1.00576900	−2.58002800
Si	−5.21576300	1.78857900	0.53023200
Si	−4.61208900	−1.97584600	−0.68751100
C	−1.46787900	0.15554700	−3.18919700
H	−1.57254600	−0.93459200	−3.21022800
H	−1.23170000	0.48754800	−4.20829900
H	−0.61398500	0.40801400	−2.55180900
C	−4.46244300	0.62273900	−3.82908100
H	−4.18348400	1.01042900	−4.81720000
H	−4.64170300	−0.45213100	−3.93218600
H	−5.40491900	1.09738800	−3.53756100
C	−3.71182700	−2.93776300	−2.07254900
H	−3.68105500	−2.37637100	−3.01119000
H	−2.68265500	−3.17805500	−1.78510300
H	−4.23783300	−3.88230400	−2.26191500
C	−6.42929500	−1.72832800	−1.23013700
H	−6.87730000	−2.70097400	−1.47003700
H	−7.02591500	−1.27251400	−0.43268800
H	−6.50409900	−1.09291600	−2.11784400
C	−4.61489500	−3.09666600	0.85455300
H	−5.16888600	−2.65249800	1.68647300
H	−5.09027400	−4.05290500	0.60135000
H	−3.59694000	−3.30717600	1.19685200
C	−6.58238200	2.16036300	−0.75335200
H	−7.14788200	1.26251400	−1.02042300
H	−7.28636100	2.89161300	−0.33593500
H	−6.16433300	2.58679200	−1.67109700
C	−6.07358500	1.12327700	2.10227200
H	−6.86750500	1.81486200	2.41117600
H	−6.53076000	0.14409800	1.92452700
H	−5.37328800	1.02416900	2.93690300

C	-4.31814100	3.42105500	0.93859800
H	-3.37690000	3.24022500	1.46535500
H	-4.07961200	3.96948600	0.02200000
H	-4.95209500	4.06134400	1.56469700
C	-2.79581500	2.89421200	-2.58128300
H	-2.06011400	3.19172700	-1.82916500
H	-2.43022300	3.21829900	-3.56386400
H	-3.73086200	3.42763800	-2.37868800
Si	-1.87026800	0.09077500	3.08127100
C	-3.16681200	-1.21279200	3.56444200
H	-2.86400700	-2.21134400	3.23556400
H	-3.27353700	-1.23346000	4.65680500
H	-4.14735800	-0.99956600	3.13215700
C	-2.29800700	1.75645200	3.89545000
H	-1.56156400	2.51792500	3.62060400
H	-3.28561500	2.11779700	3.59531900
H	-2.29264400	1.65033700	4.98767300
C	-0.18560700	-0.49596700	3.75341000
H	-0.21093600	-0.49381100	4.85064700
H	0.04663600	-1.51715000	3.43007000
H	0.63409500	0.15295800	3.43414100
P	-1.58681500	0.49737300	0.77235400
Sn	-0.33550300	-1.72633200	0.08428300
P	2.07390400	-1.11089600	-0.36638900
Si	3.50401900	0.72618800	-0.13592600
Si	3.07006300	-3.23387000	-0.33567800
Si	4.99656400	0.41350400	1.73363200
Si	4.67104500	1.13037300	-2.21649800
Si	2.25932900	2.76006300	0.26206400
C	4.79941400	-3.28004400	-1.11868000
H	5.43979800	-2.46396700	-0.77996600
H	5.28332900	-4.22705200	-0.84780700
H	4.73331500	-3.23151000	-2.20849500
C	3.17284700	-3.86676800	1.45800500
H	3.58149200	-4.88513000	1.47982100
H	3.81333100	-3.22975600	2.07587600
H	2.17860000	-3.88742300	1.91639700
C	1.94778700	-4.39478600	-1.34609900
H	0.97204400	-4.54229700	-0.87385500
H	1.78145700	-3.99602800	-2.35159200
H	2.43164700	-5.37538300	-1.44126200
C	3.52545700	2.06250400	-3.42628300
H	4.04733500	2.21387100	-4.37961800
H	2.61599200	1.48618300	-3.62558400
H	3.23060900	3.04427000	-3.04407300
C	5.26436400	-0.43313100	-3.12668600
H	4.43095600	-1.11232600	-3.32865500
H	5.70480100	-0.13819800	-4.08759600
H	6.02309400	-0.97888100	-2.55964900
C	6.20754100	2.21068200	-1.85727400
H	6.69413300	2.48451500	-2.80205400
H	5.94769000	3.13434100	-1.33211000
H	6.94059300	1.66785500	-1.25030200
C	5.84250100	2.07510900	2.15338800
H	5.11608400	2.82034100	2.49298900
H	6.56714500	1.92165100	2.96298000
H	6.37920500	2.48729300	1.29340400
C	4.00012500	-0.16097900	3.25409800
H	3.36502600	-1.01858400	3.01230100
H	4.67778700	-0.45007500	4.06700600
H	3.34929700	0.63816200	3.62291100
C	1.57984600	2.85491500	2.03971600
H	2.35728000	2.70772400	2.79581000
H	1.12935900	3.84198900	2.20374300
H	0.79780600	2.10323900	2.18090100
C	3.46431500	4.22586800	0.00886200
H	4.34944400	4.15578800	0.64751700
H	3.79711000	4.30061800	-1.03139100
H	2.94206400	5.15858500	0.25792100
C	0.80415400	2.96682200	-0.94256200
H	1.09575600	2.81836400	-1.98539900

H	0.01249300	2.25489800	-0.68657700
H	0.39273300	3.97989000	-0.84307300
C	6.37950700	-0.85873300	1.39251900
H	5.98824200	-1.87923000	1.34263000
H	6.90724900	-0.64904600	0.45616300
H	7.11410000	-0.82268000	2.20696100

[HypP(SiMe$_3$)]$_2$Sn 16

Energy = -4458.9680851

Si	-3.98706800	-0.23534500	0.02281000
Si	-3.98845900	-2.63779800	-0.16250600
Si	-5.41092600	0.68584700	-1.67743200
Si	-4.70719500	0.38176000	2.23595900
C	-3.14194100	-3.41803900	1.36049000
H	-3.68759700	-3.19138100	2.28263600
H	-3.10314000	-4.50889800	1.25013500
H	-2.11552200	-3.05469100	1.47522800
C	-5.79826700	-3.24907200	-0.23467300
H	-5.81883800	-4.34280600	-0.14918600
H	-6.40673400	-2.83589800	0.57507400
H	-6.26874700	-2.98169500	-1.18713500
C	-3.25503400	0.17629400	3.45107600
H	-2.92488800	-0.86631400	3.50172900
H	-2.39881600	0.78001300	3.13355000
H	-3.55049600	0.49239900	4.45913300
C	-6.15375800	-0.73973200	2.79002900
H	-6.51114900	-0.41991400	3.77696200
H	-6.99770000	-0.68585200	2.09409500
H	-5.84457700	-1.78711300	2.87096300
C	-5.32587800	2.18699100	2.29388700
H	-6.20522300	2.32836600	1.65609400
H	-5.61184300	2.44844100	3.32046600
H	-4.55308500	2.88970200	1.96972500
C	-7.22879800	0.30320500	-1.22775100
H	-7.51311700	0.78512100	-0.28572500
H	-7.89546500	0.68336300	-2.01191300
H	-7.40802900	-0.77118600	-1.12458500
C	-5.22946200	2.57974600	-1.80539000
H	-5.89749900	2.96439000	-2.58613400
H	-5.49197100	3.07236900	-0.86379500
H	-4.20666500	2.86487300	-2.06822200
C	-4.99577300	-0.08653800	-3.37029100
H	-3.92986300	0.01716400	-3.59812000
H	-5.24556400	-1.15241500	-3.39261000
H	-5.56604000	0.40986300	-4.16508900
C	-3.10993000	-3.23697600	-1.74470800
H	-2.04127100	-3.00158900	-1.72502000
H	-3.21314400	-4.32588300	-1.83382700
H	-3.53780100	-2.77863400	-2.64127700
Si	-1.13559600	2.61893600	-0.57164500
C	-2.20665800	3.86269700	0.39920500
H	-2.17433700	3.64720300	1.47129900
H	-1.83175800	4.88134800	0.24183100
H	-3.24921100	3.83261500	0.06899500
C	-1.08063800	3.05214000	-2.42631100
H	-0.42155700	2.35090000	-2.94704400
H	-2.07141300	2.99978600	-2.88870500
H	-0.68690300	4.06581200	-2.57028500
P	-1.79191000	0.43813600	-0.24597900
Sn	0.11998600	-1.18595600	-0.31577200
P	1.90489400	0.65454200	-0.79588100
Si	3.93527200	-0.22038100	-0.00309700
Si	1.09311200	2.54540400	0.29400200
Si	4.58485100	-1.59712700	-1.86652500
Si	5.55182400	1.54475500	0.20259200

Si	3.85844900	-1.56123300	1.99425300
C	2.02190100	4.12013100	-0.25809500
H	1.49450300	5.01145400	0.10393800
H	3.04100700	4.15032600	0.13935900
H	2.07967400	4.17321000	-1.34933100
C	1.05810900	2.44974900	2.19575900
H	2.06107500	2.28877500	2.60367700
H	0.66356100	3.38290100	2.61674900
H	0.41900200	1.62597500	2.52710600
C	5.31479300	2.49983000	1.84067300
H	6.06875900	3.29240100	1.92565300
H	4.32695800	2.96624800	1.90400300
H	5.42853600	1.83431200	2.70335700
C	5.42560500	2.74440500	-1.27499900
H	4.38606700	2.97474400	-1.52184000
H	5.94691900	3.68382600	-1.05311200
H	5.88529800	2.30373900	-2.16509600
C	7.31174600	0.79923600	0.21424800
H	8.05100600	1.59634300	0.36354800
H	7.43863300	0.06505000	1.01542600
H	7.53936500	0.30738000	-0.73739300
C	6.07152900	-2.70527100	-1.40112500
H	5.81473300	-3.41063000	-0.60360500
H	6.38766100	-3.28974500	-2.27438600
H	6.92829600	-2.11229200	-1.06536600
C	3.13986500	-2.71470400	-2.41749100
H	2.30322800	-2.10875000	-2.78170300
H	3.46494200	-3.36640000	-3.23842600
H	2.77581100	-3.35021300	-1.60405700
C	3.15857200	-3.29967200	1.62387800
H	3.78881900	-3.84174600	0.91117800
H	3.11491200	-3.88697400	2.54982000
H	2.14647900	-3.24912300	1.20838500
C	5.63213600	-1.77480300	2.67402600
H	6.29423900	-2.23510500	1.93339800
H	6.06546500	-0.81275200	2.96726500
H	5.61603900	-2.42081700	3.56078700
C	2.78552600	-0.75879600	3.35084800
H	3.18730900	0.21266200	3.65654600
H	1.75750300	-0.60302200	3.00794200
H	2.75315300	-1.40760200	4.23500100
C	5.07555400	-0.49240200	-3.34190800
H	4.28535500	0.23331100	-3.55998900
H	6.00039300	0.05823200	-3.14010000
H	5.23629100	-1.10550800	-4.23750000

