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Novel Low Valent Main Group Element Compounds -

From Molecules Toward Materials

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2 Kurzfassung

Im Fokus der vorliegenden Arbeit steht die Stabilisierung von niedervalenten Verbindungen von Elementen der Hauptgruppen 3 (Gallium, Indium) und 4 (Germanium, Zinn, Blei) des Periodensystems und die Untersuchung der entsprechenden Strukturen, Stabilitäten und Reaktivitäten. Zwei unterschiedliche Ligandenklassen wurden eingesetzt, um die sterischen und elektronischen Effekte bei der Stabilisierung der niedervalenten Verbindungen vergleichen zu können. Einerseits wurden Silylamid-Liganden verwendet, die sich von den bisher in der Literatur publizierten Systemen durch größeren sterischen Anspruch (zwei Phenyl-Gruppen am Silizium-Atom) unterscheiden. Zwei unterschiedliche Substitutionsmuster am Stickstoff-Atom wurden ausgewählt, um den sterischen Effekt der flankierenden Phenyl-Gruppe zu untersuchen. Andererseits wurden Phenyl-basierte Ligandensysteme (Biphenyle und Terphenyle) eingesetzt. Die Biphenyl-Liganden, die in der vorliegenden Arbeit beschrieben werden, wurden bisher nicht im Zusammenhang mit der Stabilisierung von niedervalenten Verbindungen von schwereren Elementen der Hauptgruppe 4 erwähnt. Im Gegensatz dazu sind die hier gezeigten Terphenyl-stabilisierten Verbindungen der Gruppen 13 und 14 literaturbekannt. Sie wurden in die Arbeit aufgenommen, um ihre Stabilität und Reaktivität zu untersuchen. Wie bei den Silylamid-Liganden erfolgten auch hier Modifikationen an den Ligandensystemen, um deren Auswirkungen zu untersuchen. Die niedervalenten Verbindungen, die in der vorliegenden Arbeit erstmalig beschrieben werden, zeigen eine große Vielfalt an Strukturmotiven: $LGaI_2$, L_2InCl, $(LIn)_4$, LECl, L_2E, $Li^+(EL_3)^-$, $LEEL_3$ (L = Ligand, E = Ge, Sn, Pb). Die erhaltenen Verbindungen wurden mittels Multi-Kern-NMR und Einkristallstrukturanalysen charakterisiert. Die Untersuchung der Stabilität und Reaktivität der erhaltenen niedervalenten Hauptgruppenelementverbindungen erfolgte durch Umsetzung mit einer Serie an Reagenzien (z.B. Adamantylphosphaalkin, unterschiedliche Reduktionsmittel). Die Reaktionen zeigten, dass die Silylamid-basierten Verbindungen signifikant stabiler (und somit weniger reaktiv) als ihre Terphenyl-stabilisierten Analoga sind. Letztere eröffneten den Weg zu einer Vielfalt an neuen Strukturmotiven (z.B. Tetrole, Cluster) bei der Umsetzung mit den entsprechenden Reagenzien.

3 Abstract

The present work focuses on the stabilization of low valent main group 3 (gallium, indium) and 4 (germanium, tin, lead) element compounds and the study of their structures, stability and reactivity. Two different ligand classes were deployed in order to compare the sterical and electronic effects of the moieties in stabilizing the low valent compounds. On the one hand, silylamide ligands were used. The systems described in the present work differ significantly from those already published in literature due to their greater sterical hindrance (bearing two phenyl groups at the silicon atom). Different substitution patterns at the nitrogen atom were chosen in order to compare the sterical effect of the flanking phenyl group. On the other hand, phenyl based ligands (biphenyl and terphenyl ligands, respectively) were deployed. While the biphenyl ligands described herein have not been previously discussed in literature in terms of stabilization of heavier main group 4 derivatives (as in the present work), the low valent main group 3 and 4 terphenyl-stabilized compounds have been published earlier and were preferentially studied concerning their stability and reactivity. In analogy to the silylamide ligands, variation of these ligand systems was performed in order to study the effects of the modifications. The low valent group 13 and 14 derivatives first described in the present work include the following structural motives: $LGaI_2$, L_2InCl, $(LIn)_4$, LECl, L_2E, $Li^+(EL_3)^-$, $LEEL_3$ (L = ligand, E = Ge, Sn, Pb). The obtained low valent derivatives were characterized by multinuclear magnetic resonance and single crystal X-ray diffraction measurements. Further studies included conversion of the derivatives with a broad range of reagents (including e.g. adamantylphosphaalkyne, reducing agents) in order to study their stability and reactivity. These investigations showed that the silylamide derivatives are significantly more stable (and hence less reactive) than their terphenyl based analogs. Reactions of the latter led to a broad range of novel structural motives (including tetrole and cluster derivatives) upon conversion with the corresponding reagents.

Contents

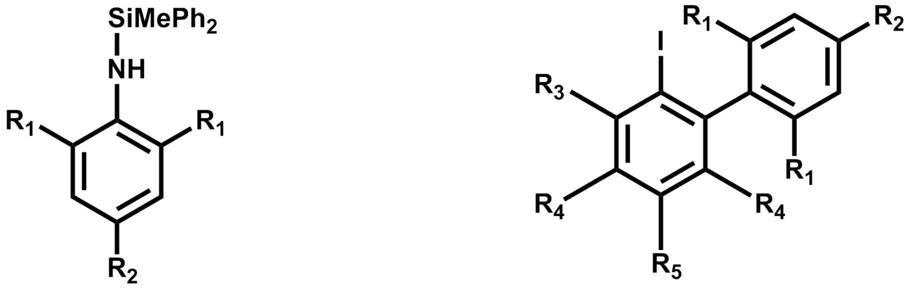
4 Abbreviations

Ada	adamantyl, tricyclo[3.3.1.1^{3,7}]decanyl
Ar	aryl
^{o}bip	ortho-biphenyl, iso-biphenyl
Bu	butyl
^{t}Bu	tert-butyl
^{t}BuDipp	2,6-$^{i}Pr_2$-4-$^{t}BuC_6H_2$
diglyme	bis(2-methoxyethyl)ether, $CH_3OCH_2CH_2OCH_2CH_2OCH_3$
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
DIBAL	$^{t}Bu_2AlH$
Dipp	2,6-diisopropylphenyl, 2,6-$^{i}Pr_2C_6H_3$
dme	1,2-dimethoxyethane
Et	ethyl
K-selectride	potassium tri-*sec*-butyl(hydrido)borate, $K^+[BHCH(CH_3)CH_2CH_3]^-$
L	ligand; in the experimental section: 2,6-$Mes_2C_6H_3$
L-selectride	lithium tri-*sec*-butyl(hydrido)borate, $Li^+[BHCH(CH_3)CH_2CH_3]^-$
^{m}	meta
Me	methyl
Mes	mesityl, 2,4,6-$Me_3C_6H_2$
Mes'	2,4,6-$^{t}Bu_3C_6H_2$
Naph	naphtyl
NICS	nucleus-independent chemical shift
NMR	nuclear magnetic resonance
^{o}	ortho
^{p}	para
Ph	phenyl
Pr	propyl
^{i}Pr	iso-propyl
Quin	quinuclidine
R	alkyl or aryl
Ter	terphenyl
tmeda	N,N,N',N'-tetramethylethylenediamine, $Me_2NCH_2CH_2NMe_2$
TMS	tetramethylsilane
TMSTrip	2-(2,3,5-$^{i}Pr_3$-6-$SiMe_3C_6H_1$)-6-Trip-C_6H_3
tolyl	MeC_6H_4
Trip	2,4,6-triisopropylphenyl, 2,4,6-$^{i}Pr_3C_6H_2$
$\Sigma\Theta(Z)$	sum of the bond angles about atom Z

5 Introduction

Low valent main group element compounds have been in the focus of intensive research for decades.*see e.g.* [1,2] The diversity of ligands deployed in literature is impressive, the variety of structural motives obtained is enormous.

The present work focuses on the deployment of two different ligand systems on the way toward low valent main group 3 (gallium, indium) and 4 (germanium, tin, lead) derivatives. On the one hand, silylamide derivatives were deployed, on the other hand phenyl based ligands (including biphenyl and terphenyl structural motives) were used in order to stabilize the low valent derivatives. The structural main features of the ligands are depicted in figure 1.



R_1 = Me, R_2 = Me
R_1 = ^{i}Pr, R_2 = H

R_1 = R_2 = Me, R_3 = R_4 = R_5 = H
R_1 = ^{i}Pr, R_2 = R_3 = R_4 = R_5 = H
R_1 = R_2 = Me, R_3 = Mes, R_4 = R_5 = H
R_1 = R_2 = Me, R_3 = Mes, R_4 = ^{i}Pr, R_5 = H
R_1 = R_2 = Me, R_3 = Mes, R_4 = H, R_5 = Cl
R_1 = R_2 = Me, R_3 = Mes, R_4 = H, R_5 = $SiMe_3$

Figure 1: Schematic representation of the two ligand classes deployed in the present work: Silylamide ligands (left) and phenyl based ligand systems (right) - including biphenyl and terphenyl ligands.

As shown in figure 1 the ligand systems were modified in comparison to derivatives known in literature. The silylamide based ligands are sterically more demanding than their already published analogs (due to the silicon substitution by two phenyl groups), while the biphenyl ligands deployed in the present work represent less sterically hindered structures than their terphenyl analogs, that have been intensively studied in the past concering the stabilization of low valent main group element compounds.

Two central questions form the basis of the present work: On the one hand, the synthesis and characterization of the low valent main group 3 and 4 derivatives is one point of interest, in particular the structures of the novel compounds are significant. The present work describes novel compounds of the following structural motives: $LGaI_2$, L_2InCl, $(LIn)_4$, $LECl$, L_2E, $Li^+(EL_3)^-$, $LEEL_3$ (L = ligand, E = Ge, Sn, Pb). One of the most important features discussed in the present work in order to characterize the structures of the synthesized compounds is the sum of angles about the central atom (nitrogen or central metal, respectively). Figure 2 gives an overview on the possible structural motives and the significance of the named sum of angles in case of threefold and fourfold coordination.

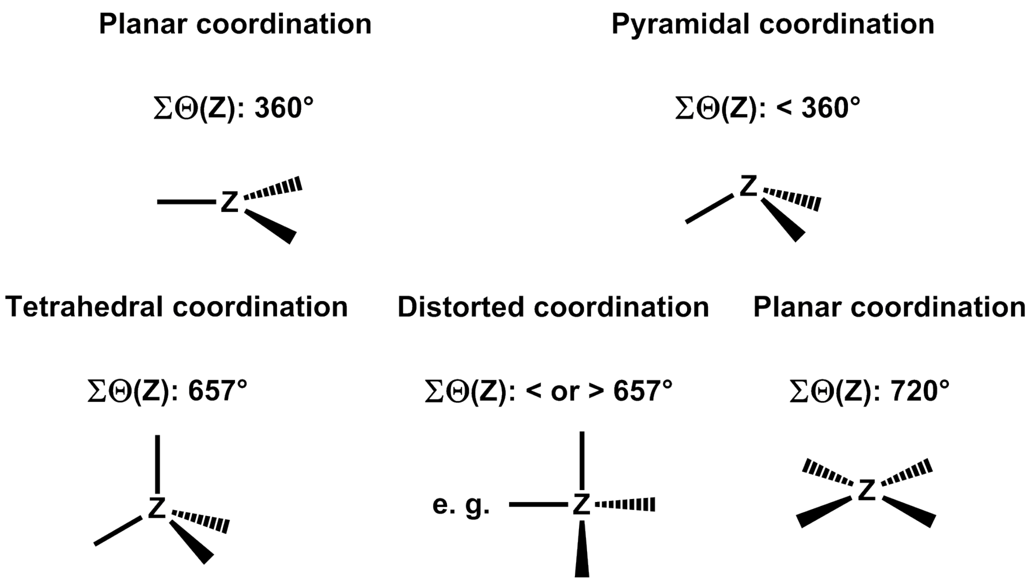


Figure 2: Sum of the angles about the central atom (Z) in case of threefold and fourfold coordination.

On the other hand, the stability and reactivity of the obtained derivatives is appealing due to the broad range of reactivity patterns described in literature. Despite the fact that literature data is extensive, novel structure and reactivity types keep being published constantly. The present work was formed in order to contribute to this fascinating field of research. The investigation of the subsequent reactions also allows a comparison of the different types of ligands deployed herein. While the silylamide based systems lead to main group element derivatives of high stability (and low reactivity), subsequent reactions of the low valent main group 3 and 4 derivatives stabilized by terphenyl ligands readily lead to novel structural motives including germoles and gallium clusters. Two of the novel structural motives described in the present work are depicted in figure 3.

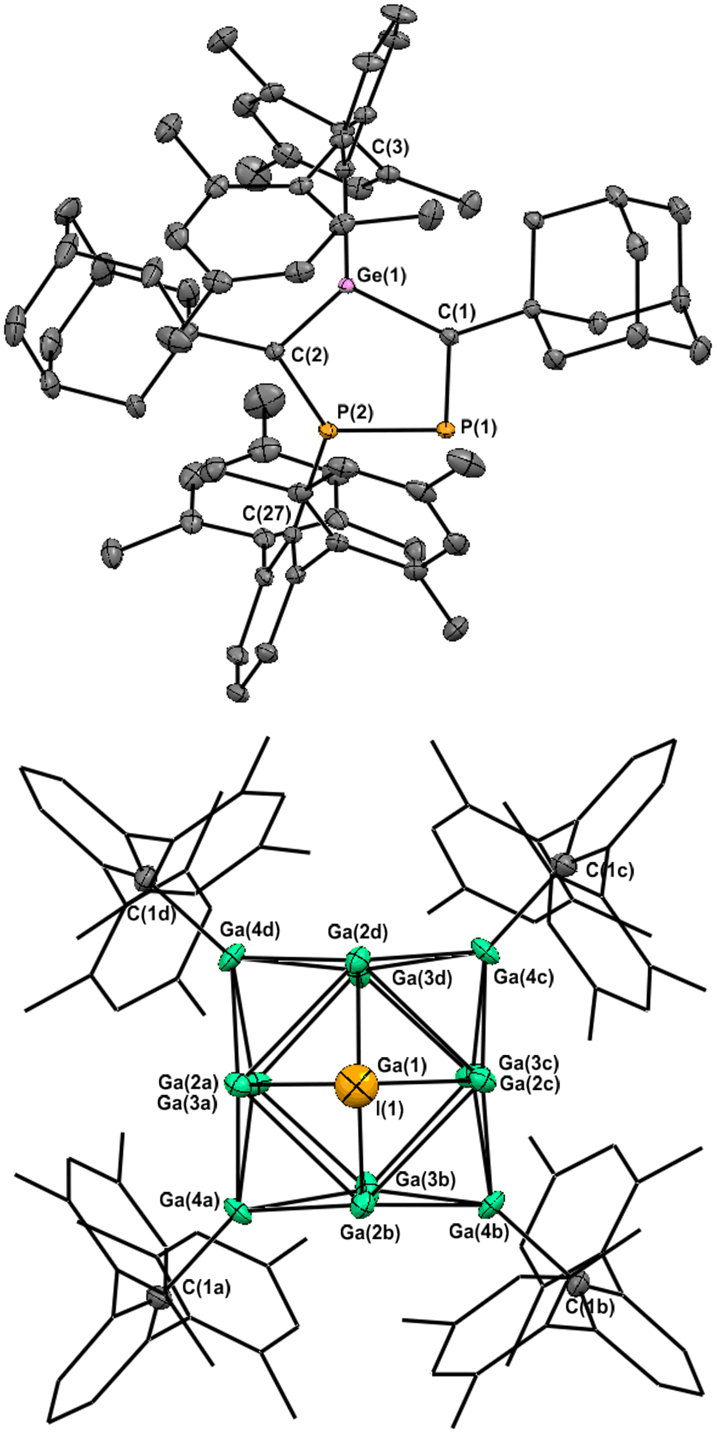


Figure 3: Two crystal structures obtained in the present work representing novel structural motives.

6 Literature

6.1 Silylamide Ligands as Stabilizing Systems

6.1.1 On the Way Toward Aryl-Substituted Silylamines

For similarity (to the compounds deployed in the present work) reasons only silylamines of the type $Ar_nR_{3-n}SiNHAr$ (n = 0 - 3) are discussed in this section. This chapter makes no claim to be complete, instead a rough overview shall be given. Compounds with aryl substitution at the silicon atom are highlighted in red. $PhNHSiEt_3$ was observed as reduction product of $NO_2NHSiEt_3$ by Dolgov et al. in 1948.[3] Most of the other syntheses discussed herein can be assigned to one of the following categories:

Synthesis Routes

- Method a) Reaction of Amines with Silylamines
- Method b) Reaction of Amides with Halosilanes or Silanes via Salt Elimination
- Method c) Reaction of Amines with Halosilanes in the Presence of an Auxiliary Base
- Method d) Reaction of Azides with Grignard Reagents Followed by Hydrolysis
- Method e) Reaction of Azides with Silanes
- Method f) Reactions in the Presence of a Catalyst
- Method g) Reactions of Amines with Silylsulfides or Silylthioles (Evolution of H_2S)
- Method h) Ring Opening Reactions

Method a) Reaction of Amines with Silylamines

In 1950 Mjorne reported the synthesis of $PhNHSiMe_3$, obtained by conversion of $NH(SiMe_3)_2$ with $PhNH_2$.[4]

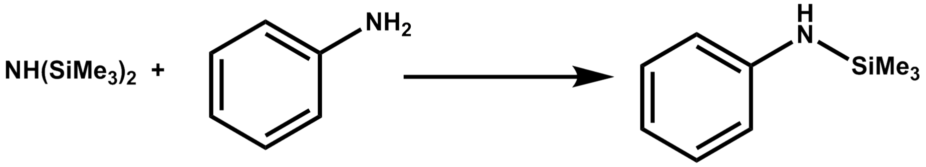


Figure 4: Synthesis of $PhNHSiMe_3$ conducted by Mjorne in 1950.[4]

In the same year Larsson and Carlsson obtained a series of silylamines by conversion of Et_3SiNH_2 with the corresponding RNH_2 (R = Ph, ^{o}tolyl, ^{p}tolyl) derivatives.[5]

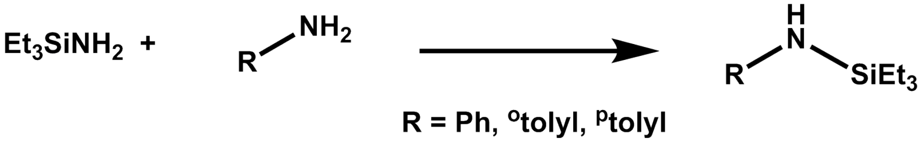


Figure 5: Dry mixtures of the starting materials were refluxed by Larsson and Carlsson in 1950 to obtain $RNHSiEt_3$ derivatives.[5]

Larsson and Marin described the syntheses of $RNHSiPr_3$ (R = Ph, $PhCH_2$ and $PhCH_2CH_2$) by conversion of the aniline based precursor with a primary or secondary amine in 1951.[6] $PhNHSiBu_3$ was described by Larsson in the year 1958. (Bu_3SiNH_2 was refluxed in aniline.)[7] $3\text{-}NO_2C_6H_4NHSiEt_3$ was obtained by converting $3\text{-}NO_2C_6H_4NH_2$ with Me_2NSiEt_3 by Ali et al. in 1974, $4\text{-}NO_2C_6H_4NHSiEt_3$ analogous to this route. $4\text{-}CNC_6H_4NHSiEt_3$ was accessible via conversion of Et_3SiNH_2 with $4\text{-}CNC_6H_4NH_2$.[8] Arai et al. published the synthesis of $2\text{-}BrC_6H_4NH$ $SiMe_3$ by conversion of $2\text{-}BrC_6H_4NH_2$ with hexamethyldisilazane (in the presence of trimethylsilyl chloride) in 1976.[9]

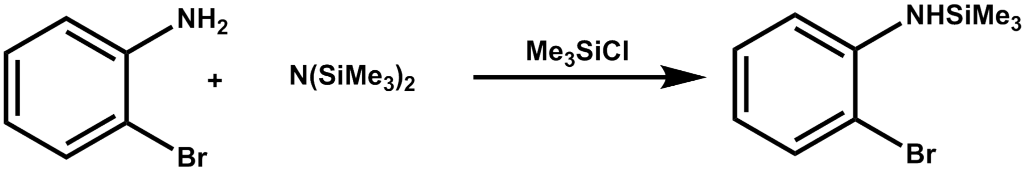


Figure 6: The synthesis of $2\text{-}BrC_6H_4NHSiMe_3$ was described by Arai et al. in 1976.[9]

A series of halogen-substituted phenylsilylamine derivatives obtained by reaction of the corresponding amine with hexamethyldisilazane and reported by Lebedev et al. is shown in table 1. $4\text{-}HOC_6H_4NHSiMe_3$ was obtained by Mojtahedi et al. in 2007 by the reaction of $4\text{-}HOC_6H_4NH_2$ with hexamethyldisilazane and activation via ultrasound.[10]

Compounds		
2-$FC_6H_4NHSiMe_3$	3-$FC_6H_4NHSiMe_3$	4-$FC_6H_4NHSiMe_3$
2,4-$F_2C_6H_3NHSiMe_3$	2,5-$F_2C_6H_3NHSiMe_3$	2,3,5,6-$F_4C_6H_1NHSiMe_3$
3-F-4-$MeC_6H_3NHSiMe_3$	3-Cl-4-F-$C_6H_3NHSiMe_3$	4-Br-2-$FC_6H_3NHSiMe_3$
2-$CF_3C_6H_4NHSiMe_3$	3-$CF_3C_6H_4NHSiMe_3$	

Table 1: Silylamine derivatives obtained by Lebedev et al. in 2006.[11]

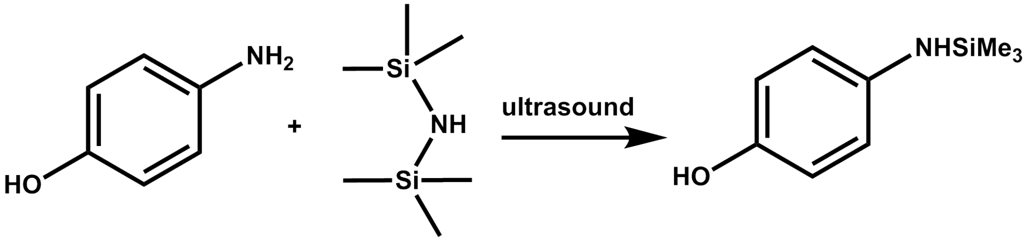


Figure 7: Conversion of 4-$HOC_6H_4NH_2$ with hexamethyldisilazane performed by Mojtahedi et al. in 2007.[10]

Method b) Reaction of Amides with Halosilanes or Silanes via Salt Elimination

Two routes can be distincted in case of method b): On the one hand, the reaction can be performed in a one-pot synthesis (reaction of an amine and a halosilane or silane in the presence of an alkali metal). Reactions of this type were performed by Chugunov[12] and Fink.[13] The preparation of $PhNHSi(Naph)_3$ was published by Chugunov in 1953.[12]

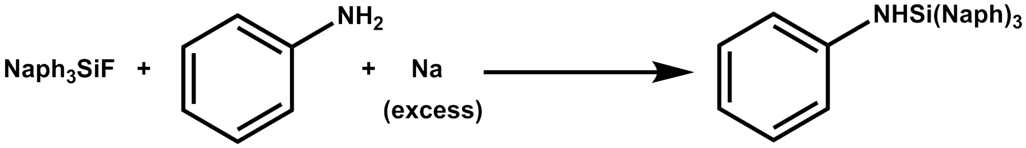


Figure 8: Synthesis route toward $PhNHSi(Naph)_3$ published by Chugunov in 1953.[12]

Fink described the synthesis of $PhNHSiMePh_2$ in 1966.[13]

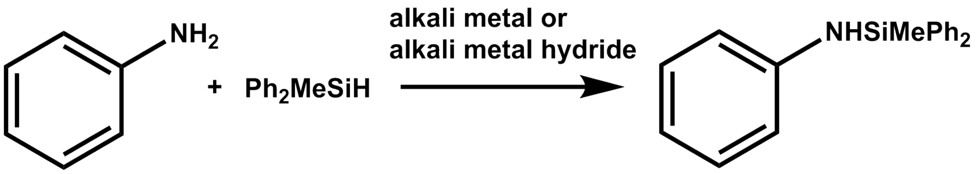


Figure 9: Fink published the synthesis of PhNHSiMePh$_2$ in 1966.[13]

On the other hand, precedent metallation of the amine (yielding the corresponding amide) and subsequent conversion with a halosilane is another route leading to silylamines. There is a great number of reactions performed through this route.

PhNHSiPh$_3$ was first synthesized by Wannagat et al. by conversion of lithiated aniline with a chlorosilane.[14]

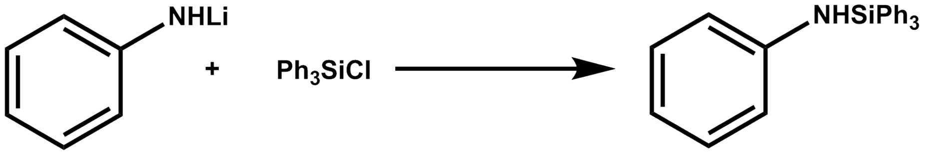


Figure 10: Reaction of lithiated aniline with a chlorosilane yielding PhNHSiPh$_3$, performed by Wannagat et al. in 1962.[14]

PhNHSiMe$_2$(C$_6$F$_5$) was obtained by Oliver and Graham in 1969. They converted the lithiated aniline with the bromosilane precursor,[15] in analogy to the reaction described by Wannagat et al.[14] Bassindale et al. reported the synthesis of a series of silylamines in the same year. The named compounds are listed in table 2. All of these compounds were obtained from the conversion of the lithiated aniline derivative with ^{i}Pr$_3$SiX (X = Br or F).[16]

Compounds		
PhNHSi^{i}Pr$_3$	^{o}tolylNHSi^{i}Pr$_3$	^{m}tolylNHSi^{i}Pr$_3$
^{p}tolylNHSi^{i}Pr$_3$	2-ClC$_6$H$_4$NHSi^{i}Pr$_3$	3-ClC$_6$H$_4$NHSi^{i}Pr$_3$
4-ClC$_6$H$_4$NHSi^{i}Pr$_3$	2-MeOC$_6$H$_4$NHSi^{i}Pr$_3$	4-MeOC$_6$H$_4$NHSi^{i}Pr$_3$
2-FC$_6$H$_4$NHSi^{i}Pr$_3$	4-FC$_6$H$_4$NHSi^{i}Pr$_3$	2,3-Me$_2$C$_6$H$_4$NHSi^{i}Pr$_3$
2,6-Me$_2$C$_6$H$_4$NHSi^{i}Pr$_3$	2-EtC$_6$H$_4$NHSi^{i}Pr$_3$	4-EtC$_6$H$_4$NHSi^{i}Pr$_3$

Table 2: Aryl-substituted silylamines obtained by Bassindale et al. in 1970.[16]

Haiduc and Gilman published the synthetic preparation of C$_6$F$_5$NHSiMe$_2$Ph also in the year 1971. They converted the lithiated amine precursor (the least basic amine) with the chlorosilane.[17] In the year 1974 Ali et al. succeeded in the preparation of a series of aryl-substituted silylamines, a list of which is given in table 3.[8]

Compounds		
$PhNHSiEt_3$	$^{o}tolylNHSiEt_3$	$^{m}tolylNHSiEt_3$
$^{p}tolylNHSiEt_3$	$2\text{-}ClC_6H_4NHSiEt_3$	$3\text{-}ClC_6H_4NHSiEt_3$
$4\text{-}ClC_6H_4NHSiEt_3$	$4\text{-}FC_6H_4NHSiEt_3$	$4\text{-}MeOC_6H_4NHSiEt_3$
$4\text{-}MeSC_6H_4NHSiEt_3$	$PhNHSiMeEt_2$	$PhNHSiMe_2^{i}Pr$
$PhNHSiMe_2tBu$	$PhNHSi^{i}Pr_3$	$PhNHSi(4\text{-}MeOC_6H_4)_3$
$PhNHSi(4\text{-}ClC_6H_4)_3$	$PhNHSi(3\text{-}ClC_6H_4)_3$	

Table 3: Aryl-substituted silylamines obtained by Ali et al. in 1974.[8]

All these compounds were obtained by conversion of the appropriate halosilane with the lithiated aniline derivative.[8] $2\text{-}EtC_6H_4NHSiMe_3$ was prepared by lithiation of $2\text{-}EtC_6H_4NH_2$ and subsequent conversion with Me_3SiCl.[18] Phillion et al. published the successful synthesis of $2,6\text{-}Et_2C_6H_4NHSiMe_3$ via conversion of $2,6\text{-}Et_2C_6H_4NH_2$ with BuLi and Me_3SiCl in the year 1986.[19] The reaction of aniline with BuLi and $Ph_2^{t}BuSiCl$ yielding $PhNHSiPh_2^{t}Bu$ was described in 1988 by Bowser et al.[20] Petrie et al. published the synthesis of $DippNHSiPh_3$ by conversion of the lithiated aniline derivative with the chlorosilane in 1993.[21] Gauvin et al. published the synthesis of $H_2NCH_2C_6H_4NHSiMe_3$ via conversion of $H_2NCH_2C_6H_4NH_2$ with BuLi and subsequent trimethylsilylation (with Me_3SiCl) in 2001.[22] Also in 2001, $2\text{-}PhOC_6H_4NHSiMe_3$ was obtained by Deacon et al.[23] In the year 2008 $2,4,6\text{-}Br_3C_6H_2NHSiMe_3$ and $2,6\text{-}Br_2C_6H_3NHSiMe_3$ were obtained via conversion of the aniline derivative with EtMgBr and subsequent addition of Me_3SiCl by Storozhenko et al.[24] Further reaction of these products with BuLi, Me_3SiCl and HCl led to the synthesis of $2\text{-}Br\text{-}6\text{-}SiMe_3C_6H_3NHSiMe_3$, $2\text{-}Br\text{-}4,6\text{-}(SiMe_3)_2C_6H_2NHSiMe_3$, $2,4\text{-}Br_2\text{-}6\text{-}SiMe_3C_6H_2NHSiMe_3$ and $4\text{-}Br\text{-}2,6\text{-}(SiMe_3)_2 C_6H_2NHSiMe_3$.[24] Li et al. obtained $2,6\text{-}(CHPh_2)_2\text{-}4\text{-}MeC_6H_2NHSiMePh_2$, $2,6\text{-}(CHPh_2)_2\text{-}4\text{-}MeC_6H_2NHSiPh_3$ and $2,6\text{-}(CHPh_2)_2\text{-}4\text{-}MeC_6H_2NHSiMe_3$ by lithiation of $2,6\text{-}(CHPh_2)_2\text{-}4\text{-}MeC_6H_2NH_2$ and subsequent conversion with $Ph_2MeSiCl$, Ph_3SiCl and Me_3SiCl, respectively, in the year 2011.[25] In the same year Pace et al. presented a series of silylamines as products of the ^{t}butyldimethylsilyl protection of the corresponding aniline derivative.[26]

Compounds	
$PhNHSiMe_2^tBu$	$2,3\text{-}Me_2C_6H_3NHSiMe_2^tBu$
$3,5\text{-}(MeO)_2C_6H_3NHSiMe_2^tBu$	$3\text{-}MeOC_6H_4NHSiMe_2^tBu$
$3,4\text{-}F_2C_6H_3NHSiMe_2^tBu$	$3\text{-}CF_3C_6H_4NHSiMe_2^tBu$
$4\text{-}NO_2C_6H_4NHSiMe_2^tBu$	3-F-4-morpholino-$C_6H_3NHSiMe_2^tBu$
$2\text{-}IC_6H_4NHSiMe_2^tBu$	$4\text{-}BrC_6H_4NHSiMe_2^tBu$
$4\text{-}CH_3COC_6H_4NHSiMe_2^tBu$	$4\text{-}CH_3CH_2OCOC_6H_4NHSiMe_2^tBu$
$4\text{-}CNC_6H_4NHSiMe_2^tBu$	$3\text{-}H_2NCH_2C_6H_4NHSiMe_2^tBu$

Table 4: Aryl-substituted silylamines investigated by Pace et al. in 2011.[26]

Stewart et al. described the synthesis of oily $3,5\text{-}(CF_3)_2C_6H_3NHSiMe_3$ by lithiation of $3,5\text{-}(CF_3)_2C_6H_3NH_2$ and subsequent conversion with Me_3SiCl in 2012.[27]

Method c) Reaction of Amines with Halosilanes in the Presence of an Auxiliary Base

Larsson and Mjorne obtained $PhNHSiEt_3$ (that had already been described by Dolgov et al. one year earlier[3]) by converting Et_3SiCl with $PhNH_2$ in 1949. The same paper described the analogous synthesis route toward ^{p}tolylNHSiEt$_3$ in C_6H_6.[28]

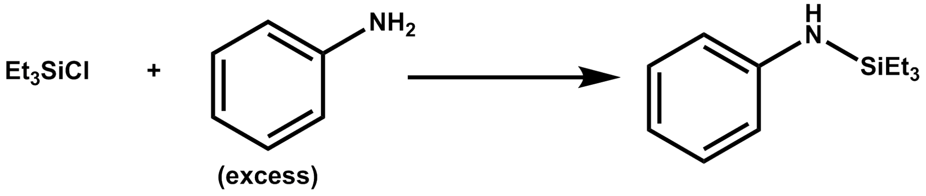


Figure 11: The synthesis route toward $PhNHSiEt_3$ described by Larsson and Mjorne in 1949.[28]

Klebe et al. published the synthesis of $PhNHSiMe_2Ph$ by conversion of the amine and the chlorosilane in presence of triethylamine as auxiliary base in 1964. They also described the analogous procedure for the preparation of ^{m}tolylNHSiMe$_3$.[29]

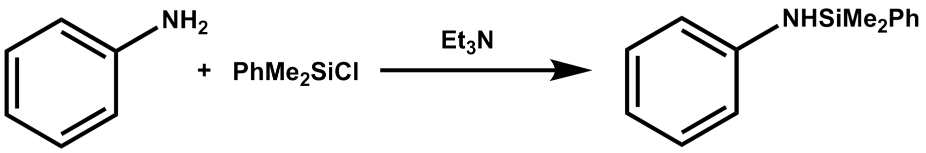


Figure 12: Conversion of an amine with a chlorosilane in the presence of Et_3N as reported by Klebe et al. in 1964.[29]

In 1967 Andrianov et al. published the syntheses of PhNHSiMeEtPh, PhNHSiMe$_2$Ph and PhNHSiMePh$_2$. The syntheses were performed in analogy to Klebe et al.'s procedure,[29] but deployed Et$_2$O as additional solvent.[30] PhNHSiMe$_3$ was obtained by Pikies et al. in 1978 trough reaction of the corresponding amine with the chlorosilane.[31] In the year 1985 Aizpurua and Palomo reported the synthesis of ^{p}tolylNHSiMe$_2^t$Bu by conversion of Me$_2^t$BuSiCl with ^{p}tolylNH$_2$ in the presence of the base 1,8-diazabicyclo[5.4.0]undec-7-ene.[32] In the year 2007 Levin et al. published the synthesis route toward PhNHSi(C$_6$F$_5$)$_3$ via conversion of aniline with (C$_6$F$_5$)$_3$SiCl in the presence of Et$_3$N.[33] PhNHSi^{t}Bu$_2^i$Bu was obtained by Liang et al. in 2011 by the reaction of aniline with ^{t}Bu$_2^i$BuSiOSO$_2$CF$_3$ in the presence of Et$_3$N.[34]

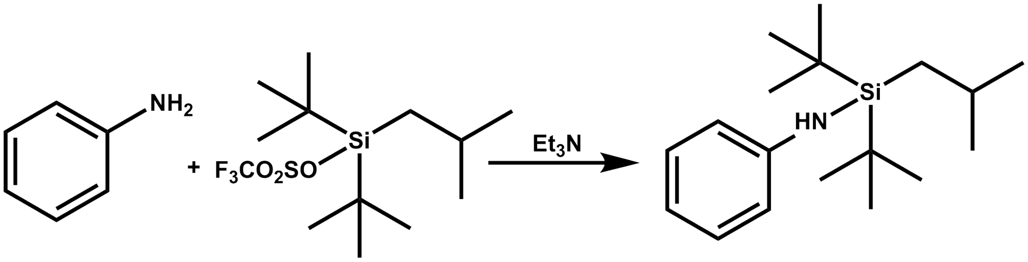


Figure 13: Synthesis of PhNHSi^{t}Bu$_2^i$Bu performed by Liang et al. in 2011.[34]

Method d) Reaction of Azides with Grignard Reagents Followed by Hydrolysis

In the year 1970 Wiberg and Joo obtained MesNHSiPh$_3$, ^{m}tolylNHSiPh$_3$, ^{o}tolylNHSiPh$_3$ and ^{p}tolylNHSiPh$_3$ by conversion of Ph$_3$SiN$_3$ with the corresponding RMgBr compound followed by careful hydrolysis in H$_2$O/Et$_2$O.[35]

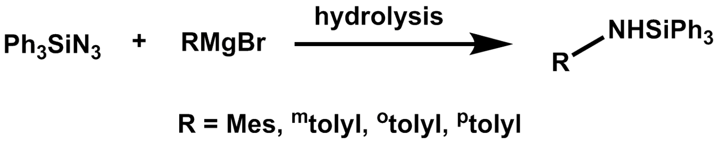


Figure 14: The synthesis route via conversion of Ph$_3$SiN$_3$ with grignard reagents followed by Wiberg and Joo in 1970.[35]

Method e) Reaction of Azides with Silanes

PhNHSiMePh(Naph) was described in a paper by Carey and Hsu in the year 1970.[36]

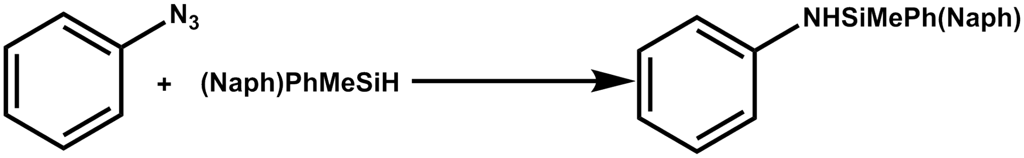


Figure 15: Conversion of phenyl azide with a silane yielding PhNHSiMePh(Naph).[36]

Benati et al. obtained a series of aryl-substituted silylamines by conversion of the corresponding amine with Et_3SiH in the presence of NaN_3 or the conversion of the corresponding azidobenzene with Et_3SiH. The compounds obtained are listed in table 5.[37]

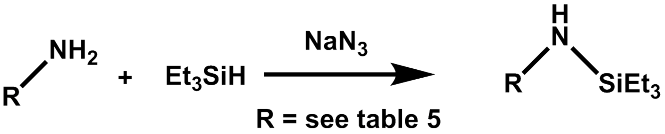


Figure 16: One of the two routes followed by Benati et al. in 2006 on the way toward aryl-substituted silylamines.[37]

Compounds		
$PhNHSiEt_3$	^{o}tolylNHSiEt$_3$	^{p}tolylNHSiEt$_3$
$2\text{-}MeOC_6H_4NHSiEt_3$	$3\text{-}MeOC_6H_4NHSiEt_3$	$4\text{-}MeOC_6H_4NHSiEt_3$
$2\text{-}ClC_6H_4NHSiEt_3$	$3\text{-}ClC_6H_4NHSiEt_3$	$4\text{-}ClC_6H_4NHSiEt_3$
$2\text{-}FC_6H_4NHSiEt_3$	$4\text{-}FC_6H_4NHSiEt_3$	$4\text{-}NO_2C_6H_4NHSiEt_3$
$4\text{-}CNC_6H_4NHSiEt_3$	$2\text{-}PhC_6H_4NHSiEt_3$	$1\text{-}/2\text{-}NaphNHSiEt_3$

Table 5: Aryl-substituted silylamines obtained by Benati et al. in 2006.[37]

Method f) Reactions in the Presence of a Catalyst

Dennis and Speier published the synthesis of $PhNHSiMe_2Hex$ by conversion of $PhNHSiMe_2H$ and 1-hexene in the presence of H_2PtCl_6 in 1970.[38] A series of silylamine derivatives was obtained by Smith et al. in 1986 by reacting the corresponding ^{o}toluidine derivative with $(Me_3Si)_2NH$ in the presence of catalytic amounts of LiI and Me_3SiCl. ('Silylation, which occurs without the added lithium iodide, is much faster in the presence of iodide, presumably due to the *in situ* formation of a catalytic amount of the more reactive trimethylsilyl iodide.')[39] The products of these syntheses are listed in table 6.

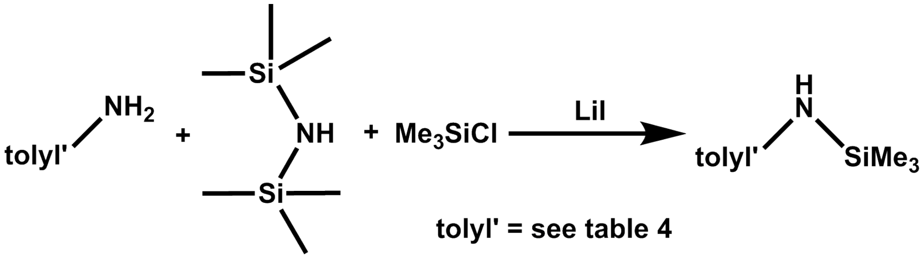


Figure 17: Synthesis of a series of toluidine derivatives, conducted by Smith et al. in 1986.[39]

Compounds	
^{o}tolylNHSiMe$_3$	2,6-Me$_2$C$_6$H$_3$NHSiMe$_3$
2-Me-4-MeO-C$_6$H$_3$NHSiMe$_3$	6-Me-3-MeO-C$_6$H$_3$NHSiMe$_3$
4-F-2-Me-C$_6$H$_3$NHSiMe$_3$	4-Cl-2-Me-C$_6$H$_3$NHSiMe$_3$
2,3-Me$_2$C$_6$H$_3$NHSiMe$_3$	2,4-Me$_2$C$_6$H$_3$NHSiMe$_3$
2,5-Me$_2$C$_6$H$_3$NHSiMe$_3$	2-EtC$_6$H$_4$NHSiMe$_3$

Table 6: Aryl-substituted silylamines obtained by Smith et al. in 1986.[39]

$PhNHSiMePh_2$ and $PhNHSiMe_2Ph$ were obtained by heating of equimolar quantities of the organosilane (Ph_2MeSiH or $PhMe_2SiH$, respectively) and aniline in the presence of a catalytic quantity of sodium hydride by Breed et al. in 1971.[40] In 2013 Koenigs et al. published the conversion of Me_2PhSiH with ^{o}tolylNH$_2$, $MesNH_2$, 4-CF$_3$C$_6$H$_4$NH$_2$ and 2-BrC$_6$H$_4$NH$_2$ in the presence of a ruthenium catalyst yielding ^{o}tolylNHSiMe$_2$Ph, $MesNHSiMe_2Ph$, 4-CF$_3$C$_6$H$_4$NHSiMe$_2$Ph and 2-BrC$_6$H$_4$NHSiMe$_2$Ph, respectively.[41]

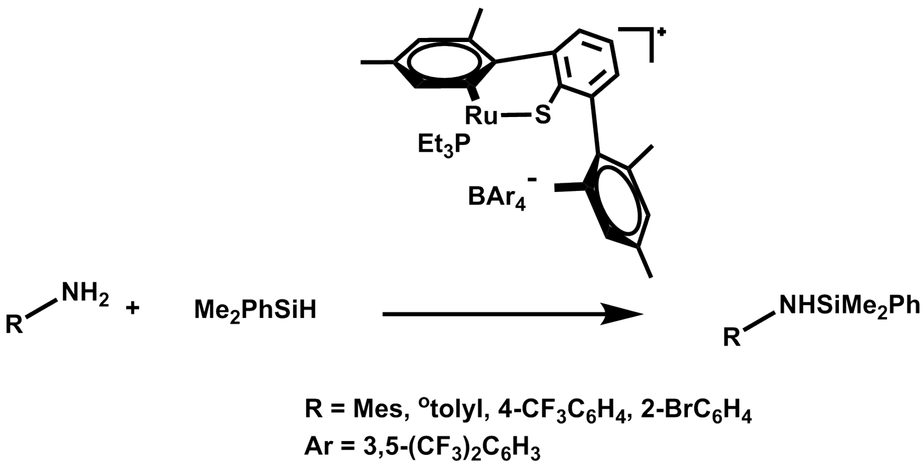


Figure 18: Series of silylamine derivatives published by Koenigs et al. in 2013.[41]

^{p}tolylNHSiPh$_2$Me was observed by Stahl et al. in 2013 following an analogous route.[42]

Method g) Reactions of Amines with Silylsulfides or Silylthioles (Evolution of H_2S)

In 1975 Lebedev and Baburina converted $(Me_3Si)_2S$ with RNH_2 (R = Ph, Naph), respectively, yielding the corresponding silylamines.[43]

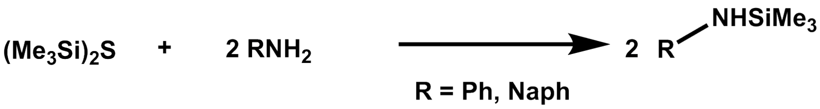


Figure 19: RNHSiMe$_3$ derivatives described by Lebedev and Baburina in 1975.[43]

Furthermore, they obtained 3-HOC$_6$H$_4$NHSiMe$_3$ by conversion of 3-HOC$_6$H$_4$NH$_2$ with $(Me_3Si)_2S$ via 3-Me$_3$SiOC$_6$H$_4$NHSiMe$_3$.[43] 4-ClC$_6$H$_4$NHSiPh$_3$ was synthesized by deploying triphenylsilanethiole and the corresponding amine by Pikies et al. (see figure 20). PhNHSiPh$_3$ was obtained by the analogous route.[31]

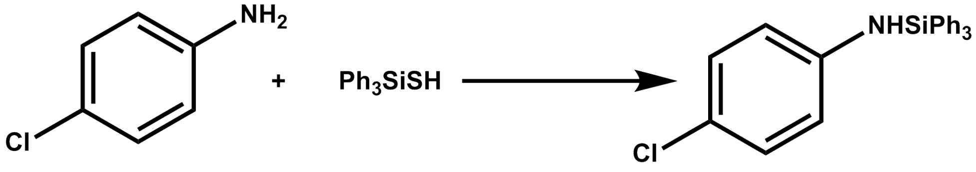


Figure 20: Conversion of triphenylsilanethiole with an amine yielding 4-ClC$_6$H$_4$NHSiPh$_3$.[31]

Method h) Ring Opening Reactions

Seyferth et al. described the synthesis of PhNHSiMe$_2$(CMe$_2^i$Pr) by ring opening of hexamethylsilirane via aniline in the same year.[44]

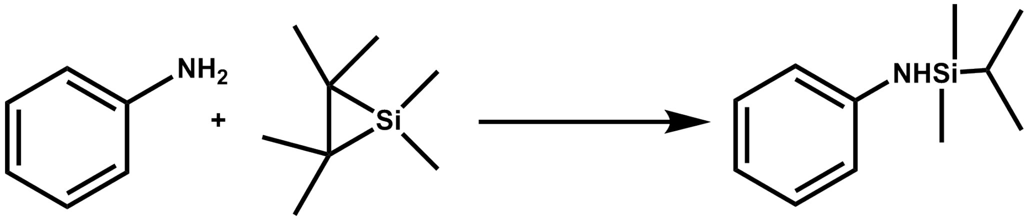


Figure 21: The ring opening of hexamethylsilirane by aniline published by Seyferth et al. in 1982.[44]

As can be seen from this chapter, synthesis routes toward silylamides are manifold. A Science of Synthesis article by Chiara from the year 2007 even named 15 methods of preparation of N-silylarylamines, one of which is the 'reaction of halosilanes with arylamines' (or lithium amides).[45] This method has been cited several times in this chapter, which shows the significance of the route. This method was also deployed to yield the silylamines described in the present work.

