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Synthesis and Reactivity of Siloles, Germoles, Yttrium Complexes, and Silatranes

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AFFIDAVIT

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ABBREVIATIONS

18-cr-6	18-crown-6 [$(C_2H_4O)_6$]
AIE	aggregation-induced emission
ASE	aromatic stabilization energy
Cp	cyclopentadienyl ($-C_5H_5$)
D	degree of C-C bond equalization
d	days
DCM	dichloromethane
equiv.	equivalents
h	hours
HOMO	highest occupied molecular orbital
HypSi	hypersilyl [$-Si(SiMe_3)_3$]
KC_8	potassium graphite (intercalation compound)
Li[Naph]	lithium naphthalenide
LUMO	lowest unoccupied molecular orbital
min	minutes
NICS	nuclear independent chemical shift
NMR	nuclear magnetic resonance
ppm	parts per million
rt	room temperature
S_a	silatrane [$-Si(OCH_2CH_2)_3N$]
Tf	triflate ($-SO_2CF_3$)
THF	tetrahydrofuran
TiPS	triisopropylsilyl [$-Si(^iPr)_3$]
TLC	thin layer chromatography
TMEDA	N,N,N’,N’-tetramethylethylenediamine
TMS	trimethylsilyl ($-SiMe_3$)

1. INTRODUCTION

The chemistry of f-elements and especially lanthanides is a fast growing discipline[1] with many topics, fundamental questions and novel compounds yet to be discovered. Recently, Evans and *co*-workers reported a new type of reaction, the sterically induced reduction, which enables lanthanocenes to process a two electron reduction with involvement of the Cp ligand.[2] Participation of the Cp ligand is quite unusual, since it is typically considered as a spectator ligand.

This behavior of lanthanocenes raised the question, whether germole- or silole containing lanthanocenes can be synthesized. If so, how is the Cp-analogous compound bound to the lanthanide and does it have any other specific reactivity from the original lanthanocenes (Cp_3Ln)?

Therefore, we focused on the synthesis of siloles and germoles along two possible reaction pathways, which were developed by Tamao and *co*-workers[3] and by Fagan and *co*-workers[4].

Additionally, we chose yttrium(III) as the very first “lanthanide” to study certain reactivity and behavior of lanthanides on less complex compounds.

As a side project, we focused on the synthesis of a tetrasilatrane-disilene, because of the interest in the specific electrochemical behavior of this compound.

Silatranes were synthesized for the very first time by Voronkov and *co*-workers already some 50 years ago.[5] Nevertheless, they are a highly interesting class of compounds, due to the hypervalent penta-coordinated silicon atom within this system. Furthermore, they are very bulky substituents and therefore seem to be very suitable for the synthesis of disilenes.

2. THEORETICAL PART

2.1. Siloles

This chapter will focus on the chemical properties and different ways of synthesis towards siloles. The term “silole” is used to describe a cyclopentadiene derivative containing a silicon atom (silacyclopentadiene). There are also related structure motifs, which exhibit similar chemical patterns like 1-silaindene and silafluorene that are not going to be discussed in detail in this thesis. (Figure 2-1)

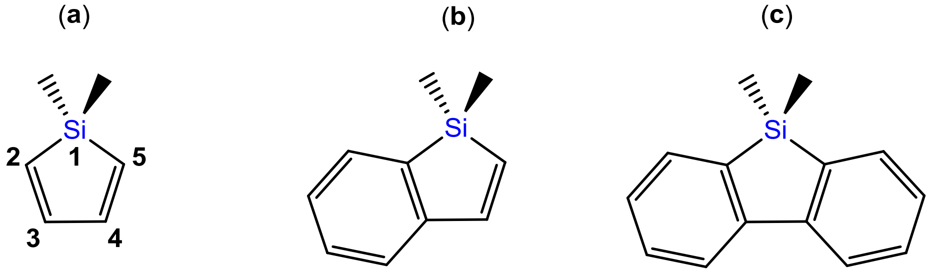


Figure 2-1. Chemical structure of a Silole (a) with numbering of the ring atoms and related structure motifs (b) 1-silaindene and (c) silafluorene.

Siloles have found great scientific attention and application[6–8] in recent years due to their quite unique electronic behavior.[9] For this reason they are of special interest as building blocks in the synthesis of organic semiconductors and polymer light-emitting diodes,[10] field-effect transistors,[11] explosives detection[12] and for photovoltaic applications.[13] Moreover, they can be thought of as interesting precursors towards ligands for lanthanides and group 4 metals (Ti, Zr, Hf).[14,15]

2.1.1. Chemical Properties of Siloles

In general, siloles have an energetically low lying LUMO orbital and a very little HOMO-LUMO gap compared to other heteroles like furan, thiophene or pyrrole.[16] This is caused by a well interaction of the π^* orbital of the butadiene fragment with the antibonding σ^* orbitals of the two exocyclic Si-X bonds.[17] (Figure 2-2) Out of this σ^*-π^* conjugation are siloles a highly regarded building block for electron-transporting materials.[18]

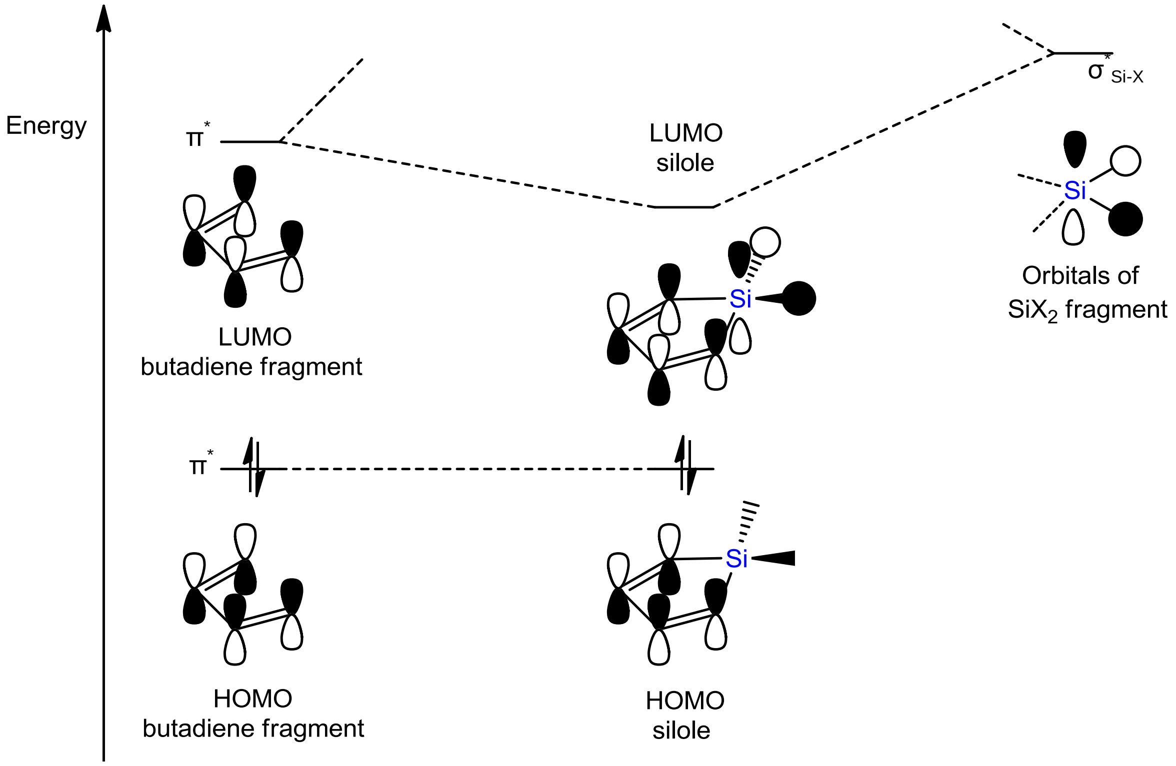


Figure 2-2. Schematic extract of the silole MO diagram, originating from orbital overlap of the π* butadiene fragment and the $\sigma^{*}_{Si\text{-}X}$ of the SiX_2 fragment.[8,17]

Additionally, Tang *et al.* discovered on a TLC that a wet spot is only scarcely fluorescent, whereas the dry spot is clearly visible under UV-light.[19] This phenomenon, called aggregation-induced emission (AIE), was quite a surprise at that time, since solids were expected to exhibit quenching of photoluminescence processes (aggregation caused quenching).[20] Within brief time siloles have found great applicability in optoelectronic devices.[21]

The electronic properties of siloles can be tuned to some extent by variation of the donor/acceptor strength of the exocyclic substituents, which have been summarized in a review by Zhan, Barlow and Marder.[8] Typically, substituents in 2,5-position have the biggest impact on redox and optical properties, since strong π-interactions with the silole core can be observed. The HOMO-LUMO gap of siloles can be influenced by stabilizing the LUMO with π-acceptors or *via* destabilizing the HOMO with π-donors.

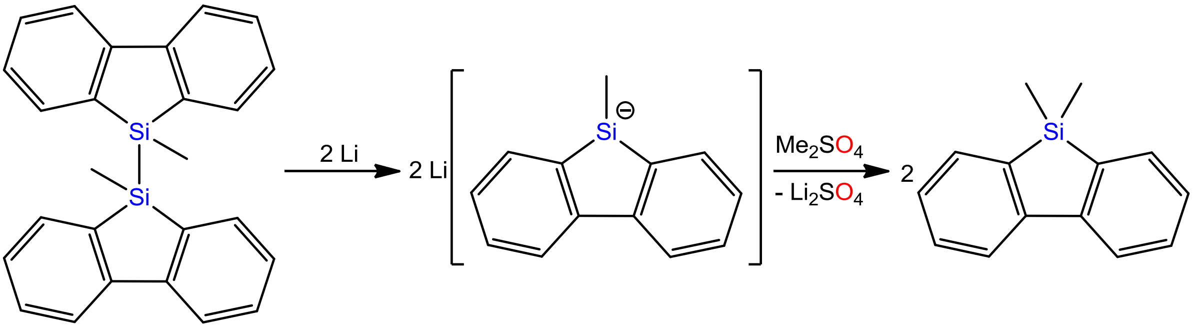
Substitution in 1,1-position has little effect on the electronic properties and is mainly referred to inductive effects. Strong σ-acceptors ease the accessibility towards reduction.

Investigation of substituent effects of the 3,4-position has shown to be difficult, due to synthetic limitations. The reaction path by Tamao and *co*-workers relies on phenyl moieties in 3,4-position.[22] However, DFT calculations show significantly less extension of both HOMO and LUMO interactions onto 3,4-aryl groups compared to 2,5-aryl groups. This is supported by the crystallographic observation of larger dihedral angles between 3,4-rings and the silole than 2,5-rings and the silole.

Aromaticity is a key property in the use of conjugated ring systems as potential multi haptic ligands. Cyclopentadienyl illustrates a typical example as it is a η^5, six π-electron donating (4n + 2), planar ligand with significant aromatic stabilization energy (ASE), C-C bond equalization (D) and a typical aromatic nucleus independent chemical shift[23] (NICS). Such aromatic ligands have broad application in transition metal catalysis.

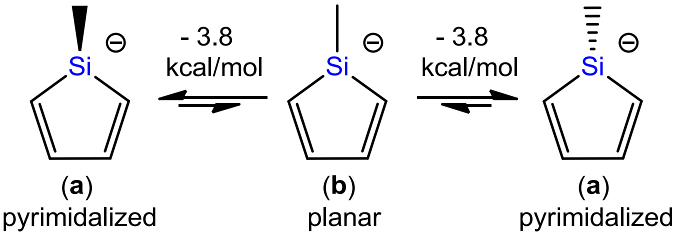
Since siloles are congeners of cyclopentadiene, the question of aromaticity of silole monoanions and dianions suggests itself.

Already in 1958 Gilman *et al.* synthesized the first silole monoanion intermediary in the preparation of a dimethylsilafluorene.[24] (Scheme 2-1)



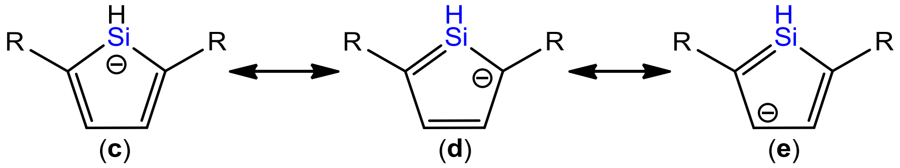
Scheme 2-1. Intermediary synthesis of the very first silole monoanion by Gilman and *co*-workers.

Later studies revealed that silole monoanions are drastically less aromatic than cyclopentadienyl,[25] which is caused by pyrimidalization of the silicon atom leading to less planarity and less conjugation of the electrons within the ring system.[26] However, the planar form (**b**) of the silole monoanion is a transition state in the inversion reaction of the pyrimidalized form (**a**). (Scheme 2-2)



Scheme 2-2. Inversion reaction between the pyrimidalized silole monoanions (a) over the planar form (b).

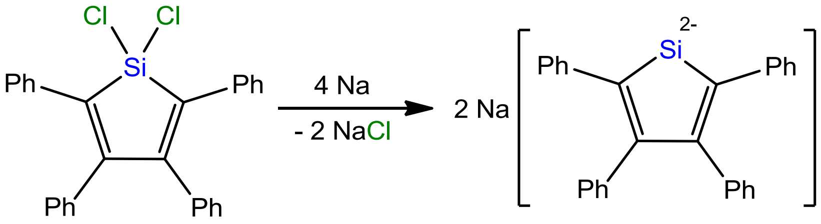
It has to be mentioned that **b** has 55% of the ASE of cyclopentadienyl, whereas **a** is basically nonaromatic.[27,28] This aromaticity can even be enhanced by reduction of the inversion barrier with π-acceptors (e.g. SiH_3, TMS) in α-position.[15] (Scheme 2-3)



Scheme 2-3. Mesomeric structures of silolide. π-acceptors in α-position enhance the probability of d and e.

Furthermore, should not be forgotten that the silolide has a counterion, which is essential for the right explanation of the system. A η^1-lithium silolide, where the lithium is complexed with dioxane or crown ether, is nonaromatic.[29–31] In contrast to that has a η^5-lithium silolide 80% of the ASE of LiCp.[27] Solvent coordination to the Li^+ reduces this "aromatizing" effect. Freeman et al. have been the first to synthesize transition metal complexes with η^5-silolide, showing that they can be planar and aromatic ligands.[32]
The structure of delocalized silole monoanions would suggest a charge transfer from the less electronegative silicon to the butadiene fragment. This effect is observable with NMR spectroscopy resulting in a downfield shift for the silicon (^{29}Si) and an upfield shift for the butadiene fragment (^{13}C). Unfortunately, this hypothesis is more complex, since substituent effects decisively influence chemical shifts.[15]

Silole dianions have been synthesized for the very first time by Joo *et al.* in 1990 through reduction of 1,1-dichloro-2,3,4,5-tetraphenylsilole with sodium.[33] (Scheme 2-4)



Scheme 2-4. First synthesis of a silole dianion by Joo and *co*-workers.

Such dianions are highly aromatic since pyrimidalization is in contrast to the monoanions irrelevant.[34,35] The ASE of silole dianions (η^5-$LiC_4H_4Si^-$ 36.4 kcal/mol) even outperforms isoelectronic compounds such as phosphole (η^5-$LiC_4H_4P^-$ 34.1 kcal/mol) or thiophene (η^5-

$LiC_4H_4S^+$ 27.1 kcal/mol).[27] The counterion coordination towards the silole dianion can differ between η^1/η^5 and η^5/η^5 depending on the solvent.[29,36] (Figure 2-3)

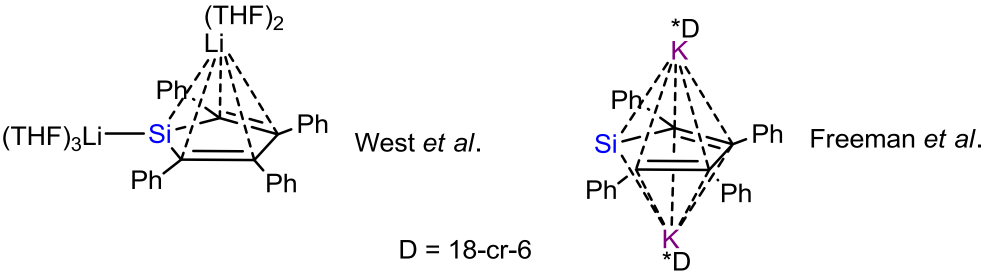
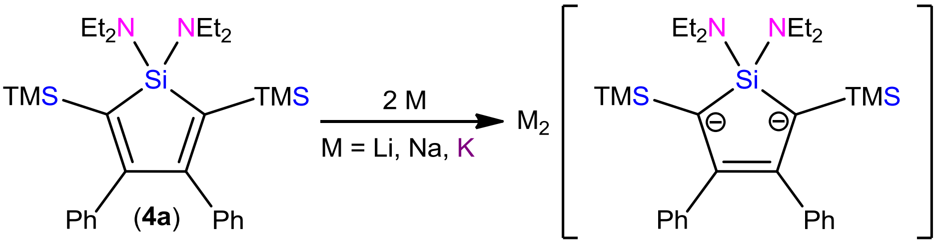


Figure 2-3. Synthesized η^1/η^5 and η^5/η^5 silole dianions by West and *co*-workers and Freeman and *co*-workers.

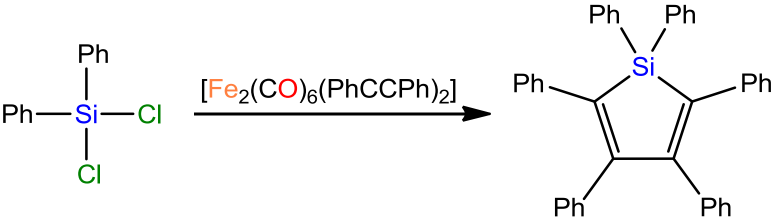
More recently, published Han and *co*-workers the synthesis of a 1,1-disubstituted dianionic silole, (Scheme 2-5) which is able to act as a two electron reducing agent. However, this compound is not aromatic at all, because it has neither equal C-C bond distances, nor is it planar.[37]



Scheme 2-5. Synthesis of a nonaromatic 1,1-disubstituted dianionic silole by Han and *co*-workers.

2.1.2. Synthesis of Siloles

The first silole was synthesized some 60 years ago by Braye *et al.* in 1959, with a quite unconventional method.[38] The reaction of dichlorodiphenyl silane with a binary iron complex formed hexaphenylsilole. (Scheme 2-6)

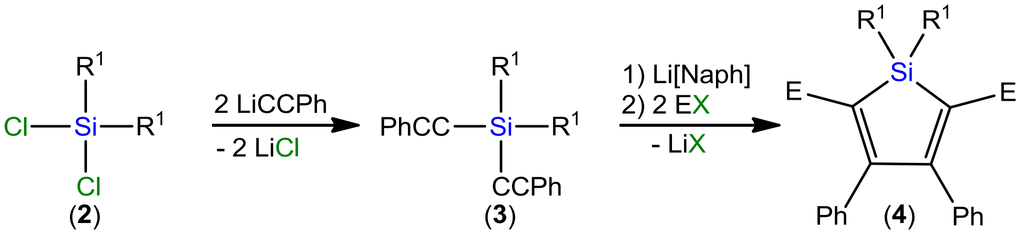


Scheme 2-6. Reaction scheme for the very first synthesis of a silole in 1959 by Braye and *co*-workers.

Today we have a set of different reaction pathways towards the synthesis of siloles, which are still increasing and under development. The main reaction paths are going to be discussed in the following chapters. However, it has to be mentioned that all listed methods show differences towards the scope of substituents in the final silole.

