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Synthesis of Bidentate *N*–heterocyclic Carbene–Phosphinidene Ligands and Complexation of Group 14 Elements

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"Agassiz does recommend authors to eat fish, because the phosphorus in it makes brains. But I cannot help you to a decision about the amount you need to eat. Perhaps a couple of whales would be enough."

Mark Twain

"A scientist in his laboratory is not a mere technician: He is also a child confronting natural phenomena that impress him as though they were fairy tales."

Marie Curie

Publication List and Conference Contributions

Publications included in this thesis:

- V. Nesterov, <u>R. Baierl</u>, F. Hanusch, A. Espinosa Ferao, and S. Inoue
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- R. Baierl and S. Inoue
  Oral Presentation: "*Synthesis and Coordination Chemistry of Bidentate N–Heterocyclic Carbene–Phosphinidene Ligands towards Group 14 Metals*"
  51st Silicon Symposium, San Diego, USA, March 2022

Abstract

In contrast to the intensely studied *N*–heterocyclic carbenes (NHCs), the research on the related *N*–heterocyclic carbene–phosphinidenes (NHCPs) is still in its infancy. Owning to their σ–donor as well as π–acceptor properties and the availability of two free electron lone pairs at the phosphorus atom, NHCPs qualify as ligands to stabilize electron deficient compounds. Even though this compound class was discovered in 1997 by Arduengo, neutral phosphinidene (NHCP–R) and anionic phosphinidenide (NHCP$^-$) ligands have only found scarce applications. In the literature various transition metal complexes (e.g., Cr, Mo, W, Ir, Rh, Hg, Zn, Fe, Cu), as well as a small number of main group complexes (e.g., B, Al, Sn, Ge) can be found. During the course of this project, the first bidentate NHCP ligand (bisNHCP) was published by Hadlington and Driess opening up new possibilities.

The first part of this thesis focuses on the synthesis of heavier nitrile analogues (RE≡P with E = Ge, Sn). Making use of NHCs as excellent donor–ligands and a sterically demanding terphenyl ligand, we could isolate an NHC–stabilized tetrylene–phosphinidene. Spectroscopic data as well as theoretical calculations reveal a double bond character of the E=P bond accounting for a heavier nitrile analogue. The isolated germylene– and stannylene– phosphinidenes react with diphenylketene in a [2+2] cycloaddition reaction confirming the E=P double bond character. Additionally, activity of the stannylene–phosphinidene in catalytic hydroboration of carbonyls and reactivity towards tris(pentafluorophenyl)borane has been investigated.

The second part of this thesis concentrates on the synthesis of a bisNHCP ligand and its application in coordination chemistry. The ligand was synthesized from treating 1,1'– bis(dichlorophosphine)ferrocene with a NHC and subsequent dechlorination with sodium naphthalenide. A variety of bisNHCP–stabilized stannyliumylidene cations could be isolated from Sn(II) precursors (SnX_2 with X = Cl, Br, I, OTf) and were successfully characterized. Spectroscopic and theoretical data displayed a double bond character (NHC=P:) in the free ligands, while the double bond character is lost upon coordination (NHC–P→). Reactivity studies investigated the Sn(II) transfer to a bidentate *N*–heterocyclic imine (bisNHI) ligand and the transmetallation from a Sn(II) complex to a bisNHCP–CuCl complex.

The last part of this thesis investigates the ability of the previous synthesized bisNHCP ligand to stabilize Si(IV) dications, expanding the NHCP chemistry towards silicon. Treatment of the bisNHCP with bistriflate silanes $R_2Si(OTf)_2$ (R = H, Ph) readily forms the dicationic complexes. Both complexes show expected high Lewis acidity, confirmed *via* Gutmann Beckett method,

and irreversible reduction potentials in the CV. Furthermore, both compounds are highly thermally stable up to 80 °C (for R = H) and 100 °C (for R = Ph) in CD_3CN solution. The $H_2Si(OTf)_2$ complex exhibits reactivity towards diphenylketene at elevated temperature with the CO of the diphenylketene inserting into the Si–P bond.

These investigations expand the chemistry and properties of NHCPs and open ways for further investigations, as the properties of the bisNHCP ligand has not yet been fully analyzed.

Zusammenfassung

Im Gegensatz zu den umfassend untersuchten *N*–heterocyclischen Carbenen (NHCs) steckt die Forschung zu den verwandten *N*–heterocyclischen Carben–Phosphinidenen (NHCPs) noch in den Kinderschuhen. Aufgrund ihrer σ–Donor– sowie π–Akzeptor Eigenschaften und der Verfügbarkeit von zwei freien Elektronenpaaren am Phosphoratom eignen sich NHCPs als Liganden zur Stabilisierung elektronenarmer Verbindungen. Obwohl diese Verbindungsklasse bereits 1997 von Arduengo entdeckt wurde, haben neutrale Phosphiniden– (NHCP–R) und anionische Phosphinidenid– (NHCP⁻) Liganden nur wenig Anwendungen gefunden. In der Literatur lassen sich verschiedene Übergangsmetallkomplexe (z. B. Cr, Mo, W, Ir, Rh, Hg, Zn, Fe, Cu), sowie wenige Hauptgruppenkomplexe (z. B. B, Al, Sn, Ge) finden. Im Laufe dieses Projekts wurde der erste zweizähnige NHCP–Ligand (bisNHCP) von Hadlington und Driess veröffentlicht, der neue Möglichkeiten eröffnet.

Der erste Teil dieser Arbeit konzentriert sich auf die Synthese von schwereren Nitril–Analoga (RE≡P mit E = Ge, Sn). Unter Verwendung von NHCs als exzellente Donor–Liganden und einem sterisch anspruchsvollen Terphenylliganden konnten wir ein NHC–stabilisiertes Tetrylen–Phosphiniden isolieren. Spektroskopische Daten sowie theoretische Berechnungen zeigen einen Doppelbindungscharakter der E=P Bindung, der ein schwereres Nitrilanalogon charakterisiert. Die isolierten Germylen– und Stannylen–Phosphinidene reagieren mit Diphenylketen in einer [2+2]–Cycloadditionsreaktion, was den E=P Doppelbindungscharakter bestätigt. Außerdem wurde die Aktivität des Stannylen–Phosphinidens bei der katalytischen Hydroborierung von Carbonylen und die Reaktivität gegenüber Tris(pentafluorphenyl)boran untersucht.

Der zweite Teil dieser Arbeit konzentriert sich auf die Synthese eines bisNHCP–Liganden und seine Anwendung in der Koordinationschemie. Der Ligand wurde durch Behandlung von 1,1'–Bis(dichlorphosphin)ferrocen mit einem NHC und anschließender Dechlorierung mit Natriumnaphthalenid synthetisiert. Eine Vielzahl von bisNHCP–stabilisierten Stannylium-ylidenkationen konnte aus Sn(II)–Vorstufen (SnX$_2$ mit X = Cl, Br, I, OTf) isoliert und erfolgreich charakterisiert werden. Spektroskopische und theoretische Daten zeigten einen Doppelbindungscharakter (NHC=P:) in den freien Liganden, während der Doppelbindungscharakter bei der Koordination verloren geht (NHC–P→). Reaktivitätsstudien untersuchten den Sn(II)–Transfer auf einen zweizähnigen *N*–heterocyclischen Imin (bisNHI)–Liganden und die Transmetallierung von einem Sn(II)–Komplex zu einem bisNHCP–CuCl Komplex.

Der letzte Teil dieser Arbeit untersucht die Fähigkeit des zuvor synthetisierten bisNHCP–Liganden, Si(IV)–Dikationen zu stabilisieren, wodurch die NHCP–Chemie in Richtung Silizium erweitert wird. Die Behandlung des bisNHCP mit Bistriflat–Silanen $R_2Si(OTf)_2$ (R = H, Ph) bildet die entsprechenden Dikationen. Beide Komplexe zeigen eine erwartet hohe Lewis–Azidität, bestätigt durch die Gutmann–Beckett Methode, und irreversible Reduktionspotentiale im CV. Darüber hinaus sind beide Verbindungen in CD_3CN–Lösung bis 80 °C (für R = H) und 100 °C (für R = Ph) thermisch sehr stabil. Der $H_2Si(OTf)_2$–Komplex zeigt bei erhöhter Temperatur Reaktivität gegenüber Diphenylketen, wobei das CO des Diphenylketens in die Si–P–Bindung insertiert. Diese Untersuchungen erweitern die Chemie und Eigenschaften von NHCPs und öffnen Wege für weitere Untersuchungen, da die Eigenschaften des BisNHCP–Liganden noch nicht vollständig analysiert wurden.

List of Abbreviations

Ad	Adamantyl
Ar	Aryl
ATP	Adenosine triphosphate
Bbt	2,6–Bis[bis(trimethylsilyl)methyl]–4–[tris(trimethylsilyl)methyl]–phenyl
BCF	Tris(pentafluorophenyl)borane
BisNHCP	Bidentate *N*–heterocyclic carbene–phosphinidene
BisNHI	Bidentate *N*–heterocyclic imine
cAAC	Cyclic alkyl amino carbene
cat	Catalyst
Ch	Chalcogen
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
DBU	1,8–Diazabicyclo[5.4.0]undec–7–ene
ΔE_{ST}	Singlet–triplet gap energy
DABCO	1,4-Diazabicyclo[2.2.2]octane
DBU	1,8-Diazabicyclo(5.4.0)undec-7-ene
DG	Directing group
Dipp	2,6–Di*iso*propylphenyl
DLA	D–lactide
DMAP	4–Dimethylaminopyridine
DNA	Deoxyribonucleic acid

Do	donor
E	Tetrel (Si, Ge, Sn)
EA	Elemental analysis
Eind	1,1,3,3,5,5,7,7–octaethyl–s–hydrindacen–4–yl
El	Electrophile
eq.	Equivalents
Et	Ethyl
Et_2O	Diethyl ether
FT–IR	Fourier–transform infrared spectroscopy
HDF	Hydrodefluorination
IMe_4	1,3,4,5–Tetramethylimidazol–2–ylidene
IMes	1,3–Dimesitylimidazol–2–ylidene
*i*Pr	*iso*–propyl
I*t*Bu	1,3–Di–*tert*–butyllimidazol–2–ylidene
L	Neutral ligand
LG	Leaving group
LIFDI–MS	Liquid injection field desorption ionization mass spectrometry
LLA	L–lactide
M	Metal atom
Me	Methyl
[Me]IMes	1,3–Dimesityl–4,5–dimethylimidazol–2–ylidene
Mes	Mesityl (2,4,6–trimethylphenyl)

NaBArF$_4$	Sodium tetrakis[3,5–bis(trifluoromethyl)phenyl]borate
NHC	*N*–heterocyclic carbene
NHCP	*N*–heterocyclic carbene–phosphinidene
NHI	*N*–heterocyclic imine
NMR	Nuclear magnetic resonance
PDLA	Poly(D–lactide)
Ph	Phenyl
PLLA	Poly(L–lactide)
ppm	Parts per million
ROP	Ring–opening polymerization
rt	Room temperature
SC–XRD	Single–crystal X–ray diffractometry
*t*Bu	*tert*–butyl
THF	Tetrahydrofuran
TMS	Trimethylsilane
UV–Vis	Ultraviolet–visible spectroscopy
WBI	Wiberg bond index
X	Halogen substituent

Table of Contents

1.   Introduction

Phosphorus is ubiquitous in nature and everyday life. It makes up about 1 w% of the human body with most of it being in bones and teeth. The bone mineral consists of calcium phosphate being important for the mechanical strength.[1-2] In addition to that, phosphorus is contained in, for instance, adenosine triphosphate (ATP), which provides energy in cells and in the backbone of our DNA (deoxyribonucleic acid). In more than one aspect, phosphorus is essential for living organisms.

> *"Life can multiply until all the phosphorus has gone and then there is*
> *an inexorable halt which nothing can prevent."*
>
> *Isaac Asimov 1974*

As important phosphorus is in the human body, as important it is in chemistry. Phosphorus is a group 15 element located in the third period as heavier homologue of nitrogen. It was accidentally discovered by the German alchemist Hennig Brand in 1669. In the search for the "philosopher's stone" he distilled urine and received a white substance, which later turned out to be ammonium sodium hydrogen phosphate $(NH_4)NaHPO_4$.[3-4]

Elemental phosphorus exists in gas phase as P_2 and in different allotropes. White (P_4), red, black and violet phosphorus can be found, all exhibiting different crystal structures as well as physical properties.[5] Phosphorus has diverse applications, for instance, in Germany over 80% is used for production of fertilizers. However, in form of phosphorus–based ligands it additionally plays a key role in catalysis. Phosphine ligands (R_3P:) have the advantage to easily associate and dissociate, thus bearing an essential feature for most catalytic cycles. To name just a few, the Grubb's catalyst, catalyzing olefin metathesis, the Suzuki–Miyaura crosscoupling, the Wilkinson's catalyst, catalyzing hydrogenation, hydroformylation, and hydrosilylation, and the Noyori's catalyst, used for asymmetric hydrogenation.[6-9]

However, all these catalysts are based on transition metals, bearing high costs, low accessibility, and often even high toxicity. Therefore, one of the main targets in modern main group chemistry is the synthesis of new catalysts based on abundant, non–toxic, and economic main group elements like silicon. This research field is still in its infancy and different methods to successfully isolate catalytically active main group catalysts are developed. Recently, *N–*heterocyclic carbene–phosphinidene ligands received increasing attention and are yet to be further investigated.

2.   *N*–Heterocyclic Carbene Phosphinidenes

For a long time, phosphines and phosphanes dominated as ligands in transition metal coordination chemistry. However, with the first isolation of *N*–heterocyclic carbenes (NHCs) and their superior properties in comparison to electron–rich organophosphanes being discovered, the NHCs replaced the phosphorus ligands to yield next–generation organometallic catalysts.[10-11] The first "bottleable" NHC has been isolated by Arduengo and coworkers in 1991.[12] This ground–breaking isolation led to the synthesis of a plethora of new NHCs and their application in transition metal, as well as in main group chemistry being the subject of various publications and reviews.[13-21] Like organophosphanes, NHC ligands demonstrate strong σ–donor as well as weak π–acceptor properties.

Structure

With the discovery of *N*–heterocyclic carbene–phosphinidenes (NHCPs) by Arduengo in 1997, a combination of NHCs and phosphine ligands has evolved.[22-24] NHCPs are the heavier analogues of *N*–heterocyclic imines (NHIs) and are considered as inversely polarized phosphaalkenes, which show a partial negative charge on the phosphorus instead of at the carbene carbon atom in classical phosphaalkenes. In the classical phosphaalkenes the difference in electronegativity in the Pauling scale of phosphorus (2.1) and carbon (2.5) results in polarization and the mesomeric structures **1** and **1'** (Scheme 1). However, depending on the substituents, the electron distribution can be changed to yield an inversely polarized phosphaalkene. For instance, the introduction of an NHC substituent bearing electron donating nitrogen atoms, results in the formation of an NHCP being an inversely polarized phosphaalkene. NHCPs feature strong σ–donor and weak π–acceptor properties (Figure 1).[25] The in plane occupied carbenic sp^2 hybrid orbital interacts with the empty σ–type orbital (p_x orbital) of the phosphinidene in a σ–donation interaction. Additionally, there is a π–backdonation from the occupied π–type orbital of the phosphorus (p_y orbital) towards the empty p-orbital of the carbene.[26-27] These effects contribute to a pronounced polarization of the P–C bond, which can be visualized in resonance structures **2-2''**.[23, 28-30] Depending on the phosphorus substituent and the nature of the carbene, resonance structure **2** with a P=C double bond, zwitterion **2'** with a P–C single bond, or **2''** with a dative C→P donor–acceptor interaction is predominant.[25]
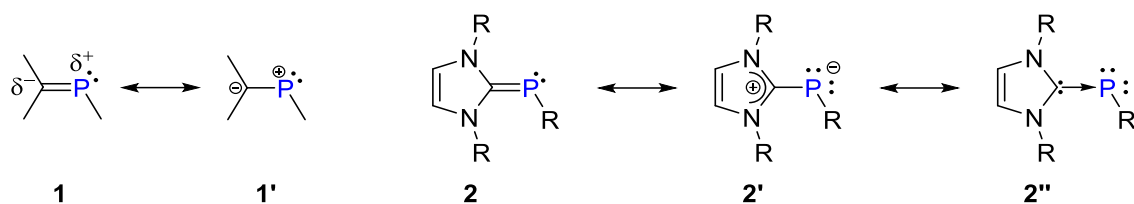
Scheme 1 Canonical forms of phosphaalkenes and *N*–heterocyclic carbene–phosphinidenes.

singlet
carbene

singlet
phosphinidene

σ donation

π back-donation
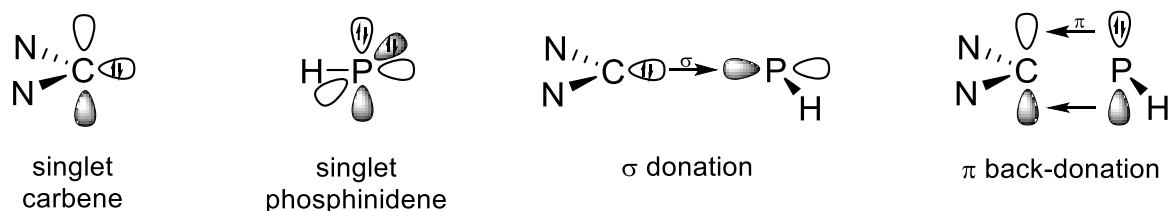
Figure 1 Schematic orbital representation of a singlet phosphinidene and C–P bond orbital interactions in NHCPs.

Due to the availability of two lone pairs at the phosphorus, NHCPs qualify as ligands to stabilize electron deficient compounds. The two phosphorus lone pairs in resonance structure **3** could be confirmed the first time by treatment of IMesP–Ph with two equivalents of BH$_3$·THF isolating the P–bonded bis(borane) adduct **4** (Scheme 2, left).[24] Later various bis(group 11 metal) complexes **5** could additionally verify the ability of NHCPs to have two available lone pairs at the phosphorus and the potential to coordinate metal halides (Scheme 2, right).[31]
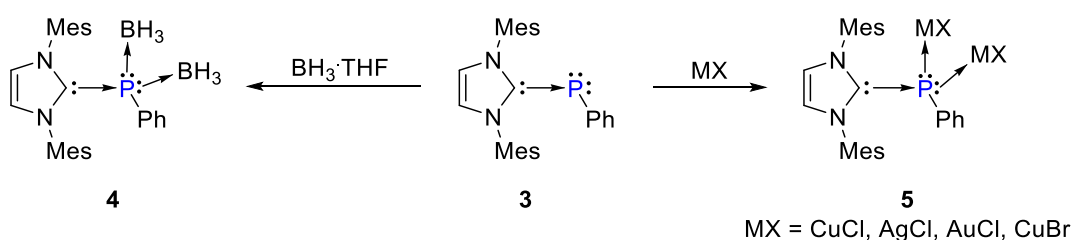
Scheme 2 Reactivity of IMesP–Ph towards BH$_3$·THF and group 11 metal halides.

Synthesis

To synthesize NHCPs, several pathways have been explored. In general, the combination of a suitable carbene **6** or carbene precursor **13** and a phosphorus source is needed. As phosphorus source, amongst others, cyclopolyphosphines (e.g., (PPh)$_5$),[23] diphosphenes (e.g., Ar–P=P–Ar),[32] chlorophosphines (e.g., PhPCl$_2$),[23, 30] phosphines (e.g., PhPH$_2$),[33]

polyphosphorus (e.g., Na_3P_7),[34] or phosphides (e.g., NaOCP)[35] compounds are utilized and treated with a carbene or imidazolium salt (Scheme 3).[25] With these different synthetic approaches a variety of NHCPs (**7**, **9**–**11**, **14**, **15**) are accessible. The substituents on the carbene as well as on the phosphorus can be exchanged to yield different steric as well as electronic properties.
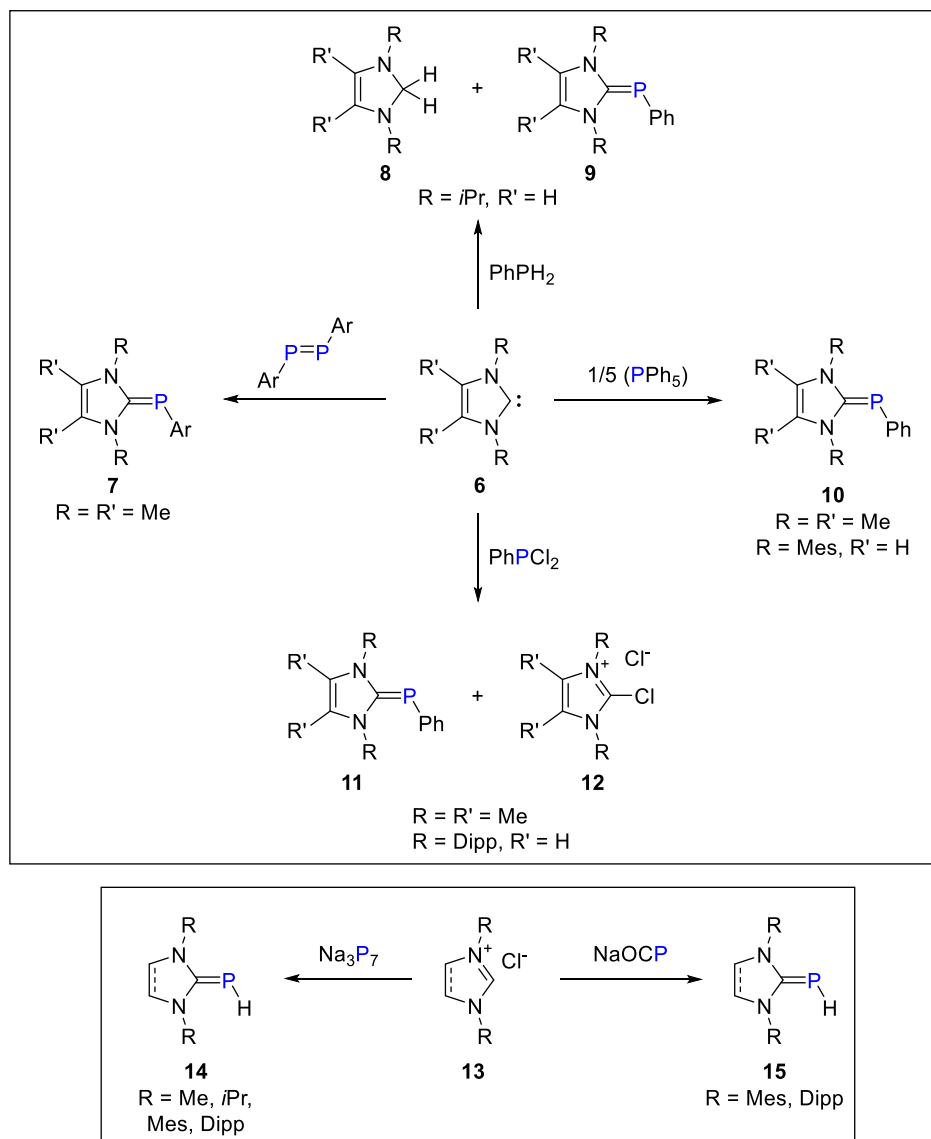
Scheme 3 Synthesis pathways to isolate a NHCP.

Reactivity

Despite the coordination of BH_3 and different group 11 metal halides, NHCPs proved to be suitable neutral (NHC–phosphinidene) or monoanionic (NHC–phosphinidenide) ligands in a plethora of transition metal and main group compounds. Figure 2 shows selected examples of transition metal complexes **16-19**.[36-39] The group of Tamm isolated the tungsten and

molybdenum pentacarbonyl complexes **16** from treatment of the respective NHCP with the photochemically prepared THF adduct [(thf)W(CO)$_5$] or the trimethylamine complex [(Me$_3$N)W(CO)$_5$] and with thermally generated [(thf)Mo(CO)$_5$]. Characterization of the complexes with IR revealed the strong electron–donating properties of the NHCP, observed in a lower CO stretching frequency.[36] The NHC–phosphinidene and analogue NHC–phosphinidenide rhenium and iridium complexes **17** and **18** are synthesized from NHCP–H and NHCP–TMS with the respective dichloro–rhenium and dichloro–iridium precursor complex. Grützmacher presented the Hg(II) complex **19** from treatment of NHCP–H with HgCl$_2$ in the presence of 1,8–diazabicyclo[5.4.0]undec–7–ene (DBU).[38]
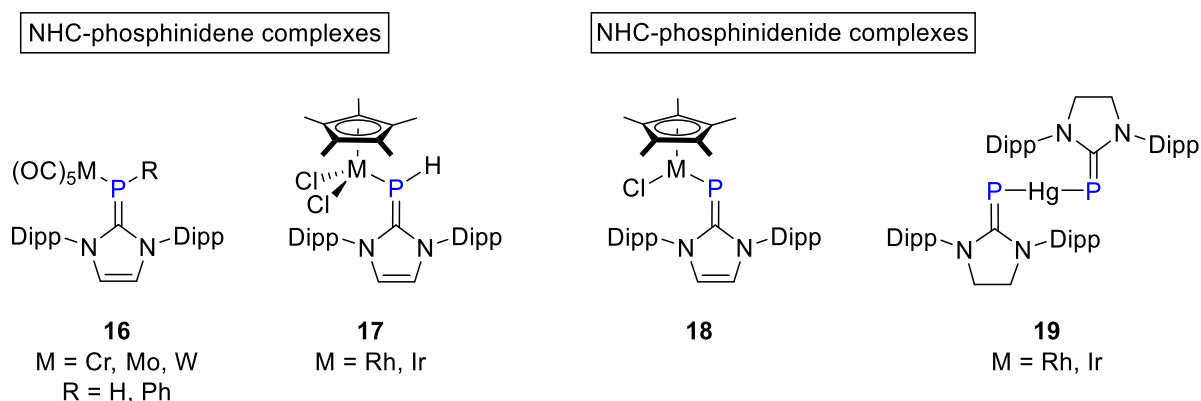
Figure 2 Selected examples of NHC–phosphinidene and –phosphinidenide transition metal complexes.

Recently, Tamm and coworkers isolated the NHC–phosphinidene iridium complexes **20** and **21** from NHCP–H and [Ir(cod)Cl$_2$] followed by chloride abstraction using sodium tetrakis[3,5–bis(trifluoromethyl)phenyl]borate (NaBAr$^F_4$) (Scheme 4). Both complexes present application in *ortho*–directed hydrogen isotope exchange reactions, expanding the scope of possible reactivities of NHCP complexes. Substrates with different directing groups were tested, all showing a high degree of deuteration of above 90%.[40]

20

21

DG = directing group

selected examples of substrates:
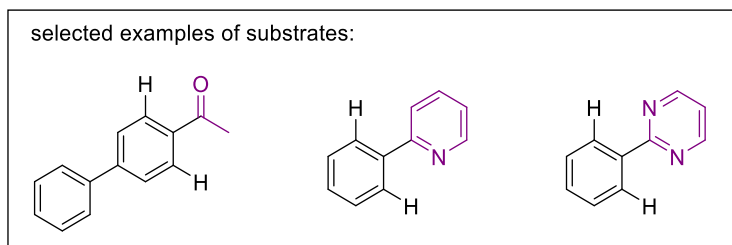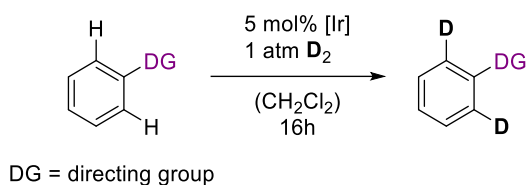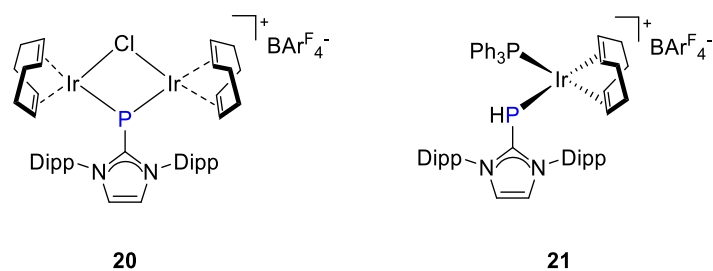
Scheme 4 Catalytic H/D exchange reaction.