Reactions of Silylamines

Aryl-substituted silylamines have been precursors for a wide variety of reactions as indicated by the following section.

PhNHSiMeEtPh was deployed as polymerization precursor by Andrianov's working group in the year 1966.[46] Yoder discussed the ^{19}F NMR spectrum of 4-FC$_6$H$_4$NHSiMe$_3$ in a paper from the year 1971.[47] An article published by Pestunovich et al. from the year 1977 described a series of silylanilines studied concerning their ^{29}Si NMR shifts (compounds are listed in table 7).[48]

Compounds		
PhNHSiMe$_3$	^{p}tolylNHSiMe$_3$	^{m}tolylNHSiMe$_3$
3-MeOC$_6$H$_4$NHSiMe$_3$	4-MeOC$_6$H$_4$NHSiMe$_3$	3-ClC$_6$H$_4$NHSiMe$_3$
4-ClC$_6$H$_4$NHSiMe$_3$	4-BrC$_6$H$_4$NHSiMe$_3$	4-NO$_2$C$_6$H$_4$NHSiMe$_3$
3-NO$_2$C$_6$H$_4$NHSiMe$_3$		

Table 7: Aryl-substituted silylamines obtained by Pestunovich et al. in 1977.[48]

4-MeOC$_6$H$_4$NHSiMe$_3$ had also been described in an earlier paper by Couch and Williams from the year 1972.[49] A series of silylamines RNHSiMe$_3$ (R = 2,6-

$Me_2C_6H_3$, Mes, 3-$CF_3C_6H_4$, 2-FC_6H_4, 3-$CF_3C_6H_4$, Ph) was described by Maringgele and Meller in 1978 as starting materials in the synthesis of borane derivatives. The authors obtained amidinoboranes via silylamidines.[50] Kaufmann et al. studied the ethanolysis rate constants of 4-$RC_6H_4NHSiMe_3$ (R = MeO, Me, H, F, Cl, I), $PhNHSiMe_2Ph$, $PhNHSiMe_2(4\text{-}MeOC_6H_4)$, $PhNHSiMe_2(4\text{-}ClC_6H_4)$ and $PhNHSiMe_2^{p}tolyl$ in 1981.[51] The selective bromination of 2,5-$Me_2C_6H_3NHSiMe_3$ with bromosuccinimide was investigated by Ando and Tsumaki in 1982.[52] Clegg et al. published the preparation of $MesNHSiMes_2^{t}Bu$ via conversion of $^{t}BuLi$ and $MesNHSiMes_2F$ in the year 1984.[53] 2-$EtC_6H_4NHSiMe_3$ and 2-$MeC_6H_4NHSiMe_3$ were deployed as starting materials on the way toward indole derivatives by Smith and Visnick in 1985.[18] 4-$^{t}BuC_6H_4NHSiMe_3$ was mentioned in a patent from the same year by Findeisen and Fauss.[54] 3-$CH{\equiv}CC_6H_4NHSiMe_3$ was described in 1988 by Evers et al. as precursor for polyamides.[55] A patent by Pearson et al. from the same year mentioned 2,6-$Cl_2C_6H_3NHSiMe_3$ and 2,6-$F_2C_6H_3NHSiMe_3$ as amidation reagents.[56] Kokorev et al. investigated the reactions of $PhNHSiMe_3$, 2-$MeOC_6H_4NHSiMe_3$, 2-$ClC_6H_4NHSiMe_3$ and 4-$ClC_6H_4NHSiMe_3$ (after lithiation) with chloroarsines in 1991. A schematic reaction pathway is shown in figure 22. Also, $^{p}tolylNHSiMe_3$ and $^{o}tolylNHSiMe_3$ were mentioned in the same paper.[57]

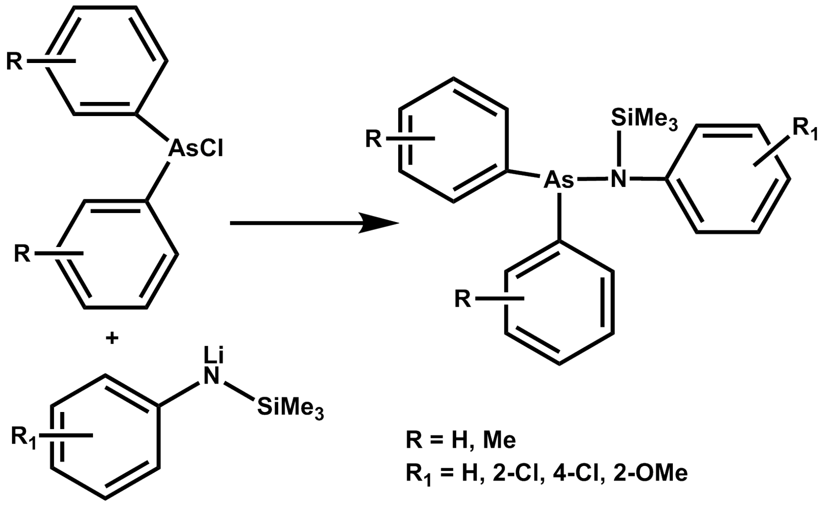


Figure 22: Kokorev et al.'s reactions of silylamides with chloroarsines from the year 1991.[57]

In 1994 Bryce et al. deployed 4-$CNC_6H_4NHSiMe_3$ and 2-$CNC_6H_4NHSiMe_3$ in the reaction with chlorosulfanylphthalimide. One of the reactions is depicted in figure 23.[58]

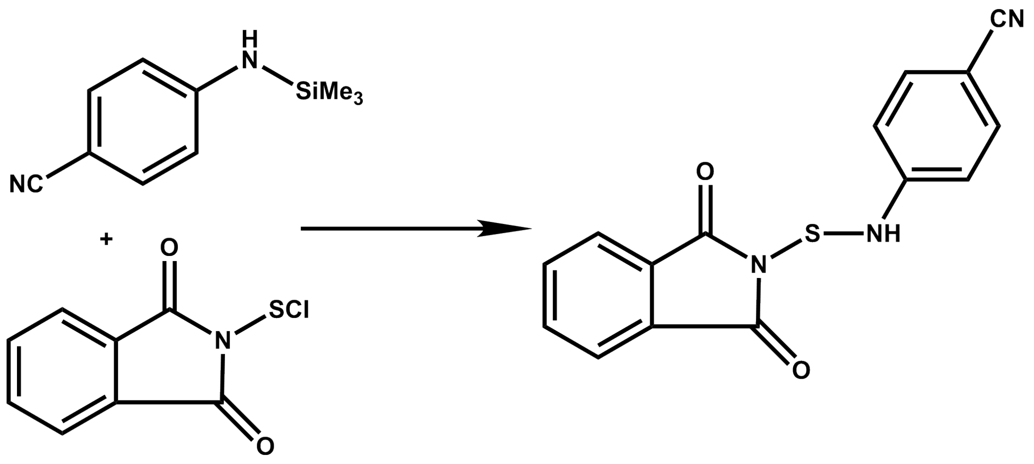
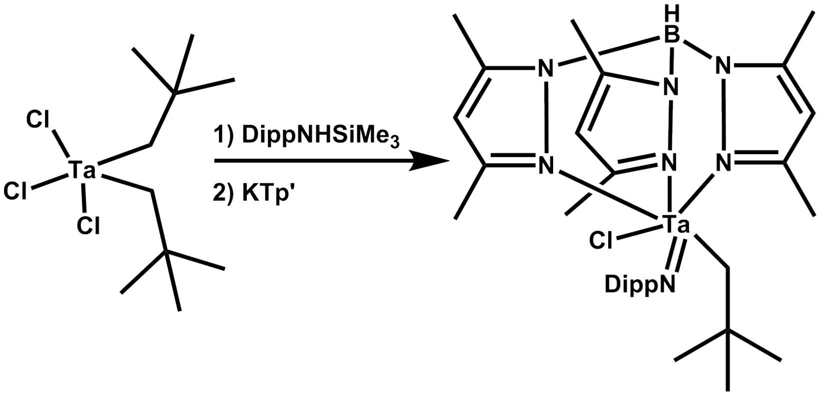


Figure 23: Reaction of a silylamine with chlorosulfanylphthalimide published by Bryce et al. in 1994.[58]

The same group published the reactions of the compounds $RNHSiMe_3$ (R = 2-BrC_6H_4, 4-BrC_6H_4, ^{p}tolyl, 2-PrC_6H_4) toward the corresponding sulfenyl chlorides ($RN(SCl)SiMe_3$) by conversion with SCl_2 in the presence of Et_3N in the same year.[59] Hamada et al. published the deployment of 3-$BrC_6H_4NHSiMe_3$ (amongst others) toward the corresponding N,N-disilylamine 3-$BrC_6H_4N(SiMe_3)_2$ in the year 1996.[60] $DippNHSiMe_3$ was deployed as imidation reagent of a tantalum neopentyl halide complex by Boncella et al. also in 1996.[61]



= $Tp'Ta(CH_2C(CH_3)_3)(NDipp)Cl$

Figure 24: Imidation of a tantalum neopentyl halide complex described by Boncella et al. in 1996.[61]

Waezsada et al. described the reaction of $AlMe_3$ with 2,6-$Me_2C_6H_3NHSiMe_2^tBu$, 2,6-$Me_2C_6H_3NHSiMe_2Mes$, $DippNHSiMe_2^tBu$, $DippNHSiMe_2^iPr$ and $DippNHSiMe_3$, respectively, in 1997. As products the corresponding diorganoaminodimethylalanes were obtained.[62] In 1998 Chan et al. investigated the reaction of 2-^{t}BuC_6H_4NHSiMe$_3$ with (C_5H_5)NbCl$_4$ in the presence of 2,6-dimethylpyridine yielding 2-^{t}BuC_6H_4N Nb(C_5H_5)Cl$_2$.[63] Schrock et al. mentioned the phosphination of 2,6-Me$_2$C$_6$H$_3$NH SiMe$_2$CH$_2$Cl in 1999.[64]

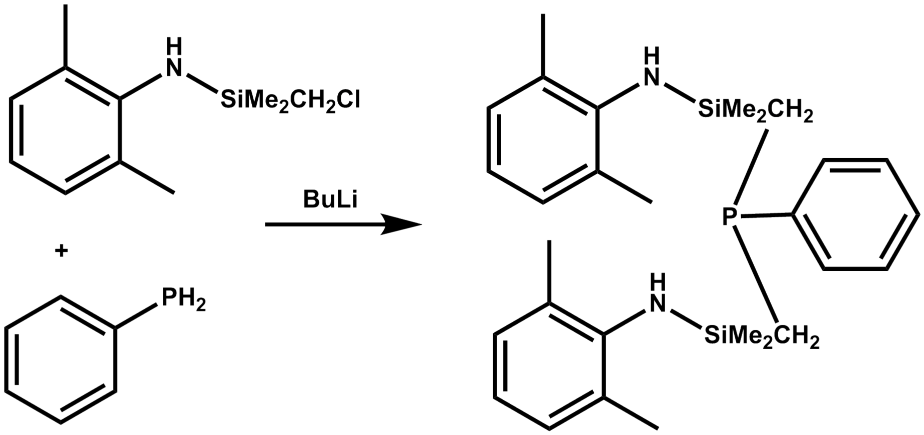


Figure 25: Silylamine phosphination described by Schrock et al. in 1999.[64]

Ernst mentioned 4-CH≡CC_6H_4NHSiMe$_3$ in the synthesis of starting materials on the way toward cp*ruthenacyclopentatrienes in 2002.[65] In the year 2005 Zakharov et al. used 2-Br-4-MeC_6H_3NHSiMe$_3$ on the route toward ditelluride derivatives.[66]

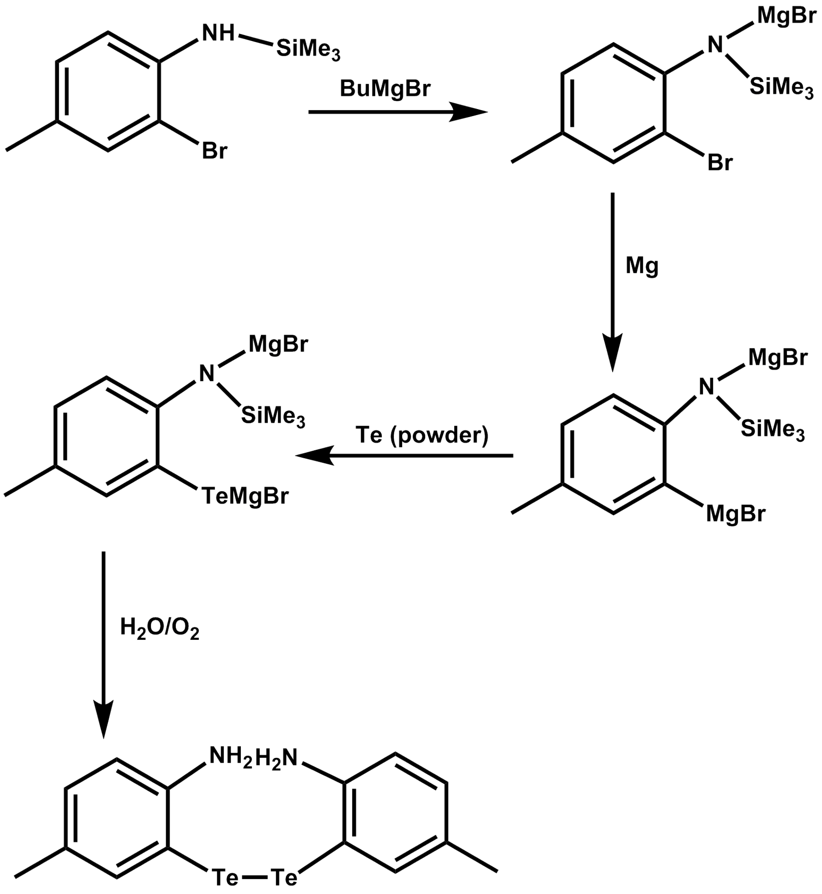


Figure 26: Deployment of a silylamine on the route toward ditelluride derivatives, described by Zakharov et al. in 2005.[66]

A patent from the year 2010 lists ^{m}tolylNHSiMe$_2$Ph as one reagent deployed for ethylene polymerization.[67]

The diversity of deployments of silylamines in subsequent reactions can be clearly seen from this chapter. The use of this interesting compound class as polymer precursors, as reagents toward boron, bromine, arsenic, aluminum or phosphorus derivatives or as amidation reagents are only some important examples shown in this section.

6.1.2 The Use of Aryl-Substituted Silylamides in Stabilizing Main Group 1, 3 and 4 Element Compounds

6.1.2.1 Lithium, Sodium and Potassium Derivatives

Antolini et al. discussed the diversity of structural motives of crystalline metal amides in their publication from the year 2000: 'In the absence of a neutral coligand, they are polymers [...], trimers [...] or tetramers [...].'[68] While a great number of e.g. disilylamides is known in literature, examples following the herein discussed structural motive $Ar_nR_{3-n}SiNMAr$ (M = alkali metal) are not too excessively present. In 2009 Lappert et al. discussed the preparation and synthesis of metal amides in their book 'Metal Amide Chemistry'. They stated in the introduction of chapter 2 ('Alkali Metal Amides') that 'Amido derivatives of the alkali metals enjoy the most widespread use of all metal amides. This is a result of their central importance as amide ligand transfer agents for the synthesis of other element amido derivatives throughout the Periodic Table.'[69] While a number of lithium amides of the described structures is known in literature, sodium and potassium derivatives are rare. Lappert et al. reported that 'Lithium amides are the most important of the alkali metal amides. This is mainly due to the facility with which they can be prepared in solution by the simple reaction of the amine with commercially available ^{n}BuLi. An analogous reaction with heavier metal alkyls is much more difficult due to the high reactivity of heavier alkali metal alkyls which attack many solvents. Another advantage of lithium amides is that they tend to be more soluble in hydrocarbons than their heavier element congeners. This is due to the small size (and hence greater polarizing power) of the lithium ion, which induces greater covalent character.'[69] The correlation of gaseous state, solubility and reactivity is one of the most interesting ones when focussing on this class of compounds, which is why the molecular structures of the aryl-substituted silylamide derivatives are of special interest. The reason for the significance of this correlation lies amongst others in the importance of obtaining the amides free from coordinating solvent molecules. Those could e.g. lead to subsequent ether cleavage in the following reactions. One can state, that – while a great variety of structural motives of the main group 1 amides is known (including e.g. monomeric to tetrameric, ladder and polymeric structural motives) – not too many examples of aryl-substituted silylamide derivatives have been characterized up to the present. Like in the previous chapter, only the first appearance of each structure or their later first structural description in literature shall be discussed herein.

The monomeric (due to the 'very large substituents at the amido ligand'[69]) structure of Mes'NLiSi^{i}Pr$_2$X{thf}$_3$ (X = F, Cl) was published by Boese and Klingebiel in 1986 [ΣΘ(N): 359.9°].[70] C_6F_5NLiSi^{t}Bu$_2$F{thf}$_2$ was described as a monomeric derivative (due to the same reason) by Stalke et al. in 1988.[71] In the year 1991 Kennepohl et al. published the dimeric, solvent-free crystal structure of [DippNLiSiMe$_3$]$_2$ [ΣΘ(N): 643.8/645.5°].[72] PhNKSiMe$_3$ was first described by Hitchcock et al. in 2002, obtained via conversion of PhNHSiMe$_3$ with an excess of KH. Furthermore, this compound was used as reactant for the preparation of ytterbium(II) phenyl(trimethylsilyl)amido thf complexes.[73] DippNKSiMe$_3$ was mentioned as precursor toward LaBr{DippNSiMe$_3$}$_2${thf} by Hitchcock et al. in 2004[74] and had been already described in a patent from the year 2000.[75] Antolini et al. published the crystal structure of a tetrameric lithium derivative [LiN(SiMe$_3$)Ph]$_4$ in the year 2000.[68] This compound had been synthesized by lithiation of the amine precursor with BuLi by Barnett et al. in 1991.[76]

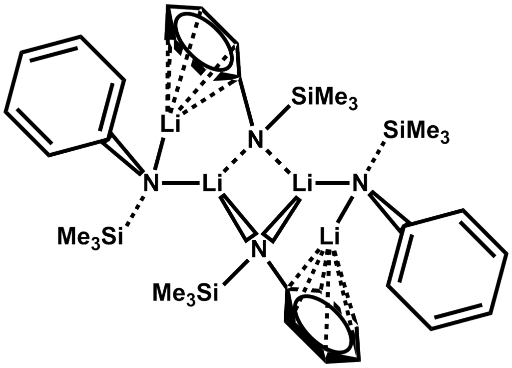


Figure 27: The tetrameric lithium derivative obtained by Barnett et al. in 1991[76] and structurally characterized by Antolini et al. in 2000.[68]

The structure of the lithium amide can be described as follows: 'the structure [...] in which there is a dimeric {LiN(SiMe$_3$)Ph}$_2$ core wherein each lithium is also bound to the nitrogen of another LiN(SiMe$_3$)Ph unit whose lithium has η^6 by the phenyl contacts from the core {LiN(SiMe$_3$)Ph}$_2$ dimer.'[69] The group published a novel sodium amide in the same paper, the structure of which is shown in figure 28.[68]

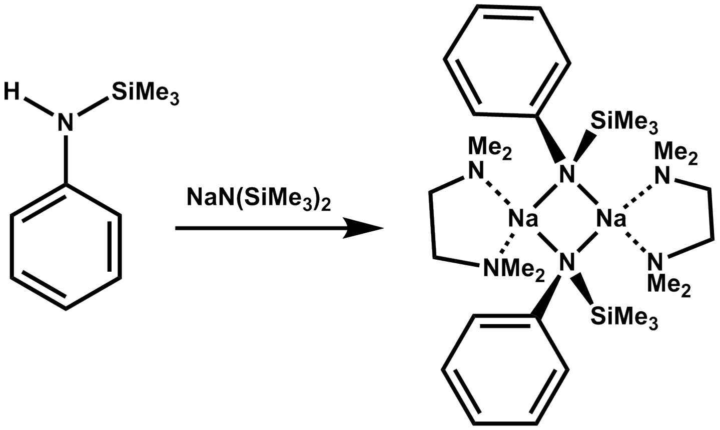


Figure 28: The sodium amide obtained by Antolini et al. in 2000.[68]

The crystal structure of the lithium derivative changes significantly in the presence of the chelating bidentate ligand tmeda: Bezombes et al. described the polymeric structure of [{LiN(Ph)($SiMe_3$)}{tmeda}]∞ [ΣΘ(N): 648.2°] in the year 2001.[77]

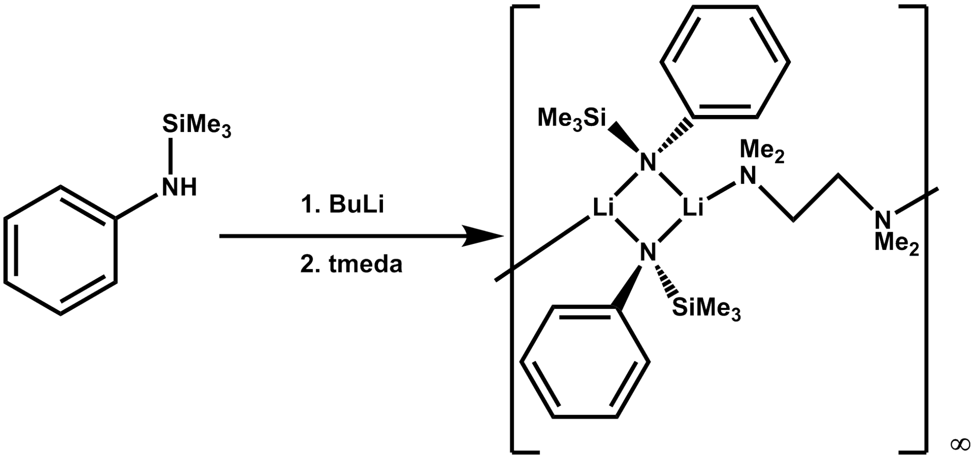


Figure 29: The polymeric lithium amide structure published by Bezombes et al. in 2001.[77]

Lappert et al. described the structure of this compound as follows: 'the bridging mode of the bidentate tmeda ligand [...] facilitates the formation of infinite chains of planar [...] $(LiN)_2$ units. [...] The lithium ions are three-coordinate with nearly planar, distorted trigonal geometry.'[69] Also in 2001, Deacon et al. published the synthesis of a series of 'structurally diverse organoamides and organoamido-, organo-metallic-lithium aggregates' deploying their ligand already mentioned above. Their results pointed out the diversity of lithium derivatives stabilized by silylamides [ΣΘ(N): 359.7° for compound **b**].[23]

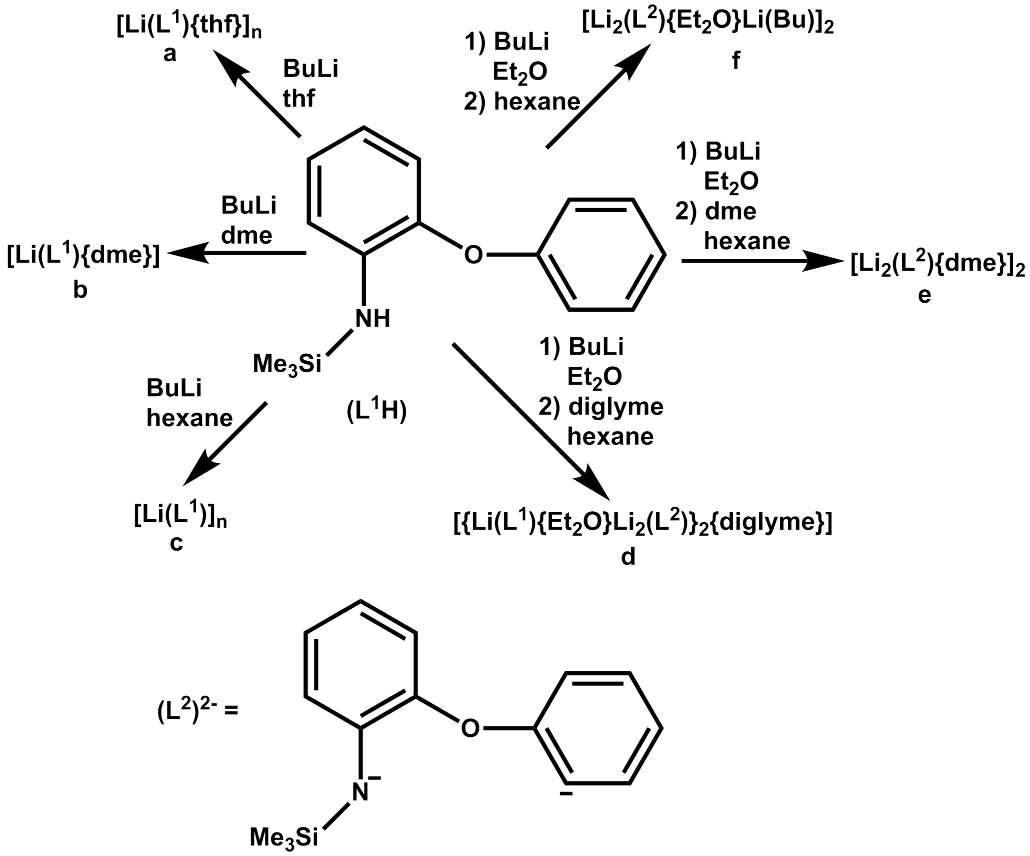


Figure 30: Lithium derivatives published by Deacon et al. in 2001. (n in compounds **a** and **c** indicates that the composition was determined via elemental analyses only and X-ray data was not obtained, which is why only the stoichiometry is known.)[23]

In 2007 Hitchcock et al. published the syntheses of the sodium and potassium salts of $PhNHSiMe_3$. These compounds were used as precursors on the reaction pathway toward metal benzamidinates. No structural information on the derivatives was given, since they were deployed in-situ for further reactions.[78] Zhou et al. reported the use of the Li/Na (1:1) salt of $DippNHSiMe_3$ for the synthesis of lanthanide amide complexes in 2009.[79] $PhNKSiMe_3\{thf\}$ was obtained by Thomson et al. in 2010 via reduction of $PhNHSiMe_3$ with $K[N(SiMe_3)_2]$ in hexanes/thf and deployed for the subsequent synthesis of uranium mixed-ligand metallocene complexes.[80] Schädle et al. published the crystal structure of monomeric $DippNLiSiMe_3\{thf\}_3$ in a paper from the same year [$\Sigma\Theta(N)$: 359.0°].[81] In 2011 Li et al. described the synthesis of 2,6-$(CHPh_2)_2$-4-$MeC_6H_2NLiSiMe_3\{L\}$ (L = Et_2O or thf) [$\Sigma\Theta(N)$: 359.90° for L = Et_2O, note: this compound shows η^1-interactions of the lithium atom toward one phenyl group of the ligand; $\Sigma\Theta(N)$:

358.04° for L = thf, note: this compound shows η^3-interactions of the lithium atom toward one phenyl group of the ligand], 2,6-$(CHPh_2)_2$-4-$MeC_6H_2NNaSiMe_3\{thf\}_3$ [$\Sigma\Theta$(N): 359.95°] and 2,6-$(CHPh_2)_2$-4-$MeC_6H_2NKSiPh_3\{Et_2O\}$ [$\Sigma\Theta$(N): 359.97°, note: this compound shows two η^3- and one η^1-interaction of the potassium atom toward the flanking phenyl rings] via conversion of the amines with BuLi, NaH and KH, respectively. The authors stated that the crystal structures of these compounds were obtained proving that the amides are monomeric in the solid state.[25] Dange et al. published the synthesis of 2,6-$(CHPh_2)_2$-4-$MeC_6H_2NKSiMe_3\{\eta^6$-toluene$\}$ by conversion of 2,6-$(CHPh_2)_2$-4-$MeC_6H_2)NHSiMe_3$ with $K[N(SiMe_3)_2]$ in 2012. The structure was found to be monomeric in the solid state and showed η^4- and η^6-coordination toward the flanking phenyl groups in addition to the η^6-coordination toward a toluene molecule. The related structure 2,6-$(CHPh_2)_2$-4-$MeC_6H_2NKSiMe_3\{Et_2O\}$ was also described as showing two η^6-coordinations of the metal toward flanking phenyl groups.[82] The crystal structure of LiNa(quinolyl $NSiMe_2^tBu)_2$−NHC was described by Chen and Yuan in 2012. This compound was obtained by conversion of quinolyl$NHSiMe_2^tBu$ with BuLi/BuNa (in a molar ration of 1:1). The structure of the complex is shown in figure 31 [$\Sigma\Theta$(N): 648.3°].[83]

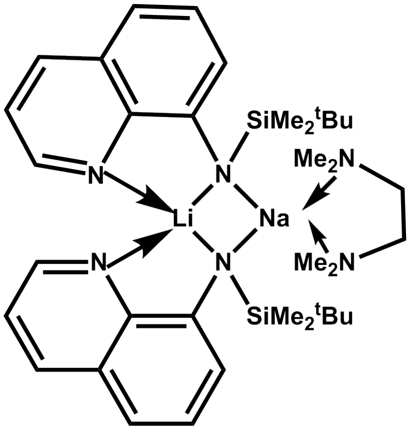


Figure 31: The sodium/lithium complex obtained by Chen and Yuan in 2012.[83]

In the same year Stewart et al. published the synthesis of 3,5-$(CF_3)_2C_6H_3$-$NLiSiMe_3\{thf\}_3$. A crystal structure of this compound was obtained and described as showing 'a distorted tetrahedral Li cation bound to the nitrogen of the [...] ligand along with the oxygen atoms of the three coordinated thf ligands' [$\Sigma(\Theta$(N): 357.2°].[27] $MesNKSiMe_3$ was obtained via reaction of $MesNHSiMe_3$ with KH and subsequently deployed to generate dinitrosyl iron amide comlexes and aminyl radical-stabilized derivatives via reversible one-electron redox reactions by Tsou et al. in 2013.[84] In the same year Wong et al. reported the synthesis and structural characterization (via X-ray diffraction) of 2,6-$(CHPh_2)_2$-4-$^iPrC_6H_2NKSi^iPr_3$. This compound was obtained via deprotonation of 2,6-$(CHPh_2)_2$-4-$^iPrC_6H_2NHSi^iPr_3$\{η^6-toluene\} by KH and deployed in the synthesis of boron and aluminum derivatives. The structure of this compound was described as 'monomeric and possesses a K centre that is coordinated by an amido N-atom, while having approximately η^6-interactions with a molecule of toluene and one benzhydryl phenyl group. Another phenyl group from the other benzhydryl substituent η^2-coordinates the potassium centre'.[85] In addition, the structural similarity to Dange et al.'s potassium silylamide[82] was pointed out. Also in 2013 Hicks and Jones published the synthesis of a series of 'extremely bulky amido first row transition metal(II) halide complexes'. One of the precursors deployed was 2,6-$(CHPh_2)_2$-4-$MeC_6H_2NKSiPh_3$, which had been obtained via reaction of $K[N(SiMe_3)_2]$ with the parent compound.[86, *compare* 25]

This chapter shows that the range of structural motives of the aryl-substituted main group 1 silylamides is broad. The highest diversity can be found in the lithium derivatives (monomeric, dimeric, tetrameric and polymeric structures), while sodium (monomeric and dimeric structures) and potassium (monomeric structures only) derivatives are rarer than their lithium congeners and therefore less manifold.

6.1.2.2 Gallium and Indium Derivatives

The aim of the present work referring to main group 3 derivatives was the generation of oxidation state +I compounds, either directly from the reactions or, alternatively, through subsequent reduction of the +III derivatives. In the following chapter E(III) and E(I) derivatives will be discussed separately.

E(III) Derivatives

In 1993 Petrie et al. reported the synthesis and characterization of the monomeric In(III) species $^tBu_2In(DippNSiPh_3)$, obtained by conversion of $^tBu_2InCl$ and the lithium amide. The structure turned out to show a planar coordination environment at the indium and nitrogen atoms [$\Sigma\Theta(N)$: 359.6°, $\Sigma\Theta(In)$: 359.6°].[87] In 1997 Linti and Frey reported the synthesis of a series of N-trimethylsilyl substituted aminogallanes. They described the reaction of R_2GaCl (R = Me, Et) with $DippNLiSiMe_3$ yielding $R_2Ga(DippNSiMe_3)$. The same publication mentioned the synthesis of $(MesNSiMe_3)_2GaCl$ by conversion of $GaCl_3$ with $MesNLiSiMe_3$. Furthermore, they discussed the route toward an oligosilazane (see figure 32).[88]

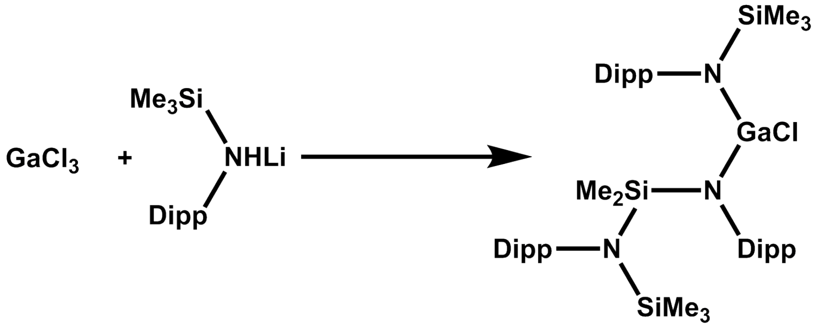


Figure 32: An oligosilazane obtained by Linti and Frey in 1997.[88]

The structure of this oligosilazane was described as having an '[...] extrem verzerrte trigonal planare Umgebung am zentralen Gallium-Atom [...]'. Furthermore, the authors stated that 'Alle Stickstoff-Atome [...] sind planar koordiniert.'[88] Kim et al. described the synthesis of a series of indium amide compounds in the year 1998. Amongst others, $PhNLiSiMe_3$ was converted with $InCl_3$ yielding $In(PhNSiMe_3)_3\{Et_2O\}$. This compound was characterized by X-ray diffraction and was found to be centered around a 'nearly planar $In(amide)_3$ core' [$\Sigma\Theta$(N): 359.8/359.9°, $\Sigma\Theta$(In): 648.24°, including oxygen coordination of Et_2O].[89] Also in 1998, Waezsada et al. discussed the synthesis route toward three gallium derivatives, shown in figure 33.[90] One of those had already been described by Linti and Frey in 1997.[88] A crystal structure of the phenyl derivative was obtained and described as a dimer in the solid state with a Ga_2N_2 ring core structure.[90]

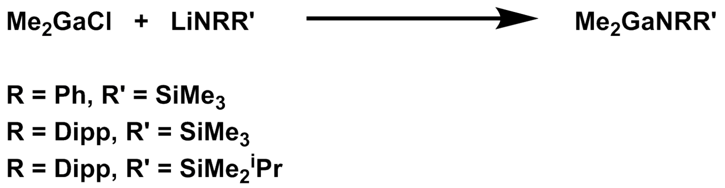


Figure 33: Three gallium derivatives described by Waezsada et al. in 1998.[90]

Prust et al. published the synthesis of a $RR'N \rightarrow InCl_3^-$ derivative in 1999 [$\Sigma\Theta$(N): 359.6°, $\Sigma\Theta$(In): 656.02°, app. tetrahedral coordination]. The reaction pathway is shown in figure 34.[91] The Cl_3InN core of the structure was described as distorted tetrahedra by Carmalt in her review from the year 2001.[92]

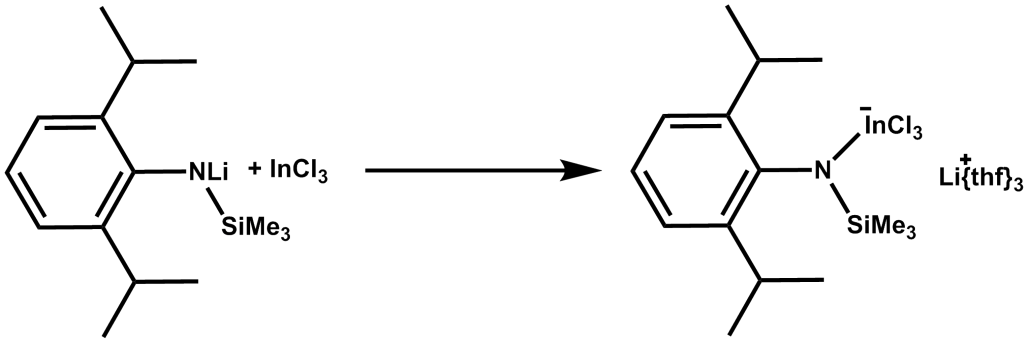


Figure 34: The RR'N→$InCl_3^-$ derivative obtained by Prust et al. in 1999.[91]

Luo et al. described the synthesis and thermolysis of $Cl_2Ga(DippNSiMe_3)\{Quin\}$ in 2002. The target compound was obtained by converting the lithiated precursor with $GaCl_3\{Quin\}$. Figure 35 shows the described compound.[93]

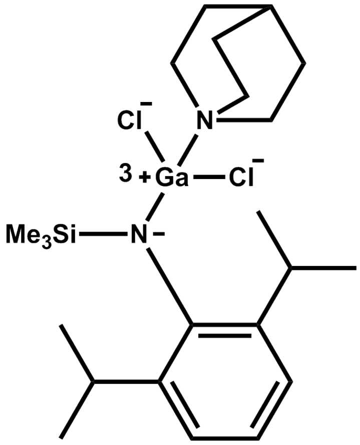


Figure 35: The gallium derivative obtained by Luo et al. in 2002.[93]

In 2003 Schiefer et al. reported the synthesis of a series of 'neutral and ionic aluminum, gallium and indium compounds', e.g. the gallium derivative shown in figure 36 (analogous to Prust's indium derivative).[94]

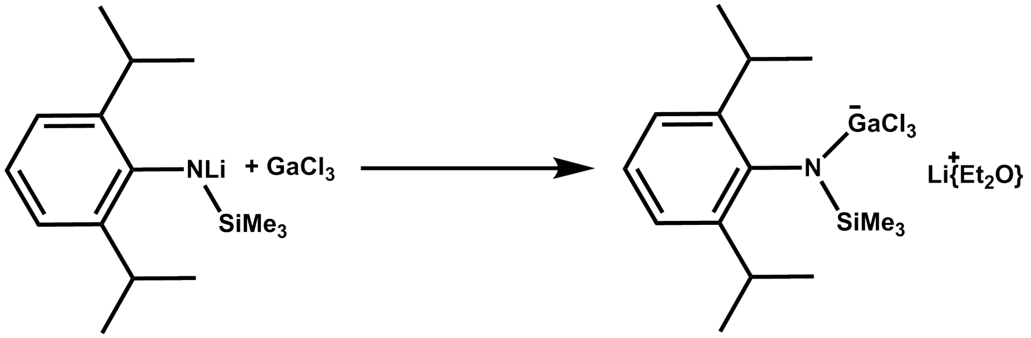


Figure 36: The RR'N→$GaCl_3^-$ derivative obtained by Schiefer et al. in 2003.[94]

The conversion of this (and the analogous indium) precursor with $Me_3SiC{\equiv}CLi$ toward $[(Li^+)_2\{dioxane\}_7]_{0.5}[DippNSiMe_3Ga(C{\equiv}CSiMe_3)_3]^-\{dioxane\}_{1.5}$ [ΣΘ(N): 360.0°, ΣΘ(Ga): 656.6°] and $[(Li^+)_2\{dioxane\}_7]_{0.5}[DippNSiMe_3In(C{\equiv}CSiMe_3)_3]^-\{dioxane\}_{1.5}$ [ΣΘ(N): 359.86°, ΣΘ(In): 656.62°] and the crystal structures of these derivatives were described in the same paper.[94]

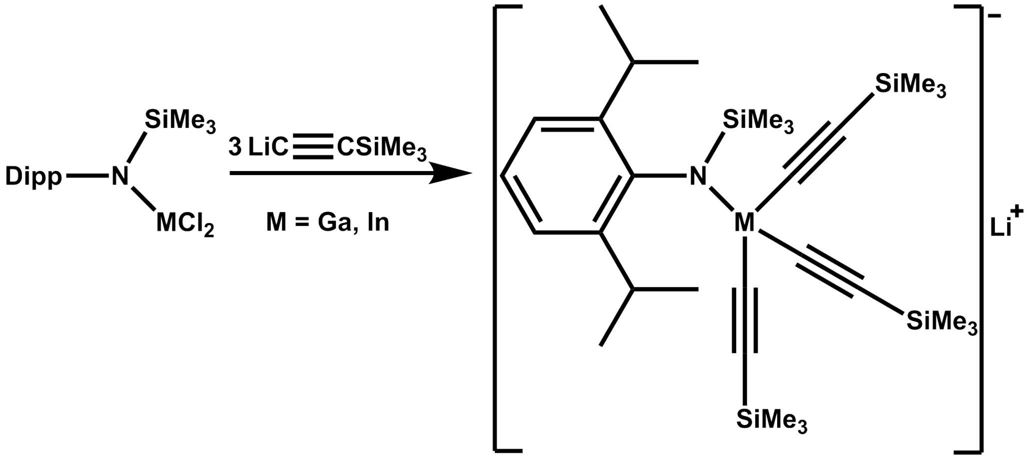


Figure 37: A gallium and an indium derivative carrying three terminal ethynyl groups published by Schiefer et al. in 2003.[94]

In 2007 Hartig et al. reported the isolation of $Li\{thf\}_4GaBr(DippNH)_2(DippNSiMe_3)$ as side product when synthesizing gallium clusters. The structure was determined via X-ray diffraction measurements [ΣΘ(N): 360.0°, ΣΘ(Ga): 656.22°].[95]

It is noteworth that all these Ga(III) derivatives were obtained starting from materials with the same oxidation state.