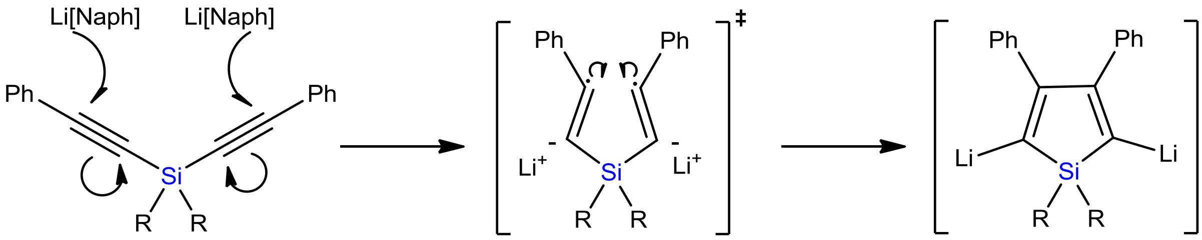
2.1.2.1. Tamao *et al*. Method

Today's most common reaction path was published by Tamao and *co*-workers in 1994.[22] It was described herein as an *endo-endo* intramolecular reductive cyclization of a bis(phenylethynyl)silane with lithium naphthalenide followed by subsequent quenching of the intermediary 2,5-dianionic silole with an electrophile (e.g. Me_3SiCl, Bu_3SnCl, Br_2). (Scheme 2-7) The Tamao *et al*. method allows a fast and efficient introduction of three different sets of substituents to the silole.



Scheme 2-7. A typical reaction path towards the synthesis of a silole provided by Tamao and *co*-workers. EX = halogen containing electrophile (e.g. Me_3SiCl, Bu_3SnCl, Br_2).

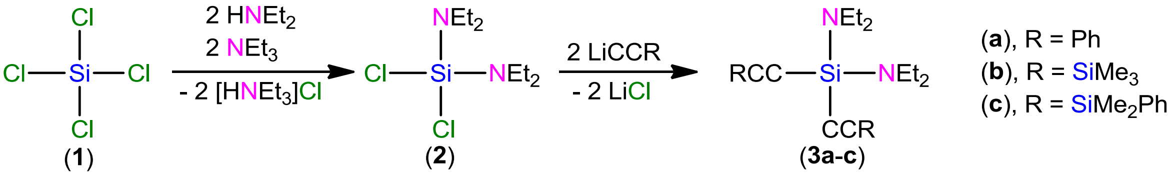
Substituents in 3,4-position are limited to aromatic substituents, since a certain stabilizing ability to the highly reactive diradical-dianionic transition state is needed. (Scheme 2-8) Therefore, phenyl groups are by far the most frequent substituents next to some more complex derivatives.[39] Nevertheless, it would be of interest to introduce different motifs than aryl groups in these positions, although, Tamao and *co*-workers briefly mention that alkyl- and silyl-groups are incapable of stabilizing the postulated transition state.[22]



Scheme 2-8. Postulated reaction mechanism by Tamao and *co*-workers for the *endo-endo* intramolecular reductive cyclisation.[22]

However, it is known from other reactions that silyl-moieties have a stabilizing effect on radicals,[40] attempts to perform reductive cyclization with trimethylsilyl groups in 3,4-position were carried out. Similar stabilizing effects were assumed to a phenyl-group linked via a dimethylsilyl-moiety to the alkynyl functionality.

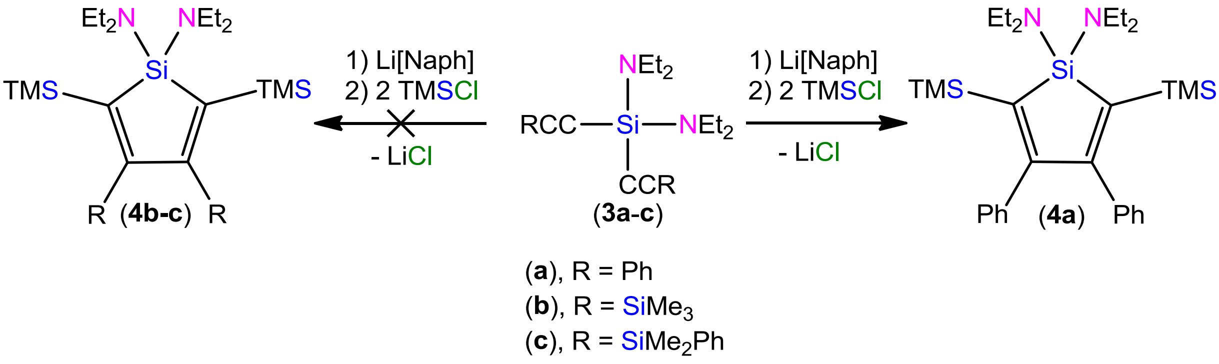
Preparation of the bisalkynylsilanes can be achieved in two steps. (Scheme 2-9)



Scheme 2-9. Preparation of 2 and subsequent synthesis of 3a-c.

Starting with $SiCl_4$ (**1**), two chlorides can be converted to diethylamines through treatment with $HNEt_2$ (2.5 equiv.) and NEt_3 (2.5 equiv.).[3] Attempts to react **1** with an large excess (8 equiv.) $HNEt_2$[41] and without NEt_3 were not successful as small amounts of the 'overamination' product tris(diethylamino)chlorosilane formed along with **2**, leading to a more time consuming protocol for purification.

The preparation of **3a-c** was accomplished by deprotonating the respective alkynyl derivative with *n*-butyl lithium at 0 °C and further reaction with **2**. The reaction was accelerated by traces of copper(I)cyanide and was driven towards the product through precipitation of LiCl. The two new compounds **3b** and **3c** were synthesized in good yields with 66% and 68%, respectively.



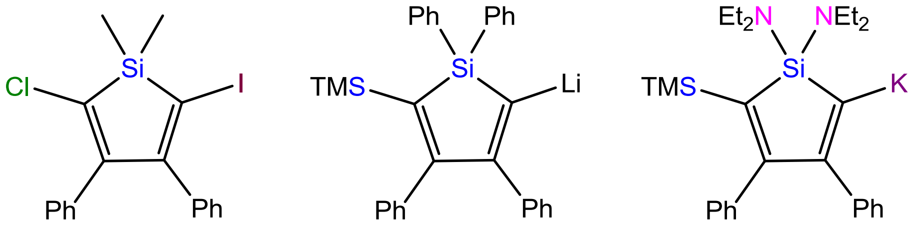
Scheme 2-10. Reductive cyclization of 3a-c with the Tamao *et al.* protocol.

Unfortunately, the *endo-endo* reductive cyclization with excess lithium naphthalenide gave a variety of silylated naphthalene derivatives and the starting alkynyl educts. It seems either, that the trimethylsilyl- as well as the dimethylphenylsilyl-group is only scarcely able to stabilize the very reactive transition state or they are too bulky to allow coplanar arrangement of the two alkynyl units. (Scheme 2-10)

Also of interest is the preparation of various 2,5-substituted siloles. One option is to directly quench the intermediary 2,5-dianionic silole with an electrophile,[39,42] as was already mentioned above. Another one is to perform transmetallation with $ZnCl_2$/TMEDA to synthesize an intermediary 2,5-ZnCl-silole, which can be used for Negishi-type cross-coupling. This method allows the introduction of various aromatic substituents in 2,5-position.[17,43] The third option is to synthesize a 2,5-dibromosilole[22,44] and subsequent use for cross-coupling.[45]

Moreover, there are options to obtain an 2,5-asymmetric silole. The first was again described by Tamao and *co*-workers in his first paper on the synthesis of siloles.[22] A 2,5-dibromosilole can be transmetallated with *n*-butyl lithium once and subsequently quenched with an electrophile to give a 2,5-asymmetricsilole.

The second one was developed by Boydston and Pagenkopf *et al.*[7,44,46] and proceeds *via* an 2-Chloro-5-iodosilole, which is able to perform stepwise cross-coupling with the use of different reaction conditions. (Figure 2-4)



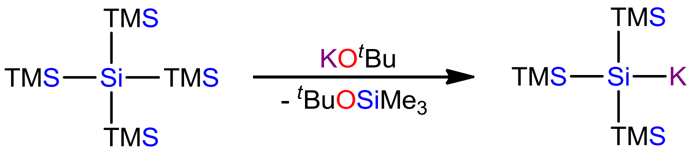
Boydston and Pagenkopf et al.

Tamao et al.

(**5**)

Figure 2-4. Synthesized 2,5-asymmetric siloles by Boydston and Pagenkopf and *co*-workers[46] and by Tamao and *co*-workers.[47] The pictured β-carbanionic silole on the right side (5) can be thought of as another reactive intermediate towards the synthesis of 2,5-asymmetric siloles.

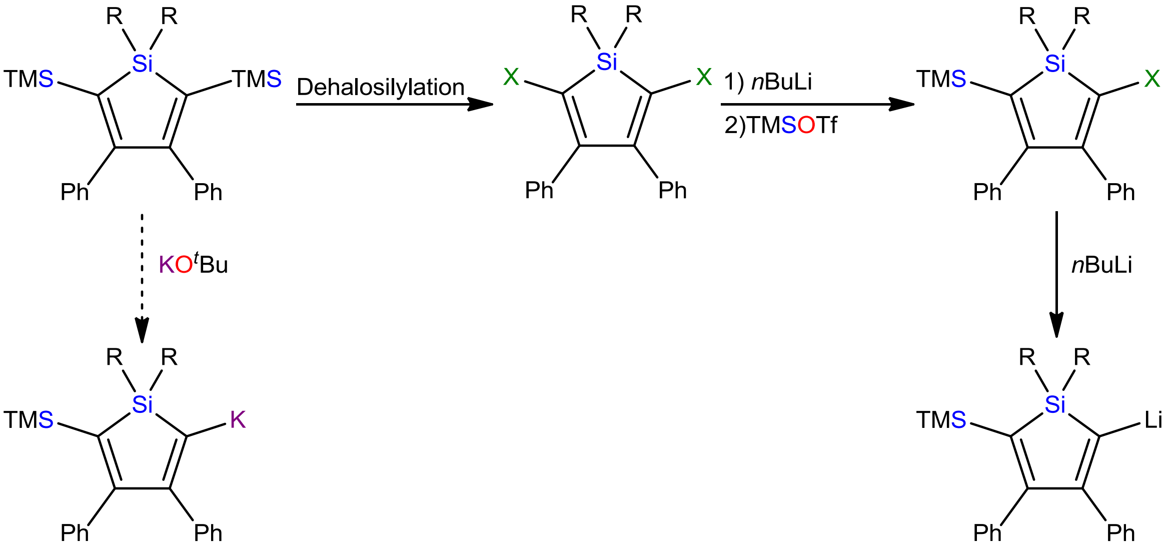
Alternatively, it can be thought of a shorter reaction pathway towards the synthesis of a Tamao and *co*-workers 2,5-asymmetric silole. Potassium *tertiary* butoxide is capable of cleaving trimethylsilyl groups of bulky silanes through formation of a very stable silyl ether and a highly reactive silanide (Scheme 2-11).[48] Typically, these silanides are used in the preparation of oligosilanes.



Scheme 2-11. Typical formation of a silanide with KO^{t}Bu using the example of the potassium hypersilyl formation.

However, the clean formation of a carbanion through a similar reaction with KO^{t}Bu is energetically less favored, since the C-Si bond is stronger (Si-Si ~222 kJ/mol, C-Si ~318 kJ/mol) and the carbanion is much more reactive. Nevertheless, siloles, synthesized by Tamao and *co*-workers,[3] have various opportunities to stabilize a carbanion in 2-position (β-carbanionic silole) via mesomeric stabilization of the attached conjugated system, which is supported by the various existing lithium compounds in 2- or 2,5-position.

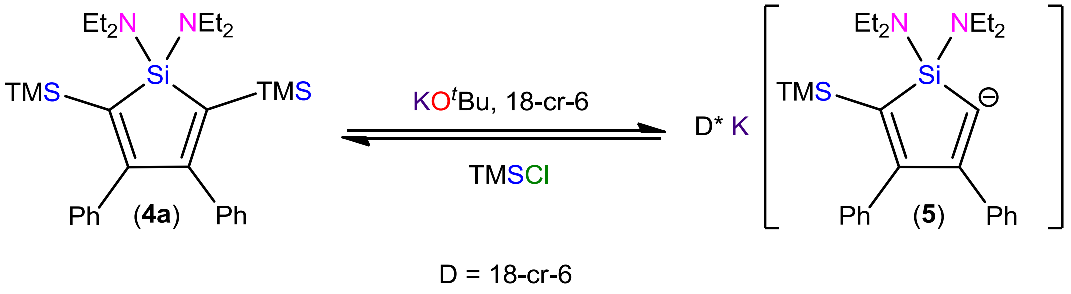
Therefore a shorter reaction path can be suggested. (Scheme 2-12)



Scheme 2-12. The reaction path of Tamao and *co*-workers towards a 2,5-asymmetric β-carbanionic silole starting from a 2,5-bis(trimethylsilyl)silole proceeds over 3 steps. The newly suggested reaction path utilizing the principle of cleaving trimethylsilyl-groups with tertiary butoxide by Marschner et al. performs the desired transformation in a single step. (dotted arrow)

The Tamao *et al*. reactionpath relies on a 2,5-dihalo silole, which can be synthesized by dehalosilylation[49] or direct synthesis from bis(alkynyl)silane.[22] Asymmetrization is achieved through lithium-halogen exchange followed by metathesis reaction with trimethylsilyl triflate. A second lithium-halogen exchange gives the final product. The use of potassium *tertiary* butoxide reduces the effort to a single step and is by far more atom-economic.

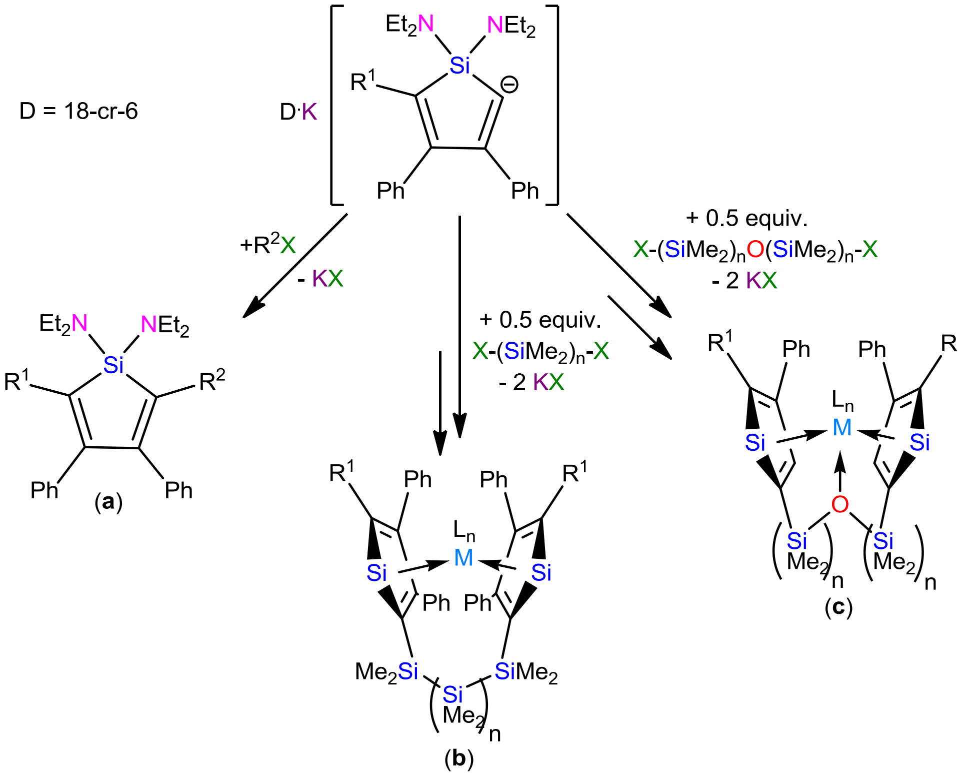
To synthesize the desired asymmetric precursor **5**, 1 equiv. of KO^{t}Bu was added to a THF solution of **4a**, but even after 12 days no silyl cleavage reaction was observed (Scheme 2-13). Therefore, a further equiv. of 18-cr-6 was added to enhance the nucleophilicity of the ^{t}butanolate ("naked anion") and immediately a color change from slightly yellow to strong brownish and the formation of a precipitate was observed. The reaction mixture was subjected to NMR-spectroscopy, showing only solvent, 18-cr-6 and silyl ether signals. To obtain clarity, an excess of trimethylsilyl chloride was added and the sample was subjected to NMR-spectroscopic analysis, which showed educt **4a** and small amounts of 1,1-alkoxide substituted silole derivatives.



Scheme 2-13. Back and forth reaction of 4a *via* an intermediary β-anionic silole.

This reaction, however, provides no distinct evidence for the clean formation of a β-anionic silole, since parts of observed **4a** could be unreacted educt. Admittedly, no **4a** could be observed after addition of crown-ether, which would fit the behavior of an insoluble intermediary ionic species. Repetition of this experiment with a different electrophile (e.g.: dimethylphenylchloride) will give clarity to how clean the reaction is.

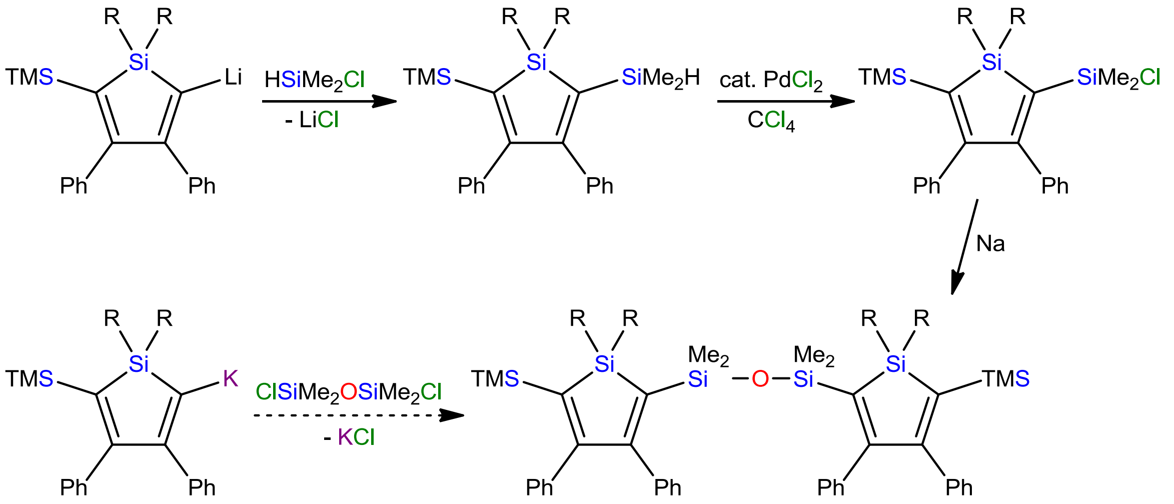
Accordingly, **4a** was reacted with KO^{t}Bu and again nothing but the silylether was detectable through NMR spectroscopy. This time, 0.5 equiv. dichlorotetramethyldisilane were chosen as electrophile and were added dropwise to a solution of **5**. However, mainly **4a** was formed, which hints that the order of addition may be key to a successful reaction.



Scheme 2-14. Three examples how a β-anionic silole could function as possible precursor are shown. (a) asymmetric silole, (b) *ansa*-type ligand and (c) *multi*-dentate ligand. At (c) the two phenyl-groups in 3-position were left out for more clarity.