[HypP-(SiMe$_3$)]$_2$Sn·THF

Energy = -4771.1321722

Si	3.58132900	-0.84456100	-0.30083600
Si	2.90888600	-2.53518200	-1.87915000
Si	5.19546400	-1.89542100	1.14126000
Si	4.64526900	0.90421200	-1.58187500
C	1.32579400	-2.01063900	-2.80440100
H	1.45283500	-1.04772300	-3.31083500
H	1.07555300	-2.75854800	-3.56798200
H	0.46818800	-1.93027600	-2.12844100
C	4.27813400	-2.83382100	-3.18359500
H	3.97712300	-3.65912600	-3.84171300
H	4.44129200	-1.95200300	-3.81218600
H	5.23281900	-3.10470400	-2.72166900
C	3.74554300	1.23258100	-3.23655100
H	3.68844000	0.32741500	-3.84964000
H	2.72531000	1.59693700	-3.07728500
H	4.29574700	1.99089000	-3.80876300
C	6.42318500	0.33890900	-2.00754700

H	6.90006300	1.08456700	-2.65649500
H	7.03855300	0.23509000	-1.10764000
H	6.42620900	-0.61941400	-2.53579500
C	4.78523700	2.56637700	-0.65548500
H	5.43012400	2.47936900	0.22475400
H	5.21936700	3.32336400	-1.32094300
H	3.80687100	2.92168700	-0.31958000
C	6.45034100	-2.91346600	0.11783300
H	6.95795600	-2.30044800	-0.63266200
H	7.21332900	-3.32918500	0.78844000
H	5.96602800	-3.75112400	-0.39478600
C	6.20281500	-0.58917300	2.10916100
H	6.86653700	-1.08008800	2.83196600
H	6.82805900	-0.00352200	1.42577900
H	5.56296200	0.10844500	2.65695400
C	4.31421700	-3.09394200	2.33553000
H	3.39728800	-2.65941000	2.74062300
H	4.03822500	-4.01332000	1.80905600
H	4.97280900	-3.36275500	3.17073300
C	2.58078800	-4.18784700	-0.98514600
H	1.88913600	-4.05192000	-0.14916900
H	2.13501500	-4.90819600	-1.68263600
H	3.50798500	-4.62398000	-0.59825300
Si	1.99277300	0.80841200	2.84495200
C	3.05862800	2.36757400	2.61033300
H	2.57953200	3.05880600	1.91034500
H	3.19006400	2.87764100	3.57375100
H	4.04972000	2.12135700	2.21938400
C	2.78301300	-0.28724000	4.18771400
H	2.19293900	-1.19785100	4.33140700
H	3.81023400	-0.57895600	3.95826500
H	2.79115100	0.26494800	5.13667200
C	0.28668600	1.31880500	3.53456300
H	0.39842700	2.19373300	4.18756000
H	-0.43461000	1.56080400	2.75023000
H	-0.13354500	0.50670200	4.13473100
P	1.58425800	-0.45941700	0.91142500
Sn	0.35777400	1.17335800	-0.82249800
P	-2.07468900	0.28191400	-1.03792300
Si	-3.56816800	-1.02881300	0.19768800
Si	-3.06433900	2.10303200	-2.11865000
Si	-4.96908300	0.24745900	1.68247000
Si	-4.84064000	-2.43011000	-1.31503900
Si	-2.36862200	-2.64415600	1.53582700
C	-4.82756300	1.79615900	-2.75864600
H	-5.47415500	1.33543600	-2.00898500
H	-5.26812700	2.76114000	-3.04075600
H	-4.81982300	1.15421400	-3.64266900
C	-3.12035200	3.64432500	-0.99602200
H	-3.51070300	4.50710600	-1.55147900
H	-3.76511700	3.47895200	-0.12648100
H	-2.11622500	3.88476600	-0.63529900
C	-1.96514100	2.49202600	-3.62753400
H	-0.94960300	2.77767700	-3.33494300
H	-1.88914200	1.61497000	-4.27793700
H	-2.40257700	3.31545100	-4.20651600
C	-3.79630700	-3.93776100	-1.85138300
H	-4.37595600	-4.54406400	-2.55916100
H	-2.87955500	-3.61436000	-2.35548200
H	-3.51657000	-4.57865400	-1.01060400
C	-5.40794200	-1.60288900	-2.93365800
H	-4.55438700	-1.17743100	-3.46986800
H	-5.87012900	-2.36334000	-3.57595700
H	-6.14122100	-0.81017600	-2.76476900
C	-6.40158200	-3.04878500	-0.39717600
H	-6.93219800	-3.78135000	-1.01856700
H	-6.15368800	-3.52846700	0.55417500
H	-7.09194800	-2.22283800	-0.19231100
C	-5.79038800	-0.89480700	2.97806300
H	-5.04619700	-1.38412800	3.61497000
H	-6.44663200	-0.30029000	3.62645300

H	-6.39854400	-1.67153900	2.50388200
C	-3.90341100	1.53152200	2.60866300
H	-3.35065400	2.15684400	1.90041600
H	-4.53724700	2.18058400	3.22580200
H	-3.17371600	1.04293400	3.26179600
C	-1.61238600	-1.86373400	3.09841000
H	-2.34532100	-1.30803100	3.69206200
H	-1.18447100	-2.65062100	3.73236800
H	-0.80366400	-1.18912100	2.80616400
C	-3.60145900	-3.99644300	2.09998100
H	-4.41620600	-3.58534900	2.70394200
H	-4.04088900	-4.53260900	1.25342500
H	-3.06316200	-4.72885800	2.71549200
C	-0.96019200	-3.45831100	0.55311300
H	-1.28330300	-3.81522600	-0.42770500
H	-0.14995500	-2.73421800	0.41797000
H	-0.56243400	-4.31205200	1.11706300
C	-6.37317300	1.17898300	0.77897500
H	-5.98532200	1.99254300	0.15793900
H	-6.95649700	0.50991600	0.13742500
H	-7.05633200	1.61702500	1.51771700
C	-0.35183900	4.20130100	1.58358600
O	0.33694300	3.56380400	0.43944900
C	0.91625200	4.61057200	-0.43107200
C	0.80955400	5.91114400	0.37075700
C	-0.45537800	5.68454200	1.21963100
H	-1.31674500	3.70798700	1.70753000
H	0.25813300	4.04213800	2.47672200
H	1.94235700	4.32480900	-0.66703000
H	0.33050800	4.64892000	-1.35548100
H	1.68471000	6.03806900	1.01579200
H	0.73303700	6.78659000	-0.27801400
H	-0.48996300	6.32176500	2.10637000
H	-1.35447200	5.87387800	0.62551300

[HypP-(SiMe$_2$)-]$_2$Ge

Energy = -4790.5333505

Ge	0.11922200	0.66126500	-0.25397900
P	1.99171200	-0.93332200	-0.60576900
Si	2.01112700	-0.75245200	-2.96221300
Si	3.82622900	0.25455700	0.29334600
Si	4.31763500	2.50466800	-0.39677400
Si	3.26289000	0.22729200	2.63845900
Si	5.79541500	-1.12962300	0.10077400
C	1.32746500	0.90968500	-3.60458200
H	1.54086500	1.01208700	-4.67638600
H	0.23969400	0.95256900	-3.47787400
H	1.76152400	1.76988300	-3.08752100
C	0.87357000	-2.13107000	-3.60390400
H	1.26663200	-3.12041400	-3.35222600
H	-0.12875300	-2.04078900	-3.17311200
H	0.78606300	-2.06155000	-4.69559600
C	3.77277400	-1.02419500	-3.61717700
H	3.74912500	-1.11667100	-4.71029000
H	4.42772700	-0.18754800	-3.36117900
H	4.20515500	-1.94270500	-3.20872200
C	2.88508800	3.69287000	0.02611500
H	1.95087000	3.38420700	-0.45436100
H	2.70945000	3.73148700	1.10662600
H	3.12460400	4.70852200	-0.31295000
C	4.70558300	2.63914300	-2.26116900
H	4.95737500	3.67815100	-2.50895100
H	5.56139000	2.01251100	-2.53175300
H	3.85762900	2.34217600	-2.88403400
C	5.88659700	3.07263500	0.53679800

H	5.74612600	3.05977500	1.62143600
H	6.74074100	2.42949400	0.29827600
H	6.14528900	4.09699100	0.24011800
C	4.44429900	1.30623800	3.68338400
H	4.24629800	1.13679600	4.74940600
H	5.49614700	1.07418100	3.49423300
H	4.28715400	2.37133900	3.48143100
C	1.49560700	0.88787400	2.93427600
H	1.34629100	1.87661500	2.48823000
H	0.73972800	0.20423900	2.52913100
H	1.30788100	0.97444000	4.01239200
C	3.32428500	−1.57081300	3.27651700
H	2.74105600	−2.23252700	2.62816300
H	4.34964500	−1.95235700	3.31187200
H	2.90766100	−1.62751100	4.28993400
C	6.90930300	−0.86642500	1.63410400
H	7.23527100	0.17582600	1.71823800
H	6.40412300	−1.14147600	2.56462900
H	7.80612600	−1.49221900	1.54157200
C	6.89027400	−0.70566900	−1.40738300
H	7.77523200	−1.35490800	−1.40073100
H	6.37054400	−0.85660000	−2.35669600
H	7.24038900	0.33169200	−1.36794600
C	5.28418000	−2.96340900	0.01502300
H	6.17178100	−3.60368600	−0.06316700
H	4.72482100	−3.25585200	0.90903200
H	4.64060800	−3.15502900	−0.84925600
P	−1.63557700	−0.89240600	−0.28882100
Si	−1.37241600	−3.08101700	0.49593900
C	−0.23073900	−4.04285000	−0.66983300
H	−0.08777000	−5.05955400	−0.28138800
H	−0.65730000	−4.11558800	−1.67426100
H	0.74431200	−3.55240400	−0.73925900
C	−0.61680400	−3.00230400	2.23694100
H	0.34491600	−2.48231100	2.20347300
H	−1.27092800	−2.47255100	2.93621100
H	−0.44534800	−4.01396100	2.62584300
C	−3.06576400	−3.94235600	0.56019800
H	−2.93971900	−4.93772500	1.00532800
H	−3.78778500	−3.39279200	1.16817100
H	−3.48372500	−4.07476300	−0.44184500
C	−2.89145800	2.48608800	−2.38466700
H	−2.88515900	3.52745700	−2.72632800
H	−1.86801600	2.10162800	−2.43906300
H	−3.50950200	1.90492000	−3.07604900
C	−2.48573900	3.46616000	0.55603900
H	−2.43600700	4.48501400	0.15366300
H	−2.91312300	3.52582000	1.56200500
H	−1.46640300	3.07614500	0.63221100
Si	−3.71650900	0.08633700	0.12873400
Si	−5.31078300	−1.02110300	−1.31723100
Si	−4.21665100	0.13022600	2.48749800
C	−6.42140900	−2.24560000	−0.36226100
H	−7.16663900	−2.67156500	−1.04585700
H	−5.85428600	−3.07226200	0.07354200
H	−6.96091800	−1.73669300	0.44394900
C	−4.36104000	−1.91919000	−2.70382400
H	−3.82979700	−1.19749200	−3.33305100
H	−3.61422700	−2.61234200	−2.30713900
H	−5.05970700	−2.48088000	−3.33651500
C	−6.48550700	0.23455700	−2.14787000
H	−7.11170800	−0.29426900	−2.87788900
H	−7.15004700	0.71050100	−1.42072800
H	−5.94562700	1.02188300	−2.68385300
C	−4.74100900	−1.56536400	3.19187400
H	−5.06592400	−1.43549400	4.23201800
H	−5.57249000	−2.00530400	2.63281000
H	−3.91112900	−2.27887600	3.19202000
C	−5.64198000	1.35998900	2.80806800
H	−6.55180400	1.08015900	2.26733800
H	−5.87719900	1.37886300	3.87967000