NHCPs have not only been used in transition metal coordination chemistry, recently they have grown into the field of main of main group coordination chemistry. The formation of a bis(borane) adduct has already been shown, however, in 2021 the group of Tamm followed this direction of group 13 chemistry with the isolation of the respective aluminum complexes **23** and **24** (Scheme 5). Treatment of NHCPs **22a** with equimolar amounts of trimethylaluminum yielded formation of the 1:1 adduct **23**. Interestingly, the methylated backbone NHCP **22b** has a higher tendency to form the 1:2 adduct **24**, therefore the monoadduct could not be isolated.[41] The mono– and the bisadducts show similar ^{31}P NMR shifts of −137.9 ppm, −147.4 ppm, and −142.9 ppm. Comparison of the P–C$_{Carbene}$ bond lengths of free NHCP and the adducts shows significant elongation upon coordination of one and two equivalents trimethylaluminum.
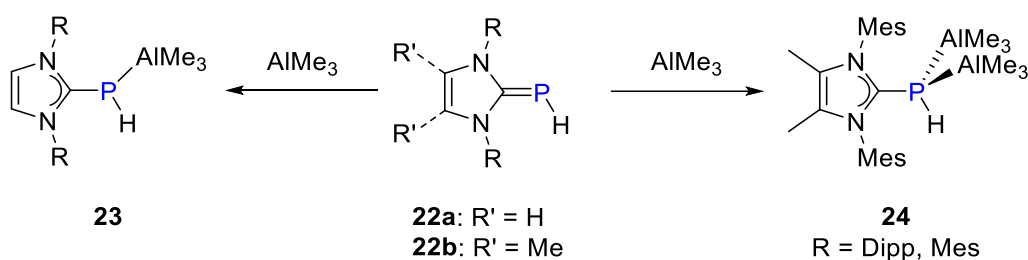
Scheme 5 Synthesis of NHCP trimethylaluminum complexes.

These NHCP aluminum adducts were tested for application as initiators in ring–opening polymerization (ROP) of *rac*–lactide (Scheme 6). At 60 °C in toluene with a monomer to catalyst ratio of 100–500, conversions of 82–97% could be achieved within 12 h, yielding isoselective polymerization.[41]
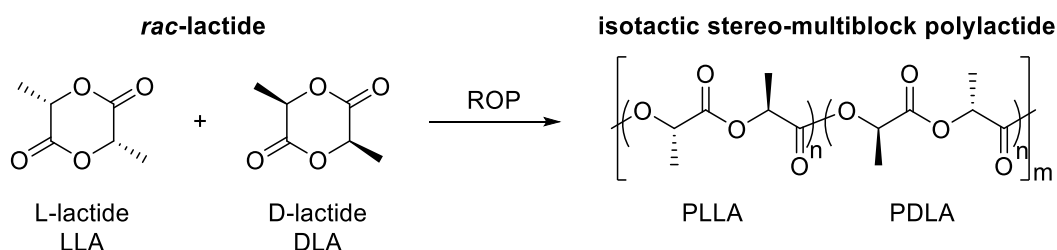
Scheme 6 Ring–opening polymerization of *rac*–lactide.

Until 2021 only monodentate NHCP ligands have been known. Hadlington and Driess published the first example of a bidentate, xanthene bridged NHCP ligand **25** (Scheme 7). The bisNHCP ligand **25** is able to stabilize transition metal halides as well as Ge(II) and Sn(II) halides to form cationic complexes **26** and **27**.[42]
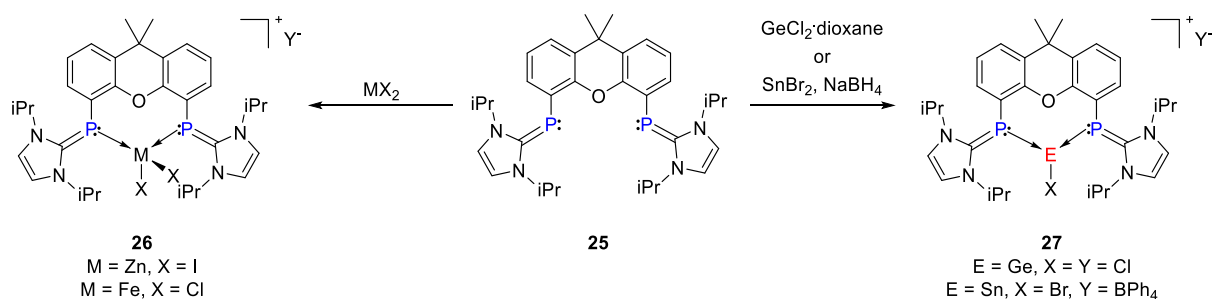
Scheme 7 Reactivity of xanthene–bridged bisNHCP **25**.

In recent years, NHCPs proved to exhibit great potential in the stabilization of low–valent as well as low oxidation state main group compounds and their full potential has not yet been fully discovered.

3. Low–coordinate and Low–valent Group 14 Complexes

3.1 Tetrylium Ions

Structure

Tetrylium ions display the heavier analogues of the comprehensively studied carbenium ions R_3C^+. The three–coordinate tetrylium ions **28** of the form R_3E^+ possess six valence electrons, one vacant p–orbital, and a positive charge at the central atom (Figure 3, left), making them highly electrophilic and therefore extremely Lewis acidic. Since tetrylium ions tend to react with most σ– and π–electron donors (e.g., solvent molecules, nucleophiles), isolation in the condensed phase is difficult. For stabilization highly sterically demanding substituents and/or donor stabilization is necessary to protect the reactive tetrylium ion center sterically from nucleophilic attack, as well as electronically by quenching the electrophilicity.[43] Additionally, non–coordinating solvents and counter anions need to be used in all the reactions. For instance, perfluorinated, weakly coordinating anions, like tetrakis(pentafluorophenyl)borate, proofed to be successful.[44] To stabilize the positive charge, electronic stabilization can be introduced with inter– or intramolecular σ– or π–donors yielding the stabilized tetrylim ions **29** and **30** (Figure 3, middle and right).[45]

unstabilized/free	σ-donor-stabilized	π-donor-stabilized
28	**29**	**30**
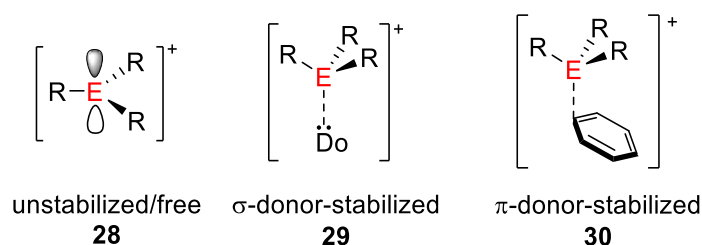
Figure 3 Classification of tetrylium ions (with E = Si, Ge, Sn, Pb) (counter anions are omitted).

In 1993 Lambert and Reed independently isolated the first examples of silylium ions **31** and **32** (Figure 4).[46-47] Both silicon centers adopt a pyramidal geometry and an upfield shifted ^{29}Si NMR signal (92.3 ppm and 105.0 ppm) compared to the calculated shift of Et_3Si^+ in the gas phase (354.6 ppm)[48], accounting for σ– or π–donor stabilization. Since silylium ion **31** shows coordination to the solvent toluene and **32** coordination to the counter anion, both are not considered to be free silylium cations. Only in 2002, finally the first three–coordinated tetrylium ion **33** has successfully been isolated by the groups of Reed and Lambert.[49] This mesityl–substituted silylium ion shows a trigonal planar structure with well separated ion pairs and

9

solvent molecules. In 2003, these results are followed by the isolation of the first germylium ion **34** reported by Sekiguchi and the first stannylium ions **35** by Lambert and Müller.[50-51]
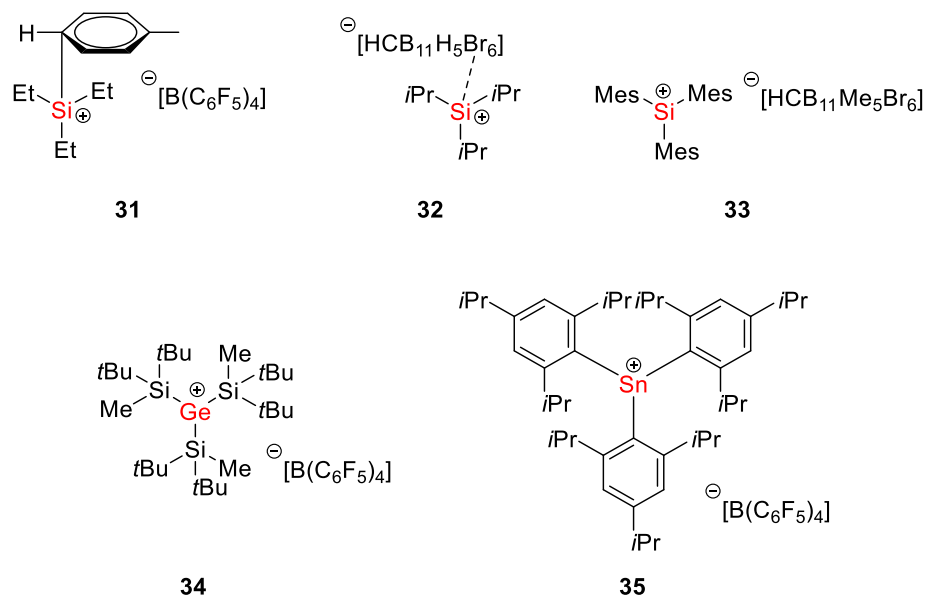
Figure 4 Selected examples of tetrylium cations.

Synthesis

Until now, numerous synthetic strategies have been evolved to isolate tetrylium ions. Predominantly, the abstraction of a leaving group (X, H, benzyl, allyl, CR_3, ER_3) with an electrophile is applied (Scheme 8 **(I)**–**(VI)**). Furthermore, the oxidative addition of an electrophile R^+ to a silylene **(VII)** or a one–electron oxidation of a silyl radical **(VIII)** can be applied.[45, 52-53]
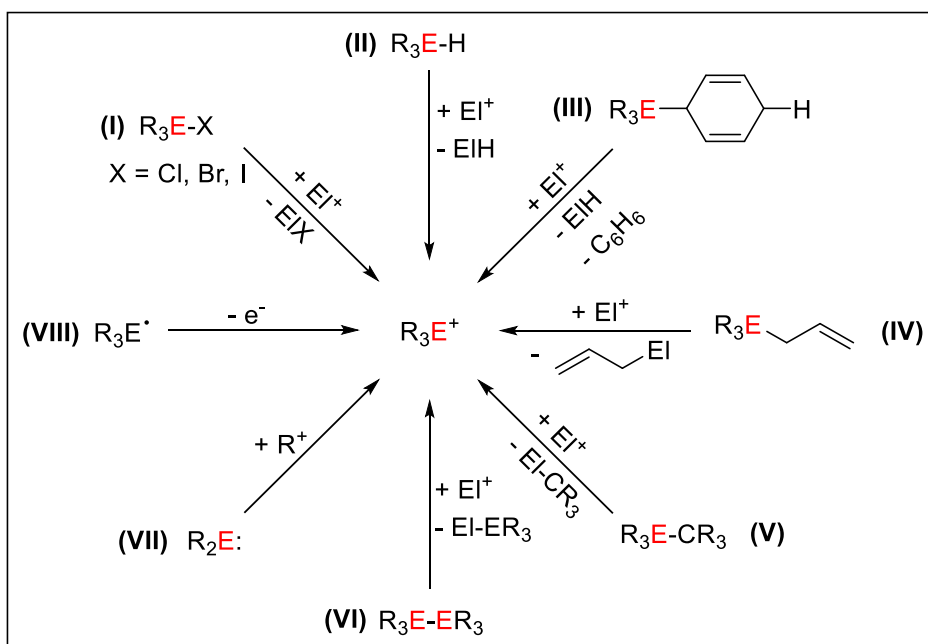
Scheme 8 Selected synthetic routes for preparation of tetrylium ions (E = Si, Ge, Sn).

In order to minimize interaction of the cationic E(IV) center with the counter anion, the application of weakly coordinating anions is necessary. Especially fluorinated tetracoordinated boranes emerged successful, such as $[B(C_6F_5)_4]^-$ and $[B(3,5–(CF_3)_2C_6H_3)_4]^-$, or halogenated *closo*–carborates and perhalogenated *closo*–borates, like $[HCB_{11}H_5Br_6]^-$ and $[B_{12}X_{12}]^-$ (X = Cl, Br).[53]

Reactivity and Catalytic Application

Amongst others, tetrylium ions have found application as Lewis acid catalysts, due to their high electrophilic character. One of the many catalytic applications of silylium ions is the hydrodefluorination (HDF) of fluorinated and perfluorinated alky groups. In HDF reactions selectively $C(sp^3)$–F bonds are transformed to C–H bonds commonly using triethylsilane.[54] In 2005, Ozerov reported the first room–temperature HDF of aliphatic C–F bonds applying a silylium ion catalyst.[55] However, the used tetrakis(pentafluorophenyl)borate anion $[B(C_6F_5)_4]^-$ limited the substrate scope as well as the turnover numbers. After change of the counter anion to monocarboranes, the longevity of the catalysis improved and it was even possible to activate perfluoroalkyl groups, presenting high selectivity for aliphatic C–F bonds. Scheme 9 shows the selective HDF of perfluorotoluene (**36**) using a silylium ion catalyst, selectively producing **37**.[56]
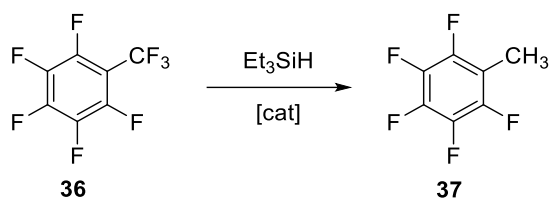
Scheme 9 Hydrodefluorination of perfluorotoluene.

In Scheme 10 the proposed mechanism is reported. The catalytic process requires the generation of a carbo cation and a silylium cation. Both cations are highly Lewis acidic and therefore the counter anion needs to be chosen carefully. A suitable counter anion should be weakly coordinating but also stable towards decomposition *via* transfer of an anionic group. Ozerov discovered monocarboranes (e.g., $[HCB_{11}H_5Cl_6]^-$, $[HCB_{11}Cl_{11}]^-$, $[HCB_{11}H_5Br_6]^-$) to be potent counter anions. In the catalytic cycle, the carbenium ion R'_3C^+ is formed *via* fluoride abstraction by the electrophilic silylium ion forming $R_3Si–F$. This step is followed by reaction of the carbenium ion R'_3C^+ with stoichiometrically added silane $R_3Si–H$, acting as hydride source. $R'_3C–H$ and R_3Si^+ are formed regenerating the silylium cation.[54-56]
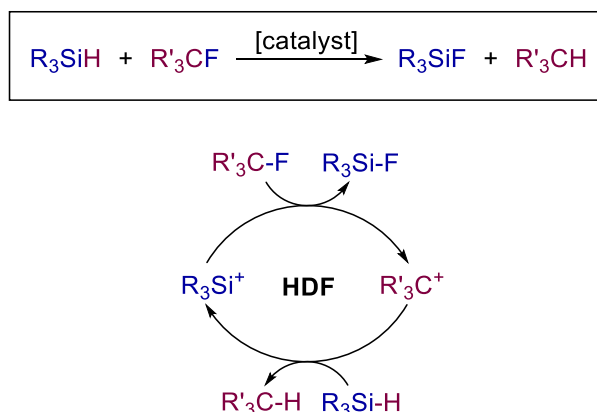
Scheme 10 Proposed mechanism for silylium–catalyzed hydrodefluorination.

Silyl Dications

All in all, suitable methods in stabilizing silyl cations have been developed and these species emerged to be valuable catalysts. The in general even more Lewis acidic silyl dications, however, are less investigated. In 2014, Filippou and coworkers presented the first example of a tetracoordinated Si(IV) dication **38** using NHCs for stabilization (Figure 5).[57] These results were followed by the groups of Driess and Inoue isolating further examples of NHC–stabilized

Si(IV) dications **39** and **40** [58-59]. Driess additionally presented various penta–coordinated dications **41**, stabilized by a terpyridine ligand. [60]
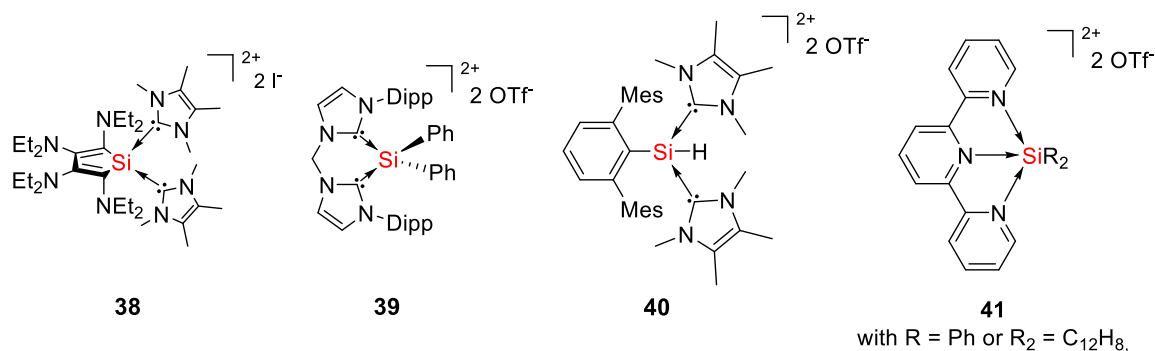
Figure 5 Selected examples of Si(IV) dications.

Different synthetic approaches were used to isolate mononuclear silyl dications **45–47**. Three possible pathways are **(I)** addition of NHC to a diiodosilane **42**, **(II)** use of a neutral bidentate ligand **43** to complex a bistriflatesilane, and **(III)** the addition of triflic acid to a silyliumylidene ion **44** (Scheme 11).[57-60]
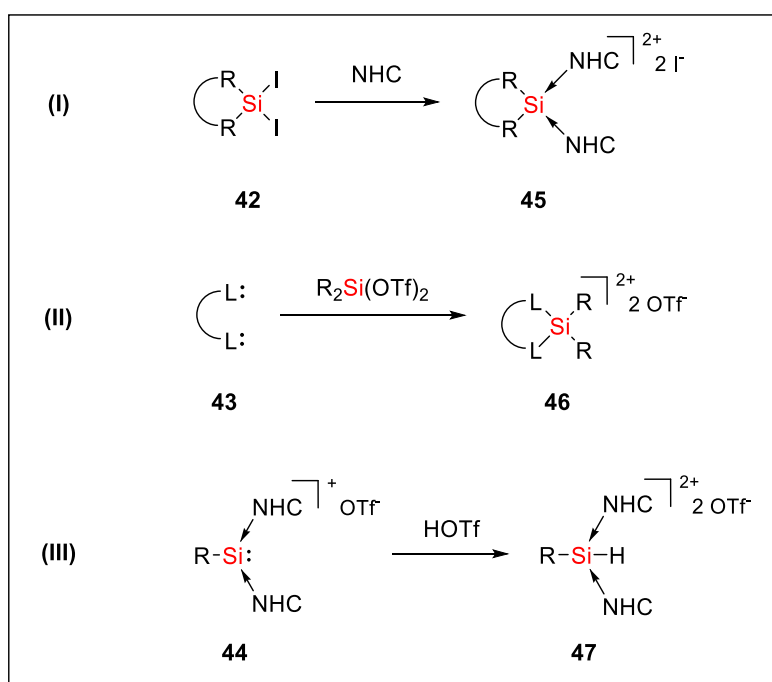
Scheme 11 Synthetic strategies to yield Si(IV) dications.

13

All mononuclear silyl dications show different reactivity. For instance, dications **41** are able to catalyze hydrodefluorination of 1–fluoroadamantane, which is attributed to their high Lewis acidity (Lewis superacidity), quantified by the Gutmann–Beckett method.[60] In the Gutmann–Beckett method triethylphosphine oxide is added to the substrate in a non–coordination solvent (commonly dichloromethane is used). Triethylphosphine oxide coordinates to the Lewis acidic substrate *via* the oxygen atom shifting the ^{31}P NMR signal. According to this NMR shift, the Lewis acidity of a substrate can be quantified. The higher the downfield shift, the higher the Lewis acidity.[61-62] Dication **40** shows reactivity towards CO_2 resulting in the single or double insertion product. The CO_2 inserts into the Si–C^{NHC} bond. At elevated temperatures, the second CO_2 insertion is reversible resulting in a 1:1 equilibrium of single and double insertion product.[59]

Mononuclear Si(IV) dications proved to offer great potential in small molecule activation as well as catalytic application. However, this research is still in its infancy and needs further investigations.

3.2   Tetrylenes

<u>Structure and properties</u>

Tetrylenes are the heavier analogues of carbenes bearing one electron lone pair, however, possessing different properties. Unlike carbon, the heavier group 14 elements do not have a high tendency to form hybrid orbitals. This results in a singlet ground state in tetrylenes in contrast to the triplet ground state in carbenes (Figure 6). For comparison, the singlet–triplet gap ΔE_{ST} for the simplest carbene H_2C: is −14.0 kcal mol^{-1}, while the ΔE_{ST} for the heavier tetrylenes is much higher (H_2Si: 16.7 kcal mol^{-1}, H_2Ge: 21.8 kcal mol^{-1}, H_2Sn: 24.8 kcal mol^{-1}, H_2Pb: 34.8 kcal mol^{-1}). Therefore, tetrylenes predominantly exhibit a singlet ground state.[63-64]

Tetrylenes are not only reactive towards other molecules, however, also to themselves. To yield stabilization, dimerization often occurs. The stability of the monomer over the dimer ascends down the group 14 elements (C < Si < Ge < Sn < Pb). To enhance the monomer stability, sterically demanding substituents are introduced hindering oligomerization. Additionally, the sterically demanding substituents hinder nucleophilic attack at the highly reactive vacant p–orbital, yielding kinetic stabilization of the tetrylene. Further stabilization can be realized either *via* intra– or intermolecular π–donors and σ–acceptors (thermodynamic

stabilization) (Figure 6, right). For thermodynamic stabilization for instance Cp* ligands or heteroatoms like N, O, and P are introduced.[63]
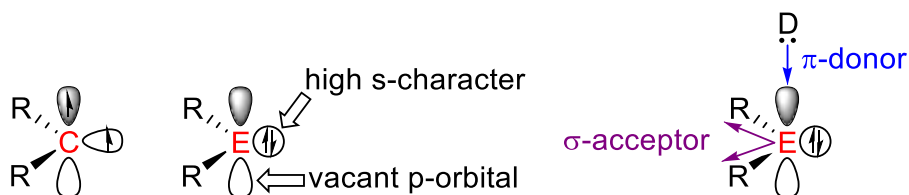
Figure 6 Molecular orbitals or carbenes and tetrylenes.

While Ge(II), Sn(II), and Pb(II) substrates have already been accessible, the stabilization of Si(II) compounds in condensed phase turned out to be more challenging.[65-66] For a long time silylenes were considered to be too reactive to be able to isolate them at room temperature. Nevertheless, in 1986 Jutzi and coworkers isolated the first formal Si(II) compound **48** (Figure 7) opening a new research field.[67] Jutzi's Si(II) compound is thermodynamically stabilized by two Cp* ligands. Due to the hyper coordination (η^{10}), however, it does not meet the definition of a silylene. Therefore, the *N*–heterocyclic silylene **51** published by Denk in 1994 is considered to be the first (dicoordinate) silylene.[68] These results inspired the research generating a variety of new cyclic and acyclic tetrylenes **49**–**53** with a variety of stabilizing substituents (Figure 7).[67-77]

48
Jutzi **1986**

49
E = Si, R = R' = S*m*Ter: Tuononen, Power **2012**
E = Ge, R = R' = [Dipp]NHI: Inoue **2021**
E = Sn, R = mTer, R' = Si(*t*Bu)$_3$: Inoue **2021**
E = Pb, R = R' = CH(Me$_3$Si)$_2$: Lappert **1973**
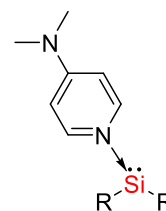
50
R = Si(TMS)$_3$, Si*t*Bu$_2$Me
Inoue **2020**
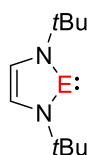
51
E = Si: Denk **1994**
E = Ge: Herrmann **1992**
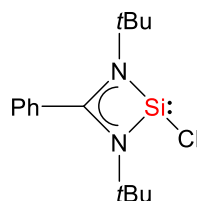
52
Roesky **2006**
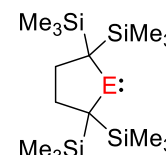
53
E = Si: Kira **1999**
E = Ge: Kira **1999**
E = Sn: Kira **1991**

Figure 7 Selected examples of acyclic and cyclic tetrylenes.

Besides these tetrylenes, the dihalogen–substituted tetrylenes exhibit versatile employable starting materials, amongst others for the synthesis of different substituted tetrylenes or for the synthesis of tetryliumylidenes, which will be discussed in detail in chapter 3.3. While all PbX$_2$, SnX$_2$ (with X = Cl, Br, I), and GeX$_2$ (with X = Br, I) compounds are stable without further stabilization, GeCl$_2$ and SiX$_2$ (with X = Cl, Br, I) need stabilization *via* electron donation. Commonly, dichlorogermylene is stabilized with 1,4–dioxane and SiX$_2$ (with X = Cl, Br, I) with IDipp.[78-81]

Synthesis

Tetrylenes have been investigated intensely over the last few decades and therefore, a plethora of synthetic methods to isolate them has evolved. In Scheme 12 the most important ones are summarized.[63]

(I) Halogen exchange in dihalotetrylenes using organolithium reagents.

(II) Reductive dehalogenation (e.g., with KC$_8$ or sodium naphthalenide) of a dihalogen– substituted E(IV) substrate.

16

(III)   Photochemical reductive elimination of $Me_3Si-SiMe_3$ from a bis(trimethylsilane)–substituted E(IV) substrate.

(IV)   Photochemical or thermal reductive elimination of an alkene or alkyne.

(V)   Photochemical, thermal, or donor–induced splitting of ditetrenes.

(VI)   Photochemical, thermal, or donor–induced splitting of trimers.
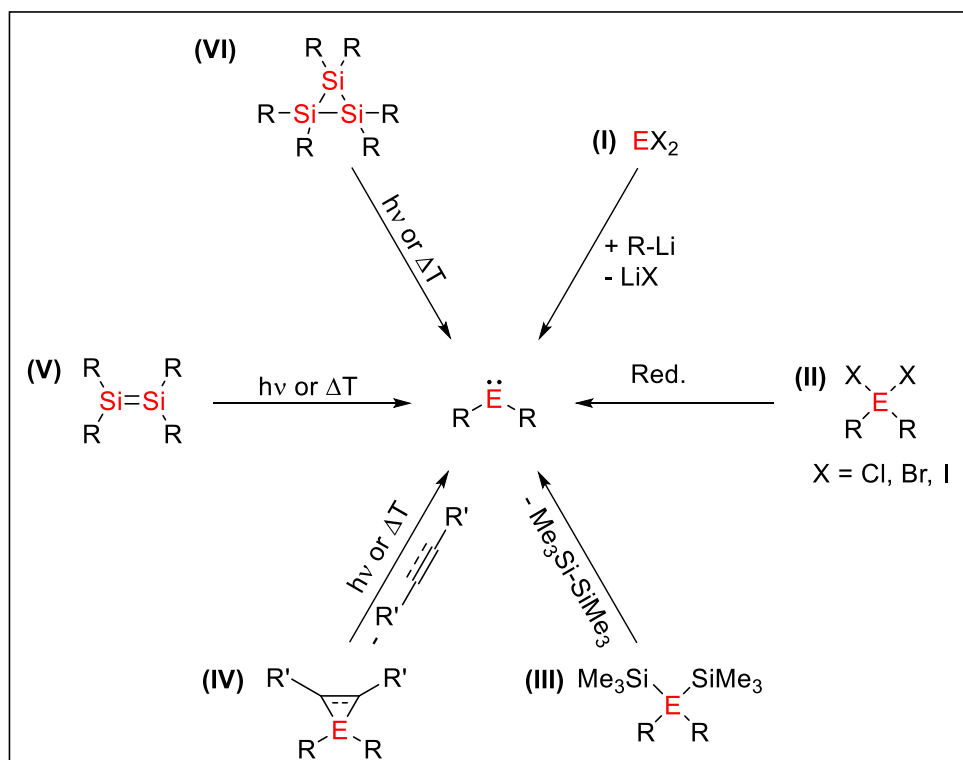
Scheme 12 Various synthetic methods to isolate tetrylenes.