Besides scientific curiosity, a β-carbanionic silole would be a very useful building-block in the formation of asymmetric siloles, *ansa*-type siloles and might be even considered as a precursor for a *multi*-dentate ligand (Scheme 2-12). Furthermore, substitution of the diethylamino-moieties by chloride-groups and reduction to the dianionic silole rings might be envisioned. If this could be accomplished with a (**c**)-type ligand, it would create a 14 electron ligand, with two tightly bound siloles and a more flexible extra coordination site at the bridging-chain. Group 14 metals (Ti, Zr, Hf) and lanthanides would be interesting substrates for this ligand.

A related compound to a (**c**)-type ligand was already prepared by the group of Tamao *et al*. in a *multi*-step synthesis from a 2,5-asymmetric β-carbanionic silole.[47] However, a much shorter synthesis can be suggested. (Scheme 2-15)



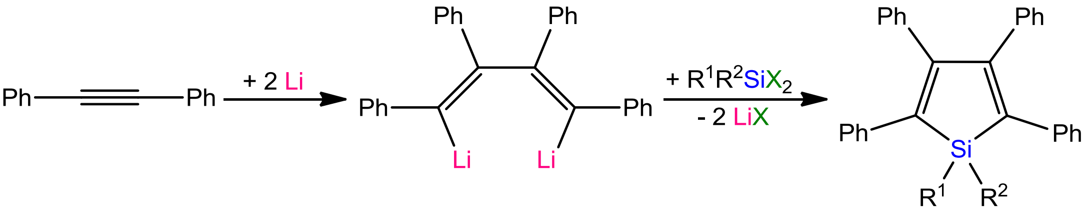
Scheme 2-15. Synthesis of a (c)-type ligand related compound according to Tamao and *co*-workers (R = Ph)[47] and a possible alternative reaction path towards a precursor with R = NEt_2. (dotted arrow)

In contrast to asymmetrization, we also thought of shortening the reaction time for the formation of the silole by switching the reducing agent from Li[Naph] to the intercalation compound KC_8 and spare the approximately two hours for the formation of Li[Naph]. Unfortunately, the *endo-endo* intramolecular reductive cyclization with potassium graphite resulted only in a crude reaction mixture. KC_8 seems too strongly reducing for this type of reaction.

Finally, has to be mentioned that the 1,1-position of siloles can be prearranged to some extent with the respective bis(phenylethynyl)silane and also modification of siloles afterwards is feasible. Since modification of the 1,1-position is not exclusive to the Tamao *et al*. method it will be discussed in a following chapter.

2.1.2.2. Curtis *et al*. Method

The synthetic approach of Curtis and *co*-workers towards the synthesis of siloles utilizes the reductive dimerization of 1,2-diarylalkynes with lithium followed by metathesis reaction of a dihalidesilane.[50] (Scheme 2-7) The key step of this reaction is the formation of the intermediary 1,4-dilithio-1,3-butadiene derivative, which has already been synthesized by Schlenk *et al*. some 90 years ago.[51] However, the clean formation of this dilithio compound is still not fully understood. An improper ratio of lithium to tolan and/or a too long reaction time promotes the rearrangement towards 1,2,3-triphenylnaphthalene.[52–55] Chen *et al*. described that this unwanted rearrangement can be diminished by using an excess tolan, which enables longer reaction times and enhances yields.[56,57] Despite this, there are still manifold ratios of lithium to tolan used and published, which are summarized along with various differently 1,1-substituted siloles by Corey *et al.*[17]



Scheme 2-16. Schematic reaction path towards a silole by Curtis and *co*-workers.

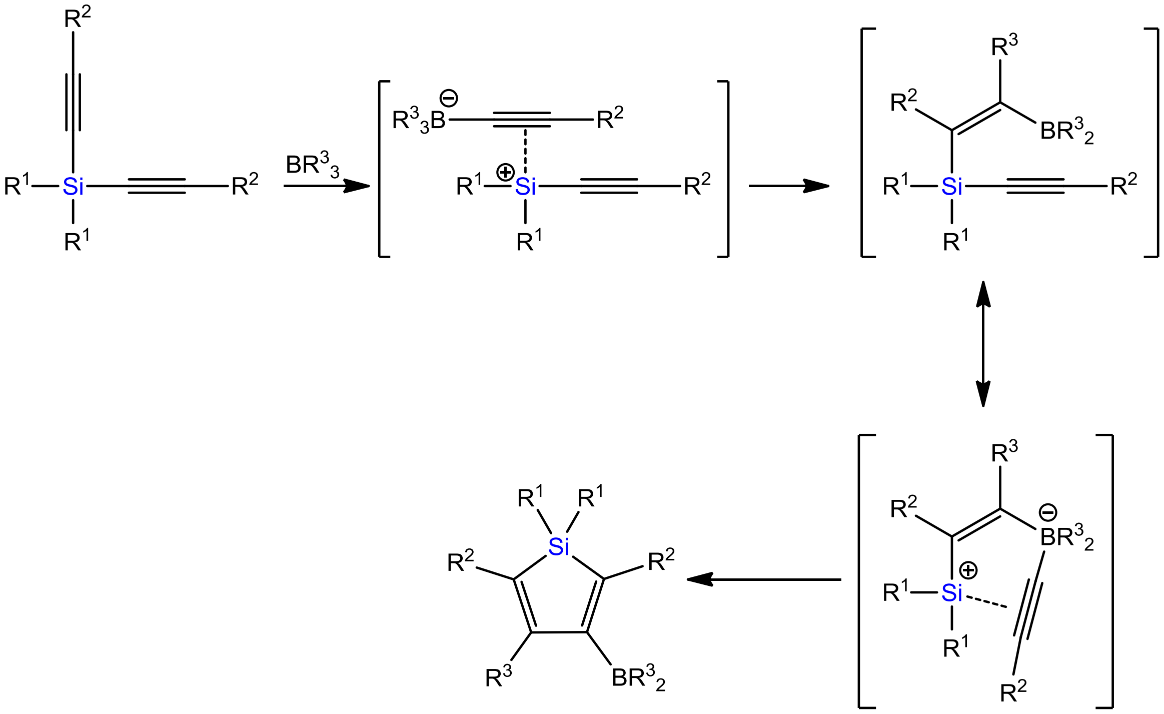
The method by Curtis *et al.* relies on two aromatic substituents on the alkyne, which minimizes the scope of available siloles drastically as the 2,3,4,5-positions are limited to aromatic substituents, which need not to be phenyl moieties.[58]

Li *et al.* investigated the reactivity of a mixed substituted alkyne in this reaction path by choosing a sterically demanding substituent next to the phenyl group. In a hideous work-up with 20 chromatographies, all three different isomers were isolated and quantified. The isomer with the bulky substituent in 2,4-position (92%) was dominant over the 2,5- (5%) and 3,4-isomer (2%).[59] This study revealed, that with the reaction path established by Curtis *et al.* 2,5/3,4-different substituted siloles are not feasible in sufficient yields.

2.1.2.3. Wrackmeyer *et al.* Method

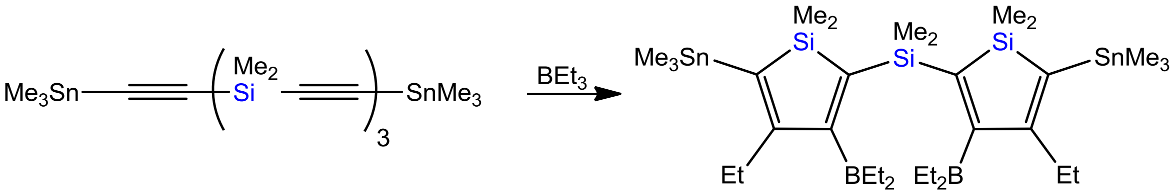
Wrackmeyer *et al.* were able to demonstrate in several papers, that siloles can be synthesized by double organoboration of bis(alkynyl)silanes, the same starting materials as for the Tamao *et al.* method, and the following mechanism was proposed.[60] (Scheme 2-17) The first reactions were done with triethylborane and several different substituted bis(alkynyl)silanes giving mainly oils in high yields as products.[61] The Wrackmeyer *et al.* method provides several options towards a broad scope of possible substituents of the silole, even for the 3,4 position. In contrast, the methods by Tamao and *co*-workers and Curtis and *co*-workers rely on aryl substituents (mainly phenyl groups). However, the reaction path by Wrackmeyer *et al.* gives 3,4-asymmetric compounds, depending on the substituents of the used borane. Next to BEt_3, have been used BPh_3[62] and $B(C_6F_5)_3$,[63] which above all lead to crystallizable products. The attached boryl moiety can be modified by deborylation[61,64,65] or cross-coupling.

Moreover, have been introduced several different substituents in 2,5-position, such as hydrogen-,[60] trimethylsilyl-,[66] phenyl-,[63] chloride groups[67] and more which are summarized by Corey and *co*-workers.[17]



Scheme 2-17. Proposed mechanism for the double organoboration of a bis(alkynyl)silane.

Additionally, 1,1- and/or 2,5-asymmetric siloles are known, if an asymmetric substituted bis(alkynyl)silane is used.[64,67–69] The preparation of 1,1-asymmetric siloles is straight forward as even chloride is tolerated, which has to be protected with a diethylamine in the Tamao *et al.* reaction path. More problematic is the preparation of 2,5-asymmetric siloles, which often give inseparable mixtures out of a lack of options for purification. Chromatographic methods and distillation are not feasible, due to thermal instability and hydrolizability of the borylated siloles. Therefore, Corey *et al.* suggest a derivatization of the boryl substituents of the resulting product mixture before purification.[17]

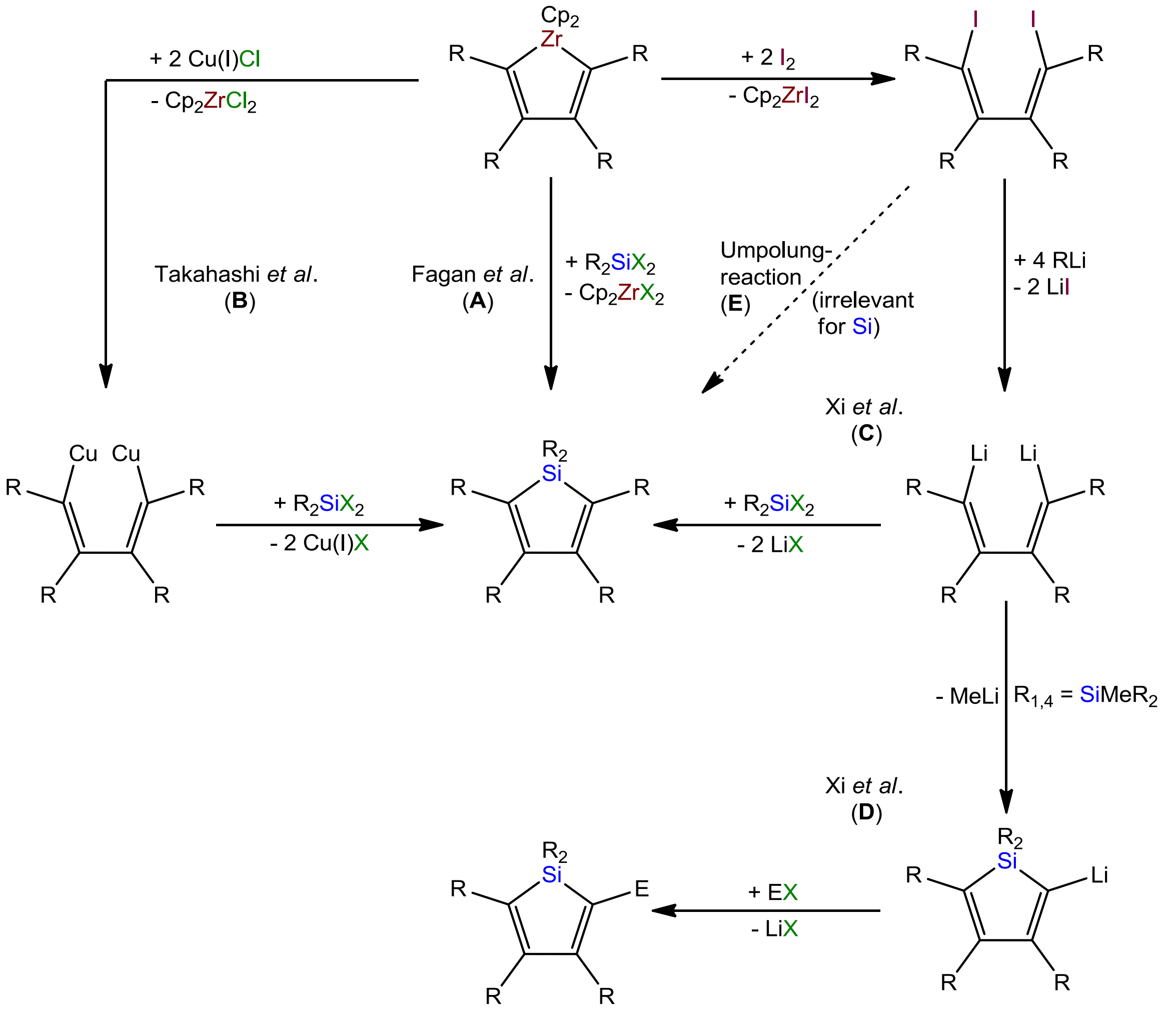


Scheme 2-18. Single step quantitative synthesis of a dimethyldisiloyl silane from a tetrayne and triethyl borane.

Another fascinating topic of this method is the formation of more complex ring systems using tetraynes as starting material. Wrackmayer *et al.* were able to synthesize a dimethyldisiloyl silane quantitatively in a single step.[70] (Scheme 2-18)

2.1.2.4. Direct and Indirect Synthesis of Siloles from Five-Membered Zirconocenacycles

Both the direct- as well as the indirect reaction path in the formation of siloles use the ability of Negishi-zirconocene to form five-membered metallocenacycles with alkynes.[71–74] Direct synthesis proceeds *via* transmetallation with corresponding halogensilanes. (**A**, Fagan and *co*-workers)[4,75]

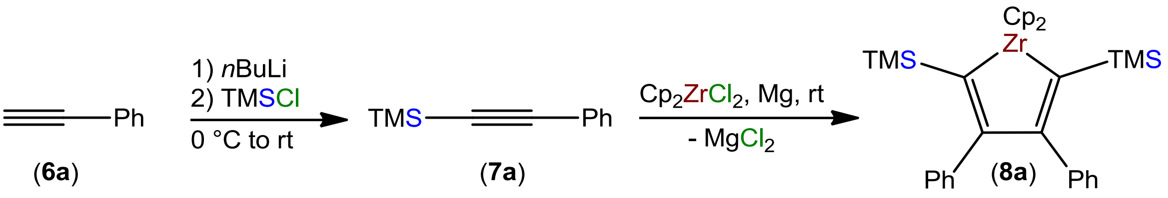


Scheme 2-19. Schematic reaction paths towards the synthesis of a silole starting from a five-membered zirconocenacycle. (A) direct transmetallation by Fagan and *co*-workers, (B) transmetallation with Cu(I) followed by metathesis by Takahashi and *co*-workers, (C) ring-opening iodination followed by lithium-halogen exchange and metathesis by Xi and *co*-workers, (D) rearrangement by Xi and *co*-workers and (E) Umpolung reaction, which is by now irrelevant for siloles. The scheme is inspired by Yan and *co*-workers.[75]

Takahashi *et al*. were able to improve this method significantly by *prior* transmetallation with Cu(I)Cl. (**B**) [76,77] The indirect synthesis utilizes ring-opening iodination, followed by lithium-halogen exchange. Depending, if the substituents in 1- or 4-position are silyl groups, either metathesis with halogensilanes, (**C**, Xi and *co*-workers)[78] or rearrangement followed by reaction with an electrophile is possible. (**D**, Xi and *co*-workers)[79,80] Option **E** is in the case of siloles just of theoretical nature, because no such reaction was performed by now. (Scheme 2-19)

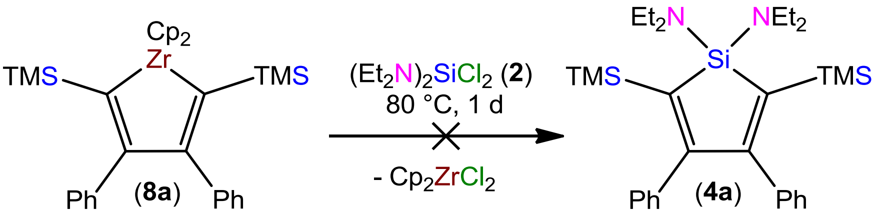
Reaction path **A** proceeds not smoothly on a broad scope of electrophiles. Me(H)$SiCl_2$ and H_2SiCl_2 show transmetallation at rt after a brief period of time in good yields, 88% (24 h) and 92% (5 min) respectively, but the reaction with $SiBr_4$ gives even after 2 d at 150 °C only 28% yield. $SiCl_4$ and Me_2SiCl_2 do not react at all under the tested reaction conditions[76] and even method **B** did not lead to the desired silole.[75] This weak nucleophilicity of the zirconocenacycle suggests the need of small and/or electron withdrawing substituents on the silane.

Accordingly, was questioned if the electrophilic silicon center of bis(diethylamino)dichloro silane (**2**) is able to perform the transmetallation of **A**. Out of this purpose was synthesized the following five-membered zirconocenacycle **8**. (Scheme 2-20)



Scheme 2-20. Deprotonation of 6a and subsequent quenching with trimethylsilyl chloride gives 7a, which can be oligomerized with the Rosenthal procedure to the five-membered zirconocenacycle 8a.

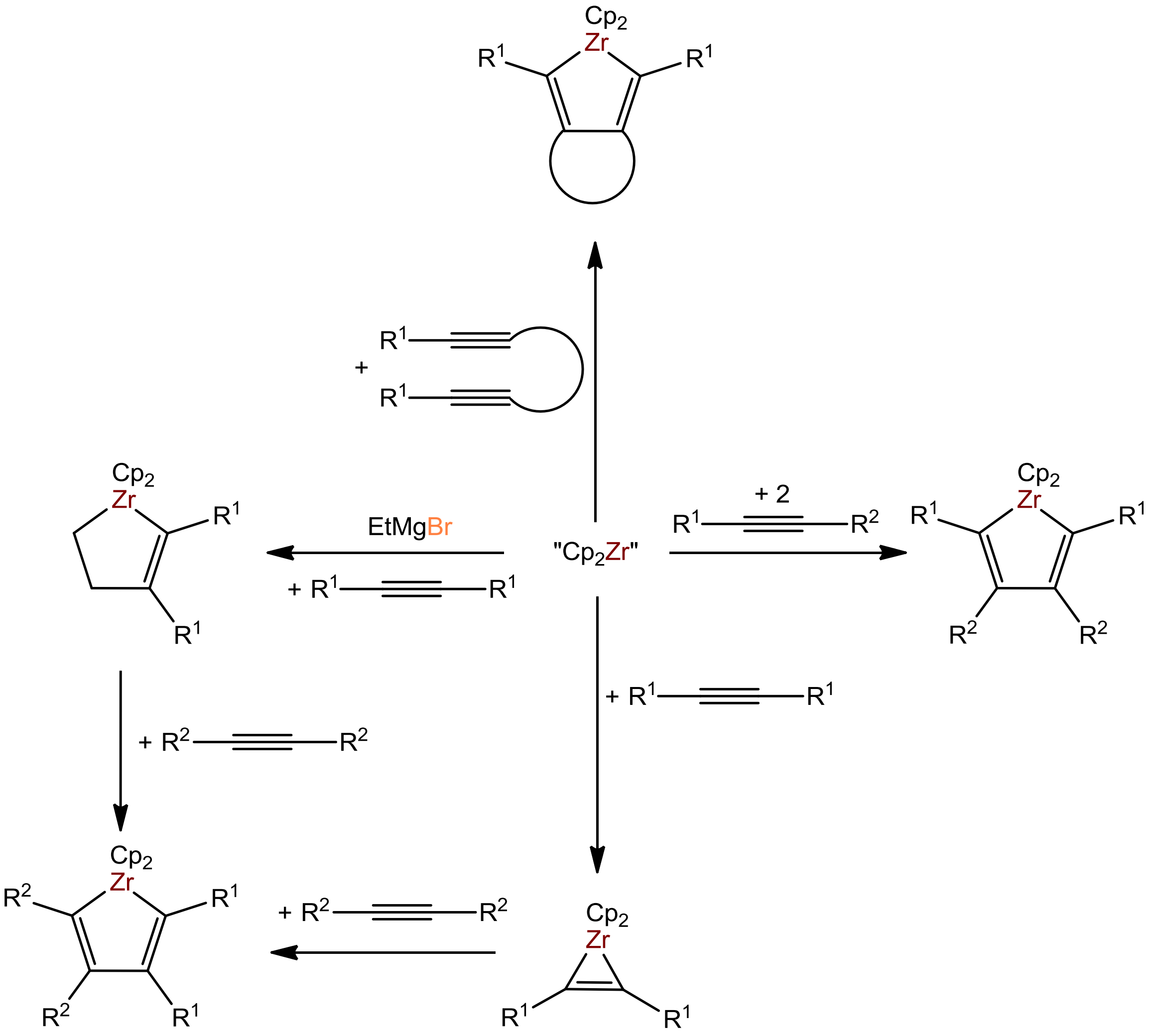
Reaction of **8a** with **2** did not show any reaction after 1 day at rt and 1 day at 80 °C. Hence, **2** can be considered as too sterically demanding and/or too little electronically activated for reaction path **A**. (Scheme 2-21)



Scheme 2-21. 4a cannot be synthesized by transmetallation of 8a with 2.