H	-5.37347900	2.37804500	2.50726600
C	-2.66739900	0.71393000	3.43066300
H	-1.81781300	0.05201800	3.23698400
H	-2.37177300	1.72565000	3.13762600
H	-2.86156600	0.71462700	4.51062700
Si	-3.55807000	2.37733400	-0.59580700
Si	-5.71142800	3.43218200	-0.58604600
H	-5.60467600	4.73883200	0.14312500
H	-6.16146700	3.73040800	-1.98336700
H	-6.79076700	2.64197700	0.07941700

[HypP(SiMe$_3$)]$_2$Ge

Energy = -4459.3850598

Si	3.78475200	-0.32441100	0.00577500
Si	4.01901700	-2.07287600	-1.63901200
Si	3.80962200	-1.24754200	2.22529600
Si	5.56470700	1.26183200	-0.28652400
C	3.51254600	-1.40524400	-3.35020900
H	4.17777800	-0.59878900	-3.67444400
H	3.55441100	-2.20708200	-4.09805300
H	2.49516100	-1.00315000	-3.32556900
C	5.82932900	-2.67975600	-1.72901200
H	5.89252400	-3.54455200	-2.40138400
H	6.48957700	-1.90097900	-2.12497500
H	6.20928600	-2.98553900	-0.74911700
C	5.60433200	1.87345300	-2.09213500
H	5.89333100	1.06644500	-2.77387400
H	4.62245400	2.24152700	-2.40632700
H	6.33098200	2.68745500	-2.20515100
C	7.22383400	0.41235500	0.13644500
H	8.05323700	1.10401600	-0.05799100
H	7.26400600	0.13406100	1.19535500
H	7.39004000	-0.49057700	-0.45759100
C	5.40416300	2.75687900	0.89000900
H	5.39839300	2.43516000	1.93592500
H	6.25997800	3.42877500	0.74751700
H	4.49270500	3.33261500	0.71054400
C	5.17013300	-2.58864400	2.31580600
H	6.15149000	-2.18681900	2.04274100
H	5.23902200	-2.98163700	3.33789600
H	4.95053600	-3.42879900	1.64862200
C	4.19908000	0.07768600	3.54355900
H	4.13404400	-0.36578200	4.54504800
H	5.21027700	0.48033700	3.42140200
H	3.49067000	0.91066400	3.49749900
C	2.13115800	-2.04352600	2.64913100
H	1.33719400	-1.28942200	2.69202700
H	1.84231600	-2.79907100	1.91128300
H	2.18366500	-2.52970300	3.63154800
C	2.91266800	-3.56604800	-1.20208600
H	1.85779600	-3.27871300	-1.13968000
H	3.00915900	-4.33898900	-1.97508400
H	3.19788200	-4.01203100	-0.24331200
Si	1.18557800	2.73483400	0.20046200
C	2.02044800	4.09452800	-0.84805800
H	1.74566100	3.97548600	-1.90043500
H	1.69630700	5.08811500	-0.51530100
H	3.11147600	4.05478700	-0.78103900
C	1.52199600	2.96042100	2.06091500
H	1.00071400	2.18509000	2.63047500
H	2.59219900	2.89464200	2.28130200
H	1.16197000	3.93825200	2.40283800
P	1.75144100	0.64637700	-0.61377400
P	-1.69701900	0.60685200	0.52168000
Si	-3.78619000	-0.32128300	0.02355400

```
 Si      -1.15822200    2.71667100   -0.27050800
 Si      -4.04962800   -1.98688400    1.74053300
 Si      -5.50539800    1.32843300    0.31225300
 Si      -3.87807700   -1.35049400   -2.14464000
 C       -2.06143000    4.08478000    0.70468300
 H       -1.65040900    5.06650400    0.43957800
 H       -3.13234300    4.09818100    0.47943400
 H       -1.93909000    3.93943400    1.78192800
 C       -1.42574900    2.95367600   -2.14141300
 H       -2.47611200    2.82039000   -2.41863400
 H       -1.11872800    3.96339700   -2.44111200
 H       -0.82811700    2.23250000   -2.70643000
 C       -5.55470700    2.53071700   -1.17102500
 H       -6.37340200    3.25003800   -1.04445100
 H       -4.62257200    3.09569900   -1.26875300
 H       -5.72253400    1.99178400   -2.10974200
 C       -5.24830600    2.30959300    1.92763300
 H       -4.21017700    2.62925500    2.04936300
 H       -5.88783600    3.20106400    1.93667000
 H       -5.50891700    1.69728600    2.79627100
 C       -7.19758600    0.44649400    0.41370700
 H       -7.99820700    1.18979300    0.51616500
 H       -7.40160400   -0.14909700   -0.48135800
 H       -7.24588700   -0.21813700    1.28287000
 C       -5.49516700   -3.15481000    1.29091900
 H       -5.28655600   -3.71369100    0.37233300
 H       -5.64939800   -3.88313400    2.09702800
 H       -6.43237400   -2.60706400    1.14879800
 C       -2.46624400   -3.02836000    1.94408300
 H       -1.62884700   -2.40568600    2.27560100
 H       -2.62995500   -3.80471100    2.70231400
 H       -2.17408000   -3.51906900    1.01094800
 C       -2.95461800   -3.02103600   -2.11870300
 H       -3.44362600   -3.73887700   -1.45160600
 H       -2.93681500   -3.45509000   -3.12632500
 H       -1.91867800   -2.90018600   -1.78420400
 C       -5.69838400   -1.67532500   -2.63172800
 H       -6.21703700   -2.27819200   -1.87929700
 H       -6.25261100   -0.73907600   -2.75947200
 H       -5.73662900   -2.21883300   -3.58416400
 C       -3.08183400   -0.23668700   -3.46986800
 H       -3.61500400    0.71444200   -3.56886900
 H       -2.03918800   -0.01351200   -3.22284200
 H       -3.10018600   -0.74036100   -4.44433700
 C       -4.42921700   -1.14556800    3.40993000
 H       -3.67538300   -0.38624200    3.64160200
 H       -5.41165700   -0.66197400    3.40258800
 H       -4.42550600   -1.88939700    4.21643200
 Ge       0.00412400   -0.92034600   -0.18174200
```

A.4. Compounds 18-23: Synthesis and Characterization of 1,1-dihalogenated cyclopentasilanes

1-chloro-3,3,4,4-tetramethyl-2,2,5,5-tetrakis(trimethylsilyl)-cyclopentasilane 18

```
Energy = -3704.7411991

 Si      -1.16005300   -1.02933500    1.97073400
 Si      -1.99002200   -0.05836300   -0.05993300
 Si      -3.04093600    2.06903800    0.31173500
```

Si	-3.39053700	-1.57129900	-1.29032400
Si	1.98722800	-0.05028600	-0.04029300
Si	1.15213100	-0.38423100	2.18024800
Si	3.41617200	1.86939400	-0.23550500
Si	3.01043500	-2.02950000	-0.93564800
C	-4.58286800	1.80827500	1.40889800
H	-5.07066100	2.77340500	1.59542100
H	-5.31337100	1.15372100	0.92194300
H	-4.32478800	1.36816600	2.37668600
C	-1.83332000	3.24502300	1.19986700
H	-1.51773500	2.84311600	2.16791900
H	-0.94278700	3.42104800	0.58887400
H	-2.31843800	4.21272800	1.37834800
C	-3.58913300	2.85732400	-1.33221000
H	-4.32779800	2.23917100	-1.85128300
H	-4.04574600	3.83570600	-1.13554400
H	-2.73579900	3.00472000	-1.99991000
C	-4.88066700	-2.09528400	-0.21699100
H	-4.55878100	-2.60723200	0.69610200
H	-5.48473400	-1.23037500	0.07575800
H	-5.52548700	-2.78235000	-0.77898400
C	-2.41127200	-3.13003700	-1.79181700
H	-1.55007900	-2.87398500	-2.41789600
H	-2.05140600	-3.67933500	-0.91706600
H	-3.05736300	-3.80184000	-2.37079900
C	-4.02982500	-0.72928500	-2.87774400
H	-3.20947900	-0.30094100	-3.46250100
H	-4.54858600	-1.46321700	-3.50699300
H	-4.73507200	0.07548500	-2.64822800
C	-1.25524800	-2.94135500	1.91661000
H	-2.29288400	-3.28242600	1.83140300
H	-0.69041600	-3.34940800	1.07381000
H	-0.83797700	-3.36062000	2.83997600
C	-2.14047400	-0.44000900	3.50834600
H	-2.09048800	0.64656200	3.62708100
H	-3.19469000	-0.72867800	3.43403400
H	-1.72751300	-0.89900100	4.41454500
C	1.26016200	1.22876900	3.20612900
H	0.80634800	1.07734900	4.19276200
H	2.30344500	1.52795200	3.35740500
H	0.73739900	2.05330400	2.71359300
C	2.13074900	-1.74094600	3.11535600
H	3.18747400	-1.46492100	3.20474900
H	1.72868200	-1.86757000	4.12764700
H	2.07176200	-2.70679900	2.60439400
C	2.51392400	3.46473300	0.27920100
H	1.65322300	3.64704800	-0.37051500
H	2.16717500	3.42065800	1.31554600
H	3.19836600	4.31756600	0.18674600
C	4.91163800	1.59952100	0.92334200
H	5.57825800	2.47004700	0.88332200
H	4.59231300	1.46740700	1.96257600
H	5.49132800	0.71727700	0.63429000
C	4.03149600	2.05350100	-2.02922400
H	4.62512600	2.97134900	-2.12499900
H	4.66356300	1.21203300	-2.33024400
H	3.18869000	2.12050400	-2.72390300
C	1.84758600	-3.52783800	-0.72110700
H	1.65546000	-3.74241000	0.33500500
H	0.88644200	-3.36186300	-1.21880800
H	2.30533600	-4.41962800	-1.16718000
C	3.34129300	-1.79696900	-2.79935600
H	4.06938600	-1.00153600	-2.98414900
H	3.73836100	-2.72612900	-3.22710900
H	2.42285600	-1.54228900	-3.33822400
C	4.65794500	-2.40508300	-0.04775800
H	5.09616300	-3.32703100	-0.45011200
H	5.38385000	-1.59848900	-0.19265400
H	4.51219200	-2.54186500	1.02844100
Si	0.00412700	0.21418200	-1.33508400
Cl	0.02378200	2.21653600	-2.36516800