Reactivity

Owning to their high reactivity, silylenes are prone to react intramolecularly to decompose at higher temperature, as demonstrated for the DMAP–stabilized silylenes **58a–c**. Depending on the silyl substituent, silylenes **58a–c** undergo C–H activation of one *tert*–butyl group to form the disiletane **59**, insertion into the pyridine ring of DMAP forming the azasilepin **60**, or isomerization to the cyclic silane **61** (Scheme 13, left). At lower temperature, however, these silylenes are able to activate a variety of small molecules. For instance, activation of dihydrogen, ethylene, as well as trimethylsilyl azide yield the depicted silanes **62–64** (Scheme 13, right).[72]
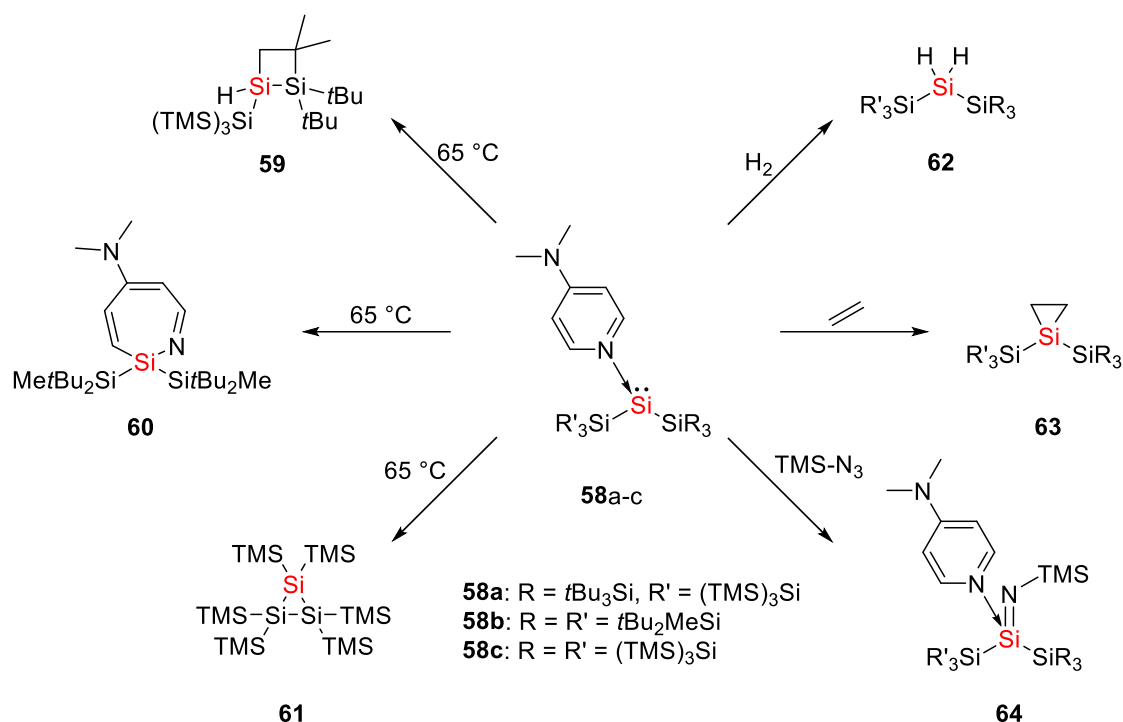
Scheme 13 Thermal decomposition of DMAP–stabilized silylenes and reactivity towards small molecules.

As discussed above, silylenes undergo oligomerization in cases where the steric demand of the substituents is not large enough. However, those disilenes are often in equilibrium with the free silylene in solution.[63] This can for instance be verified by treating the disilene **65** with CO to yield one of the first silicon–carbonyl complexes **66** (Scheme 14). Like transition metal carbonyl complexes, the silicon–carbonyl complex exhibits a strong Si–CO bonding, with Si←CO σ–donation and Si→CO π–backdonation. Thermal or photochemical activation leads to release of CO and formation of the disiletane **67**.[82]
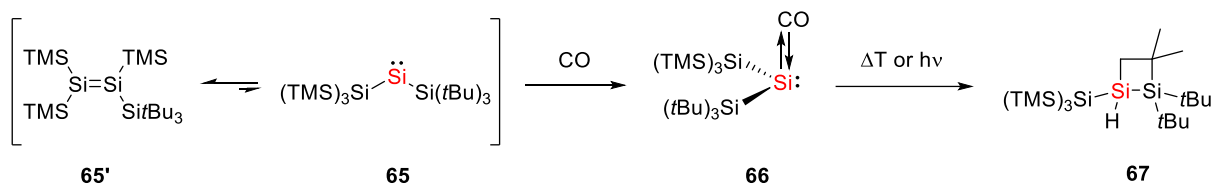
Scheme 14 Activation of CO forming silicon–carbonyl complex **66** and thermal or photochemical CO release.

Schulz *et al.* simultaneously discovered a similar route to trap the reactive silylene intermediate **69** by forming the stable silicon-carbonyl complex **70** under CO atmosphere (Scheme 15). In argon atmosphere the silylene intermediate immediately undergoes intramolecular C-C bond activation forming a silane.[83]
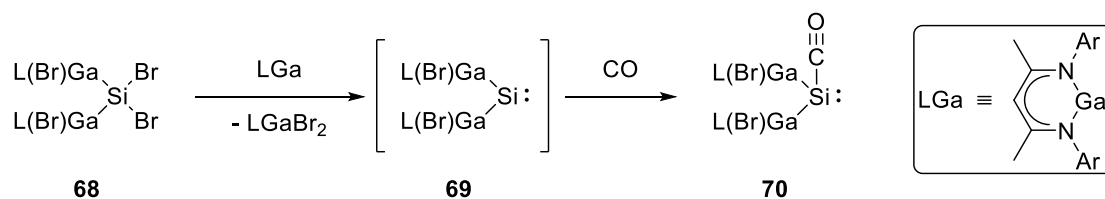
Scheme 15 Synthesis of silicon-carbonyl complex via trapping the free silylene with CO.

3.3 Tetryliumylidenes

Structure

Tetryliumylidenes are E(II) (E = Si, Ge, Sn, Pb) species with only four valence electrons, bearing a lone–pair, two vacant p–orbitals and a positive charge at the central atom (Figure 8, left). Due to their electronic properties, tetryliumylidenes are related to tetrylium ions as well as tetrylenes. The two vacant p–orbitals account for the electrophilic (Lewis acidic) part and the lone–pair for the nucleophilic (Lewis basic) one, classifying an ambiphilic character. Due to the high reactivity, stabilization *via* inter– or intramolecular electron donation and the use of a sterically demanding substituent are necessary to be able to isolate tetryliumylidene ions in the condensed phase. Donation of electron density into the vacant LUMO results in the reduction of the localized positive charge and consequently results in kinetic stabilization (Figure 8, middle and right). The use of sterically demanding R group shields the E(II) center from nucleophilic or electrophilic attacks (thermodynamic stabilization). In general, however, germyliumylidenes and stannyliumylidenes are easier to be stabilized as a result of the increasing s–p orbital energy separation.[84-85]
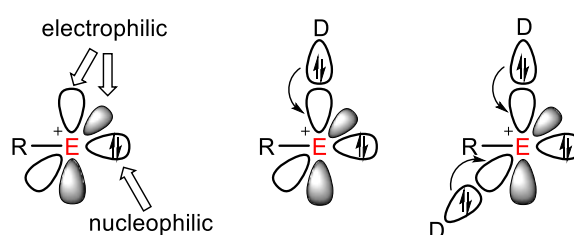
Figure 8 Molecular orbitals of free and donor–stabilized tetryliumylidenes.

The variety of R substituents and donor ligands were successfully used for tetryliumylidene stabilization. Especially imine and carbene–based donors proved suitable. Figure 9 depicts selected examples of published tetryliumylidenes **71–76**.[86-101]
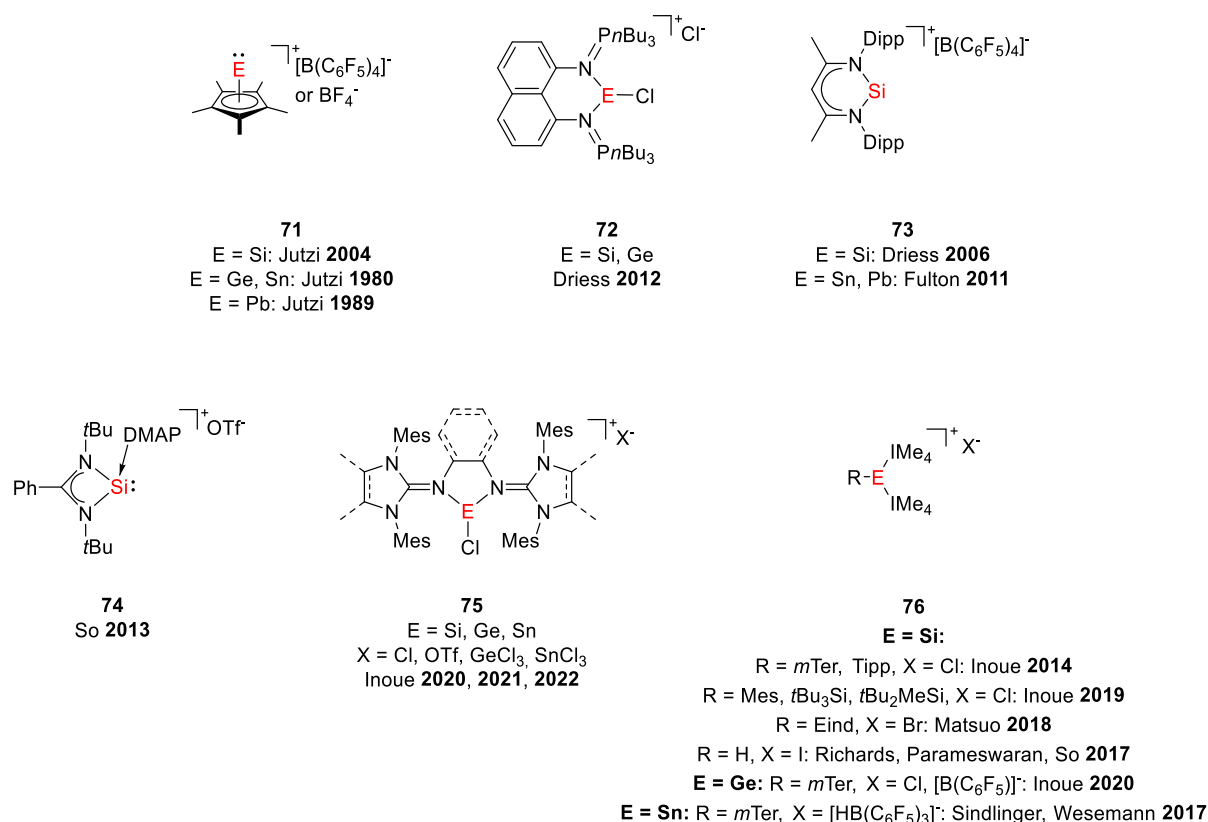
Figure 9 Selected examples of tetryliumylidene ions.

Synthesis

Over the years various synthetic pathways have been explored to isolate tetryliumylidenes. Only the most common ones are selected to be discussed in detail in this work.

The landmark synthesis of the first E(II) compounds dates back to 1980 when Jutzi and coworkers isolated the (pentamethylcyclopentadienyl)germanium(II) and –tin(II) cations **78** *via* protonation of the neutral bis(pentamethylcyclopendadienylgermanium and –tin complexes **77** (Scheme 16).[87] In 2004, Jutzi used the same approach to isolate the silicon(II) derivative, marking the beginning of Si(II) cation chemistry.[86]
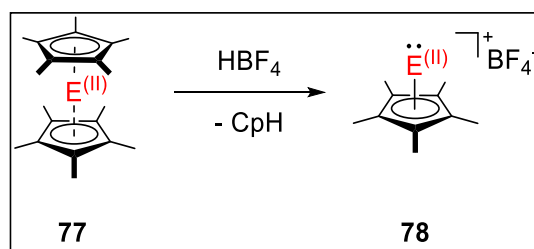
Scheme 16 Synthesis of Cp*E+ *via* protonation of Cp*E:.

Another way is the treatment of a neutral and bidentate Lewis basic ligand **79** with a NHC–stabilized dihalosilylene, donor–stabilized (e.g., 1,4–dioxane, NHC, or DMAP) germanium(II)– or tin(II)dihalide in a ligand exchange reaction. This approach is for example used for tetryliumylidenes **80**, bearing carbene or imine (NHI, phosphaimine)–based ligands (Scheme 17).[89-90, 94-95, 102-103]
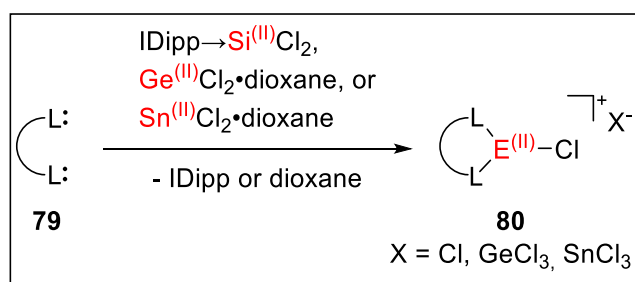
Scheme 17 Synthesis of tetryliumylidene ions **80** *via* ligand exchange reaction from E(II) dihalides.

A third synthetic approach is the treatment of an aryl– or silyl–substituted dichlorosilane **81** with 3 eq NHC in a reductive dehydrochlorination (Scheme 18), yielding an aryl–/silyl–substituted, NHC–supported silyliumylidene **82** with the respective imidazolium salt as side product. The analogue germyliumylidenes and stannyliumylidenes **84** are prepared from the chlorotetrylene **83** with the addition of NHC.
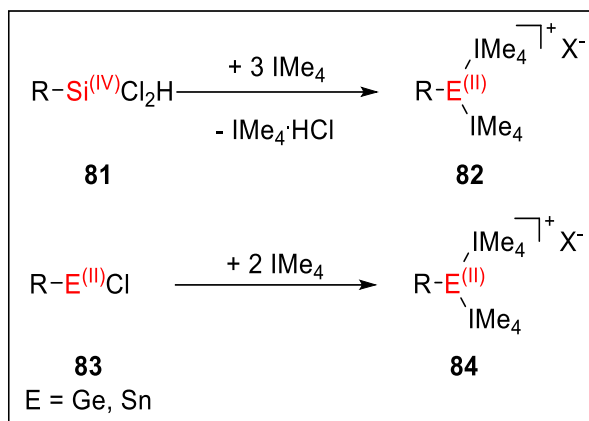
Scheme 18 Synthesis of tetryliumylidenes **82** and **84** *via* dehydrochlorination using NHC.

Tetryliumylidene synthesis is not only possible starting from a E(IV) or E(II) complex but also by treatment of a E(I) dimer **85** or **87** with an additional donor (Scheme 19). As donor for instance NHCs or DMAP are used, as demonstrated for silyliumylidenes **86** and **88**.[93, 104]
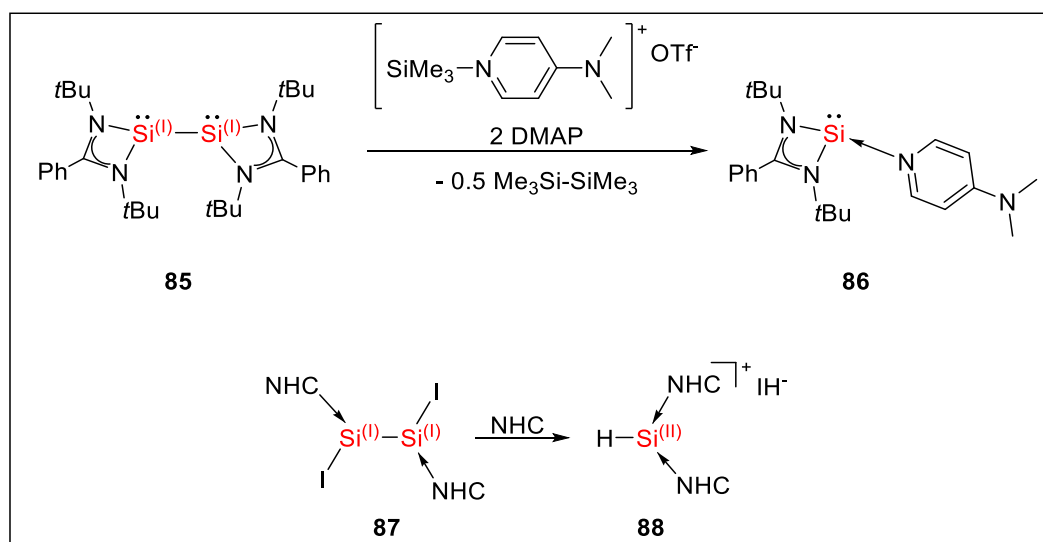
Scheme 19 Synthesis of silyliumylidene from Si(I) dimers **85** and **87**.

Reactivity

Since tetryliumylidenes show an ambiphilic character, they can react either as Lewis acids or Lewis bases. A typical Lewis base reactivity is the reactivity towards chalcogens (Ch = S, Se, Te). Indeed, silyliumylidene ion **89** readily forms the heavier silaacylium ions **90** with elemental chalcogens (Scheme 20). The ^{29}Si NMR shifts present an increasing upfield shift going down the heavier chalcogen group (^{29}Si δ [ppm] = –26.7, –31.0, and –59.1).[94]
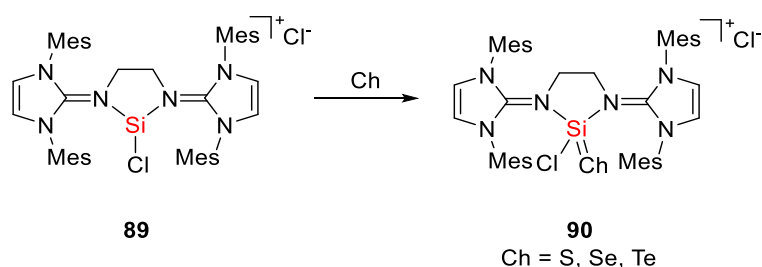
Scheme 20 Reactivity of silyliumylidene **89** towards heavy chalcogens.

The NHC–stabilized silyliumylidene published by Inoue in 2014, has been examined thoroughly towards small molecule activation. While silylenes tend to react with alkynes in a cycloaddition reaction, silyliumylidene **91** presented the reaction to silane **95** when treated with phenylacetylene (Scheme 21). The calculated reaction mechanism suggests the C−H activation and oxidative addition of phenylacetylene as first step to form silylene **92** and imidazolium salt. The silylene **92** reacts with two further molecules of phenylacetylene in a second C−H activation followed by acetylene–hydrogenation showing Z–selectivity to form the silane **95**.[97]
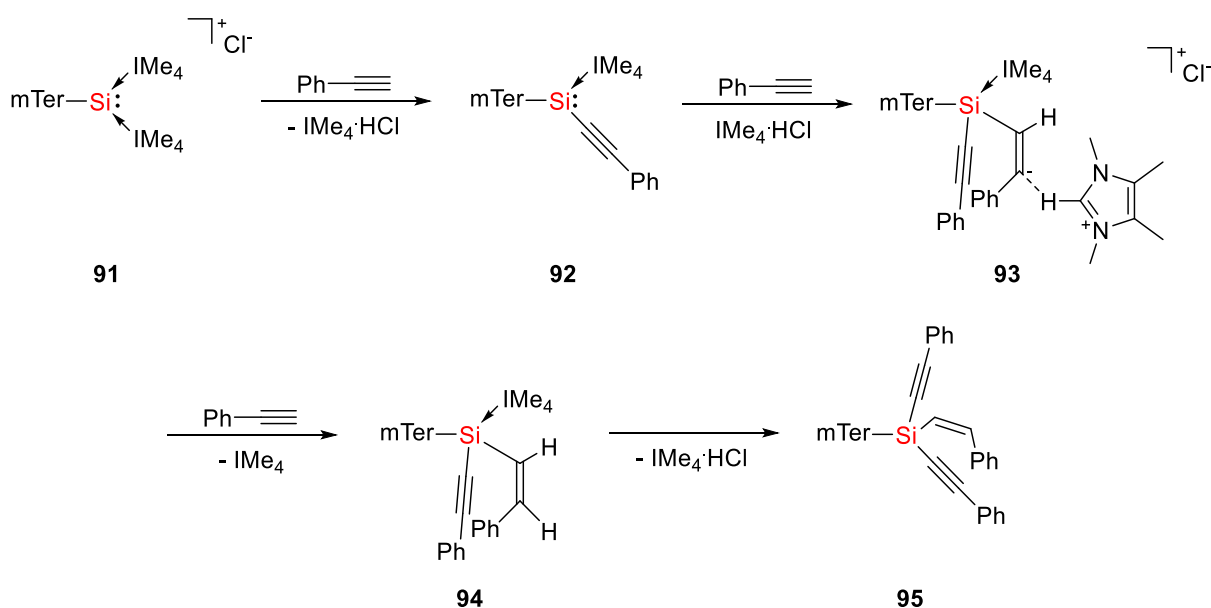
Scheme 21 Reaction of silyliumylidene **91** with phenylacetylene.

Further selected examples of reactivity towards small molecule, transition metal halides, and Lewis acidic GaCl₃ are depicted in Scheme 22. Treatment with different transition metal salts resulted in the coordination complexes **96** with the downfield effect in the ²⁹Si NMR shift getting stronger with descending the group from copper to gold.[105] Furthermore, the silaaldehyde **97**

was achieved with $GaCl_3$ and water, the thiosilaaldehyde **98** with hydrogen sulfide and the silaacyclium ion **99** *via* reaction with CO_2.[106-108]
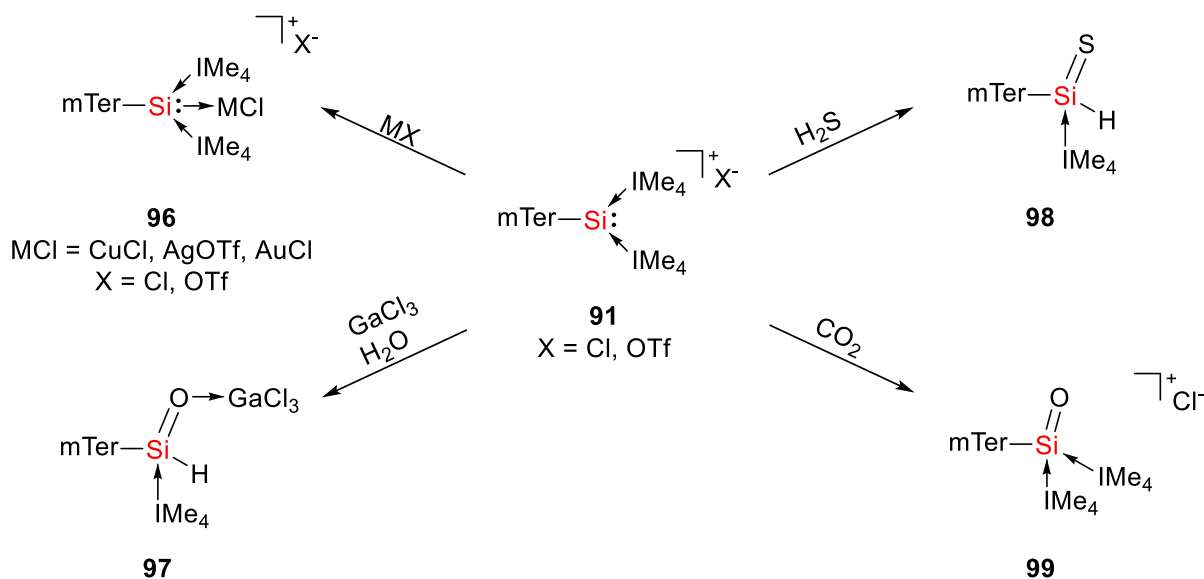
Scheme 22 Selected reactivity of silyliumylidene **91**.

Tetryliumylidenes can furthermore be reduced from E(II) to E(0) yielding a tetrylone, which will be discussed in detail in the following chapter (3.4).

The quest to substitute toxic and expensive transition metal catalysts with economic, non–toxic and earth abundant silicon–based catalysts is one of the main targets in main group silicon chemistry. For instance, the hydrosilylation is commonly catalyzed with platinum catalysts such as Karstedt's catalyst.[109] To substitute the platinum complex, Fritz–Langhals further investigated the properties of pentamethylcyclopentadienylsilicon(II) cation Cp*Si:+ for application in catalysis. Jutzi *et al.* could already proof its catalytic application in specific degradation of oligo(ethyleneglycol) diethers.[110] Indeed the Si(II) complex additionally offers excellent activity in hydrosilylation of alkenes and alkynes at a catalyst loading of lower than 0.1 mol%. A mechanism similar to the tris(pentafluoro–phenyl)borane (BCF)–catalyzed hydrosilylation is suggested (Scheme 23).[111-113] In the hydrosilylation of α–methylstyrene with pentamethylsiloxane and 0.0013 mol% catalyst, full conversion was achieved at room temperature. Interestingly, the addition of further starting material again resulted in full conversion, verifying the presence of an active catalyst species.[111]

$$Cp^*Si^+ \, X^- \; + \; H{-}SiR_3$$
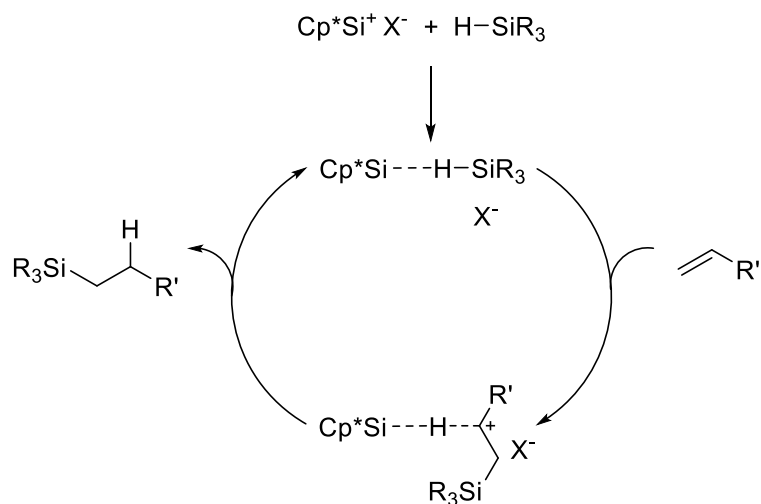
Scheme 23 Suggested mechanism for catalytic hydrosilylation of olefins.

Si(II) Dications

The last chapter summarized the properties of monocationic tetryliumylidenes. However, the related dicationic E(II) complexes possess similar properties with an even higher electrophilicity and therefore high reactivity. These E(II) species exhibit a lone–pair and three vacant p–orbitals (Figure 10).[85]
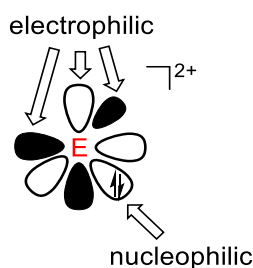
Figure 10 Molecular orbitals and electronic features of E(II) dications.

Due to the difficult stabilization, only scarce examples are known in the literature. A strategy to trap these species, is the application of three strongly Lewis basic ligands to compensate the strong electrophilicity of the unoccupied p-orbitals. The first one to achieve an isolation in condensed phase was the group of Baines in 2007 isolating the NHC stabilized Ge(II) dication **101** from addition of excess NHC to the NHC–stabilized GeI_2 **100** (Scheme 24). [114]
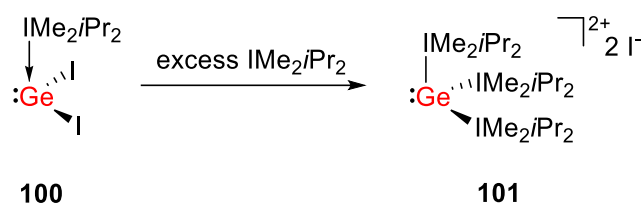
Scheme 24 Synthesis of Ge(II) dication **101**.

Only one year later, Baines accomplished the striking isolation of new a compound class, the cryptand–stabilized Ge(II) dication **103**, presenting the first non–metal cryptand complex (Scheme 25).[115] Four years later, the analogue Sn(II) dication complex was reported by Herber, Huang, and Baines.[116] The electron rich macrobicyclic cryptand stabilizes the dicationic center not *via* discrete but with multiple weak donor–acceptor interactions.
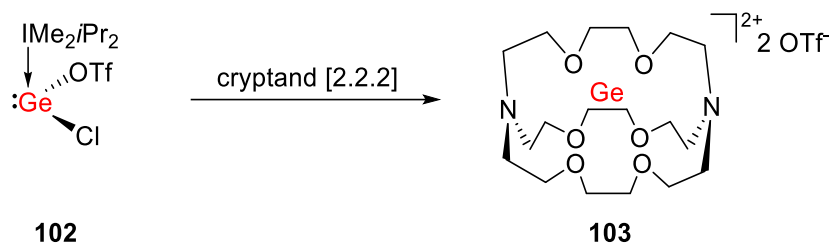
Scheme 25 Synthesis of cryptand stabilized Ge(II) dication **103**.