Alternatively, method **C** could have been used to synthesize **4a** from **8a**, but was not performed, due to easier availability of **4a** by the Tamao *et al*. method.[3]

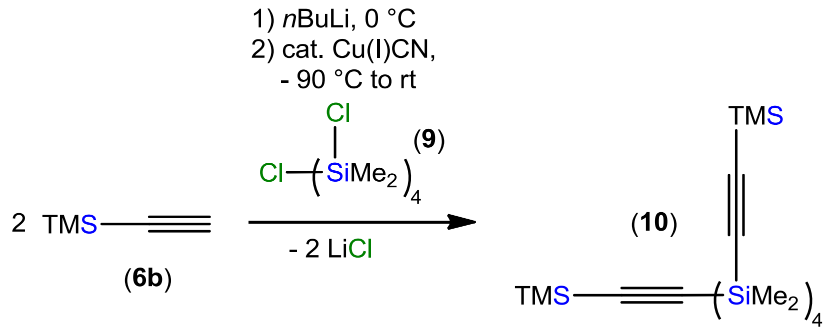
An advantage of the formation of siloles from zirconocenacycles is that the structure can be well modeled by the various opportunities towards different zirconocenacycle skeletons. (Scheme 2-22) Which are summarized well by the reviews of Rosenthal *et al*.,[72,81–83] Negishi *et al*.,[73,74,84] Ma *et al*.[71] and Yan and Xi.[75]



Scheme 2-22. Examples towards possible substituent arrangements in a zirconocenacycle skeleton.[75]

To enhance the structural variety of synthesized siloles, compound **10** was synthesized by reaction of 2 equiv. **6b** with **9**. (Scheme 2-23) The preparation of **10** was somehow more complex than the comparable synthesis of other silylated alkynes. (**7a**, Scheme 2-20) If the reaction was performed at rt and **9** was added to deprotonated **6b**, an inseparable product mixture was observed. Similar behaviour was detected for the reaction at – 80 °C.

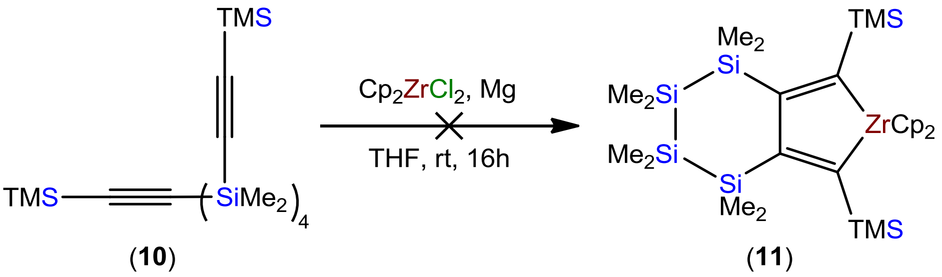
However, if deprotonated **6b** was added to **9** at -90 °C, the unknown compound **10** formed as colorless oil in good yields (80%).



Scheme 2-23. Synthesis of 10 through reaction of 9 with 2 equiv. of deprotonated 6b at – 90 °C.

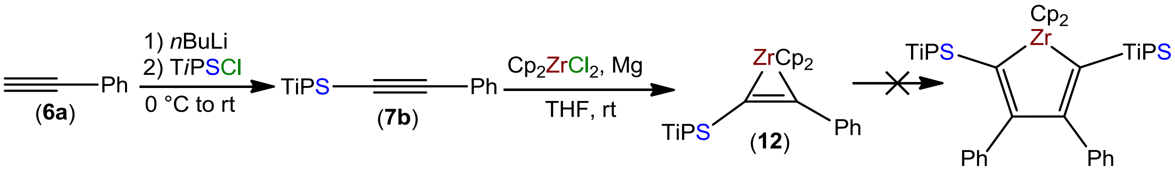
A reason for the obtained product mixtures at the beginning might be occurring lithium-halogen exchange. It is likely that the order of addition and low temperatures kinetically suppress exchange reactions.

To form the bicyclic zirconocenacycle, **10** was reacted with 1 equiv. of Negishi-Zirconocene to form **11**. (Scheme 2-24) Uexpectedly, only little conversion was detected after 16 h at rt, so higher reaction temperatures or a prolonged reaction time have to be considered.



Scheme 2-24. After 16 h at rt, only little amounts of 10 reacted with *in-situ* generated Negishi-Zirconocene.

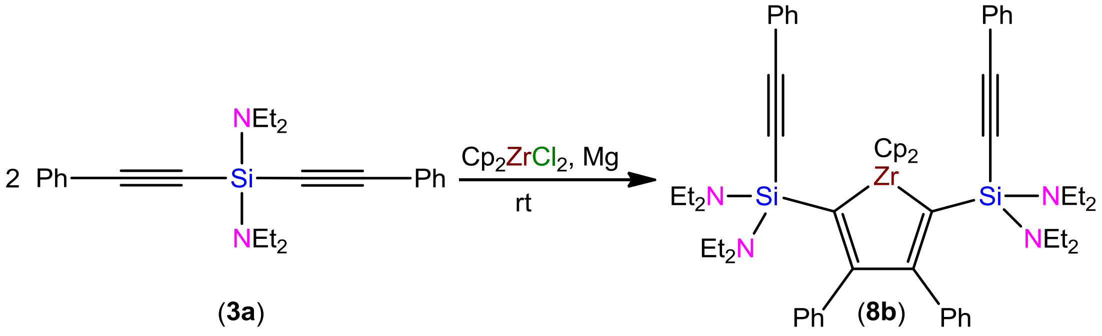
Furthermore, a bulky substituted alkyne (**7b**) was synthesized from deprotonation of **6a** and subsequent reaction with triisopropylsilyl chloride. (T*i*PSCl, Scheme 2-25)



Scheme 2-25. 7b was synthesized by deprotonation of 6a and subsequent quenching with T*i*PSCl. Reaction of *in-situ* generated Negishi-Zirconocene with 7b should give the zicenocenirene 12 instead of a 5-membered zircenocenacycle, but was not distinctly observed with NMR-spectroscopy.

7b should react with 1 equiv. of Negishi-Zirconocene to a 3-membered- instead of a 5-membered zircenocenacycle. The insertion of the second equiv. **7b** is sterically hindered by the large T*i*PS substituent. Although separation of **12** from excess **7b** was not possible, an additional peak in the ^{29}Si-NMR-spectra at 1.1 ppm was observable. Unfortunately, some ^{1}H-NMR peaks of **7b** superimpose the peaks of **12**. The reaction has to be redone with a single equivalent of **7b** for spectra of pure **12** and eventual crystallographic data.

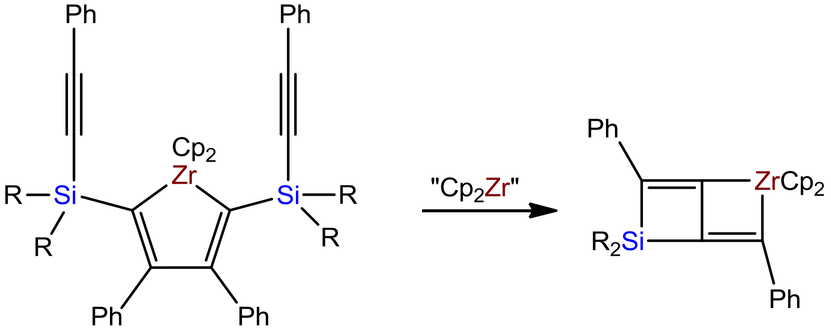
To complete the set of various zirconocene skeletons, 2 equiv. of the bulky 1,1-diyne **3a** were reacted with 1 equiv. of *in-situ* generated Negishi-Zirconocene. (Scheme 2-26)



Scheme 2-26. Synthesis of 8b through reaction of *in-situ* generated Negishi-Zirconocene with 3a.

Unfortunately, **8b** crystallizes as bright orange lamella and hence was not suited for XRD, but for some NMR spectroscopic measurements, which correlate with the suggested structure.

Liu *et al*. published similar structures with phenyl- or alkyl groups instead of diethylamino as substituents and furthermore describe the tendency of this compounds towards skeleton rearrangement.[85] (Scheme 2-27)



Scheme 2-27. 2,5-bisalkynylzirconocenacycles can perform skeleton rearrangement with excess Negishi-Zirconocene.

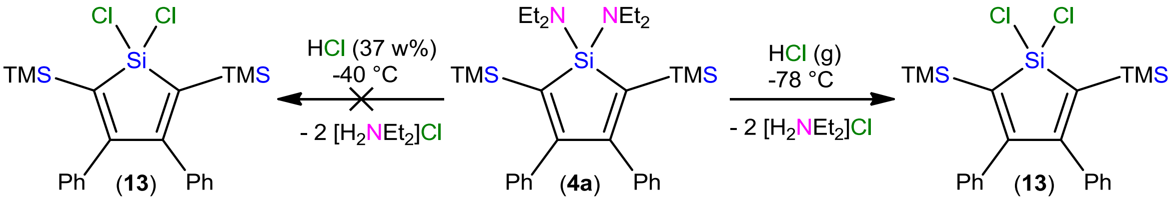
The compound class of 2,5-bisalkynylzirconocenoles and especially **8b** have manifold options of modification: Rearrangement with excess Negishi-Zirconocene, "Click-Reaction" of the alkyne functionality to give triazoles, direct transmetallation (e.g. with $GeCl_4$), indirect transmetallation (**C**) and halogenation of the diethylamino groups with HCl after transmetallation of the zirconocenole, to name a few.

2.1.3. Modification of Siloles in 1,1-Position towards formation of a dianionic silole

The 1,1-position of siloles can be prearranged to some extent, with the choice of the right silane as starting material or introduced electrophile. In some cases as in the method by Tamao *et al*. prearrangement of chloride groups in 1,1-position is not possible, but since they are important to facilitate reduction towards mono- or dianions, a modification of functional groups in 1,1-position was developed. The papers of Braddock-Wilking *et al*.[86] and by Yamaguchi et al.[3] give a nice overview of this topic.

The focus of this chapter will be kept on the afforded modifications in 1,1-position to synthesize silole dianions from **4a**, synthesized with the Tamao *et al*. procedure.

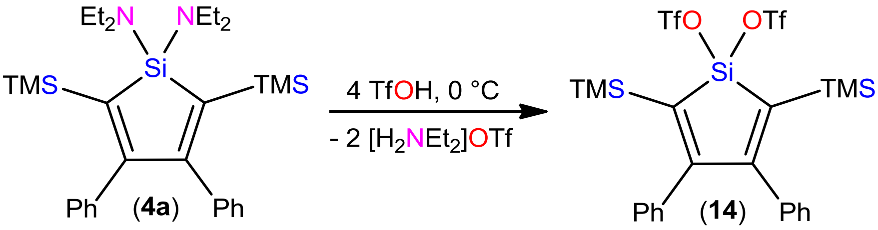
The 1,1-diethylamino groups of **4a** can be considered to some extent as a protecting-group. They can be converted into chlorides by bubbling gaseous HCl through an ethereal solution of **4a** at -78 °C (Scheme 2-28).[3] For practical reasons it is recommended to use a large excess of HCl (g) to obtain full conversion.



Scheme 2-28. Substitution of the two 1,1-diethylamino moieties with chloride.

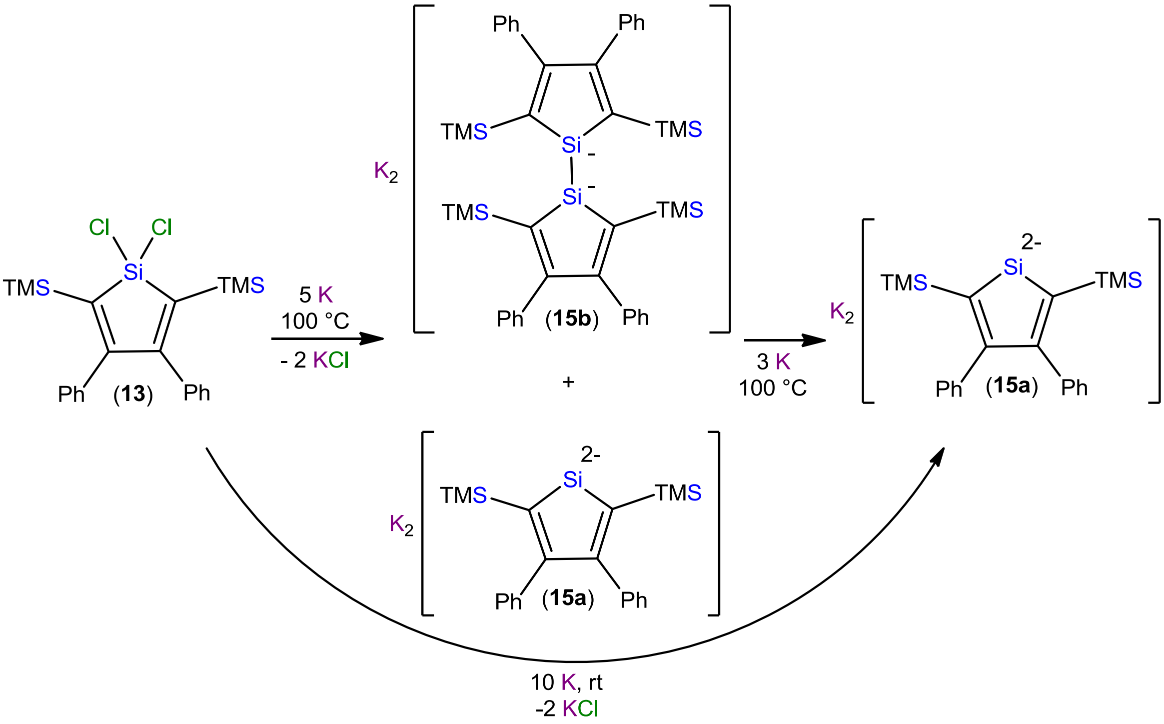
Since this is a quite elaborate method, it was tried to simplify this step by heavy stirring an ethereal solution of **4a** with an excess of concentrated HCl (37 w%) at -40 °C. Unfortunately, this resulted mainly in formation of 1-chloro-1-diethylaminosilole and many side products.

Moreover, the reaction of **4a** with trifluoromethanesulfonic acid was investigated as alternative reaction path. (Scheme 2-29) The compound **14** was obtained in quantitative yield.



Scheme 2-29. Substitution of the two 1,1-diethylamino moieties with triflate groups works quantitative.

The use of the much stronger trifluoromethanesulfonic acid (pK_a (H_2O) = - 14) instead of gaseous HCl (pK_a (H_2O) = - 8) gives several advantages aside from chemical costs. Most importantly the reaction works quantitative compared to roughly 80% yield, if HCl (g) is used. Secondly, the preparative effort is much easier, since no gas introduction and low temperature cooling bath is required. Another key point is that the amounts of reacting acid can be better controlled. However, it has to be discovered if **14** is accessible to reduction, but since triflate is an even better leaving group than chloride this should not be a problem.



Scheme 2-30. Two possible reaction pathways for the formation of 15a starting from 13.

As in former chapters explained, silole dianions are aromatic and hence are interesting ligands for early transition- and rare earth metal complexes. They are able to coordinate to metal centers either as η^5- or η^4-ligands[87,88] or even in η^1-coordination mode with the ionic lone pair.[89]

Preparation of dipotassio-silole dianions from **13** proceeds according to literature *via* addition of 5 equiv. potassium in 1,4-dioxane at 100 °C and stirring for 8 hours.[34]

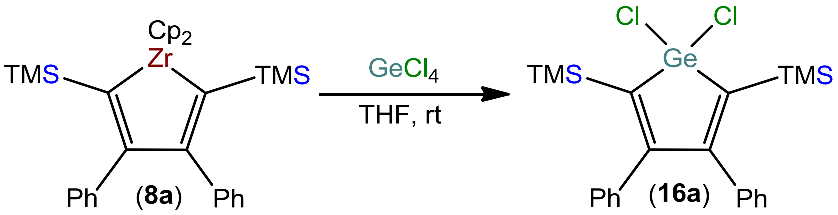
In doing so, NMR-spectroscopic reaction control showed that next to the dianionic silole **15a** a dimeric dianion **15b** formed, (Scheme 2-30) which is known from various similar reactions.[29,35,90–93] **15b** can be converted to **15a** with another excess of potassium. However, its formation can be avoided by reaction of **13** with 10 equiv. potassium in THF at room temperature overnight.