H	0.01302000	-0.71391600	-2.51568300

3,3,4,4-tetramethyl-2,2,5,5-tetrakis-(trimethylsilyl)cyclopentasilane 19

Energy = -3245.1059021

Si	-1.15306500	-0.34448100	2.03424800
Si	-1.95854700	-0.00803800	-0.19749500
Si	-3.00539300	2.12983900	-0.46922900
Si	-3.38258200	-1.78550200	-0.93866800
Si	1.95852900	0.00806300	-0.19751200
Si	1.15307600	0.34434300	2.03426300
Si	3.38260300	1.78555300	-0.93856000
Si	3.00535800	-2.12980100	-0.46940500
C	-4.69146700	2.17623200	0.42658200
H	-5.15154100	3.16569700	0.31251700
H	-5.38202400	1.43478600	0.01103000
H	-4.58222500	1.97481300	1.49704300
C	-1.89433600	3.51186900	0.23763700
H	-1.74610000	3.39596300	1.31599500
H	-0.91097500	3.51602300	-0.24401500
H	-2.35835400	4.49088900	0.06417300
C	-3.28041100	2.48104100	-2.32430500
H	-3.96695500	1.75774300	-2.77485600
H	-3.70679600	3.48316000	-2.45805100
H	-2.33599100	2.43753100	-2.87651800
C	-4.86646500	-1.99260500	0.24660000
H	-4.53407600	-2.21140200	1.26686300
H	-5.48121200	-1.08715100	0.28075400
H	-5.50368600	-2.82157300	-0.08590400
C	-2.40691600	-3.42364100	-1.00523400
H	-1.53041900	-3.33282400	-1.65553400
H	-2.06655400	-3.72776800	-0.01091100
H	-3.04277600	-4.22312700	-1.40559700
C	-4.03922500	-1.41056000	-2.69138400
H	-3.21757200	-1.20612500	-3.38575300
H	-4.60169700	-2.27114000	-3.07460400
H	-4.70836500	-0.54399000	-2.69226800
C	-1.25247100	-2.18726800	2.55240000
H	-2.29207400	-2.53293500	2.57447200
H	-0.69166700	-2.83263000	1.87064000
H	-0.83397000	-2.31253400	3.55830300
C	-2.15845900	0.66570600	3.31692600
H	-2.09378000	1.74064300	3.12309400
H	-3.21548400	0.37742100	3.29496900
H	-1.77897500	0.47992600	4.32878400
C	1.25249600	2.18709400	2.55253500
H	0.83401700	2.31229600	3.55845500
H	2.29210100	2.53275200	2.57460300
H	0.69168000	2.83250100	1.87082800
C	2.15847800	-0.66593600	3.31686200
H	3.21550700	-0.37766500	3.29490200
H	1.77901500	-0.48020900	4.32873900
H	2.09377700	-1.74086000	3.12297000
C	2.40698500	3.42372600	-1.00499900
H	1.53047500	3.33297800	-1.65529100
H	2.06664900	3.72779900	-0.01065000
H	3.04286300	4.22321900	-1.40532000
C	4.86650900	1.99253100	0.24670200
H	5.50375000	2.82150200	-0.08575600
H	4.53414900	2.21126900	1.26698700
H	5.48123000	1.08705600	0.28077900
C	4.03922400	1.41070900	-2.69130400
H	4.60171800	2.27129700	-3.07447300
H	4.70834000	0.54412000	-2.69224000

```
 H       3.21756100    1.20633600   -3.38568100
 C       1.89429800   -3.51187900    0.23736600
 H       1.74606300   -3.39604200    1.31573100
 H       0.91093600   -3.51600500   -0.24428500
 H       2.35831700   -4.49088800    0.06383900
 C       3.28038200   -2.48087400   -2.32450500
 H       3.96692200   -1.75753900   -2.77500600
 H       3.70677600   -3.48298100   -2.45831800
 H       2.33596300   -2.43733500   -2.87671800
 C       4.69142800   -2.17626100    0.42640900
 H       5.15149200   -3.16572400    0.31229000
 H       5.38199400   -1.43479800    0.01090100
 H       4.58218100   -1.97489900    1.49688000
 Si     -0.00001300    0.00008400   -1.55969300
 H       0.00614100   -1.19543400   -2.47496600
 H      -0.00617600    1.19570900   -2.47482700
```

1,1-dichloro-3,3,4,4-tetramethyl-2,2,5,5-tetrakis(trimethylsilyl)cyclopentasilane 21

```
Energy = -4164.3763754
```

```
 Si     -1.15535800   -0.34557500    2.30887900
 Si     -2.02925500   -0.02533700    0.09339400
 Si     -3.08101200    2.13013600   -0.13028400
 Si     -3.43624600   -1.81383000   -0.69338600
 Si      2.02926700    0.02536000    0.09333400
 Si      1.15542600    0.34559000    2.30884400
 Si      3.43605600    1.81398900   -0.69348800
 Si      3.08118400   -2.13004800   -0.13026700
 C      -4.57472700    2.20461900    1.05708200
 H      -5.08906300    3.16634100    0.93554400
 H      -5.29758500    1.40975800    0.84992900
 H      -4.26460400    2.11804200    2.10240300
 C      -1.86271500    3.51680200    0.34014900
 H      -1.51966100    3.41694200    1.37494200
 H      -0.99103800    3.51368000   -0.32028800
 H      -2.35774200    4.49115900    0.24334600
 C      -3.69936500    2.38981800   -1.91145800
 H      -4.50739000    1.69431200   -2.15938600
 H      -4.08896600    3.40985800   -2.02021000
 H      -2.89094800    2.25414800   -2.63506900
 C      -5.04704100   -1.77774400    0.33354800
 H      -4.84579500   -1.85576800    1.40716000
 H      -5.61515800   -0.85826100    0.16038200
 H      -5.68434300   -2.62405100    0.04797400
 C      -2.60829000   -3.51347800   -0.47217500
 H      -1.66785000   -3.56519400   -1.02786900
 H      -2.40717400   -3.73544100    0.57943200
 H      -3.27497300   -4.29340800   -0.86150600
 C      -3.85090600   -1.54976000   -2.53222000
 H      -2.94263800   -1.56757800   -3.14153200
 H      -4.51133800   -2.35403000   -2.88038000
 H      -4.35888300   -0.59650200   -2.70413600
 C      -1.25532300   -2.18064600    2.84363600
 H      -2.29910400   -2.50514600    2.91985600
 H      -0.74389300   -2.84091700    2.13816400
 H      -0.78974000   -2.30621800    3.82843900
 C      -2.11137800    0.68884400    3.60729400
 H      -2.03851100    1.76128800    3.40365300
 H      -3.17122600    0.41284300    3.62527100
 H      -1.69819300    0.50470300    4.60624300
 C       1.25538500    2.18065800    2.84361500
 H       0.78993000    2.30618800    3.82848300
 H       2.29915800    2.50521600    2.91969800
 H       0.74382200    2.84091400    2.13822500
```

C	2.11148700	-0.68882600	3.60723000
H	3.17128500	-0.41263600	3.62535100
H	1.69816800	-0.50488700	4.60616100
H	2.03883400	-1.76125600	3.40344400
C	2.60801800	3.51357100	-0.47207500
H	1.66766700	3.56535700	-1.02791300
H	2.40671200	3.73532800	0.57953900
H	3.27474200	4.29359700	-0.86114200
C	5.04695900	1.77792900	0.33327200
H	5.68426900	2.62418100	0.04754900
H	4.84582500	1.85606700	1.40689500
H	5.61501800	0.85840400	0.16014600
C	3.85053400	1.55009200	-2.53238900
H	4.51082200	2.35447200	-2.88057100
H	4.35861500	0.59691200	-2.70443400
H	2.94219300	1.56783800	-3.14159500
C	1.86298400	-3.51675700	0.34029600
H	1.52014000	-3.41698400	1.37516800
H	0.99117400	-3.51358700	-0.31996600
H	2.35799300	-4.49110400	0.24331000
C	3.69949200	-2.38980100	-1.91144400
H	4.50724700	-1.69404900	-2.15955300
H	4.08944200	-3.40972100	-2.02007000
H	2.89096500	-2.25452000	-2.63500500
C	4.57495600	-2.20435900	1.05703700
H	5.08904100	-3.16626600	0.93590500
H	5.29799500	-1.40977800	0.84943500
H	4.26495700	-2.11721100	2.10234600
Si	-0.00001400	-0.00012300	-1.16393400
Cl	-0.02296100	1.73073000	-2.58951700
Cl	0.02288500	-1.73138000	-2.58903700

1,1-difluoro-3,3,4,4-tetramethyl-2,2,5,5-tetrakis(trimethylsilyl)cyclopentasilane 20

Energy = -3443.6693271

Si	1.14087200	0.33184800	2.14792500
Si	1.98517600	0.00743000	-0.04956200
Si	3.00513600	-2.11744700	-0.34194300
Si	3.37297200	1.78191700	-0.79755600
Si	-1.98517400	-0.00737200	-0.04958000
Si	-1.14087000	-0.33156000	2.14794400
Si	-3.37272100	-1.78209100	-0.79744900
Si	-3.00540000	2.11736800	-0.34212200
C	4.66006200	-2.17965900	0.57791600
H	5.11265900	-3.17197100	0.46092300
H	5.36976000	-1.44545200	0.18365600
H	4.54395100	-1.99175600	1.64990300
C	1.89754800	-3.49868600	0.32725300
H	1.71556400	-3.39880800	1.40170100
H	0.92910700	-3.52234300	-0.18194300
H	2.37998100	-4.47018300	0.16347100
C	3.31534500	-2.45514200	-2.17533700
H	4.01267300	-1.73739400	-2.61723200
H	3.74651200	-3.45637600	-2.29806500
H	2.38416400	-2.41560200	-2.74791300
C	4.86499300	1.97290400	0.35582600
H	4.56172300	2.19149200	1.38486100
H	5.48733000	1.07273000	0.37669500
H	5.49513300	2.80308500	0.01369400
C	2.42003700	3.41418300	-0.82833300
H	1.54435600	3.34705500	-1.48069300
H	2.08444100	3.71467300	0.16854300
H	3.06657200	4.21135900	-1.21542000
C	4.00369900	1.43466300	-2.54667000