E(I) Derivatives

The key challenge in preparing main group 3 derivatives in oxidation state +I is to sterically or electronically stabilize the compounds in order to avoid coordination, which is favored due to the electron deficiency of the main group element. This fact led to the relatively late appearance of gallium and indium aryl-substituted silylamides with oxidation state +I in literature. In 2006 Wright et al. succeeded in the synthesis of the 'first stable monomeric Ga(I) amide' that was also 'the first one-coordinate gallium species to be characterized in the solid state', 2,6-$Mes_2C_6H_3NGaSiMe_3$ [$\Sigma\Theta$(N): 358.8°], by reaction of 2,6-$Mes_2C_6H_3NLiSiMe_3$ with 'GaI'. The structure of this compound is monomeric in the solid state and 'there is a long interaction between gallium with [...] the flanking mesityl ring of the terphenyl nitrogen substituent'.[96] Seifert and Linti published the synthesis of a Ga_4 core based compound in 2007. The structure was described by the authors as follows: 'The cores [...] are distorted tetrahedra of gallium atoms. The gallium-gallium distances [...] spread over a range of 10 pm [$d_{\text{Ga-Ga}}$ = 258.6(1) - 268.5(1) pm]. [...] The nitrogen atoms [...] are coordinated in a nearly planar manner [...].' The reaction yielding this Ga_4 cluster is shown in figure 38.[97]

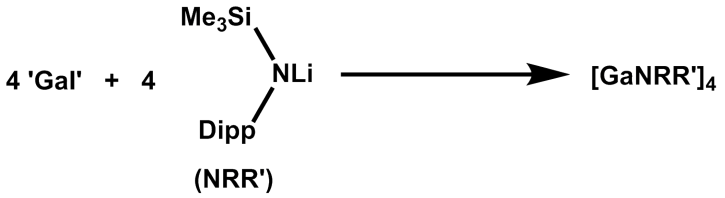


Figure 38: The Ga_4 cluster obtained by Seifert and Linti in 2007.[97]

Dange et al. reported the synthesis of a number of gallium, indium and thallium compounds stabilized by their very bulky ligand system in 2012. The structures of the gallium and indium derivatives are shown in figure 39. X-ray diffraction revealed the structures to be monomeric. The authors stated that 'it is apparent that the metal centers [...] are all essentially one-coordinate' [$\Sigma\Theta$(N): 360.0° for M = Ga, R = Me].[82]

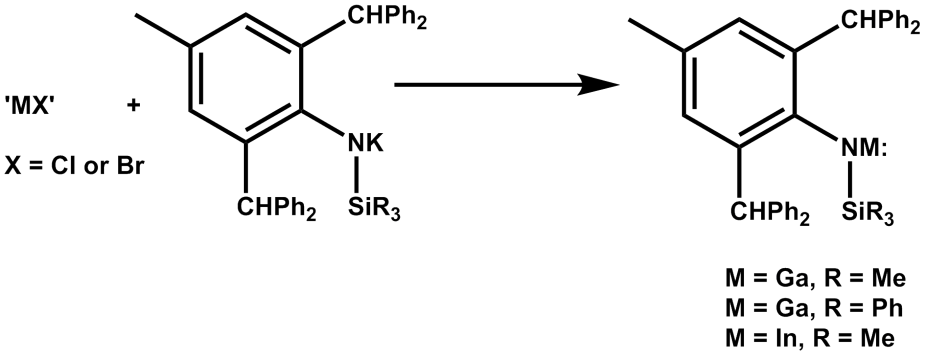


Figure 39: Gallium and indium compounds obtained by Dange et al. in 2012.[82]

In analogy to the E(III) compounds, all of the E(I) derivatives shown herein derive from E(I) precursors.

The only – to the best of the author's knowledge – known In(II) silylamide derivative shall be mentioned here in order to complete this chapter: In 2010 Brown et al. described the synthesis of an In(II)-In(II) bound amide dimer, the structure of which is given in figure 40.[98]

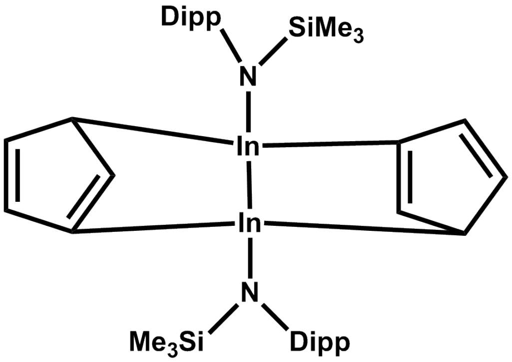


Figure 40: The indium-indium bound dimer obtained by Brown et al. in 2010.[98]

6.1.2.3 Germanium, Tin and Lead Derivatives

Like in the previous chapter E(IV) and E(II) derivatives will be discussed separately in this section.

E(IV) Derivatives

The most basic tin aryl silylamide, $Me_3Sn(PhNSiMe_3)$, was first described by Schumann and Ronecker in 1970. It was obtained by conversion of Me_3SnCl with lithium and subsequent reaction with Me_3SiCl.[99] The analogous lead derivative, $Me_3Pb(PhNSiMe_3)$, was mentioned in literature 20 years later in a publication by Wrackmeyer and Zhou. They also described the syntheses of a broad range of further derivatives, that are listed in table 8.[100]

Compounds	
$Me_3Sn(PhNSiMe_3)$	$Me_3Pb(PhNSiMe_3)$
$Me_3Sn(2\text{-}MeC_6H_4NSiMe_3)$	$Et_3Sn(2\text{-}MeC_6H_4NSiMe_3)$
$Et_3Pb(2\text{-}MeC_6H_4NSiMe_3)$	$Me_3Sn(2,6\text{-}Me_2C_6H_3NSiMe_3)$
$Me_3Pb(2,6\text{-}Me_2C_6H_3NSiMe_3)$	

Table 8: Tin and lead derivatives obtained by Wrackmeyer and Zhou in 1990.[100]

The same authors had published a series of main group 4 derivatives one year earlier. $Me_3Sn(4\text{-}MeC_6H_4NSiMe_3)$, $Me_3Sn(2\text{-}MeC_6H_4NSiMe_3)$ and $Me_3Sn(2,6\text{-}Me_2C_6H_3NSiMe_3)$ were among these compounds.[101] In the same year Pfeiffer et al. reported the syntheses of two new structures: $\{2,6\text{-}Me_2C_6H_3NSiMe_3\}_2Ge\{N(SiMe_3)_2\}N_3$ and $\{MesNSiMe_3\}_2Ge\{N(SiMe_3)_2\}N_3$.[102] In 1992 Meller et al. discussed the syntheses of $\{2,6\text{-}Me_2C_6H_3NSiMe_3\}_2Ge(OPh)NCO$, $\{2,6\text{-}Me_2C_6H_3N\,SiMe_3\}_2Ge(NMe_2)NCO$, $\{DippNSiMe_3\}_2Ge(OPh)NCO$ [$\Sigma\Theta$(N): 358.9/359.3°] and $\{MesNSiMe_3\}_2Ge(OPh)NCO$ [$\Sigma\Theta$(N): 359.8/359.9°].[103] The tripodal triamidostannate $\{MeN(CH_2CH_2NMe_2)_2Li\}_2Cl\{HC(SiMe_2N^{p}tolyl)_3Sn\}$ was published by Hellmann et al. in 1994.[104] The crystal structure of this compound was reported one year later by the same group. They also described the syntheses of further corresponding tripodal triamidostannates and -plumbates in the same paper. $\{SiMe_2N^{p}tolyl\}_3SnLi\{thf\}_3$ was obtained by conversion of $HC\{SiMe_2N(Li)\,^{p}tolyl\}_3\{thf\}_2$ with $SnCl_2$, while the analogous lead derivative (coordinated by $\{thf\}_4$) was obtained via reaction with Cp_2Pb (LiCp elimination).[105] Another publication by the same group from the year 1998 dealt with the consecutive reactions of lithium triamidostannates toward allyltriamidostannanes. In addition, $HC\{SiMe_2N^{p}tolyl\}_3SnMe$ was obtained by conversion of the lithium stannate with MeI.[106] On the basis of the group's findings, Lutz et al. reported the synthesis of the hexaaminodistannane shown in figure 41 in 2003.[107]

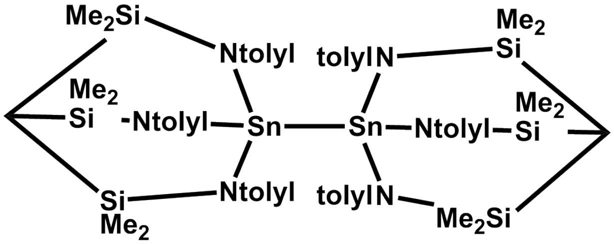


Figure 41: Hexaaminodistannane described by Lutz et al. in 2003.[107]

Belay et al. described the synthesis of $\{2,6\text{-}Me_2C_6H_3NSiMe_3\}_2Ge(CCl_3)Cl$ by conversion of $\{2,6\text{-}Me_2C_6H_3NSiMe_3\}_2Ge$ (preparation published by Meller and Gräbe in 1985[108]) with :CCl_2 in 1998.[109] In 1999 Wraage et al. described the synthesis of $(DippNSiMe_3)GeBr_3$ via conversion of $DippNLiSiMe_3$ with $GeBr_4$.[110] The crystal structure of $\{PhNSiMe_3\}_3SnCl$ was published by Valet and Hoffman in 2005 [$\Sigma\Theta$(N): 359.7/359.9/360.0°].[111]

E(II) derivatives (Synthesis)

In 1985 Meller and Gräbe reported the synthesis of a series of GeL_2 compounds via salt elimination reactions of $GeCl_2$\{dioxane\} and the lithium amide (in a molar ratio of 1:2). An overview of the ligands deployed is given in table 9.[108] A crystal structure of $\{DippC_6H_3NSiMe_3\}_2Ge$ was published by Meller et al. in 1992 [$\Sigma\Theta$(N): 358.1/359.4°].[103]

Compounds		
$2\text{-}MeC_6H_4NHSiMe_3$	$2,6\text{-}Me_2C_6H_3NHSiMe_3$	$MesC_6H_2NHSiMe_3$
$DippC_6H_3NHSiMe_3$	$2\text{-}FC_6H_4NHSiMe_3$	

Table 9: Ligands deployed for the synthesis of Ge(II) derivatives by Meller and Gräbe in 1985.[108]

In addition, Meller and Gräbe described the syntheses of $2,6\text{-}Me_2C_6H_3N(SiMe_3)GeO^tBu$, $MesN(SiMe_3)GeO^tBu$, $DippN(SiMe_3)GeO^tBu$, $DippN(SiMe_3)GeBr$ and $2,6\text{-}Me_2C_6H_3N(SiMe_3)GeCl$.[108] The same group published the syntheses of $\{2,6\text{-}Me_2C_6H_3NSiMe_3\}_2Ge$ and $\{MesNSiMe_3\}_2Ge$ in their paper from the year 1992.[103] In 1998 Babcock mentioned $\{2,6\text{-}Me_2C_6H_3NSiMe_3\}_2Sn$ in his Ph.D. thesis [^{119}Sn NMR: δ 655 ppm].[112] The same group published the synthesis of the monomeric orange solid $\{DippNSiMe_3\}_2Sn$ [$\Sigma\Theta$(N): 359.0/359.6°; ^{119}Sn NMR: δ 440 ppm] in 1999. The reactivity of the compound was described as follows: 'Regarding heterocumulene metathesis, in solution, compound **1** was found to be inert toward both carbon dioxide and *tert*-butylisocyanate, ^tBuNCO, even at elevated temperatures up to 80℃.'[113] In 2004 Tang et al. published the conversion of $MesNHSiMe_3$

with $SnCl_2$ via precedent lithiation of the former, yielding two different compounds when varying the reaction stoichiometry. The results of these reactions are shown in figure 42 [monomer: $\Sigma\Theta(N)$: 359.1/359.5°, ^{119}Sn NMR (93.275 MHz, Me_4Sn): δ 473 ppm; trimer: $\Sigma\Theta(N)$: 358.8/360.0°, ^{119}Sn NMR (93.275 MHz, Me_4Sn): δ 67 ppm].[114]

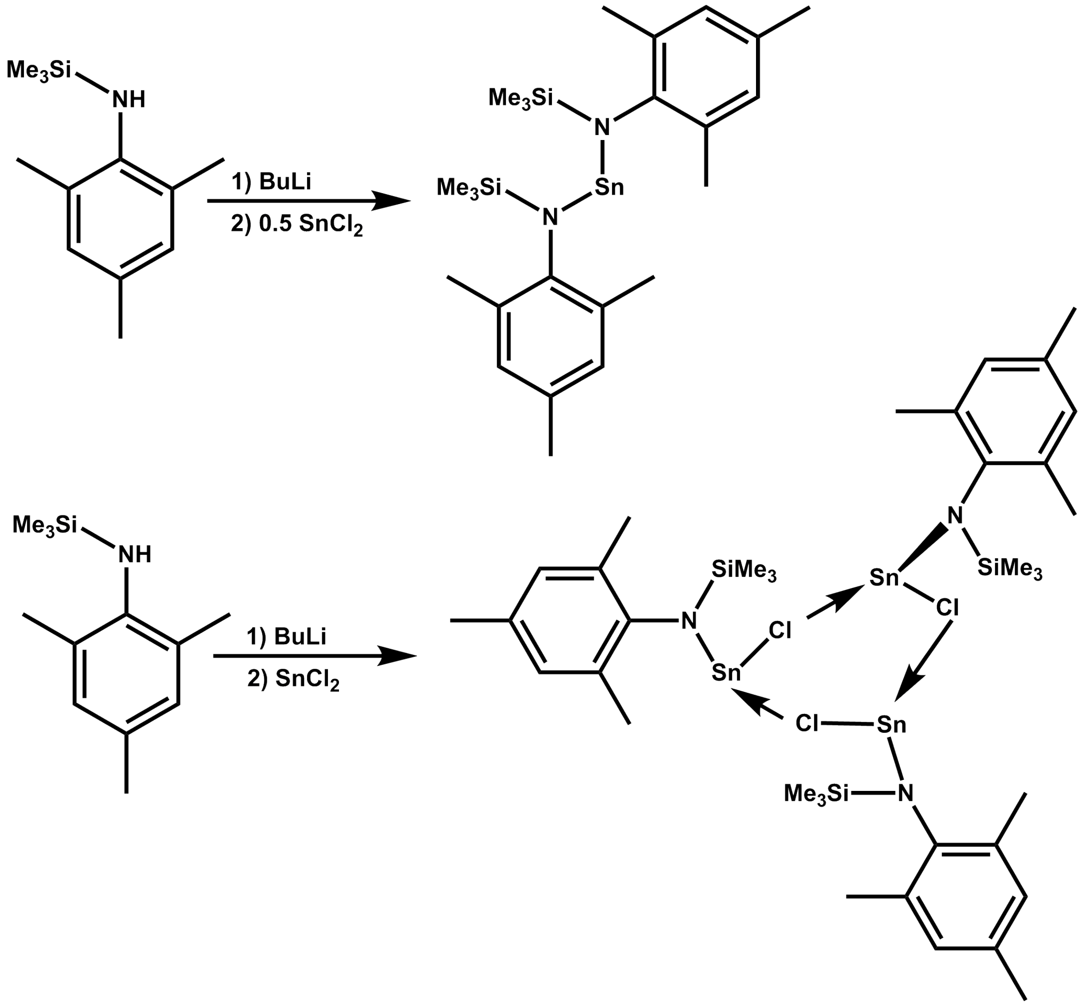


Figure 42: Conversions of $MesNHSiMe_3$ with $SnCl_2$ (in varying stoichiometries) performed by Tang et al. in 2004.[114]

In 2006 Brynda et al. described the synthesis of $[\{DippNSiMe_3\}SnCl]_2$ [^{119}Sn NMR (C_6D_6/Me_4Sn): δ 14.3 ppm, $\Sigma\Theta(N)$: 360.0°] by conversion of the lithium derivative and $SnCl_2$ (via salt elimination). Alternatively, the route via $\{DippN SiMe_3\}_2Sn$ with $SnCl_2$ (metathetical ligand exchange) was discussed. In addition, the reaction of $\{DippNSiMe_2Ph\}_2Sn$ with $SnCl_2$ yielding the $SiMe_2Ph$ analog was published in the same paper.[115] Bares et al. published the synthesis of

{DippNSiMe$_3$}$_2$Pb in 2010.[116] Li et al. described the syntheses of the monomeric compounds {2,6-CHPh$_2$-4-MeC$_6$H$_2$NSiR$_3$}ECl (E = Ge, Sn, R$_3$ = Me$_3$, Ph$_3$, MePh$_2$) [ΣΘ(N): 359.9/360°; ^{119}Sn NMR (149 MHz, C$_6$D$_6$/Me$_4$Sn): δ 173.7 ppm for E = Sn, R$_3$ = Me$_3$; ^{119}Sn NMR (149 MHz, C$_6$D$_6$/Me$_4$Sn): δ 104.5 ppm for E = Sn, R$_3$ = MePh$_2$; ΣΘ(N): 359.9°; ^{119}Sn NMR (149 MHz, C$_6$D$_6$/Me$_4$Sn): δ 185.4 ppm for E = Sn, R$_3$ = Ph$_3$] and the dimeric structures [{2,6-CHPh$_2$-4-MeC$_6$H$_2$NSiR$_3$}PbCl]$_2$ (R$_3$ = Me$_3$, MePh$_2$) [ΣΘ(N): 359.9° for R$_3$ = Me$_3$] by conversion of the parent amine with BuLi and subsequent conversion with the corresponding ECl$_2$ in 2011. (All of these compounds were isolated as pale yellow crystals.) In the same paper the isolation of [{2,6-CHPh$_2$-4-MeC$_6$H$_2$NSiMe$_3$}Ge]$_2$ was described [ΣΘ(N): 360.0°].[25] The synthesis of oily {3,5-(CF$_3$)$_2$C$_6$H$_3$NSiMe$_3$}$_2$Sn [^{119}Sn NMR (112 MHz, DMSO-d$_6$/Et$_4$Sn): δ -12 ppm] deriving from 3,5-(CF$_3$)$_2$-C$_6$H$_3$NLiSiMe$_3$ and SnCl$_2$ was described by Stewart et al. in 2012. The authors stated as follows: 'In an attempt to purify [...] by distillation we observed an unexpected cyclization reaction with activation of an aromatic H atom.' The product obtained from this procedure is shown in figure 43.[27]

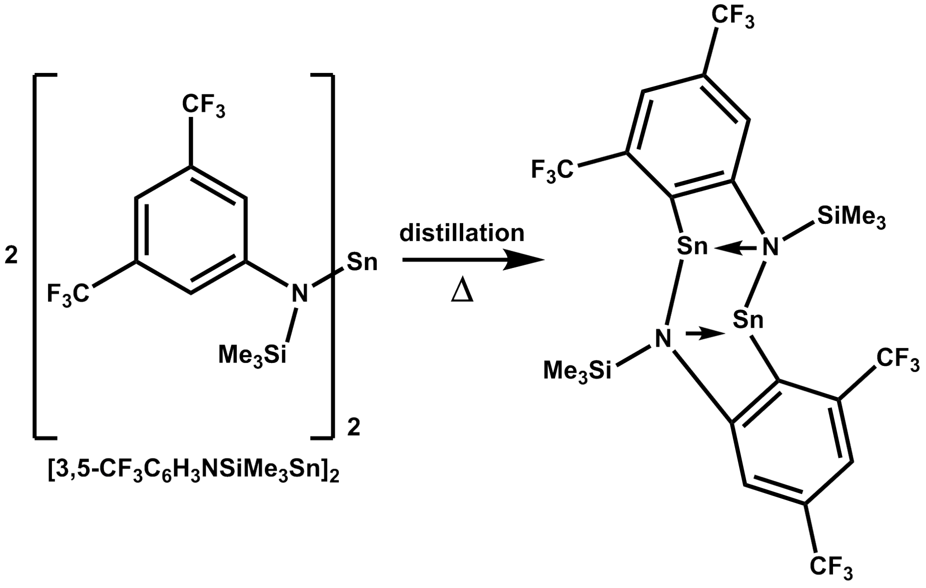


Figure 43: Cyclization of {3,5-(CF$_3$)$_2$C$_6$H$_3$NSiMe$_3$}$_2$Sn upon distillation observed by Stewart et al.[27]

Hadlington and Jones published the synthesis of the 'first amido-distannyne' [{2,6-CHPh$_2$-4-^{i}PrC$_6$H$_2$NSi^{i}Pr$_3$}Sn]$_2$ [ΣΘ(N): 360/360.2°] in 2014.[117]

E(II) Derivatives (Reactivity)

In 1991 Meller et al. reported the conversion of two of the discussed compounds ($\{DippNSiMe_3\}_2Ge$ and $\{MesNSiMe_3\}_2Ge$) to germaimines (reaction shown in figure 44) [ΣΘ(N): 356.4/358.5° for R=R'=Dipp, ΣΘ(N): 356.8/359.6° for R=R'=Mes].[118]

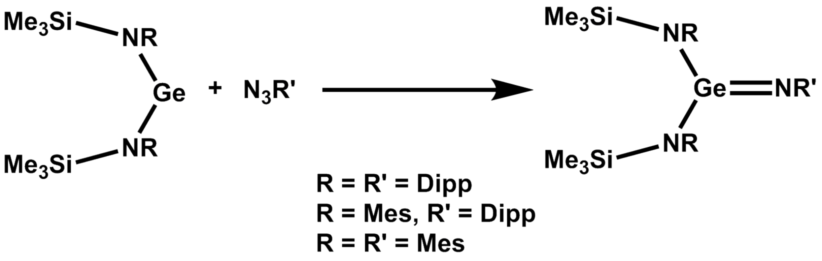


Figure 44: Conversion of $\{DippNSiMe_3\}_2Ge$ and $\{MesNSiMe_3\}_2Ge$ to germaimines.[118]

Another report by the same group described a series of consecutive reactions of germylenes with acid azides affording Ge(IV) species, a selection of which is presented in figure 45.[103]

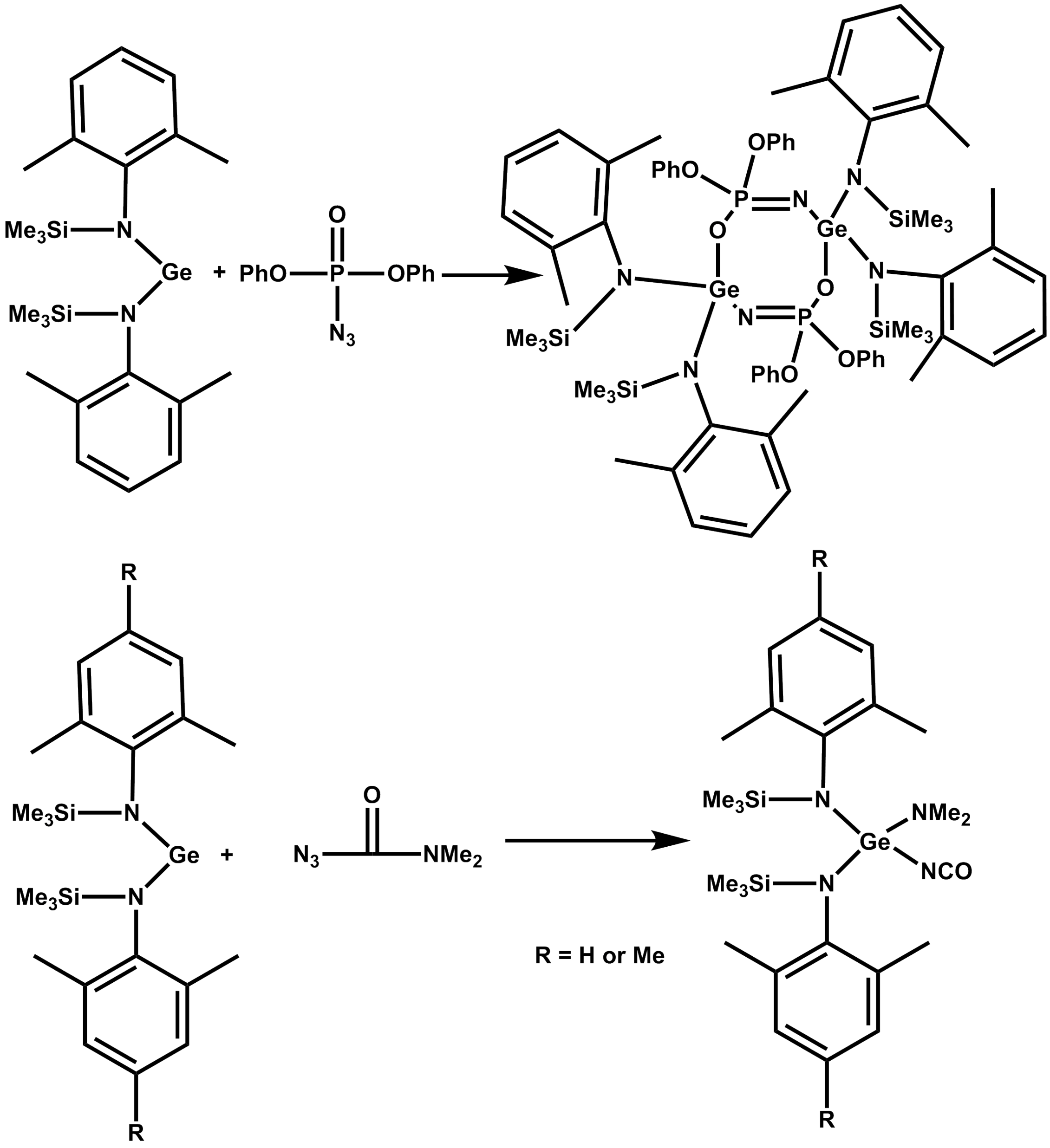


Figure 45: Some examples of reactions of $\{2,6\text{-}Me_2C_6H_3NSiMe_3\}_2Ge$ and $\{MesNSiMe_3\}_2Ge$ conducted by Meller et al. in 1992.[103]

The reduction of $[\{DippNSiMe_3\}SnCl]_2$ with KC_6, performed by Brynda et al. in 2006, led to the synthesis of a $Sn_{15}\{DippNSiMe_3\}_6$ cluster. Another structure of the same compound was obtained by in-situ conversion of $Sn\{DippNSiMe_3\}_2$ with $SnCl_2$ and subsequent addition of $Li[BH^sBu_3]$. $Sn_{15}\{DippNSiMe_2Ph\}_6$ was obtained by analogous reactions.[115] The clusters were described in the book by Lappert et al. as follows: 'These are the first body-centred clusters of a Group 14 element. Single crystals of **80** [note: $Sn_{15}\{DippNSiMe_3\}_6$] were isolated in four different space groups, but the molecular structure deduced from each is essentially identical and closely similar to that of **81** [note: $Sn_{15}\{DippNSiMe_2Ph\}_6$].'[69] The reduction of a germylene derivative discussed above was performed by Li et al. in the year 2011. The reaction pathway is shown in figure 46.[119]

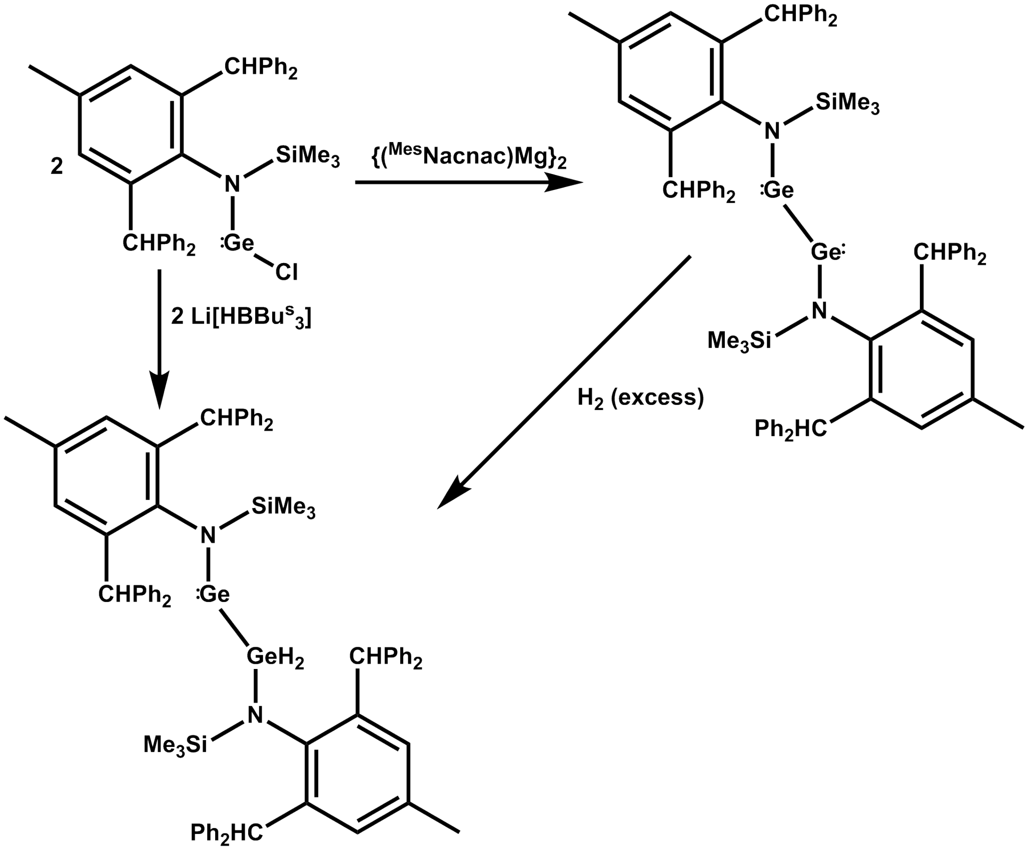


Figure 46: Reaction pathway toward 'the first example of a digermyne with a Ge-Ge single bond'.[119]

Corresponding germylene cations were obtained one year later by the same group.[120] Also in 2012 the group published the conversion of the LGeCl precursor shown in figure 46 with $Na[CpMo(CO)_3]$ yielding the 'first examples of structurally characterized two-coordinate molybdenum substituted germylenes [...].'[121] The insertion of CO_2 and CS_2 into the precursor $\{3,5\text{-}(CF_3)_2C_6H_3NSiMe_3\}_2Sn$ was performed successfully by Stewart et al. in 2012, while the conversion with OCS yielded an 'unidentified mixture of products'. A schematic presentation of these conversions is given in figure 47.[27]

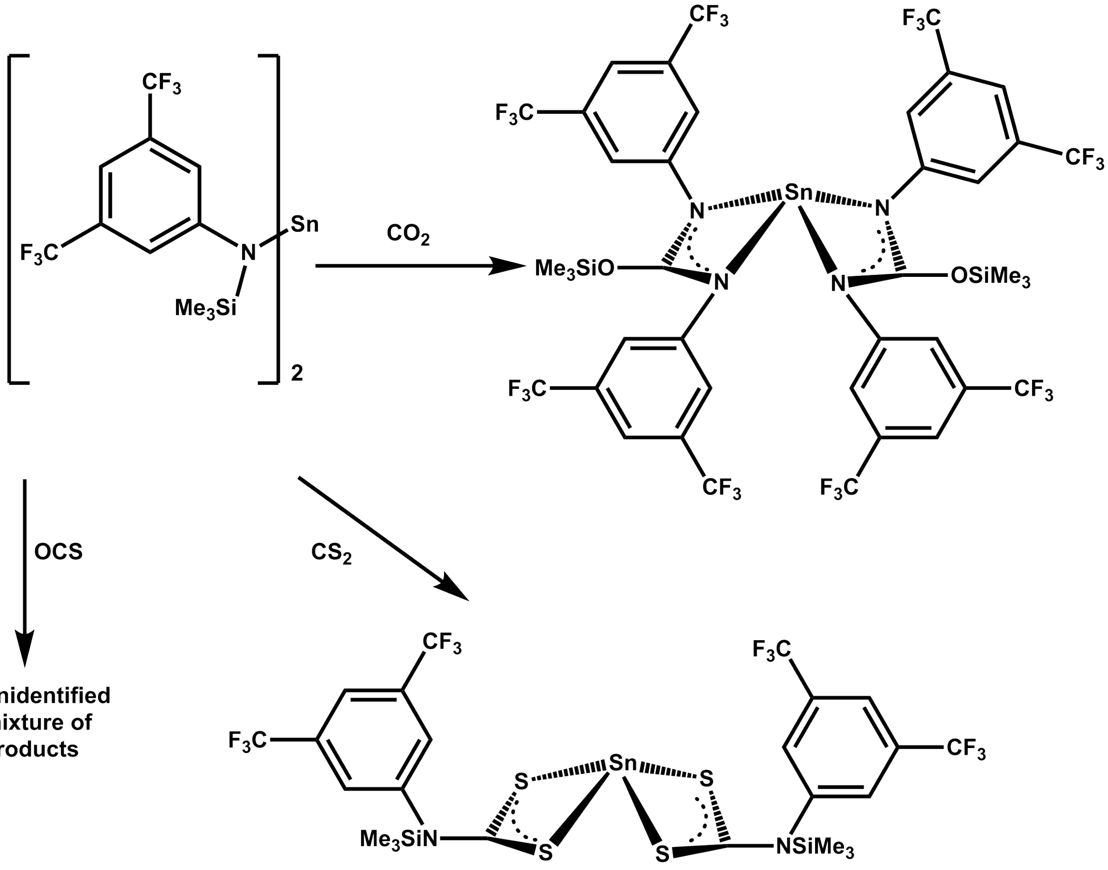


Figure 47: Reactions of CO_2, CS_2 and OCS with $\{3,5\text{-}(CF_3)_2C_6H_3NSiMe_3\}_2Sn$ described by Stewart et al. in 2012.[27]

The addition reactions of H_2 and $^{t}BuNC$ to $[\{2,6\text{-}CHPh_2\text{-}4\text{-}^{i}PrC_6H_2NSi^{i}Pr_3\}Sn]_2$ were published by Hadlington and Jones in 2014 (see figure 48).[117]

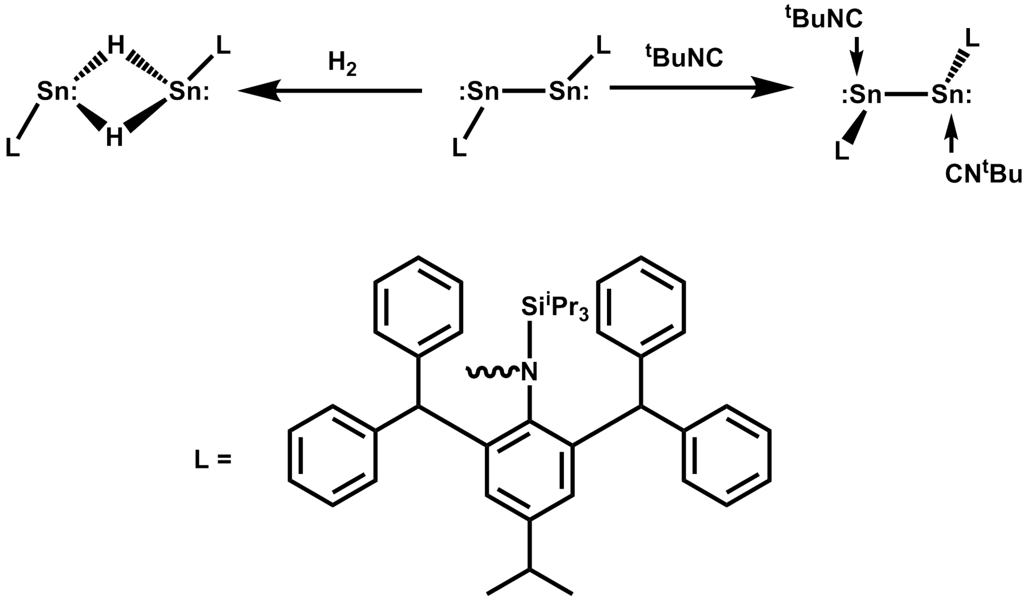


Figure 48: H_2 activation and isocyanide coordination of $[\{2,6\text{-}CHPh_2\text{-}4\text{-}{}^{i}PrC_6H_2NSi{}^{i}Pr_3\}Sn]_2$ published by Hadlington and Jones in 2014.[117]

6.2 Phenyl Ligands as Stabilizing Systems

6.2.1 ^{o}Biphenyl-Substituted Tetryltetrylenes

6.2.1.1 The Use of ^{o}Biphenyls in Stabilizing Tin and Lead Derivatives

An easily applicable synthesis route toward biphenyls was published by Hartman et al. in 2001[122] and only modified slightly for the present work. A range of subsequent derivatives was presented in literature following this procedure, including a series of transition metal compounds.*see e.g.* [123]
A series of biphenyl-stabilized tin compounds and halogenated analogs can be found in literature: The first reactions to obtain ^{o}bip$_4$Sn were published by Talalaeva and Kocheshkov in 1942[124] and by Bahr and Gelius in 1958,[125] respectively. ^{o}bip$_2$SnCl$_2$ and ^{o}bip$_2$SnBr$_2$ followed two years later,[126] the corresponding X-ray structure of the former was published in 1985.[127] ^{o}bip$_3$SnCl was described by Gelius in 1960,[126] the corresponding bromine analog had been published by Bahr and Gelius in 1958.[125] Stern's paper from the year 1964 names alternative routes toward ^{o}bip$_{4-n}$SnX$_n$ (X = Cl, Br) derivatives.[128] Synthesis of ^{o}bip$_3$SnSn^{o}bip$_3$ was also reported by Bahr and Gelius in 1958.[129]
The corresponding lead analogs are – to the best of the author's knowledge – not present in literature up to date.

6.2.1.2 Heavier Tetryltetrylenes

This chapter gives a short overview on the heavier tetryltetrylenes (including germanium, tin and lead centers) known in literature, that have been experimentally isolated. Comprehensive theoretical studies on group 14 X_2H_4 derivatives can e.g. be found in the publications by Trinquier.[130,131]

The first germylgermylenes published in literature were PhCl$_2$GeGePh and Ph(MeO)$_2$GeGePh, described by Riviere et al. in 1973. These intermediates were obtained by thermal decomposition of trigermanes. Decomposition of tetragermanes led to the synthesis of PhCl$_2$GeGePh and PhMe$_2$GeGePh, respectively. An alternative route toward the latter was also described. The group proved the structures of the tetryltetrylenes by trapping reactions deploying dimethylbutadiene.[132] The germylgermylenes $(C_6F_5)_3$GeGeF and $(C_6F_5)_3$GeGeCl were trapped by the same reaction and published a few years later by the same group. As described above, the compounds were obtained by thermal decomposition reactions of trigermanes.[133] Baines et al. reported the synthesis of Mes$_3$GeGeMes in 1992. The compound was obtained from Mes$_2$GeGeMes$_2$ undergoing a 1,2-mesityl shift ('digermene-to-germylgermylene rearrangement') in the absence of a compound reactive toward the Ge=Ge bond and was trapped deploying Et_3SiH.[134]

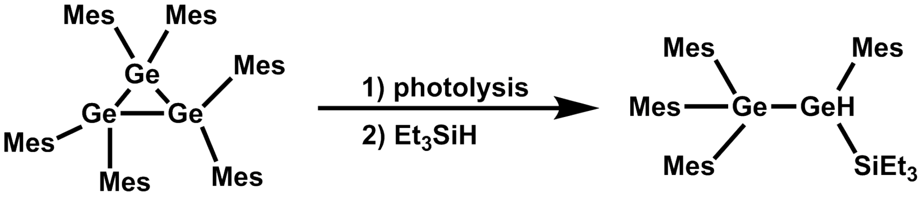


Figure 49: The synthesis and trapping of $Mes_3GeGeMes$ conducted by Baines et al. in 1992.[134]

The analogous silylgermylene was described by Baines et al. in the same year.[135] Further studies on these two and the parent compounds were conducted by the named working groups in the following years.*see e.g.* [136–141] Setaka et al. published the synthesis and structural characterization (by X-ray diffraction) of a germylgermylene stabilized by a terphenyl ligand in 2001.[142]

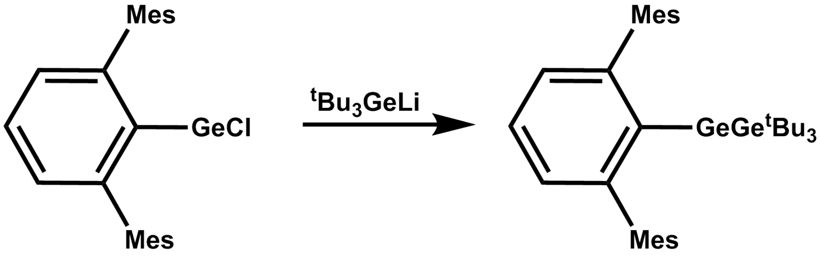


Figure 50: Synthesis of the terphenyl-stabilized germylgermylene obtained by Setaka et al. in 2001.[142]

Fukaya et al. published the observation of the germylgermylene shown in figure 51 in 2001 and trapped it with diphenylacetylene.[143]

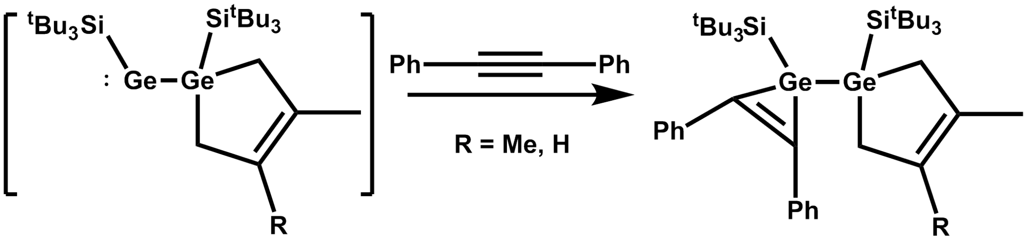


Figure 51: Trapping reaction of the germylgermylene observed by Fukaya et al. in 2001.[143]

A study on the 'photochemical generation of chlorine-substituted digermenes and their rearrangement to germylgermylenes' was published by the same group in 2002.[144] A base-stabilized germylgermylene was published by Richards et al. in 2003. The route to obtain the target compound 2,6-$Dipp_2C_6H_3(PMe_3)GeGeH_2$-2,6-$Dipp_2C_6H_3$ is shown in figure 52.