2.2. Synthesis of Germoles

Germoles are higher homologs of siloles with related properties, but retrieve by far less attention than siloles. Goldfuss and Schleyer *et al*. computed that germoles have a smaller C-M-C angle, but longer C-M bonds than siloles, originating from the larger ionic radius of germanium.[14] Additionally, showed Yamaguchi *et al*. that germoles have a similar HOMO-LUMO gap as siloles with both HOMO as well as LUMO slightly higher in energy.[94] In a review by Lee and Sekiguchi are mono- and dianionic structures of germoles summarized,[26] and also in the review by Saito and Yoshioka.[95]

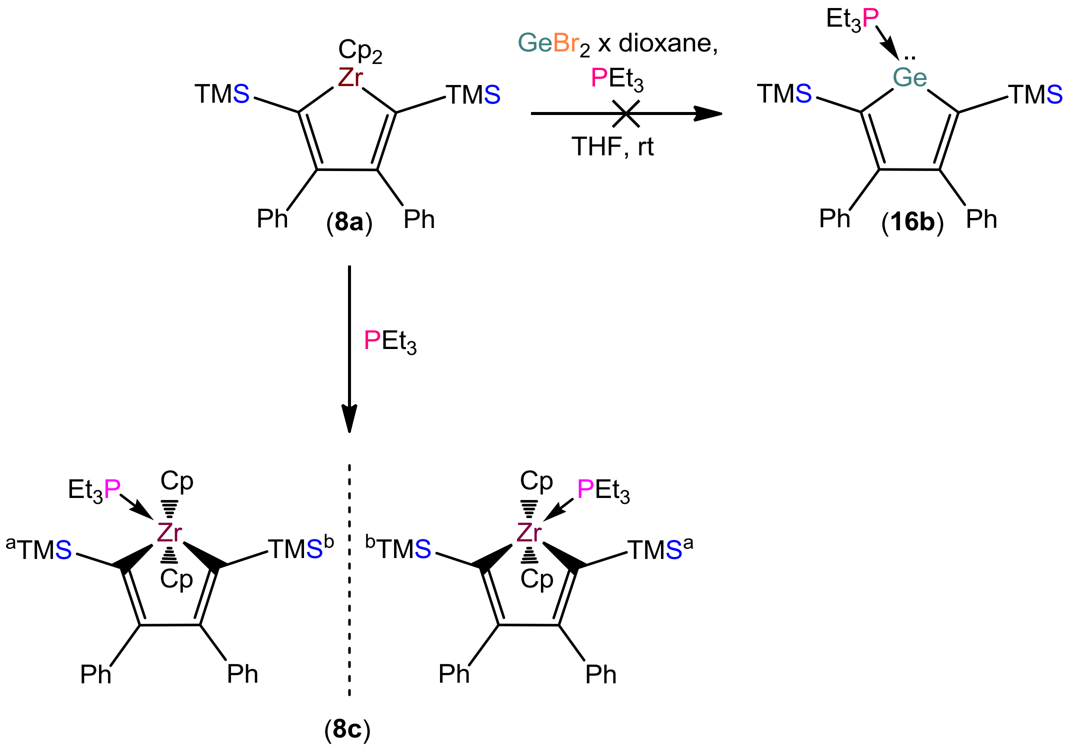
The synthesis of dianionic germoles is more straightforward than the synthesis of dianionic siloles, since 1,1-dichlorogermoles can be prepared directly from zircenocenoles[4] followed by reduction.[96]

Synthesis of **16a** was achieved by direct transmetallation of **8a** with $GeCl_4$. (Scheme 2-31)[97]



Scheme 2-31. Synthesis of 16a *via* direct transmetallation of 8a with $GeCl_4$.

Moreover, a direct transmetallation attempt with Ge(II)Br_2 x dioxane in the presence of 1 equiv. triethylphosphine was carried out. (Scheme 2-32) The used reaction condition leads to a phosphine adduct **8c** instead.



Scheme 2-32. In the direct transmetallation reaction of 8a with Ge(II)Br_2 x dioxane in the presence of PEt_3 formed the zircnocenacycle-phosphine adduct 8c instead of 16b.

Triethylphosphine is able to coordinate to **8a** giving a stable 18-valence-electron-complex, which was detected with NMR-spectroscopy in the crystallized fraction. Triethylphosphine can coordinate from two sites showing a clear site differentiation in the ^{1}H- and 13C-NMR-spectrum with two singlets for the two trimethylsilyl-groups.

To overcome the unreactive adduct formation and to prepare **16b**, it can be considered to perform the reaction at reflux temperatures and also to switch the used phosphine to the more volatile trimethylphosphine.

An alternative path might be *prior* solvation of $GeBr_2$ x dioxane in PEt_3 to form a stable $GeBr_2$ x PEt_3 complex. Afterwards unneeded solvent (dioxane and PEt_3) can be removed. However, PEt_3 might dissociate from $GeBr_2$ and coordinate to **8a** to give again **8c**.

Another option could be direct reaction of $GeBr_2$ x dioxane with **8a** and trapping of the reactive cyclicgermylene with PEt_3 afterwards.

2.3. Synthesis of Various Metallocenes and Yttrium Complexes with a Direct Y-Si Bond

The rise of metallocenes in organometallic chemistry with the famous cyclopentadienyl ligand started with the fortunate discovery of ferrocene by Pauson and Kealy[98] and the structural characterization of E. O. Fischer, G. Wilkinson[99] and R. B. Woodward. Today the use of the Cp-ligand has found broad application in modern catalysis and is often referred to as a so-called spectator ligand for d-group elements. However, in some cyclopentadienyl-rare-earth-metal complexes the Cp is no longer a spectator ligand, but participates directly in reductive reactions (e.g. sterically induced reduction).[2,100] This behavior of lanthanocenes raised the question, whether germole- or silole containing lanthanocenes can be synthesized.

However, since such complexes are unknown by now and lanthanide chemistry is not very well investigated, less complex target molecules were aimed at as a start.

For this reason, Y was chosen as a starting ion and should extend our gathered knowledge on other lanthanides later on. Yttrium(III) has a similar ionic radius as holmium(III) and has also an empty d-orbital.[101] Furthermore, it is in the same group as lanthanum, diamagnetic (100% spin ½ *nuclei*, ^{39}Y) and behaves chemically similar to lanthanides.

2.3.1. Synthesized Metallocenes

For the preparation of metallocenes, magnesocene (**17**) as a “Cp-transferring” agent was synthesized according to literature.[102]

Although the field of metallocenes is well investigated and new compounds are not likely to be found, we reacted magnesocene with In(III)-, W(VI)- and Nb(V) chlorides to eventually form unknown metallocene compounds.

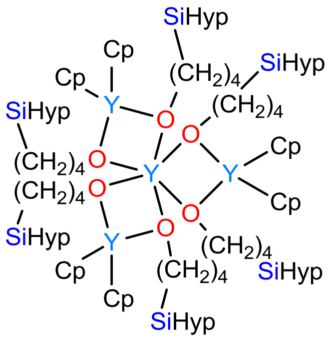
In the reaction with $InCl_3$ the more stable $InCp_3$ (**18b**) instead of the unknown Cp_2InCl (**18a**) formed. The spectra of investigated reaction mixtures of WCl_6 or $NbCl_5$ with magnesocene gave no clear results.

Cp_2YCl (**20**) can be prepared by reaction of YCl_3 (**19**) with $MgCp_2$ (**17**) in toluene at rt for 2 days.[103] Interestingly, **20** is only badly soluble in toluene and precipitates along with $MgCl_2$. Therefore, an alternative work-up method than extraction with toluene should be considered.

2.3.2. Synthesis of [$Cp_2Y(HypSi)$] (**22a**)

To approach the synthesis of desired K[Cp_2Y(silole dianion)] and K[Cp_2Y(germole dianion)] compounds, less sophisticated system were investigated first.

Cp_2YCl (**20**) dissolved in THF at rt was subjected to reaction with 1 equiv. of hypersilyl potassium (**21**). After 18 h, NMR-spectroscopy revealed that **21** was fully consumed and aside from small amounts of tetrakis(trimethylsilyl)silane (**23**) formation, four different Cp signals along with **20** were observed. The amount of Cp signals in the ^{1}H-NMR-spectrum may be explained by incomplete reaction and through formation of a K[$Cp_2Y(HypSi)_2$] (**22b**) ate-complex. This hypothesis would explain three of the five observed signals. Since crystallization gave no suitable crystals for XRD-analysis, the experiment was repeated with 2 equiv. **21**.



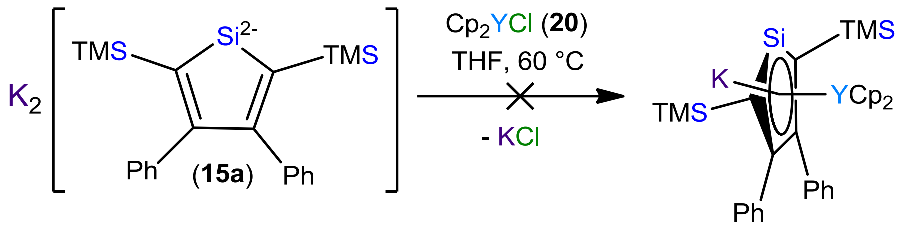
(**22c**)

This time the reactions progress was controlled over 1 week with NMR-spectroscopy. After that time roughly 50% of **21** had formed **23**. Crystallization from pentane revealed, that the other half had opened THF and formed the tetrameric complex (**22c**). To avoid THF-opening, solvents towards toluene/TMEDA were switched. Therefore, coordinated THF was removed from 2 equiv. **21** under reduced pressure before 1 equiv. **20** in 10 equiv. TMEDA and toluene was added.

Unfortunately, the drying step was not complete, since the last THF molecules are very tightly bound to **21**. However, the yielded product mixture looked significantly more promising than the previous attempts with less amounts of **22c** (20%) and **23** (10%), but a set of unknown peaks in the ^{29}Si-NMR-spectrum (-6.3, -7.4, -7.6, -7.8, -170.5, -172.3), two of them could be **22b**. It has to be mentioned that none of these peaks is **21** (-5.0 ppm in TMEDA-toluene). The first reaction control after 17 h, showed that **21** is consumed very fast by this reaction and **22c** is formed very slowly later on (no **21** and **22c** observable). From day 6 to day 13, the peak at -6.3 ppm shrunk by the same amount as **22c** grew within that time. This indirect proportionality might indicate that the product with the peak at -6.3 ppm is able to slowly transform towards **22c**. It seems that **22c** is thermodynamically- but not kinetically favoured.

The reaction will be redone with totally coordinating-solvent-free **21**, to further minimalize the possibility of **22c** formation.[104]

2.3.3. Reaction of Dipotassio-Silole (**15a**) with Cp_2YCl (**20**)

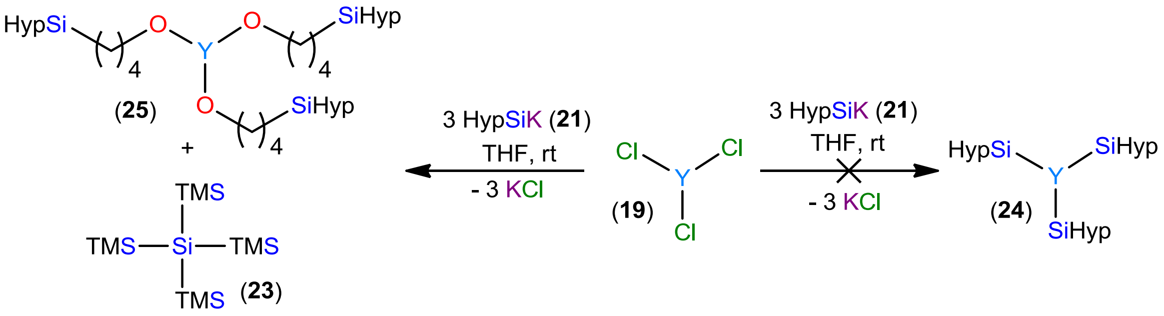


Scheme 2-33. 15a undergoes no reaction with 20 in THF at 60 °C, but decomposes.

To synthesize the aimed $K[Cp_2Y(\text{silole-dianion})]$ complex, **15a** and **20** were dissolved in THF at rt, but no reaction occurred after 1 day. Therefore, we kept the reaction mixture for 26 h at 60 °C, which resulted in decomposition of **15a**. (Scheme 2-33)

2.3.4. Reactions of YCl_3 (**19**) with Silanides

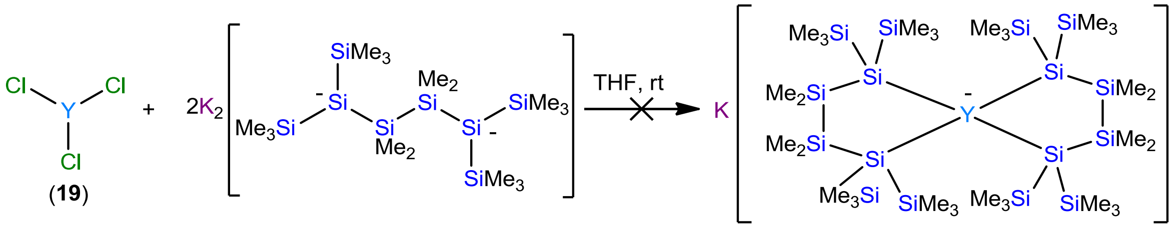
The reaction of YCl_3 with 3 equiv. **21** gives roughly 50% of **23** and another product with peaks at -13.0 and -82.2 ppm in the ^{29}Si-NMR spectrum. These two peaks are very similar to the signals found for THF-opening complex **22c**, therefore again THF-opening is very likely. Attempts to crystallize the complex out of pentane at -45 °C were unsuccessful. The dried compound has a foamy pattern. (Scheme 2-34)



Scheme 2-34. Reaction of 19 with 3 equiv. 21 gives products 23 and 25 in a rough 1:1 ratio, instead of 24.

Noticeably, the reaction of **19** towards **25** is complete within 4 h, which is in strong contrast to THF-opening of **20** towards **22c**, which typically takes multiple days to weeks. Apparently, the Cp ligands suppress THF-opening of yttrium-complexes to some extent, by providing 6 electrons with one coordination site and therefore lowering the lewis acidity of yttrium(III). To prepare **24**, a solvent switch towards a non-coordinating solvent has to be considered.

Additionally, we reacted **19** with 2 equiv. of 1,4-dipotassio-2,2,3,3-tetramethyl-1,1,4,4-tetrakis(trimethylsilyl)disilanide (Scheme 2-35).

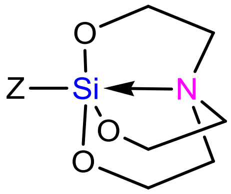


Scheme 2-35. Reaction of 19 with 2 equiv. of a 1,4-tetrasilandiide leads not to a "spiro-type"-ytterate complex .

The reaction progress was monitored with NMR-spectroscopy. After 1 week only 2,2,3,3-tetramethyl-1,1,1,4,4,4-hexakis(trimethylsilyl)silane was found in the reaction mixture. Probably, THF as solvent was not ideal for this reaction.

2.4. Synthesis of Silatranes

Silatranes are a class of hypervalent silicon compounds with three Si-O bonds within a plane and a dative N-Si bond, besides a Si-Z bond, where Z is a residue (Scheme 2-36).[5]



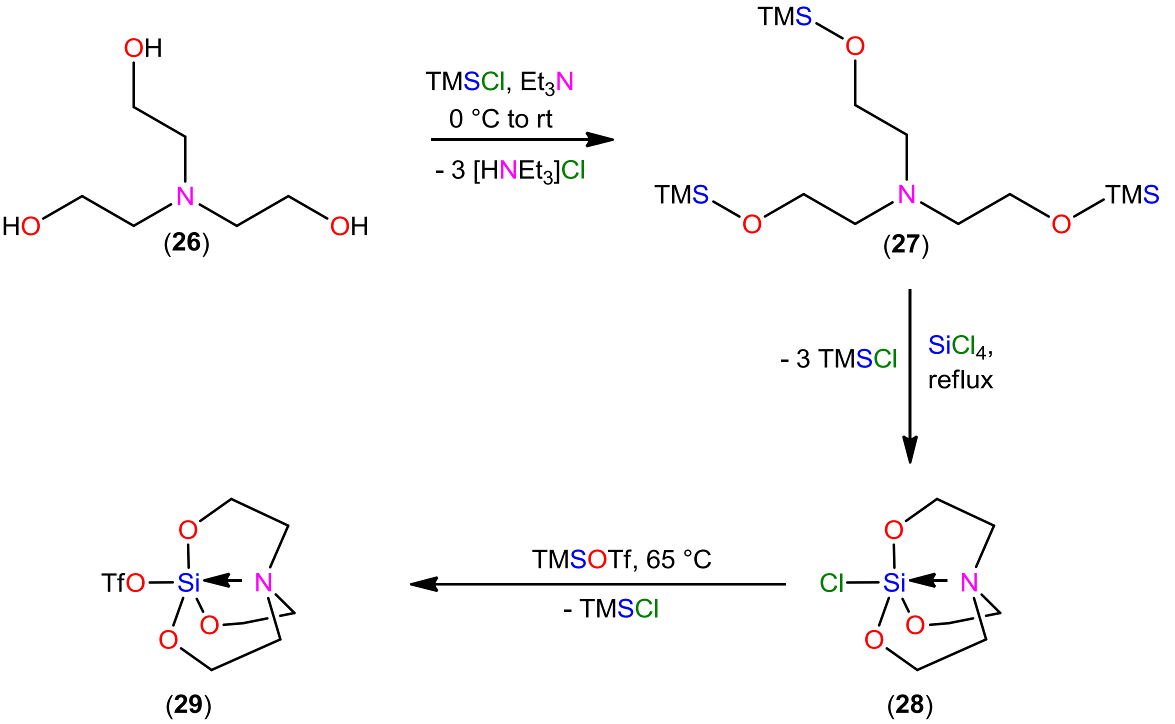
Scheme 2-36. Typical structure of a silatrane, with a plane of three Si-O bonds, an orthogonal dative N-Si bond and a Si-Z bond to a residue.

The dative bond and the Si-Z bond influence each other. If the N-Si bond becomes very strong (short Si-N distance) the Si-Z bond lengthens (weaker Si-Z bond). Therefore, we can speak of a 3-center-4-electron bond.[105] Furthermore, we can influence this bond by the nature of Z, *via* protonation of the N lone pair with strong acids[106] or even electrochemically.[107] The central Si atom of the silatrane should be a good electrophile, but in the case of 1-chlorosilatrane it has a very low reactivity towards nucleophiles. The unique geometry of the silatrane cage blocks the possibility of a backside attack on the Si-Cl and lowers the reactivity drastically.[108]

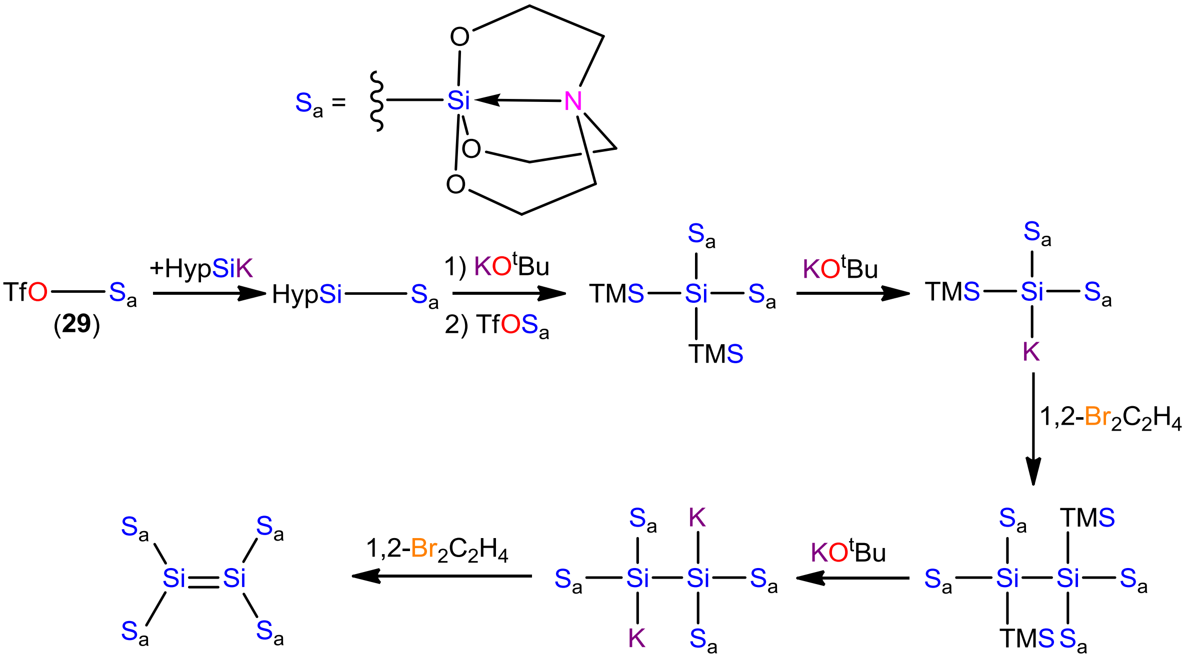
The possible applications of this interesting compound class are manifold and reach from anchors for catalysts on metal oxide surfaces[109] over molecular switches[110] to “molecular muscles” if many silatrane units are linked to each other.