H	3.17983700	1.25308800	-3.24394800
H	4.56806800	2.30030900	-2.91469500
H	4.67127000	0.56808900	-2.57789800
C	1.25031300	2.15500800	2.68065200
H	2.28939400	2.50035900	2.70244600
H	0.68865100	2.82032300	2.01928500
H	0.84219400	2.26909800	3.69175600
C	2.11745500	-0.66802400	3.43931200
H	2.08179800	-1.74384400	3.24511100
H	3.16981100	-0.36360800	3.45529200
H	1.70899000	-0.49622300	4.44199000
C	-1.25029600	-2.15467500	2.68084600
H	-0.84218500	-2.26866400	3.69196400
H	-2.28937500	-2.50003700	2.70266700
H	-0.68862200	-2.82005300	2.01954800
C	-2.11748100	0.66841700	3.43922900
H	-3.16982900	0.36397700	3.45523700
H	-1.70901600	0.49672600	4.44192500
H	-2.08185100	1.74422000	3.24492100
C	-2.41945200	-3.41415600	-0.82837400
H	-1.54385100	-3.34682500	-1.48082400
H	-2.08368300	-3.71460100	0.16845500
H	-3.06586200	-4.21145500	-1.21541500
C	-4.86455300	-1.97340500	0.35612400
H	-5.49456800	-2.80370600	0.01405500
H	-4.56110000	-2.19195400	1.38511600
H	-5.48706900	-1.07335900	0.37709600
C	-4.00372100	-1.43492100	-2.54648500
H	-4.56796500	-2.30067000	-2.91445900
H	-4.67146600	-0.56847700	-2.57762500
H	-3.17997800	-1.25317600	-3.24385700
C	-1.89808000	3.49879300	0.32713800
H	-1.71620500	3.39899100	1.40161100
H	-0.92958600	3.52256700	-0.18194900
H	-2.38063200	4.47021500	0.16325800
C	-3.31548700	2.45495600	-2.17555300
H	-4.01268700	1.73710500	-2.61748200
H	-3.74676600	3.45613300	-2.29835800
H	-2.38424900	2.41550400	-2.74803900
C	-4.66042300	2.17938200	0.57757400
H	-5.11315800	3.17162000	0.46048900
H	-5.36997000	1.44504900	0.18328000
H	-4.54438900	1.99155100	1.64958200
Si	0.00001000	0.00006500	-1.32637000
F	0.00013400	1.27947000	-2.35596900
F	-0.00009600	-1.27934000	-2.35596700

1,1-dibromo-3,3,4,4-tetramethyl-2,2,5,5-tetrakis(trimethylsilyl)cyclopentasilane 22

Energy = -3270.7748784

Si	-1.14565100	-0.37125400	2.57655300
Si	-2.02978600	-0.03648800	0.36599300
Si	-3.12675800	2.10621300	0.20728800
Si	-3.46913400	-1.81378600	-0.39386600
Si	2.02977200	0.03672400	0.36600000
Si	1.14560900	0.37269800	2.57636200
Si	3.46907500	1.81364000	-0.39485500
Si	3.12681000	-2.10604400	0.20848800
C	-4.56986600	2.14112400	1.45800800
H	-5.11168500	3.08999700	1.35559100
H	-5.28092800	1.32878400	1.28156600
H	-4.21563400	2.06480400	2.48951500
C	-1.92263600	3.51592400	0.64405800
H	-1.54416400	3.41452300	1.66633300

H	-1.07239200	3.53887000	-0.04328400
H	-2.44255400	4.47946600	0.57255900
C	-3.84883300	2.37460900	-1.53395100
H	-4.66215800	1.67053300	-1.73776400
H	-4.25866200	3.39003100	-1.60635400
H	-3.08810700	2.25790800	-2.30992600
C	-5.07208100	-1.74133600	0.64455300
H	-4.86555600	-1.78430600	1.71916100
H	-5.64155400	-0.82857800	0.44321500
H	-5.71054800	-2.59676400	0.39018000
C	-2.67902500	-3.52900000	-0.15195600
H	-1.73030000	-3.61009000	-0.68924600
H	-2.50163600	-3.74639300	0.90494300
H	-3.35751500	-4.29610000	-0.54646700
C	-3.90502100	-1.56316500	-2.22991900
H	-3.00751700	-1.59202500	-2.85414200
H	-4.57726400	-2.36472000	-2.56146000
H	-4.40787400	-0.60694800	-2.40143900
C	-1.20730100	-2.21426000	3.08864100
H	-2.24531900	-2.55022300	3.19042200
H	-0.71006200	-2.86037700	2.36057300
H	-0.71339200	-2.34683200	4.05863900
C	-2.10794800	0.62265800	3.90223000
H	-2.05045800	1.70028500	3.72231100
H	-3.16371300	0.33221500	3.92441500
H	-1.68250400	0.42163800	4.89287100
C	1.20722000	2.21598100	3.08747600
H	0.71325800	2.34904300	4.05738000
H	2.24522600	2.55201700	3.18913500
H	0.71000200	2.86170700	2.35904800
C	2.10791800	-0.62047000	3.90259200
H	3.16370500	-0.33008600	3.92454300
H	1.68254700	-0.41880900	4.89313500
H	2.05034400	-1.69820500	3.72334600
C	2.67887200	3.52896800	-0.15408700
H	1.73017500	3.60966700	-0.69148600
H	2.50141200	3.74703900	0.90266000
H	3.35734700	4.29584700	-0.54905500
C	5.07191700	1.74185000	0.64376100
H	5.71037300	2.59716900	0.38900100
H	4.86526200	1.78537800	1.71832000
H	5.64145100	0.82900800	0.44297700
C	3.90510700	1.56191800	-2.23072200
H	4.57745000	2.36322400	-2.56266600
H	4.40788600	0.60555700	-2.40165000
H	3.00765900	1.59050000	-2.85503800
C	1.92271000	-3.51554400	0.64601200
H	1.54422600	-3.41361200	1.66823100
H	1.07247400	-3.53886900	-0.04133000
H	2.44264500	-4.47911500	0.57502500
C	3.84888600	-2.37539100	-1.53260700
H	4.66222700	-1.67144400	-1.73680100
H	4.25869700	-3.39086000	-1.60445200
H	3.08816700	-2.25910600	-2.30865100
C	4.56993600	-2.14022700	1.45920300
H	5.11182700	-3.08910800	1.35723200
H	5.28093000	-1.32791700	1.28234700
H	4.21572400	-2.06343400	2.49068000
Si	0.00000200	-0.00028200	-0.90645000
Br	0.05136400	-1.83802900	-2.43916200
Br	-0.05130100	1.83651500	-2.44029800

1,1-diiodo-3,3,4,4-tetramethyl-2,2,5,5-tetrakis(trimethylsilyl)cyclopentasilane 23

Energy = -3266.8478909

Si	1.13443000	-2.82719200	0.39983100
Si	2.03142600	-0.62331000	0.04834000
Si	3.16894100	-0.51946700	-2.08210900
Si	3.50536700	0.09143400	1.81963100
Si	-2.03124500	-0.62384300	-0.04854000
Si	-1.13370900	-2.82702400	-0.40248600
Si	-3.50617400	0.09228000	-1.81843100
Si	-3.16782900	-0.52191800	2.08249600
C	4.57608300	-1.81168200	-2.08409700
H	5.14105000	-1.71839300	-3.02047400
H	5.27353400	-1.65846000	-1.25587400
H	4.19356100	-2.83370500	-2.02227100
C	1.98527600	-0.94239200	-3.51316400
H	1.59267300	-1.95949800	-3.41296800
H	1.14390800	-0.24530300	-3.55909200
H	2.52620100	-0.88331600	-4.46598900
C	3.96217200	1.19139800	-2.35043100
H	4.79229100	1.35167700	-1.65444700
H	4.36383600	1.25039700	-3.36999000
H	3.24182100	2.00296000	-2.22145800
C	5.08006000	-0.98866200	1.71860600
H	4.84558300	-2.05841000	1.71783500
H	5.66532700	-0.76620800	0.82106000
H	5.71481800	-0.78451400	2.59019200
C	2.74457800	-0.15813800	3.54742500
H	1.78810700	0.36101900	3.64945400
H	2.59060500	-1.21845300	3.76641500
H	3.43070500	0.24777200	4.30175900
C	3.99847300	1.91486100	1.58112900
H	3.12545000	2.57192400	1.62621500
H	4.69204000	2.21482900	2.37699400
H	4.49545200	2.07610000	0.61995700
C	1.14910600	-3.30566300	2.25229300
H	2.17797400	-3.44016700	2.60455600
H	0.67185000	-2.54667200	2.87714900
H	0.61813300	-4.25420900	2.39626500
C	2.11275600	-4.17873700	-0.54285000
H	2.07210900	-4.02969300	-1.62592400
H	3.16388800	-4.19426500	-0.23573700
H	1.68236400	-5.16267500	-0.32010700
C	-1.14802000	-3.30317800	-2.25555300
H	-0.61569700	-4.25076500	-2.40083300
H	-2.17676100	-3.43874800	-2.60778200
H	-0.67201400	-2.54268800	-2.87954200
C	-2.11182500	-4.17993100	0.53845600
H	-3.16324800	-4.19440900	0.23229500
H	-1.68207600	-5.16363000	0.31342700
H	-2.07011300	-4.03300400	1.62178300
C	-2.74667100	-0.15613100	-3.54695600
H	-1.78926600	0.36134800	-3.64872400
H	-2.59485900	-1.21642100	-3.76759000
H	-3.43239600	0.25220500	-4.30034500
C	-5.08091200	-0.98771500	-1.71713400
H	-5.71610100	-0.78307700	-2.58829100
H	-4.84646600	-2.05747200	-1.71705500
H	-5.66570300	-0.76569600	-0.81916800
C	-3.99874900	1.91560600	-1.57816300
H	-4.69407600	2.21591000	-2.37236300
H	-4.49353700	2.07649400	-0.61581100
H	-3.12578000	2.57262900	-1.62493200
C	-1.98329300	-0.94502500	3.51277700
H	-1.59063300	-1.96205900	3.41206300
H	-1.14198800	-0.24784400	3.55845900
H	-2.52369900	-0.88629800	4.46591800
C	-3.96183100	1.18839700	2.35218300
H	-4.79311800	1.34819200	1.65747000
H	-4.36202100	1.24697800	3.37234500
H	-3.24224200	2.00049000	2.22229300
C	-4.57433500	-1.81483200	2.08450200
H	-5.13960400	-1.72148700	3.02069300

H	-5.27164200	-1.66226200	1.25603800
H	-4.19129000	-2.83669400	2.02316600
Si	-0.00008800	0.66683900	0.00011000
I	-0.07688600	2.35857700	2.00503000
I	0.07609700	2.35892000	-2.00455800

A.5. Compounds 24-30: Reductive dehalogenation of 1,1-dihalogenated cyclopentasilanes.