Before this landmark synthesis, cyclic ethers have already been applied in stabilization of tin and lead dications like **104** and **105** (Figure 11).[117-118] Inspired by this results, a further example of macrocyclic Ge(II) and Sn(II) dications **106** have been published by Baines and McDonald.[119-120]

104	**105**	**106**
Hough **1989**	Drew, Nicholson **1992**	E = Ge: McDonald, Baines **2009**
		E = Sn: McDonald **2010**
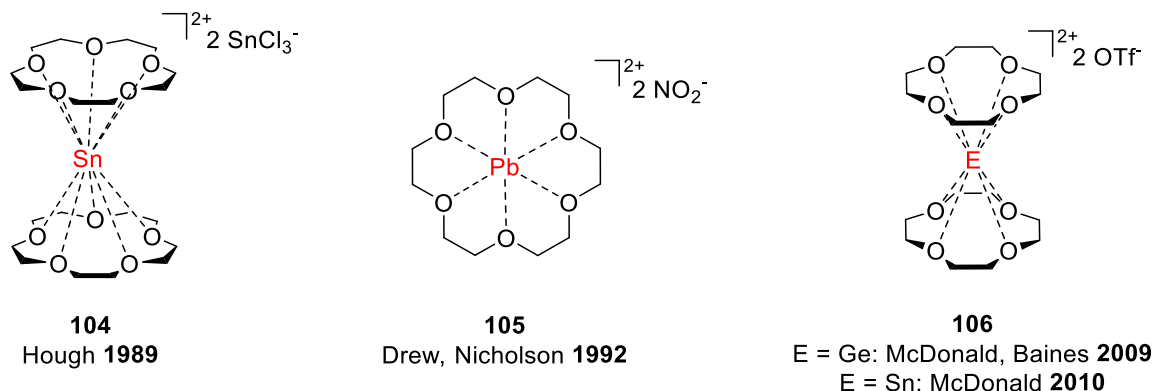
Figure 11 Polyether stabilized E(II) dicationic complexes.

Filippou used NHCs to successfully stabilize the first Si(II) dication **108**, generated from the NHC–stabilized diiodosilylene **107** (Scheme 26).[81]
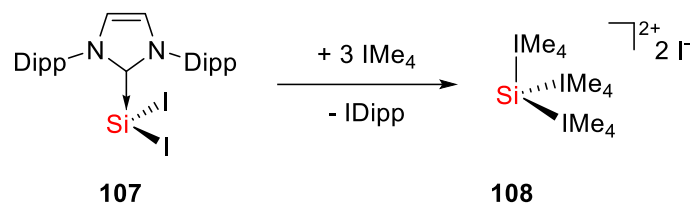
Scheme 26 Synthesis of Si(II) dication **108**.

3.4 Tetrylones

Structure

Tetrylones, also called ylidones, are divalent group 14 complexes of the formal oxidation state 0, exhibiting two free electron pairs. Stabilization of the reactive E(0) center is realized using neutral donor ligands (L). Scheme 27 displays the different resonance structures of tetrylones. Depending on the ligand, the complex has a predominant ylidone, ylidene, or bent allene character.[121-122] Strong π–backbonding to the ligand results in an increasing allene character and therefore increasing stability, yet decreasing reactivity. In Figure 12, selected examples of literature known tetrylones **109**–**115** are shown and depicted according to the predominant resonance structure.[102-103, 123-135] For stabilization of the E(0) center, especially carbene, silylene, germylene, or imine based ligands proved successful due to their strong σ–donor and sufficient π–acceptor properties.
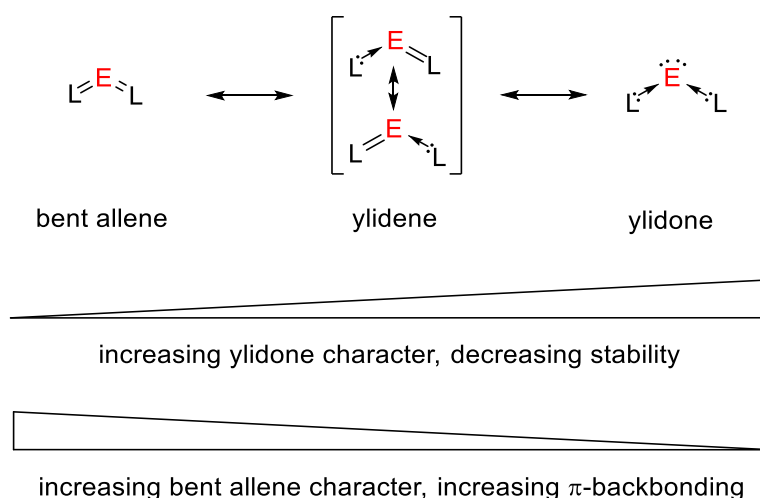
Scheme 27 Resonance structures of divalent E(0) compounds (with E = Si, Ge, Sn, Pb).

27

109
Wiberg **1999**

110
E, E' = Si: Kira **2003**
E = Si, E' = Ge: Kira **2005**
E = Ge, E' = Si: Kira **2005**
E, E' = Ge: Kira **2005**

111
E = Si: Stalke, Roesky, Frenking **2013**
E = Ge: Roesky, Zhu, Stalke, Andrada **2013**

112
E = Si, Ge
Driess **2013**

113
Tokitoh **2017**

114
E = Ge: Nikonov **2014**
E = Sn: Fischer, Flock **2013**

115
E = Si: Driess **2019**
E = Ge: Driess **2019**
E = Sn: Driess **2022**
E = Pb: Driess **2022**
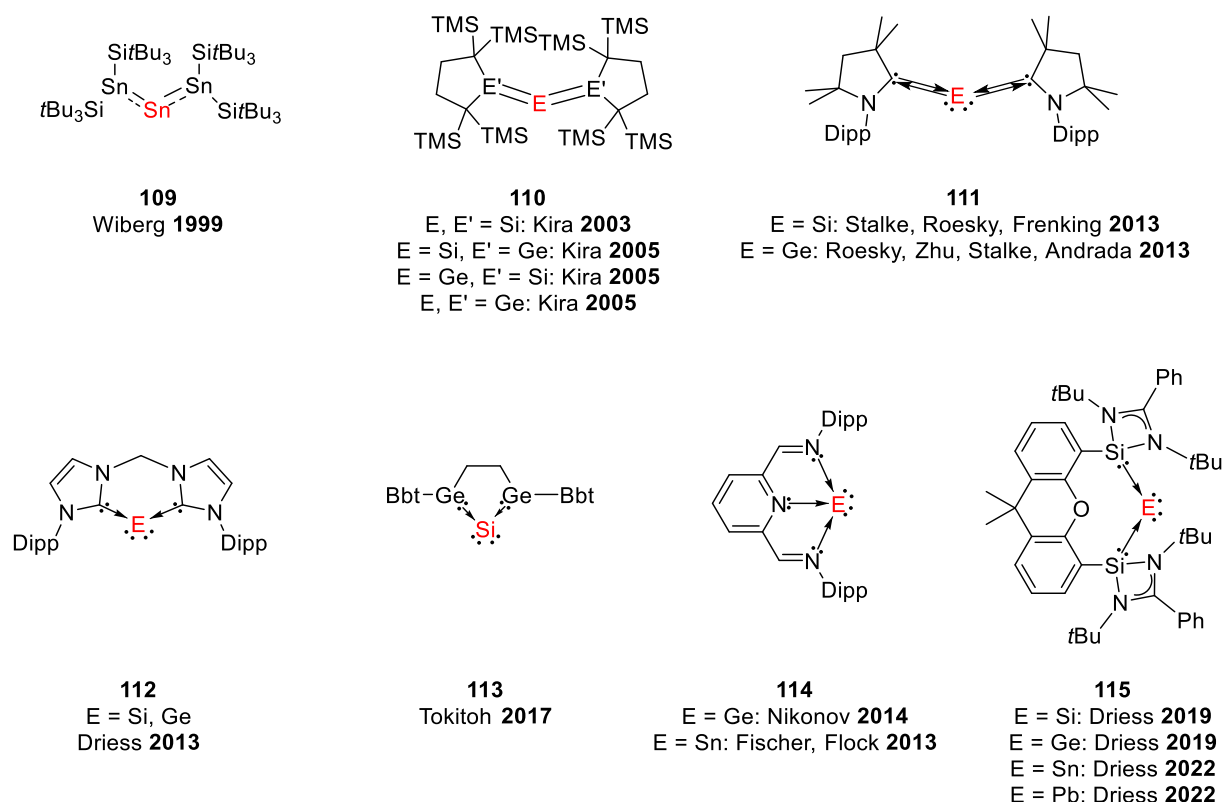
Figure 12 Selected examples of divalent E(0) compounds (with E = Si, Ge, Sn, Pb).

Theoretical calculations by Frenking investigated the bonding situation in divalent E(0) compounds (with E = C, Si, Ge, Sn) to get an insight into the geometric and electronic properties.[121, 136] The calculations revealed a best description of the bonding situation as donor–acceptor interaction between the E(0) center in EL_2 (E = Si, Ge, Sn, Pb) and the ligand L, with L being a five–membered cyclic ylidone or NHC. Additionally, silylene and germylene–stabilized silylones and germylones reveal E(0) character as well, showing two free lone pairs in molecular orbital analysis, calculated by the groups of Phukan and Gadre. However, allenes with dialkylsilylene ligands as in **110** are exceptions thereof, revealing two Si=Si and Ge=Ge bonds in their equilibrium geometries.[137] In Figure 13 the general electronic structure of the two resonance structures of tetrylone and allene are depicted. Tetrylones exhibits two electron lone pairs, one in an s–type orbital, one in a p–type orbital. The vacant p–orbitals are occupied by the σ–donating electron pair of the ligand. Consequently, the L–E–L angle should be close to 90°. Free p–orbitals of the ligand (e.g., in carbenes and silylenes) are stabilized by the π–backdonation from the free p lone pair at the E(0) center. In case of an increasing bulk of the ligands, the L–E–L angle increases and the structure changes towards an allene character. Additionally, the s–character of the lone pair at the E(0) center changes towards an sp–type hybridization, resulting in a more pronounced π–bonding character between E(0) and L.[122]
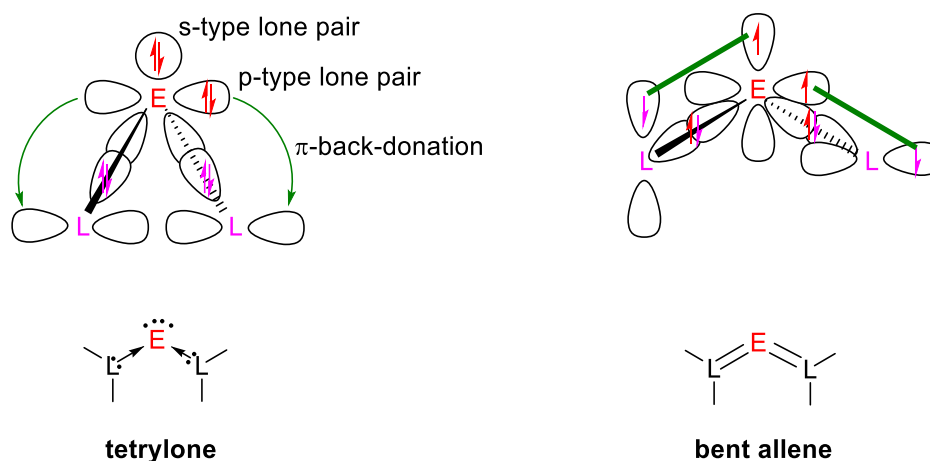
Figure 13 Resonance structures of tetrylones and bent allenes.

To visualize the differences in the E(0) structures, and the impact on the L–E–L bond angle as well as on the ^{29}Si NMR shift, trisilaallene **116**, cAAC–stabilized silylone **117** and NHC–stabilized silylone **118** are compared in Table 1.[102, 124, 127] As expected, the trisilaallene **119** shows the largest L–Si–L bond angle of 136.49(6)° and a low–field shifted ^{29}Si NMR signal at 157.0 ppm.[124] Interestingly, the two carbene–stabilized silylones **117** and **118** reveal large differences. According to calculations by Driess and coworkers, the tremendous ^{29}Si NMR upfield shift of the NHC–stabilized silylone compared to the cAAC–stabilized one accounts for stronger σ–donor und weaker π–acceptor properties of the NHC resulting in a more shielded Si(0) center. Additionally, the NHC–stabilized silylone exhibits a smaller L–Si–L bond angle close to 90°.[102]

Table 1 ^{29}Si NMR shifts and L–Si–L bond angles of selected silylones.

	^{29}Si NMR δ[ppm]	Bond angle L–Si–L [°]
116	157.0	136.49(6)
117	66.7	117.70(8)
118	−83.8	89.1(1)

Synthesis

To synthesize tetrylones, various methods have been evaluated. The first E(0) species to be isolated is considered to be the stannylone published by Wiberg $et\ al.$[123] in 1999. Either Lappert's stannylene $Sn(NTMS_2)_2$[138] or $(Sn(OtBu)_2)_2$[139] (**119**) are treated with sodium tri($tert$–butyl)silanide to yield the stannylone **120**, which exhibits a half–life time of only 9.8 h (Scheme 28). Due to the high steric demand of the supersilyl substituents, a rearrangement to the isomeric cyclotristannene **121** takes place. Since the central tin atom shows a ^{119}Sn NMR shift of 2233 ppm, which is in the range of reported stannylenes, and additionally the SC–XRD analysis revealed a short Sn–Sn bond length of 2.682 Å, the compound is better described as a stannylene adduct of a distannavinylidene (**120'/120''**).[123]
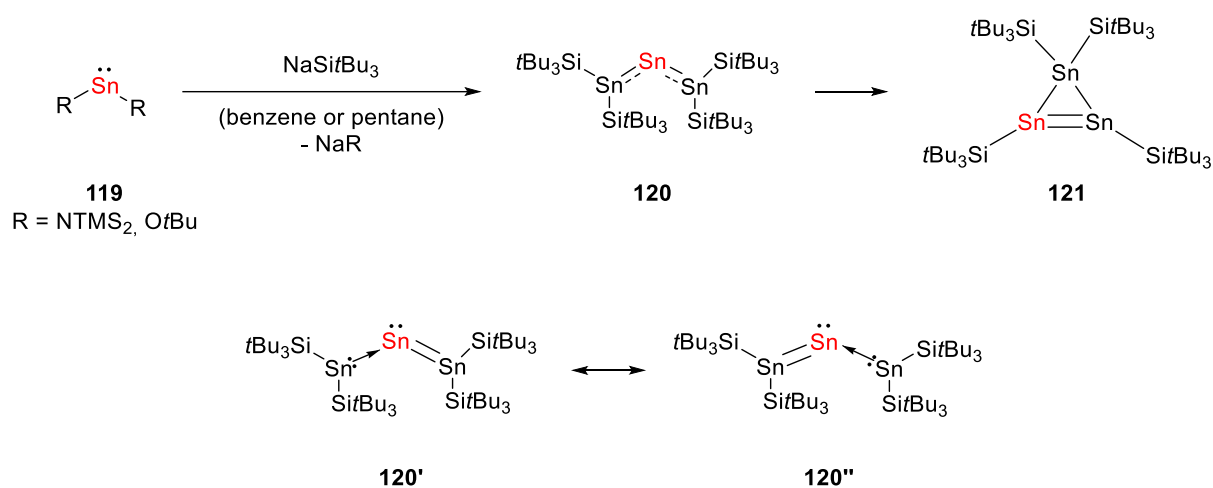
Scheme 28 Synthesis of stannylone **120** and rearrangement to cyclotristannene **121** and suggested resonance structures of **120'/120''**.

A different, most commonly used strategy to isolate tetrylones is the reductive dehalogenation of E(IV) and E(II) compounds shown in Scheme 29 and Scheme 30.[124, 127-128] As reducing agents often KC_8 or sodium naphthalenide are used. This strategy was not only used in the isolation of formal Si(0) complex **124**, which is best described as trisilaallene, but also in the isolation of the first so–called silylone **127** by Roesky, Stalke, and Fenking, using carbenes for stabilization and the germylone **129** by Roesky, Zhu, Stalke, and Andrada.[124, 127-128] The same strategy was used to synthesize the first cyclic silylone and germylone by Driess.[102-103]
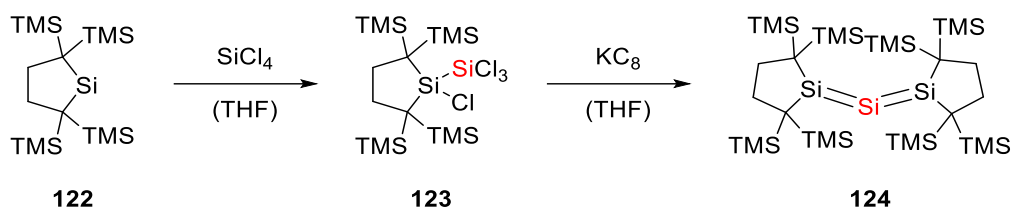
Scheme 29 Synthesis of Si(0) complex *via* reductive dehalogenation from Si(IV).
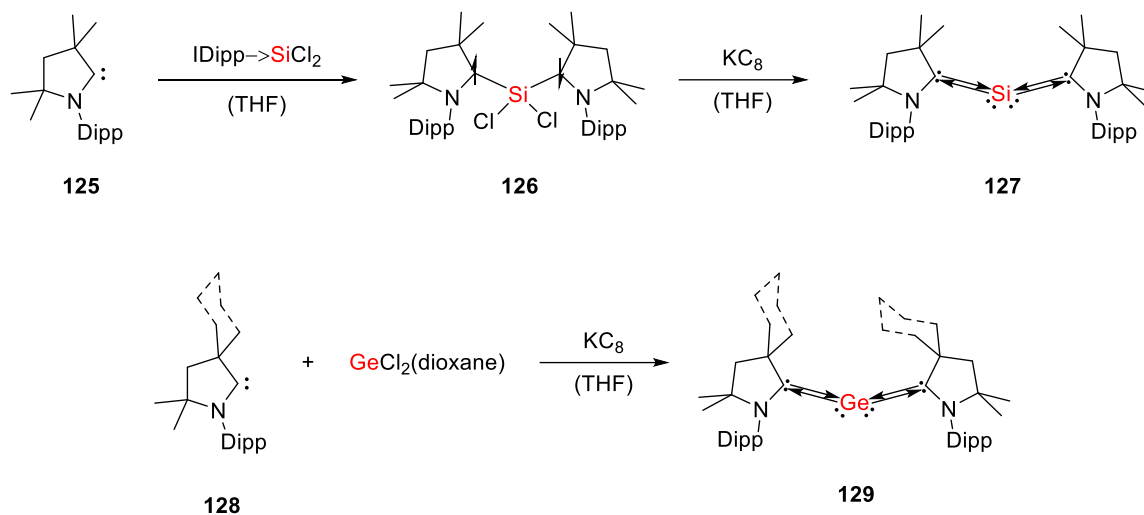
Scheme 30 Synthesis of cAAC–stabilized silylone **127** and germylone **129** *via* reductive dehalogenation from diradical **126** or Ge(II).

A third reaction pathway used for stannylone synthesis, is the transamination displayed in Scheme 31. Lappert's stannylene Sn(NTMS$_2$)$_2$ is used as Sn(II) source and deprotonation reagent to yield the planar tricoordinate formal stannylone **131**.[131]
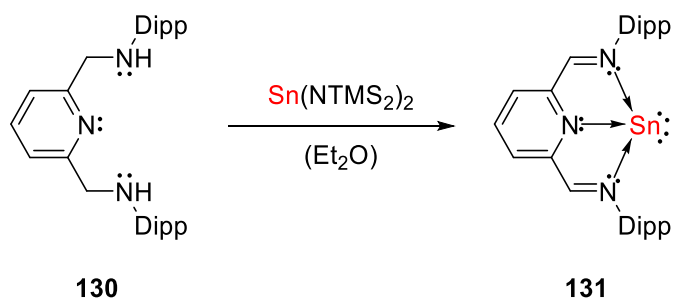
Scheme 31 Synthesis of stannylone **131** *via* transamination.

31

Reactivity

Tetrylones possess two free electron pairs and therefore are expected to react with Lewis acids and be able to activate small molecules. For instance, Driess and coworkers were able to isolate the mono– and bis–AlBr$_3$ adduct (**133** and **134**) of germylone **131** (Scheme 32). Interestingly, the formation of the bis–adduct is only possible in non–coordinating solvents such as benzene. The use of coordinating solvents like Et$_2$O or THF does only result in the formation of the monoadduct even with an 20–fold excess of the Lewis acid, since the coordination ability of the donor solvent towards AlBr$_3$ is stronger.[132]
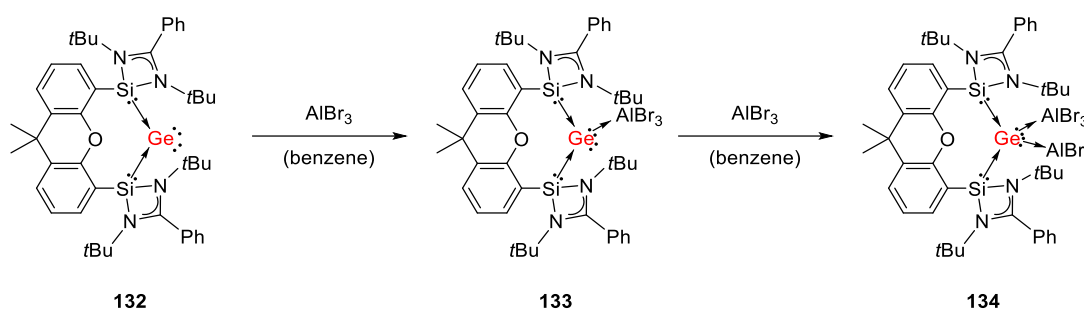
Scheme 32 Reactivity of germylone **132** towards AlBr$_3$.

Among the small molecule activations, CO$_2$ activation is an often–targeted goal. Carbon dioxide is one of the main greenhouse gases. Hence, towards the capturing, storage, and utilization of CO$_2$ considerable research efforts is invested. Additionally, CO$_2$ presents a non–toxic, abundant, and economical C1 feedstock. However, due to the high thermodynamic stability, activation is necessary. In 2017, Driess and coworkers presented the synthesis of a bisNHC–supported silicon decarbonate complex **138** by activation of carbon dioxide with silylone **135** (Scheme 33). The formation *via* silicon monoxide **136** and the dioxide complex **137** is proposed and verified with quantum chemical calculations.[140]
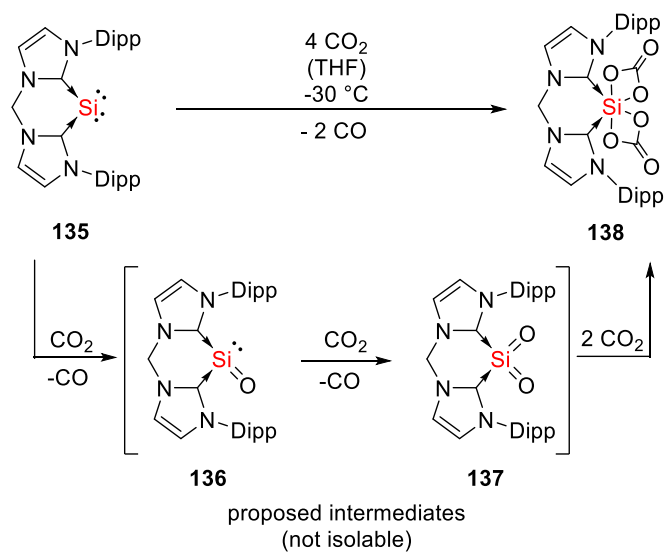
Scheme 33 Reactivity of silylone **135** towards CO_2.

4. Scope of this Work

4.1 Synthesis and Reactivity of Heavier Nitrile Analogues

The first part of this thesis focuses on the synthesis of a stable tin and germanium heavier nitrile analogues. As suitable phosphorus source, the *N*-heterocyclic carbene-phosphinidene were selected, featuring the advantage of the introduction of a NHC as stabilization. Analogue to literature known procedures used to synthesize NHCP-transition metal complexes, there are different methods to functionalize a NHCP. One way is the treatment of a TMS substituted NHCP **139** with a chloro-tetrylene to eliminate TMSCl and form the NHCP-stabilized tetrylene **140** (Scheme 34). A second path is the utilization of a parent NHCP **141** and treatment with a chloro-tetrylene and an amine base (e.g., DABCO, DBU).[37-38] Depending on the used NHCs and substituents R', the mesomeric structure **140**, **140'**, or **140''** with a P-E single, double, or triple bond character is predominant. The multiple bond character can be confirmed chemically, with theoretical calculations, or with SC-XRD analysis.
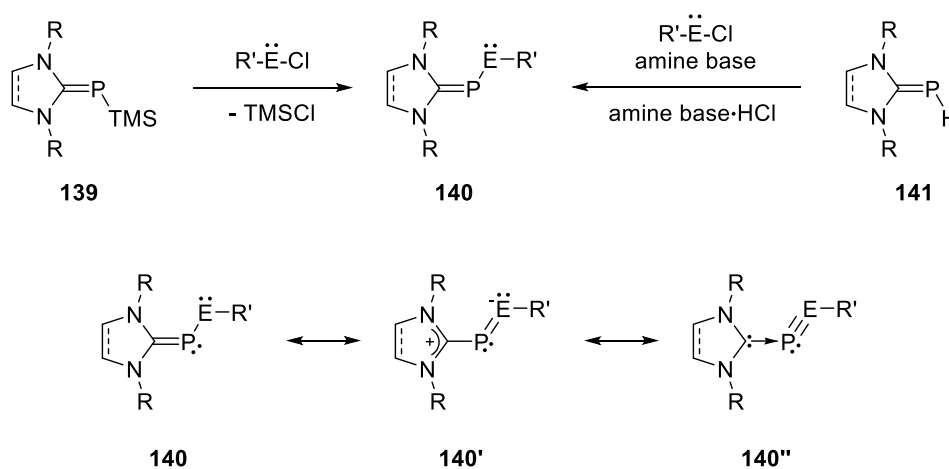
Scheme 34 Synthetic methods to isolate a NHC stabilized heavier nitrile and mesomeric structures of heavier nitrile analogue **140**.

34

4.2 Synthesis and Application of Bidentate N-heterocyclic Carbene-Phosphinidene Ligands

In order to be able to isolate low–valent, low–oxidation state group 14 complexes, a suitable ligand system needs to be evaluated. Previous research on the isolation of tetryliumylidenes and tetrylones has been conducted in the group of Inoue using a bidentate *N*–heterocyclic imine ligand system, resulting in the isolation of a variety of tetryliumylidene ions **142**–**145** (Figure 14).[94-96]
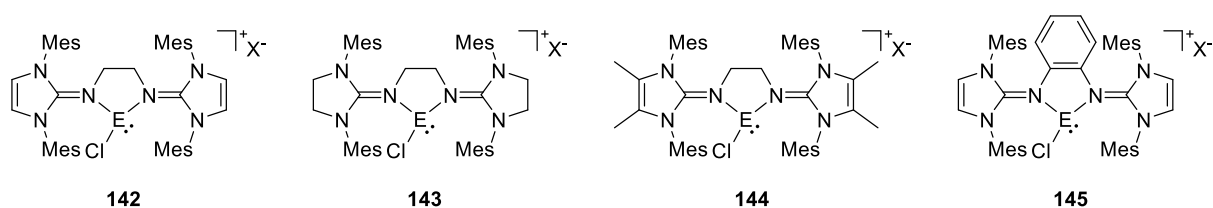
Figure 14 BisNHI stabilized tetryliumylidenes (with E = Si, Ge, Sn and X = Cl, OTf, $SnCl_3$, $GaCl_3$).

However, reduction of the tetryliumylidenes to the corresponding tetrylone was not possible. Supposably, the highly reactive and electron rich E(0) center could not be stabilized by the bisNHI ligand. NHIs are strong σ–donor ligands, however they do not have π–acceptor properties. All literature–known tetrylones are stabilized for example with carbene, silylene, or germylene based ligands, allowing strong π–backdonation to the ligand. This results in a lower electron density at the E(0) center, resulting in higher stability but also lower reactivity. Therefore, a new ligand system based on NHCPs, offering strong σ–donor and weak π–acceptor properties, is synthesized and tested for its application in complexation.