The synthesis of silatranes was done according to literature.[106] (Scheme 2-37)

Starting from triethanolamine, **27** can be formed by formation of three silylether with trimethylsilyl chloride and base. Initial cooling prevents a too violent reaction and vaporization of solvent. Further reaction of **27** with tetrachloro silane at reflux of chloroform (61 °C) gives **28**. This reaction step is entropically-driven with the generation of 3 equiv. trimethylsilyl chloride. The substitution of chloride by a triflate is done to enhance the electrophilicity of the central silicon atom by introducing a better leaving group.



Scheme 2-37. Three step synthesis of silatrane 29. First, the hydroxyl groups of triethanolamine 26 are transformed to a silylether. Next, the silatrane structure 28 is built with tetrachloro silane at reflux of chloroform. In the last step, the chloride is substituted by a triflate, which is a better leaving group.



Scheme 2-38. Possible reaction path for the synthesis of a tetrasilatrane substituted disilene starting from 29 as precursor. S_a = silatrane

Moreover, **29** can be reacted further towards a disilene along the hypothetic reaction path provided in Scheme 2-38. The final tetrasilatrane disilene would be a very interesting compound for electro-spectroscopic analysis.

3. SUMMARY

In this thesis were discussed different options towards the preparation of siloles with a focus on the reaction path by Tamao and *co*-workers. For this purpose were synthesized the new compounds bis(diethylamino)bis(trimethylsilylethynyl)silane (**3b**) and bis(diethylamino)bis((dimethylphenylsilyl)ethynyl)silane (**3c**). It was demonstrated, that this two compounds are not suitable for the *endo-endo* reductive cyclization.

Moreover, it was developed a reaction concept towards a shorter and more atom-efficient synthesis of a 2,5-asymmetric β-carbanionic intermediate by utilizing the cleavage of trimethylsilyl groups with potassium *tertiary*-butoxide and crown-ether. First synthesis studies are shown herein.

Furthermore, the quantitative preparation of the new compound 3,4-diphenyl-1,1-ditriflate-2,5-bis(trimethylsilyl)silole (**14**) was achieved, which is a considerable alternative towards the synthesis of dianionic siloles.

In the synthesis of germoles along the reaction path provided by Fagan and *co*-workers, the interesting compound 2,5-bis[bis(diethylamino)phenylethynylsilyl]-3,4-diphenyl-1-zirconocenacyclopenta-2,4-diene (**8b**) was reported together with several modification options.

Additionally, we were able to prepare a 1,1-dichlorogermole (**16a**) suitable for reduction and further reactivity towards yttrium-germole-complexes.

With the identification of THF-opening products **22c** and **25** in the reaction of Y-Cl complexes with hypersilyl potassium in THF, the need for a different solvent like toluene/TMEDA was reported.

In addition, the preparation of 1-chloro-silatrane and a concept towards the synthesis of a tetrasilatrane substituted disilene was shown.

4. EXPERIMENTAL SECTION

General Remarks. All reactions involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen using either Schlenk techniques or a glove box. All solvents were dried using column based solvent purification system.[111]

Chemical substances used as starting materials like, tetrakis(trimethylsilyl)silane[112], hypersilyl potassium,[48,104] 1,4-dipotassio-1,1,4,4-tetrakis(trimethylsilyl)-2,2,3,3-tetramethyldisilanide,[113] and dimethylphenylchlorosilane[114] were prepared according to literature procedure.

Other used chemicals were obtained from different suppliers (MERCK, ABCR, Sigma-Aldrich, Riedel-de Haen, Fluka, Lactan) and used without further purification.

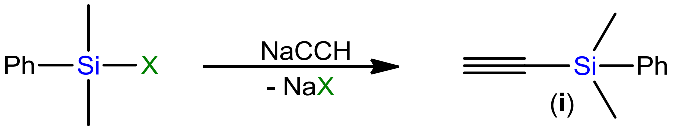
^{1}H (300 MHz), ^{13}C (75.4 MHz), ^{19}F (282.2 MHz), ^{31}P (121.4 MHz) and ^{29}Si (59.3 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer. To compensate for the low isotopic abundance of ^{29}Si the INEPT pulse sequence was used for the amplification of the signal.[115,116]

Measured samples were dissolved in benzene-d_6, chloroform-d_1, DMSO-d_6 or were objected to NMR spectroscopy neat or in a non-deuterated solvent with a D_2O filled capillary. Shifts are given in ppm and are referenced to solvent residuals.

X-ray structure analysis was performed with a BRUKER-AXS SMART APEX CCD diffractometer (λ = 0.71073 Å). Gathered data was reduced to F^2_0 and corrected for absorption effects with SAINT[117] and SADABS,[118] respectively. Solved structures were obtained using direct methods and refined by full-matrix least-squares method (SHELXL97).[119] Refinement of all non-hydrogenatoms was done with anisotropic displacement parameters and positions of the hydrogen atoms were obtained applying standard bond angles and lengths.

4.1. Synthesis of Siloles

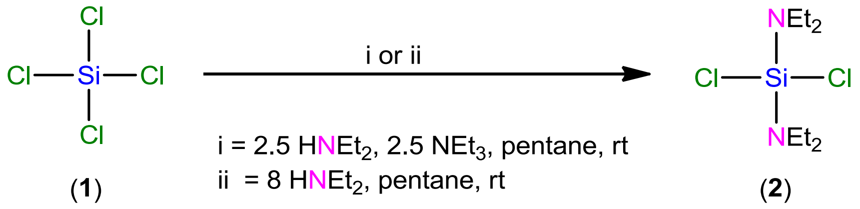
4.1.1. Synthesis of Ethynyldimethylphenylsilane[120] (**i**)



Sodium-acetylide (18.74 g, 1.0 equiv., 70.2 mmol, 18% slurry in xylene: mineral oil) was dissolved in THF (35 mL) and cooled to 0 °C. Then $XSiMe_2Ph$-mixture (13.06 g, 1.04 equiv., 72.7 mmol, 4:1 = $ClSiMe_2Ph$:$BrSiMe_2Ph$) was added dropwise. The yellow suspension was stirred for 20 min at 0 °C before it was allowed to warm to rt and was stirred for another 12 h. The reaction was quenched by slow addition of water (50 mL). The two phases were separated and the aqueous phase was extracted three times with Et_2O. The combined organic phases were treated with brine (70 mL) and dried with Na_2SO_4. After filtration and concentration of the solution, **i** was subjected to bulb-to-bulb distillation at 60 °C (1 mbar). For further purification, the product was dissolved in pentane and was subjected to column chromatography with pentane as eluent. The volatiles were removed under vacuo and **i** was obtained as colorless liquid (3.87 g, 34%).

NMR (δ in ppm): ^1H (Neat/D_2O-Lock): 7.64 (m, 2H), 7.28 (m, 3H), 2.35 (s, 1H), 0.41 (s, 6H). ^{29}Si (Neat/D_2O-Lock): -21.7 (s, $SiMe_3$).

4.1.2. Synthesis of Bis(diethylamino)dichlorosilane (**2**)[3,41]



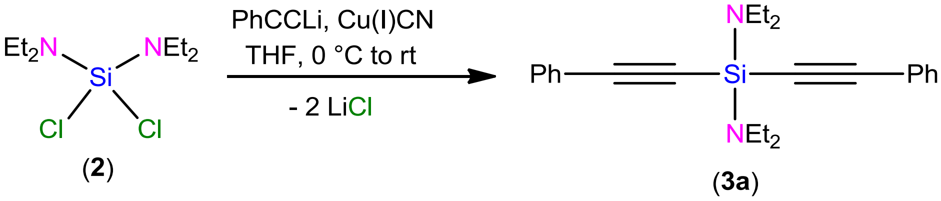
i)

1 (9.23 g, 1 equiv., 54.3 mmol, 6.2 mL) was dissolved in pentane (200 mL). The colorless solution was cooled with a cold water bath (approx. 10 °C). Then triethylamine (13.36 g, 2.4 equiv., 132 mmol, 18.4 mL) was added dropwise, followed by dropwise addition of diethylamine (8.32 g, 2.1 equiv., 114 mmol, 11.8 mL). The suspension was stirred for 1d at rt. The cloudy, voluminous precipitate was filtered and washed with pentane three times. The solvent and the remaining reactants were removed under reduced pressure. **2** was obtained as slightly yellow liquid (8.51 g, 65%). NMR (δ in ppm): ^{1}H (Neat/D_2O-Lock): 2.89 (q, *J* = 7.1 Hz, 8H), 0.96 (t, *J* = 7.2 Hz, 12H). ^{13}C (Neat/D_2O-Lock): 39.0, 14.2. ^{29}Si (Neat/D_2O-Lock): -31.1 (s, Si_q)

ii)

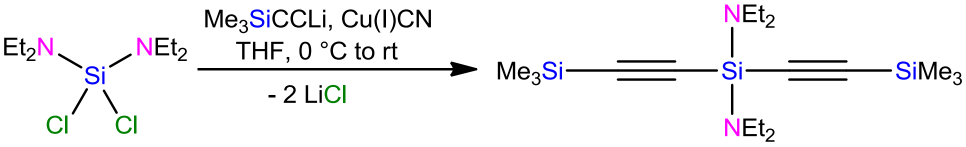
1 (5.0 g, 1 equiv., 29.4 mmol, 3.4 mL) was dissolved in pentane (110 mL). Then diethylamine (17.75 g, 8.3 equiv., 243 mmol, 25.0 mL) was added dropwise. The suspension was stirred for 1 d at rt. The cloudy, voluminous precipitate was filtered and was washed with pentane three times. The solvent and the remaining reactants were removed under reduced pressure. (**2**) was obtained as dark yellow liquid (3.06 g, 43%) contaminated with (0.77 g, 9%) tris(diethylamino)chlorosilane. NMR of contaminant (δ in ppm): ^{1}H ($CDCl_3$): 2.89 (q, *J* = 7.0 Hz, 8H), 1.01 (t, *J* = 7.1 Hz, 12H). ^{29}Si ($CDCl_3$): -30.2 (s, Si_q)

4.1.3. Synthesis of Bis(diethylamino)bis(phenylethynyl)silane[3] (**3a**)



Phenylacetylene (**6a**, 6.30 g, 2 equiv., 61.69 mmol, 6.77 mL) was dissolved in THF (100 mL) and the solution was cooled to 0 °C. Then *n*-butyllithium (28 mL, 2.3 equiv., 70.0 mmol, 2.5 M in hexane) was added dropwise. The solution was stirred for 80 min in which color changes from orange to dark green and finally to dark brown were observed. Next **2** (7.45 g, 1 equiv., 30.63 mmol) and copper(I)cyanide (0.28 g, 0.1 equiv., 3.13 mmol) were added. The reaction mixture was allowed to warm to rt and was stirred additional 72 h. The solvent was removed in vacuo and the residue was extracted three times with pentane (3 x 40 mL). The solution was again diluted in pentane (1:1) and filtrated. After pentane was removed under reduced pressure, **3a** was obtained as bronze colored oil (11.27 g, 98%). NMR (δ in ppm): ^{1}H (Neat/D_2O-Lock): 7.32 (m, 4H), 7.09 (m, 6H), 3.03 (q, J = 6.8 Hz, 8H), 1.07 (t, J = 7.0 Hz, 12H). ^{13}C (Neat/D_2O-Lock): 131.5, 128.4, 128.0, 122.8, 104.0, 90.9, 39.0, 15.0. ^{29}Si (Neat/D_2O-Lock): -56.0 (s, Si_q)

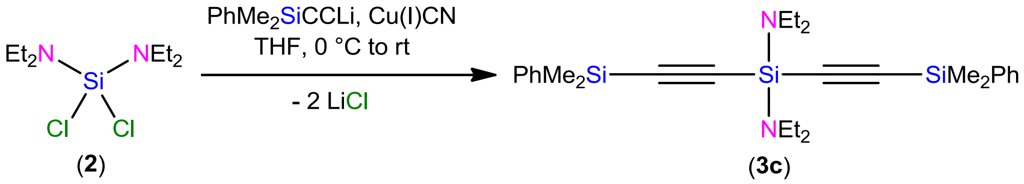
4.1.4. Synthesis of Bis(diethylamino)bis(trimethylsilylethynyl)silane (**3b**)



(**2**) (**3b**)

Trimethylsilylacetylene (**6b**, 210 mg, 2.1 equiv., 2.14 mmol) was dissolved in THF (8 mL) and the solution was cooled to 0 °C. Then *n*-butyllithium (1.0 mL, 2.4 equiv., 2.5 mmol, 2.5 M in hexane) was added dropwise. The solution was stirred for 1 h, in which a color change from colorless to slightly bronze-colored was observed. Next **2** (250 mg, 1 equiv., 1.0 mmol) and copper(I)cyanide (14 mg, 0.15 equiv., 0.16 mmol) were added. The reaction mixture was allowed to warm to rt and was stirred for additional 24 h. The now yellowish solution with brown precipitate was dried under reduced pressure. Pentane was added and the suspension was centrifuged and filtrated. After the orange filtrate was concentrated in vacuo, **3b** was obtained as a dark red liquid (250 mg, 66%). NMR (δ in ppm): ^{1}H ($CDCl_3$): 2.93 (q, J = 7.0 Hz, 8H), 1.03 (t, J = 7.0 Hz, 12H), 0.16 (s, 9H). ^{13}C ($CDCl_3$): 113.2, 110.1, 38.8, 14.8, -0.41. ^{29}Si ($CDCl_3$): -18.7 (s, $SiMe_3$), -59.9 (s, Si_q)

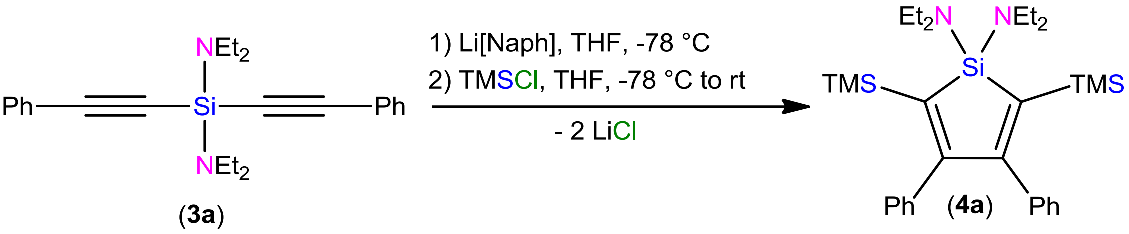
4.1.5. Synthesis of Bis(diethylamino)bis((dimethylphenylsilyl)ethynyl)silane (**3c**)



i (200 mg, 2.0 equiv.; 1.25 mmol) was dissolved in THF (8 mL) and the solution was cooled to 0 °C. Then *n*-butyllithium (0.52 mL, 2.1 equiv.; 1.31 mmol; 2.5 M in hexane) was added dropwise. The colorless solution was stirred for 1 h. Next **2** (154 mg, 1.0 equiv.; 0.63 mmol) and copper(I)cyanide (10 mg, 0.17 equiv.; 0.11 mmol) were added. The reaction mixture was allowed to warm to rt and was stirred for 16 h. The now reddish suspension was dried under reduced pressure. Pentane was added and the suspension was centrifuged and filtrated. After the yellow filtrate was concentrated in vacuo, **3c** was obtained as a yellow liquid (210 mg, 68%).

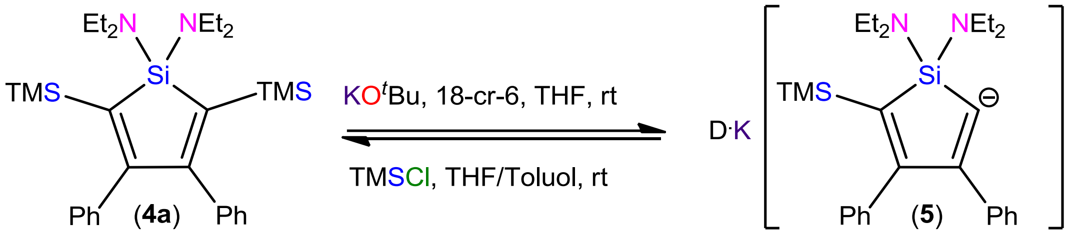
NMR (δ in ppm): ^{1}H ($CDCl_3$): 7.92 (m, 4H), 7.62 (m, 6H), 3.28 (q, *J* = 7.0 Hz, 8H), 1.33 (t, *J* = 7.0 Hz, 12H), 0.69 (s, 12H). ^{13}C ($CDCl_3$): 136.9, 133.9, 129.5, 127.9, 112.5, 111.1, 39.0, 15.1, -0.9. ^{29}Si ($CDCl_3$): -22.1 (s, $SiMe_3$), -59.5 (s, Si(q)).

4.1.6. Synthesis of 1,1-Bis(diethylamino)-3,4-diphenyl-2,5-bis(trimethylsilyl)silole[3] (**4a**)



Naphthalene (6.25 g, 4.7 equiv.; 48.8 mmol) was dissolved in THF (100 mL) and small pieces of lithium-ribbon (0.36 g, 5.0 equiv.; 51.9 mmol) were added. The dark green solution was stirred for 4 h. Afterwards the solution was cooled to -80 °C and **3a** (3.88 g, 1.0 equiv.; 10.4 mmol) dissolved in THF (20 mL) was added dropwise within 15 min. The solution was stirred at -80 °C for 1 h and a dark purple color was observed. Then trimethylsilyl chloride (6.42 g, 5.7 equiv.; 59.1 mmol; 7.5 mL) was added within 10 minutes and the solution was allowed to warm to rt. The brownish reaction mixture was stirred for 12 h. The solvent and the excess of trimethylsilyl chloride were removed under reduced pressure. The residue was subjected to sublimation at 80 °C and 1 mbar to remove the majority of naphthalene (5.25 g; 84%). The remaining solid was extracted three times with pentane. The yellow solution was concentrated and was kept at -45 °C for crystallization. **4a** was obtained as slightly yellow crystals (4.15 g (77%) yield. NMR (δ in ppm): ^{1}H (C_6D_6): 6.78 – 6.95 (m, 10H), 3.12 (q, J = 7.0 Hz, 8H), 1.14 (t, J = 7.0 Hz, 12H), 0.10 (s, 18H). ^{13}C (C_6D_6): 168.7, 142.9, 140.4, 128.7, 126.9, 126.0, 38.9, 14.2, 1.1. ^{29}Si (Pentane/D_2O-Lock): 3.0 (s, Si_q), -10.5 (s, $SiMe_3$)

4.1.7. Synthesis of 1,1-Bis(diethylamino)-3,4-diphenyl-2-potassium-5-trimethylsilylsilole (**5**)



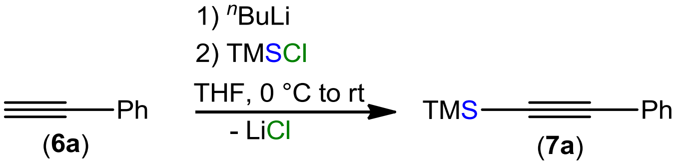
D = 18-cr-6

[APM8; p.16]

KO^{t}Bu (45 mg, 1.05 equiv., 0.40 mmol) and **4a** (200 mg, 1.0 equiv., 0.38 mmol) were dissolved in cold THF (4 mL). After 12 days, 18-cr-6 (107 mg, 1.08 equiv., 0.41 mmol) was added and the solution immediately turned dark red and was subjected to NMR-spectroscopy. After 60 min, TMSCl (112 mg, 2.7 equiv., 1.13 mmol) was added and the reaction mixture was subjected to NMR-spectroscopy showing signals of **4a**.