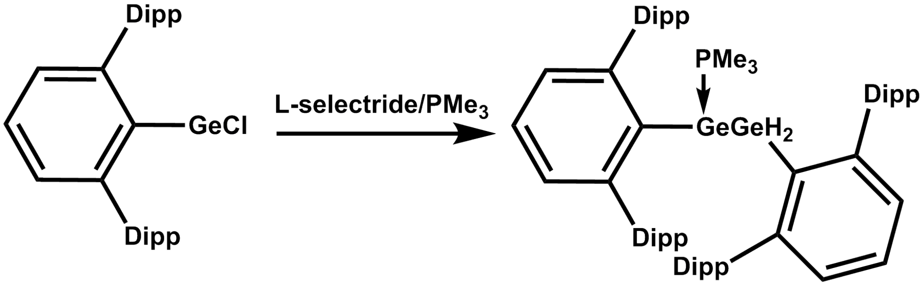


Figure 52: The base-stabilized germylgermylene obtained by Richards et al. in 2003.[145]

Conversion of NHC-$GeMes_2$ with NHC-Ge:Cl_2 did not yield the expected heteroleptic complex NHC-GeClMes but the NHC-stabilized germylgermylene NHC-GeClGeMes_2Cl as published by Rupar et al. in 2008.[146]

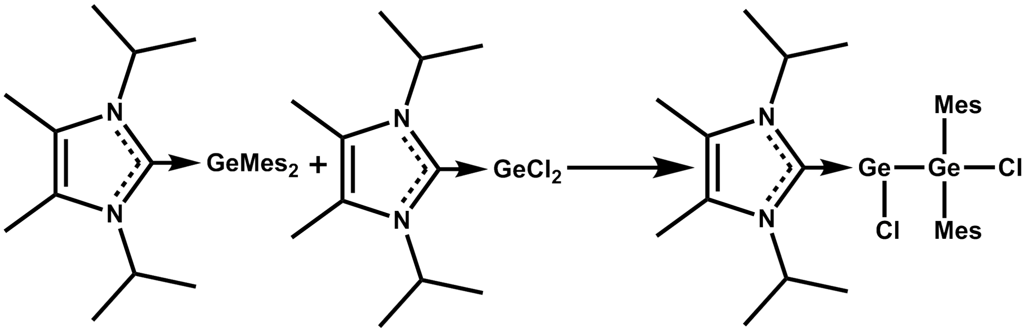


Figure 53: Synthesis of the first NHC-stabilized germylgermylene by Rupar et al. in 2008.[146]

Another carbene-stabilized germylgermylene was described by Katir et al. in the year 2011.[147]

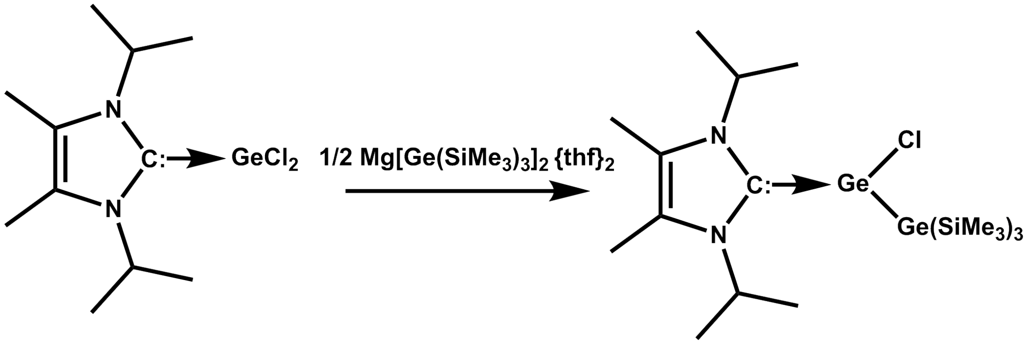


Figure 54: A carbene-stabilized germylgermylene obtained by Katir et al. in 2011.[147]

In 2011 Li et al. published the synthesis of a silylamide-stabilized germylgermylene.[119] The reaction toward this compound was discussed earlier and is shown in figure 46. The synthesis of a germylstannylene was published by Setaka et al. in 2001. This structure is analogous to the germylgermylene obtained by the same group in the year (see figure 50).[142] A series of ditetryltetrylenes was synthesized by Katir et al. in the year 2011. An overview of these derivatives is given in figure 55.[147]

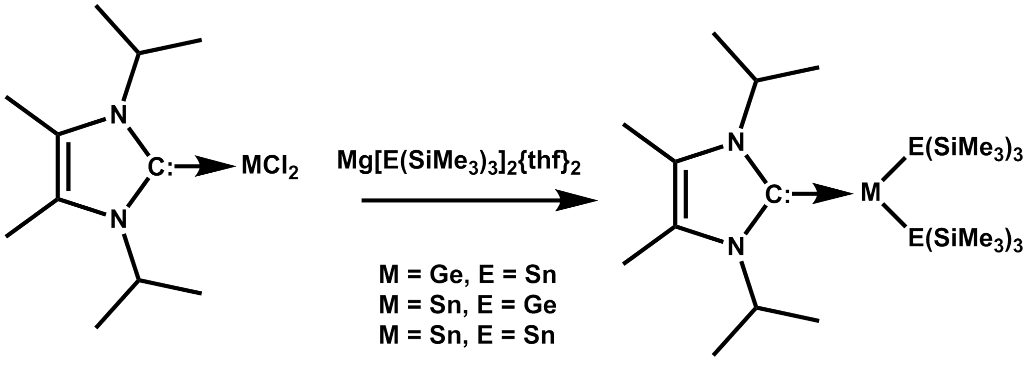


Figure 55: Ditetryltetrylenes obtained by Katir et al. in 2011.[147]

A digermylplumbylene was published as a precursor on the way toward Pb(III) radicals by Kurzbach et al. in 2010. The same paper also mentioned the observation of $K^+[Sn\{Ge(SiMe_3)_3\}_3]^-$.[148]

$$\mathrm{Pb[N(SiMe_3)_2]_2 + 2\ KGe(SiMe_3)_3} \longrightarrow \mathrm{Pb[Ge(SiMe_3)_3]_2}$$

Figure 56: A digermylplumbylene described by Kurzbach et al. in the year 2010.[148]

In 1986 Jurkschat et al. reported the isolation of a 'tin(II)-tin(IV) containing compound', the structure of which had not been determined by X-ray diffraction measurements but on the basis of NMR and Mössbauer spectroscopy.[149]

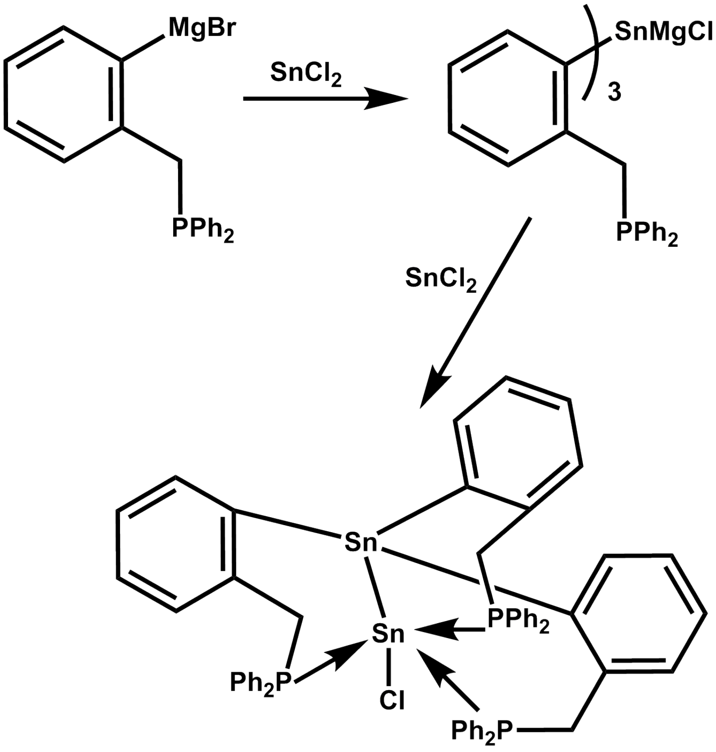


Figure 57: The 'tin(II)-tin(IV) containing compound' characterized by Jurkschat et al. in 1986.[149]

Cardin et al. published the synthesis of the 'first structurally authenticated compound containing a bond between divalent tin and tetravalent tin' in 1998. The synthetic route they followed is shown in figure 58.[150,151] The authors mentioned that two structures of this type had already been published in 1977, but had turned out to be Ag/As derivatives.[152,153]

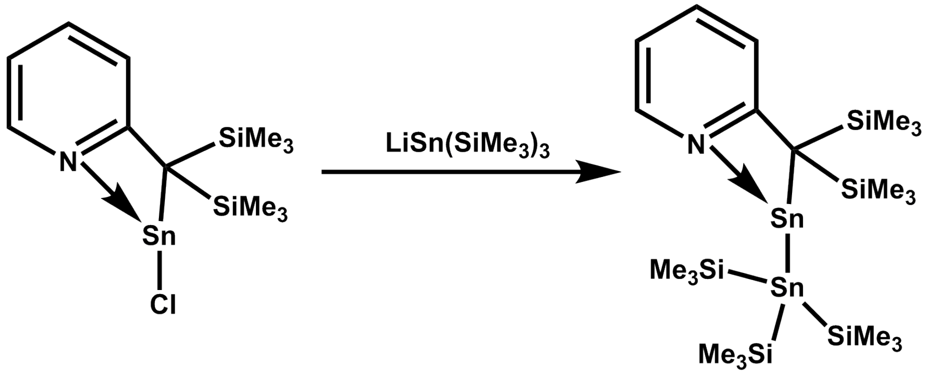


Figure 58: Synthesis of the 'first structurally authenticated compound containing a bond between divalent tin and tetravalent tin' published by Cardin et al. in 1998.[150]

The first stannylstannylene without nitrogen stabilization was synthesized by Eichler et al. and published in the year 2000. They described the compound as 'the first stable group 14 element methylmethylene (i.e., CH_3CH) analogue of ethylene (H_2CCH_2)'. Figure 59 shows the reaction pathway on the way toward the named structure.[154]

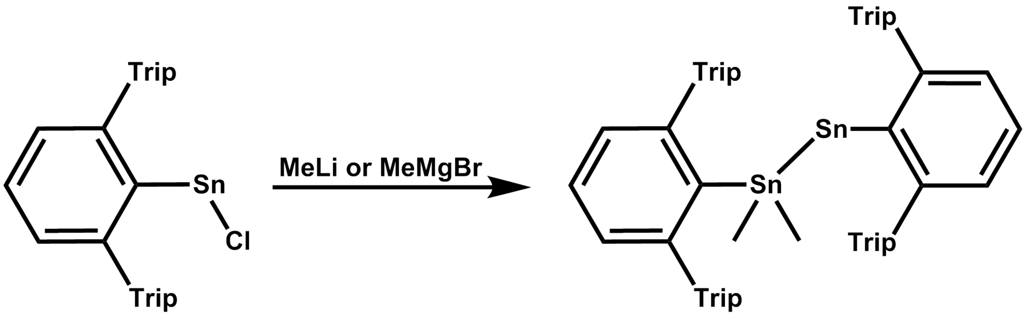


Figure 59: The synthesis of the first stannylstannylene without nitrogen stabilization, obtained by Eichler et al. in 2000.[154]

In the same year Mehring et al. reported the synthesis of two stannylstannylene derivatives, shown in figure 60.

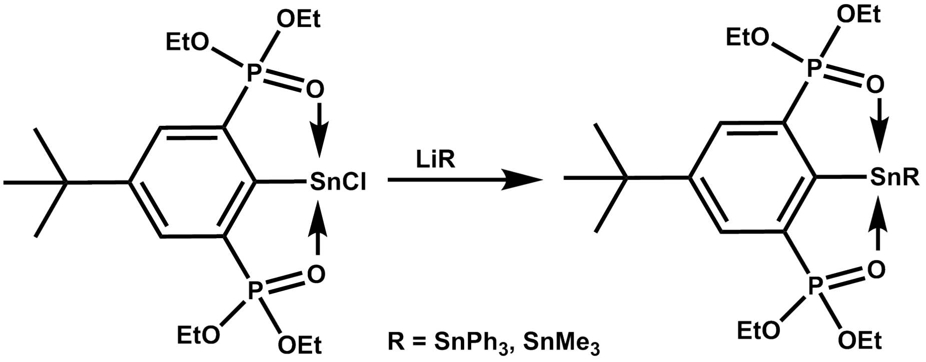


Figure 60: Stannylstannylenes obtained by Mehring et al. in the year 2000.[155]

In the year 2002 Drost et al. published the synthesis of the distannylstannanediyl $Sn[Sn\{2,6\text{-}(O^iPr)_2C_6H_3\}_3]_2$. The proposed reaction pathway is depicted in figure 61. Alternatively, the compound was also obtained via the reaction of $SnCl_2$ with $\{2,6\text{-}(O^iPr)_2C_6H_3\}$ (in a molar ratio of 1:2).[156] The authors stated in a later paper, that the compound is probably desintegrating into the corresponding arylstannylstannylene in solution, which explains the presence of two ^{119}Sn NMR peaks in the ratio of 1:1.[157]

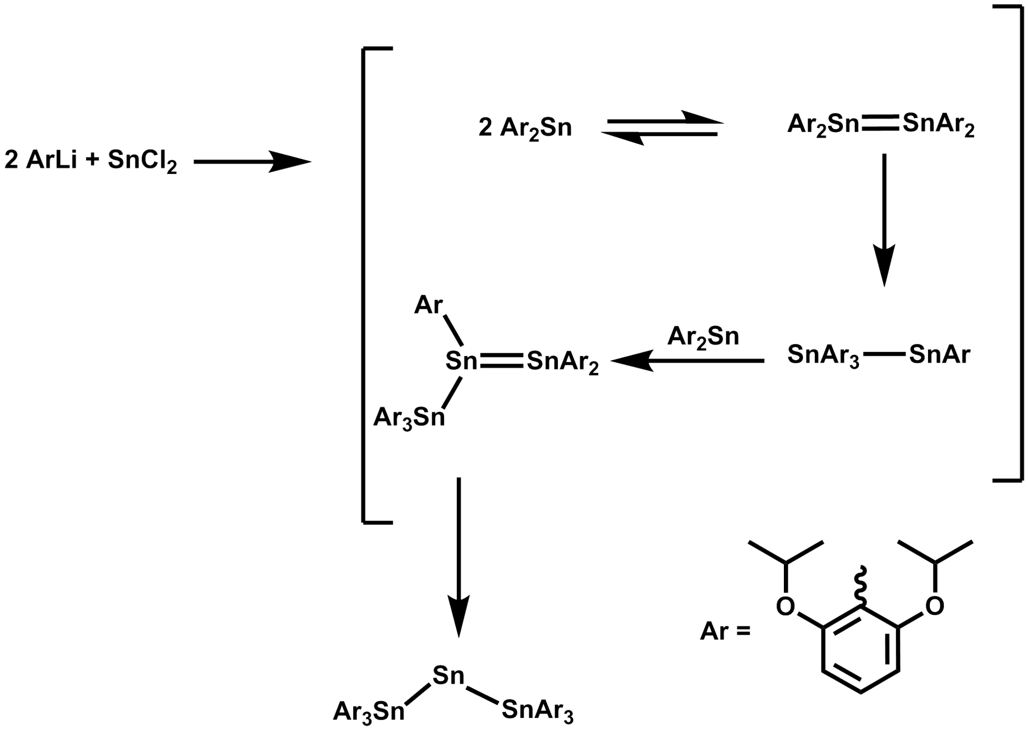


Figure 61: The distannylstannanediyl described by Drost et al. in 2002.[156]

Phillips et al. published the stannylstannylene (2,6-Trip$_2$C$_6$H$_3$)SnSnPh$_2$(2,6-Trip$_2$C$_6$H$_3$) one year later. The corresponding reaction is shown in figure 62.[158]

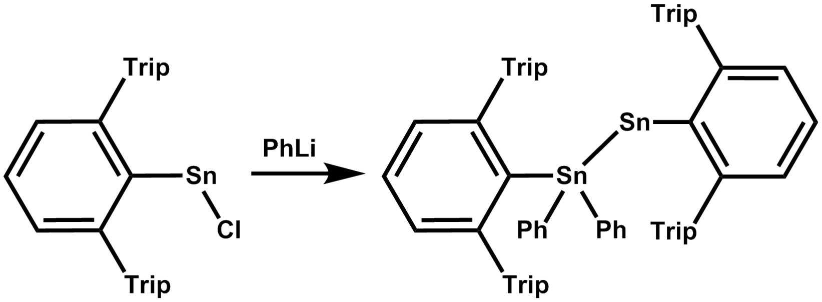


Figure 62: The reaction affording a heteroleptic stannylstannylene obtained by Phillips et al. in 2003.[158]

The same working group described the formation of the distannylstannylene Sn(SnPh$_2$-2,6-Trip$_2$C$_6$H$_3$)$_2$ in the same year.[159]

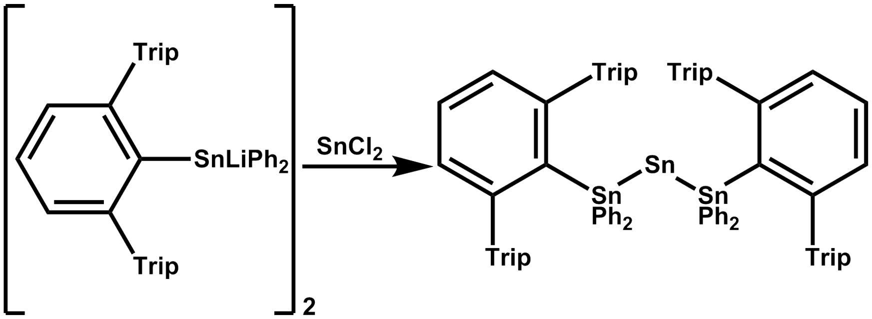


Figure 63: The distannylstannylene described by Eichler et al. in 2003.[159]

Rivard et al. published the synthesis and characterization of their terphenyl based stannylstannylene in 2007.[160]

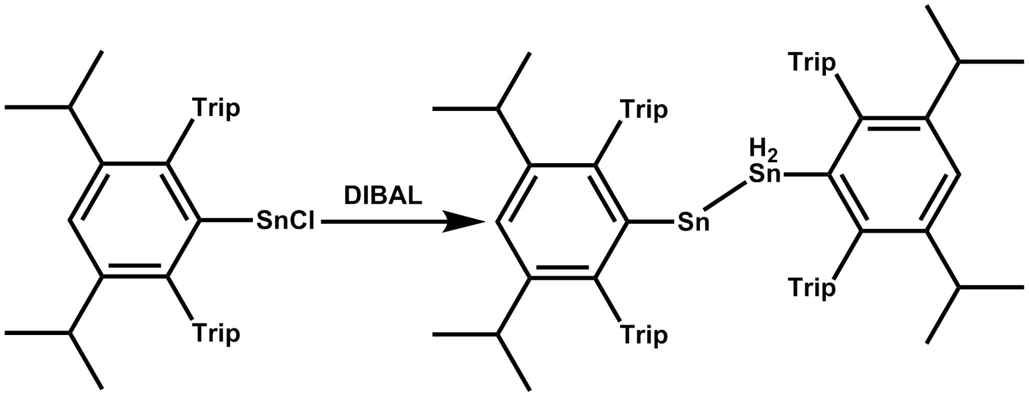


Figure 64: The terphenyl based stannylstannylene obtained by Rivard et al. in 2007.[161]

In 2008 Setaka et al. published the characterization of another stannylstannylene, that had been obtained by the group 'via intramolecular carbene addition of a transient stannaacetylene'.[162]

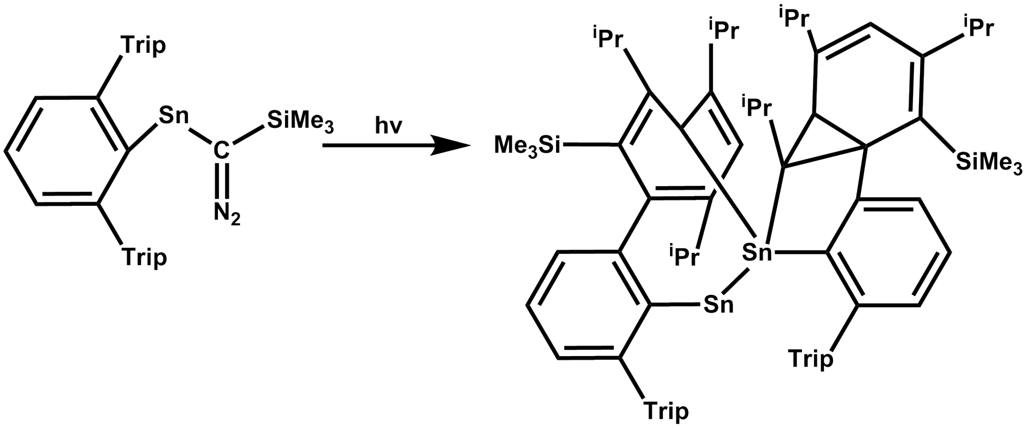


Figure 65: The stannylstannylene formed 'via intramolecular carbene addition of a transient stannaacetylene' by Setaka et al. in 2008.[162]

A stannylstannylene stabilized by terphenyl substituents as well as by CC^tBu fragments was reported by Lei et al. in 2010 as shown in figure 66.[163]

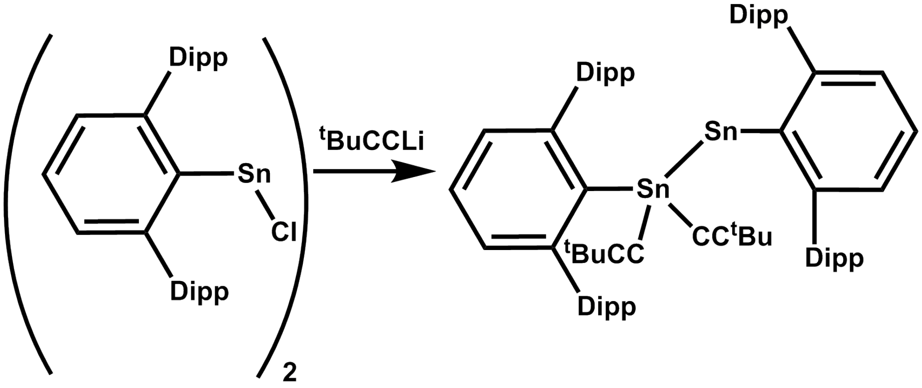


Figure 66: The reaction pathway toward the stannylstannylene obtained by Lei et al. in 2010.[163]

The first stannylplumbylene was obtained by Drost et al. in 2012. They reacted their distannylstannanediyl described above (see figure 61) with the corresponding diaryllead derivative as shown in figure 67.[157]

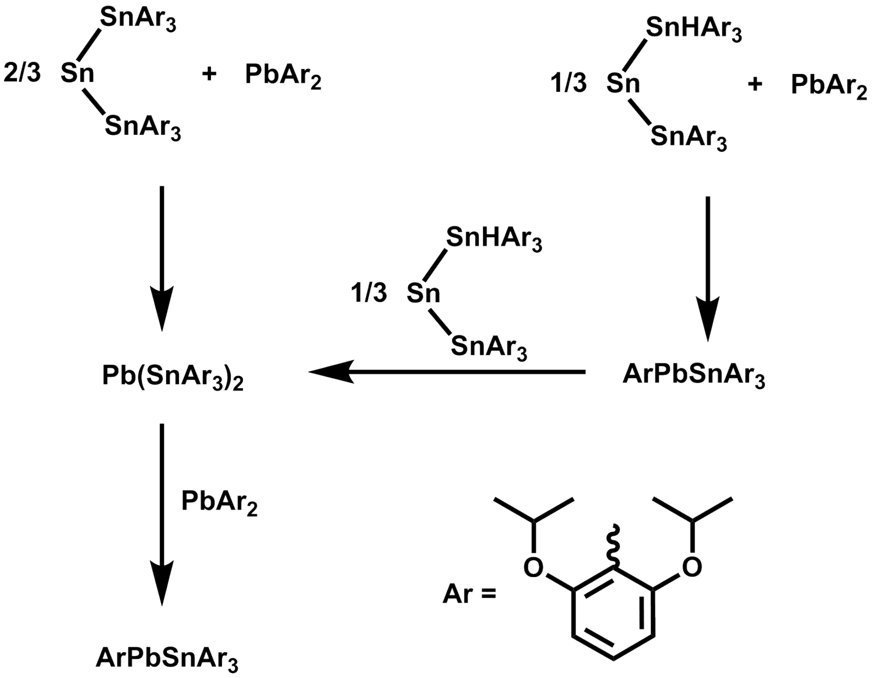


Figure 67: The first stannylplumbylene described by Drost et al. in 2012.[157]

The only stable (to the best of the author's knowledge) plumbylplumbylene known in literature was published by Hino et al. in 2005. The group obtained the named structure by the reaction of a lead precursor with Me_3SiN_3 as shown in figure 68. The compound was formed via activation of the methyl group of the triisopropyl substituent.[164]

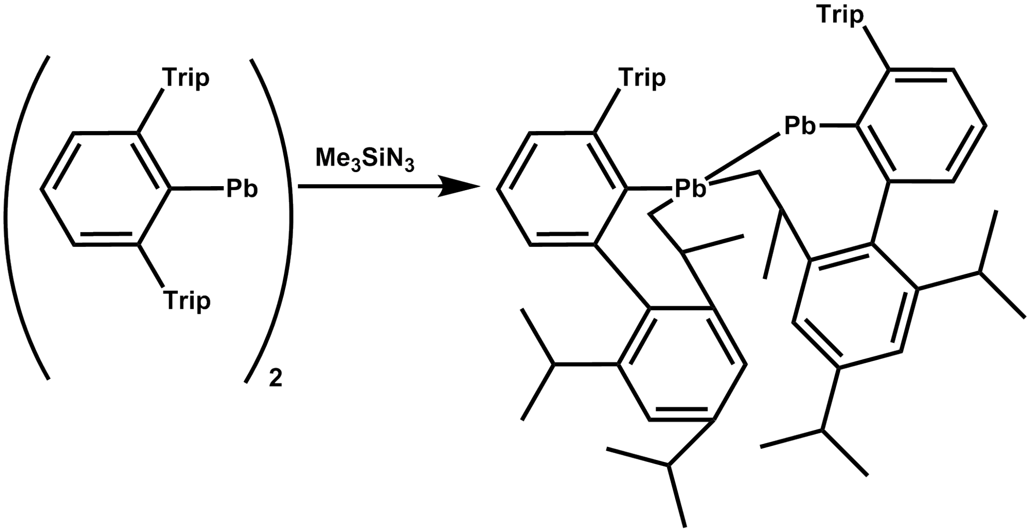


Figure 68: The reaction performed by Hino et al. yielding the first stable plumbylplumbylene known in literature.[164]

Table 10 gives an overview on the heavier tetryltetrylenes known in literature and selected properties of these compounds.

Compound	**E-E** [Å]	**Color**	**^{119}Sn/^{207}Pb shift [ppm]**	**Ref.**
^{t}Bu$_3$GeGe(2,6-Mes$_2$C$_6$H$_3$)	2.5439(7)	blue	—	142
2,6-Dipp$_2$C$_6$H$_3$(PMe$_3$)GeGeH$_2$-(2,6-Dipp$_2$C$_6$H$_3$)	2.5304(7)	yellow	—	145
NHC-ClGeGeClMes$_2$	2.5355(19)	pale yellow	—	146
NHC-ClGeGe(SiMe$_3$)$_3$	n.a.	red-orange	—	147
^{t}Bu$_3$GeSn(2,6-Mes$_2$C$_6$H$_3$)	2.7224(11)	blue	2960	142
NHC-Ge{Sn(SiMe$_3$)$_3$}$_2$	2.686(1)/2.703(1)	orange	-589.76	147
NHC-Sn{Ge(SiMe$_3$)$_3$}$_2$	n.a.	red-orange	-115.0	147
NHC-Sn{Sn(SiMe$_3$)$_3$}$_2$	2.864(1)/2.883(1)	brown	-138.3/-655.5	147
Pb[Ge(SiMe$_3$)$_3$]$_2$	2.733(2)	black	n.a.	148
2-(CHPPh$_2$C$_6$H$_4$)$_3$SnSnCl	n.a.	yellow	-102.4/-226.0	149
{2-[(SiMe$_3$)$_2$C]-C$_5$H$_4$N}SnSn(SiMe$_3$)$_3$	2.8689(5)	red	-502/897	150
2,6-Trip$_2$C$_6$H$_3$SnSnMe$_2$(2,6-Trip$_2$C$_6$H$_3$)	2.8909(2)	green	257/2857	154,165
4-^{t}Bu-2,6-{P(OEt)$_2$O}$_2$C$_6$H$_2$SnSnPh$_3$	n.a.	red-brown*	-43/109	155
4-^{t}Bu-2,6-{P(OEt)$_2$O}$_2$C$_6$H$_2$SnSnMe$_3$	n.a.	red-brown*	11/217	155
Sn[Sn{2,6-(O^{i}Pr)$_2$C$_6$H$_3$}$_3$]$_2$	2.865(1)/2.867(1)	brownish-red	-14.6/1302.1, -14/1296	156,157
(2,6-Trip$_2$C$_6$H$_3$)SnSnPh$_2$(2,6-Trip$_2$C$_6$H$_3$)	2.9688(5)	blue-green	245/2870	158
Sn(SnPh$_2$-2,6-Trip$_2$C$_6$H$_3$)$_2$	2.9630(3)/2.9644(3)	pale orange	398/3752	159
(3,5-^{i}Pr$_2$-2,6-Trip$_2$C$_6$H)SnSnH$_2$-(3,5-^{i}Pr$_2$-2,6-Trip$_2$C$_6$H)	2.916(1)	dark-blue	34/1727	161
TMSTripSnSnTMSTrip (intramolecular bonding)	2.9034(13)	red	71/789	162
(2,6-Dipp$_2$C$_6$H$_3$)SnSn(CC^{t}Bu)$_2$(2,6-Dipp$_2$C$_6$H$_3$)	2.9038(2)	blue	n.a.	163
{2,6-(O^{i}Pr)$_2$C$_6$H$_3$}PbSn{2,6-(O^{i}Pr)$_2$C$_6$H$_3$}$_3$	2.8784(4)	purple	1270 (^{119}Sn)/6905 (^{207}Pb)	157
(2,6-Trip$_2$C$_6$H$_3$)PbPb(2,6-Trip$_2$C$_6$H$_3$) (intramolecular bonding)	2.9928(3)	green	n.a.	164

Table 10: Selected properties of the heavier tetryltetrylenes known in literature. *Color in thf solution.

6.2.2 Deployment of Low Valent Terphenyl-Stabilized Compounds

Syntheses of the low valent main group 3 and 4 element compounds deployed in the present work were previously described in literature.[166,167]

6.2.2.1 Reactions of Tetrylenes with Adamantylphosphaalkyne

Addition Reactions of Low Valent Terphenyl-Stabilized Compounds

The reactivity of tetrylenes, i.e. compounds with formal composition R_2E:, has been one focus of main group and transition metal chemistry for decades. An extensive review on the topic ('Stable Heavier Carbene Analogues') was given by Mizuhata et al. in 2009. The authors stated that 'The diverse range of reported reactivities of stable metallylenes can be roughly categorized into five types: (i) insertion, (ii) cycloaddition, (iii) reduction, (iv) oxidation, and (v) coordination reactions. A valid explanation of this diverse range of reactions is the initial formation of a Lewis acid-base complex between the metallylene and the reagent with the metallylene acting as a Lewis acid with high electrophilicity. As described above, a metallylene has two reactive sites, namely, the vacant p orbital and the lone pair of electrons based on its singlet ground state. However, the lone pair is expected to be relatively 'inert' as a nucleophile, since it exhibits high s character due to its $(ns)^2(np)^2$ valence electron configuration. On the other hand, due to the 6 valence electrons and the octet rules, the vacant p orbital should make the metallylene highly electrophilic. Thus, almost all the metallylene reactivity can be initiated by the nucleophilic reaction of the reagents toward the vacant p orbital. For example, reactions of the stable metallylenes R_2M: with haloalkanes (R'X, X = halogen) such as MeI or MeOH (R'OH) are known to give the corresponding insertion products $R_2MR^{'}X$ (X = halogen or OH) [reactivity (i)]. Such insertion reactions can be initiated by the nucleophilic attack of the halogen or oxygen lone pair, leading to the formation of the Lewis-acid-base complex, e.g. $R_2M^{\delta -}{-}X^{\delta +}{-}R^{'}$. [...] Since the nucleophilicity of the central metallylene moiety (M) should be enhanced by this coordination, the next step in the nucleophilic reaction is expected to be that of the M toward the R' moiety. [...] Other unique metallylene insertion reactions toward systems such as Si-H, Si-Cl, B-H, and B-B bonds [...] can also be explained by an initial interaction between the vacant p orbital and the reactive bond with a high highest occupied molecular orbital (HOMO) level.'[168]

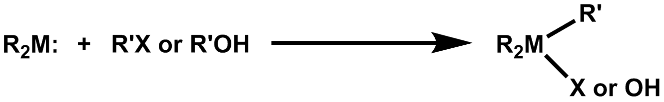


Figure 69: Reactivity (i) of metallylenes: Insertion reactions.[168]

'In case of cycloadditions with unsaturated organic compounds such as alkenes and alkynes, the corresponding [1 + 2]-cycloadducts, metalliranes and metallirenes, are obtained, while the [1 + 4]-cycloadducts are obtained when the butadiene derivatives are reacted with the metallylenes [reactivity (ii)]. In these reactions, the p-bonds of unsaturated compounds attack the vacant p orbitals of the metallylenes. The reaction with 1,3-butadiene, leading to the formation of the corresponding cycloadducts, can be explained by two possible mechanisms: a direct [1 + 4] pericyclic reaction between the HOMO of the 1,3-butadiene and the lowest unoccupied molecular orbital (LUMO), the vacant p orbital of the metallylene, or an initial [1 + 2] cycloaddition reaction followed by a rearrangement leading to the formation of the corresponding four-membered ring system, the formal [1 + 4]-cycloadduct.'[168]

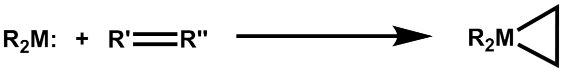
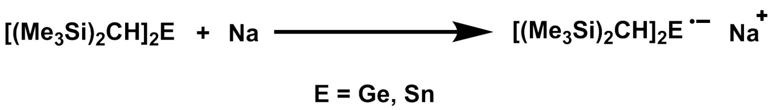


Figure 70: Reactivity (ii) of metallylenes: Cycloaddition reactions, shown here: a [1 + 2] cylcloaddition reaction of a tetrylene and an alkene.[168]

'Interestingly, some carbon-substituted metallylenes were reported as reacting with phosphaalkyne derivatives to give the corresponding heterocyclic compounds, which are quite unique. Such unusual reactions can also be explained by an initial coordination of the reagents toward the vacant p orbitals of the metallylenes.'[168] One of the reactions referred to by the authors is discussed later in the present work (compare figure 83).

Concerning reactivity (iii) the authors stated that 'On the other hand, the vacant p orbital of a metallylene can also accept an electron. Some photoinduced insertion reactions of dialkylsilylene [...] have been reported. [...] In addition, the generation of a radical anion species of carbon-substituted metallylenes has also been reported. [...] Again this suggests electronic structures where one electron is in the vacant p orbital of the corresponding metallylene [(iii) reduction reactions].'[168]

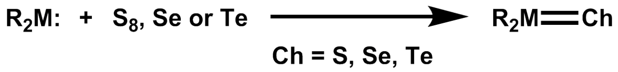


$$[(Me_3Si)_2CH]_2E + Na \longrightarrow [(Me_3Si)_2CH]_2E^{\bullet -}\ Na^{+}$$

$$E = Ge, Sn$$

Figure 71: Reactivity (iii) of metallylenes: Reduction reactions, shown here: generation of germylene and stannylene anionic radicals performed by Egorov et al. in 1995.[168,169]

'Although reactions of metallylenes leading to the formation of the corresponding tetravalent species should also strictly be categorized as "oxidation reactions", since the oxidation number of the central metal atom is changed from M^{II} to M^{IV} during the reaction, "(iv) oxidation reactions" here actually means chalcogenation (O, S, Se, Te) reactions of the metallylenes [...]. In these cases, however, the nucleophilic oxidant acts as an oxidant toward the vacant p orbital of the metallylene. Thus, the lone pairs of the chalcogen atoms such as (S_8, Se, Te) and the phosphine chalcogenides can react with the vacant p orbital of the metallylenes. This gives the heavier ketone analogues, the so-called "heavy ketones" $R_2M{=}Ch$ [...], or the cyclic polychalcogenides containing the heavier group 14 elements. The latter have been shown to be precursors for producing the corresponding "heavy ketones".'[168]



$$R_2M: + S_8,\ Se\ or\ Te \xrightarrow[Ch\ =\ S,\ Se,\ Te]{} R_2M{=}Ch$$

Figure 72: Reactivity (iv) of metallylenes: Oxidation reactions, shown here: formation of "heavy ketones".[168]

'Metallylenes can, therefore, be characterized by their vacant p orbital. Accordingly, one can conclude that metallylenes can be stabilized by the coordination of a Lewis base, giving the corresponding donor-stabilized metallylenes [...]. For example, the reaction of isocyanides with silylenes gave the corresponding silylene-isocyanide complexes, which can be formulated as the silaketenimine resonance structure.'

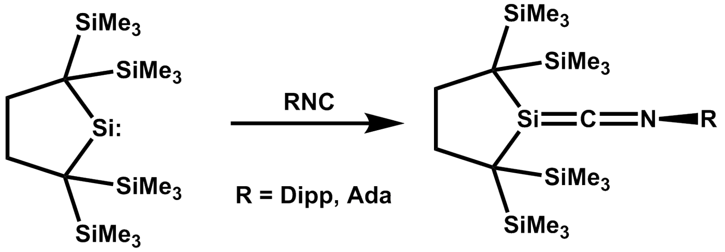


Figure 73: Reactivity (v) of metallylenes: Coordination reactions, shown here: formation of a silylene-isocyanide complex described by Abe et al. in 2006.[168,170]

Another point of view concerning the reactivity of tetrylenes has been a special point of interest in the last years: The activation of small molecules has become a topic of great interest. A review by Power from the year 2010 stated that '[...] a gradually increasing realization that the chemistry of the heavier main-group elements more resembles that of transition-metal complexes than that of their lighter main-group congeners [...]' had taken place in the past years. 'The similarity is underlined by recent work, which has shown that many of the new compounds react with small molecules such as H_2, NH_3, C_2H_4 or CO under mild conditions [...]'.[171] One example cited by Power is given in figure 74.

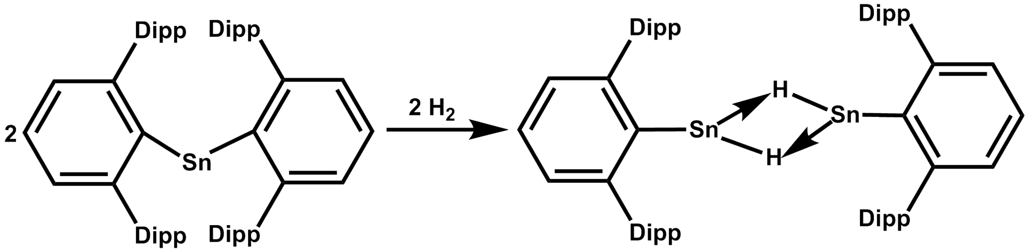


Figure 74: Activation of H_2 by a stannylene cited by Power in his review from the year 2010.[171] The reaction had been previously published by Peng et al. in 2008.[172] (The analogous reaction deploying NH_3 was also described in the same paper.)

A report by Brown and Power from the year 2013 gave further insight into the deployment of tetrylenes regarding the reactions with 'isocyanides, CO, ammonia, and related molecules'.[173] The conversion of a germylene with CO cited in this article (and performed by Wang et al. in 2009[174]) is shown in figure 75.

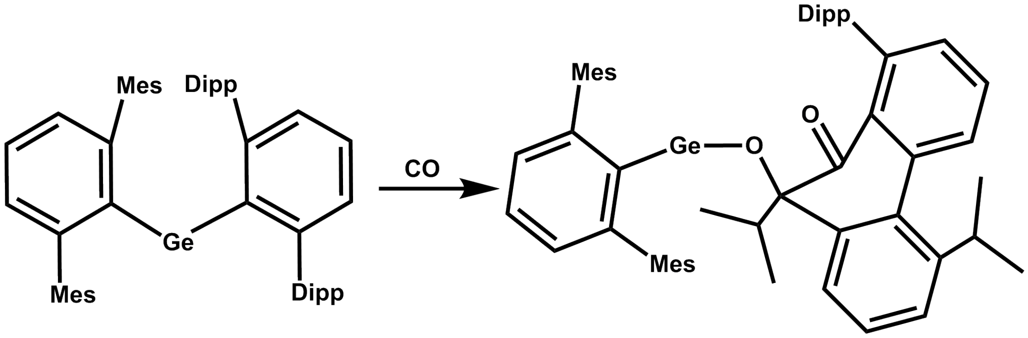


Figure 75: Activation of CO by a germylene described by Wang et al.[174] and Brown and Power.[173]

Another example cited by Brown and Power was the reaction of a germylene with an isocyanide (performed by Brown et al. in 2012[175]), as depicted in figure 76.

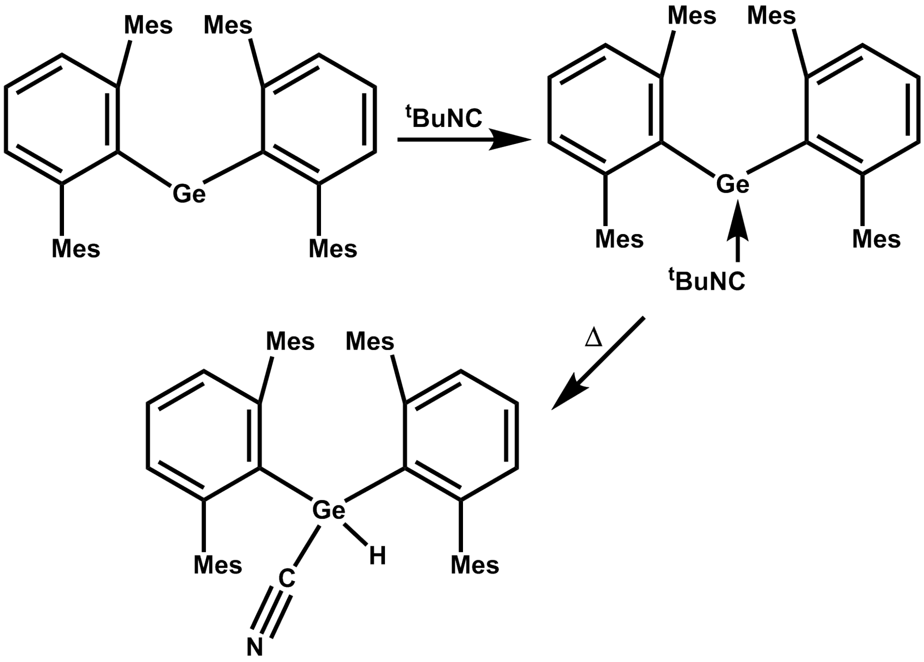


Figure 76: Activation of an isocyanide by a germylene described by Brown et al.,[175] cited by Brown and Power.[173]

Phosphaalkynes – Versatile Building Blocks in Organic, Inorganic, and Organometallic Chemistry

Starting with the successful and selective synthesis of HC≡P reported by Gier in 1961,[176] the history of phosphaalkynes has been a rich and successful one. The significance and utility of this class of compounds, that had been believed to be non-existant for decades, has been continuously explored and reviewed since the late 80s.[*see e.g.* 177–187] Especially the duality of participation of either the triple bond or the phosphorus lone-pair electrons in reactions has led to a vast number of compounds deriving from reactions of phosphaalkynes with transition metal and main group element precursors. Reaction of the triple bond is generally preferred, the lone pair at the phosphorus atom is only active with special substrates offering "pockets" for end-on reactions.