Synthesis of bidentate NHCP ligand

To synthesize a bisNHCP ligand, two different strategies are tested (Scheme 35). The first method is conducted analogue to the synthesis of bisNHI ligands. The parent or TMS substituted NHCP is treated with a triflate–substituted alkane, followed by deprotonation/TMS abstraction using a base. Commonly, bases such as NaHMDS, KHMDS, *n*BuLi, or KO*t*Bu are used. The second method is treating a bis(dichlorophosphine) with NHC followed by reductive dehalogenation. Reductive dehalogenation can be realized e.g., with KC_8 or sodium/potassium naphthalenide. In both methods the ligand bridge as well as the substituents on the NHC can be varied to yield different steric and electronic properties. For stabilization of a low–valent

and/or low–oxidation state central atom, bulky substituents are chosen in order to sterically hinder an attack at the central atom.
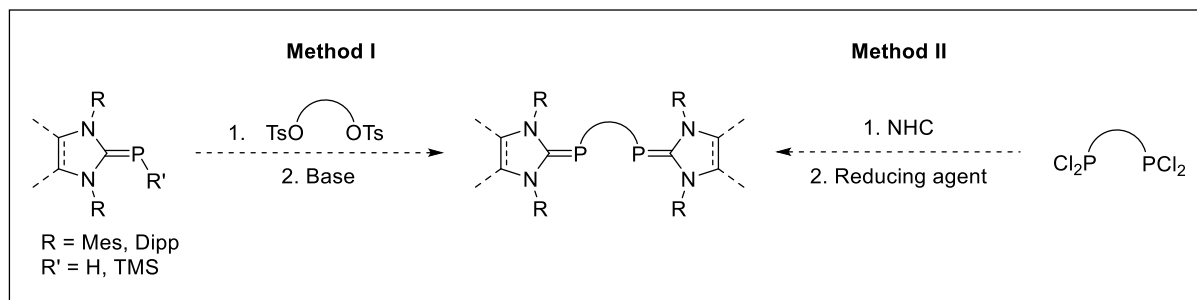
Scheme 35 Possible pathways to synthesize a bisNHCP ligand.

<u>Synthesis and reactivity of bisNHCP–stabilized E(IV) and E(II) complexes</u>

In order to test the capability of the new bisNHCP ligand to stabilize E(IV) and E(II) complexes, various precursors are tested (Scheme 36). As E(IV) precursors, different halosilanes and triflate–substituted silanes are tested to yield mono–, di–, or tricationic E(IV) complexes. To isolate tetryliumylidene ions, the bisNHCP ligand is treated with NHC–stabilized dihalosilylenes or EX_2 (with E = Ge, Sn and X = Cl, Br, I, OTf).
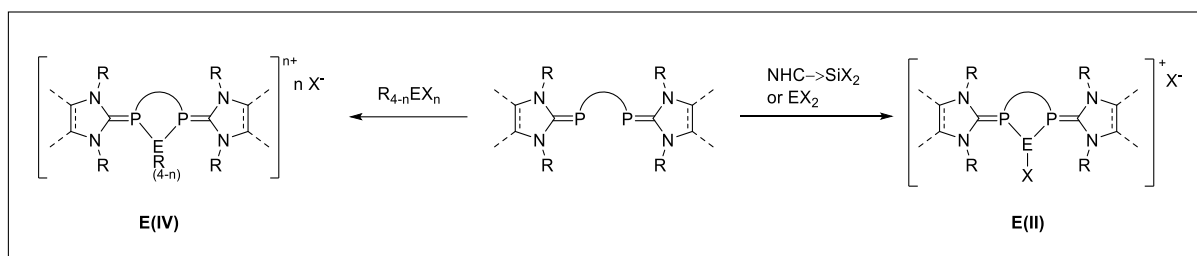
Scheme 36 Synthesis of bisNHCP**–**stabilized E(IV) and E(II) complexes (with E = Si, Ge, Sn and X = Cl, Br, I, OTf).

Reactivity of the formed complexes towards small molecules and application in catalysis is examined.

Reduction of bisNHCP–stabilized E(IV) and E(II) complexes to E(0) complexes

To get to the target complex of a tetrylone, either stepwise or direct reduction is investigated (Scheme 37). For the reduction a suitable reducing agent needs to be evaluated, e.g., KC_8, sodium or potassium naphthalenide, $(NacnacMg(I))_2$, Mg^*, metallic lithium, sodium, or potassium, or their alloys.
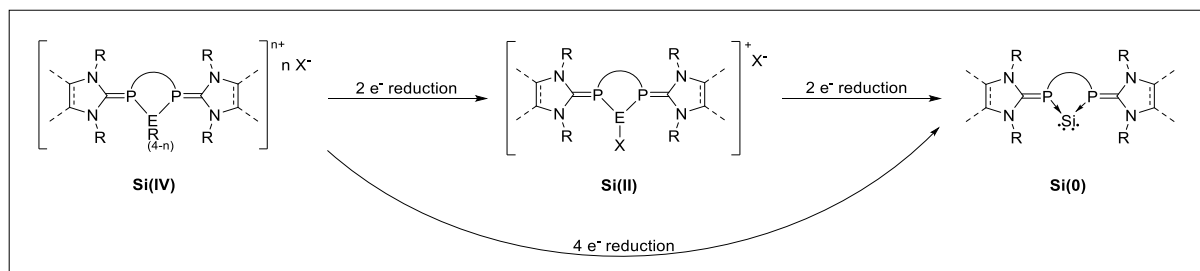
Scheme 37 Stepwise reduction from Si(IV) to Si(0).

As for the E(IV) and E(II) complexes, the terylones will be tested for small molecule activation, application in catalysis and for oxidation towards monomeric 'SiO' and 'SiO$_2$' complexes.

5.   *N*–Heterocyclic Carbene–Stabilized Germanium and Tin Analogues of Heavier Nitriles: Synthesis, Reactivity, and Catalytic Application

[a]V. Nesterov and R. Baierl planned and executed all experiments to synthesize compounds **1−4**. A. Espinosa Ferao performed the theoretical calculation. V. Nesterov performed the catalytic experiments and wrote the manuscript. F. Hanusch conducted SC–XRD measurements and processed the respective data. All work was done under the supervision of S. Inoue.

Content: The synthesis of a stable heavier nitrile analogue was achieved by coordination of a NHC to a low–valent phosphorus center and the use of a sterically demanding terphenyl substituent protecting the Ge(II)/Sn(II) center. Both compounds display [2+2] cycloaddition reaction with diphenylketene and demonstrated potential in catalytic hydroboration of carbonyl compounds.

Towards the synthesis of heavier analogues of alkenes, alkynes, or nitriles considerable effort has already been made, however, it remains challenging. In contrast to carbon, in the heavier analogues the stability of multiple bonds decreases. Aiming the isolation of a heavier nitrile

derivative, different strategies have been explored, for instance, attachment of electronegative groups at the group 14 element or the use of sterically demanding amido groups. This publication further explores the synthetic pathway to introduce a Lewis base at the phosphorus center. Treating NHCP–TMS with germylene or stannylene mTerECl (E = Ge, Sn) at 75 °C resulted in the formation of a tetrylene–phosphinidene. SC–XRD analysis as well as theoretical calculations revealed a E–P double bond character. While the tetrylene–phosphinidenes are unreactive towards several small molecules, a formation of a [2+2] cycloaddition product occurs with diphenylketene. NMR–spectroscopically a reversible reaction at elevated temperature could be proved. Additionally, both tetrylenes exhibit ability to catalyze hydroboration of aromatic aldehydes and ketones with pinacolborane.

N-Heterocyclic Carbene-Stabilized Germanium and Tin Analogues of Heavier Nitriles: Synthesis, Reactivity, and Catalytic Application

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S *Supporting Information*

ABSTRACT: The synthesis of stable heavier analogues of nitriles as monomeric tetrylene−phosphinidenes ^{Mes}TerEP(IDipp) (E = Ge, Sn; ^{Mes}Ter = 2,6-Mes$_2$C$_6$H$_3$, IDipp = C([N-(2,6-*i*Pr$_2$C$_6$H$_4$)CH]$_2$) was achieved by taking advantage of NHC (N-heterocyclic carbene, here IDipp) coordination to the low-valent phosphorus center. Multiple bonding character of the E−P bonds was examined experimentally and computationally. Both germanium and tin compounds undergo [2+2] cyclo-addition with diphenylketene, whereas reaction of the tin derivative with *tris*(pentafluorophenyl)borane provided unique "push−pull" phosphastannene (^{Mes}Ter)(Ar)Sn = P(IDipp) (Ar = C$_6$F$_4$[B(F)(C$_6$F$_5$)$_2$]). Going further, we demonstrated the potential of tetrylene−phosphinidene complexes in catalytic hydroboration of carbonyl compounds.

S table heavier main group alkene, alkyne, nitrile analogues and their derivatives continuously attract increased research attention due to unique synthetic potential and growing application in catalysis.[1,2] Among these compounds, heavier nitrile analogues RE≡P **IA** (E = Si, Ge, Sn, Pb; Chart 1A) still remain very challenging synthetic targets due to low

Chart 1. (A) Heavier Nitrile (I) and Isocyanide (II) Analogues; (B) Dimers III−VII, and Germylene VIII

thermodynamic stability and tendency to oligomerize. Theoretical calculations[3] on model compounds with small substituents suggest higher stability of the linear form RE≡P (**IA**) over the isomeric bent structure RP=E: (**II**) only for silicon derivatives (E = Si) with electronegative groups.[3a] For the silicon compounds with electropositive substituents[3a] and tin analogues independent from the substitution pattern,[3b] the isomer **II** is energetically more favored.[4] Low thermodynamic stability of heavier nitriles is attributed to drastically decreased ability of heavier elements to form multiple covalent bonds. This can be viewed as increased contribution of the valence isomer tetrylene−phosphinidene resonance structure **IB** into the ground state of the molecule descending the group 14. Although sufficiently bulky aryl substituents were predicted to stabilize the heavier nitrile form **IA** (E = Si, Sn),[3b,c] reported experimental attempts to access these compounds using this strategy alone were not successful so far.[5] Most recently, an approach using very sterically demanding amido ligands resulted in tetrylene−phosphinidenes dimers, diphosphenes **III** (Chart 1B).[5d]

Alternative approach, implying coordination of a Lewis base to a heavier low-coordinate group 14 element, have also been explored. Several groups independently reported isolation of [LSiP]$_2$ cyclobutadiene analogue **IV** (Chart 1B)[6] considered as a phosphasilyne dimer. Related heterocyclic system [LGeP]$_2$ **V** (Chart 1B),[7] as well as cationic derivatives **VI** and **VII** (Chart 1B)[8] were obtained after UV irradiation of the corresponding L[Ge]PCO phosphaketenes. Cyclic germylene **VIII** was synthesized using similar synthetic approach.[9]

NHCs are widely recognized as excellent ligands for stabilization of low-valent main group elements.[10] Herein, we describe the synthesis and isolation of NHC-stabilized tetrylene−phosphinidenes, as well as first insights into the structure, bonding, and reactivity of these heavier nitrile analogues, including application in catalysis.

Recently, we developed a number of synthetic methods to stabilize low-coordinate group 14 element compounds using N-heterocyclic imines (NHIs) as supporting ligands.[11] To expand this chemistry, we approached the problem exploring synthetic potential of their heavier analogues, NHC−phosphinidene (NHCP) adducts.[10,12] Aiming at target

14576
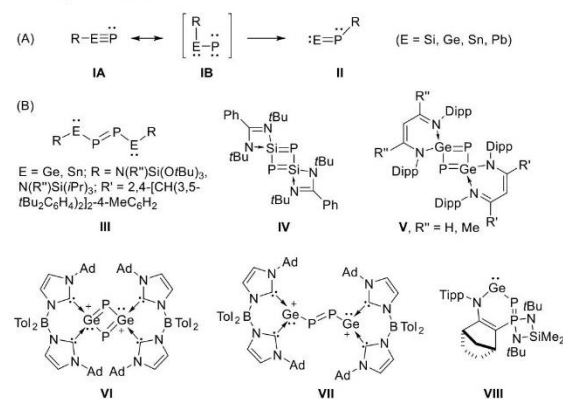
compounds with aryl substituents, which would provide some "pull" effect and steric protection, we reacted germylene and stannylene chloride dimers [^{Mes}TerECl]$_2$[13] with trimethylsilyl phosphinidene complex (IDipp)PSiMe$_3$[14] (Scheme 1). At

Scheme 1. Synthesis of Germylene, and Stannylene, Phosphinidene NHC Complexes 1 and 2

1 (E = Ge, 82 %)
2 (E = Sn, 72 %)
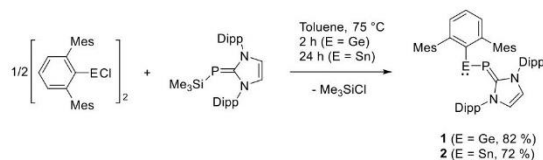
elevated temperature, the reaction led to elimination of trimethylsilyl chloride and selective formation of stable tetrylene–phosphinidenes **1** and **2** isolated in good yields as red and orange crystals, respectively. Their signals in the ^{31}P NMR spectra (C$_6$D$_6$) appeared at 216.8 ppm (**1**) and 176.4 ppm (^1J(^{119}Sn,P) = 1648 Hz) (**2**) lying downfield related to the starting material (δ(^{31}P) = −129.5 ppm)[14] and within the range reported for phosphagermenes (175−416 ppm) and phosphastannenes (170−204 ppm).[1] The ^{119}Sn NMR spectrum of **2** showed a doublet at 1689.8 ppm (^1J(^{119}Sn,P) = 1648 Hz), which falls into the region reported for bis(aryl)stannylenes (980−2323 ppm)[15] and significantly downfield shifted related to phosphastannenes signals (499− 658 ppm)[2] indicating pronounced tetrylene character of this compound. The ^1J(^{119}Sn,P) coupling constant lies between the typical values for Sn−P single (ca. 1000 Hz) and double (2208−2295 Hz) bonds.[2]

Single crystal X-ray diffraction analysis revealed similar structural features of **1** and **2** (Figure 1). The bond angles

Figure 1. Molecular Structures of **1** (left) and **2** (right). Thermal ellipsoids are shown with 50% probability; hydrogen atoms are omitted for clarity.

around the group 14 metals are very acute (89.56(5)° at Ge, and 86.69(6)° at Sn) and close to those reported for (amido)tetrylenes (^{Mes}Ter)(NHDipp)Ge: (88.6(2)°)[16a] and (^{Mes}TerNH)$_2$E: (88.6(2)° at Ge, and 87.07(8)° at Sn).[16b] The E−P bond distances in **1** (2.2364(6) Å) and **2** (2.4562(7) Å) are shorter than those in (aryl)(phosphido)-tetrylenes (^{Tipp}Ter)[(Me$_3$Si)$_2$P]E: (Ge−P: 2.291(4) Å, Sn−P: 2.527(1) Å; ^{Tipp}Ter = 2,4-(2,4,6-iPr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$),[5c] but very close to the bond lengths between a planar phosphorus of one of the phosphido ligands and a tetrylene atom in bis(phosphido)tetrylenes [(Dipp)$_2$P]$_2$E: (Ge−P$_{(planar)}$: 2.2337(11) Å, Sn−P$_{(planar)}$: 2.4458(8) Å).[17] The Ge−P bond distance in **1** is also shorter than that in cyclic germylene **VIII** (2.247(2) Å),[9] but longer than those in phosphagermenes R$_2$Ge=PR' (2.138(3)−2.1748(14) Å).[2] Altogether, this strongly suggests multiple bond character of the E−P bonds

in **1** and **2** due to the lone pair delocalization from the monovalent phosphorus into the vacant p-orbitals of the divalent germanium or tin atoms. It should be noted that so far reported related tetrylenes supported by P-donor ligands with two-coordinate phosphorus (except **III** and **VIII**) are limited to the examples with three-coordinate group 14 elements and intrinsic single E−P bonds (E = Si−Pb).[18]

To understand the bonding nature in **1** and **2** better, quantum chemical calculations were carried out using simplified model compounds **1a** and **2a** (2,6-Me$_2$C$_6$H$_4$ groups at N atoms). The optimized geometries at B3LYP-D3/def2-TZVP(ecp) level of theory showed good agreement with the experimental structural data. The highest occupied molecular orbitals (HOMOs) in both germanium and tin model compounds correspond to the respective σ(Ge−P) and σ(Sn−P) bonds, unlike to cyclic germylene **VIII**, where the HOMO is the π(Ge−P) orbital. The HOMO−1 of the germanium derivative **1a** displays a π(E−P) symmetry and mainly located at the more electronegative phosphorus, while in the heavier analogue **2a** it is mostly a phosphorus' p orbital (Figure 2A). Relatively low singlet−triplet gaps of 34.9 and
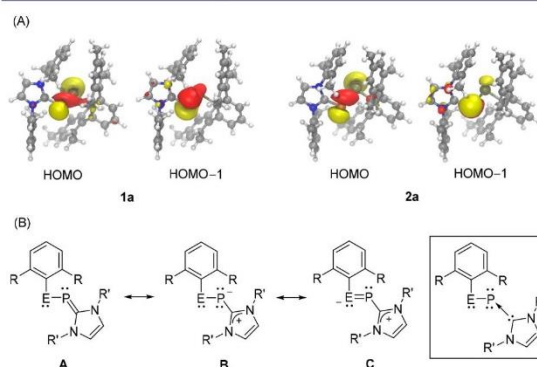
Figure 2. (A) HOMO and HOMO−1 in **1a** and **2a**; (B) resonance Lewis structures of **1** and **2**.

34.2 kcal/mol were found for **1a** and **2a**, respectively at B3LYP-D3/def2-TZVPP(ecp) level of theory. The HOMO−LUMO separation of the germanium derivative is slightly higher than that of its tin congener (3.49 vs 3.34 eV). Wiberg bond indices (WBIs) of the E−P (**1a**: 1.300 **2a**: 1.063) and C$_{NHC}$−P bonds (**1a**: 1.122; **2a**: 1.194) indicate a presence of partial double bond character.

Natural bond orbital (NBO) analysis of **1a** revealed the absence of a formal (natural) π(Ge−P) orbital, while second-order perturbation theory (SOPT) unveiled strong electron donation from s-type lone pair at P (1.915e), as well as from the π and π* (C$_{NHC}$−P) MOs (occupancies 1.672e and 0.398e, respectively) to a scarcely filled p-type orbital at Ge (0.398e), amounting altogether to 82.0 kcal/mol. Natural population analysis (NPA) indicates substantial net electron transfer from the NHC moiety to the phosphorus atoms (0.27e and 0.21e in **1a** and **2a**, respectively) suggesting significant dative bond character of the C$_{NHC}$−P bonds. Thus, the calculations suggest essential contribution of the resonance structure **B** into the ground state of these molecules, whereas the contribution of the structure **C** is not negligible and higher for the lighter germanium analogue (Figure 2B).

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Evidence for dative nature of the C_{NHC}–P bonds in **1** and **2** was also obtained from the analysis of the bond dissociation energies and using Bader's quantum theory of atoms in molecules (QTAIM).[19]

Further experimental study revealed inertness of complexes **1** and **2** toward small molecules (H_2, CO, CO_2) and equimolecular amounts of 1,3-dimethyl-1,3-butadiene, benzaldehyde, and pinacolborane. Surprisingly, reactions with diphenylketene $Ph_2C=C=O$ afforded selectively the formal [2+2] cycloaddition products, heterocycles **3** and **4** (Scheme 2).

Scheme 2. Synthesis of Heterocycles 3 and 4
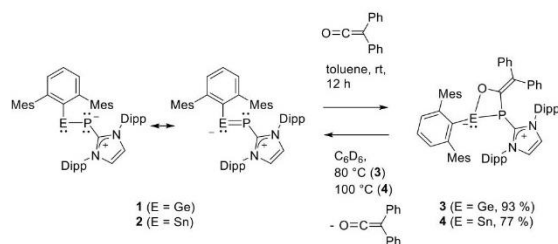
Spectroscopic evidence for reversible retro-cycloaddition was obtained after consecutive heating and cooling of the C_6D_6 solutions of **3** and **4**. Similar reactivity is known for compounds with genuine Ge–P and Sn–P double bonds.[20] The mechanism for the formation of **3** and **4** was confirmed as concerted [2+2] cycloaddition by quantum chemical calculations using model compounds.[19]

Heterocycles **3** and **4** were isolated as pale yellow solids in good yields. They displayed very similar chemical shifts in the ^{31}P NMR spectra (**3**: 18.2 ppm; **4**: 20.2 ppm). The signal of **4** in the ^{119}Sn NMR spectrum was observed as a doublet at 344.2 ppm ($^1J(^{119}Sn,P) = 253$ Hz).

Molecular structures of **3** and **4** were confirmed using single crystal X-ray diffraction analysis (Figure 3). The four-
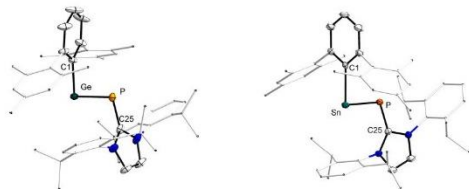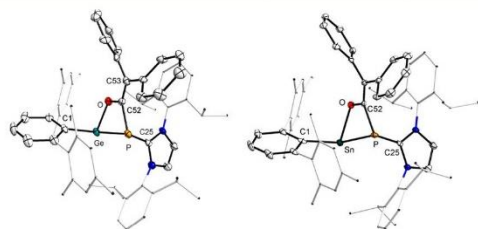
Figure 3. Molecular Structures of **3** (left) and **4** (right). Thermal ellipsoids are shown with 50% probability; hydrogen atoms are omitted for clarity).

membered rings in **3** and **4** are nonplanar, the bulky aryl and NHC ligands are *trans*-oriented. Both compounds contain elongated single E–P (Ge–P: 2.5319(14) Å; Sn–P: 2.7299(10) Å) and E–O (Ge–O: 1.946(4) Å; Sn–O: 2.126(2) Å) bonds exceeding the sum of covalent radii of the corresponding atoms.[21,22]

Catalytic application of low-valent group 14 element compounds is an emerging field of main group chemistry.[1] Only few examples of catalytic hydroboration of carbonyl compounds using tetrylenes (neutral species) are reported to

date.[23,24] Our preliminary study on catalytic application of complexes **1** and **2** revealed high activity of the latter in hydroboration of aromatic aldehydes and ketones with pinacolborane (Table 1).

Table 1. Hydroboration of Aldehydes or Ketones RC(O)R′ with Pinacolborane, Catalyzed by 2 or 1[a]

R	R′	Cat.	Loading, mol %	Time, h	Conv., %
Ph	H	**2**	0.05	<0.3	50[b]
Ph	H	**2**	0.1	<0.25	>99
4-MeOPh	H	**2**	0.1	5	75[c]
Ph	Me	**2**	0.05	0.3	>99
Ph	Ph	**2**	0.5	2.5	>99
Ph	H	**1**	4	3	67[c]
Ph	H	(IDipp)PH	5	3	47[c]

[a]Reaction conditions: RC(O)R′ (0.5 mmol), HBpin (0.55 mmol), C_6D_6 (0.4 mL), ambient temperature. Catalyst loading relative to a carbonyl substrate. [b]No further conversion was observed. [c]Full reaction time was not estimated.

Benzaldehyde reduction in the presence of 0.1 mol % of **2** was completed in 15 min and in a few minutes using 2 mol % of the catalyst. Reduction of acetophenone in the presence of only 0.05 mol % of **2** led to full conversion within 30 min. All reductions in the presence of **2** are selective and clean. Catalytic activity of the germanium analogue **1** appeared to be significantly lower than that of **2** (Table 1). Interestingly, comparable acceleration of the benzaldehyde reduction was also observed in the presence of 5 mol % of (IDipp)PH.

Finally, we attempted to remove the NHC from **1** and **2** using *tris*(pentafluorophenyl)borane (BCF) as a strong Lewis acid, but no formation of $(IDipp)B(C_6F_5)_3$ adduct was observed for both reactions after heating at 65 °C. Instead, reaction of **1** gave an unstable product ($\delta(^{31}P) = -111.5$ ppm, $\delta(^{11}B) = -15.2$ ppm, C_6D_6), while providing a stable adduct **5** in the case of **2** (Scheme 3).[25,26]

Scheme 3. Synthesis of Phosphastannene 5
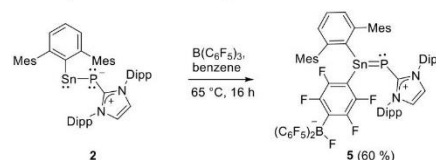
Structural analysis of the single crystals revealed phosphastannene **5** (Figure 4) showing a planar geometry at the tin atom (sum of the bond angles is 359.9°). Compared to **2**, the
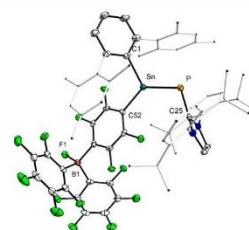
Figure 4. Molecular structure of **5** (thermal ellipsoids are shown with 50% probability; hydrogen atoms are omitted for clarity).

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C_{NHC}–P bond in **5** (1.816 (3) Å) is elongated, while the Sn–P bond distance (2.3450(10) Å) is substantially shorter (4.5%) indicating a double bonding character. To the best of our knowledge, this is the shortest Sn−P bond distance reported to date.

Due to the unique "push–pull" zwitterionic structure, phosphorus and tin nuclei in **5** are significantly shielded compared to those in the starting material and known aryl phosphastannenes. Unusual high-field resonances at $\delta(^{31}P) = -93.05$ ppm ($^1J_{Sat}(^{119}Sn,P) = 3046$ Hz, $^1J_{Sat}(^{117}Sn,P) = 2919$ Hz) and $\delta(^{119}Sn) = 152.2$ ppm ($^1J(^{119}Sn,P) = 3069$ Hz) were observed in the ^{31}P and ^{119}Sn NMR spectra (tetrahydrofuran-d_8). The $^1J(^{119/117}Sn,P)$ coupling constants are significantly greater than those reported for two known phosphastannenes (2295/2191 and 2208/2110 Hz).[2]

The density functional theory calculations at the B3LYP-D3/def2-TZVPP(ecp) level support a presence of a weak Sn=P double bond in **5a** with WBI = 1.170. The HOMO is located at fluorinated aromatic rings, while the HOMO−1 and LUMO are essentially p_z atomic orbitals at phosphorus and tin atoms, respectively.

In conclusion, we described the synthesis and electronic structure of germylene, and stannylene−phosphinidenes stabilized by NHC at the phosphorus atom. These compounds contain reactive P−E bonds (E = Ge, Sn), and open an access to zwitterionic heavier imine analogues, as was demonstrated for the tin derivative. Notably, the latter showed high catalytic activity in the hydroboration of aromatic aldehydes and ketones, drastically different to that of the germanium congener. Further coordination chemistry and catalytic applications are currently under investigation.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b08741.

> Full synthetic and characterizing data for new compounds, representative NMR spectra, details of computational studies (PDF)

> Crystallographic data (CCDC Compound **1**: 1946724, Compound **2**: 1946725, Compound **3**: 1946726, Compound **4**: 1946727, Compound **5**: 1946728) (CIF)

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Notes
The authors declare no competing financial interest.

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6. Application of ferrocene–bridged *N*–heterocyclic carbene stabilised bis–phosphinidenes in Sn(II) complexation

Title: "Application of ferrocene–bridged *N*–heterocyclic carbene stabilised bis–phosphinidenes in Sn(II) complexation"[141]

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[a]R. Baierl planned and executed all experiments and wrote the manuscript. A. Kostenko performed the theoretical calculation and wrote the theoretical part of the manuscript. F. Hanusch conducted SC–XRD measurements and processed the respective data. All work was done under the supervision of S. Inoue.

Content: Newly synthesized bidentate NHCP ligands proved to successfully stabilize various Sn(II) halides as well as Sn(II) bistriflate. The stannyliumylidenes showed reactivity in transmetallation to a CuCl complex as well as Sn(II) transfer to a bisNHI ligand.

Despite the discovery of *N*–heterocyclic carbene–phosphinidenes in 1997 by Arduengo, this compound class has only lately found broad application in transition metal as well as main group chemistry. Until recently only monodentate NHCP ligands have been known. This paper presents the second example of a bisNHCP ligand using a ferrocene backbone, synthesized from treatment of 1,1'–bis(dichloro–phosphine)ferrocene and NHC (IMes or ^{Me}IMes) followed by reductive dehalogenation with sodium naphthanenide. SC–XRD analysis of the two ligands revealed a shortened P–C bond accounting for a double bond character, which was verified by theoretical calculations. NBO analysis shows a σ– and a π–bond between the phosphorus atom and the NHC with a Wiberg bond index (WBI) of 1.29. Treatment of the bisNHCP ligands

with different SnX_2 (with X = Cl, Br, I, OTf) compounds shows successful complexation and stabilization of the Sn(II) moieties. All complexes are analyzed *via* multinuclear NMR spectroscopy as well as mass spectrometry. The SnI_2 complex bearing a methylated backbone bisNHCP ligand was successfully crystallized and analyzed *via* SC–XRD. The complex shows elongated P–C bonds compared to the free ligand. Reactivity investigations demonstrated a transmetallation from the SnI_2 complex to the CuCl complex. Additionally, Sn(II) transfer from the bisNHCP ligand to a bisNHI ligand is possible.