3,3,4,4-tetramethyl-2,2,5,5-tetrakis(trimethylsilyl)cyclopentasil-1-ylene 24

Energy = -3244.4564999

Si	1.14029100	0.31905700	2.08388300
Si	1.80895600	0.02058800	-0.17176000
Si	0.00000500	0.00006400	-1.70587700
Si	2.78024900	-2.13023400	-0.54202100
Si	3.36827300	1.64495700	-0.92861700
Si	-1.80892000	-0.02055400	-0.17173900
Si	-1.14022000	-0.31906200	2.08388600
Si	-3.36820100	-1.64493200	-0.92860800
Si	-2.78036100	2.13021200	-0.54197600
C	4.51819300	-2.20233300	0.20693200
H	4.93126600	-3.21188900	0.08931100
H	5.20130600	-1.50494800	-0.28783600
H	4.51088800	-1.96562100	1.27542600
C	1.73996600	-3.49781400	0.25372700
H	1.65343900	-3.37463400	1.33739100
H	0.72828100	-3.53151500	-0.16322700
H	2.20704000	-4.47298600	0.06794600
C	2.89965900	-2.51491100	-2.39114900
H	3.46607100	-1.75596500	-2.93787000
H	3.40142500	-3.47960100	-2.53708400
H	1.90918400	-2.57965600	-2.85338900
C	4.80373100	1.84284900	0.29305000
H	4.45319000	2.14879500	1.28380900
H	5.36984200	0.91405100	0.41367100
H	5.49855300	2.61268200	-0.06497000
C	2.50345600	3.32240900	-1.10155500
H	1.68661500	3.27519600	-1.83008400
H	2.08850900	3.67045500	-0.15039500
H	3.21447400	4.08120400	-1.45092700
C	4.08075900	1.18996200	-2.62300800
H	3.29070800	0.97729900	-3.35035500
H	4.67546100	2.02662500	-3.01010800
H	4.73788600	0.31575100	-2.57229400
C	1.29796900	2.14129700	2.61472600
H	2.34560500	2.46083500	2.63078000
H	0.75181800	2.81574300	1.94954600
H	0.89686300	2.27441900	3.62629300
C	2.16121600	-0.69553000	3.33121900
H	2.09103600	-1.77175700	3.14870600
H	3.21952000	-0.41518900	3.28852500
H	1.81064200	-0.50778100	4.35300000
C	-1.29787900	-2.14132500	2.61465300
H	-0.89675900	-2.27449100	3.62620900
H	-2.34551500	-2.46086800	2.63070600
H	-0.75173700	-2.81574000	1.94943200
C	-2.16115200	0.69546200	3.33126800
H	-3.21945500	0.41511900	3.28856200
H	-1.81057700	0.50767300	4.35304100
H	-2.09097800	1.77169700	3.14880100

C	-2.50325200	-3.32226700	-1.10203700
H	-1.68656000	-3.27483000	-1.83071700
H	-2.08808100	-3.67045800	-0.15102700
H	-3.21426300	-4.08106400	-1.45141900
C	-4.80341400	-1.84319300	0.29328700
H	-5.49823700	-2.61301300	-0.06475800
H	-4.45266000	-2.14930900	1.28391900
H	-5.36958000	-0.91446700	0.41420100
C	-4.08102500	-1.18965000	-2.62277900
H	-4.67576500	-2.02626400	-3.00992700
H	-4.73817100	-0.31546700	-2.57177900
H	-3.29111800	-0.97681800	-3.35023300
C	-1.73986200	3.49794600	0.25321600
H	-1.65295900	3.37493200	1.33686800
H	-0.72832500	3.53162700	-0.16409300
H	-2.20704000	4.47307100	0.06744900
C	-2.90040900	2.51459600	-2.39112600
H	-3.46698500	1.75554400	-2.93753500
H	-3.40225200	3.47924800	-2.53704500
H	-1.91009200	2.57929700	-2.85371200
C	-4.51806000	2.20236100	0.20753400
H	-4.93121300	3.21188300	0.08989800
H	-5.20130500	1.50487400	-0.28690700
H	-4.51039200	1.96580700	1.27606200

1-(triethylsilyl)-3,3,4,4-tetramethyl-2,2,5,5-tetrakis(trimethylsilyl)cyclopentasilane 25

Energy = -3772.3383367

Si	0.91450400	-2.89512100	0.16646300
Si	1.92070600	-0.73630600	0.04606100
Si	3.33301800	-0.64534000	-1.86181400
Si	3.19522700	-0.25755900	1.99336500
Si	-1.98606800	-0.45809200	-0.03267200
Si	-1.28083000	-2.63102000	-0.68140200
Si	-3.62340000	0.29771100	-1.58143800
Si	-3.00531700	-0.54666000	2.11675100
C	4.85069500	-1.74465200	-1.60795800
H	5.48495100	-1.71647200	-2.49984600
H	5.45597000	-1.40980200	-0.76210100
H	4.57190100	-2.78546600	-1.43066100
C	2.42906300	-1.21627700	-3.41804900
H	2.08314400	-2.24887100	-3.34833600
H	1.56244000	-0.58284900	-3.62051500
H	3.10150300	-1.14681900	-4.27922200
C	3.93771600	1.11114200	-2.20495900
H	4.48091700	1.53702800	-1.35931700
H	4.61429100	1.10165800	-3.06584200
H	3.10608500	1.77681500	-2.44784000
C	4.11766700	-1.80005800	2.57742600
H	3.43457600	-2.57830100	2.92091300
H	4.74306800	-2.22354200	1.78781300
H	4.77287000	-1.53801500	3.41456600
C	2.08816400	0.33948600	3.40241500
H	1.53522200	1.24024000	3.12605700
H	1.36339600	-0.42480500	3.69216300
H	2.69311600	0.57513400	4.28368600
C	4.51368600	1.05932500	1.67541900
H	4.09511200	1.99375900	1.29948000
H	5.03703500	1.27875400	2.61197200
H	5.26008600	0.71125000	0.95723700
C	0.84577700	-3.56601700	1.94222100
H	1.83278200	-3.91770000	2.25221700
H	0.50916100	-2.82204400	2.66429800
H	0.16293600	-4.41914300	1.99453500

C	1.84236800	-4.22005600	-0.82910900
H	1.92676500	-3.97388400	-1.88831500
H	2.85053600	-4.36931500	-0.43340700
H	1.31277800	-5.17442800	-0.74931000
C	-1.20842500	-2.74799000	-2.57350300
H	-0.80558000	-3.71814300	-2.87905700
H	-2.20373800	-2.64892500	-3.01358300
H	-0.57156300	-1.97063000	-2.99939800
C	-2.40155300	-4.03596800	-0.06935600
H	-3.41892500	-3.92743400	-0.45448500
H	-2.01595400	-4.99847200	-0.41898800
H	-2.45473600	-4.07584300	1.02060800
C	-2.84957100	0.77723100	-3.23470600
H	-2.14072600	1.60104700	-3.13343600
H	-2.31890200	-0.06352200	-3.68636900
H	-3.63484400	1.09143700	-3.93010500
C	-4.88796100	-1.06782100	-1.92051200
H	-5.65198900	-0.70095600	-2.61369100
H	-4.42155100	-1.94383900	-2.37735000
H	-5.39384400	-1.39624300	-1.01051500
C	-4.56830400	1.79378500	-0.91360100
H	-5.27688900	2.15229800	-1.66718900
H	-5.14005400	1.54040400	-0.01762800
H	-3.90258400	2.62289600	-0.66287800
C	-1.94992600	-1.44393200	3.39854500
H	-1.75463600	-2.48077100	3.11924700
H	-0.99032200	-0.94504300	3.55077300
H	-2.47547700	-1.45101400	4.35900900
C	-3.44030100	1.13708200	2.84994100
H	-4.02097900	1.75622600	2.16361000
H	-4.04492000	0.98050600	3.74952800
H	-2.55141100	1.69813300	3.14086000
C	-4.63023700	-1.49985600	1.94316700
H	-5.06752500	-1.65408900	2.93508100
H	-5.35946000	-0.94744700	1.34588900
H	-4.48990200	-2.47946100	1.48256800
Si	0.06595200	0.69594300	-0.42553600
H	0.07879800	0.64879300	-1.92984600
Si	0.15301200	3.03891500	0.00887600
C	-0.90173100	3.42863400	1.53546000
H	-1.91675600	3.08432200	1.31339000
H	-0.55335300	2.78959800	2.35475300
C	-0.94445700	4.88499700	2.00490900
H	-1.25852900	5.56264000	1.20688400
H	-1.64844100	5.01266700	2.83241100
H	0.03167000	5.22459400	2.35866100
C	1.94324000	3.62466900	0.27011400
H	2.23345500	3.32834700	1.28435700
H	2.59621700	3.05748000	-0.39950900
C	2.19531900	5.12315800	0.07672900
H	1.59521600	5.73326800	0.75433400
H	3.24480900	5.37334900	0.25761000
H	1.95847000	5.44399400	-0.94035900
C	-0.58925100	3.94145800	-1.49063900
H	-1.62787000	3.61284700	-1.60718800
H	-0.64793700	5.00539100	-1.22971500
C	0.16315900	3.77594700	-2.81148000
H	1.19388900	4.13185000	-2.73555100
H	0.20514300	2.72886700	-3.11990500
H	-0.31501400	4.33738200	-3.61903000

3,3,4,4-tetramethyl-2,2,5,5-tetrakis(trimethylsilyl)cyclopentasil-1-ylene·Isoprene 26