Conversion of Phosphaalkynes with Low Valent Main Group 4 Element Compounds

The reaction of a carbene with a phosphaalkyne (^{t}BuC≡P) was first published by Wagner et al. in 1987.[188,189] The first successful conversions of phosphaalkynes (^{t}BuC≡P, AdaC≡P) with a heavier low valent main group 4 element compound (^{t}Bu$_2$Si:) were published by Schäfer et al. in 1987. The oily products obtained were the first known phosphasilirenes, namely the first three-membered ring compounds containing a carbon-phosphorus double bond. An X-ray structure of the latter (R = Ada) was obtained after conversion with W(CO)$_5${thf} in form of the adduct [^{31}P NMR (C$_6$D$_6$): δ 274.0 ppm for R = ^{t}Bu; ^{31}P NMR (C$_6$D$_6$): δ 272.6 ppm for R = Ada].[190,191]

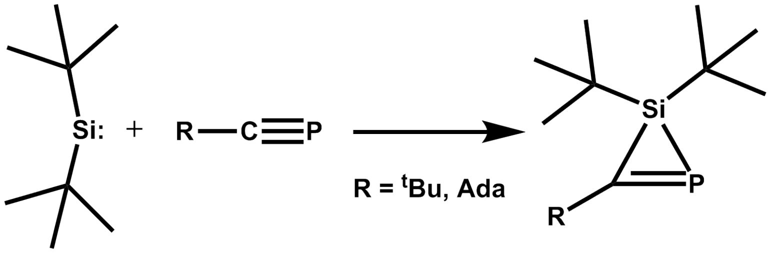


Figure 77: Trapping reactions of a silanediyl by phosphaalkynes as published by Schäfer et al. yielding phosphasilirenes.[190,191]

An analogous structure bearing bulkier ligand systems was published by Tokitoh et al. in 2002. While an X-ray structure could not be obtained, the 'molecular structures [...] were satisfactorily confirmed by ^{1}H, ^{13}C, ^{29}Si and ^{31}P NMR spectroscopy, and DFT calculations [...]' [^{31}P NMR (109 MHz, $CDCl_3$/85 % H_3PO_4): δ 287.39 ppm].[192]

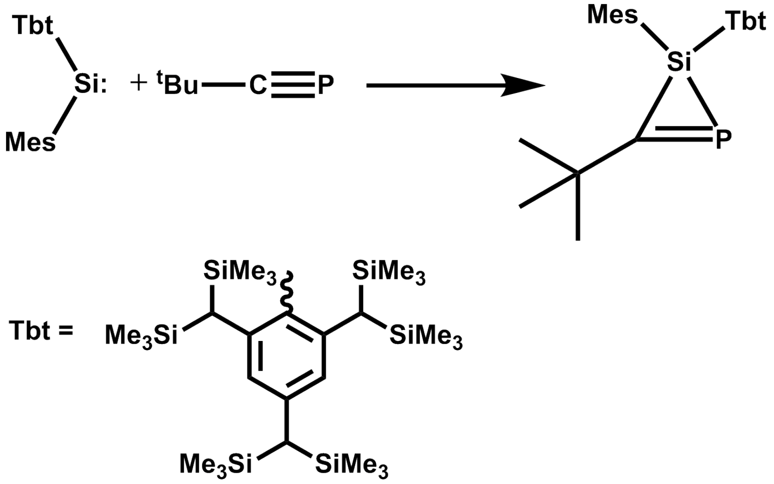


Figure 78: Analogous conversion of an in-situ obtained silylene with a phosphaalkyne published by Tokitoh et al.[192]

The 'stepwise silylene addition to phosphaalkynes', yielding phosphadisilacyclobutenes, was reported by Weidenbruch et al. in 1997.[193] They proposed that the reaction proceeds via addition of one equivalent of dimesitylsilylene to the carbon-phosphorus triple bond, followed by the insertion of a second equivalent of the silylene transforming the three-membered ring (an analog to the one obtained by Schäfer et al.) into a four-membered system. The difference in the products obtained is explained by the effects of the aryl groups at the silicon atom compared to the ^{t}Bu substitution deployed by Schäfer et al. The structure of the adamantyl-substituted compound was confirmed by X-ray crystallography [^{31}P NMR: δ 441.2 ppm for R = Ada, 442 ppm for R = 1-methylcyclohexyl].[193]

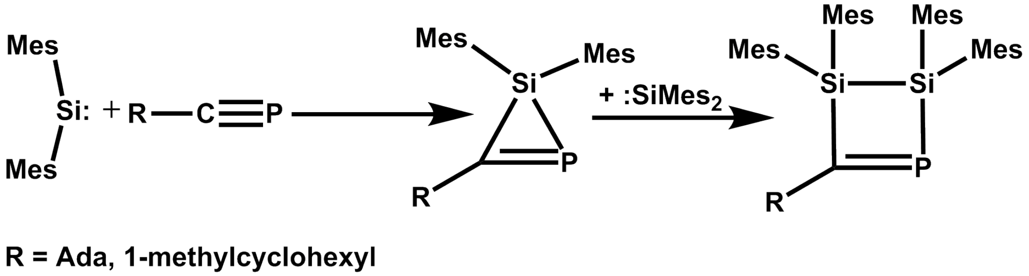


Figure 79: Stepwise silylene addition to phosphaalkynes, published by Weidenbruch et al. in 1997.[193]

In analogy to the conversions performed by Schäfer et al., reaction of a germylene ($[(Me_3Si)_2CH]_2Ge:$) with ${}^tBuC{\equiv}P$ yielded the corresponding phosphagermirene as proven by Cowley et al. in 1988. The structure of this compound was confirmed by X-ray analysis [^{31}P NMR (121.5 MHz, hexane/85% H_3PO_4): δ 315 ppm].[194]

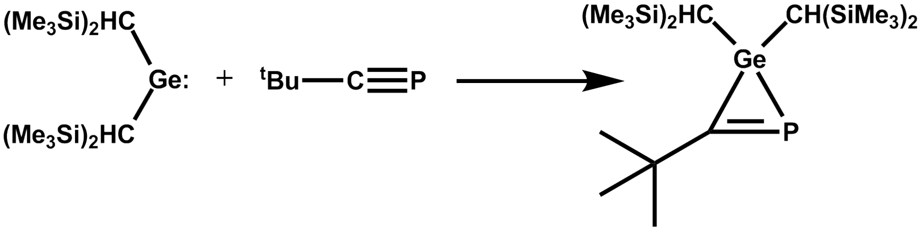


Figure 80: A phosphagermirene obtained by Cowley et al. by conversion of a germylene with a phosphaalkyne.[194]

The reaction of ${}^tBuC{\equiv}P$ with an arylgermane yielded – in contrast to the result shown above – a polycyclic product as reported by Lazraq et al. in 1993.[195] Another conversion of ${}^tBuC{\equiv}P$ with a diarylgermylene performed by Meiners et al. in 2001 yielded a germadiphosphacyclobutene. The formation of this four-membered ring system was explained by the dimerization of two equivalents of the phosphagermirene, obtained in the first step of the reaction, similar to the conversion conducted by Cowley et al. The structure was determined via X-ray diffraction measurements [^{31}P NMR: δ 271.5 ppm, -34.4 ppm (d, $^1J_{\mathrm{PP}} = 16$ Hz), 269.0 ppm, -8.1 ppm (d, $^1J_{\mathrm{PP}} = 21$ Hz), due to two conformers in solution].[196]

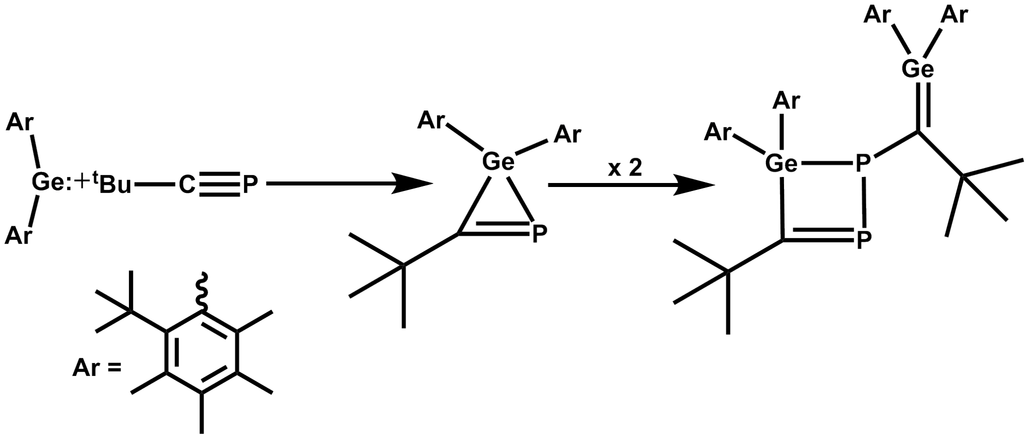


Figure 81: The germapdiphosphacyclobutene, obtained by Meiners et al. in 2001, presumeably by dimerization of two equivalents of the phosphagermirene (first step of the reaction).[196]

Cowley et al. published the successful addition of the distannene $\{[(Me_3Si)_2CH]_2Sn\}_2$ to $^tBuC{\equiv}P$ in 1988. A phosphadistannacyclobutene was obtained – in contrast to the three-membered ring systems described in case of germanium. Despite evidence that the distannene takes part in the reaction in an equilibrium with the corresponding monomer stannylene, the reacting species seems to be the distannene itself due to several indications. The structure was confirmed by X-ray analysis [^{31}P NMR (121.5 MHz, C_6D_6/85% H_3PO_4): δ 459.0 ppm (s, $^1J_{\mathrm{SnP}}$ = 830.0 (^{117}Sn), 796.0 (^{119}Sn) Hz, $^2J_{\mathrm{SnP}}$ = 278.3 Hz); ^{119}Sn NMR (111.9 MHz, C_6D_6/Me_4Sn): δ 58.6 ppm (d, $^1J_{\mathrm{PSn}}$ = 827.2 Hz), 160.4 (d, $^2J_{\mathrm{PSn}}$ = 281.9 Hz, $^1J_{\mathrm{SnSn}}$ = 892.2 Hz)].[197,198]

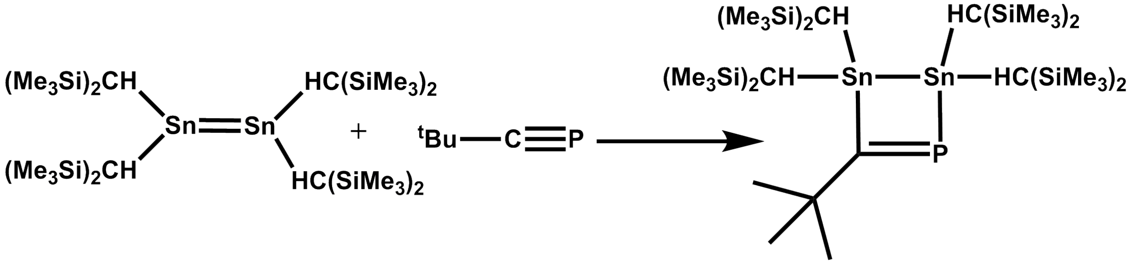


Figure 82: Cowley et al.'s conversion of a distannene with a phosphaalkyne yielding a phosphadistannacyclobutene performed in 1988.[197,198]

Jones et al. compared the reactivity of MeC≡P toward :ER_2 and R_2EER_2 (E = Si, Ge, Sn, Pb) species with the already well-studied reaction behaviour of ^{t}BuC≡P in 2008.[199] In addition, they deployed and compared the two different ligand systems $CH(SiMe_3)_2$ (R') and Trip. While the reactions deploying the disilene $Mes_2Si{=}SiMes_2$, the diplumbene $Trip_2Pb{=}PbTrip_2$ or the plumbylene :PbR'$_2$ led to 'intractable mixtures of phosphorus containing products', conversions of R'$_2$Ge=GeR'$_2$, R'$_2$Sn=SnR'$_2$ and $Trip_2Sn{=}SnTrip_2$ yielded bridged 2,3,5,6-tetraphospha-1,4-dimethylidenecyclohexanes. Most important, the reaction of R'$_2$Ge=GeR'$_2$ was claimed to proceed via a phosphagermirene [^{31}P NMR (121.6 MHz, thf-d_8/85% H_3PO_4): δ 436.6], analogous to the one obtained by Cowley et al. in 1988. Addition of a second equivalent of MeC≡P was discussed to lead to the formation of a 2,4-diphosphagermole [^{31}P NMR (121.6 MHz, thf-d_8/85% H_3PO_4): δ 308.5, 319.8 ppm, $^2J_{PP}$ = 29.8 Hz (AB spin system)], which was converted into the final product via 1,3-H shifting [^{31}P NMR (121.6 MHz, thf-d_8/85% H_3PO_4): δ -13.7 ppm (br. d, $^1J_{PP}$ = 303.1 Hz, *P*Ge), 31.7 ppm (br. d, $^1J_{PP}$ = 303.1 Hz, P*P*CCH$_2$) for E = Ge, R = R'; CD_2Cl_2 instead of thf-d_8, -63.2 ppm (br. d, $^1J_{PP}$ = 311.2 Hz, $^1J_{SnP}$ = 621.2 Hz, *P*Sn), 16.5 ppm (br. d, $^1J_{PP}$ = 311.2 Hz, P*P*CCH$_2$) for E = Sn, R = R'; C_6D_6 instead of CD_2Cl_2, -76.3 ppm (d, $^1J_{PP}$ = 320 Hz, $^1J_{SnP}$ = 614 Hz, *P*Sn), 15.8 ppm (d, $^1J_{PP}$ = 320 Hz, *P*P) for E = Sn, R = Trip]. The existence of the germole could be proved by coordinating $W(CO)_5$. ('1:1 and 1:2 adducts of the heterocycle with the $W(CO)_5$ fragment' were observed.) Molecular structures of the complexes were obtained and proved the existance of the germole.[199]

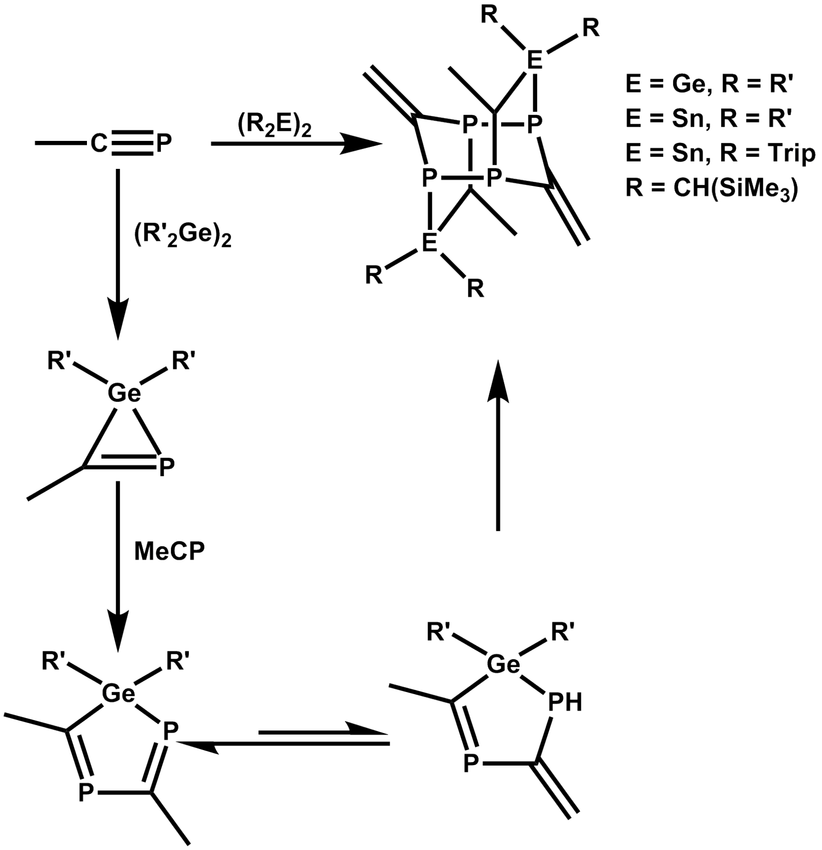


Figure 83: Conversions of a series of digermenes and distannenes with methylphosphaalkyne published by Jones et al.[199]

Formation of Polyphosphaphospholes

The formation of polyphosphaphosphole derivatives (phosphole = phosphacyclopentadiene) was first described in 1985 by Becker et al.[200] and subsequently proved in 1989 by Cowley et al.[201] and Bartsch et al.,[202] respectively. Unfortunately, X-ray crystal data were not published by these authors.

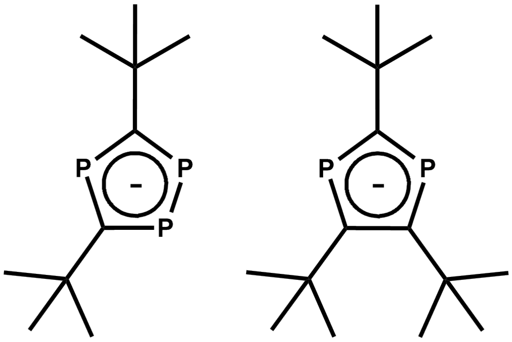


Figure 84: Polyphosphaphospholides obtained by Cowley et al.[201] and Bartsch et al.[202] [^{31}P NMR (thf/85 % H_3PO_4): δ 245.5 (d, $^2J_{PP} = 47$ Hz), 252.5 ppm (t, $^2J_{PP} = 47$ Hz) (left); 187.6 ppm (right) according to Cowley et al.].

Further investigation of the products led to a rich variety of compounds based on polyphosphaphospholide ligands,*see e.g.*[203] including heteroatom substitution in the aromatic ring system.*see e.g.*[204,205]

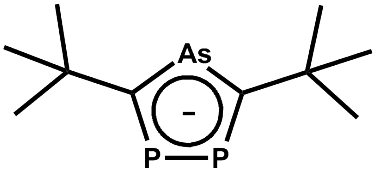


Figure 85: The $AsP_2C_2^tBu_2^-$ anion obtained by Bartsch et al. by conversion of ^{t}BuC≡P with $LiAs(SiMe_3)_2$.[204]

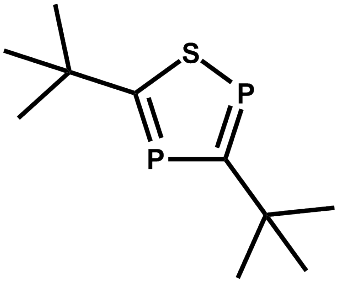


Figure 86: $SP_2C_2^tBu_2$, an example of a 1,2,4-thiadiphosphole, synthesized by Dietz et al. by reaction of ^{t}BuCP with S_8 and $STaCl_3$ in the presence of Ph_3P [^{31}P NMR (C_6D_6/85 % H_3PO_4): δ 254.7, 266.8 ppm ($^2J_{PP} =$ 49.5 Hz)].[205]

Dietz et al.'s thiadiphosphole was also deployed for subsequent reactions, including conversion with trisacetonitrile complexes yielding half-sandwich complexes as depicted in figure 87.[205]

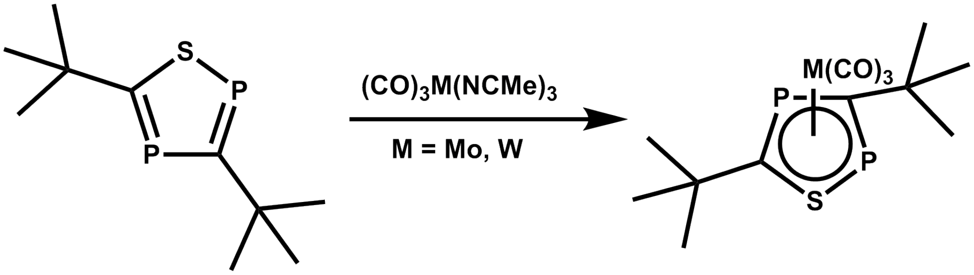


Figure 87: One of the subsequent reactions deploying a thiadiphosphole derivative published by Dietz et al.[205]

Aromaticity of Five-Membered Heavier Group 14 Organometallic Ring Systems

'Although aromaticity has been extensively studied for more than a century, there is still no generally acceptable definition. [...] The most general point of view on aromaticity combines the geometric (bond length equality), energetic (aromatic stabilization energy) and magnetic (diamagnetic susceptibility exaltations and nucleus-independent chemical shifts) criteria.'[206(*referring to* 207–210)] 'The theory of aromaticity has also undergone a spectacular evolution since the first definition of aromaticity by Hückel; the classification of aromaticity now requires the consideration of versatile criteria: energetic, structural, magnetic, among others.'[211] 'Experimental and theoretical investigations have established that aromaticiy of the heavier Group 14 element analogues of the cyclopentadienyl anion strongly depends on the nature of the counter anion and substituents. Not all metallole anions and dianions are aromatic.'[206 *and references therein*] A series of aromatic five-membered ring systems containing heavier Group 14 elements ist known. Here, not all of them shall be discussed, but the author will focus on the availability of crystal structures and further methods of characterization. (For an early general review on metalloles see the publication by Dubac et al. from the year 1990.[212])

As early as 1990 Dufour et al. investigated the potential aromaticity of the germacyclopentadienyllithium compound shown in figure 88. The lithium derivative had been obtained by conversion of the germole precursor with BuLi in thf. The group stated that 'the negative charge is localized on the germanium atom' [^{13}C NMR (50.32 MHz, thf-d_8/TMS): δ 128.2 (GeCC), 148.9 (GeCC) ppm for the germole ring].[213]

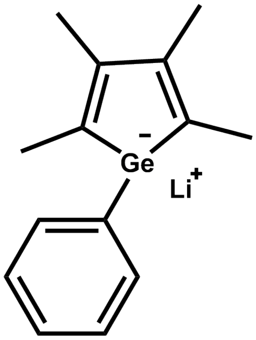


Figure 88: The germacyclopentadienyllithium derivative described by Dufour et al. in 1990.[213]

In 1995 Freeman et al. published the synthesis and characterization of [Li(12-crown-4)$_2$][$C_4Me_4GeSi(SiMe_3)_3$] [^{13}C NMR (100.6 MHz): δ 136.95 (GeCC), 157.03 (GeCC) ppm] and [K(18-crown-6)][$C_4Me_4GeSi(SiMe_3)_3$] [^{13}C NMR (75.5 MHz): δ 137.13 (GeCC), 157.06 (GeCC) ppm]. ('The NMR parameters for these compounds suggest that the anions have identical structures.') The germole analog (complexed by K(18-crown-6)) with a $SiMe_3$ substituent instead of the $Si(SiMe_3)_3$ group was also presented in the same paper [^{13}C NMR (100.6 MHz): δ 136.72 (GeCC), 158.56 (GeCC) ppm]. The X-ray crystal structure of the lithium compound was obtained and described as follows: 'A pyramidalization at the germanium center is clear, as evidenced by the angle between the C_4Ge plane and the Ge-Si bond of only 100.1°. Furthermore, the carbon portion of the ring has considerable diene character, as indicated by the C1-C2, C2-C3, and C3-C4 bond lengths of 1.36(6), 1.46(6), and 1.35(5) $\mathring{A}$, respectively. [...] These data therefore suggest that $[Me_4C_4GeSi(SiMe_3)_3]^-$ gains very little stabilization by π-delocalization of the negative charge' [Ge(1)-C(1) 2.01(3), Ge(1)-C(4) 1.96(3) $\mathring{A}$]. The group concluded that their compound is 'a non-aromatic ring with a pyramidal germanium center'[214,215] – in sharp contrast to the ruthenium complex shown in figure 91 published by the same group.[216,217] Amongst others, Lee et al. mentioned $Ph_4C_4GeLi_2$ as a metalloaromatic example in their review from the year 2000.[206] Details on this compound were described by Hong et al. in 1995[218] and West et al. in 1996.[219,220] The aromaticity of this germole dianion was established on the basis of the ^{13}C NMR spectrum ('NMR studies [...] give evidence of a high degree of π-delocalization'[218]), as well as of the nearly planar geometry of the five-membered ring and the equal C-C bond lengths. Interestingly, two products were obtained when employing varying crystallization temperatures: One type of product showed an η^5-η^5-structure, while in the other one an η^1-η^5-bonding pattern (η^1 to Ge) was observed [^{13}C NMR (75.403 MHz, dioxane): δ 119.45, 122.03, 125.89, 128.04, 129.19, 131.93, 143.83, 150.07, 165.17 ppm; Ge(1)-C(1) 1.957(3), Ge(1)-

C(4) 1.956(3), C(1)-C(2) 1.429(4), C(2)-C(3) 1.449(4), C(3)-C(4) 1.431(4) for η^5-η^5-coordination, Ge(1)-C(1) 1.930(2), Ge(1)-C(4) 1.930(2), C(1)-C(2) 1.423(2), C(2)-C(3) 1.435(2), C(3)-C(4) 1.421(2) for η^1-η^5-coordination].[219,220]

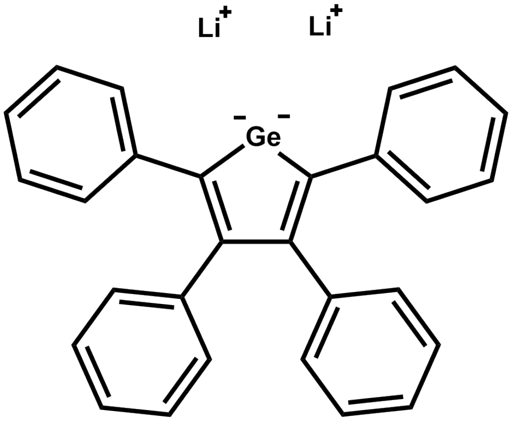


Figure 89: One compound showing metalloaromaticity described by Hong et al.[218] and West et al.[219,220]

Freeman et al. synthesized a series of metallole species and investigated the aromaticity of some of the compounds by NMR and X-ray diffraction in 1996. An obtained bisgermole dianion complex was [K_4(18-crown-6)$_3$][C_4Me_4Ge]$_2$ [Ge(1)-C(1) 1.846(9), Ge(1)-C(4) 1.959(8), C(1)-C(2) 1.451(11), C(2)-C(3) 1.431(10), C(3)-C(4) 1.417(10)], a series of monoanions is shown in figure 90. The group claimed that for the dianionic structure (obtained as thf adduct) 'the structural analyses [...] reveal the presence of delocalized π-systems, as indicated by roughly equivalent C-C distances in the ring', while in case of the (silolyl and) germolyl anions 'NMR data are consistent with a significant localization of charge on the heavy group 14 element (Si or Ge) and a nonaromatic, bond-localized structure'. The group also reasoned that the 'NMR parameters for **23** – **27** [note: compounds **a** – **d** in figure 90 plus the lithium derivative described by Freeman et al. in 1995 (see page 72)[214,215]] indicate that the anions have very similar structures in solution. For example, the ^{13}C NMR shifts for the ring carbons [...] of compounds **23** [note: compound **a** in figure 90] and **25** [note: the lithium derivative described by Freeman et al. in 1995[214,215]] are nearly equivalent [...], and somewhat downfield shifted relative to analogous resonances for the corresponding germoles. Such shifts seem to be associated with bond localization in the rings, and considerable localization of negative charge onto the germanium atom [...]. Note that the analogous ^{13}C shifts for **27** [note: compound **d** in figure 90] are similar [...], indicating that interaction of the lithium cation with the ring does not greatly perturb its electronic structure.' Furthermore, the authors concluded (concerning compound

c) that the 'anion possesses a pyramidal germanium center, which results in an angle between the C_4Ge plane and the Ge–C(Mes) bond of 113.4°. For comparison the analogous angle in **25** is considerably smaller, at 100.1°. In addition the C_4Ge ring possesses pronounced bond localization, as indicated by the variation in C–C bond lengths.' On compound **e** they commented as follows: 'The ^{13}C NMR data [...] indicate that the anionic ring, like those in **25** and **26** [note: compound **c** in figure 90], is bond-localized and nonaromatic [...]. [...] This structure differs from those for **25** and **26**, in that there is a strong interaction between the cation and anion. This interaction brings the sodium atom in contact with only the germanium atoms of the ring; there are no sodium-carbon bonding interactions in the structure. Thus, the germanium atom is in a distorted tetrahedral environment. Bond distances in the ring reflect a nonaromatic diene structure, and are very similar to the corresponding distances in **25** and **26**, despite the presence of the Na···Ge bonding interaction. The angle between the Ge–C(Me) bond and the C_4Ge plane, 110.0°, is very close to the corresponding value for the free anion **26** (113.4°).' Though, Freeman et al. mentioned that 'an important question that remains, therefore, is whether or not the ground state properties of silolyl and germolyl anions can be greatly influenced by the nature of substituents on the five-membered ring.' They also stated that 'coordination of a transition metal fragment induces considerable π-delocalization and apparent aromatic character for silolyl and germolyl rings'.[221] Selected bond lengths of the compounds that yielded crystals suitable for X-ray diffraction and NMR data of all compounds are cited in tables 11 and 12, respectively.

Compound	Ge-C1/Ge-C4 (av) [$\AA$]	C1-C2/C3-C4 (av) [$\AA$]	C2-C3 [$\AA$]
c	1.98	1.34	1.47(1)
e	1.96	1.33	1.48(1)

Table 11: Bond lengths of the central core of the germolyl monoanions published by Freeman et al. in 1996.[221]

Compound	ν_0 [MHz]	solvent	δ [ppm]	δ [ppm]
a	75.5	C_6D_6	137.13	157.06
b	100	C_6D_6	145.94	156.40
c	100	C_6D_6/thf	145.49	155.21
d	100	thf-d_8	141.29	156.90
e	100	C_6D_6	136.10	156.89
f	100	C_6D_6	131.31	135.26
g	100	thf-d_8	141.10	157.40
h	100	C_6D_6	136.72	158.56
i	100	C_6D_6	140.63	156.43
j	100	thf-d_8	142.45	166.84
k	100	thf-d_8	141.05	168.62

Table 12: ^{13}C NMR data (C_4Ge^- core) of germolyl monoanions published by Freeman et al. in 1996.[221]

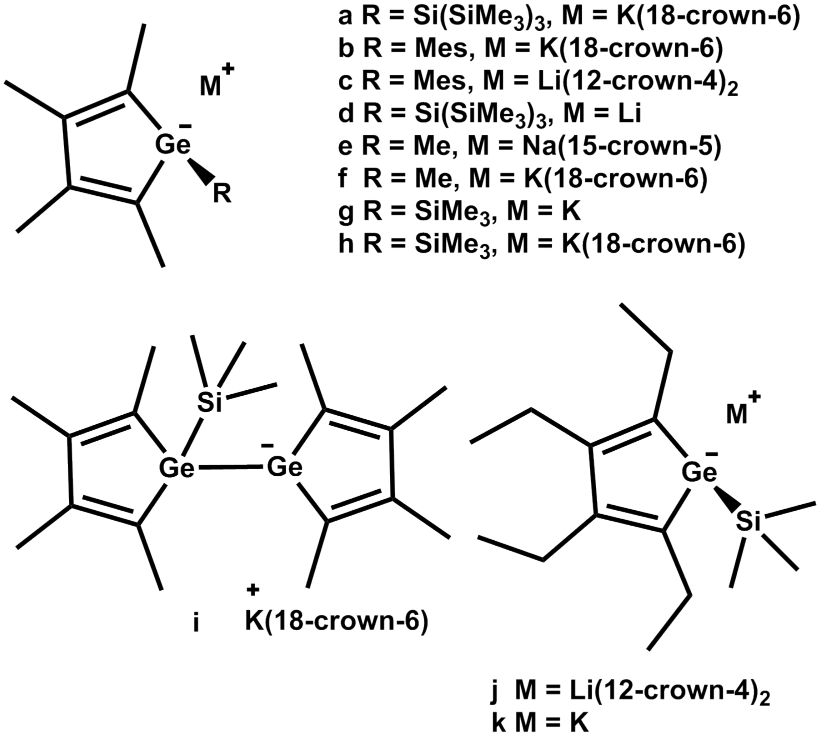


Figure 90: The series of germolyl monoanions described by Freeman et al. in 1996.[221]

A uniquely bound structure was observed by Choi et al. in 1999, when they obtained $[\eta^5\text{-Li}\{\text{tmeda}\}][\eta^5\text{-Li}]_{0.5}[\eta^1\text{-Li}]_{0.5}[Et_4C_4Ge]$. In the introduction to their paper the authors described that 'Until now, only two types of metal coordination to silole and germole dianions have been characterized by experimental or theoretical methods: η^5, η^5 [...] and η^1, η^5 [...].' The structure of the new lithium derivative was explained as follows: 'One lithium ion [...] is η^5-coordinated to the C_4Ge ring and to TMEDA while the other [...] is η^5-coordinated to the C_4Ge ring fragment and also η^1-coordinated to a germanium atom of another C_4Ge ring. This combination of linkages results in a polymeric network [...].' The authors summed up that 'The nearly equal carbon–carbon bond lengths in the GeC_4 ring (bond distances of the C_1-C_2, C_2-C_3, C_3-C_4 are 1.417, 1.444, and 1.416 $\AA$, respectively), and its planar geometry (bond angle summation of the GeC_4 ring; 540.0°) is consistent with a high degree of aromaticity' [^{13}C NMR (100 MHz, thf-d_8): δ 126.44, 167.35 ppm for the GeC_4 fragment].[222]

The review by Tokitoh (2004) named a number of six-membered ring systems containing Ge$^{e.g.}$,[223–227] but did not discuss any five-membered analogs.[228]

A review by Lee and Sekiguchi from the year 2007 cited numerous publications discussing 'analogues of the cyclopentadienide ion, incorporating one heavy element of Group 14 (Si-Sn) [...].'[211] The paper gave a broad overview on this interesting class of compounds pointing out the differences in structure and stability depending on the heteroelement. Lee and Sekiguchi also mentioned the tin analog of the germanium containing structure shown in figure 89. This stannole derivative was first prepared and described by Saito et al. and showed an η^5-η^5 structural motive[229–231] [^{119}Sn NMR: δ 186.7 ppm according to reference 229, ^{13}C NMR (101 MHz, Et_2O/C_6D_6): δ 187.68 ppm for C1/C4, ^{119}Sn NMR (149 MHz, Et_2O/C_6D_6): δ 163.3 ppm according to references 230,231; Sn(1)-C(1) 2.179(4), Sn(1)-C(4) 2.133(4), C(1)-C(2) 1.422(6), C(2)-C(3) 1.442(5), C(3)-C(4) 1.446(6) $\AA$[230,231]]. The group discussed that ' The stannole ring is almost planar and the C–C distances within the ring are nearly equal, ranging from 1.422(6) to 1.446(6) $\AA$, which suggests a considerable aromatic character of [the] dianion [...].' Natural population analysis also led to the conclusion that 'a considerable delocalization of negative charges into the stannole ring' should be present. The corresponding stannole monoanion was also identified by the same group [^{119}Sn NMR: δ -30.3 ppm].[229,232] Further discussion on this interesting class of compounds can be found in later publications of the group.$^{see\ e.g.\ 233\ and\ references\ cited\ therein}$ Saito stated in a communication from the year 2002 that 'the germolyl anions do not show aromaticity because the negative charge localizes on the germanium. [...] On the contrary, the negative charges in the dianions of siloles and germoles significantly delocalize in the C_4M (M = Si, Ge) ring.'[232]

The first plumbole – dilithiotetraphenylplumbole [^{13}C NMR: δ 147, 228 ppm for the PbC_4 fragment, ^{207}Pb NMR: δ 1712.8 ppm] – was obtained by Saito et al. in 2010 and was found to be aromatic, in contrast to the corresponding lithiomesityltetraphenylplumbole [^{207}Pb NMR: δ 1095.7 ppm]. The differences in aromaticity of the two structures were discussed as follows: On the dilithioplumbole: 'The molecular structure of dilithioplumbole **1** was established by x-ray crystallographic analysis [...]. One Li atom is coordinated by the plumbole ring in an η^5 fashion, whereas the other Li atom is coordinated by three DME molecules. Because the distance between the Pb and DME-solvated Li atoms is more than 10 $\AA$, the solvated Li atom has no interaction with the plumbole ring. The plumbole ring is planar with a 539.8° sum of the internal angles. The C–C distances within the ring are almost equal [1.410(6), 1.412(6), and 1.431(6) $\AA$], as was observed in the aromatic dilithiostannole, suggesting that dilithioplumbole **1** has considerable aromatic character.' On the lithiomesitylplumbole: 'The structure of lithiomesitylplumbole **4** was established by x-ray diffraction analysis [...] after crystallization with 12-crown-4. The Li atom is coordinated by two molecules of crown ether, and the distance between the Li and the Pb atoms of more than 6 $\AA$ suggests no interaction between them. The C–C bonds within the plumbole ring of **4** differ [1.347(8), 1.498(8), and 1.354(8) $\AA$]. The pyramidalization of the Pb center is clearly evident from the angle between the plumbole ring and the Pb–C(mesityl) bond of 103.4°. These geometric features clearly show that lithiomesitylplumbole **4** is nonaromatic, even though the plumbole ring is planar with a sum of internal angles of 539.8°.'[234]

The utilizability of germole based compounds in acting as ligands when converted with transition metals has also been described in literature, based on the presumed aromaticity of these compounds. A relatively early review focused on the topic of 'Group 14 Metalloles – Ionic Species and Coordination Compounds' and described the attempts to deploy sila- and germaaromatic compounds as ligands in transition metal complexes. These attempts starting from η^4-complexes were not successful in yielding the desired η^5-compounds.[235] In 1993 Freeman et al. succeeded in the synthesis of the first stable η^5-germacyclopentadienyl transition metal complex by reacting the germole precursor with BuLi and subsequently with Cp*RuCl. The aromaticity of the complex was discussed as follows: 'Das ^{13}C{^{1}H}-NMR-Spektrum weist zwei Resonanzsignale für die C-Atome des Germacyclopentadienylrings mit ähnlichen chemischen Verschiebungen bei δ = 80.23 und 87.82 auf. Die δ-Werte deuten an, daß der C_4Ge-Ligand aromatischen Charakter hat, da die C-Atome des Cp*-Liganden bei δ = 85.38, d.h. im gleichen Bereich, in Resonanz treten. Hierfür spricht darüber hinaus, daß sich die chemischen Verschiebungen der zwei Signale der C_{Ring}-Atome in η^4-Germol-

Komplexen stärker unterschieden [...]' [Ge(1)-C(1) 1.900(6), Ge(1)-C(4) 1.899(7), C(1)-C(2) 1.425(11), C(2)-C(3) 1.415(11), C(3)-C(4) 1.424(9)]. The crystal structure of the complex is described as 'zwei planare Fünfringe [sind] Sandwich-artig wie in Metallocenen an das Ru-Atom gebunden. [...] Das Ge-Atom ist nur 0.02 *Å* außerhalb der besten Ebene des C_4Ge-Rings, und auch die Winkelsumme am Ge-Atom deutet mit 358.1° auf die sp^2-Hybridisierung hin.'[216,217]

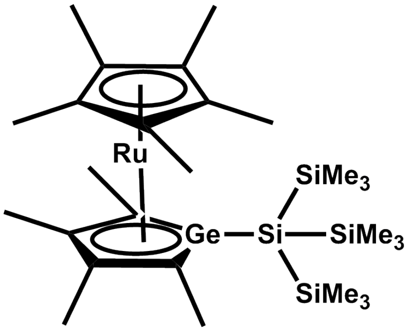


Figure 91: The first stable transition metal complex of a germacyclopentadienyl ring obtained by Freeman et al. in 1993.[216,217]

In 1998 Dysard and Tilley published the synthesis and isolation of a hafnium germolyl complex obtained by conversion of a germolyl precursor with Cp^*HfCl_3. The product obtained was analogous to the compound shown in figure 91. The structure of the hafnium complex was determined via X-ray diffraction measurements and was described as consisting 'of two planar five-membered rings coordinated in a bent fashion to the metal atom. The germolyl ring is planar, with the Ge atom deviating by only 0.001 *Å* from the C_4Ge least-squares plane. [...] The C–C bond length alternation in the germolyl ring (1.387(9) – 1.452(8) – 1.406(8) *Å*) is slight (0.04 – 0.06 *Å*), and is significantly less than in the germole $Me_4C_4Ge(H)Si(SiMe_3)_3$ (0.16 *Å*)' [^{13}C NMR: 135.8, 146.0 ppm for the GeC_4 fragment].[236] Related products were also published by the same group in the year 2000.[237]

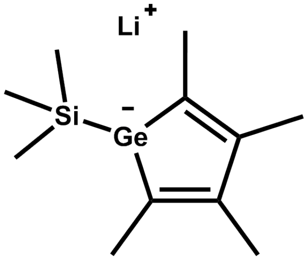


Figure 92: The germolyl precursor of the hafnium germolyl complex obtained by Dysard et al. in 1998.[236]

In 2002 Freeman et al. succeeded in the synthesis of a ferrocene analog stabilized by germolyl substituents. The working group proved the electron delocalization in the germolyl rings by X-ray crystal and NMR spectroscopic data confirming η^5-coordination in the compound. 'The molecular structure [...] consists of two coplanar η^5-germolyl rings bound in a "sandwich" fashion to the iron center. The angle between the least-squares planes of these rings is 5°, and they both lie 1.69 Å from the iron center. [...] The germanium atoms deviate by only 0.04 Å from the C_4Ge least-squares planes [...]. Further evidence for sp^2 hybridization at germanium is given in the sum of the bond angles about Ge (358.1°)' [^{13}C NMR (75.5 MHz, benzene-d_6): δ 79.51, 89.86 ppm for the GeC_4 fragment; Ge(1)-C(1) 1.891(5), Ge(1)-C(4) 1.897(5), C(1)-C(2) 1.423(8), C(2)-C(3) 1.431(8), C(3)-C(4) 1.412(7) Å]. The group also investigated and described a series of consecutive reactions of their ferrocene analog.[238]

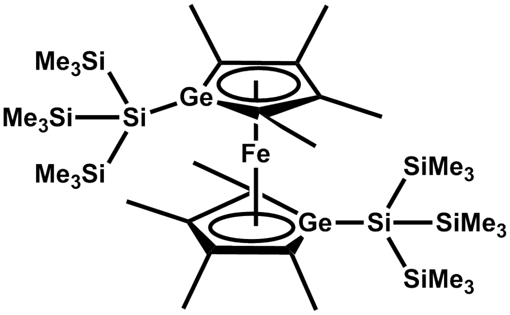


Figure 93: The bisgermolyl ferrocene complex synthesized by Freeman et al. in 2002.[238]

A theoretical study by Goldfuss et al. led to the conclusion that 'both the aromaticity and the antiaromaticity of heavier group 14 metalloles are less than those of their carbon congeners. The increasing tendency toward pyramidalization of heteroatoms in the trivalent anionic species [...] results in decreased aromaticity of the heavier metallolyl anions [...]. However, this pyramidalization bias is not present in the metallole dianions and their lithiated derivatives, and highly delocalized aromatic structures result.'[208]

Another similar class of compounds, namely disilagermacyclopentadienes, has also been investigated with regard to their aromatic behaviour. The first of these compounds was obtained by Lee et al. in 2000. They reported 'the synthesis, full characterization, X-ray structure, and reactivity of the first cyclic metalladiene consisting of Group 14 elements of the type -M=M'-C=C- (M = Si, M' = Ge).' The group was not able to find any evidence for conjugation between the double bonds in the five-membered ring: 'None of these data give any evidence for noticable conjugation between the Si=Ge and C=C double bonds in the cyclopentadiene unit [...], despite the planarity of the five-membered ring. The same conclusion has been drawn from the UV/vis spectrum [...], which showed no significant bathochromic shift in comparison with an isolated Si=Ge double bond [...]' [^{13}C NMR (C_6D_6) δ 149.8, 173.3 ppm for the GeC_2Si_2 fragment; Ge(1)-C(1) 1.972(3), Ge(1)-Si(2) 2.250(1), Si(1)-Si(2) 2.364(1), Si(1)-C(2) 1.888(3), C(1)-C(2) 1.343(5) Å].[239]

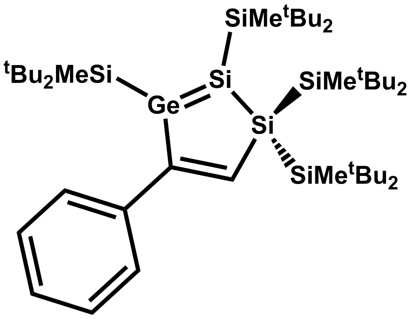


Figure 94: The first disilagermacyclopentadiene (bright orange crystals) obtained by Lee et al. in 2000.[239]

When the same working group isolated the lithium salt of the corresponding dienide in 2005, they were able to show evidence for the aromaticity of the structure: On the one hand the ring system was nearly planar (sum of the interior bond angles: 536.32°), on the other hand the lithium ion was η^5-coordinated to the anionic part and was directly bound to all skeletal atoms. Furthermore, the elongation of the double bonds (Ge-Si 2.250(1) vs. 2.3220(5)Å, C-C 1.343(5) vs. 1.402(2)Å) and the shortening of the single bonds (Ge-C 1.972(3) vs. 1.9303(17)Å, Si-Si 2.364(1) vs. 2.2403(7)Å, Si-C 1.888(3) vs. 1.8268(18)Å) upon reduction and calculated NICS values (NICS = - 12) gave further hints pointing toward aromaticity of the compound. NMR data (in toluene-d_8) also supported this theory: ^{13}C NMR measurements showed shielding of the skeletal olefinic *C*H atom compared to the starting compound (143.2 vs. 150.0 ppm), while the olefinic *C*Ph atom was deshielded (181.4 vs. 173.6 ppm). An interesting change of the properties was observed when changing to polar solvents: The compound 'is unable to benefit from such aromatic delocalization in polar solvents, thus changing the coordination from the delocalized η^5- to a localized η^1-mode. [...] in THF-d_8 solution, the anionic part [...] acquires the properties of the localized cyclopentadienide derivative, which features Si=Si and C=C double bonds and has a negative charge situated on the Ge atom [...]'.[240,241] Further chemistry of this interesting compound class was published by the group in the following years.[242–244]

A relatively recent review on the topic of group 14 metallole anions and dianions was given by Saito and Yoshioka in 2005.[245]