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Application of ferrocene-bridged N-heterocyclic carbene stabilised bis-phosphinidenes in Sn(II) complexation†

Ramona Baierl, Arseni Kostenko, [ID] Franziska Hanusch [ID] and Shigeyoshi Inoue [ID] *

Two new bidentate ferrocene-bridged bis(*N*-heterocyclic carbene–phospinidenes) (bisNHCPs) were successfully isolated by treating 1,1'-bis-(dichlorophosphine)ferrocene with *N*-heterocyclic carbenes, followed by dechlorination using sodium naphthalenide. The bisNHCPs were used in complexation of various Sn(II) halides and Sn(II) bistriflate (SnX$_2$ with X = Cl, Br, I, OTf). Transmetalation to a CuCl complex and Sn(II) transfer to a bisimine was performed to investigate the stannyliumylidenes' reactivity.

Introduction

Phosphinidenes (R-P̈:) are low valent phosphorus compounds, which can be considered as the phosphorus analogues of carbenes (R$_2$C:).[1] Free phosphinidenes are highly reactive species, even in comparison to carbenes, and isolation of the first stable phosphinidene was only accomplished in 2016 by Bertrand and coworkers.[2] Before that their isolation needed stabilisation *via* additional donor molecules *e.g. N*-heterocyclic carbenes (NHCs) forming *N*-heterocyclic carbene-phosphinidene adducts (NHCPs).[3–6] Since their discovery by Arduengo *et al.* in 1997 NHCPs have found broad application in transition metal and main group chemistry.[5,7–13] NHCPs can be considered as inversely polarised phosphaalkenes featuring two electron pairs at the phosphorus centre, demonstrated by the canonical forms **A** and **A′** (Chart 1). Treatment of IMes·PPh (**A** for R = Mes, R′ = Ph) with 2 eq. of BH$_3$·THF resulted in the P-bonded bis(borane) adduct, indicating the dominance of canonical forms **A** and **A′**.[6,14] Recently, the first bis(NHCP) compound, featuring a xanthene backbone (XantPP), was isolated and its coordination ability as a bidentate ligand was demonstrated on element dihalides, forming stannyliumylidene **H** (Chart 3), beyond others.[15]

In this work we set out to study the more flexible ferrocene backbone, which can lead to reduced distance between the NHCP moieties and enhance the chelating properties of the bis(NHCP). In general, ferrocene allows for synthetically straight forward introduction of various substituents. The flexibility of the resulting chelating ligands and the ability of the ferrocene bridge to undergo one-electron oxidation, renders this backbone an attractive option for coordination and redox chemistry.[16–18] While group 15 substituted ferrocenes are well established ligands in catalysis,[19–24] the first bis(silylenyl) and bis(germylenyl)-substituted ferrocenes **B** were introduced by Driess in 2012 (Chart 2).[25] The corresponding bis(silylene)-CpCo complex was demonstrated to catalyse [2 + 2 + 2] cycloaddition reactions. Using bis(silylenyl)-substituted ferrocenes **B**, the same group additionally isolated a bis(NHSi)-stabilised η^6(arene) Fe^0 complex and showed its application in catalytic hydrogenation of ketones.[26] Going towards the heavier tetrels, the groups of Tokitoh and Sasamori isolated, among other ferrocenyl-substituted group 14 compounds,[27–29] the redox-active bis(ferrocenyl)germylene **C** stabilised by a bulky ferrocene derivative (Chart 2).[30] Further examples of ferrocene-based tetrylenes are the redox active complexes **D** isolated by Siemeling *et al.* (Chart 2)[31–34] and a stannylene reported by Wesemann *et al.*[35] In all these cases, ferrocene-based complexes have shown to successfully stabilise low valent compounds kinetically as well as electronically. Diaconescu *et al.* additionally proved stabilization of different ferrocene diamide metal complexes *via* iron–metal donor–acceptor interaction.[36,37] However, tetryliumylidene complexes featuring a ferrocene-based ligand remained unknown up to our knowledge.

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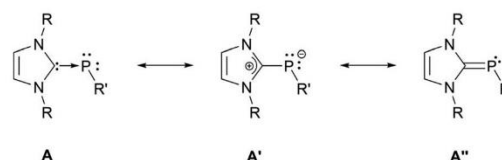
Chart 1 Canonical forms of N-heterocyclic carbene–phosphinidenes.
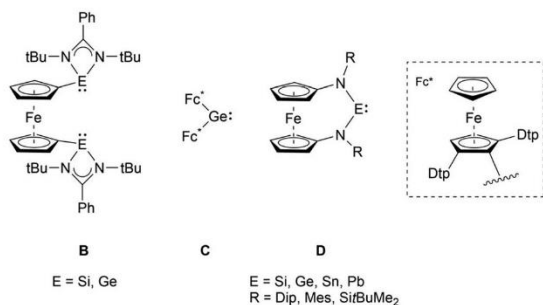
Chart 2 Selected examples of ferrocene-based tetrylenes **B–D** (Dip = 2,6-diisopropylphenyl, Mes = 2,4,6-trimethylphenyl, Dtp = 3,5-di-*tert*-butylphenyl).

Tetryliumylidenes feature a unique structure with a positive charge and a free electron pair and can be considered to be related to tetrylenes as well as tetrylium ions.[38,39] The chemistry of stannyliumylidene ions commenced with the initial isolation of $[(\eta^5\text{-}C_5Me_5)Sn]^+[BF_4]^-$ in 1980.[40] Later different stannylium-ylidenes and chloro-stannyliumylidenes like **E–H** were synthesised (Chart 3).[41–48] Chloro-substituted stannylium-ylidenes [:SnCl]$^+$ have attracted attention, since they are easily functionalised by either halide abstraction and substitution to yield modified stannyliumylidene derivatives [R'Sn:]$^+$ or reduction to Sn(0).[49–51]

Herein we report the synthesis of a new bidentate bisNHCP ligand bridged by a flexible and redox-active ferrocene backbone. The ligand was applied in stabilisation of stannyliumylidene ions and their potential in transmetalation and Sn(II) transfer reaction was explored.

Results and discussion

Synthesis of BisNHCPs

The ferrocene-bridged bisNHCP was synthesised by an approach analogous to the one described by Bertrand and co-workers.[52] 1,1'-Bis(dichloro-phosphine)ferrocene (**1**) was
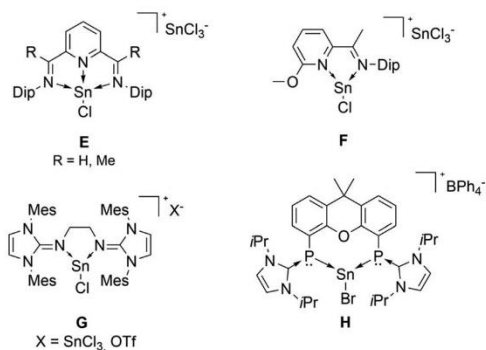
treated with 2 eq. NHC forming intermediate **2**, followed by direct reductive dechlorination using 4 eq. sodium naph-thale-nide (NaNaph). Using either 1,3-bis(2,4,6-trimethyl-phenyl)imi-dazol-2-ylidene (IMes) or 1,3-bis(2,4,6-trimethyl-phenyl)-[4,5-dimethylimidazol]-2-ylidene (^MeIMes), two diff-erent sterically demanding bisNHCPs (**3a** and **3b**) were isolated in 25% and 47% yield, respectively (Scheme 1). Compounds **3a** and **3b** were characterised by multinuclear NMR, single-crystal X-ray diffraction (SC-XRD) analysis, and LIFDI-MS (liquid injection field desorption ionization mass spectrometry) (see ESI Fig. S1–8 and S59, 60†). **3a** shows a ^{31}P NMR shift of −56.98 ppm while **3b** has a slightly upfield shifted signal at −59.76 ppm accounting for the electronical impact of the methylated backbone. These ^{31}P NMR signals are high-field shifted in comparison to typical, non-polarised phosphaalk-enes (δ = 230–420 ppm)[53] but show similar shifts compared to NHC stabilised phosphinidenes ((NHC)PPh: δ = −10.2 to −61.2 ppm; XantPP: δ = −77.2 ppm).[15,54]

Compounds **3a** and **3b** were crystallised from a concen-trated Et$_2$O solution at −35 °C forming orange-yellow crystals. SC-XRD analysis confirmed the molecular structure of both bisNHCPs (Fig. 1). The P–C$_{Carbene}$ bond lengths of **3a** are slightly shorter compared to **3b** indicating a more pronounced double bond character. In comparison to XantPP (P–C$_{Carbene}$ 1.790(5)–1.830(5) Å), **3a** and **3b** exhibit shorter P–C$_{Carbene}$ bond lengths.[15]

In order to get an insight into the electronic and structural properties of the bisNHCPs **3a** and **3b**, calculations at the B3PW91-D3 level of theory were carried out. Details about basis sets and the employed computational methods are given in the ESI.† In **3a**, the nearly degenerate HOMO and HOMO−1 correspond to the π-type lone pairs of the phosphinidene moi-eties, and the almost degenerate HOMO−5 and HOMO−6 correspond to the σ-type lone pairs at the phosphorus atoms that are conjugated with the π system of the cyclopentadienyl

Chart 3 Selected examples of halogen-substituted stannyliumylidenes.
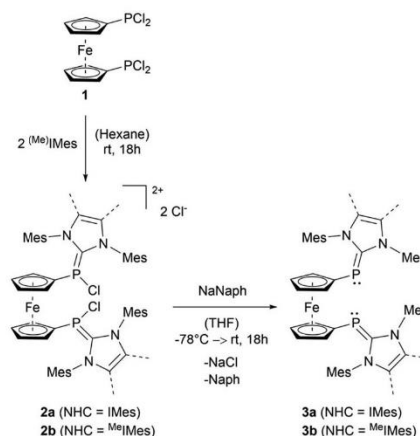
Scheme 1 Synthesis of **3a** and **3b** in a two-step procedure from 1,1'-bis-(dichloro-phosphine)ferrocene (**1**).
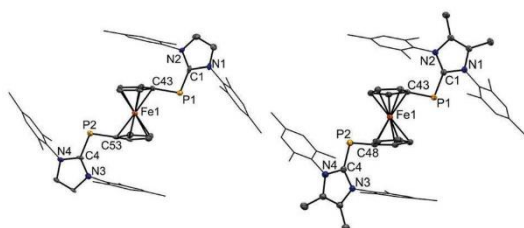
Fig. 1 Molecular structure of bisNHCP **3a** (left) and **3b** (right). Translational ellipsoids are plotted at the 50% probability level. For reasons of clarity, hydrogens are omitted and mesityl groups are depicted in wireframe models. Selected bond lengths (Å) and angles (°): **3a** P1−C1 1.731(10), P2−C4 1.808(10), P1−C43 1.863(10), P2−C53 1.803 (10), C1−N1/2 1.410(12)/1.390(13), C4−N3/4 1.366(12)/1.357(12), C1−P1−C43 102.6(4), C4−P2−C53 103.6(4); **3b** P1−C1 1.7696(18), P2−C4 1.7704 (19), P1−C43 1.8319(16), P2−C48 1.8220(17), C1−N1/2 1.3766(19)/1.372 (2), C4−N3/4 1.375(2)/1.377(2), C1−P1−C43 103.33(8), C4−P2−C48 102.92(8).

rings (Fig. 2). According to the NBO analysis, this is due to weak donor–acceptor interactions between the σ-type lone pairs of phosphorus atoms ($LP(P^1)$ and $LP(P^2)$) and the $\pi^*(C–C)$ orbitals of the adjacent carbons of the cyclopentadienyl rings (Fig. 3). NBO analysis shows that the σ-type lone pairs retain occupancy of 1.94 el., while the phosphinidene–carbene interactions are interpreted as σ and π bonds between the phosphorus atom and the NHC that total to Wiberg bond index (WBI) of 1.29 accounting for a predominance of canonical structure **A″**. For consistency, in this article in all complexes the C–P bond is depicted according to **A″**. The interpretation of the π-type lone pairs as π(P–C) bonds with occupancy of 1.95 el. is attributed to the strong interactions between the phosphinidene π-type lone pairs and the empty p orbitals of the carbene carbons.

Both SC-XRD and DFT optimised structures of **3a**, show alignment of the mesityl substituents of the NHCs and the

Fig. 3 Selected NBO of **3a** showing the σ-type lone pairs of the phosphinidene centres and the σ(C−P) and π(C−P) orbitals.

cyclopentadienyl rings of the ferrocene, indicating the presence of sandwich π–π stacking interactions. In fact, quantum theory of atom in molecules (QTAIM) molecular graph (Fig. 4) displays interactions between the mesityls and the cyclopentadienyl rings, showing four (3, −1) critical points with electron density ρ of 0.005, 0.011, 0.006, 0.011 e Bohr^{-3} and Laplacian of electron density $\nabla^2\rho$ 0.015, 0.033, 0.018, 0.033 e Bohr^{-5} respectively.

Application of the novel bisNHCPs in the synthesis of SnX_2 complexes (with X = Cl, Br, I, OTf) resulted in the direct formation of the air-sensitive stannyliumylidenes **4a–d** and **5a–d** (Scheme 2). In contrast to SnX_2 with X = Br, I, and OTf, treatment with $SnCl_2$·dioxane afforded full conversion of the bisNHCP adding 2 eq. $SnCl_2$·dioxane, due to the preferred autoionization forming the trichlorostannate anion $SnCl_3^-$. All

Fig. 2 Selected molecular orbitals of **3a**.
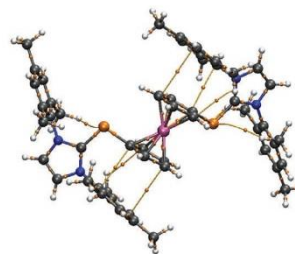
Fig. 4 QTAIM molecular graph of **3a**.

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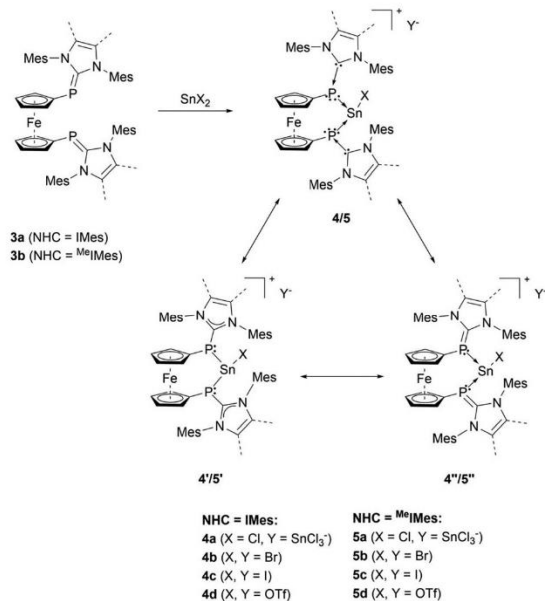
Scheme 2 Synthesis of various Sn(II) complexes (4a–e, 5a–e).

complexes were characterised by multinuclear NMR and LIFDI-MS (see ESI Fig. S9 and 50†).

The complexes **4a–d** and **5a–d** show an expected downfield shift in the ^{31}P NMR (Table 1) in comparison to the free bisNHCPs **3a** and **3b** indicating an electron donation from the phosphorus to the electron deficient Sn(II) centre. The ^{119}Sn NMR shows a triplet resulting from the coupling of the tin centre to the two phosphorus atoms with a coupling constant of $^1J_{Sn,P}$ = 1249 to 1301 Hz, being in the range of Sn–P single bonds.[55] Compared to previous reported stannylium-ylidenes (^{119}Sn NMR **E**: δ = −445.2 ppm (R = H) and −435.1 ppm (R = Me), **F**: δ = −330.4 ppm, **G**: δ = −240.42 ppm) a pronounced downfield shift is observed in the ^{119}Sn NMR. Since no ^{119}Sn NMR shift is given for the only reported bisphosphinidene stabilised stannyliumylidene **H**, a comparison as well as related discussion is not possible here. However, examination of $^1J_{Sn,P}$ coupling constants in the ^{31}P NMR of **H** and herein reported stannyliumylidenes revealed a similar range with higher values in our reported stannyliumylidenes (**H**: $^1J^{119}_{Sn,P}$

= 860 Hz, $^1J^{117}_{Sn,P}$ = 1038 Hz; **4c,d/5c,d**: $^1J^{119}_{Sn,P}$ = 1189–1211 Hz, $^1J^{117}_{Sn,P}$ = 1252–1268 Hz).

Crystallisation from a concentrated THF solution at −35 °C gave crystals of **5c**, suitable for SC-XRD analysis (Fig. 5). **5c** crystallises in the monoclinic space group $P21/c$. The structure shows a trigonal pyramidal coordinated Sn(II) cation with Sn–P bond lengths of 2.645(5)/2.659(4) Å. In comparison to the bisNHCP **3b**, the P–C$_{Carbene}$ bond lengths are elongated (**3b**: P1–C1 1.7696(18), P2–C4 1.7704(19), **5c**: P1–C1 1.824(4), P2–C4 1.828(4)), accounting for predominant canonical structures **4/5** and **4′/5′**.

The calculated free energy for complexation of SnI$_2$ by **3b** to form **5c**, using the CPCM solvation model, is −48.5 kcal mol^{-1}. Calculations show that the relative affinity of the ferrocene-bridged bisNHCP **3b** toward SnI$^+$ is by 7.5 kcal mol^{-1} higher than that of xanthene-bridged bisNHCP **H**. The optimised structure and the molecular orbitals of **5c** are presented in Fig. 6. The HOMO corresponds mainly to the lone pair of the Sn centre. The bonding HOMO−1 corresponds to the bonding interaction between the phosphinidene moieties and the tin centre (WBI for Sn–P1 and Sn–P2 is 0.77 and 0.78, respectively). According to the NBO analysis the phosphinidene centres retain their σ-lone pairs and HOMO−4 corresponds to the σ-lone pairs interacting with the empty 5p orbitals of Sn.
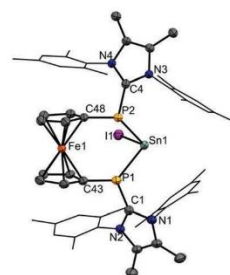
Fig. 5 Molecular structure of SnI$_2$ complex **5c**. Translational ellipsoids are set to 50% probability level. For reasons of clarity, hydrogens and the counter ion are omitted and mesityl groups are depicted in wireframe models. Selected bond lengths [Å] and angles [°]: P1–Sn1 2.645(5), P2–Sn1 2.659(4), P1–C1 1.824(4), P2–C4 1.828(4), P1–C43 1.809(4), P2–C48 1.817(4), C1–N1/2 1.374(6)/1.354(6), C4–N3/4 1.358(6)/1.357(6), I1–Sn1–P1 104.68(18), I1–Sn1–P2 102.25(14), P1–Sn1–P2 78.73(13).

Table 1 ^{31}P and ^{119}Sn NMR shifts in THF-d$_8$ of different stannyliumylidenes **4a–d** and **5a–d**

	IMes			^{Me}IMes		
		^{31}P δ [ppm]	^{119}Sn δ [ppm]		^{31}P δ [ppm]	^{119}Sn δ [ppm]
bisNHCP	**3a**	−56.98	—	**3b**	−59.76	—
SnCl$_2$·dioxane	**4a**	−46.85	236.45 (SnCl), −21.11 (SnCl$_3$)	**5a**	−49.27	243.75 (SnCl), −27.39 (SnCl$_3$)
SnBr$_2$	**4b**	−47.91	168.99	**5b**	−49.57	170.47
SnI$_2$	**4c**	−49.89	174.43 (t, $J^{Sn,P}$ = 1301 Hz)	**5c**	−52.12	262.20 (t, $J^{Sn,P}$ = 1254 Hz)
Sn(OTf)$_2$	**4d**	−29.76	432.78 (t, $J^{Sn,P}$ = 1249 Hz)	**5d**	−30.56	465.20 (t, $J^{Sn,P}$ = 1270 Hz)

Fig. 6 Molecular orbitals of **5c**.

HOMO, -6.92 eV

HOMO-1, -7.42 eV

HOMO-4, -8.01 eV

NBO analysis of the discussed interactions is presented in the ESI (Fig. S61†).

Transmetalation reaction

Treatment of the Sn(II) complex **5a** with CuCl resulted in the formation of transmetalation product **6** (Scheme 3). For comparison, complex **6** was directly prepared in a reaction of bisphosphinidene **3b** and CuCl in THF and characterised by ^1H, ^{13}C and ^{31}P NMR as well as LIDFI-MS (see ESI Fig. S55–58†). Using the CPCM solvation model, the free energy for this reaction is calculated to be −9.0 kcal mol^{-1}.

Sn(II) transfer reaction

After successful transmetalation using stannyliumylidene **5c**, the ability to transfer the central Sn(II) atom was examined for **5a**. Recently, our group established the nitrogen analogue of bisNHCP for the synthesis of tetryliumylidenes,[48,56] thus we hypothesised this bisNHI[57–59] to be an ideal candidate for Sn(II) acceptance. The addition of bisNHI to a solution of **5a** in THF-d$_8$ resulted in a quantitative formation of free bisNHCP **3b** (Scheme 4). The formed precipitate showed the reported ^1H and ^{119}Sn NMR shifts in CD$_3$CN, confirming the Sn(II) transfer from the bisNHCP to the bisNHI system. Interestingly, calculations in the gas phase show that the affinity of the bisNHCP ligand toward SnCl$^+$ is by 7.6 kcal mol^{-1} higher than that of
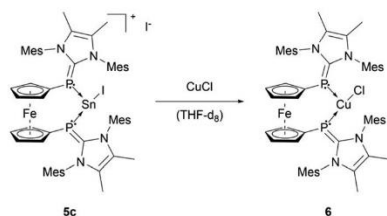
Scheme 4 Sn(II) transfer reaction between bisNHCP and bisNHI.

the bisNHI. However, in THF and acetonitrile the affinity of bisNHI toward SnCl$^+$ is higher by 0.6 and 2.2 kcal mol^{-1}, respectively. Additionally, calculations show that the full reaction presented in Scheme 4 is exergonic by 1.1 and 2.5 kcal mol^{-1} in THF and acetonitrile, respectively. Therefore it is reasonable to suggest that the described reactivity is not due to better stabilisation of the electron deficient Sn(II) centre by the bisNHI ligand, but rather caused by solvation effects, the relative solubility of the bisNHCP and bisNHI ligands, and the stannyliumylidenes **5a** and **7** in THF and acetonitrile.

While stannyliumylidene **7** is reported to be stable in CD$_3$CN solution under air for over 14 days,[48] stannyliumylidenes **4** and **5** decompose rapidly under air. Since phosphorus has a high affinity towards oxygen, the bisNHCP is supposedly oxidised rapidly.

Conclusions

In conclusion we were able to synthesise the second examples of bidentate *N*-heterocyclic carbene–phosphinidenes **3a** and **3b**. Both compounds show sandwich π–π stacking interactions between the mesityl substituents of the NHCs and the cyclopentadienyl rings of the ferrocene in the SC-XRD structure, which could additionally be confirmed by theoretical calculations. These bisNHCPs were utilised to synthesise various stannyliumylidenes **4a–d** and **5a–d**. Treatment of stannyliumylidene **5c** with CuCl resulted in formation of the transmetalation product **6**. Furthermore, stannyliumylidene **5a** was used to transfer the Sn(II) synthon from the bisphosphinidene to a bisimine, forming **7** and **3b**.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Scheme 3 Transmetalation from bisNHCP Sn(II) complex **5c** to bisNHCP CuCl complex **6**.

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7. Synthesis and Reactivity of Bidentate *N*–Heterocyclic Carbene–Phosphinidene Supported Si(IV) Dications

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Content: This paper expands the complexation abilities of the recently published bidentate *N*–heterocyclic carbene–phosphinidene ligand towards the stabilization of Si(IV) dications. Two complexes are synthesized from $R_2Si(OTf)_2$ (R = H, Ph) and their electronic properties as well as reactivity is investigated.

In previous publications the properties of NHCPs in transition metal, as well as main group chemistry has been explored. However, until now NHCP–stabilized silicon compounds remained unknown. Herein we want to report the first example of a NHCP–stabilized Si(IV) dication. Treatment of the bisNHCP ligand with bistriflate silanes $R_2Si(OTf)_2$ (R = H, Ph) readily forms the dications. The dicationic structure was confirmed *via* SC–XRD analysis. Computational investigations revealed that the +2 charge is mainly located in the imidazolium ring of the NHCP. This observation is in accordance with the high thermal stability of the

compounds (stable up to 80 °C for R = H and 100 °C for R = Ph in CD_3CN). No reactivity is observed towards ethylene, acetylene, phenyl– and diphenylacetylene. In contrast, treatment of the $[SiH_2]^{2+}$ complex with diphenylketene leads to an insertion into the Si–P bond. The optimized structure exhibits a C_2 symmetrical geometry.

Synthesis and Reactivity of Bidentate *N*-Heterocyclic Carbene-Phosphinidene Supported Si(IV) Dicationic Complexes

Ramona Baierl,[a] Arseni Kostenko,[a] Franziska Hanusch,[a] Alexander D. Beck,[b] and Shigeyoshi Inoue*[a]

Herein, we report the synthesis and isolation of Si(IV) dications stabilized by a bidentate *N*-heterocyclic carbene-phosphinidene (NHCP). Treatment of the bis(NHCP) with Si(IV) bis(triflate) $R_2Si(OTf)_2$ (with R = H, Ph) resulted in the instant formation of Si(IV) dicationic complexes [**2a**] and [**2b**] featuring a tetracoor-dinated silicon centre. The dications show expected high Lewis acidity. The bis(NHCP)-stabilized parent silyl dication **2a** (SiH_2^{2+}) presents the first isolable example of a parent SiH_2 dication. In addition, dication [**2a**] is able to react with diphenylketene by insertion into the Si–P bond.

Introduction

Development of ligand systems for stabilization of reactive intermediates is of paramount importance in organometallic chemistry. The prototypical *N*-heterocyclic carbenes (NHCs), discovered by Arduengo in 1991, offer strong σ-donor as well as π-acceptor properties. Those characteristics qualify them as efficient ligands in stabilization of electron-deficient, ambiphilic and paramagnetic species, and thus they are widely utilized for isolation of low-valent/low oxidation state main group species.[1–7] From the perspective of silicon chemistry, pivotal work in the stabilization of halosilanes and highly reactive halosilylenes by NHCs opened the way towards the synthesis of numerous novel organosilicon compounds with unusual electronic properties and bonding situations.[8–12]

Related classes of compounds, *e.g.* the *N*-heterocyclic imines (NHIs) and their heavier analogues *N*-heterocyclic carbene-phosphinidenes (NHCPs), are also gradually finding their way into main group chemistry.[13–14] NHCPs have already been discovered in 1997 by Arduengo *et al.*,[15–17] nevertheless, only in the last few years they attracted attention, as their potential as ligands in main group and transition metal

chemistry has been exemplified.[14–16,18–23] NHCPs are inversely polarized phosphaalkenes with the mesomeric structures **I**, **I'**, and **I''**, out of which **I** and **I'** exhibit two electron pairs at the phosphorus atom. This was demonstrated by the reaction with $BH_3 \cdot THF$ forming the bis(borane) adduct **II** or treatment with metal halides (*e.g.* CuCl, AgCl, AuCl, CuBr) forming the bis(group 11 metal) complexes **III** (Scheme 1).[15,24]
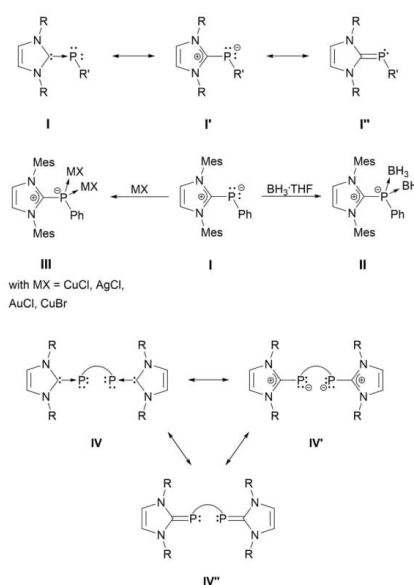
Scheme 1. Canonical forms of monodentate and bidentate *N*-heterocyclic carbene-phosphinidenes **I** and **IV** and reactivity towards borane and group 11 metal halides forming bisadducts **II** and **III** (with Mes = 2,4,6-trimethylphenyl).