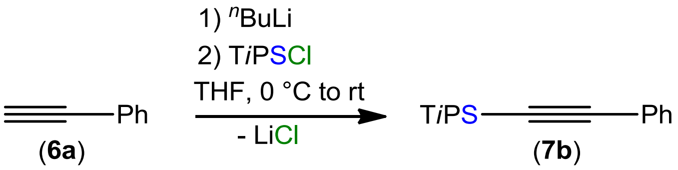
4.2. Synthesis of Cyclic Zirconocenes

4.2.1. Synthesis of Trimethyl(phenylethynyl)silane (**7a**)



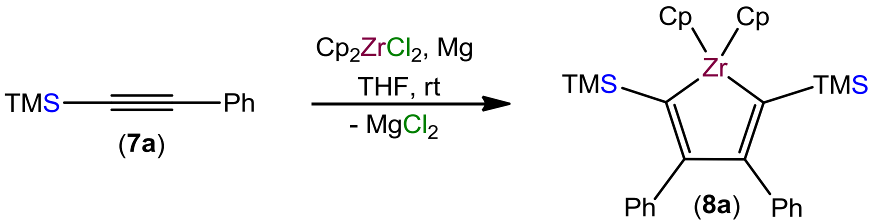
6a (5.86 g, 1.0 equiv., 57.4 mmol) was dissolved in THF (60 mL) and cooled to 0 °C. Then, *n*-butyllithium (25.2 mL, 1.1 equiv., 63.1 mmol, 2.5 M in hexane) was added dropwise and the solution was stirred for 1 h, before trimethylsilyl chloride (9.30 g, 1.5 equiv., 86.0 mmol, 10.9 mL) was added. The reaction mixture was allowed to warm to rt and was stirred for 16 h. The reaction mixture was quenched with saturated NH_4Cl solution (100 mL) and the phases were separated. The aqueous phase was washed with petroleum ether (3 x 30 mL) and the combined organic phases were dried with Na_2SO_4 before the solvent was removed under reduced pressure. **7a** was obtained as yellow oil (9.05 g, 90%) yield. NMR (δ in ppm): ^1H (Neat/D_2O-Lock): 7.50 (m, 2H), 7.20 (m, 3H), 0.31 (s, 9H). ^{29}Si (Neat/D_2O-Lock): -18.3 (s, $SiMe_3$).

4.2.2. Synthesis of Triisopropyl(phenylethynyl)silane (**7b**)



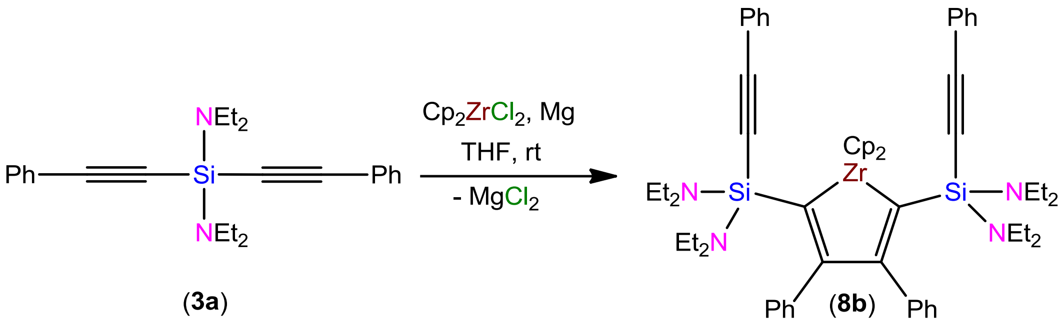
6a (1.00 g, 1.0 equiv., 9.8 mmol) was dissolved in THF (10 mL) and cooled to 0 °C. Than *n*-butyllithium (4.3 mL, 1.1 equiv., 10.8 mmol, 2.5 M in hexane) was added dropwise and the solution was stirred for 1 h, before triisopropylsilyl chloride (2.80 g, 1.5 equiv., 14.7 mmol, 3.08 mL) was added. The reaction mixture was allowed to warm to rt and stirred for 3h. The reaction mixture was quenched with saturated NH_4Cl solution (10 mL) and the phases were separated. The aqueous phase was washed with petroleum ether (3 x 5 mL) and the combined organic phases were dried with Na_2SO_4 before the solvent was removed under reduced pressure. The crude pale yellow oil was subjected to bulb-to-bulb distillation (gradually 70-140 °C, 5 mbar). **7b** was obtained as colorless oil (2.02 g, 80%). NMR (δ in ppm): ^{1}H ($CDCl_3$): 7.60 (m, 2H), 7.39 (m, 3H), 1.29 (s, 21H). ^{29}Si ($CDCl_3$): -1.8 (s, TiPS).

4.2.3. Synthesis of 3,4-Diphenyl-2,5-bis(trimethylsilyl)zirconocenacyclopenta-2,4-diene (**8a**)



Cp_2ZrCl_2 (202 mg, 1.0 equiv., 0.69 mmol), Mg-turbings (19 mg, 1.1 equiv., 0.78 mmol) and **7a** (242 mg, 2 equiv., 1.38 mmol) were dissolved in THF (4 mL) and stirred at rt. After 20 h full conversion was accomplished. The solvent was removed under reduced pressure and toluene was added. The formed precipitate was centrifuged, filtrated and recrystallized from toluene at -45 °C. **8a** was obtained as yellow crystals (320 mg, 81%) yield. NMR (δ in ppm): ^1H (C_6D_6): 6.87 (m, 4H), 6.76 (m, 2H), 6.69 (m, 4H), 6.16 (s, 10H), -0.16 (s, 18H).^{29}Si (C_6D_6): -15.6 (s).

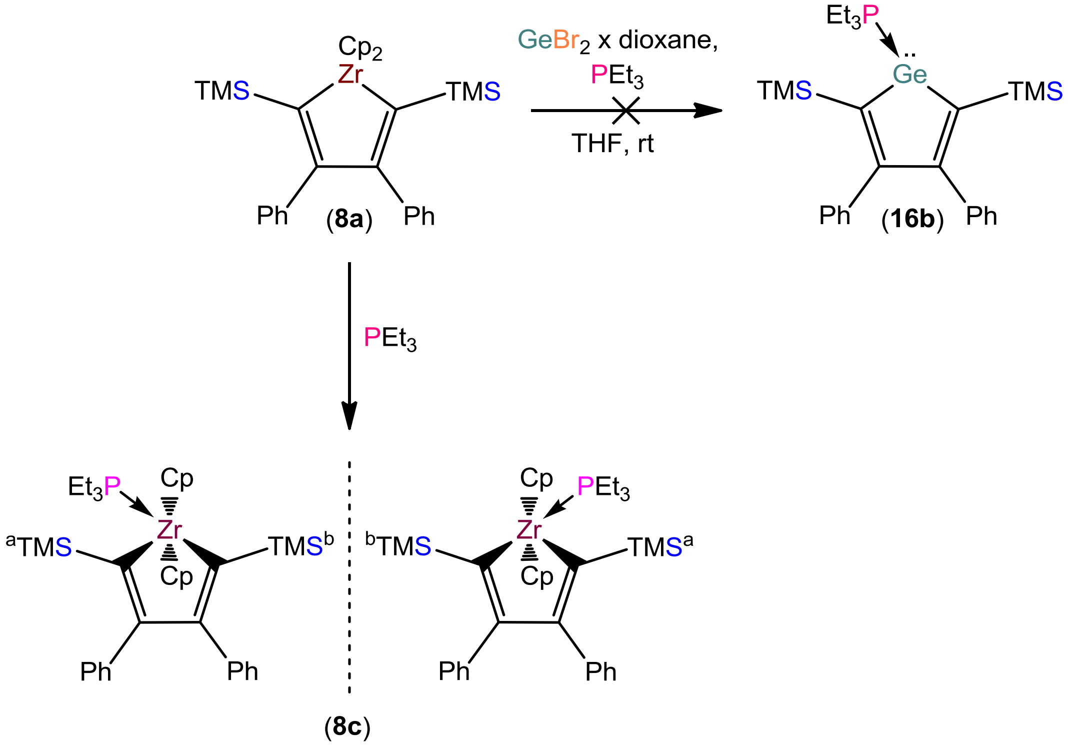
4.2.4. Synthesis of 2,5-Bis[bis(diethylamino)phenylethynylsilyl]-3,4-diphenyl-1-zirconocenacyclopenta-2,4-diene (**8b**)



3a (198 mg, 1.95 equiv., 0.53 mmol), zirconocenedichloride (79 mg, 1.00 equiv., 0.27 mmol) and Mg turnings (7 mg, 1.05 equiv., 0.29 mmol) were dissolved in THF (3 mL) and stirred at rt for 2 d. The volatiles were removed under reduced pressure, pentane added and solids removed through centrifugation and filtration. The solids were dissolved in toluene and insoluble remains removed through centrifugation and filtration. The toluene solution was put into fridge (-44 °C). After 3 d, crystallized bright orange lamellas, which were unsuitable for XRD.

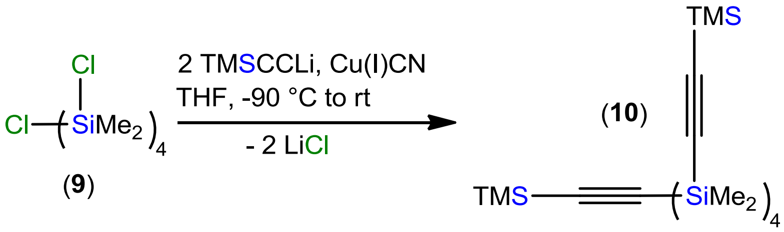
NMR (δ in ppm): ^{1}H (C_6D_6): 8.10 (m, 4H), 7.83 (m, 4H), 7.45 (m, 8H), 7.22 (m, 4H), 5.66 (s, 10H), 3.01 (q, J = 7.0 Hz, 16H), 0.94 (t, J = 7.0 Hz, 24H). ^{13}C (C_6D_6): 180.9, 167.2, 142.6, 141.7, 132.4, 130.8, 129.1, 128.6, 127.9, 127.5, 115.7, 114.2, 106.6, 38.5, 14.9.

4.2.5. Synthesis of 3,4-Diphenyl-2,5-bis(trimethylsilyl)-zirconocenacyclopenta-2,4-diene x Triethylphosphine Adduct (**8c**)



A 20 mL glasvial was charged with $GeBr_2$ x 1,4-dioxane (106 mg, 1.06 equiv., 0.33 mmol), PEt_3 (39 mg, 1.06 equiv., 0.33 mmol) and **8a** (174 mg, 1.0 equiv., 0.31 mmol) in THF (1 mL) and stirred at rt. After 3 h, the volatile were removed under reduced pressure and the residue was dissolved in toluene and subjected to NMR-spectroscopy. Due to incomplete reaction, THF (4 mL) was added and the reaction mixture was stirred for 7 d at rt. The solvents were removed and the residue was dissolved in toluene (5 mL) giving a clear brownish solution. At -45 °C colorless crystals formed in the solution, which were subjected to XRD and were identified as Cp_2ZrBr_2. The cloudy, crystals containing solution was filtrated, concentrated (to 2 mL) and was put into fridge at -43 °C for further crystallization. Again crystals were formed, which were subjected to NMR spectroscopy indicating the formation of **8c** instead of **16b**.

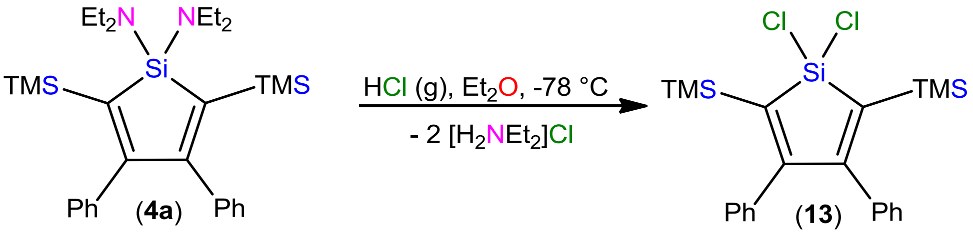
4.2.6. Synthesis of 1,1,2,2,3,3,4,4-Octamethyl-1,4-bis(trimethylsilyethynyl)tetrasilane (**10**)



Trimethylsilylacetylene (**6b**, 142 mg, 2.2 equiv., 1.45 mmol) was dissolved in THF (5 mL) and cooled to 0 °C. Then *n*-butyllithium (0.53 mL, 2.0 equiv., 1.33 mmol, 2.5 M in hexane) was added dropwise, the solution was stirred for 1 h and cooled to -90 °C. The deprotonated **6b** solution was added dropwise to **9** (200 mg, 1.0 equiv., 0.66 mmol) and Cu(I)CN (6 mg, 0.1 equiv., 0.07 mmol) in THF (4 mL) at -90 °C. The dark green solution was stirred for 1 h at -80 °C, before it was allowed to slowly warm to rt, during which a raspberry colored precipitate formed. The product solution was quenched with saturated NH_4Cl solution (10 mL) and the phases were separated. The aqueous phase was washed with petroleum ether (3 x 5 mL) and the combined organic phases were dried with Na_2SO_4 before the solvent was removed under reduced pressure. **G3** was obtained as colorless oil (230 mg, 82%). NMR (δ in ppm): ^{1}H ($CDCl_3$): 0.23 (s, 12H), 0.21 (s, 12H), 0.15 (s, 18H). ^{13}C ($CDCl_3$): 116.8, 113.3, 0.2, -1.8, -5.8. ^{29}Si ($CDCl_3$): -19.6 (s, TMS), -35.0 (s, $CCSiMe_2$), -44.0 (s, $SiMe_2$).

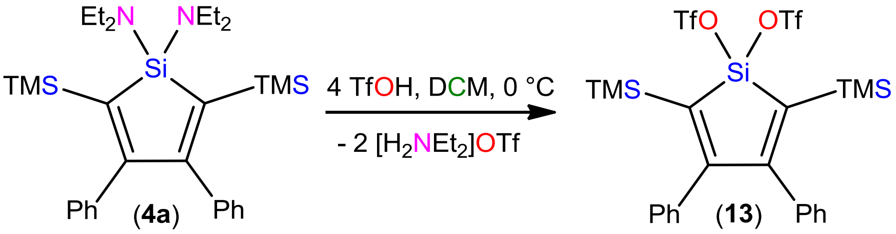
4.3. Synthesis of 1,1-Modified Siloles

4.3.1. Synthesis of 1,1-Dichloro-3,4-diphenyl-2,5-bis(trimethylsilyl)silole[3] (**13**)



In a two-neck roundbottom flask, which was equipped with a gas inlet and a bubbler, **4a** (677 mg, 1.0 equiv., 1.3 mmol) was dissolved in Et_2O (45 mL) and cooled to -80 °C. Then 40 equiv. dry HCl gas [dried with: NH_4Cl (2.80 g, 40 equiv.; 52.3 mmol) and H_2SO_4 (5.52 g, 43 equiv.; 56.3 mmol; 3.0 mL)] were bubbled through the reaction mixture within 30 min and the reaction mixture was allowed to warm to rt. Diethylether was removed under reduced pressure and the residue was extracted three times with pentane. Pentane was removed in vacuo and **13** was obtained as a yellow solid (410 mg, 71%). NMR (δ in ppm): ^{1}H (C_6D_6): 6.80 (m, 6H), 6.71 (m, 4H), 0.12 (s, 18H). ^{13}C (C_6D_6): 170.3, 140.5, 136.5, 128.4, 127.6, 127.4, 0.5. ^{29}Si (C_6D_6): 19.1 (s, Si_q), -8.1 (s, $SiMe_3$).

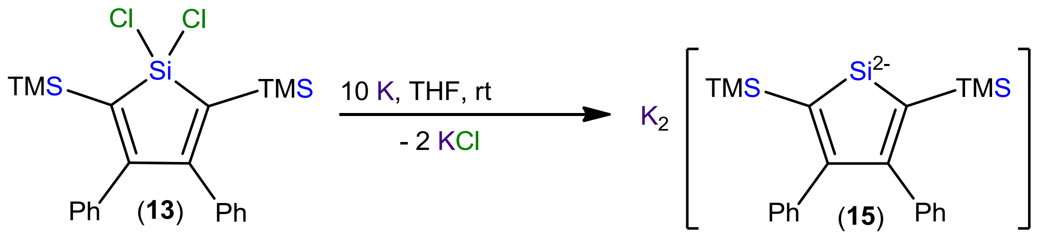
4.3.2. Synthesis of 3,4-Diphenyl-1,1-ditriflate-2,5-bis(trimethylsilyl)silole (**14**)

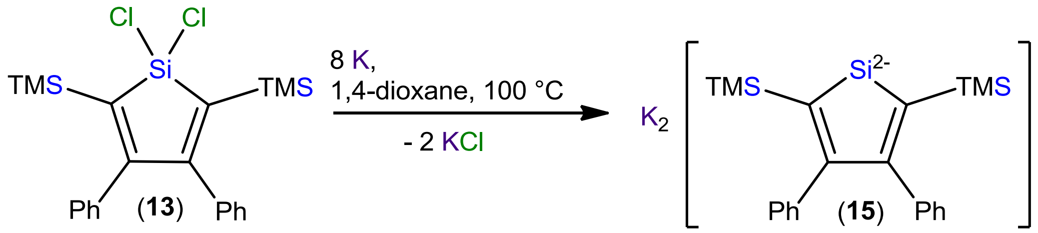


4a (305 mg, 1.0 equiv., 0.59 mmol) was dissolved in DCM (5 mL) and cooled to 0 °C. Trifluoromethanesulfonic acid (360 mg, 4.1 equiv., 2.40 mmol) was added and the reaction mixture, which was slowly warmed to rt, was stirred for 16 h. The volatiles were removed under reduced pressure, and pentane was added. The suspension was centrifuged, filtrated and concentrated. **13** was obtained as gold-yellow oil (quantitative, 395 mg).

NMR (δ in ppm): ^{1}H (C_6D_6): 6.77 (m, 6H), 6.65 (m, 4H), 0.09 (s, 18H). ^{13}C (C_6D_6): 177.0, 139.4, 130.5, 128.2, 128.1, 127.7, CF3 (not observed), 0.1. ^{29}Si (C_6D_6): -7.3 (s, $SiMe_3$), -9.5 (s, Si_q). ^{19}F (C_6D_6): -76.1.

4.3.3. Synthesis of 3,4-Diphenyl-1,1-dipotassio-2,5-bis(trimethylsilyl)silole[34] (**15**)





[1*]

13 (190 mg, 1.0 equiv., 0.424 mmol) and small potassium pieces (166 mg, 10.0 equiv.; 4.25 mmol) were dissolved in THF (5 mL). The dark red reaction mixture was stirred for 2 d at rt. The reaction mixture was centrifuged, filtrated and concentrated.

or

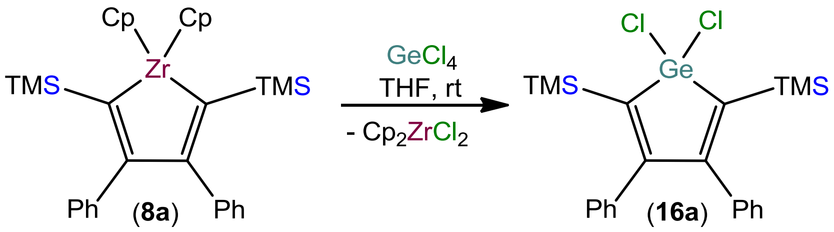
5 (200 mg, 1.0 equiv., 0.45 mmol) and small potassium pieces (88 mg, 5.0 equiv., 2.25 mmol) were dissolved in 1,4-dioxane (5 mL). The reaction mixture was stirred at 100 °C for 1 d. Then small pieces potassium (52 mg, 3 equiv., 1.33 mmol) were added and the reaction was stirred for 3 d. The reaction mixture was centrifuged, filtrated and concentrated.