Aromaticity of Polyphosphaphospholes

The aromaticity of phospholes and polyphoshaphospholes has been an intensely discussed topic in literature for decades. The idea that the aromaticity of phospholes depends strongly on the planarization of the phosphorus atom was first published by Andose et al. in 1974.[246] Mathey reviewed 'the chemistry of phospha- and polyphosphacyclopentadienide anions' in 1994.[247] In 1996 Nyulászi published a theoretical report on the aromaticity of polyphosphapholspholes in correlation with their planarization.[248] As another example, Nyulászi et al. proved this idea by theoretical studies in 1998 by taking into account a series of substituents at the phosphorus atom with varying sterical demand.[249] In the same year Dransfeld et al. conducted a theoretical study varying the number of phosphorus atoms in the ring, discovering that a higher number of phosphorus atoms leads to higher aromaticity. This is due to the greater planarization at the three-coordinate phosphorus atom when more phosphorus atoms are present in the ring.[250] A theoretical report from the year 2000 by Delaere et al. confirmed the discussed tendencies: 'Earlier computational investigations [...] have shown that the aromaticity in phopholes increases if the pyramidality of the tricoordinate phosphorus atom decreases and predicted this planar phosphole to be highly aromatic. These observations are confirmed in this work.' Further, they claim that 'in 1-BH_2-1H-phosphole the substituted π-acceptor group strongly reduces the pyramidality at the phosphorus atom', which leads to the following consequence: 'Combination of structural [...] and magnetic [...] criteria show that by putting strongly pronounced π-systems or placing a donor and acceptor substituent at the ends of the butadienic π-system, the electron delocalization over the entire system ist significantly augmented.'[251] A general report on the aromaticity of phosphorus heterocycles – including heterophospholes – was published by Nyulaszi in 2001.[252] In 2007 the influence of the phosphorus lone pair of phospholes on the order of aromaticity was discussed by Chesnut et al. The working group theoretically studied the effect of the lone pair and whose protonation and found out that 'the phosphorus lone pair is critical to the phosphole systems' aromaticity. Protonation of the lone pair results in antiaromatic systems [...]'.[253] The question whether hyperconjugation with substituents at the phosphorus atom or finite coupling of the phosphorus lone pair with the carbon π-system contribute stronger to the aromaticity of the system had also been discussed earlier in several papers and reviews.[253 *and references therein*] A more recent theoretical study dealing with the correlation of pyramidality and aromaticity of polyphosphaphospholes was conducted by Li et al. in 2008.[254] In 2011 Josa et al. discussed the effect of different locations of the phosphorus atoms in polyphosphaphospholes and found out that a direct phosphorus-phosphorus bond leads to an augmented aromaticity of the ring system. They also claimed that pyramidality of the phosphorus atom is not the only criterium to be looked at when discussing π-delocalization in this class of compounds.[255]

Experimental results confirmed the trends predicted by theoretical studies: In 1998 e.g., Cloke et al. published the first 'delocalized phosphole containing a planar tricoordinate phosphorus atom'. They stated that their phosphole is 'the first example of a neutral five-membered ring containing a tricoordinate phosphorus atom that is fully planar' ($\Sigma\Theta$(tricoordinate phosphorus atom): 358.7°) while being ' the most aromatic of all the known neutral five-membered phosphorus heterocycles'.[256]

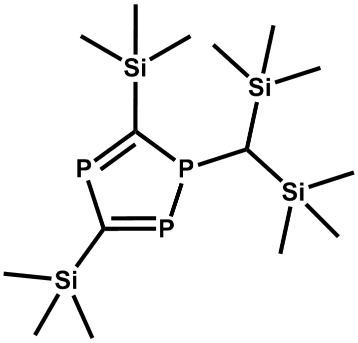


Figure 95: The first experimentally characterized delocalized phosphole with a planar tricoordinate phosphorus atom published by Cloke et al. in 1998.[256]

6.2.2.2 On the Way Toward Gallium Clusters

Gallium Compounds Stabilized by Terphenyl Substituents

Ga(III) Derivatives and Further Valencies $\neq$ I

The class of terphenyl-stabilized gallium compounds has been widely deployed in synthetic chemistry. This led e.g. to the formation of the radical derivative $[Li(12\text{-crown-}4)]_2^+[Trip_2GaGaTrip_2]^{*-}$, obtained by reducing the parent digallane with lithium powder, performed by He et al. in 1993.[257,258] Another example was the first so-called cyclogallane $Na_2[(2,6\text{-}Mes_2C_6H_3Ga)_3]$, reported by Li et al. in 1995. The group synthesized $(2,6\text{-}Mes_2C_6H_3)GaCl_2$ and deployed sodium metal as reducing agent to obtain the named structure.[259] The same working group had published the terphenyl-stabilized gallium structure $(2,6\text{-}Mes_2C_6H_3)_2GaCl$ earlier in the same year.[260] The potassium cyclogallane $K_2[(2,6\text{-}Mes_2C_6H_3Ga)_3]$ was obtained by Li et al. in 1996.[261] A series of terphenyl based mono- and dihalide gallanes has been reported since then, including $[(2,6\text{-}Mes_2C_6H_3)GaCl_2]_2$, $(2,6\text{-}Mes_2C_6H_3)_2GaBr$ *both* [262], $[(2,6\text{-}Trip_2C_6H_3)GaCl_2]_2$,[263] $[Li\{Et_2O\}_2][(2,6\text{-}Ph_2C_6H_3)GaCl_3]$, $(2,6\text{-}Ph_2C_6H_3)_2GaI$ *both* [264], $[(2,6\text{-}Trip_2C_6H_3)GaI]_2$, $[(2,6\text{-}{}^tBuDipp_2C_6H_3)GaI]_2$ $[(2,6\text{-}Dipp_2C_6H_3)GaI]_2$ *all* [265] and $[(2,6\text{-}Trip_2\text{-}4\text{-}CF_3C_6H_2)GaI]_2$.[266] Reduction of terphenyl-stabilized gallium derivatives led to interesting structural motives: The first gallyne, stabilized by the $2,6\text{-}Trip_2C_6H_3$ ligand system, was published by Su et al. in 1997. The charged target compound $Na_2[(2,6\text{-}Trip_2C_6H_3)GaGa(2,6\text{-}Trip_2C_6H_2)]$ was described as the first structure showing Ga≡Ga triple bonding and was obtained by converting $(2,6\text{-}Trip_2C_6H_3)GaCl_2$ with sodium metal.[267] The synthesis of this compound triggered an intensive discussion on the topic of multiple bonding in main group elements, including several theoretical studies on parent compounds.*see e.g.* [268–270] In contrast, the reduction of $(2,6\text{-}Trip_2C_6H_3)GaCl_2$ with potassium did not yield the expected $K_2[(2,6\text{-}Trip_2C_6H_3)GaGa(2,6\text{-}Trip_2C_6H_2)]$ but the Ga_4 cluster $K_2[Ga_4(2,6\text{-}Trip_2C_6H_3)_2]$ (published by Twamley el al. in the year 2000).[271] $Na_2[(2,6\text{-}Dipp_2C_6H_3)GaGa(2,6\text{-}Dipp_2C_6H_3)]$ was obtained via reduction of $[(2,6\text{-}Dipp_2C_6H_3)Ga]_2$ (by sodium) by Hardman et al. in 2002.[272] This compound is analogous to the structure published by Su et al. in 1997 (see above).[267]

Gallium (I) Derivatives

In 2002 the preparation of $[(2,6\text{-Dipp}_2C_6H_3)Ga]_2$ (via conversion of 'GaI' with $[(2,6\text{-Dipp}_2C_6H_3)Li]_2)$ was published by Hardman et al.[272] The isolation of the neutral monovalent gallium compounds $(2,6\text{-Trip}_2C_6H_3)Ga$ and $(2,6\text{-}^t\text{BuDipp}_2\ C_6H_3)Ga$ was reported by the same working group in 2003. The publication furthermore showed a Ga_{11} cluster to be formed in the absence of an alkali metal.[265] Another series of terphenyl-stabilized gallium derivatives was published by Zhu et al. in 2009. They described the syntheses and characterization of the dimers $[(2,6\text{-Trip}_2\text{-}4\text{-}^t\text{Bu}C_6H_2)Ga]_2$ and $[(2,6\text{-Trip}_2\text{-}4\text{-}CF_3C_6H_2)Ga]_2$ as well as of the monomers $(2,6\text{-Trip}_2\text{-}3,5\text{-}^i\text{Pr}_2C_6H_2)Ga$ and $(2,6\text{-Dipp}_2\text{-}3,5\text{-}^i\text{Pr}_2C_6H_2)Ga$.[266]

A general review focussing on the topic of 'multiple bonding in heavier element compounds stabilized by bulky terphenyl ligands' was given by Rivard and Power in 2007.[161]

In the present work, conversion of in-situ formed $(2,6\text{-Mes}_2C_6H_3)GaI_2$ with elemental sodium in the presence of PPh_3 led to the formation of crystals containing Ga_8 and Ga_{13} core structures.

Small Gallium Clusters

The term 'cluster' was defined by Cotton in the 1960s.[*see e.g. reference* 273] In 1966 he broadened his definition in stating that 'Metal atom cluster compounds can be formally defined as “those containing a finite group of metal atoms which are held together entirely, mainly, or at least to a significant extent, by bonds directly between the metal atoms even though some non-metal atoms may be associated intimately with the cluster”.'[274] This definition is still up to date, despite the fact that it was developed nearly 50 years ago. The term 'metalloid cluster' was defined by Purath et al. in 1999 as follows: 'Metalloid (metal-like) clusters should be epitomized by the property that the number of metal-metal contacts exceeds the number of metal-ligand contacts and by the presence of metal atoms which participate exclusively in metal-metal interactions.'[275,276] The gallium derivatives described in the present work can thus be classified as molecular and metalloid clusters.

The class of gallium clusters contains a large number of examples, a summary on the general topic of 'molecular clusters of the main group elements' was given by Driess in 2004.[277] Schnöckel and Schnepf gave a comprehensive overview on synthetic routes 'From AlX/GaX Monohalide Molecules to Metalloid Aluminium and Gallium Clusters' in the year 2001 including a detailed discussion of the solid state modifications of gallium.[278] A review focussing on aluminum and gallium clusters and their linking characteristics between 'the molecular and the solid-state areas' was published by Schnöckel in 2005.[279] Another review on the topic (as part of the series 'The Renaissance of Main Group Chemistry') was given by the same author in 2008.[280] The latest reviews (to the best of the author's knowledge) on this topic were published by Schnöckel in 2010[281] and 2013.[282]

A listing of small molecular gallium clusters Ga_n ($3 \leq n \leq 13$) with carbon substitution is shown in table 13. One Ga_8 cluster with silicon substitution is also included due to the presentation of a novel Ga_8 cluster in the present work.

Compound	**Ga-Ga** [Å]	**Ga-C** [Å]	**Ref.**
$Na_2[(2,6\text{-}Mes_2C_6H_3Ga)_3]$	2.441(1)	2.037(3)	259
$K_2[(2,6\text{-}Mes_2C_6H_3Ga)_3]$	2.4187(5) - 2.4317(5)	2.040(3) - 2.050(3)	261
$Ga_4[C(SiMe_3)_3]_4$	2.688	2.08	283*
$Ga_4[C(SiMe_2Et)_3]_4$	2.710	2.099	283*
$K_2[Ga_4(2,6\text{-}Trip_2C_6H_3)_2]$	2.4623(4)/2.4685(3)	2.0058(19)	271
$Li_2[Ga_8(C_{13}H_9)_8]$	2.517(3) - 2.710(3)	2.057(2)/2.088(2)	284
$Ga_8[C(SiMe_3)_3]_6$	2.6054(8) - 2.6481(9)	2.043(5) - 2.048(4)	285
$Ga_9(CMe_3)_9$	2.569(1) - 3.066(1)	2.025	286
$Ga_{11}(2,6\text{-}Mes_2C_6H_3)_4$	2.529(1) - 2.667(3)	1.991(6) - 1.996(6)	265
$[Li(thf)_4]_2[Ga_{12}(C_{13}H_9)_{10}]$	2.5827(7) - 2.6969(8)	2.059	287
$Na[Ga_{13}(Si^tBu_3)_6]$	2.400 - 2.906	—	288

Table 13: Selected small molecular gallium clusters ($3 \leq n \leq 13$). Terphenyl substitution is highlighted in red. * and references therein

A broad range of theoretical and experimental publications on the topic of small gallium clusters can be found in literature. One of the main questions discussed is the structural relation of the gallium clusters with regard to the bulk forms of the metal. Some representative examples shall be given here. Figure 96 cited from the supporting information of reference 281 gives an overview on six of the seven solid state modifications of gallium.

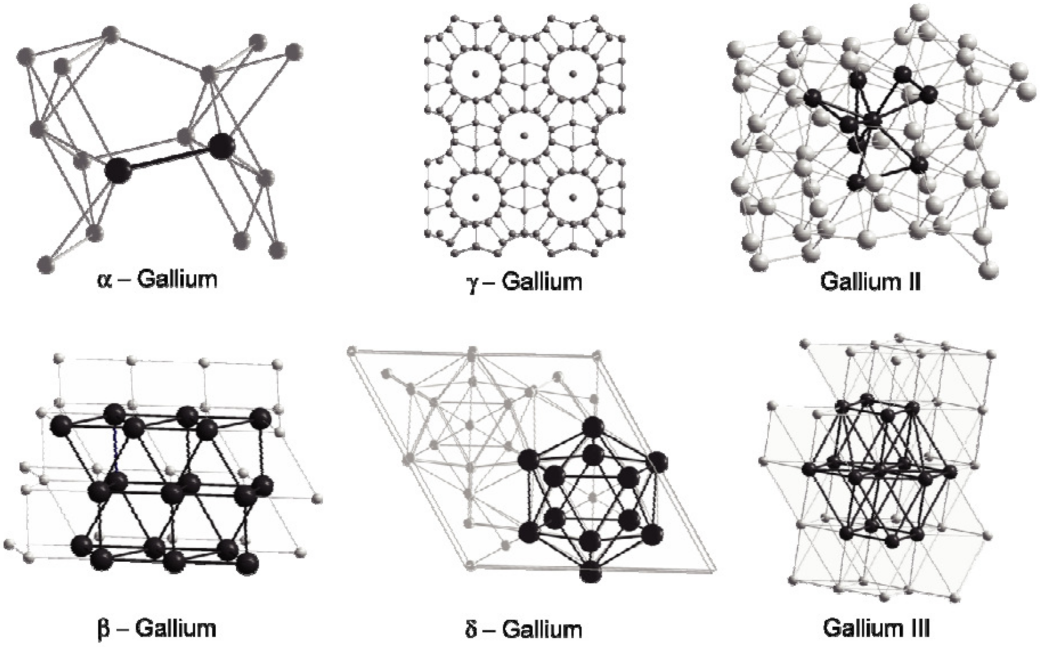


Figure 96: 'Sections of the normal-pressure modifications α-, β-, γ- and δ-gallium and the high-pressure modifications Ga^{II} and Ga^{III}. The Ga^{IV} modification (fcc) is not shown.' (Figure and description from references 281,289,290 .)

Gong and Tosatti's paper from the year 1992 presented a theoretical study on the stability of various structural motives in small gallium clusters ($2 \leq n \leq 8$). They also noted that chain-like structures found in Ga_6 and Ga_7 clusters resemble closely the zig-zag chains found in meta-stable β-gallium.[291] In the year 1993 Jones published a comprehensive study including gallium clusters Ga_n ($2 \leq n \leq 10$).[292] Yi focussed on Ga_{13} clusters in his report from the year 2000 and stated that 'Ga_{13} energetically favors a distorted decahedron'.[293] The relation between the clusters $\mathrm{Ga}_{18}(\mathrm{Si}^t\mathrm{Bu}_3)_8$ and $\mathrm{Ga}_{22}(\mathrm{Si}^t\mathrm{Bu}_3)_8$ and the solid state modifications β-gallium and Ga^{III}, respectively, were discussed by Donchev et al. in 2001. The structural analogies they pointed out are shown in figure 97.[294]

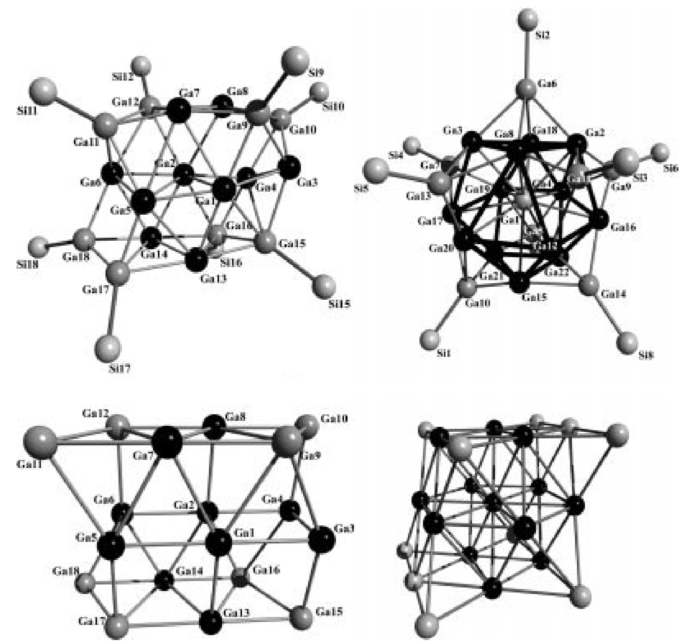


Figure 97: Structural similarity of gallium clusters and solid gallium bulk. Left column: molecular structure of $Ga_{18}(Si^tBu_3)_8$ (top), section with 18 Ga atoms out of β-gallium (bottom), right column: molecular structure of $Ga_{22}(Si^tBu_3)_8$ (top), section with 22 Ga atoms out of Ga^{III} (bottom). (Figures and description from reference 294 .)

The same group published a study on the similarity of $[Ga_6(SiPh_2Me)_8]^{2-}$ with a fragment of β-gallium ('Die Anordnung der Ga-Atome erinnert an die in β-Gallium [...]') and stated that the similarity of the target compound and β-gallium valids the labeling of the cluster as metalloid or elementoid (compare figure 98).[295]

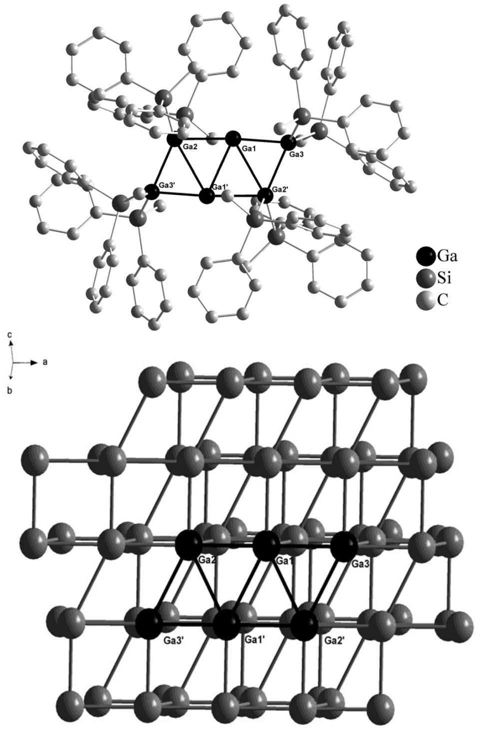


Figure 98: Comparison of $[Ga_6(SiPh_2Me)_8]^{2-}$ with β-gallium. Molecular structure of the cluster (top) vs. a fragment of β-gallium (bottom). (Figures and description from reference 295 .)

One publication by King from the year 2002 concentrated on the gallium clusters known in literature in connection with the Wade-Mingos and Jemmins electron-counting rules.[296] Song and Cao suggested a rhombic prism as the most stable structural motive for a Ga_8 cluster in their publication from the year 2005 (including Ga_n ($2 \leq n \leq 26$)). They also confirmed Yi's finding by stating that 'the ground state of the 13-atom cluster is a decahedron.' Furthermore they found out that 'Ga_8, Ga_{14} and Ga_{20} exhibit particularly higher stability.'[297] Further comparisons of gallium clusters with solid state gallium modifications can e.g. be found in the publications by Steiner et al. (e.g. $Ga_{22}(P\,^tBu_2)_{12}$ vs. δ-gallium (compare figure 99), $[Ga_{51}(P\,^tBu_2)_{14}Br_6]^{3-}$ vs. face-centered cubic Ga^{IV}, $[Ga_{18}(P\,^tBu_2)_{10}]^{3-}$ vs. Ga^{II} (compare figure 100)).[298–302]

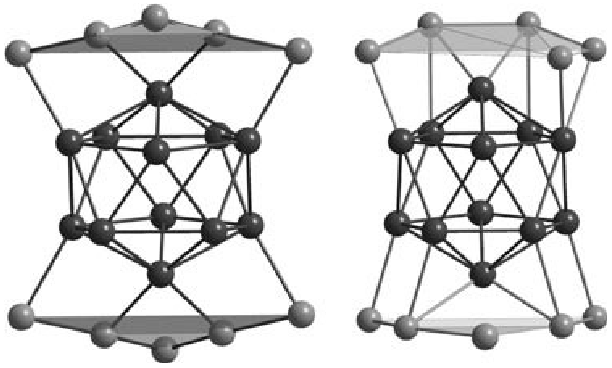


Figure 99: 'Comparison of the gallium substructure in the Ga$_{22}$ cluster ([...], left) with the corresponding section of the δ-modification of gallium (right).' (Figures and description from references 298,299 .)

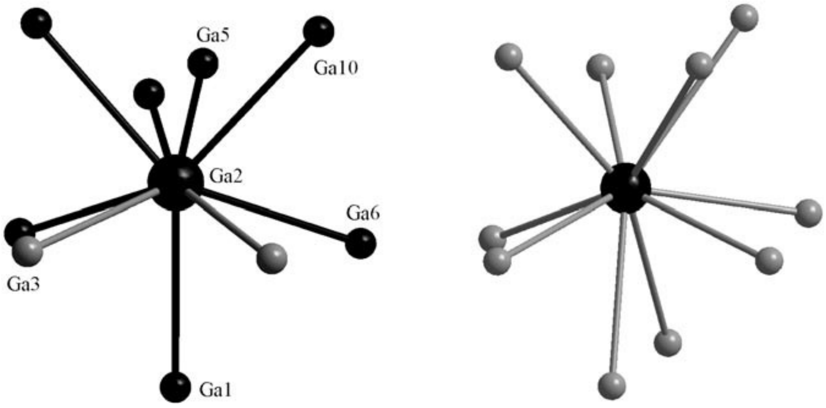


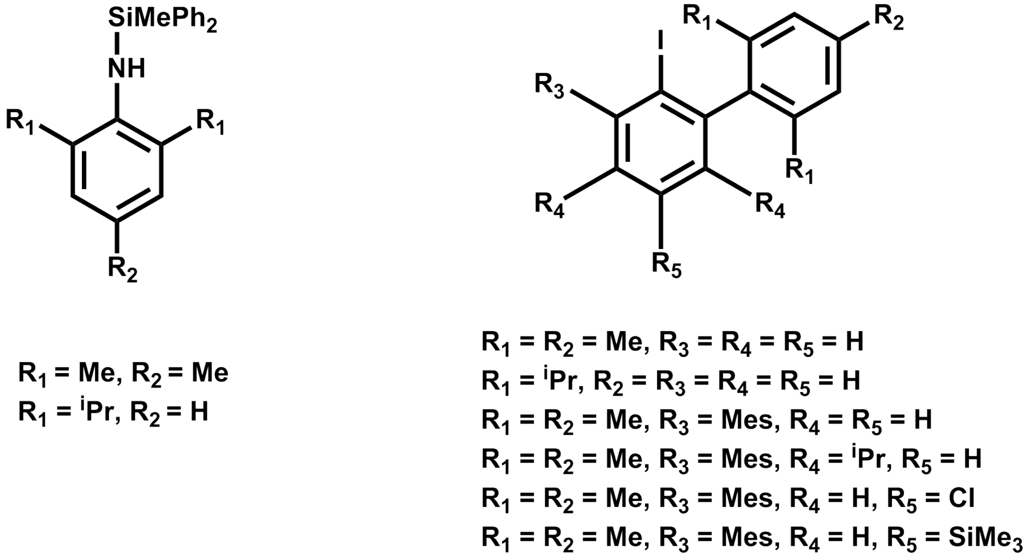
Figure 100: 'Comparison of the gallium coordination sphere [...] [note: of the cluster] (left) and the high-pressure modification Ga-II (right). [...]' (Figures and description from reference 302 .)

Drebov et al. described Ga$_{13}$ as a truncated decahedron and claimed that 'particularly stable clusters for Ga$_n$ are seen for n = 7, 14, and 20, similar to Ga$_n$' (not Ga$_8$!).[303] The relation of Ga$_{12}$ and the bulk forms of gallium was investigated by Schebarchov and Gaston in 2012.[304] In their study on Ga$_n$ ($13 \leq n \leq 37$) compounds Nunez et al. concluded that 'Ga$_{13}$ and Ga$_{13}^-$ adopt a decahedral structure'.[305]

The gallium compounds described in the present work will be discussed regarding structural relations of the crystal structures and the solid state modifications of gallium in the chapter 'Results and Discussion' (pp. 139 – 141).

7 Results and Discussion

Two ligand systems were deployed building the basis of the present work: On the one hand, silylamide ligands were used, on the other hand a series of different phenyl based ligands was synthesized and converted consecutively. The focus of the conversions of the ligands was set on group 1, 3 and 4 metal derivatives. A schematic representation of the two ligands is given in figure 101.



$R_1 = Me, R_2 = Me$
$R_1 = {}^iPr, R_2 = H$

$R_1 = R_2 = Me, R_3 = R_4 = R_5 = H$
$R_1 = {}^iPr, R_2 = R_3 = R_4 = R_5 = H$
$R_1 = R_2 = Me, R_3 = Mes, R_4 = R_5 = H$
$R_1 = R_2 = Me, R_3 = Mes, R_4 = {}^iPr, R_5 = H$
$R_1 = R_2 = Me, R_3 = Mes, R_4 = H, R_5 = Cl$
$R_1 = R_2 = Me, R_3 = Mes, R_4 = H, R_5 = SiMe_3$

Figure 101: Schematic representation of the two ligand systems deployed in the present work: Silylamide ligands (left) and phenyl based ligand systems (right) - including biphenyl and terphenyl ligands.

The main aim of the present work was to obtain novel low valent main group 3 and 4 metal derivatives (namely in oxidation states +I and +II, respectively) and to study the influence of the ligand system on stability and reactivity of the target compounds. While the phenyl based ligand systems were varied mainly by adding/removing further aromatic rings (see R_3 in figure 101), the steric bulk of the silylamide ligands was modified by varying the substituents of the flanking ring (at the nitrogen atom). Most of the phenyl ligands used had been previously discussed in literature, while the silylamide ligands deployed in this work are presented for the first time. It has to be mentioned though, that generally conversions of similar silylamide based ligand systems toward main group element compounds have played a major role in literature, while especially the class of biphenyl ligands has gained significantly less interest up to date concerning the field of main group chemistry. The main modification of the novel silylamide ligand – in comparison to literature-known systems – lies in the larger number of phenyl substituents at the silicon atom. One of the aims of the present work was to avoid the deployment of chelating ligands like e.g. nacnac based systems, which represent the majority of amide based low valent main group element compounds present in literature. The main reason for choosing two completely different ligand types was the potential comparison of the strength of electronic stabilization of the systems and the consequences concerning stability and reactivity of the products.

7.1 Novel Low Valent Main Group 3 and 4 Derivatives Stabilized by Silylamides

Ligands and Lithium, Sodium and Potassium Derivatives

As described in the literature overview, the method to obtain the silylamide ligands deployed in the present work was the 'reaction of halosilanes with arylamines' (see chapter 6.1.1, page 22), generally one of the main methods deployed in the synthesis of this ligand type. A schematic representation of the synthesis route toward the precursors and main group 1 derivatives is shown in figure 102.

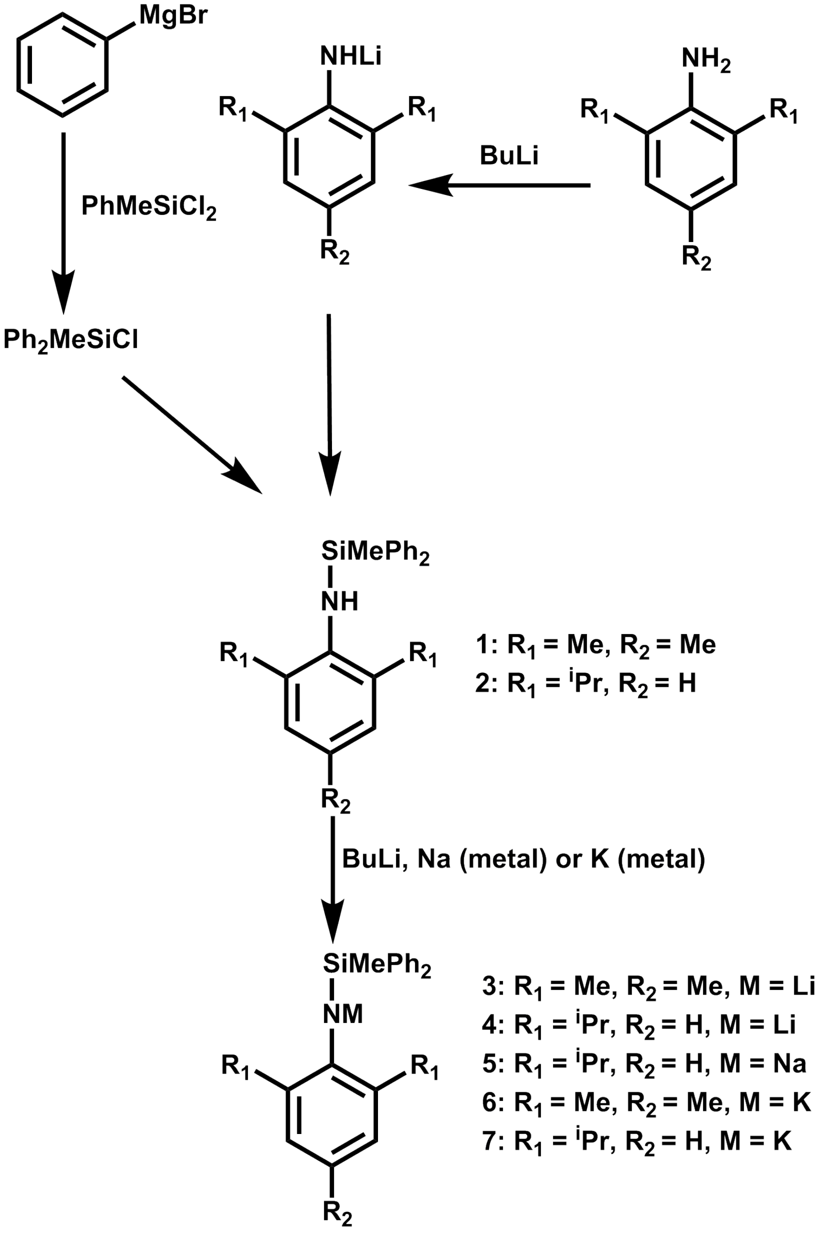


Figure 102: Schematic synthesis route toward the silylamide ligands.

Compound **1** was isolated as white crystals suitable for X-ray diffraction upon removal of the thf reaction solution. A crystal structure of the monomeric ligand was obtained and is shown in figure 103.

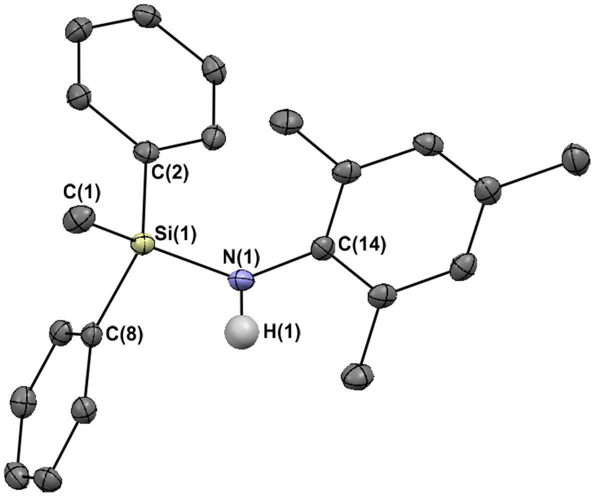


Figure 103: Thermal ellipsoid plot of compound **1** with 50% probability. Hydrogen atoms (except from the hydrogen atom at the nitrogen atom) are not shown. Selected bond distances ($\mathring{A}$) and angles (°): N(1)-H(1) 0.84(2), N(1)-Si(1) 1.741(1), Si(1)-C(1) 1.860(2), Si(1)-C(2) 1.877(1), Si(1)-C(8) 1.868(2), N(1)-C(14) 1.418(2), Si(1)-N(1)-C(14) 134.3(1).

In contrast, compound **2** was obtained as a viscous, dark brown to black liquid (due to traces of impurities). NMR studies showed the compound to be sufficiently clean for further deployment in spite of the optical appearance. Attempts to crystallize the ligand failed even at low temperatures.

The synthesis of the lithium derivatives was performed by adding BuLi to a solution of the parent ligands in heptane. Compounds **3** and **4** precipitated from the reaction solution and were obtained as white crystals after removal of the supernatant. The solubility of compounds **3** and **4** is very good in thf and Et_2O, moderate in aromatic solvents and very poor in aliphatic hydrocarbons. A crystal structure of compound **4** was obtained by X-ray diffraction measurements showing the structure to be dimeric in the solid state. Lappert et al. stated in their book from the year 2009: 'The four-membered $(LiN)_2$ ring is ubiquitous in lithium amide chemistry and is observed both in discrete dimeric structures in either planar [...] or non-planar [...] geometries as well as in oligomeric and polymeric (ladder) frameworks [...].'[69] Though, there do not seem to exist too many examples of dimeric lithium silylamide compounds of the structure type covered in the present work ($Ar_nR_{3-n}SiNHAr$ (n = 0 - 3)) in literature. The only comparable structure is the lithium derivative published by Kennepohl et al. in 1991 ($[DippNLiSiMe_3]_2$ [ΣΘ(N): 643.8/645.5°]). The sum about the nitrogen atoms of this compound and compound **4** is very similar.[72] A loose comparison can also be drawn between the structure of compound **4** and the sodium amide dimer published by Antolini et al. in 2000[68] (compare figure 28 on page 29) and the lithium/sodium complex obtained by Chen and Yuan in 2012[83] (compare figure 31 on page 31), but no corresponding pure lithium structure was published up to date. (In addition, one has to keep in mind that Antolini et al.'s and Chen and Yuan's structures bear donating ligands.) While crystals suitable for X-ray diffraction were only obtained of compound **4**, the similarity in liquid NMR data leads to the conclusion that both lithium derivatives are isomorphous. The structure of compound **4** is presented in figure 104 and shows a nearly perfectly planar $(LiN)_2$ core. One of the lithium atoms is η^1-coordinated to one of the flanking phenyl rings at the silicon atom.

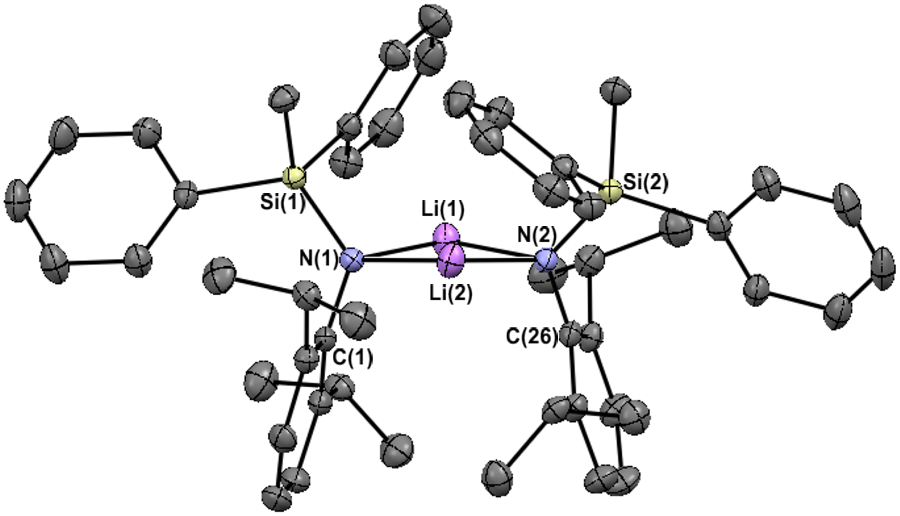


Figure 104: Thermal ellipsoid plot of compound **4** with 50% probability. Hydrogen atoms and η^1-coordination of lithium to flanking phenyl group are not shown. Selected bond distances ($\AA$) and angles (°): Li(1)-N(1) 2.006(2), Li(1)-N(2) 2.009(2), Li(2)-N(1) 2.013(2), Li(2)-N(2) 1.999(2), N(1)-Si(1) 1.697(1), N(2)-Si(2) 1.695(1), N(1)-Li(1)-N(2) 105.01(1), N(1)-Li(2)-N(2) 105.2(1), Li(1)-N(1)-Li(2) 74.10(9), Li(1)-N(1)-C(1) 97.30(9), C(1)-N(1)-Si(1) 124.52(7), Li(2)-N(1)-Si(1) 102.96(8), $\Sigma\Theta$(N(1)) 647.60, Li(1)-N(2)-Li(2) 74.34(9), Li(2)-N(2)-C(26) 95.70(9), C(26)-N(2)-Si(2) 128.15(7), Li(1)-N(2)-Si(2) 99.76(7), $\Sigma\Theta$(N(2)) 646.33.

Sodium derivative **5** was obtained in X-ray crystal quality upon deprotonation of compound **2** by metal sodium in a thf solution and storage at -30 ℃. The solubility of compound **5** in thf is good. In contrast to lithium derivative **4**, compound **5** is monomeric in the solid state. The structure is given in figure

105. The metal is complexed by three thf moieties and an η^1-coordination of sodium toward the Dipp group at the nitrogen atom is observed. The nitrogen atom is coordinated in a nearly perfectly planar way by the silicon, carbon and sodium substituents [$\Sigma\Theta$(N): 359.93°]. This planar coordination pattern was also described in literature, especially for a number of lithium derivatives. Some examples shall be cited here (for more detail see literature section, chapter 6.1.2.1): $\mathrm{Mes'NLiSi^{i}Pr_2X\{thf\}_3}$ (X = F, Cl) published by Böse and Klingebiel in 1986 shows a sum of the bond angles about the nitrogen atom of 359.9°.[70] Schädle et al. published the monomeric derivative $\mathrm{DippNLiSiMe_3\{thf\}_3}$ in 2010 [$\Sigma\Theta$(N): 359.0°].[81] Li et al.'s $\mathrm{2,6\text{-}(CHPh_2)_2\text{-}4\text{-}MeC_6H_2NLiSiMe_3\{Et_2O\}}$ [$\Sigma\Theta$(N): 359.90°] is also a close example. The same paper described $\mathrm{2,6\text{-}(CHPh_2)_2\text{-}4\text{-}MeC_6H_2NNaSiMe_3\{thf\}_3}$ [$\Sigma\Theta$(N): 359.95°] and $\mathrm{2,6\text{-}(CHPh_2)_2\text{-}4\text{-}MeC_6H_2NKSiPh_3\{Et_2O\}}$ [$\Sigma\Theta$(N): 359.97°] with high geometric similarity.[25]

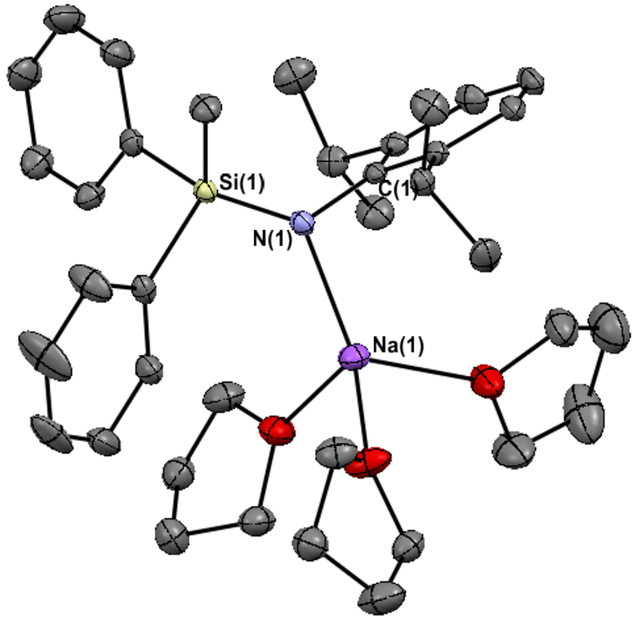


Figure 105: Thermal ellipsoid plot of compound **5** with 50% probability. Hydrogen atoms and η^1-coordination of sodium to flanking Dipp group are not shown. Selected bond distances (*Å*) and angles (°): Na(1)-N(1) 2.305(2), N(1)-Si(1) 1.664(1), Na(1)-N(1)-C(1) 99.5(1), Na(1)-N(1)-Si(1) 131.83(8), C(1)-N(1)-Si(1) 128.6(1), $\Sigma\Theta$(N(1)) 359.93.

Potassium derivatives **6** and **7** are significantly less soluble in thf and $\mathrm{Et_2O}$ than their lithium and sodium analogs. The reason for this characteristic feature was found when measuring the X-ray crystal data of the compounds: The structures both form coordination polymers that precipitate from the reaction solution upon formation. (The synthesis procedure was analogous to compound **5**.) The polymer is formed by coordination of the metal toward one phenyl ($\eta^{3\text{-}5}$) and one Mes/Dipp group (η^6) of the subsequent molecule. No solvent was found to dissolve the polymers again, which is why recording of NMR data of compounds **6** and **7** was not possible. Figure 106 presents one monomer of the polymeric structure of compound **6**, while in figure 107 a detail of the polymeric chain is shown. To the best of the author's knowledge there is no comparable polymeric structure of a potassium aryl-substituted silylamide described in literature. The only polymeric structure known (fulfilling the structural features) is [PhNLiSiMe$_3${tmeda}]∞, described by Bezombes et al. in the year 2001.[77] But the structural difference of the two compounds is obvious when keeping in mind that Bezombes et al.'s lithium amide includes one equivalent of tmeda per silylamide (compare figure 29 on page 29).

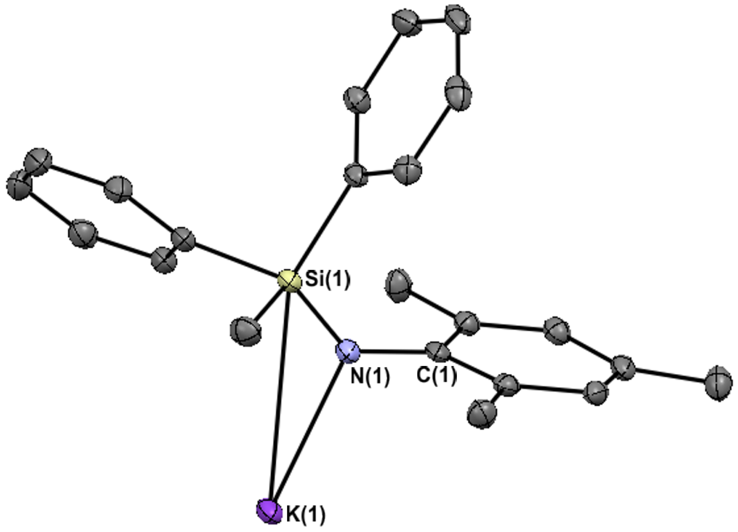


Figure 106: Thermal ellipsoid plot of compound **6** with 50% probability. Hydrogen atoms are not shown. Selected bond distances (Å) and angles (°): K(1)-N(1) 2.711(1), N(1)-Si(1) 1.661(1), K(1)-N(1)-C(1) 110.36(9), K(1)-N(1)-Si(1) 117.34(6), C(1)-N(1)-Si(1) 130.9(1), ΣΘ(N(1)) 358.6.

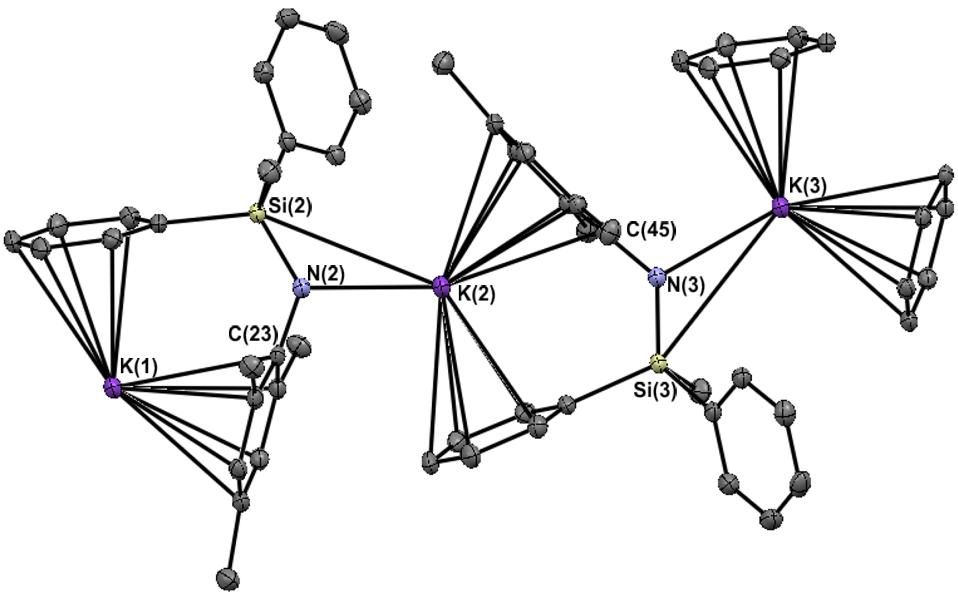


Figure 107: Polymeric structure of compound **6**.