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Recently, the first two examples of bis(N-heterocyclic carbene-phosphinidene) (bis(NHCP)) ligands have been reported.[25–26] Their coordination capabilities have been demonstrated by formation of stable Ge(II), Sn(II), and transition metal halide (CuCl, ZnI₂, FeCl₂) complexes. According to the resonance structures of bis(NHCP)s (Scheme 1, **IV**–**IV″**), they additionally appear to be an ideal ligand for stabilization of di- or polycationic main group complexes. For instance, free silicon(IV) dications (R_2Si^{2+}) are only known in the gas phase, however, not in condensed phase.[27–28] To be able to isolate an uncommon Si(IV) dication, stabilization *via* neutral Lewis bases is necessary. Up to date, NHC ligands with their σ-donor properties emerged to be suitable.

The groups of Filippou and Driess succeeded in the isolation of the four-coordinated dicationic Si(IV) complexes **V** and **VI** both using NHCs for stabilization (Figure 1).[29–30] NHC stabilization was also used in the isolation of dication **VII**, recently published by the Inoue group.[31] Additionally, in 2020 the group of Driess reported several examples of five-coordinated Si(II) dications **VIII** stabilized by a terpyridine ligand system, adding to the sparse examples of isolated Si(IV) dications.[32] To the best of our knowledge, however, an isolable example of a dicationic complex containing the parent [SiH_2]²⁺ moiety has not been reported. Additionally, the use of NHCPs for stabilization of silicon compounds is unexplored. In this work we present the expansion of the NHCP chemistry towards the stabilization of tetra-valent silicon compounds and present the first examples of bis(NHCP)-stabilized Si(IV) dications [**2a**] and [**2b**] and their reactivity.

Results and Discussion

Treatment of the recently published ferrocene bridged bis(NHCP) **1** with bis(triflate)silanes ($R_2Si(OTf)_2$, R=H, Ph) in
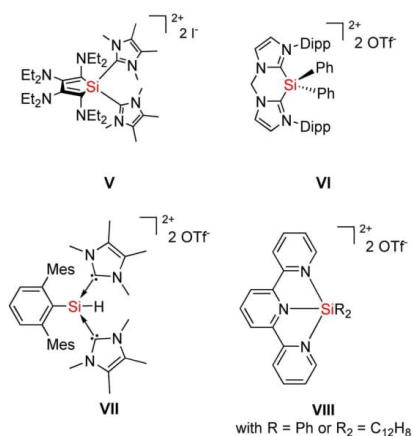
benzene at room temperature resulted in the instant formation and precipitation of complexes [**2a**][OTf]₂ and [**2b**][OTf]₂ in 70% and 88% yield respectively (Scheme 2).[26] Both complexes dissolve well in acetonitrile and 1,2-difluorobenzene. The products were characterized by multinuclear NMR spectroscopy, mass spectrometry, and elemental analysis. The ³¹P NMR signals in CD₃CN are shifted upfield in comparison to the free bis(NHCP) (−56.98 ppm[26]) with a shift of −96.68 ppm for the parent silyl dication [**2a**] and −66.01 ppm for the phenyl-substituted silyl dication [**2b**] (Table 1). In comparison to the reported bis(NHCP)-stabilized stannyliumylidenes (³¹P δ = −30.56 to −59.76 ppm),[26] the ³¹P NMR signals are upfield shifted.[26] The recorded ²⁹Si NMR spectra of [**2a**][OTf]₂ and [**2b**][OTf]₂ show the respective triplet signals at −44.09 ppm (¹$J_{P,Si}$=24.8 Hz) and −10.74 ppm (¹$J_{P,Si}$=65.7 Hz), whereby the coupling constants are in the range of ¹$J_{P,Si}$ Si–P couplings (256–16 Hz).[33] In comparison, the fourfold coordinated Si(IV) dications **V**, **VI** and **VII** (²⁹Si δ = −29.2, −36.7, and −63.4 ppm) resonate in a similar region.[29–31]

Despite numerous attempts, [**2a**] could not be crystallized successfully. However, the bis(triflate) complex of dication [**2b**] could be crystallized from a concentrated fluorobenzene solution at −35°C forming yellow needles suitable for single crystal X-ray diffraction (SC-XRD). The molecular structure of [**2b**][OTf]₂, which crystalizes in *P*21/*n* space group, reveals a distorted tetrahedral coordinated Si(IV) center with elongated Si–P single bonds (2.3137(16) Å, 2.3128(16) Å) (Figure 2). The P–C$_{Carbene}$ bond length of 1.849(4) Å and 1.851(4) Å are elongated in comparison to the free ligand (1.731(10) Å, 1.808(19) Å). Additionally, the C$_{Carbene}$–N bonds of 1.354 Å to 1.357 Å (free ligand: 1.372 to 1.377 Å) are shortened, speaking for predominant canonical forms **IV** and **IV′**. The positive charge is delocalized, hence stabilized in the NHC ring system. Analogue bond elongation/shortening has been reported in the bis(NHCP)-stabilized Sn(II) complex.[26] The sum of bond angles around P1 and P2 are 319.76° and 320.96° respectively, accounting for a trigonal pyramidal coordination of the phosphorus atoms. Similarly to the free bis(NHCP) as well as the reported bis(NHCP)-supported stannyliumylidene complex, the mesityl substituents show a sandwich π–π stacking interaction

Figure 1. Selected examples of Si(IV) dicationic complexes from the literature.
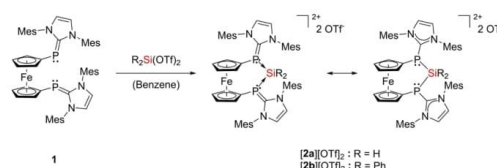
Scheme 2. Synthesis of bis(NHCP)-supported Si(IV) dications [**2a**] and [**2b**].

Table 1. ³¹P and ²⁹Si NMR shifts of Si(IV) dications in CD₃CN.

	Silane	³¹P [ppm]	²⁹Si [ppm]
[**2a**][OTf]₂	$H_2Si(OTf)_2$	−96.24	−44.09 (t, ¹$J_{P,Si}$=24.8 Hz)
[**2b**][OTf]₂	$Ph_2Si(OTf)_2$	−66.06	−10.74 (t, ¹$J_{P,Si}$=65.7 Hz)
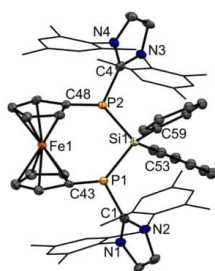
Figure 2. SC-XRD structure of [**2b**]. Translational ellipsoids are plotted at the 50% probability level. For reasons of clarity, hydrogens and triflate counter ions are omitted and mesityl groups are depicted in wireframe models. Selected bond lengths (Å) and angles (°): P1–Si1 2.3137(16), P2–Si1 2.3128(16), Si1–C53 1.807(19), Si1–C59 1.891(15), P1–C1 1.849(4), P2–C4 1.851(4), P1–C43 1.793(4), P2–C48 1.791(4), C1–N1 1.356(6), C1–N2 1.356(6), C4–N3 1.357(6), C4–N4 1.354(6), P1–Si1–P2 108.17(6), C53–Si1–C59 111.65.

with the Cp ring of the ferrocene visible in the SC-XRD structure.[26] Furthermore, the molecular structure of dication [**2b**] displays a sandwich π–π stacking interaction between the second mesityl substituent and the Si-bonded phenyl rings.

Since ferrocene is highly redox active, the free ligand **1** and both complexes [**2a**][OTf]$_2$ and [**2b**][OTf]$_2$ were examined with cyclic voltammograms recorded in 0.1 M Bu$_4$NClO$_4$/THF and all potentials (V) were referenced against ferrocene/ferrocenium (FcH/FcH$^+$) as internal standard (Figure S22–27). The free ligand **1** shows oxidation signals on a glassy carbon electrode at −0.63 V, −0.35 V, and 0.64 V vs. FcH/FcH$^+$ while only the potential at −0.63 V vs. FcH/FcH$^+$ shows a slight reversibility with a reduction potential of −1.20 V vs. FcH/FcH$^+$ followed by a chemical reaction preventing reversibility (Figure S23). The dication [**2a**][OTf]$_2$ shows an oxidation signal on a platinum electrode with a potential of 0.66 V vs. FcH/FcH$^+$ with the reduction potential of 0.22 V vs. FcH/FcH$^+$ and further reduction potentials at −0.84 V, −1.61 V, −2.33 V, and −2.61 V vs. FcH/FcH$^+$ (Figure S24 and S25). All reduction potentials are irreversible. Dication [**2b**][OTf]$_2$ shows an oxidation signal on a platinum electrode with a potential of 0.55 V vs. FcH/FcH$^+$ with the reduction potential of 0.22 V vs. FcH/FcH$^+$. A second oxidation potential at −0.42 V vs. FcH/FcH$^+$ only occurs when the substrate is reduced to over −2.37 V vs. FcH/FcH$^+$ (Figure S26 and S27). Further reduction potentials are at −0.71 V, −1.30 V, −2.15 V, and −2.64 V vs. FcH/FcH$^+$. All reduction potentials are non-reversible.

In order to investigate the electronic structure and properties of compounds [**2a**] and [**2b**], quantum chemical calculations at the B3PW91 level of theory were carried out (for details regarding the computational methods see Supporting Information). In [**2a**], the five highest occupied molecular orbitals (i.e. HOMO−5 – HOMO) do not correspond to bonding interactions involving the NHCPs and the Si center, but rather to the d orbitals of iron, bonding interactions within the ferrocene backbone and π-systems of the mesityl substituents. HOMO−6 is dispersed over the entire NHC–P^2–Si(H)$_2$–P^1–NHC fragment,

showing both phosphorus lone pairs, phosphorus silicon bonding interaction, as well as the π orbitals of the NHC moieties. The LUMO is also dispersed over the NHC–P^2–Si-(H)$_2$–P^1–NHC fragment, predominantly corresponding to the Si–H antibonding orbitals, and the π* orbitals of the NHCs. To get a more intuitive picture regarding the bonding situation [bis(NHCP)–SiH$_2$]$^{2+}$, natural bond orbital (NBO) analysis was carried out. Since [**2a**] is C_2 symmetrical, the interactions between the two NHCP moieties with SiH$_2$ as well as the internal interactions are identical, therefore only the NHCP^1 moiety will be discussed.

NBO analysis shows a Wiberg bond index (WBI) (Figure 3) of 0.91 between Si^1–P^1, which arises from a single almost non-polarized bond (Si(sp$^{3.2}$) 41.7%, P(sp$^{5.7}$) 58.3%), while P^1 retains a localized lone pair (Figure 4, top left). Second order perturbation theory analysis shows that this σ-type lone pair (s 51.4%, p 48.6%) with occupancy of 1.87 el. exhibits only minor donor-acceptor interactions (DAI) with σ*(Si^1–H^1) and σ*(Si^1–H^2) summing up to 3.8 kcal mol^{-1}. Additionally, the P^1 lone pair interacts with a σ*(C–C) orbital of the ferrocene moiety (DAI = 5.4 kcal mol^{-1}), σ*(C^1–N^1) (DAI = 3.2 kcal mol^{-1}) and π*(C^1–N^1)
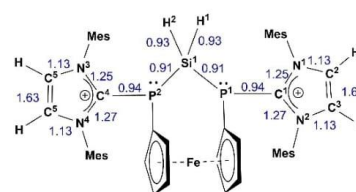
Figure 3. Lewis structure, atom labels (superscript), and Wiberg bond indices (WBI, numbers in blue) of **2a**.

LP(P^1), occ. 1.87 el.
P^1(sp$^{0.94}$)

LP(N^1), occ. 1.51 el
100% N^1(p)

σ(Si^1-P^1), occ. 1.93 el.
58.2% P(sp$^{5.69}$), 41.8% Si(sp$^{3.25}$)

π(C^2-C^3), occ. 1.84 el.
50% C^2(p), 50% C^3(p)

σ(P^1-C^1), occ. 1.97 el
34.0% P(sp$^{6.00}$), 66.0% C(sp$^{1.60}$)

π(C^1-N^2), 1.89
70.0% N^2(p), 30.0 C^1(p)
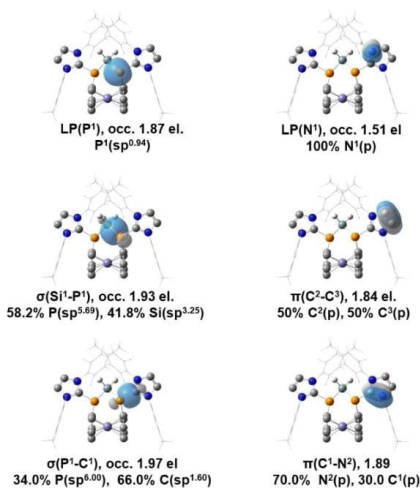
Figure 4. Selected NBOs of **2a**, their occupancy and composition.

(DAI = 11.2 kcal mol^{-1}). WBI between P^1 and C^1 of 0.94 indicates a single bond, stemming from a somewhat polarized σ(P^1–C^1) (P(sp$^{6.0}$) 34.0 %, C(sp$^{1.6}$) 66.0 %). The bonding situation within the carbene moiety is typical —C^1 and N^1 form a double bond and N^2 possess a lone pair, which is strongly delocalized to π*(C^1–N^1) (DAI = 78.4 kcal mol^{-1}), resulting in N^1–C^1–N^2 3-center-4-electron hyperbond, and to π*(C^2–N^2) (DAI = 34.2 kcal mol^{-1}). The corresponding natural localized molecular orbitals NLMOs are presented in Figure S28.

Inspection of the NPA charges of [2 a] reveals that the +2 charge of the molecule is located mainly on the atoms, which constitute the NHCP moieties with Σq(NHCP^1, NHCP^2) = +2.18 el. The SiH$_2$ moiety accommodates only +0.27 el. (+0.46 el. on Si and −0.10 el. on each hydrogen), while the ferrocene backbone is negatively charged with Σq(Fc) = −0.45 el. The calculated ^{29}Si NMR chemical shifts of [2 a] and [2 b] δ = −49.8 ppm and δ = −13.2 ppm are in good agreement with the respective experimentally observed signals at −44.1 ppm and −10.7 ppm.

In order to quantify the Lewis acidity of the isolated dicationic complexes, the Gutmann Beckett method was applied.[34–35] After addition of one equivalent triethylphosphine oxide to a 1,2-difluorobenzene solution of complexes [2 a][OTf]$_2$ and [2 b][OTf]$_2$, the difference in ^{31}P NMR chemical shifts ($\Delta\delta$ ^{31}P) between the free (^{31}P δ = 47.37 ppm) and the coordinated triethylphosphine oxide were measured. A larger difference in the shifts corresponds to a higher Lewis acidity. Adduct [2 a][OTf]$_2$(OPEt$_3$) shows a chemical shift of 81.67 ppm and a $\Delta\delta$ ^{31}P of 34.30 ppm accounting for high Lewis acidity. However, the complex [2 a][OTf]$_2$(OPEt$_3$) is not stable and fully decomposes within 20 h, therefore it eluded further investigation. While dications VIII demonstrated lower ΔP shifts (R = Ph: $\Delta\delta$ ^{31}P 23.5 ppm, R = C$_{12}$H$_8$: $\Delta\delta$ ^{31}P 28.6 ppm) compared with [2 a][OTf]$_2$ and therefore lower Lewis acidity, aryl silylium ions are even more Lewis acidic with $\Delta\delta$ ^{31}P of 39.2−44.9 ppm (Figure 5).[32,36] Addition of triethylphosphine oxide to a 1,2-difluorobenzene solution of complex [2 b][OTf]$_2$ yielded a $\Delta\delta$ ^{31}P of 53.22 ppm and 5.14 ppm. As observed in other Si(IV) dications a coordination of two equivalents triethylphosphine oxide is possible and could account for the $\Delta\delta$ ^{31}P of 5.14 ppm, while $\Delta\delta$ ^{31}P of 53.22 ppm shows the shift of a single triethylphosphine oxide coordination.[32] Since the tendency to form the bisadduct seems to be very high, the monoadduct is only visible when 0.5 eq OPEt$_3$ are added. Calculations predicts the coordination of triethylphosphine to [2 a] to be exergonic

by 6.8 kcal mol^{-1}. The computational predictions of the Gutmann–Beckett method have been previously attempted, giving poor correlations between the experimental and calculated $\Delta\delta$ ^{31}P values.[37] In the case of [2 a] the calculated $\Delta\delta$ ^{31}P accounts for 20.4 ppm.

To investigate the thermal stability as well as the reactivity of [2 a][OTf]$_2$ and [2 b][OTf]$_2$, CD$_3$CN solutions were heated for several days. While [2 a][OTf]$_2$ already shows very slow decomposition at 80 °C, [2 b][OTf]$_2$ is stable at 80 °C but slowly starts to decompose at 100 °C. The ^{1}H NMR shows only signals of the imidazolium salt after heating overnight. The other decomposition products could not be identified. Both complexes are unreactive towards ethylene, acetylene, phenyl-, and diphenylacetylene in CD$_3$CN even at elevated temperature (heating up to 80 °C for 1–2 days). However, addition of excess diphenylketene to the dication [2 a] in 1,2-difluorobenzene shows full conversion at 80 °C after 20 h, while [2 b] is unreactive. Multinuclear NMR analysis as well as LIFDI-MS indicate the formation of the compound [3] (Scheme 3). The ^{31}P NMR and the ^{29}Si NMR signal are downfield shifted in comparison to the starting material at −23.08 ppm and −53.81 ppm. Both signals do not show J(Si–P) indicating the Si–P bond cleavage via C–O insertion into the Si–P bonds. Additionally, LIFDI-MS measurement shows the mass for [2 a + 2 eq Ph$_2$CO]$^{2+}$. Similar reactivity is observed by Appel as well as by Weber and coworkers.[38–39] Treatment of PhP(SiMe$_3$)$_2$ with an equimolar amount of diphenylketene afforded the adduct Ph(Me$_3$Si)P–C(OSiMe$_3$)=CPh$_2$. The same reactivity was observed for [Fe]–P(SiMe$_3$)$_2$. According to the measured data and literature comparison, the structure of [3] was proposed.

To support the proposed structure, an optimized structure was calculated (Figure 6). DFT calculations show that [3] adopts a nearly ideal C_2 symmetry. The calculated ^{29}Si NMR and ^{31}P NMR chemical shifts of the optimized geometry at −50.2 ppm and −31.2 ppm are in a good agreement with the experiment (−53.8 ppm and −23.1 ppm). Further theoretical considerations predict the reaction of [2 a] with two equivalents of diphenylketene to form [3] to be exergonic by 57.7 kcal mol^{-1}.
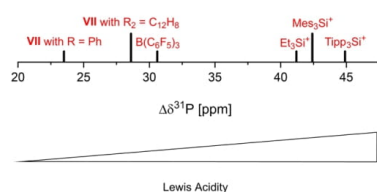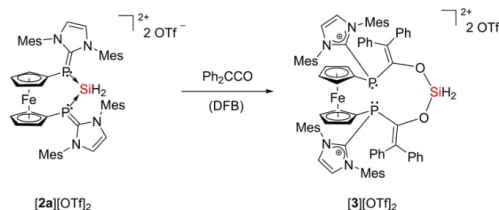

Figure 5. Lewis acidity assessment of different silyl cations and BCF via Gutmann Beckett method.

Scheme 3. Reactivity of [2 a][OTf]$_2$ towards diphenylketene in 1,2-difluorobenzene (DFB).
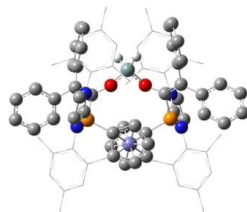
Figure 6. Optimized structure of [**3**].

Conclusion

In conclusion, we were able to isolate the first examples of bis(NHCP)-supported Si(IV) dications presenting an unique electronic nature. The dications [**2a**] and [**2b**] reveal high Lewis acidity being confirmed *via* Gutmann Beckett method. While the dications show high thermal stability in CD$_3$CN solution, [**2a**] readily reacts with diphenylketene at elevated temperature to yield a heterocyclic complex. These results further demonstrate the coordination abilities of bis(NHCP)s in main group chemistry and open the way for further investigations such as small molecule activation.

Experimental Section

Synthesis of [2a][OTf]$_2$ and [2b][OTf]$_2$: To a stirred solution of FcPIMes (**1**) (87 mg, 101.8 μmol, 1.0 eq) in benzene (1.5 mL) the silane (122.2 μmol, 1.2 eq) dissolved in benzene (0.5 mL) was added dropwise. The complex formed immediately as red oil. The solution was decanted and after washing the residue with benzene (2·2 mL), the product was dried under vacuum to yield an orange solid.

[**2a**][OTf]$_2$: ^{1}H NMR (400 MHz, CD$_3$CN, 300 K): δ[ppm] = 7.64 (s, 4H, NCH), 7.11 (s, 4H, C$_{Mes}$H), 7.07 (s, 4H, C$_{Mes}$H), 4.34 (s, 2H, C$_{Cp}$H), 4.29 (s, 2H, SiH), 4.19 (s, 2H, C$_{Cp}$H), 3.77 (s, 2H, C$_{Cp}$H), 3.72 (s, 2H, C$_{Cp}$H), 2.38 (s, 24H, o-C$_{Mes}$CH$_3$), 1.83 (s, 12H, p-C$_{Mes}$CH$_3$). ^{19}F NMR (376 Hz, CD$_3$CN): δ[ppm] = −78.94. ^{29}Si-IG NMR (99 Hz, CD$_3$CN): δ[ppm] = −44.09 (t, $^1J_{Si,P}$ = 24.8 Hz). ^{31}P NMR (162 Hz, CD$_3$CN): δ[ppm] = −96.24.

[**2b**][OTf]$_2$: ^{1}H NMR (400 MHz, CD$_3$CN): δ[ppm] = 7.58 (t, $^1J_{H,H}$ = 7.3 Hz, 6H, C$_{Ph}$H), 7.32 (d, $^1J_{H,H}$ = 7.6 Hz, 4H, C$_{Ph}$H), 7.30 (s, 4H, NCH), 6.69 (s, 8H, C$_{Mes}$H), 4.28 (s, 4H, C$_{Cp}$H), 3.94 (s, 4H, C$_{Cp}$H), 2.28 (s, 12H, p-C$_{Mes}$CH$_3$), 1.52 (s, 24H, o-C$_{Mes}$CH$_3$). ^{19}F NMR (376 Hz, CD$_3$CN): δ[ppm] = −78.88. ^{29}Si-IG NMR (79.51 Hz, CD$_3$CN): δ[ppm] = −10.74 (t, $^1J_{Si,P}$ = 65.7 Hz). ^{31}P NMR (162 Hz, CD$_3$CN): δ[ppm] = −66.06.

Synthesis of [3][OTf]$_2$: To a solution of [**2a**][OTf]$_2$ (38.0 mg, 32.12 μmol, 1.0 eq) in 1,2-difluorobenzene (0.4 mL) diphenylketene (62.4 mg, 321.20 μmol, 10.0 eq) was added. The solution was heated to 60 °C for 3 d to observe full conversion in the ^{31}P NMR. The solvent was removed and the residue washed with benzene (4·1 mL) and pentane (2·1.5 mL) to yield the diphenylketene adduct [**3**][OTf]$_2$ as yellow powder (44.0 mg, 28.0 μmol, 87 %). ^{1}H NMR (400 MHz, CD$_3$CN): δ[ppm] = 7.43 (m, 8H, C$_{Ph}$H), 7.35 (s, 4H, NCH) 7.24 (m, 8H, C$_{Ph}$H), 7.03 (s, 4H, C$_{Mes}$H), 6.90 (s, 4H, C$_{Mes}$H), 6.64 (dd, 4H, $^1J_{H,H}$ = 7.6 Hz, 2.0 Hz, C$_{Ph}$H), 4.57 (m, 2H, C$_{Cp}$H), 4.28 (m, 2H, C$_{Cp}$H), 3.90 (m, 2H, C$_{Cp}$H), 3.81 (s, 2H, SiH), 3.75 (m, 2H, C$_{Cp}$H), 2.36 (s,

12H, C$_{Mes}$CH$_3$), 1.65 (s, 12H, C$_{Mes}$CH$_3$), 1.52 (s, 12H, C$_{Mes}$CH$_3$). ^{19}F NMR (376 Hz, CD$_3$CN): δ[ppm] = −79.04. ^{29}Si-INEPT NMR (99 Hz, CD$_3$CN): δ[ppm] = −53.81 (d, $^1J_{SiH}$ = 568.0 Hz). ^{31}P NMR (162 Hz, CD$_3$CN, 300 K): δ[ppm] = −23.08.

Deposition Number 2203508 (for [**2b**][OTf]$_2$·3(C$_6$H$_5$F)) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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8.   Summary and Outlook

Since the discovery of NHCPs by Arduengo in 1997,[23] this compound class has only found scarce applications especially in main group chemistry.[24, 31, 36-39] With the isolation of the NHCP–supported germylene and stannylene, the application of phosphinidenide ligands in group 14 chemistry could be demonstrated expanding the properties of NHCP ligands.[142] At the start of this project, only monodentate NHCP ligands were known. Owning the successfully applied bisNHI ligands in our group for stabilization of group 13 and 14 elements,[94-96, 143-144] the synthesis of the heavier analogue bisNHCP was aimed for. This thesis describes the successful isolation of bisNHCP ligands and the application in Sn(II) an Si(IV) coordination.

8.1   Synthesis of NHC–Stabilized Germanium and Tin Analogues of Heavier Nitriles

In the first part of this thesis the synthesis of NHC–stabilized germanium and tin analogues of heavier nitriles **III** is presented (Scheme 38).[142] To isolate the heavier nitriles **III**, the literature known terphenyl–substituted chlorogermylene and –stannylene **I** were treated with the TMS–substituted NHCP **II** at elevated temperature reaching high yields of 82% and 72%. The products were characterized with multinuclear NMR, FT–IR, UV–Vis, EA, and SC–XRD. The SC–XRD analysis suggests an E–P (E = Ge, Sn) multiple bond character due to the short bond lengths of 2.2364(6) Å and 2.4562(7) Å. To support the experimental data, theoretical calculations were carried out. A Wiberg bond index (WBI) of 1.300 for germylene and 1.063 for the stannylene E–P bond was calculated. Therefore, especially for the germanium congener a partial double bond character was proposed.

Catalytic applications showed activity of both phosphinidene–tetrylenes in the hydroboration of aromatic carbonyls with pinacolborane. Best results of over 99% conversion were observed using the phosphinidene–stannylene as catalyst at a loading of 0.05 mol% in 0.3 h with acetophenone as substrate. The activity of the germanium analogue turned out to be notably lower. At a catalyst loading of 4 mol% in 3 h only 67% conversion of benzaldehyde was achieved.

Reactivity tests revealed both compounds to be inert towards H_2, CO, CO_2, and stoichiometric amounts of 1,3–dimethyl–1,3–butadiene, benzaldehyde, and pinacolborane. Surprisingly,

treatment with diphenylketene resulted in the selective formation of the formal [2+2] cycloaddition products **IV** in 93% (E = Ge) and 77% (E = Sn) yield. Both products display an upfield shift in the ^{31}P NMR (Ge: 18.2 ppm, Sn: 20.2 ppm) in comparison to the starting material (Ge: 216.8 ppm, Sn: 176.4 ppm). The product structure was confirmed with SC–XRD analysis. *Via* NMR spectroscopy a reversible retro–cycloaddition reaction was observed at 80 °C for E = Ge and 100 °C for E = Sn.