NMR (δ in ppm): ^{1}H (THF/D_2O-Lock): 7.22-6.95 (m, 10H), 0.36 (s, 18H). ^{29}Si (1,4-Dioxane/D_2O-Lock): XX (s, Si_q), -18.3 (s, $SiMe_3$).

[1*] Private Communication with Prof. Dr. Thomas Müller of Carl von Ossietzky-University of Oldenburg

4.4. Synthesis of a Germole

4.4.1. Synthesis of 1,1-Dichloro-3,4-diphenyl-2,5-bis(trimethylsilyl)germole (**16a**)[97]



8a (190 mg, 1.00 equiv., 0.33 mmol) was dissolved in THF (2 mL) and $GeCl_4$ (76 mg, 1.06 equiv., 0.35 mmol, 40 µL) was added dropwise. The reaction mixture was stirred at rt for 23 h. The volatile were removed under reduced pressure, toluene added and the solids removed through centrifugation and filtration. After concentration, the solution was put into fridge (-44 °C). After 4 d, colorless crystals precipitated, which were subjected to NMR-spectroscopy.

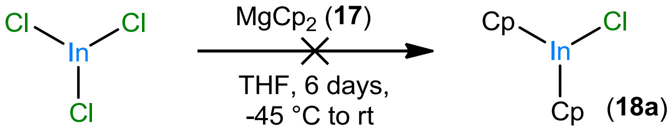
NMR (δ in ppm): ^{1}H (THF/D_2O-Lock): 7.26 (m, 6H), 7.10 (m, 4H), 0.16 (s, 18H).^{29}Si (THF/D_2O-Lock): -6.1 (s).

4.5. Synthesis of Metallocenes

4.5.1. Synthesis of Dicyclopentadienylmagnesium[102] (**17**)

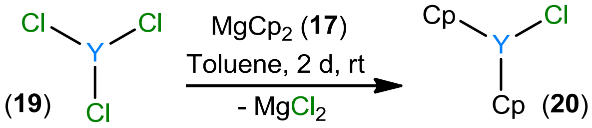
A solution of Mg(^{n}Bu)(^{s}Bu) (105 mL, 1.0 equiv., 73.5 mmol, 0.7 M in hexane) was added to freshly distilled cyclopentadiene (10.72 g, 2.2 equiv., 162 mmol, 13.4 mL) dropwise within 20 min. The reaction mixture was cooled with a cold water bath during the addition of CpH. After 12 h the precipitate was filtrated, washed two-times with pentane and dried in vacuo. **17** was obtained as colorless powder (7.00 g, 62%). NMR (δ in ppm): ^{1}H (C_6D_6): 6.01 (s, 6H). ^{13}C (C_6D_6): 107.8.

4.5.2. Synthesis of Dicyclopentadienylindium(III)chloride (**18a**)



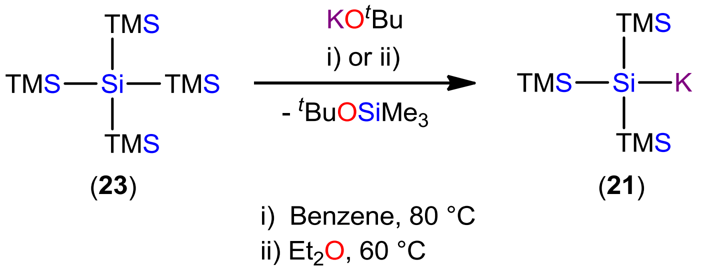
$InCl_3$ (202 mg, 1.0 equiv., 0.91 mmol) and **17** (140 mg, 1.0 equiv., 0.91 mmol) were dissolved in THF (3 mL). The suspension was kept at -45 °C in the fridge for 5 d before it was allowed to warm to rt. The bright yellow reaction mixture was subjected to NMR spectroscopy, which approved the formation of $InCp_3$ (**18b**) [121] instead of **18a**. NMR (δ in ppm): ^1H (THF/D_2O-Capillary): 6.09 (s, 6H). ^{13}C (THF/D_2O-Capillary): 110.9.

4.5.3. Synthesis of Dicyclopentadienylytrrium(III)chloride[103] (**20**)



19 (772 mg, 1.0 equiv., 3.95 mmol) and **17** (607 mg, 1 equiv., 3.93 mmol) were suspended in toluene (8 mL) and stirred for 2 d at rt. The mixture was centrifuged, which gave an only **20** containing supernatant and two types of precipitate (**20** and probably $MgCl_2$). The precipitated **20** was dissolved in toluene. The combined toluene phases were concentrated under reduced pressure and **20** was obtained as a glittering powder (710 mg, 71%). NMR (δ in ppm): ^1H (C_6D_6): 6.20 (s, 6H). ^{13}C (C_6D_6): 113.2.

4.6. Synthesis of Solvent-free Hypersilyl Potassium (**21**)



i)

23 (1.02 g, 1.05 equiv., 3.18 mmol) and KO^{t}Bu (341 mg, 1.00 equiv., 3.04 mmol) were dissolved in benzene (8 mL) and kept at 80 °C. The reaction progress was monitored with NMR-spectroscopy, showing that after 30 days the reaction rate dropped drastically. Benzene (2 mL) and a stirring bar were added and the reaction mixture was heated to 60 °C for another 4 d, before full conversion could be detected through the absence of KO^{t}Bu. The volatile were removed under reduced pressure and the remains were suspended in pentane. The suspension was centrifuged, and the slightly orange powder was thoroughly dried for several hours in vacuum, yielding **21** (680 mg, 78%) with traces of unreacted **23**.

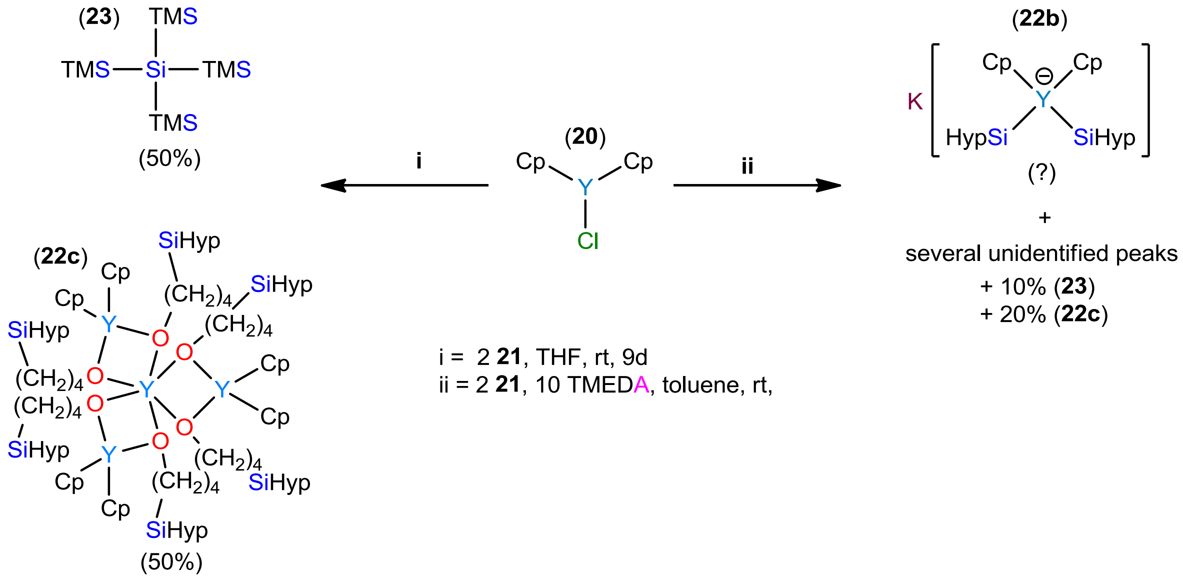
ii)

23 (747 mg, 1.05 equiv., 2.33 mmol) and KO^{t}Bu (249 mg, 1.00 equiv., 2.22 mmol) were dissolved in Et$_2$O (6 mL) and kept at 60 °C. The reaction progress was monitored with NMR-spectroscopy, showing that after 7 days full conversion, through the absence of KO^{t}Bu, was achieved. The volatile were removed thoroughly through application of vacuum for a total time of 10 h, yielding **21** as slightly yellow powder (625 mg, 98%) with traces of unreacted **23**.

NMR (δ in ppm): ^{1}H (Et$_2$O/D$_2$O-Lock): 0.66 (s, 27H). ^{29}Si (Et$_2$O/D$_2$O-Lock): -5.1 (s, SiMe$_3$), -189.8 (s, Si$_q$).

4.7. Synthesis of Yttrium Complexes

4.7.1. Synthesis of Potassium-bis(cyclopentadienyl)bis(hypersilyl)ytterate(III) (**22b**)



i)

23 (503 mg, 2.04 equiv., 1.57 mmol) and KO^tBu (185 mg, 2.14 equiv., 1.65 mmol) were dissolved in THF (3 mL) and kept at rt for 1 d. To the dark orange **21** solution, **20** (196 mg, 1.0 equiv., 0.77 mmol) was added and the reaction mixture was stirred at rt for 8 d. The solvent was removed under reduced pressure, pentane was added to the residue and the suspension was filtrated. The filter cake was suspended in THF and again filtrated. Both pentane- and THF-solutions were put in the fridge at -42 °C for crystallization. After 5 d crystals grew in both fractions. XRD-analysis of a crystal out of the pentane phase gave crystal structure (**22c**). NMR-spectroscopy revealed furthermore formation of **23** along with **22c** in a 1:1 ratio.

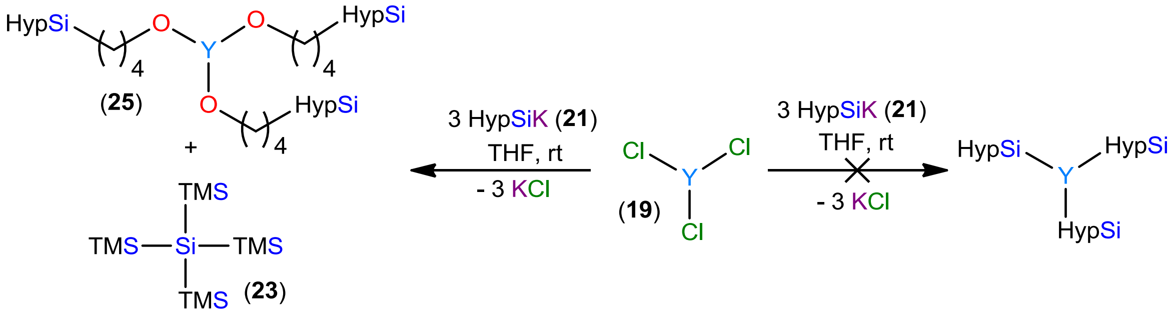
NMR (δ in ppm): **22c**: ^1H (THF/D_2O-Lock): 6.36 (s, Cp-H, 30H), 3.58 (bs, Y-O-CH_2, 12H), 1.70 (bs, -CH_2-CH_2-, 24H), 1.20 (bs, -CH_2-HypSi, 12H), 0.41 (s, HypSi, 162H). ^{29}Si (THF/D_2O-Lock): -13.0 (s, $SiMe_3$), -81.6 (s, Si_q). **23**: ^1H (THF/D_2O-Lock): 0.41 (s, 36H). ^{29}Si (THF/D_2O-Lock): -10.0 (s, $SiMe_3$), -133.0 (s, Si_q). **TMSO^{t}Bu**: ^1H (THF/D_2O-Lock): 1.41 (s, -O^tBu, 9H), 0.27 (s, TMS-O-, 9H). ^{29}Si (THF/D_2O-Lock): 6.4 (s, $SiMe_3$).

ii)

23 (268 mg, 2.1 equiv., 0.84 mmol) and KO^tBu (96 mg, 2.15 equiv., 0.86 mmol) were dissolved in THF (1 mL) and kept at rt for 1 d. The volatiles were removed under reduced pressure and the residue was dissolved in TMEDA (461 mg, 9.9 equiv., 3.97 mmol) and toluene (1 mL). **20** (101 mg, 1.0 equiv., 0.40 mmol) was added, the reaction mixture was kept at rt and reaction progress was monitored with NMR-spectroscopy. After 13 d, the suspension was centrifuged and filtrated. The colorless solid remains were rejected and the yellow supernatant was concentrated to a yellow residue. The residue was resuspended in pentane, centrifuged, filtrated and put into fridge at -45 °C. 1 hour later, crystals had formed, but were too small for XRD-analysis.

NMR (δ in ppm): **22c**: ^{1}H (TMEDA-toluene/D_2O-Lock): 6.38 (s, Cp-H, 30H), 3.57 (t, J = 6.5 Hz, Y-O-CH_2, 12H), 1.69 (bs, -CH_2-CH_2-, 24H), 1.16 (t, -CH_2-HypSi, 12H), 0.45 (s, HypSi, 162H). ^{29}Si (TMEDA-toluene/D_2O-Lock): -13.0 (s, $SiMe_3$), -81.8 (s, Si_q). **23**: ^{1}H (TMEDA-toluene /D_2O-Lock): 0.46 (s, 36H). ^{29}Si (THF/D_2O-Lock): -10.1 (s, $SiMe_3$), -135.8 (s, Si_q). **TMSO*t*Bu**: ^{1}H (TMEDA-toluene /D_2O-Lock): 1.40 (s, -O^{t}Bu, 9H), 0.30 (s, TMS-O-, 9H). ^{29}Si (THF/D_2O-Lock): 6.4 (s, $SiMe_3$).

4.7.3. Synthesis of Tris((4-hypersilylbutyl)-1-oxy)yttrium(III) (**25**)

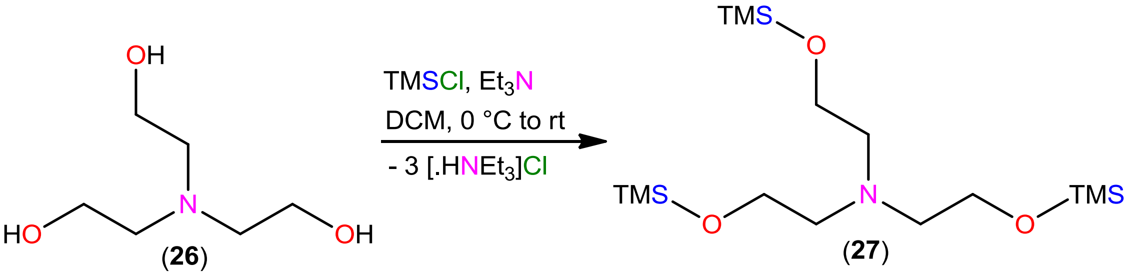


23 (982 mg, 3.0 equiv., 3.06 mmol) and KO^{t}Bu (355 mg, 3.1 equiv., 3.16 mmol) were dissolved in THF (4 mL) and kept for 1 d at rt. To the dark orange hypersilyl potassium solution, **19** (200 mg, 1.0 equiv., 1.02 mmol) was added and the reaction mixture was stirred for 4 h. The precipitate was centrifuged and the volatiles of the filtrate were removed under reduced pressure yielding foam. The foam was dissolved in 0.5 mL pentane and the highly viscous dark yellow fluid was put into a fridge at -45 °C. No crystals could be gathered with this procedure, but NMR-spectroscopy was accessible and indicated formation of **25** and **23** in a 1:1 ratio.

NMR (δ in ppm): **25**: ^{1}H (THF/D$_2$O-Lock): 4.08 (bs, Y-O-CH$_2$, 6H), 1.63 (bs, -CH$_2$-CH$_2$-, 12H), 1.08 (bs, -CH$_2$-HypSi, 6H), 0.38 (s, HypSi, 81H). ^{29}Si (THF/D$_2$O-Lock): -13.0 (s, SiMe$_3$), -82.2 (s, Si$_q$). **23**: ^{1}H (THF /D$_2$O-Lock): 0.43 (s, 36H). ^{29}Si (THF/D$_2$O-Lock): -10.0 (s, SiMe$_3$), -135.8 (s, Si$_q$). **TMSO*t*Bu**: ^{1}H (THF /D$_2$O-Lock): 1.43 (s, -O^{t}Bu, 9H), 0.28 (s, TMS-O-, 9H). ^{29}Si (THF/D$_2$O-Lock): 6.4 (s, SiMe$_3$).

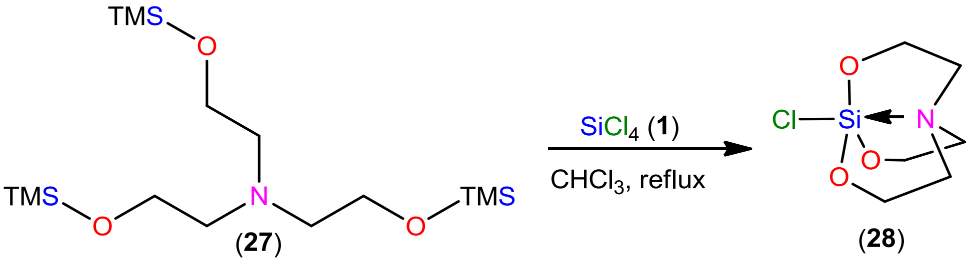
4.8. Synthesis of Silatranes

4.8.1. Synthesis of Tris(2-((Trimethylsilyl)oxy)ethyl)amine[106] (**27**)



26 (10.03 g, 1.0 equiv., 67.2 mmol, 8.9 mL) and Et_3N (30.87 g, 4.5 equiv., 305 mmol, 42.5 mL) were dissolved in DCM (100 mL) and cooled to 0 °C. Then TMSCl (25.62 g, 3.5 equiv., 236 mmol, 29.9 mL) was added dropwise within 45 min to the stirred solution. Another amount DCM (100 mL) was added for a better stirring efficiency and the whole mixture was allowed to warm to rt. After 12 h water (100 mL) was slowly added and the two-phasic system separated. The aqueous phase was extracted two times with DCM and the combined organic phases were dried with $NaSO_4$. The filtrate was dried in vacuo, which gave **27** as a gold-yellow liquid (22.93 g, 93%). NMR (δ in ppm): ^1H (Neat/D_2O-Lock): 3.91 (t, *J* = 6.5 Hz, 6H), 3.00 (t, *J* = 6.5 Hz, 6H), 0.43 (s, 18H). ^{29}Si (Neat/D_2O-Lock): 15.7 (s, Si_q).

4.8.2. Synthesis of 1-Chlorosilatrane[106] (**28**)



In a two-neck flask equipped with reflux condenser was dissolved **27** (23.81 g, 1.0 equiv., 65.1 mmol) in $CHCl_3$ (70 mL). After addition of **1** (11.72 g, 1.06 equiv., 68.98 mmol, 7.92 mL) the reaction mixture was kept at reflux for 9 h. The suspension was filtered and the slightly pink precipitate washed with pentane until it became colorless. After drying under reduced pressure, **28** was obtained as a colorless powder (1.80 g, 13%). NMR (δ in ppm): ^1H ($CDCl_3$): 3.97 (t, J = 6.0 Hz, 6H), 3.02 (t, J = 5.9 Hz, 6H). ^{13}C ($CDCl_3$): 58.1, 51.4.

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6. APPENDIX

6.1. Crystallographic Data

6.2. Curriculum Vitae

Personal Data

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Education

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03/2017 - Today	Masterstudies in Chemistry (NaWi-Studies at TU Graz and Karl Franzens University)
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10/2013 – 03/2017	Bachelorstudies in Chemistry (NaWi-Studies at TU Graz and Karl Franzens University) Bachelor Thesis: *Substratescope and Enantioselectivity of Nocardia iowensis Carboxylic Acid Reductase* at Prof. Kurt Faber
01/2013 - 09/2013	Civilian Service (Austrian Red Cross)
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