Figure 108 shows the thermal ellipsoid plot of compound **7**, the analogy of the two potassium derivatives becomes evident.

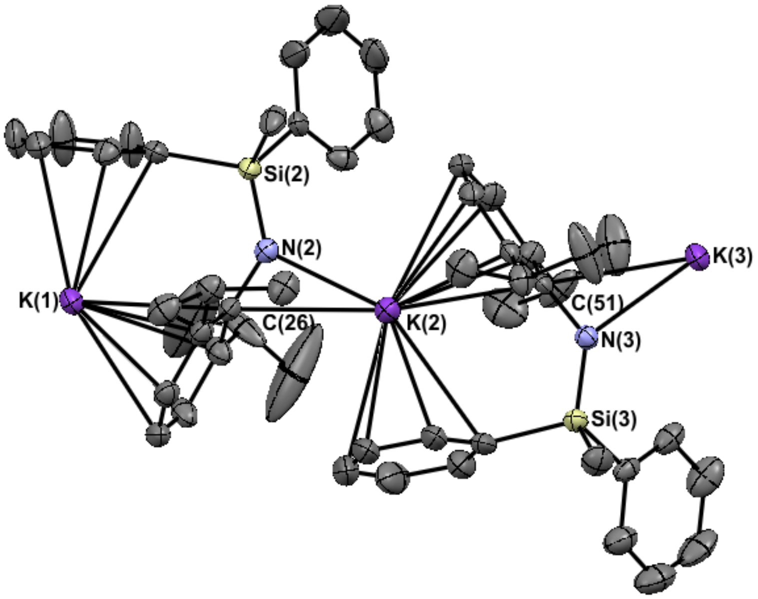


Figure 108: Thermal ellipsoid plot of compound **7** with 50% probability. Hydrogen atoms are not shown. Selected bond distances ($\AA$) and angles (°): K(1)-N(1) 2.696(3), N(1)-Si(1) 1.659(3), K(1)-N(1)-C(1) 93.4(2), K(1)-N(1)-Si(1) 133.1(1), C(1)-N(1)-Si(1) 133.5(2), $\Sigma\Theta$(N(1)) 360.0.

The versatility of the structures of the main group 1 derivatives stabilized by silylamide ligands is impressive: While the hydrogen and sodium derivatives show monomeric structures, the lithium derivatives are present as dimers in the solid state and the potassium analogs polymerize due to coordination processes. The solubility of the dervatives in ethers (thf, Et_2O) is good except for the polymeric potassium based structures. Due to this as well as to the easy synthesis route and the good storage characteristics, only the lithium derivatives were deployed for further conversions. (Compare to Lappert et al.'s statement on page 27.)

Main Group 3 Derivatives

When converting the lithium derivatives with group 13 metal precursors ('GaI' and InCl, respectively) the significance of the substitution pattern of the flanking phenyl ring (at the nitrogen atom) becomes apparent: Three different structural motives were found when varying the main group 3 element and the ligand substitution, all of which are shown schematically in figure 109.

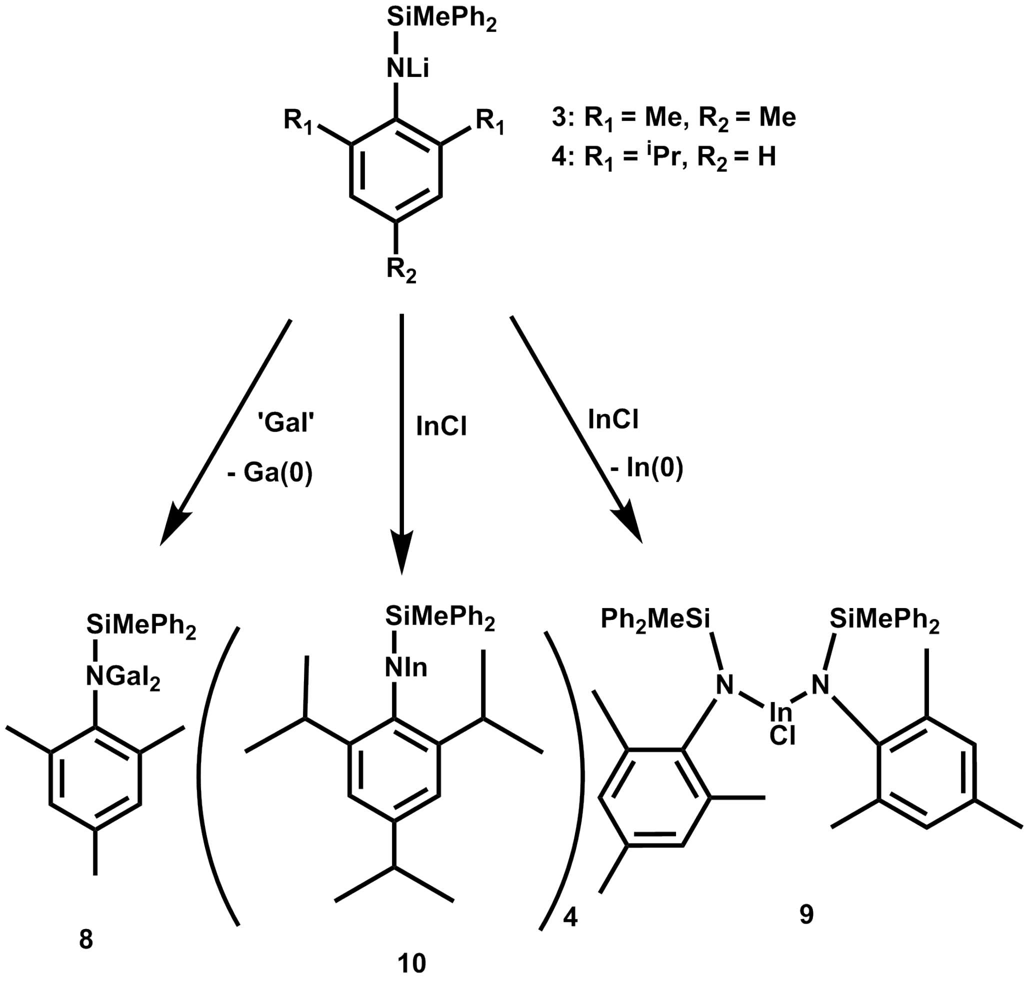


Figure 109: Synthesis of main group 3 silylamide derivatives.

Compound **3** was converted with ’GaI’ in order to obtain a low valent gallium derivative. In contrast to the expected result, oxidation of the metal led to a Ga(III) derivative, that was obtained in X-ray diffraction quality by cooling the reaction solution to -30 ℃. Parallely, Ga(0) was formed and precipitated from the reaction solution. Compound **8** crystallizes as LiI adduct, where the lithium counterion is complexed by three Et_2O moieties. The structure of compound **8** is shown in figure 110. The gallium atom is coordinated in nearly perfectly tetrahedral form in this structure. Compound **8** is structurally closely related to the $RR'N{\rightarrow}InCl_3^-$ derivative published by Prust et al. in 1999 (compare figure 34 on page 34) [$\Sigma\Theta$(N): 359.6°, $\Sigma\Theta$(In): 656.02°][91] and the gallium analog described by Schiefer et al. in 2003 (compare figure 36 on page 35).[94] Both compounds were isolated as anions due to the complexation of the halogenide because of the high Lewis-acidity of the metal center. As discussed above (LiI adduct), the same phenomenon is observed for compound **8**. An analogous complexation is also observed for the gallium and indium derivatives carrying ethynyl groups $[(Li^+)_2\{dioxane\}_7]_{0.5}[DippNSiMe_3Ga(C{\equiv}CSiMe_3)_3]^-\{dioxane\}_{1.5}$ [ΣΘ(N): 360.0°, ΣΘ(Ga): 656.6°] and $[(Li^+)_2\{dioxane\}_7]_{0.5}[DippNSiMe_3In(C{\equiv}CSiMe_3)_3]^-\{dioxane\}_{1.5}$ [ΣΘ(N): 359.86°, ΣΘ(In): 656.62°] described in the cited paper by Schiefer et al. (see figure 37).[94] Hartig et al.'s side product $Li\{thf\}_4GaBr(DippNH)_2(DippNSiMe_3)$ also shows coordination of the bromine atom due to the same reason. [ΣΘ(N): 360.0°, ΣΘ(Ga): 656.22°].[95] The gallium derivative $Cl_2Ga(DippNSiMe_3)\{Quin\}$ obtained by Luo et al. in 2002[93] (see figure 35 on page 34) also shows the same Lewis-acidic character. Presence of the base Quin leads to an interaction with the Lewis-acid and prevents the complexation of the halogenide, which leads to the isolation of a neutral derivative with a four-coordinated gallium center.

It has to be emphasized, though, that all of the compounds known in literature were obtained by deploying main group 3 element precursors in oxidation state +III ($InCl_3$ and $GaCl_3$, respectively), while the reaction described herein (starting from 'GaI') includes oxidation of the gallium atom.

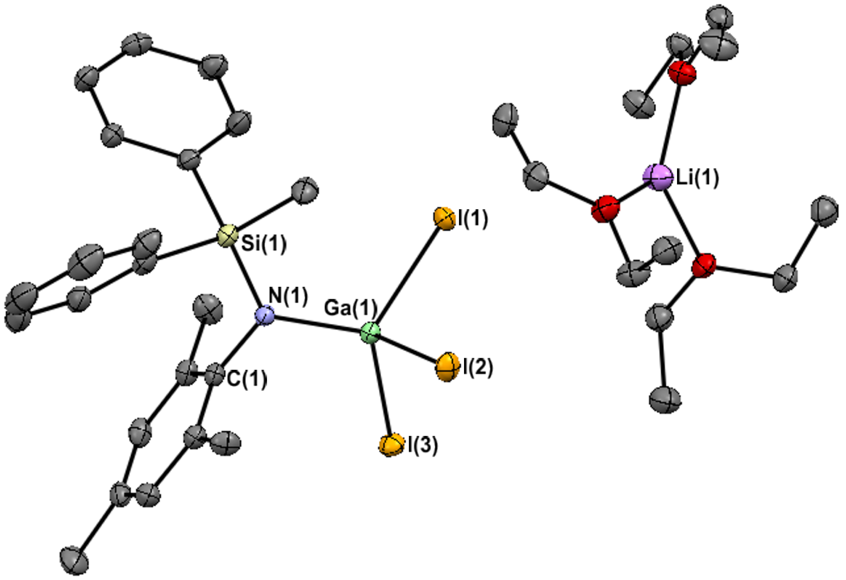


Figure 110: Thermal ellipsoid plot of compound **8** with 50% probability. Hydrogen atoms are not shown. Selected bond distances ($\AA$) and angles (°): Ga(1)-I(1) 2.5686(2), Ga(1)-I(2) 2.5874(2), Ga(1)-I(3) 2.5918(2), Ga(1)-N(1) 1.886(1), N(1)-Si(1) 1.734(1), N(1)-Ga(1)-I(1) 110.88(4), N(1)-Ga(1)-I(2) 114.92(4), N(1)-Ga(1)-I(3) 115.14(4), I(1)-Ga(1)-I(2) 105.04(1), I(1)-Ga(1)-I(3) 105.83(1), I(2)-Ga(1)-I(3) 104.11(1), Ga(1)-N(1)-C(1) 115.3(1), Ga(1)-N(1)-Si(1) 124.36(8), C(1)-N(1)-Si(1) 120.4(1), $\Sigma\Theta$(N(1)) 360.1, $\Sigma\Theta$(Ga(1)) 655.92.

Compared to compound **8**, conversion of lithium derivative **3** with InCl led to a significantly different structure: A 2:1 conversion is occuring, even if the stoichiometry of the reactants deployed is 1:1. The indium oxidation state also changes from +I to +III, which shows that the methyl substitution of the flanking phenyl group is not sufficient to stabilize In(I) derivatives. In analogy to the synthesis of compound **8**, In(0) is found as precipitate in the reaction flask. The structure of compound **9** is presented in figure 111 and shows that the InCl derivative crystallizes as LiCl adduct (again, due to the high Lewis-acidity of the metal and the absence of a base in the reaction solution). The lithium atom is moreover complexed by two Et_2O molecules. Similar structural motives can be found in Linti and Frey's $(MesNSiMe_3)_2GaCl$ and their oligosilazane (compare figure 32 on page 33).[88] Though, these compounds do not show the complexation of a halogenide in contrast to compound **9**. In terms of Lewis-acidity, the derivatives discussed above (in comparison to compound **8**) are also related to compound **9**. The only indium structure known in literature that was also characterized by X-ray diffraction (Prust et al.'s RR'N→$InCl_3^-$ derivative,[91] see page 34) shows similar bond lengths and angles compared to compound **9** (depicted in table 14).

Compound	**In-N** (Å)	**In-Cl** (Å)	**ΣΘ(In(1))**
RR'N→$InCl_3^-$	2.054(2)	2.3614(8)/2.3760(5)/2.4152(8)	656.02
Compound **9**	2.059(7)/2.089(7)	2.458(2)/2.468(2)	647.8

Table 14: Bond lengths and angles in the indium derivative described by Prust et al.[91] and in compound **9**.

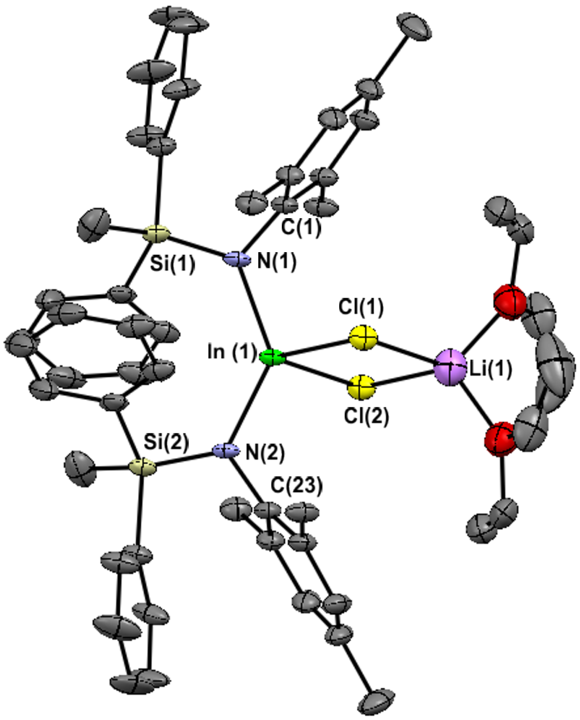


Figure 111: Thermal ellipsoid plot of compound **9** with 50% probability. Hydrogen atoms are not shown. Selected bond distances (Å) and angles (°): In(1)-N(1) 2.089(7), In(1)-N(2) 2.059(7), N(1)-Si(1) 1.699(7), N(2)-Si(2) 1.748(7), In(1)-Cl(1) 2.458(2), In(1)-Cl(2) 2.468(2), N(1)-In(1)-Cl(1) 110.0(2), N(1)-In(1)-Cl(2) 103.0(2), N(2)-In(1)-Cl(1) 102.4(2), N(2)-In(1)-Cl(2) 109.4(2), In(1)-N(1)-C(1) 113.4(5), In(1)-N(1)-Si(1) 129.2(4), C(1)-N(1)-Si(1) 117.2(5), Cl(1)-In(1)-Cl(2) 88.89(7), N(1)-In(1)-N(2) 134.1(3), ΣΘ(N(1)) 359.8, In(1)-N(2)-C(23) 117.1(5), In(1)-N(2)-Si(2) 128.4(4), C(23)-N(2)-Si(2) 114.5(5), ΣΘ(N(2)) 360.0, ΣΘ(In(1)) 647.8.

The most exciting group 13 derivative was obtained by conversion of compound **4** with InCl: Due to the sterically more demanding ligand system the oxidation state of In(I) is conserved and a weakly coordinated (In-In: 3.807 – 3.945Å) tetramer was found in the solid state, the detailed structure of which is shown in figures 112 – 114. For comparison, table 15 lists a number of indium-indium bond lengths in In_4 derivatives, summarized by Driess and Nöth in their book from the year 2004.[277]

Compound	**In-In bond length ($\AA$)**
$In_4[C(SiMe_3)_3]_4$	3.002
$In_4[C(SiMe_2Et)_3]_4$	3.004
$In_4[C(SiMeEt_2)_3]_4$	3.006/3.040
$In_4[C(SiMe_2^iPr)_3]_4$	3.152

Table 15: Indium-indium bond lengths of selected In_4 derivatives, summarized by Driess and Nöth in their book from the year 2004.[277]

The relatively long indium-indium distances of 3.8066(9) – 3.945(1) $\AA$ (compared e.g. to the lengths cited in table 15) show that the stabilization of compound **10** is rather due to Dipp-indium than to indium-indium interactions. The solvent Et_2O is co-crystallized within the crystal structure. While Wright et al.'s 2,6-$Mes_2C_6H_3NGaSiMe_3$ (see page 36)[96] and Dange et al.'s series of gallium and indium derivatives (compare figure 39 on page 37)[82] were found to be monomeric in the solid state, the Ga_4 cluster obtained by Seifert and Linti in the year 2007 (compare figure 38 on page 36) is structurally closely related to compound **10**. Seifert and Linti stated that 'The nitrogen atoms [...] are coordinated in a nearly planar manner [...].'[97] This is also true for compound **10**. It shall also be noted that Seifert and Linti's cluster also bears Dipp substituents at the nitrogen atoms (like compound **10**).

It has to be mentioned that metals of main group 3 are typically fourfold coordinated due to their high Lewis-acidity. This is also the case for compounds **8** and **9** as shown above. Compound **10** is formally one-coordinated, which leads to the interactions toward the phenyl rings in order to increase the coordination number. Comparably, the 'first stable monomeric Ga(I) amide', published by Wright et al. in 2006 (see page 36),[96] shows interactions of the gallium atom and the flanking Mes rings.

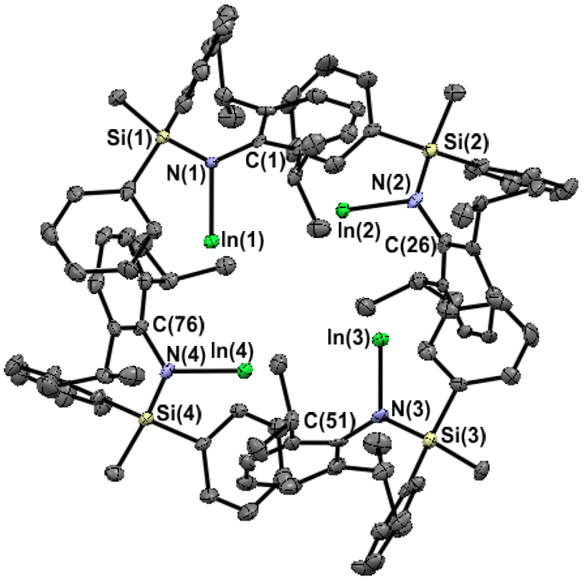


Figure 112: Thermal ellipsoid plot of compound **10** with 50% probability. Hydrogen atoms are not shown. Selected bond distances ($\mathring{A}$) and angles (°): In(1)-In(2) 3.945(1), In(1)-In(4) 3.9422(9), In(2)-In(3) 3.8066(9), In(3)-In(4) 3.9347(8), In(1)-N(1) 2.217(7), In(2)-N(2) 2.199(7), In(3)-N(3) 2.208(7), In(4)-N(4) 2.224(6), N(1)-Si(1) 1.703(8), N(2)-Si(2) 1.715(8), N(3)-Si(3) 1.696(6), N(4)-Si(4) 1.699(7), In(1)-N(1)-C(1) 108.6(5), In(1)-N(1)-Si(1) 124.0(4), C(1)-N(1)-Si(1) 127.3(6), ΣΘ(N(1)) 359.9, In(2)-N(2)-C(26) 107.2(5), In(2)-N(2)-Si(2) 126.0(4), C(26)-N(2)-Si(2) 126.7(6), ΣΘ(N(2)) 359.9, In(3)-N(3)-C(51) 108.8(5), In(3)-N(3)-Si(3) 123.3(4), C(51)-N(3)-Si(3) 127.1(6), ΣΘ(N(3)) 359.3, In(4)-N(4)-C(76) 109.2(5), In(4)-N(4)-Si(4) 122.5(4), C(76)-N(4)-Si(4) 128.3(6), ΣΘ(N(4)) 360.0.

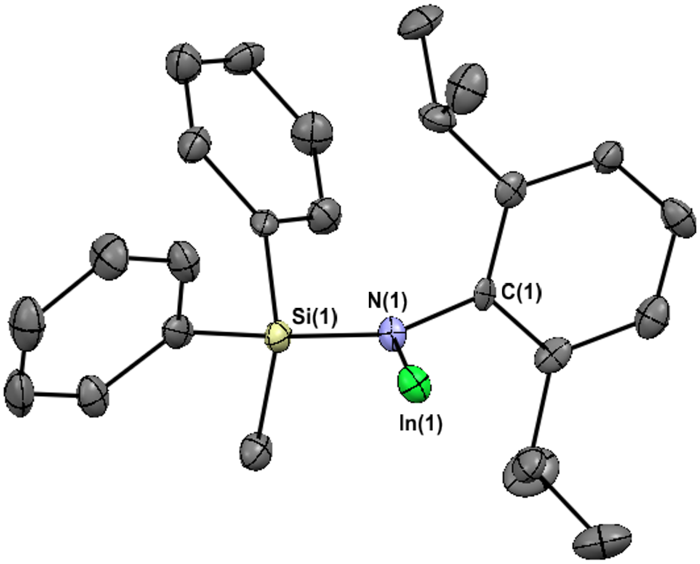


Figure 113: Thermal ellipsoid plot of one monomer fragment of compound **10** with 50% probability. Hydrogen atoms are not shown.

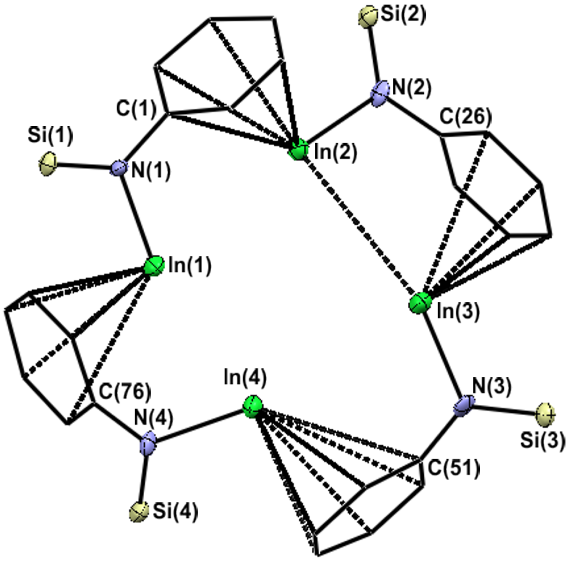


Figure 114: Thermal ellipsoid plot of compound **10** with 50% probability, showing the interactions within the tetramer. Hydrogen atoms are not shown.

As indicated by the synthesis results of main group 3 element compounds, the Mes-substituted silylamide ligand does not provide sufficient sterical hindrance to stabilize the metal in oxidation state +I. Both experiments deploying this less sterically hindered ligand system led to oxidation of the metal (see compounds **8** and **9**). The Dipp silylamide ligand – in contrast – stabilizes In(I) derivatives as proven by the crystal structure of compound **10**.

Main Group 4 Derivatives

In contrast to the main group 3 derivatives described above, ligand systems **1** and **2** both seem to be appropriate to stabilize main group 4 metal compounds in low valent oxidation state +II. A series of 1:1 and 2:1 (lithiated ligand:metal halide) conversions was performed and the desired products were obtained as outlined in figure 115. The structural analogy of the products stabilized by the two silylamide ligands deployed is obvious, no significant structural difference was observed. Compounds **11** to **18** were obtained by converting compounds **3** or **4** with $GeCl_2$\{dioxane\}, $SnCl_2$ or $PbCl_2$, respectively.

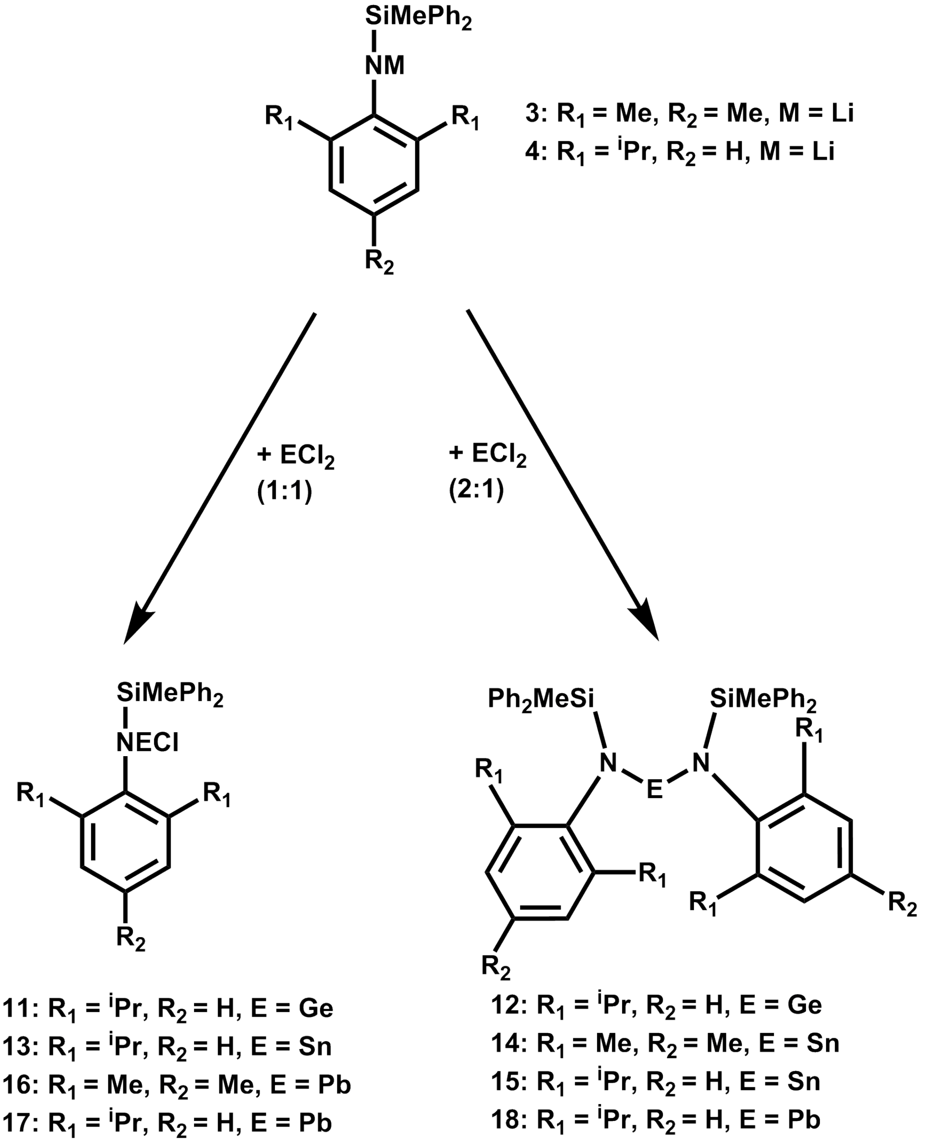


Figure 115: Synthesis of main group 4 silylamide derivatives.

Compound **11** was obtained from a thf solution of compound **4** and $GeCl_2$\{dioxane\} (1:1) after stirring the reaction overnight at room temperature. Unfortunately, X-ray quality crystals could not be isolated, which is why compound **11** was only characterized by NMR measurements. The ^{29}Si NMR shift indicates a structural analogy between compound **11** [δ -14.04 ppm] and compound **13** [δ -15.39 ppm] as well as compounds **16** and **17** (see page 109). That is the reason for the analogous structure proposed for compound **11**.

Compound **13** was synthesized following the same procedure. When repeating the reaction in Et_2O, X-ray quality crystals were obtained and the structure was found to be coordinated by a LiCl$\{Et_2O\}_2$ adduct in the solid state as shown in figure 116. A number of analogous compounds of structure type LECl (E = Ge, Sn, Pb) can be found in literature (for detailed information see pp. 39 – 46): Two early examples are DippN($SiMe_3$)GeBr and 2,6-$Me_2C_6H_3N(SiMe_3)$GeCl, described by Meller and Gräbe as early as in 1985.[108] While Tang et al. found $\{MesNSiMe_3SnCl\}_3$ to be a trimer in the solid state in 2004[114] and $[\{DippNSiMe_3\}SnCl]_2$ was found to be dimeric by Brynda et al. in 2006,[115] a series of germanium and tin chlorides was found to show monomeric structures in the solid state by Li et al. in 2011. (One corresponding lead analog turned out to crystallize as dimer, though.)[25] Some of the halides yielded X-ray diffraction data, that showed the sum of the bond angles about the nitrogen atom to be close to 360°. This is also true for compound **13** as can be seen from figure 116. The ^{119}Sn NMR shift of compound **13** is significantly deviating from the known ^{119}Sn NMR shifts of the tin halides discussed above. While shifts of 173.7 ppm (for \{2,6-$CHPh_2$-4-$MeC_6H_2NSiMe_3$\}SnCl), 104.5 ppm (for \{2,6-$CHPh_2$-4-$MeC_6H_2NSiMePh_2$\}SnCl) and 185.4 ppm (for \{2,6-$CHPh_2$-4-$MeC_6H_2NSiPh_3$\}SnCl)[25] were reported, compound **13** was found to resonate at -45.47 ppm. That is closer to Tang et al.'s trimeric $[MesNSiMe_3SnCl]_3$ [δ 67 ppm][114] and Brynda et al.'s dimeric $[\{DippNSiMe_3\}SnCl]_2$ [δ 14.3 ppm][115] (both structures in the solid state!) than to the monomeric structures discussed above. (It shall be pointed out that none of the literature-known structures bears a salt adduct.) Comparing the crystal structure data of compound **13** with Brynda et al.'s dimeric $[\{DippNSiMe_3\}SnCl]_2$ [$\Sigma\Theta$(N): 360.0°],[115] it is noticeable, that the sum about the nitrogen atoms is exactly the same.

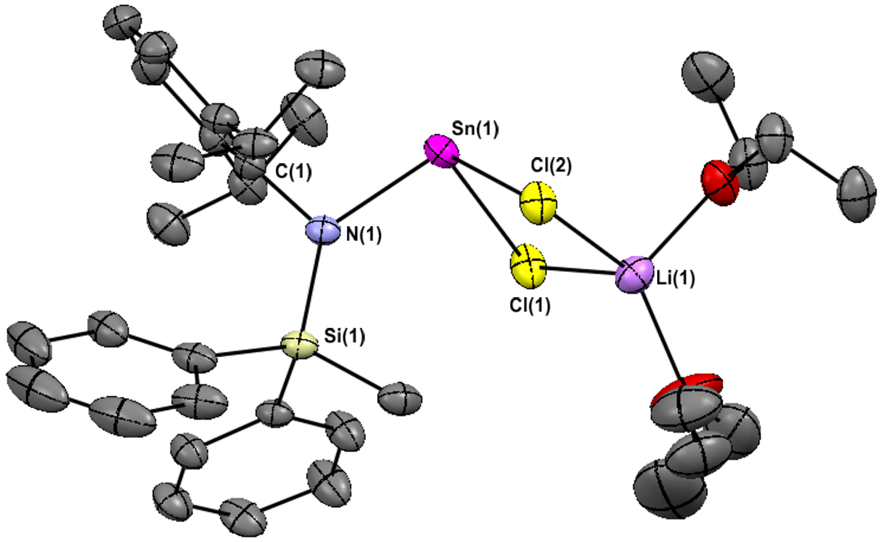


Figure 116: Thermal ellipsoid plot of compound **13** with 50% probability. Hydrogen atoms are not shown. Selected bond distances (Å) and angles (°): Sn(1)-Cl(1) 2.5598(8), Sn(1)-Cl(2) 2.5332(8), Sn(1)-N(1) 2.103(3), N(1)-Si(1) 1.724(2), N(1)-Sn(1)-Cl(1) 100.96(7), N(1)-Sn(1)-Cl(2) 96.82(7), Sn(1)-N(1)-C(1) 103.3(2), Sn(1)-N(1)-Si(1) 135.8(1), C(1)-N(1)-Si(1) 120.9(2), $\Sigma\Theta$(N(1)) 360.00.

Compounds **16** and **17** were obtained by conversion of compound **3** (in Et_2O) or **4** (in thf) with $PbCl_2$. Unfortunately, X-ray quality crystals could not be isolated, even though red crystals of compound **16** were obtained when partially evaporating the solvent. The charactization of the two compounds was performed deploying NMR measurements. The ^{29}Si NMR shift indicates a structural analogy between compounds **16** [δ -13.44 ppm] and **17** [δ -14.98 ppm] and shows similarity toward compounds **11** [δ -14.04 ppm] and **13** [δ -15.39 ppm]. A ^{207}Pb NMR shift was only obtained for compound **16** [δ 2493.79 ppm]. Since no ^{207}Pb NMR data was found for the – to the best of the author's knowledge – only lead analog published in literature (see discussion above, reference 25) and no structural information was obtained for compounds **16** and **17**, no further comparisons of these lead derivatives with literature can be drawn.

The 2:1 conversion also led to interesting structural motives. By conversion of compound **4** with $GeCl_2$\{dioxane\} compound **12** was obtained and isolated in form of yellow X-ray quality crystals after storage at -30 ℃. The structure was determined and is presented in figure 117. As indicated by the structural information given with the figure, the sum of the angle about the nitrogen atom of compound **12** is nearly 360°, which proves a nearly planar substitution environment. A number of aryl-substituted silylamide germylenes is known in literature starting with the series of germylenes synthesized by Meller and Gräbe in 1985[108] (see especially page 39). While also a number of consecutive reactions of these compounds was studied, structural information is rare in literature, which unables the author to further compare the structures of compound **12** with literature-based data. The only data available refers to $\{DippC_6H_3NSiMe_3\}_2Ge$ (published by Meller et al. in 1992) [ΣΘ(N): 358.1/359.4°].[103] The sum of the bond angles about the nitrogen atom is very similar to compound **12**. In addition, it can be stated, that the named sum is also comparable to the corresponding data of the similar stannylenes described in literature (see discussion below, page 111).

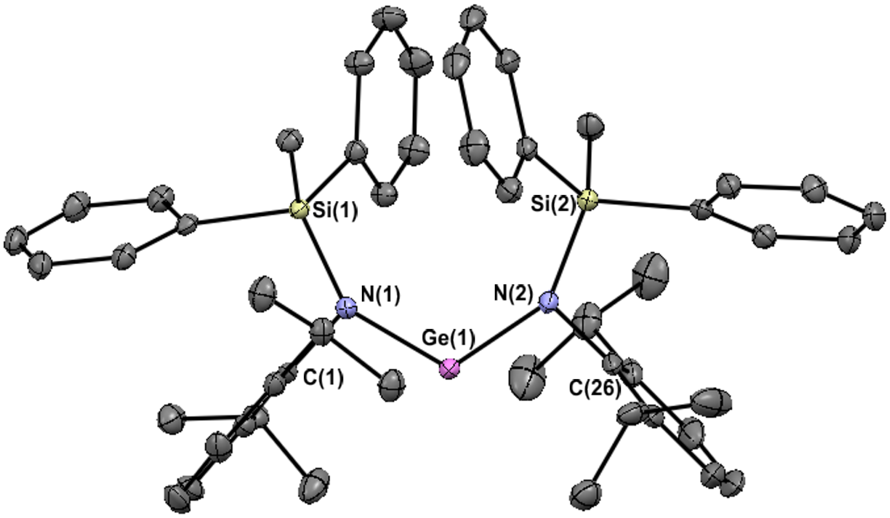


Figure 117: Thermal ellipsoid plot of compound **12** with 50% probability. Hydrogen atoms are not shown. Selected bond distances (*Å*) and angles (°): Ge(1)-N(1) 1.8944(9), N(1)-Si(1) 1.7483(8), Ge(1)-N(2) 1.884(1), N(2)-Si(2) 1.757(1), N(1)-Ge(1)-N(2) 115.78(4), Ge(1)-N(1)-C(1) 102.74(7), Ge(1)-N(1)-Si(1) 142.94(6), C(1)-N(1)-Si(1) 114.16(8), ΣΘ(N(1)) 359.84, Ge(1)-N(2)-C(26) 102.19(8), Ge(1)-N(2)-Si(2) 142.32(6), C(26)-N(2)-Si(2) 115.23(8), ΣΘ(N(2)) 359.74.

Compound **14** was synthesized by conversion of compound **3** with $SnCl_2$ in Et_2O. Yellow crystals were isolated from the reaction solution after partially evaporating the solvent, but unfortunately characterization via X-ray diffraction was not possible. Only NMR data of compound **14** is therefore available. The ^{119}Sn NMR shift of compound **14** was found at 580.65 ppm. Babcock et al. published ^{119}Sn NMR data of $\{2,6\text{-}Me_2C_6H_3NSiMe_3\}_2Sn$ [δ 655 ppm][112] and $\{DippNSiMe_3\}_2Sn$ [δ 440 ppm],[113] which are comparable to the shift of compound **14**. Tang et al.'s monomer $\{MesNSiMe_3\}_2Sn$ also resonates in the same region [δ 473 ppm].[114]

Oily $\{3,5\text{-}(CF_3)_2C_6H_3NSiMe_3\}_2Sn$ was published by Stewart et al. in 2012 and its ^{119}Sn NMR shift was found at -12 ppm – in sharp contrast to the other stannylenes discussed here.[27]

The analogous compound **15**, in contrast to compound **14**, yielded X-ray quality crystals through the same procedure as described above (deploying benzene instead of Et_2O as solvent). The structure determined is shown in figure 118. The crystal structure shows the coordination environment around the nitrogen atom to be nearly planar (compare to compound **12**). Similar results can be found in literature: E.g. Babcock et al.'s $\{DippNSiMe_3\}_2Sn$ shows a sum of the bond angles about the nitrogen atoms of 359.0 and 359.6°.[113] Also, Tang et al.'s $\{MesNSiMe_3\}_2Sn$ is similar (359.1/359.5°).[114] The ^{119}Sn NMR shift of compound **15** was found at 345.1 ppm, which is significantly shifted compared to compound **14**. Since a crystal structure of compound **14** was not obtained, explanation attempts of the NMR shift differences are difficult. It has to be mentioned, though, that some of the data available in literature (see above) also differs clearly from the value obtained for tin derivative **15**. The general difficulties in obtaining ^{119}Sn NMR data of the derivatives discussed here can be explained by the presence of LiCl formed in-situ in the reaction solution, which leads to a significant broadening of the NMR peaks. Separation of the salt is especially difficult when coordination solvents are deployed.

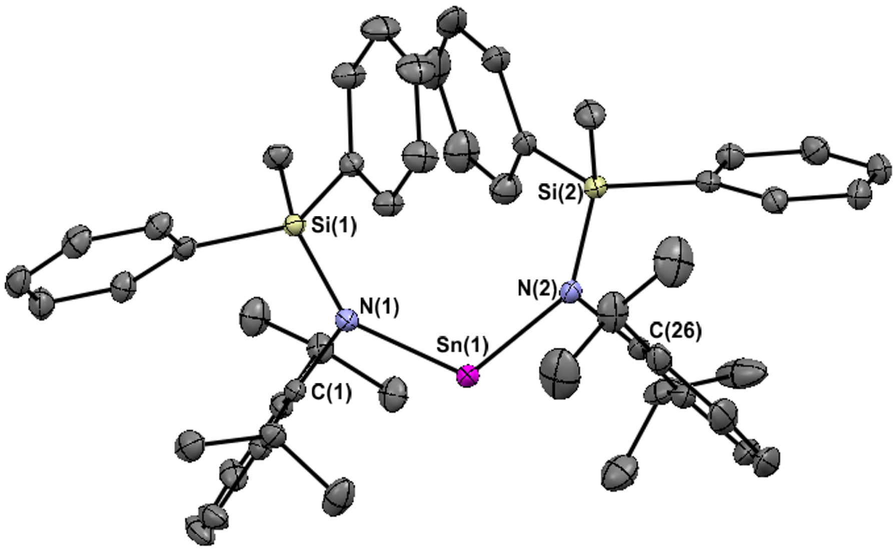


Figure 118: Thermal ellipsoid plot of compound **15** with 50% probability. Hydrogen atoms are not shown. Selected bond distances (Å) and angles (°): Sn(1)-N(1) 2.1030(9), Sn(1)-N(2) 2.094(1), N(1)-Si(1) 1.7339(9), N(2)-Si(2) 1.737(1), N(1)-Sn(1)-N(2) 115.94(4), Sn(1)-N(1)-C(1) 101.21(7), Sn(1)-N(1)-Si(1) 142.05(6), C(1)-N(1)-Si(1) 116.73(8), ΣΘ(N(1)) 359.99, Sn(1)-N(2)-C(26) 100.83(7), Sn(1)-N(2)-Si(2) 141.03(6), C(26)-N(2)-Si(2) 118.11(8), ΣΘ(N(2)) 359.87.

A solution of compound **4** and $PbCl_2$ in Et_2O yielded orange X-ray quality crystals of compound **18** after storage at -30 °C, the structure of which is presented in figure 119. Since – to the best of the author's knowledge – no corresponding plumbylenes have been published in literature up to date no structural comparison is possible here. The sum of the angles about the nitrogen atom is comparable to the similar stannylenes discussed above, though.

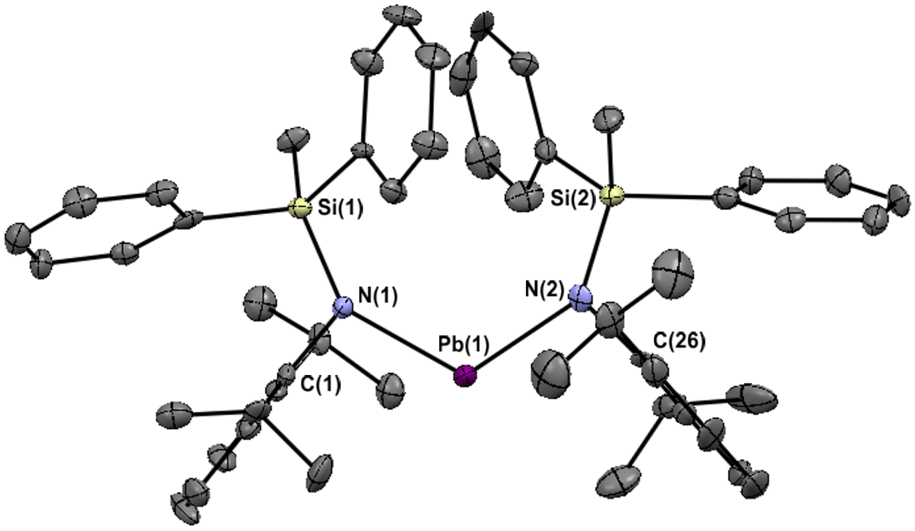


Figure 119: Thermal ellipsoid plot of compound **18** with 50% probability. Hydrogen atoms are not shown. Selected bond distances (Å) and angles (°): Pb(1)-N(1) 2.210(7), Pb(1)-N(2) 2.192(9), N(1)-Si(1) 1.731(6), N(2)-Si(2) 1.740(9), N(1)-Pb(1)-N(2) 116.7(3), Pb(1)-N(1)-C(1) 100.7(5), Pb(1)-N(1)-Si(1) 141.3(4), C(1)-N(1)-Si(1) 118.1(6), ΣΘ(N(1)) 360.1, Pb(1)-N(2)-C(26) 100.7(5), Pb(1)-N(2)-Si(2) 139.0(5), C(26)-N(2)-Si(2) 120.3(6), ΣΘ(N(2)) 360.0.

It can be concluded that the results obtained for group 14 element derivatives are the most predictable ones of the group of silylamide-stabilized compounds examined herein. While the 1:1 conversions (ligand:ECl_2 (E = Ge, Sn, Pb)) lead to compounds of the type LECl, clean reactions toward the corresponding LEL derivatives can be observed in case of the 2:1 conversions. The significance of the stoichiometry has been described in literature earlier (see e.g. the paper by Tang et al. from the year 2004, figure 42 on page 40).[114] While Tang et al. obtained a trimer of the LECl derivative in the solid state, compound **13** was found to be monomeric in the solid state, though.