Aiming for the removal of the NHC in order to enhance the E–P multiple bond character, **IIIa** and **IIIb** were treated with the strong Lewis acid BCF. Interestingly, the NHC–BCF adduct was not formed but reactivity of the tetrylenes towards BCF was observed. In contrast to the formation of an unstable product from the germylene, a stable product was observed for the stannylene resulting in the isolation of the phosphastannene **V**. The ^{31}P NMR exhibits a significantly highfield shifted signal at –93.05 ppm. SC–XRD analysis showed a planar coordinated tin center with a sum of bond angles of 359.9° and a shortened Sn–P bond in comparison to the starting material. A WBI of 1.170 for the Sn–P bond was calculated suggesting a double bond character.
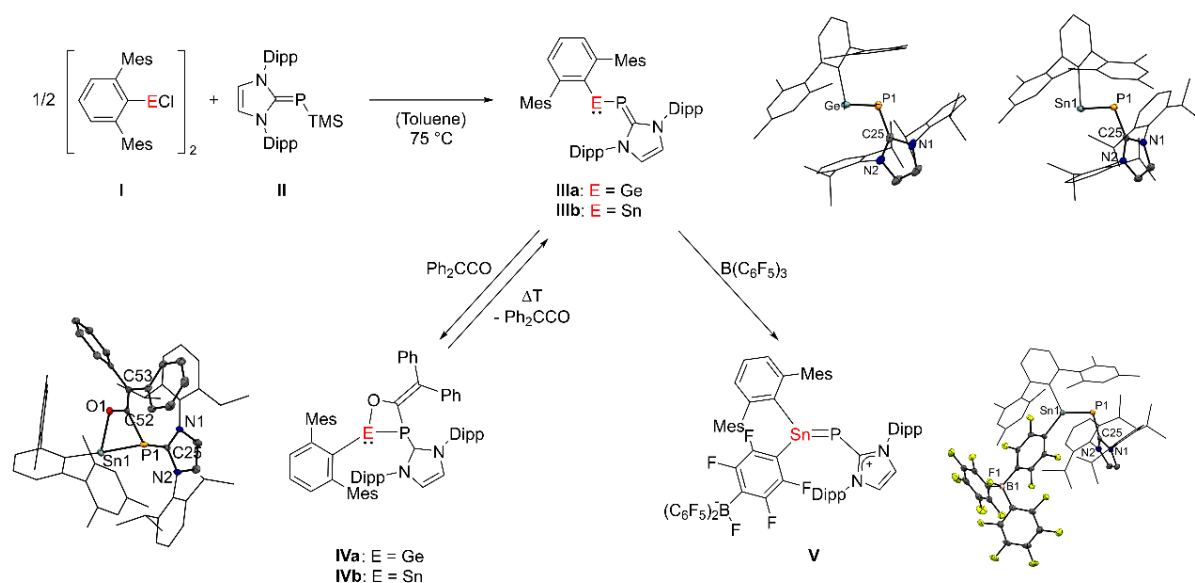
Scheme 38 Synthesis and reactivity of NHC–stabilized germanium and tin analogues of heavier nitriles.

8.2 Synthesis of Novel Bidentate NHCP Ligands and Coordination Chemistry

This thesis succeeded in the synthesis of a novel bisNHCP ligand (Scheme 39) and the application in coordination of a variety of halogen–substituted stannyliumylidene ions and Si(IV) dications.[141, 145] Until today only one other example of a bidentate NHCP ligand is known.[42] Using a ferrocene backbone and sterically demanding mesityl substituents on the NHC wingtips, different steric as well as electronic properties to the literature known bisNHCP was achieved. Treating 1,1'–bis(dichlorophosphino)ferrocene (**VI**) with NHC followed by reductive dichlorination using sodium naphthalenide resulted in the formation of the bisNHCP ligands **VIIIa** and **VIIIb**. The two new ligands differ in the NHC backbone by a methyl substituent. Full characterization with multinuclear NMR spectroscopy, LIDFI–MS, and SC–XRD analysis was performed. Both ligands revealed a P–$C_{Carbene}$ double bond character confirmed by SC–XRD analysis (P–$C_{Carbene}$ bond lengths **VIIIa**: 1.731(10)/1.808(10) Å, **VIIIb**: 1.7696(18)/1.7704(19) Å) and theoretical calculations (WBI of 1.29 for **VIIIa**). The SC–XRD structure and the DFT optimized structure show a sandwich π–π–stacking of the mesityl substituents of the NHC and the cyclopentadienyl rings of the ferrocene.
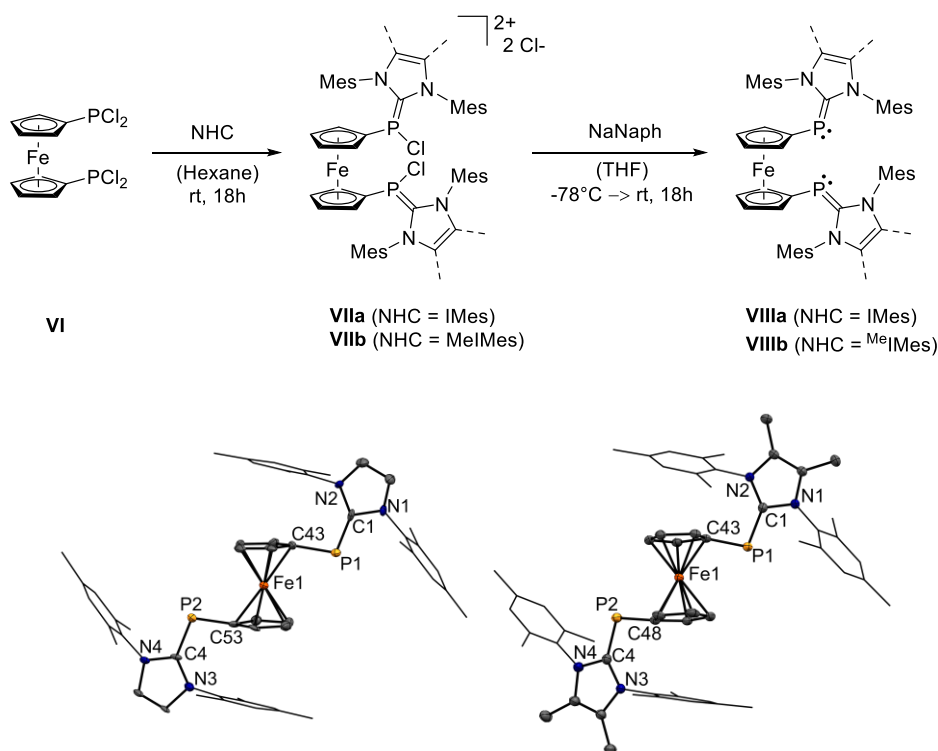
Scheme 39 Synthesis of bisNHCP ligands and SC–XRD structures.

To examine the ability of the ligands **VIIIa** and **VIIIb** to support low–valent group 14 elements, they were treated with Sn(II) precursors (SnX$_2$ with X = Cl, Br, I, OTf) to yield stannyliumylidene complexes **IX** (Scheme 40). Upon coordination, the P–C$_{Carbene}$ bonds (1.824(4)/1.828(4) Å) are elongated compared to the free ligand **VIIIb**. As discussed in chapter 2, the NHCPs display different resonance structures, which are shown in Scheme 40 for the stannyliumylidene ions. The elongated P–C$_{Carbene}$ bond lengths account for single bond character, as depicted in the mesomeric structure **IX'**. The positive charge is delocalized in the NHC rings, stabilizing the cationic complex.
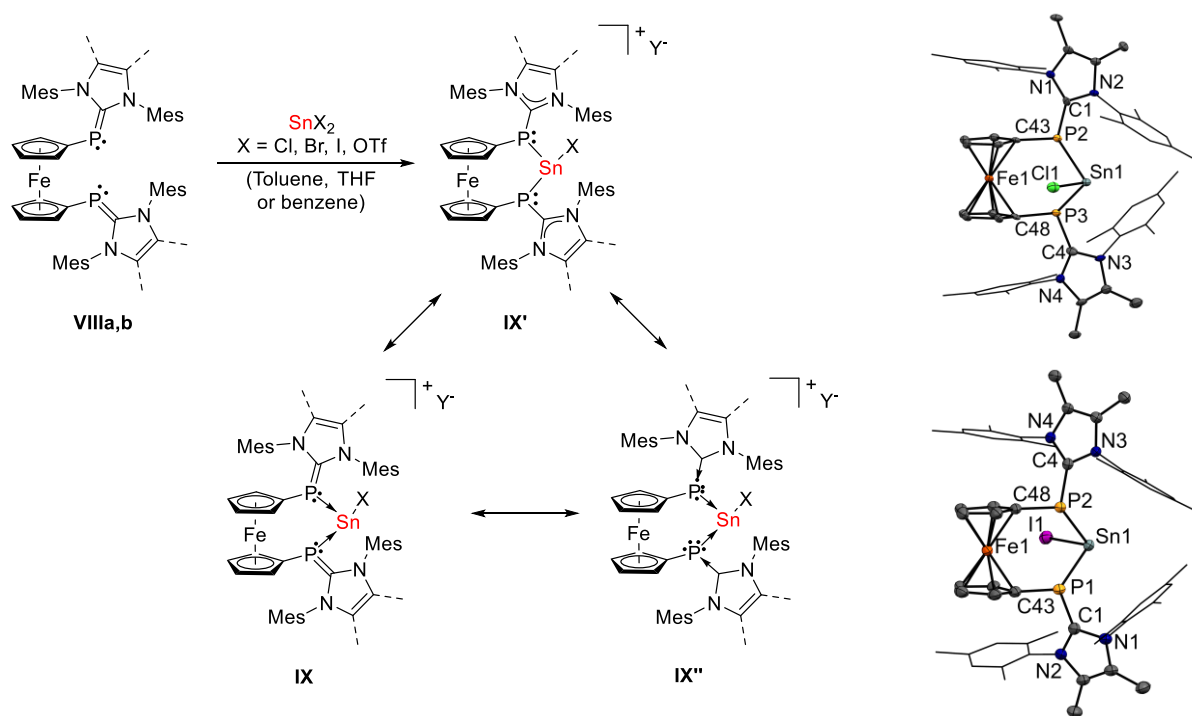
Scheme 40 Reactivity of bisNHCP ligands **VIIIa** and **VIIIb** towards Sn(II) precursors and SC–XRD structures.

These stannyliumylidene ions can be used in transmetallation as well as Sn(II) transfer. On the one hand, treatment of stannyliumylidene **IX** with CuCl in THF yields the bisNHCP CuCl complex **X**. On the other hand, addition of a bisNHI ligand to the stannyliumylidene **IX** fully transfers the Sn(II) center to form a bisNHI–supported stannyliumylidene ion **XI** (Scheme 41). Interestingly, theoretical investigations in the gas phase calculated a higher affinity of the bisNHCP ligand towards SnCl$^+$ by 7.6 kcal mol^{-1}. Therefore, it is concluded that the observed reaction takes place due to solvation effects and not due to better stabilization of SnCl$^+$ by the bisNHI ligand.
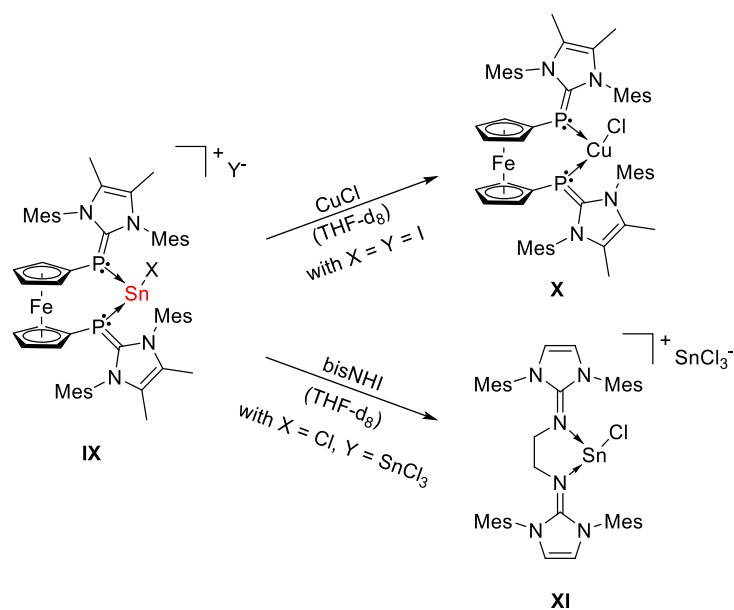
Scheme 41 Reactivity of stannyliumylidenes **IX** towards transmetallation and Sn(II) transfer.

Furthermore, the expansion of the NHCP stabilization properties towards Si(IV) dications was demonstrated. Treatment of the bisNHCP ligand with bistriflate silanes $R_2Si(OTf)_2$ (R = H, Ph) instantly resulted in the formation of dications **XIIa** and **XIIb** (Scheme 42). All compounds were characterized with multinuclear NMR spectroscopy, LIFDI–MS, and in case of $[SiH_2]^{2+}$ additionally with SC–XRD analysis. The SC–XRD structure revealed Si–P bond lengths of 2.3137(16)/2.3128(16) Å accounting for an elongated single bond character. Additionally, the $C_{carbene}$–P bonds are elongated in comparison to the free ligand. Therefore, a predominance of the mesomeric structure **XII'** was concluded. The bisNHCP ligand stabilizes the positive charge in the imidazolium ring resulting in mesomeric structure **XII'**.

To investigate the Lewis acidity of the isolated Si(IV) dications, the Gutman Beckett method was applied. To a solution of the dications in the non–coordinating solvent DFB, triethyl phosphine oxide is added and the difference in the ^{31}P NMR shifts for free and coordinated triethyl phosphine oxide is measured. A high difference $\Delta^{31}P$ accounts for a high Lewis acidity. A $\Delta^{31}P$ of 34.30 ppm for **XIIa** suggests a high Lewis acidity, however, the adduct was not stable and decomposed over time making additional characterization impossible.

Since ferrocene is known to be highly redox active, analysis of the free ligand and the dications with cyclovoltammetry (CV) was conducted. Multiple oxidation and reduction potentials were revealed, all being irreversible.
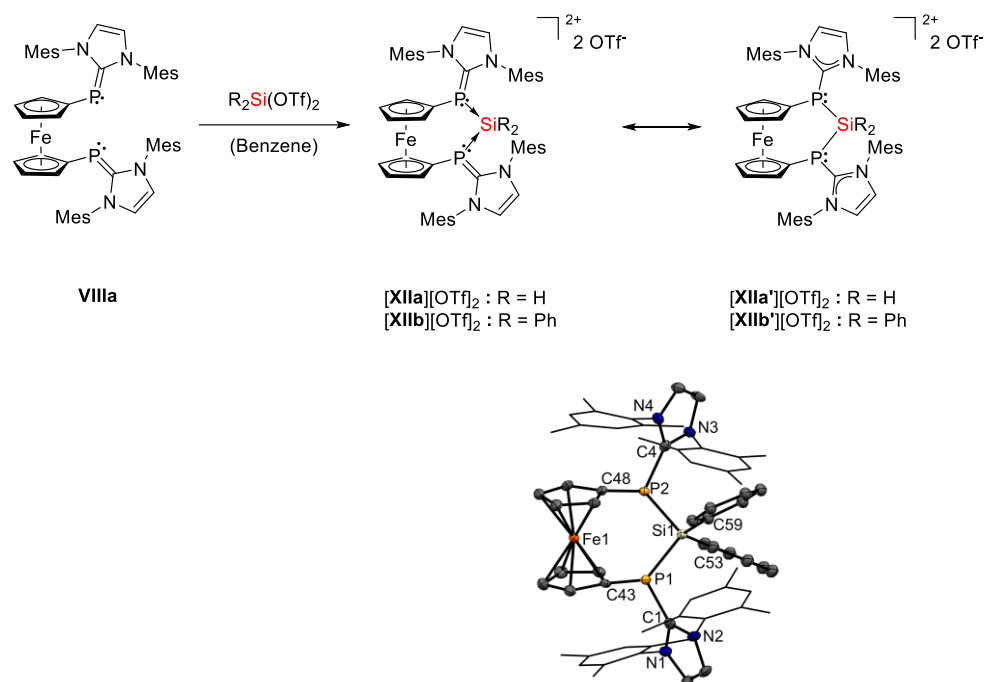
Scheme 42 Synthesis of bisNHCP–stabilized Si(IV) dications and SC–XRD structure of **XIIa** and **XIIb**.

Nevertheless, a high thermal stability of the complexes of up to 80°C and 100°C in CD_3CN solution was observed. The dications are inert towards ethylene, acetylene, phenylacetylene and diphenylacetylene. Towards an excess of diphenylketene, the dication $[SiH_2]^{2+}$ showed reactivity at elevated temperatures. The product was characterized *via* multinuclear NMR, and LIDFI–MS. According to LIDFI–MS two equivalents diphenylketene were activated. The ^{29}Si NMR no longer exhibited a triplet signal as in the starting material, accounting for an insertion in the Si–P bond forming **XIII**. Since no SC–XRD could be achieved, theoretical investigations were carried out to calculate the optimized structure and confirm the proposed coordination (Scheme 43). The calculated optimized structure and the ^{29}Si and ^{31}P NMR shifts agree with the proposed structure and the measured NMR data (calculated/measured: ^{29}Si δ = –50.2/–53.8 ppm, ^{31}P δ = –31.2/–23.1 ppm).
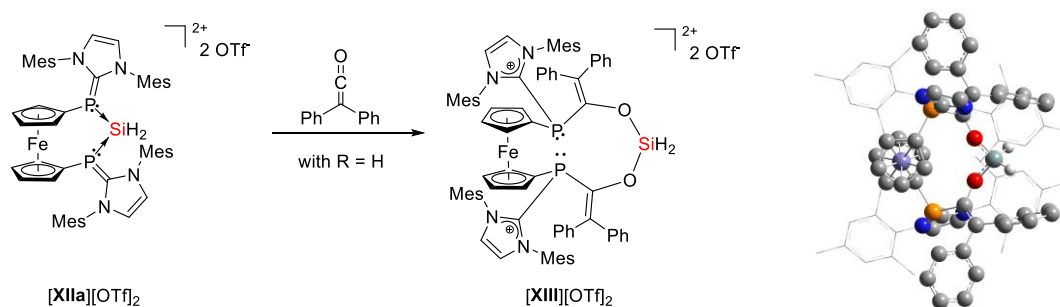
Scheme 43 Reactivity of **XIIa** towards diphenylketene and DFT optimized product structure.

8.3   Outlook

<u>Heavier nitriles</u>

Since the catalytic application in hydroboration was successful, application in other catalytic processes like hydrosilylation could be tested as well. Furthermore, to yield a more pronounced E–P multiple bond character, different methods to abstract the NHC could be investigated. Additionally, theoretical calculations suggest a higher stability of a phosphasilyne R–Si≡P using small electronegative R substituents.[146] Therefore, a variety of, for instance, fluorinated substituents R could be applied.
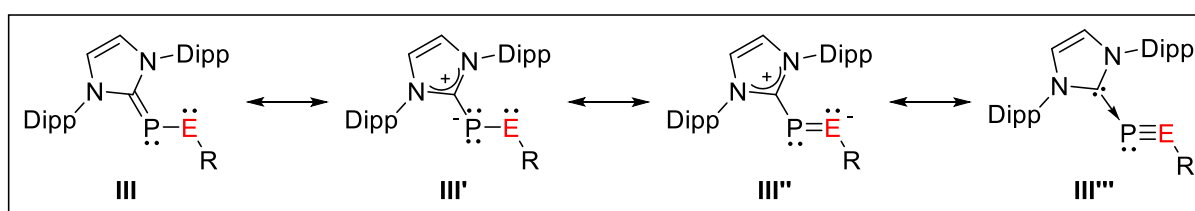
Scheme 44 Resonance structures of heavier nitriles.

Despite the fact that the NHC provides stabilization, a free P≡E triple bond is targeted. The coordinated NHC could be removed by treatment with a Lewis base like a borane to achieve the free triple bond compound **XIV**. Depending on the steric demand of the substituent on the tetrel, an oligomerization to form trimer **XVa** or cluster formation to form **XVb** is possible.
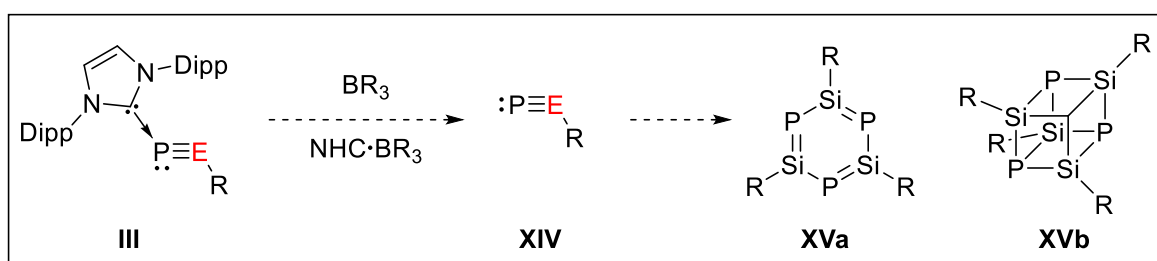
Scheme 45 Removal of the coordinated NHC and oligomerization/cluster formation.

Modification of the bisNHCP ligand

In the course of this thesis only the backbone of the NHC in the ligand was modified. However, several additional modifications are possible to vary the electronic as well as steric properties (Figure 15). For instance, a saturated NHC backbone could be introduced or different substituents on the NHC wingtips. Instead of mesityl, substituents like 2,6–diisopropylphenyl, *iso*–propyl, *tert*–butyl, methyl, or sterically more demanding groups like adamantyl or triphenylmethyl could be implemented. Additionally, different ligand backbones instead of ferrocene are possible (e.g., carborane, naphthalene). These modifications will change the steric and electronic properties and therefore could possibly give access to new structures.

R = Dipp, *i*Pr, *t*Bu, Me, Ad, CPh$_3$
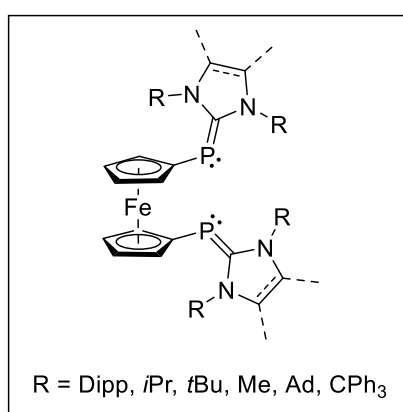
Figure 15 Possible modifications of the bisNHCP ligand.

Expansion of bisNHCP Coordination Chemistry

The new bisNHCP ligands have already shown great potential in stabilizing Si(IV) as well as Sn(II) compounds. Preliminary results on expanding the chemistry towards Ge(II) revealed a complexation of GeI$_2$ while decomposition occurs with GeCl$_2$·dioxane and GeX$_2$ (X = Br, OTf) (Scheme 46). The germyliumylidene **XVI** was characterized by NMR and LIDFI–MS. The reactivity of this complex could, for instance, be examined towards small molecules, transmetallation, Ge(II) transfer, or catalytic applications.
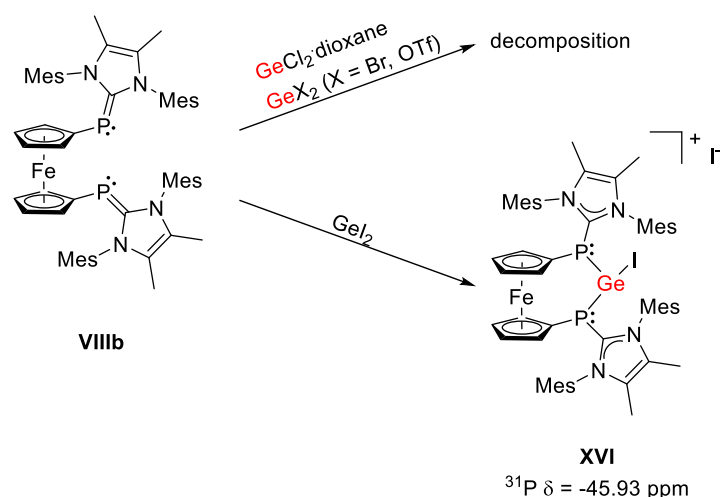
Scheme 46 Reactivity of bisNHCP ligand towards Ge(II) precursors.

NHCPs have previously shown Lewis acidic properties. Therefore, the coordination to a Lewis acid like boranes or tricoordinate aluminum compounds seems possible (Scheme 47). These (frustrated) Lewis acid–base adducts could be used to activate small molecules like CO_2 and H_2, or to catalyze polymerization as described for NHCP–AlMe$_3$ adducts.[41, 147-148]
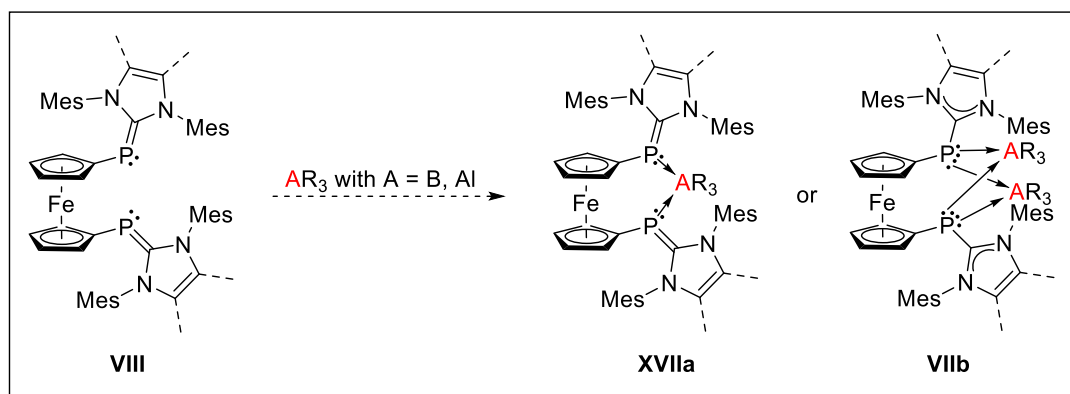
Scheme 47 Reactivity of bisNHCP towards boranes and aluminum substrates.

In the transmetalation reaction of stannyliumylidene **IX** the bisNHCP–supported CuCl complex **X** was synthesized. Motivated by the theoretical calculations proposing a possible coordination of two centers, the reactivity of the bisNHCP (with NHC = ^{Me}IMes) towards an excess of CuCl was investigated. First results revealed a broad upfield shifted ^{31}P NMR signal at −85.57 ppm compared to the mono CuCl complex **X** (^{31}P δ = −82.34 ppm). LIDFI–MS revealed the highest mass accounting for [**VIIIb**·Cu$_5$Cl$_4$]$^+$ suggesting a cluster type compound formation. Additionally, different m/z values for various CuCl contents are shown in the LIFDI–MS spectra

(Figure 16) and compared to the calculated values (Table 2). Since a SC–XRD structure could not be measured, further research needs to be done to identify and characterize the product.
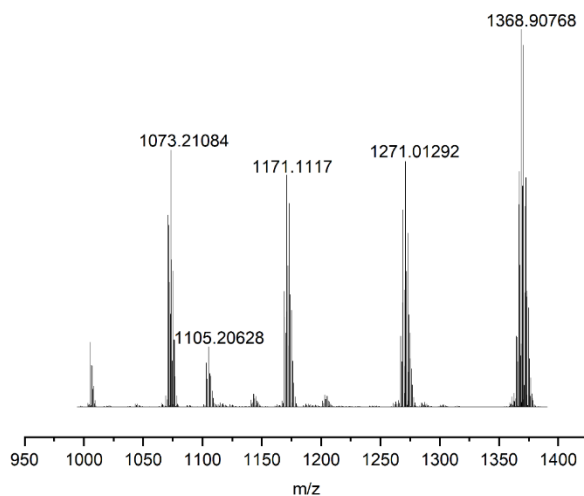
Figure 16 LIFDI-MS of excess CuCl product.

Table 2 Calculated and measured m/z for CuCl products.

	Calculated m/z	Measured m/z
[**VIIIb**·Cu$_2$Cl]$^+$	1073.2218	1073.21084
[**VIIIb**·Cu$_2$Cl$_2$]	1106.19247	1105.20628
[**VIIIb**·Cu$_3$Cl$_2$]$^+$	1171.12026	1171.1117
[**VIIIb**·Cu$_4$Cl$_3$]$^+$	1271.01576	1271.01292
[**VIIIb**·Cu$_5$Cl$_4$]$^+$	1368.91421	1368.90788

Apart from CuCl, the formation of different transition metal complexes can be attempted. Neutral monodentate NHCPs proofed to be suitable ligands in complexation of for instance two equivalents of AgCl, and AuCl, transition metal carbonyls (Cr(CO)$_5$, Mo(CO)$_5$, W(CO)$_5$, Fe(CO)$_4$), or ruthenium, osmium, iridium, and rhenium.[31, 36, 39, 149-152] Analogue to the reactivity of the bisNHCP towards boranes and aluminum substrates in Scheme 47 a single or double/multiple coordination is possible. The different transition metal complexes could be examined for catalytic activity, small molecule activation or reduction.

To sum up, during this thesis the properties of the NHCP and bisNHCP ligands was investigated towards the coordination of group 14 elements. The potential of the ferrocene–bridged bisNHCP ligand has not yet been fully discovered and interesting follow–up chemistry could be performed.

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10.   Appendix

10.1   License for Chapter 5

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Article Title	Synthesis and Reactivity of Bidentate N-Heterocyclic Carbene-Phosphinidene Supported Si(IV) Dicationic Complexes	Rightsholder	John Wiley & Sons - Books
		Publication Type	e-Journal
Author/Editor	Gesellschaft Deutscher Chemiker., Koninklijke Nederlandse Chemische Vereniging., Koninklijke Vlaamse Chemische Vereniging., Société royale de chimie (Belgium), Società chimica italiana., Société française de chimie., ChemPubSoc Europe.	URL	http://www2.lib.udel.edu/Acq/terms/wileyintro.htm
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