Energy = -3439.8685286

Si	-1.01700900	-2.38259200	-0.65155800
Si	-1.90447600	-0.27031100	-0.02860800
Si	-3.06442100	-0.45191700	2.03781200
Si	-3.38948500	0.54590300	-1.69077500
Si	1.98751500	-0.16082000	0.00621800
Si	1.23959800	-2.41482400	0.06782300
Si	3.51902700	0.32186600	1.76092800
Si	3.04992400	0.34163400	-2.06256500
C	-4.54215300	-1.62495000	1.91216000
H	-5.00820200	-1.72589500	2.89791500
H	-5.30374600	-1.24716600	1.22640000
H	-4.25307200	-2.62238100	1.57647200
C	-1.92099800	-1.13054900	3.38208200
H	-1.57099000	-2.13602000	3.13685400
H	-1.04301500	-0.50003700	3.53793900
H	-2.46070900	-1.19051000	4.33270900
C	-3.74058200	1.21988100	2.60610400
H	-4.58103600	1.53405800	1.98318000
H	-4.10578000	1.13804000	3.63507500
H	-2.99429200	2.01546900	2.57438300
C	-4.79273400	-0.68831900	-1.97431600
H	-4.41368200	-1.66370200	-2.28782500
H	-5.39370600	-0.83883000	-1.07543800
H	-5.45809100	-0.32104200	-2.76234900
C	-2.53961500	0.81129300	-3.35823000
H	-1.72159100	1.53208400	-3.30254400
H	-2.13783200	-0.11893000	-3.76359900
H	-3.27153000	1.19790500	-4.07522100
C	-4.14620000	2.19383100	-1.15978500
H	-3.38213300	2.91237500	-0.85479700
H	-4.71103900	2.63071700	-1.98962800
H	-4.83390800	2.06872800	-0.32060100
C	-1.05060700	-2.62339000	-2.53552200
H	-2.07635200	-2.66024000	-2.91237700
H	-0.52984000	-1.82143400	-3.06147100
H	-0.56694800	-3.56831200	-2.80001000
C	-1.96814100	-3.85155800	0.08575700
H	-1.99875600	-3.82212500	1.17655800
H	-2.99802300	-3.87314200	-0.28074900
H	-1.49333400	-4.79205400	-0.20993000
C	1.33233800	-3.13699300	1.81959600
H	0.87941300	-4.13273200	1.83461800
H	2.37157400	-3.24200800	2.14238300
H	0.81153900	-2.51903500	2.55271100
C	2.23168000	-3.58873500	-1.04664000
H	3.29203300	-3.59306400	-0.78188100
H	1.85609200	-4.61007700	-0.93083100
H	2.14668100	-3.32220900	-2.10199100
C	2.83992400	-0.14932000	3.46032700
H	1.89868100	0.35625800	3.68548900
H	2.67150800	-1.22381800	3.54790600
H	3.56321900	0.13951500	4.23003000
C	5.12335900	-0.64328500	1.49736700
H	5.80793100	-0.46814300	2.33345200
H	4.94342300	-1.71922200	1.43381300
H	5.63322600	-0.33459400	0.58175200
C	3.94653600	2.16272500	1.80738200
H	4.61823000	2.36230300	2.64871500
H	4.45013300	2.48628800	0.89483500
H	3.06019300	2.78830200	1.93390700
C	1.80451200	0.35589300	-3.48222200
H	1.34688500	-0.62567800	-3.62387000
H	1.00356900	1.07928100	-3.31487900
H	2.30778000	0.62409900	-4.41673400
C	3.88822000	2.03621800	-2.00149500
H	4.76391400	2.01890100	-1.34846100
H	4.23156300	2.30859300	-3.00482300
H	3.22470300	2.82829900	-1.64904000
C	4.39674100	-0.91481200	-2.48217600
H	4.91715300	-0.59900600	-3.39225800
H	5.13967200	-0.99722000	-1.68587000

H	3.98718900	-1.91018900	-2.66022700
Si	0.00424500	1.14026300	0.26285000
C	-0.77023700	5.17710100	-0.33657500
H	0.07767900	5.59417500	-0.89039300
H	-1.61065100	5.13726200	-1.03761400
H	-1.02685300	5.86933500	0.46742000
C	-0.44380100	3.81329600	0.18700700
C	-0.44405600	3.49431700	1.48665300
H	-0.69424300	4.24217100	2.23670900
C	-0.06396200	2.10651800	1.92059700
H	0.90698400	2.10910800	2.42698700
H	-0.77511000	1.69224100	2.63915500
C	-0.06594200	2.73418900	-0.80070700
H	-0.78995900	2.67948700	-1.61882500
H	0.89892000	2.96486100	-1.26708600

3,3,4,4-tetramethyl-2,2,5,5-tetrakis(trimethylsilyl)cyclopentasil-1-ylene·PMe$_3$ 27

Energy = -3705.6243651

Si	1.11363500	-2.16002700	1.03311700
Si	1.93355400	-0.19291700	-0.02507600
Si	3.25340400	-0.81203100	-1.90649400
Si	3.34101900	0.92627500	1.53100500
Si	-1.94124400	-0.16143500	-0.02780000
Si	-1.13798800	-2.37086200	0.33919500
Si	-3.67491900	-0.35078300	-1.64759700
Si	-2.90406500	0.70770200	1.95996500
C	4.86619100	-1.70337200	-1.47386900
H	5.33688800	-2.07612800	-2.38951000
H	5.58159000	-1.03718200	-0.98607500
H	4.69696500	-2.55724300	-0.81461400
C	2.25669400	-1.93597900	-3.05183200
H	1.99802900	-2.88571700	-2.57970800
H	1.33054900	-1.44535600	-3.36099500
H	2.83926500	-2.15834200	-3.95184700
C	3.70599700	0.71816400	-2.92476000
H	4.32219200	1.42706200	-2.36659000
H	4.26971800	0.41788000	-3.81399500
H	2.80397700	1.23465800	-3.26174000
C	4.73400200	-0.23463300	2.07349500
H	4.35068500	-1.13268600	2.56266900
H	5.35208600	-0.55421600	1.23295000
H	5.38233800	0.28139400	2.78958900
C	2.46215500	1.47404600	3.11412300
H	1.62667600	2.15197500	2.93319800
H	2.07772800	0.61430100	3.66539800
H	3.17597800	1.99207600	3.76313900
C	4.18271600	2.45328200	0.78700000
H	3.47345400	3.23229800	0.49789000
H	4.86570200	2.89072800	1.52256900
H	4.77132700	2.19468300	-0.09621900
C	1.16194500	-2.05095400	2.92920800
H	2.18733200	-1.98070600	3.30110100
H	0.60258900	-1.19671600	3.31183600
H	0.71999000	-2.95750500	3.35421200
C	2.09288500	-3.72800000	0.59246400
H	2.10327700	-3.92599900	-0.48049000
H	3.12970100	-3.65223600	0.93195900
H	1.64591800	-4.59557700	1.08788600
C	-1.15786800	-3.36147100	-1.27995700
H	-0.71602400	-4.34951900	-1.11898200
H	-2.17617900	-3.50762000	-1.64797300
H	-0.58494600	-2.86116200	-2.06299900
C	-2.14252300	-3.35585000	1.61447500

H	-3.18438700	-3.46175800	1.30118700
H	-1.72407600	-4.36091500	1.72545600
H	-2.13067200	-2.88014600	2.59722200
C	-2.95414100	-0.66984800	-3.36226100
H	-2.23138200	0.10208500	-3.63666600
H	-2.43589300	-1.62954900	-3.40781700
H	-3.75325200	-0.68029100	-4.11071300
C	-4.86339100	-1.76446500	-1.22910500
H	-5.65417800	-1.81832000	-1.98457700
H	-4.35683300	-2.73188700	-1.21236100
H	-5.34141200	-1.62324000	-0.25717200
C	-4.73812300	1.21460600	-1.76969900
H	-5.49287300	1.08183600	-2.55185200
H	-5.26744700	1.42426300	-0.83706700
H	-4.14843900	2.09634400	-2.03026400
C	-1.71166500	0.64505200	3.42327400
H	-1.53107700	-0.38533700	3.73730800
H	-0.74566300	1.09373700	3.18231400
H	-2.13228200	1.18332000	4.27868300
C	-3.47234900	2.50765100	1.77395100
H	-4.17485300	2.63035800	0.94661200
H	-3.98614500	2.81605200	2.69052100
H	-2.64505800	3.20283700	1.61878100
C	-4.45292700	-0.26940600	2.43741900
H	-4.83882300	0.09593100	3.39504700
H	-5.24734100	-0.15218800	1.69635200
H	-4.24899000	-1.33657800	2.54395600
Si	-0.00510900	0.66537000	-1.16951400
C	0.25523500	3.74914500	0.80082400
H	-0.46836700	3.37190900	1.52170500
H	1.25563400	3.52628200	1.16919400
C	1.31103800	3.66721000	-1.85574900
H	1.31337800	4.75363100	-1.74262600
H	2.28748900	3.27217900	-1.57664400
C	-1.52673900	3.65043100	-1.45509600
H	-2.36423800	3.36992300	-0.81739500
H	-1.44410100	4.73902000	-1.48351200
P	0.01463400	2.91170800	-0.81327700
H	-1.70805800	3.27186900	-2.46125300
H	1.12095100	3.40646300	-2.89679800
H	0.14127700	4.83167200	0.70023500

3,3,4,4-tetramethyl-2,2,5,5-tetrakis(trimethylsilyl)cyclopentasil-1-ylene·PEt_3 28

Energy = -3823.5578653

Si	1.10636100	-2.62086000	0.57514600
Si	1.93549800	-0.47308800	-0.03582600
Si	3.28139600	-0.70447300	-1.98370100
Si	3.35639400	0.22944100	1.74280100
Si	-1.92468800	-0.41547900	-0.02986900
Si	-1.14127500	-2.65722100	-0.14864600
Si	-3.76030400	-0.34337300	-1.54907100
Si	-2.85112900	0.01044100	2.11857000
C	4.88113700	-1.68922600	-1.74778500
H	5.35705600	-1.84257700	-2.72206200
H	5.59597500	-1.15643000	-1.11655700
H	4.70711900	-2.67216600	-1.30560600
C	2.28287000	-1.54039400	-3.35309200
H	2.05291200	-2.58210200	-3.11978300
H	1.34044500	-1.01285800	-3.52017800
H	2.85141000	-1.52627200	-4.28874600
C	3.78389100	0.99699600	-2.64473100
H	4.40099400	1.55516300	-1.93626000
H	4.36348200	0.87916200	-3.56621900

H	2.90381800	1.59807700	-2.88309600
C	4.69371500	-1.08444500	2.00911100
H	4.26294800	-2.06796000	2.20875800
H	5.35485400	-1.18212100	1.14664800
H	5.30875800	-0.80956700	2.87265600
C	2.49209200	0.43187900	3.41465400
H	3.21725000	0.80136300	4.14758000
H	1.65765200	1.13408900	3.39219200
H	2.11163800	-0.52352600	3.77945200
C	4.27324900	1.85228900	1.39236600
H	3.60616800	2.71414600	1.31787500
H	4.97322000	2.05229900	2.21049000
H	4.85462200	1.79933100	0.46891700
C	1.14996300	-2.92815300	2.44990400
H	2.17470800	-2.97221600	2.82703600
H	0.61501000	-2.16206300	3.01143000
H	0.67838000	-3.89183600	2.66555600
C	2.08883800	-4.05787100	-0.18714400
H	2.11092800	-4.02071100	-1.27729600
H	3.12172400	-4.05588400	0.17136700
H	1.64060000	-5.01225600	0.10631000
C	-1.15861600	-3.27369800	-1.94400500
H	-0.69261300	-4.26202600	-2.00264500
H	-2.17670100	-3.36372100	-2.32982100
H	-0.60564000	-2.60232200	-2.60376900
C	-2.15791000	-3.88732100	0.88175600
H	-3.20231100	-3.90411000	0.56005000
H	-1.75707000	-4.89864000	0.76255100
H	-2.13554800	-3.64376800	1.94617700
C	-3.16283600	-0.26025800	-3.33949900
H	-2.48213300	0.57611100	-3.51110500
H	-2.62637000	-1.17115800	-3.61348400
H	-4.01619300	-0.15435000	-4.01726900
C	-4.83794200	-1.89142400	-1.37956100
H	-5.68027100	-1.83157800	-2.07667700
H	-4.28369500	-2.80400800	-1.60829200
H	-5.24643000	-1.99415100	-0.37211800
C	-4.91927100	1.12379900	-1.23569500
H	-5.71375400	1.13043600	-1.98921700
H	-5.39774700	1.04927100	-0.25602600
H	-4.40668200	2.08596700	-1.28658200
C	-1.65567900	-0.35901700	3.53479000
H	-1.47002600	-1.43202800	3.62010700
H	-0.69038800	0.13561000	3.40906000
H	-2.08644900	-0.02216700	4.48335700
C	-3.41620300	1.81104900	2.31610500
H	-4.11325300	2.10664800	1.52876900
H	-3.93376200	1.92168100	3.27486800
H	-2.58456000	2.51861400	2.31418500
C	-4.39697100	-1.04210400	2.41374100
H	-4.75393200	-0.88258900	3.43682400
H	-5.20976500	-0.76961200	1.73676600
H	-4.20061800	-2.10895300	2.29125300
Si	0.01026100	0.62017500	-1.01546300
C	0.27511000	3.03191800	1.66165700
H	-0.39838400	2.33067700	2.15743200
H	1.28778600	2.69304200	1.89205800
C	0.04894100	4.45471800	2.16299300
H	-0.98358900	4.77757600	2.01866000
H	0.26127800	4.51018400	3.23345800
H	0.69948400	5.17886300	1.66723000
C	1.54347500	3.61790100	-0.84701700
H	1.74806800	4.47470300	-0.19845200
H	2.37915200	2.92348200	-0.72934300
C	1.43245500	4.06728200	-2.29829000
H	0.70406700	4.87169500	-2.41615900
H	2.39705800	4.44486200	-2.64410900
H	1.14204100	3.24216900	-2.95072300
C	-1.41120000	3.71251600	-0.60461200
H	-2.16724800	3.45253100	0.14156600
H	-1.16952900	4.76889900	-0.45181500

C	-1.96109300	3.47450100	-2.00557200
H	-1.26933400	3.79866300	-2.78178300
H	-2.16378900	2.41671100	-2.17185400
H	-2.89424700	4.02774400	-2.13654500
P	0.08320800	2.73083000	-0.15017600

1-hydroxy-3,3,4,4-tetramethyl-2,2,5,5-tetrakis(trimethylsilyl)cyclopentasilane 29

Energy = -3320.9860832

Si	1.13876400	0.02139000	2.09551900
Si	1.95014900	-0.01987500	-0.13261800
Si	3.05443600	-2.05348700	-0.64466100
Si	3.32895200	1.84953000	-0.61572000
Si	-1.94762600	-0.02847600	-0.13576500
Si	-1.12405100	-0.68736100	1.99237100
Si	-3.42652400	-1.63745900	-1.05578700
Si	-2.95802000	2.11947300	-0.10607600
C	4.69642500	-2.18936200	0.27910700
H	5.16940400	-3.15286800	0.06431300
H	5.39209300	-1.40376800	-0.02530700
H	4.56077000	-2.11618500	1.36035300
C	1.97851400	-3.53628500	-0.18603700
H	1.76705900	-3.57705300	0.88451600
H	1.02534800	-3.51541100	-0.72022300
H	2.49032300	-4.46484600	-0.45884000
C	3.40097300	-2.16520300	-2.49818600
H	4.05613600	-1.36377900	-2.84509200
H	3.89008700	-3.11780700	-2.72602600
H	2.47657400	-2.11909500	-3.07878600
C	4.78120500	1.94707900	0.58992600
H	4.44384100	2.07110600	1.62145900
H	5.40576100	1.05180800	0.54890800
H	5.41329900	2.80635900	0.34324600
C	2.34303600	3.45386800	-0.50749000
H	1.48074300	3.43211700	-1.17754600
H	1.98023300	3.63607800	0.50615500
H	2.97631800	4.30052900	-0.79174100
C	4.04372000	1.72177100	-2.36242600
H	3.26711700	1.60673600	-3.12255100
H	4.60438100	2.63197900	-2.59860200
H	4.72999200	0.87735000	-2.45760800
C	1.20458000	1.76756000	2.83237400
H	2.23488300	2.12242400	2.91716400
H	0.64703600	2.48760900	2.23176900
H	0.77216300	1.76337200	3.83735300
C	2.14003200	-1.09957400	3.25471200
H	2.13305200	-2.14191200	2.93002700
H	3.18116500	-0.77019400	3.31044300
H	1.72655000	-1.06277300	4.26702600
C	-1.19504800	-2.57252700	2.20125100
H	-0.78426500	-2.85730100	3.17454300
H	-2.22553300	-2.93508500	2.15976700
H	-0.62418100	-3.09604100	1.43264200
C	-2.13423700	0.05453900	3.41796000
H	-3.17453000	-0.27835300	3.36898600
H	-1.72709200	-0.27135500	4.37975500
H	-2.12954600	1.14605800	3.40595700
C	-2.50935700	-3.24173800	-1.44265800
H	-1.69244800	-3.07245300	-2.14788400
H	-2.09234000	-3.69873600	-0.54276800
H	-3.19774500	-3.96292500	-1.89501500
C	-4.82579000	-2.02832800	0.15251500
H	-5.50071200	-2.77192500	-0.28327800
H	-4.44354200	-2.43677100	1.09072700

H	-5.41627900	-1.14120400	0.39174500
C	-4.18672900	-0.99550200	-2.66057400
H	-4.78018100	-1.78412800	-3.13429300
H	-4.84919800	-0.14573200	-2.48030300
H	-3.42060800	-0.67879400	-3.37219000
C	-1.87601300	3.37689300	0.79405400
H	-1.69462300	3.09672300	1.83385200
H	-0.91107400	3.49799200	0.29702500
H	-2.37321600	4.35239800	0.79578100
C	-3.23515600	2.73942400	-1.86300300
H	-3.92785100	2.10283500	-2.41702600
H	-3.65419000	3.75064400	-1.83859500
H	-2.28987900	2.76492900	-2.40885800
C	-4.62275500	2.02759800	0.78466200
H	-5.07077300	3.02507100	0.83977600
H	-5.32542200	1.37996500	0.25484900
H	-4.52049100	1.65060500	1.80476400
Si	-0.00483300	0.06458700	-1.47780500
H	0.03116300	-1.10409300	-2.42257500
O	-0.09197700	1.45316400	-2.44108800
H	0.52819000	1.50280500	-3.16863800

1-methoxy-3,3,4,4-tetramethyl-2,2,5,5-tetrakis(trimethylsilyl)cyclopentasilane 30

Energy = -3360.2809239

Si	1.15542100	-0.63196000	2.12920100
Si	1.98960700	-0.03897200	-0.01008100
Si	3.14622800	-1.81874000	-1.06650000
Si	3.26528300	1.96012000	-0.01556000
Si	-1.92202200	-0.04812300	-0.05713300
Si	-1.10368500	-1.28255400	1.79789600
Si	-3.50217400	-1.32250500	-1.28526700
Si	-2.87209500	2.02310300	0.60437900
C	4.81482100	-2.15171800	-0.24473300
H	5.31983900	-2.98350000	-0.74629100
H	5.47279700	-1.28150600	-0.30414400
H	4.70237900	-2.41671900	0.80897600
C	2.12138300	-3.40433100	-1.00855100
H	1.93559400	-3.73859000	0.01430200
H	1.15650800	-3.26885900	-1.50335100
H	2.65106100	-4.20821400	-1.52994200
C	3.44426400	-1.40688300	-2.88496200
H	4.08183800	-0.52975300	-3.00961700
H	3.93490400	-2.25120700	-3.37994300
H	2.50383300	-1.21434200	-3.40662800
C	4.70689700	1.81234900	1.19781000
H	4.35958000	1.67181200	2.22396700
H	5.36289900	0.97448900	0.95044600
H	5.30946100	2.72610500	1.17380900
C	2.19218400	3.42761700	0.48125300
H	1.34221500	3.52120800	-0.19827400
H	1.81472000	3.33131700	1.50137300
H	2.77481800	4.35296300	0.42765000
C	3.95934700	2.29888600	-1.73636800
H	3.15831100	2.33919400	-2.47743200
H	4.47677100	3.26375200	-1.74262100
H	4.67703000	1.53638400	-2.04663800
C	1.22889500	0.82295500	3.34323100
H	2.26256700	1.12301500	3.53297300
H	0.68576100	1.69479300	2.97709700
H	0.78708000	0.53094400	4.30064300
C	2.13655900	-2.04759300	2.92710100
H	2.12157600	-2.95620200	2.32235100

H	3.18030500	-1.75865600	3.07724100
H	1.71691500	-2.29190100	3.90763800
C	-1.13993500	-3.14778800	1.44592200
H	-0.71573100	-3.69449000	2.29343500
H	-2.16317200	-3.50366100	1.30101900
H	-0.56277500	-3.41049600	0.55761900
C	-2.13230600	-1.00238900	3.36805700
H	-3.16173100	-1.34134800	3.22348900
H	-1.71047100	-1.56935100	4.20329800
H	-2.16223200	0.04920900	3.65977500
C	-2.66193200	-2.77449700	-2.15170200
H	-1.87950200	-2.43526500	-2.83413900
H	-2.20883300	-3.46456300	-1.43677000
H	-3.39875800	-3.33489900	-2.73620200
C	-4.84443900	-2.01112600	-0.14609700
H	-5.56672500	-2.59166800	-0.72909500
H	-4.42478700	-2.67398700	0.61421900
H	-5.39161200	-1.21769700	0.36778300
C	-4.34511400	-0.26524000	-2.60626500
H	-5.03122100	-0.88379600	-3.19376100
H	-4.92819400	0.54644200	-2.16504600
H	-3.62176800	0.17496300	-3.29680400
C	-1.80327400	2.92526500	1.87078400
H	-1.69715000	2.35995000	2.79911200
H	-0.80497300	3.12820900	1.47773000
H	-2.26390100	3.88686300	2.11950600
C	-3.07758600	3.16787800	-0.88195100
H	-3.68898700	2.71993900	-1.66832400
H	-3.56476700	4.09683100	-0.56845100
H	-2.10688800	3.42544900	-1.31083800
C	-4.57358100	1.73153500	1.37419100
H	-4.99618400	2.68431700	1.70927000
H	-5.27289400	1.29448200	0.65748200
H	-4.52130000	1.06770700	2.24026500
Si	0.05584400	0.26020600	-1.33809100
H	0.04854400	-0.77367900	-2.43066900
O	0.17458200	1.74072900	-2.13256600
C	-0.44801700	1.98606500	-3.37357300
H	-0.12789600	2.96738800	-3.72919900
H	-0.16375500	1.23518900	-4.12055200
H	-1.54044200	1.99163600	-3.28594000