In order to investigate the stability and reactivity of the obtained derivatives, a series of reactions was performed, mainly deploying the tin based compounds **13** – **15**. The outcome of reduction reactions of compound **13** depended on the reduction reagent used. While deployment of potassium or C_8K led to the synthesis of a tinamidocubane, an undefined mixture of reaction products was obtained upon reduction of the starting compound by L- or K-selectride. The reduction attempts are graphically depicted in figure 120.

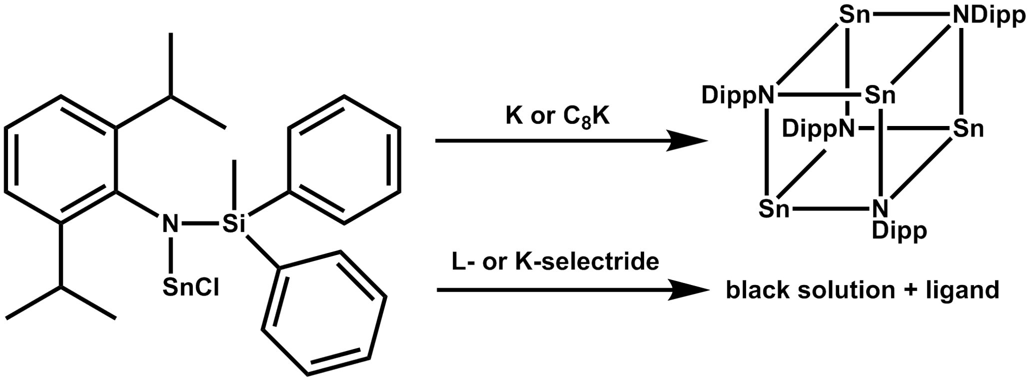


Figure 120: Reduction reactions deploying compound **13** as starting material.

Compounds **14** and **15** were converted with a number of reagents, including main group 6 elements, CS_2, transition metal derivatives (namely $Fe(CO)_5$, $Ni(PPh_3)_4$, $Pd(PPh_3)_4$), P_4 and AdaCP. An overview of these reactions is given in figure 121.

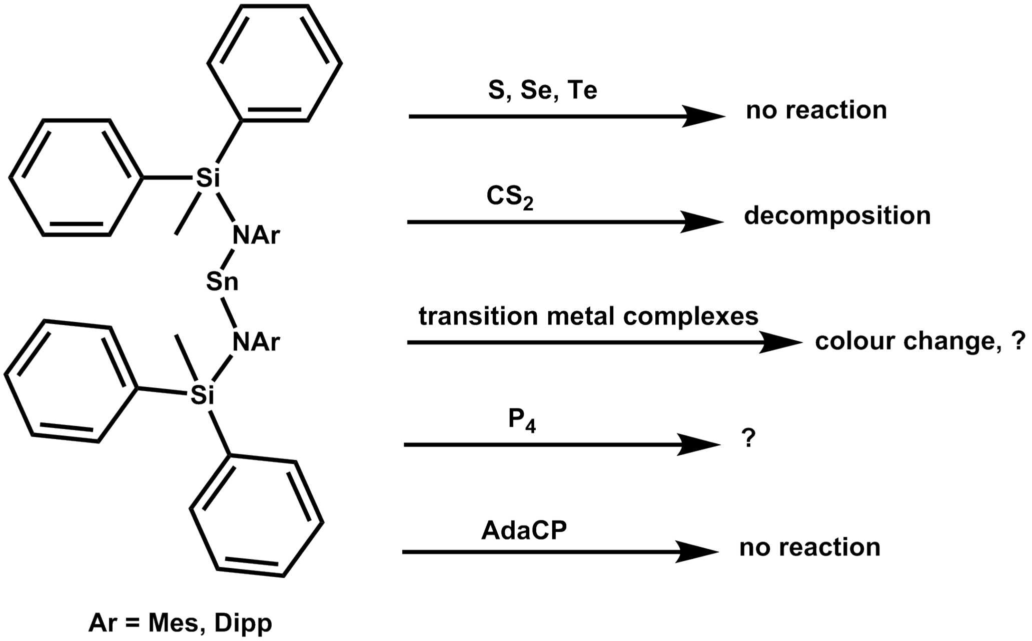


Figure 121: Reactions deploying compounds **14** and **15** as starting materials.

It can be concluded from the reaction results that the silylamide-stabilized low valent main group element derivatives are significantly more stable than their terphenyl-stabilized analogs. Especially the conversions with AdaCP did not lead to any reaction in sharp contrast to the analogous syntheses of compounds **26** – **33** described on pages 121 – 132.

7.2 Synthesis of Biphenyl-Stabilized Tetryltetrylenes and Anionic Compounds

The synthesis route toward ligand systems **19** and **20** and lithium derivatives **21** and **22** is shown in figure 122.

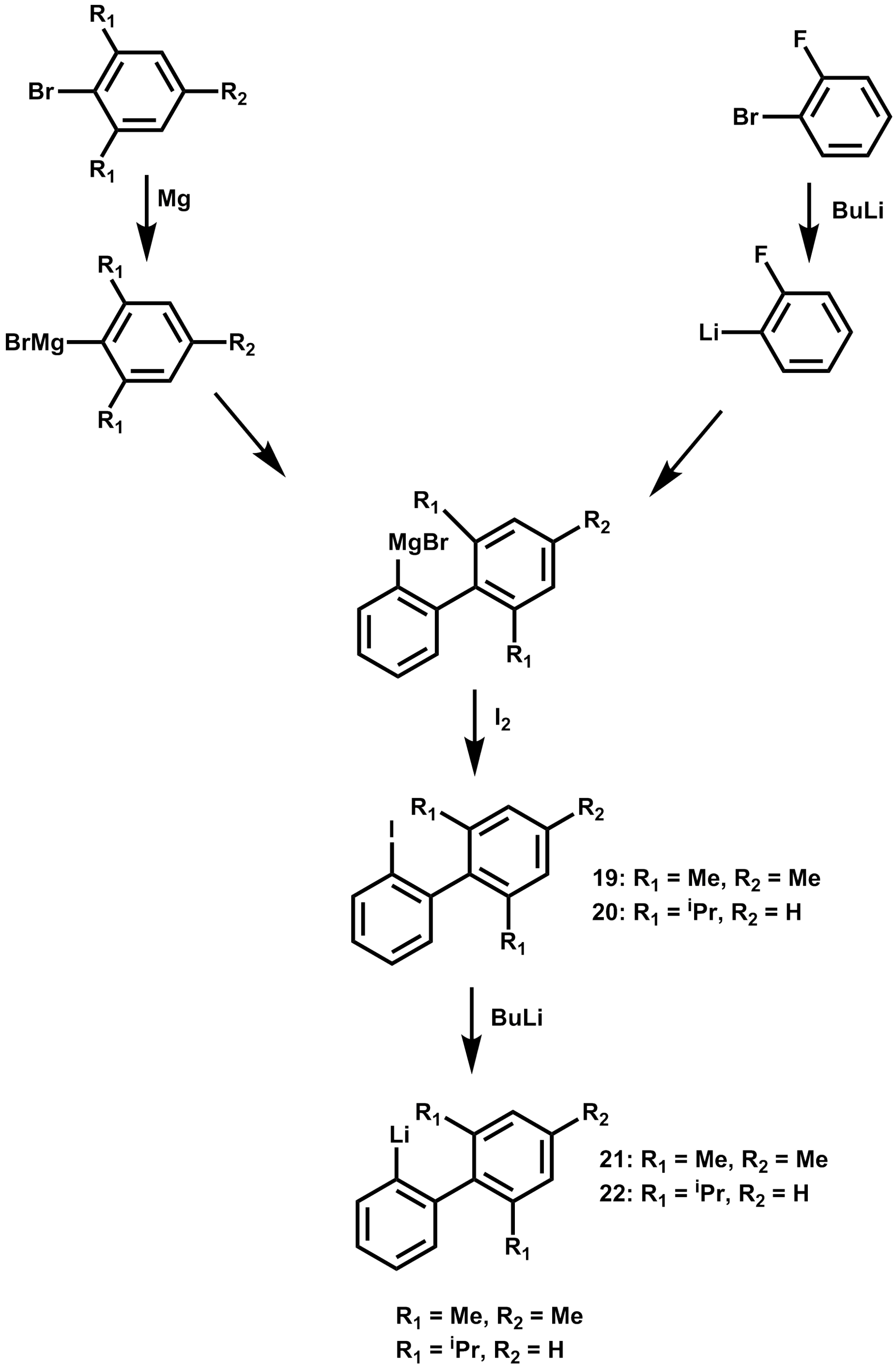


Figure 122: Schematic synthesis route of the biphenyl ligands.

While compound **19** had been described in literature before[122] and had also been crystallographically characterized,[306] the present work describes the novel ligand **20** for the first time. A crystal structure of this compound was obtained and is shown in figure 123. The comparison of compounds **19** and **20** shows that the I(1)-C(1) bond lengths are very similar to each other (2.105(4) *Å* in compound **19** vs. 2.104(2)/2.109(2) *Å* in compound **20**). The two phenyl rings of the biphenyl are approximately orthogonal to each other in both structures. The only significant difference can be seen in the presence of only one molecule in the unit cell (compound **19**) vs. two molecules in the unit cell (compound **20**).

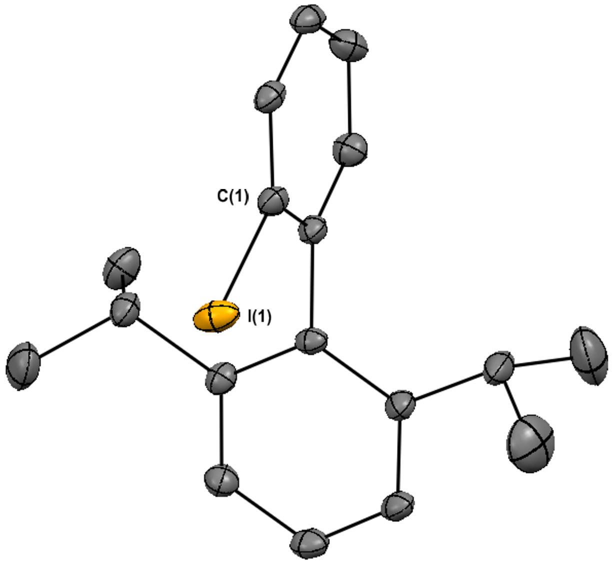


Figure 123: Thermal ellipsoid plot of compound **20** with 50% probability. Hydrogen atoms are not shown. Selected bond distance (*Å*): I(1)-C(1) 2.104(2)/2.109(2) (two molecules in the unit cell).

Following literature procedures[122,123] (with minor changes, see experimental section) lithium derivatives **21** and **22** were obtained and deployed as precursors for the further reactions. Since the two compounds were used as precursors on the way toward tin and lead derivatives, their characterization was performed only by means of NMR measurements in order to check the purity and quality of the products.

Conversion of compounds **21** and **22**with tin and lead precursors led to stannide and plumbide anions and a plumbylplumbylene, depending on reaction stoichiometry. A 3:1 conversion of the lithium derivatives with $SnCl_2$ or $PbCl_2$, respectively, led to the formation of stannide/plumbide anions, coordinated by one lithium cation. The plumbylplumbylene was obtained via 2:1 conversion of compound **21** with $PbCl_2$.

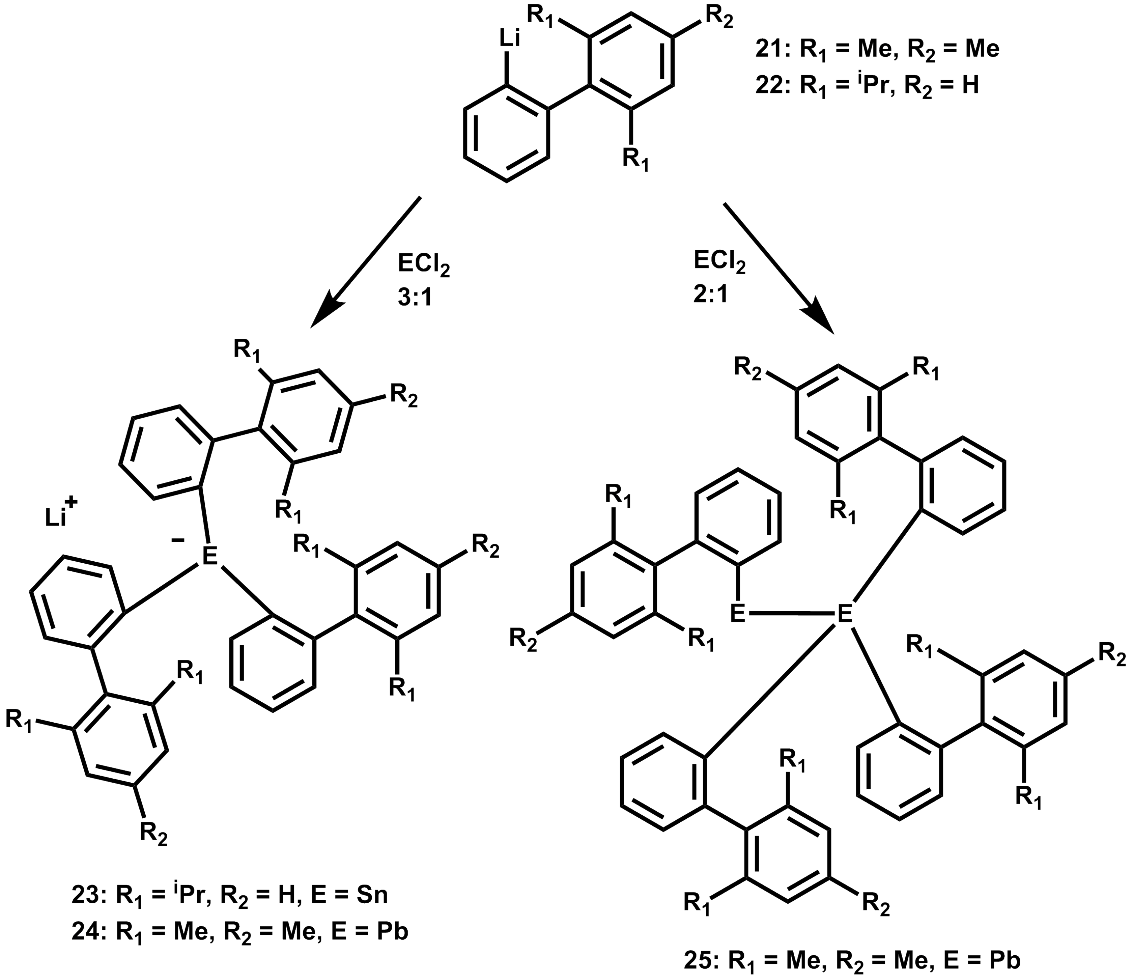


Figure 124: Conversion of the biphenyl precursors to the target compounds.

The structures of compounds **23**, **24** and **25** are presented in figures 125 – 127.

Compound **23** was obtained by reaction of compound **22** with $SnCl_2$ (in a molar ratio of 3:1) in Et_2O (or thf) at -70°C. Yellow X-ray quality crystals of the anion were obtained after removal of the salts, addition of pentane and storage of the reaction solution at -30°C. The characterization of compound **23** was also performed by ^{1}H, ^{13}C and ^{119}Sn NMR measurements. [^{119}Sn {^{1}H} NMR (111.92 MHz, thf/D_2O): δ -137.23 ppm.] The crystal structure of the stannide anion shows that the lithium counterion is solvated by three thf and one Et_2O moieties. In addition, one equivalent of Et_2O is co-crystallized within the crystal lattice. A pyramidal structural motive is present, with angles about the tin atom varying between 92.62° and 93.28°.

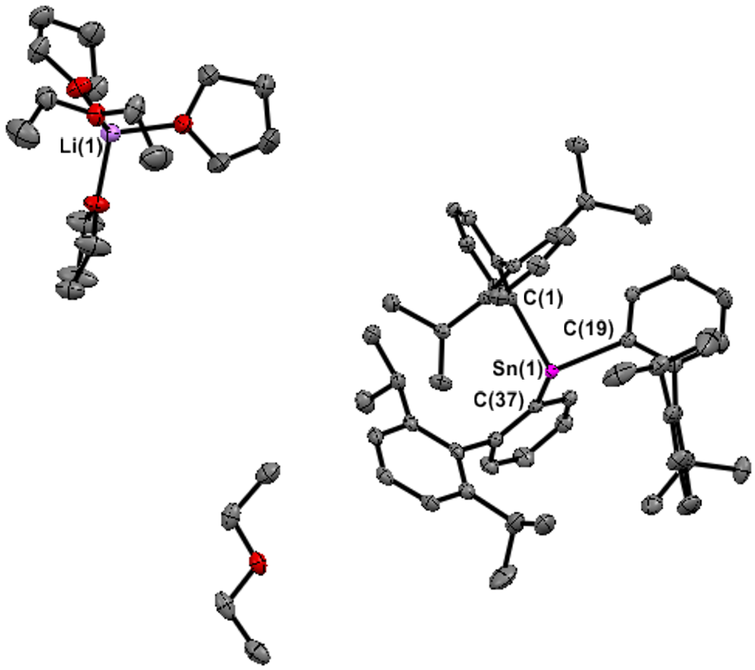


Figure 125: Thermal ellipsoid plot of compound **23** with 50% probability. Hydrogen atoms are not shown. Selected bond distances ($\mathring{A}$) and angles (°): Sn(1)-C(1) 2.268(2), Sn(1)-C(19) 2.249(2), Sn(1)-C(37) 2.259(2), C(1)-Sn(1)-C(19) 93.28(6), C(1)-Sn(1)-C(37) 92.69(7), C(19)-Sn(1)-C(37) 92.62(6), $\Sigma\Theta$(Sn(1)) 278.59.

Compound **24** was obtained by the analogous route as described for compound **23**. Though, compound **21** was deployed as precursor. Interestingly, neither the change in the ligand back bone nor the different metal used led to significant structural changes of the products. In analogy with compound **23**, a pyramidal structure of compound **24** was proven by X-ray diffraction measurements. (Angles about the lead atom: 90.3° – 90.9°.) The lithium counterion is solvated by two Et_2O moieties. It has to be noted that the crystal structure of compound **24** could not be perfectly solved up to the present date. (See the non-ellipsiod plot of several carbon atoms in figure 126.)

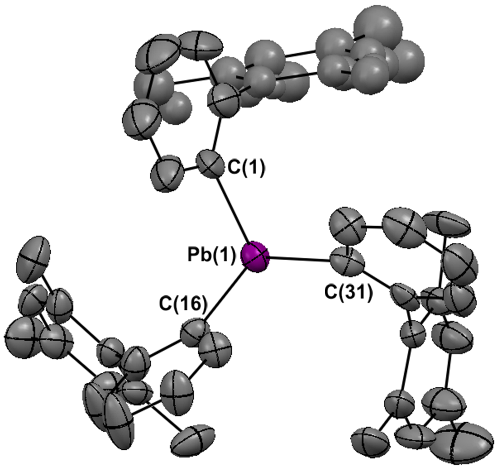


Figure 126: Thermal ellipsoid plot of compound **24** with 50% probability. Hydrogen atoms and solvated counterion are not shown. Selected bond distances ($\mathring{A}$) and angles (°): Pb(1)-C(1) 2.37(1), Pb(1)-C(16) 2.346(9), Pb(1)-C(31) 2.35(1), C(1)-Pb(1)-C(16) 90.3(4), C(1)-Pb(1)-C(31) 90.9(4), C(16)-Pb(1)-C(31) 90.4(4), $\Sigma\Theta$(Pb(1)) 271.6.

2:1 conversion of compound **21** with $PbCl_2$ led to the synthesis of compound **25**, the crystal structure of which is shown in figure 127. Since the precursors and conditions were the same as described above for compound **24**, is shall be noted that the difference in the resulting structure is definitely a question of stoichiometry of the reactants.

The only plumbylplumbylene known in literature was discussed in the corresponding section on pp. 57 – 57. The lead-lead distance within that molecule was determined to be 2.9928(3) $\mathring{A}$, which is similar to the value obtained for compound **25** (3.0187(3) $\mathring{A}$). The closest examples (in terms of only bearing phenyl substituents) of stannylstannylenes are the phenyl/terphenyl-stabilized derivative published by Phillips et al. in 2003 (see figure 62 on page 54)[158] and the terphenyl-stabilized compound obtained by Setaka et al. in 2008 (see figure 65 on page 55).[162] Also, the stannylplumbylene described by Drost et al. in 2012 shall be mentioned here as a similar example.[157]

The reaction pathway toward compound **25** is presumed to proceed via formation of the plumylene in solution followed by rearrangement of the biphenyl groups in order to form the final product. As shown in the literature section (see pp. 47 – 59) migration of groups like in case of compound **25** has been observed several times and is one of the main routes toward the formation of tetryltetrylenes.

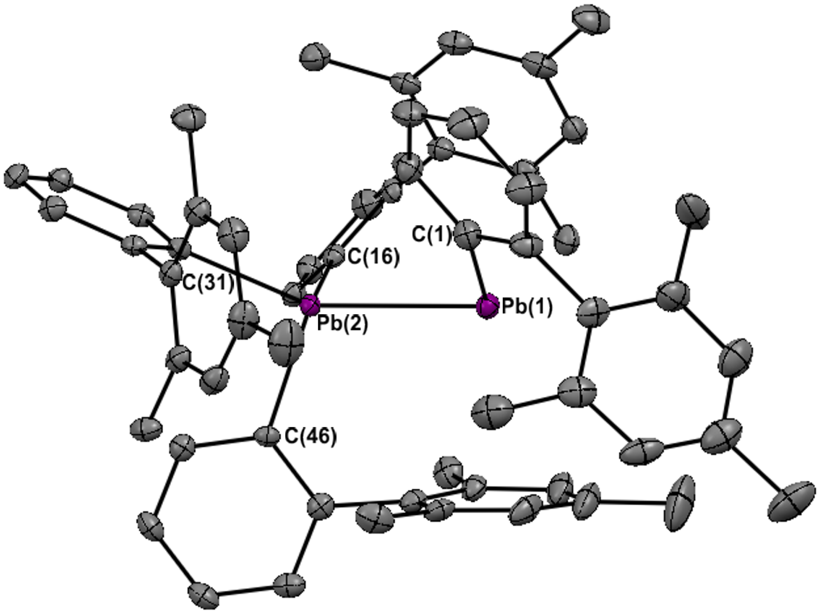
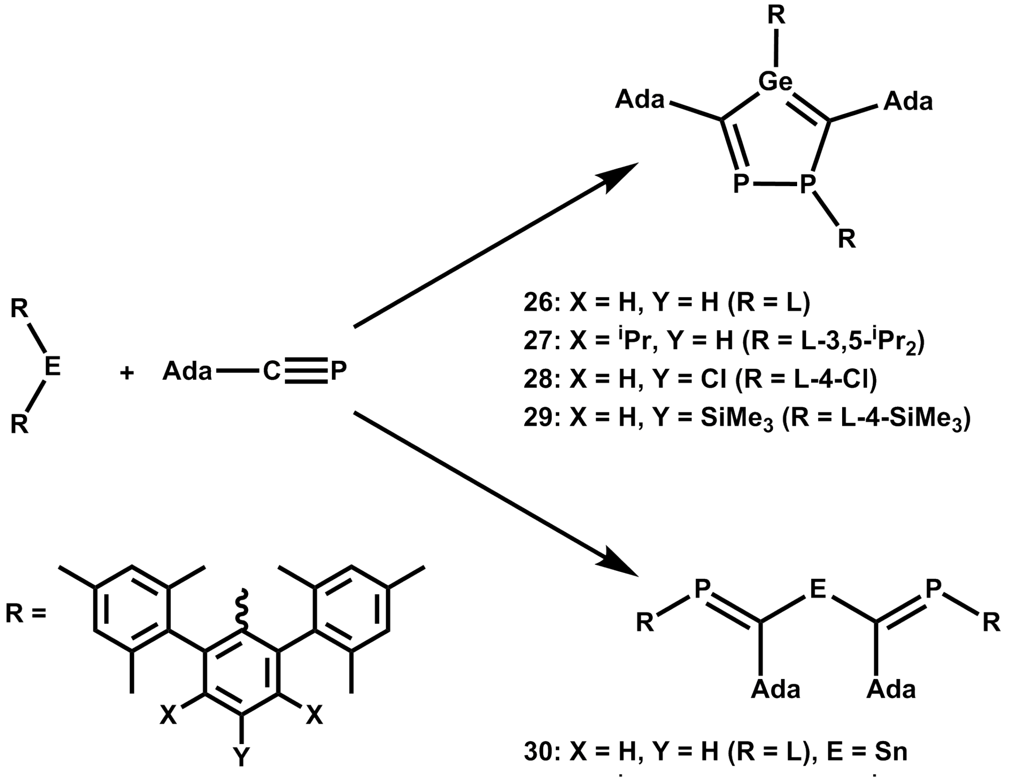


Figure 127: Thermal ellipsoid plot of compound **25** with 50% probability. Hydrogen atoms are not shown. Selected bond distances (Å) and angles (°): Pb(1)-Pb(2) 3.0187(3), Pb(1)-C(1) 2.280(4), Pb(2)-C(16) 2.279(3), Pb(2)-C(31) 2.275(3), Pb(2)-C(46) 2.280(4), Pb(2)-Pb(1)-C(1) 100.41(9), Pb(1)-Pb(2)-C(16) 100.81(9), Pb(1)-Pb(2)-C(31) 112.33(9), Pb(1)-Pb(2)-C(46) 142.63(9), C(16)-Pb(2)-C(31) 95.8(1), C(16)-Pb(2)-C(46) 98.4(1), C(31)-Pb(2)-C(46) 97.2(1), $\Sigma\Theta$(Pb(1)) 408.74.

Summarizing the results of deployment of biphenyl ligands in the present work, it can be stated that the small sterical hindrance of this ligand type allows the migration of the phenyl moieties and hence the synthesis of mixed-valence species (like compound **25**), which is not possible when deploying the sterically more hindered terphenyl ligands. The importance of reaction stoichiometry has to be emphasized.

7.3 Formation of Germoles and Corresponding Tin and Lead Derivatives Stabilized by Terphenyls

Figure 128 gives an overview on the reactions of a series of tetrylenes with AdaCP, yielding tetroles or further tetrylenes, respectively, depending on the kind of metal center.



26: X = H, Y = H (R = L)
27: X = ^{i}Pr, Y = H (R = L-3,5-^{i}Pr$_2$)
28: X = H, Y = Cl (R = L-4-Cl)
29: X = H, Y = SiMe$_3$ (R = L-4-SiMe$_3$)

30: X = H, Y = H (R = L), E = Sn
31: X = ^{i}Pr, Y = H (R = L-3,5-^{i}Pr$_2$), E = Sn
32: X = H, Y = Cl (R = L-4-Cl), E = Sn
33: X = ^{i}Pr, Y = H (R = L-3,5-^{i}Pr$_2$), E = Pb

Figure 128: Conversion of terphenyl-stabilized tetrylenes with adamantylphosphaalkyne.

The subsequent pages (figures 129 – 137) will present and discuss the cystal structures and NMR data of compounds **26** – **33** followed by a chapter on the potential aromaticity of the germole derivatives.

All of the compounds described here were obtained by addition of a solution of AdaCP in Et$_2$O or thf to a solution of the parent tetrylene in the same solvent. X-ray quality crystals of the compounds were obtained upon storage of the reaction solutions at -30°C or at room temperature.

Compound **26** is the most basal germole derivative obtained, bearing no further substituents (other than hydrogen) at the back bone of the central aromatic ring of the terphenyl ligand. A yellow solution of the compound was obtained after conversion of the parent germylene with AdaCP. At first, based on the ^{31}P NMR data [^{31}P {^{1}H} NMR (121.54 MHz, C_6D_6): δ 12.66 (d,^{1}J $_{\text{31P-31P}}$: 420 Hz), 276.67 (d, ^{1}J $_{\text{31P-31P}}$: 420 Hz ppm], a four-membered ring system similiar to the one synthesized by Meiners et al. in 2001 (see page 67) [^{31}P NMR: δ -34.4 ppm, 271.5 ppm (d, ^{1}J $_{\text{31P-31P}}$ = 16 Hz), -8.1 ppm, 269.0 ppm (d, ^{1}J $_{\text{31P-31P}}$ = 21 Hz), due to two conformers in solution][196] was proposed. The deviation in the coupling constants and appearance of only one set of signals (in contrast to the two sets observed by Meiners et al.) could not be explained at this time. The real structure of the compound was not found until X-ray quality crystals of compound **26** were obtained by storage of the reaction solution at -30℃. As illustrated in figure 129, a five-membered germadiphosphaphosphole bearing two adamantyl and two terphenyl groups was obtained (1:2 conversion of germylene:AdaCP). The most similar structure, that can be found in literature, is the germole trapped by Jones et al. in 2008 [^{31}P NMR (121.6 MHz, thf-d_8/85% H_3PO_4): δ 308.5, 319.8 ppm, ^{2}J $_{\text{PP}}$ = 29.8 Hz (AB spin system)] (see page 68).[199] It has to be pointed out, though, that Jones et al.'s germole is a 2,4-diphosphole, while compound **26** is a 3,4-diphosphole. Unfortunately, Jones et al. did not report any structural information (e.g. bond lengths or angles) on their germole. Comparison of the ^{31}P NMR shifts of compound **26** and the polyphosphaphospholes reported by Cowley et al.[201] and Dietz et al.[205] shows that the low-field shift of compound **26** is comparable to the data reported by the other authors (see page 70). Further comparison of the derivatives is not possible, though, due to the missing structural data in literature.

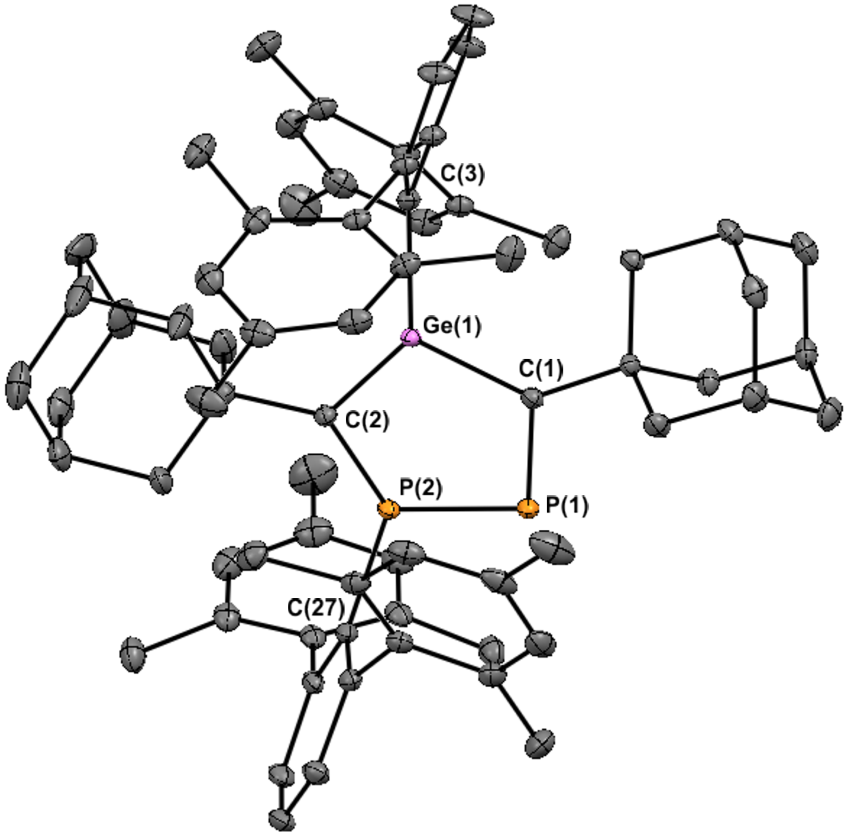


Figure 129: Thermal ellipsoid plot of compound **26** with 50% probability. Hydrogen atoms are not shown. Selected bond distances ($\AA$) and angles (°): Ge(1)-C(1) 1.922(1), Ge(1)-C(2) 1.8532(9), Ge(1)-C(3) 1.979(1), C(1)-P(1) 1.713(1), C(2)-P(2) 1.762(1), P(1)-P(2) 2.1289(4), P(2)-C(27) 1.8615(9), C(1)-Ge(1)-C(2) 106.85(4), C(1)-Ge(1)-C(3) 117.56(4), C(2)-Ge(1)-C(3) 130.77(4), Ge(1)-C(1)-P(1) 113.46(5), Ge(1)-C(2)-P(2) 108.38(5), C(1)-P(1)-P(2) 100.99(4), C(2)-P(2)-P(1) 107.85(4), C(2)-P(2)-C(27) 118.99(5), P(1)-P(2)-C(27) 104.55(3), $\Sigma\Theta$(Ge(1)) 355.18.

For better recognizability, the framework of compound **26** is shown as combined wireframe and thermal ellipsoid plot in figure 130. The (almost) planarity of the germole ring can also be seen from this depiction.

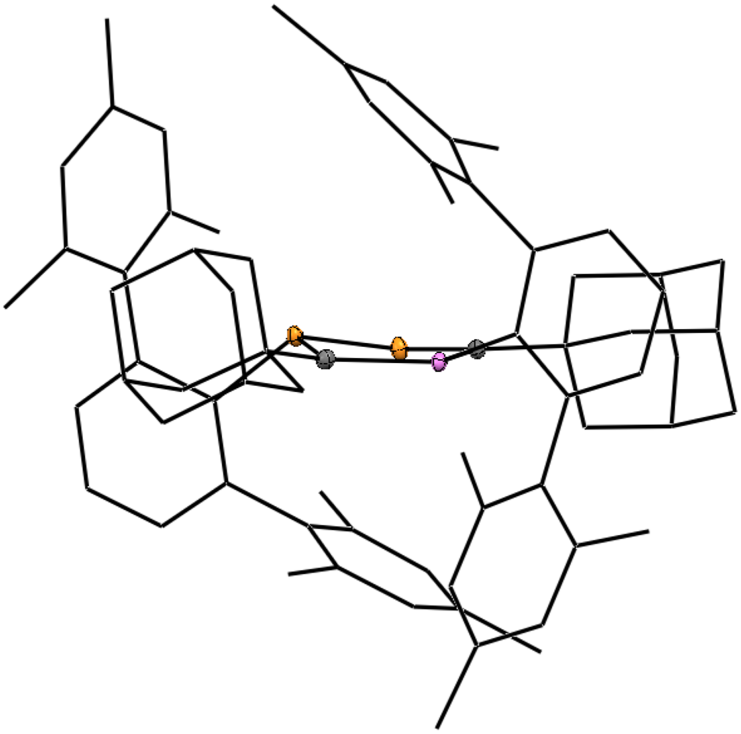


Figure 130: Wireframe and thermal ellipsoid plot of compound **26**.

The synthesis of compound **27** was performed analogous to compound **26**. X-ray quality crystals were obtained at room temperature from the reaction solution. The structural similarity of all the germoles described in the present work is supported by the resemblance of ^{31}P NMR data as well as of structural parameters obtained by X-ray diffraction measurements. The ^{31}P NMR data of compound **27** [^{31}P {^{1}H} NMR (121.54 MHz, thf/D_2O): δ 19.65 (d,^{1}J $_{31P\text{-}31P}$: 449 Hz), 259.62 (d, ^{1}J $_{31P\text{-}31P}$: 449 Hz) ppm] is very similar to that of compound **26** [^{31}P {^{1}H} NMR (121.54 MHz, C_6D_6): δ 12.66 (d,^{1}J $_{31P\text{-}31P}$: 420 Hz), 276.67 (d, ^{1}J $_{31P\text{-}31P}$: 420 Hz ppm]. Also, bond lengths and angles of the germole structures turned out to be extremely similar. It has to be noted, though, that in case of compound **27** Et_2O is co-crystallized within the crystal structure.

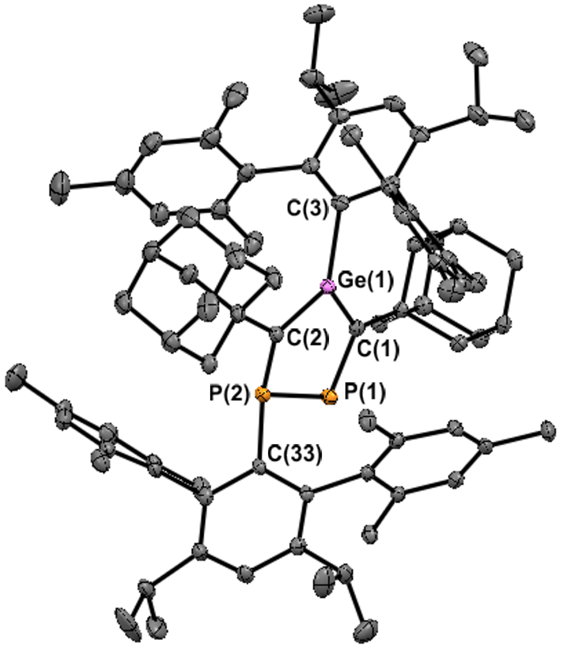


Figure 131: Thermal ellipsoid plot of compound **27** with 50% probability. Hydrogen atoms are not shown. Selected bond distances (Å) and angles (°): Ge(1)-C(1) 1.916(2), Ge(1)-C(2) 1.838(2), Ge(1)-C(3) 1.972(2), C(1)-P(1) 1.716(2), C(2)-P(2) 1.759(2), P(1)-P(2) 2.1375(9), P(2)-C(33) 1.862(2), C(1)-Ge(1)-C(2) 107.8(1), C(1)-Ge(1)-C(3) 118.5(1), C(2)-Ge(1)-C(3) 131.5(1), Ge(1)-C(1)-P(1) 112.7(1), Ge(1)-C(2)-P(2) 108.3(1), C(1)-P(1)-P(2) 101.40(9), C(2)-P(2)-P(1) 107.09(8), C(2)-P(2)-C(33) 118.8(1), P(1)-P(2)-C(33) 107.38(8), ΣΘ(Ge(1)) 357.8.

Compound **28** was obtained by an analogous route, again Et_2O is co-crystallized within the crystal structure. In case of this germole, recording of ^{31}P NMR data was unsuccessful. The characterization via X-ray diffraction suggests, that similar NMR data to compounds **26** and **27** can be expected. Crystal data is again very similar to the germoles discussed above.

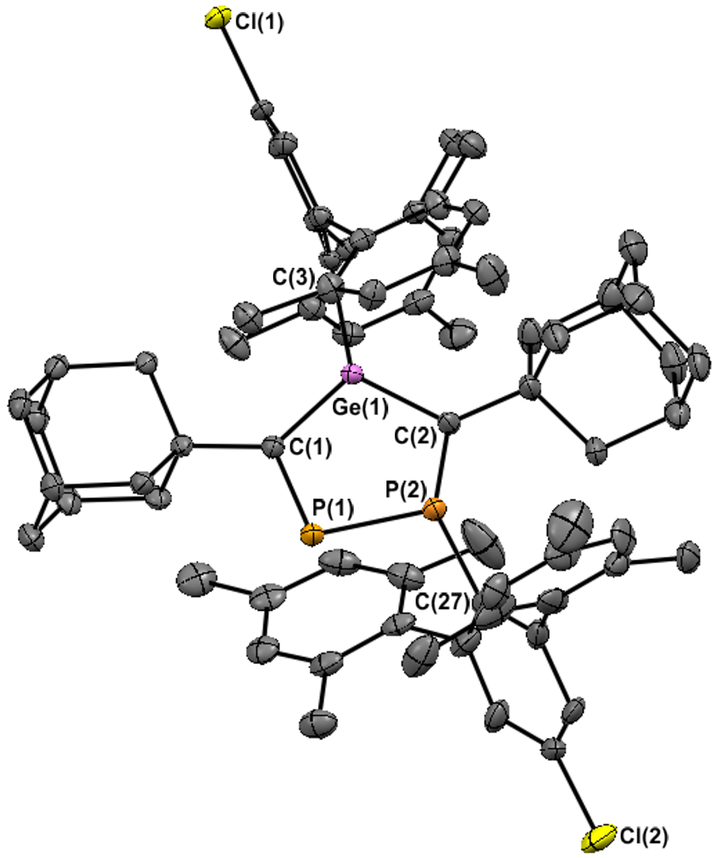


Figure 132: Thermal ellipsoid plot of compound **28** with 50% probability. Hydrogen atoms are not shown. Selected bond distances ($\mathring{A}$) and angles (°): Ge(1)-C(1) 1.924(2), Ge(1)-C(2) 1.855(2), Ge(1)-C(3) 1.982(2), C(1)-P(1) 1.717(2), C(2)-P(2) 1.762(2), P(1)-P(2) 2.1264(7), P(2)-C(27) 1.862(2), C(1)-Ge(1)-C(2) 107.57(9), C(1)-Ge(1)-C(3) 120.71(9), C(2)-Ge(1)-C(3) 127.61(9), Ge(1)-C(1)-P(1) 112.6(1), Ge(1)-C(2)-P(2) 107.5(1), C(1)-P(1)-P(2) 101.58(7), P(1)-P(2)-C(2) 107.82(8), P(1)-P(2)-C(27) 104.70(8), C(2)-P(2)-C(27) 118.9(1), ΣΘ(Ge) 355.89

The yellow X-ray quality crystals of compound **29** were obtained by the same procedure as described above. Again, NMR data [^{31}P {^{1}H} NMR (121.54 MHz, C_6D_6): δ 12.80 (d,^{1}J $_{31P\text{-}31P}$: 419 Hz), 276.98 (d, ^{1}J $_{31P\text{-}31P}$: 419 Hz) ppm] and structural parameters are very close to the other germoles.

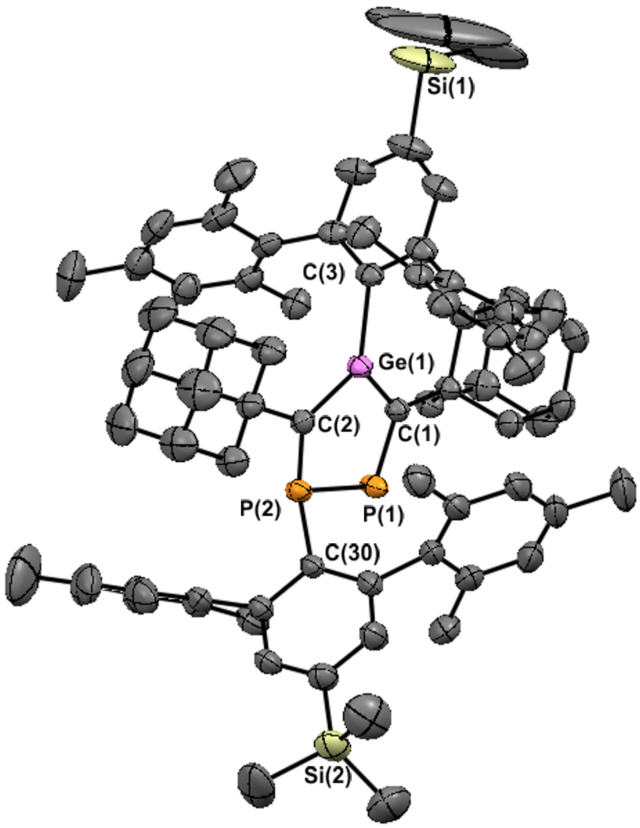


Figure 133: Thermal ellipsoid plot of compound **29** with 50% probability. Hydrogen atoms are not shown. Selected bond distances (*Å*) and angles (°): Ge(1)-C(1) 1.916(3), Ge(1)-C(2) 1.851(3), Ge(1)-C(3) 1.984(3), C(1)-P(1) 1.706(3), C(2)-P(2) 1.774(3), P(1)-P(2) 2.133(1), P(2)-C(30) 1.873(3), C(1)-Ge(1)-C(2) 106.5(1), C(1)-Ge(1)-C(3) 119.5(1), C(2)-Ge(1)-C(3) 131.7(1), Ge(1)-C(1)-P(1) 113.7(2), Ge(1)-C(2)-P(2) 109.5(2), C(1)-P(1)-P(2) 102.0(1), C(2)-P(2)-P(1) 106.6(1), C(2)-P(2)-C(30) 115.7(1), P(1)-P(2)-C(30) 104.4(1), ΣΘ(Ge) 357.7.

A detailed discussion of the structural parameters of the obtained germoles can be found later in the present work (see pp. 134 – 135).

The acyclic stannylene **30** was isolated in form of green crystals after conversion of the parent stannylene with AdaCP and storage at -30℃. X-ray diffraction measurements could not be performed though, which led to the only characterization of the compound by NMR [^{31}P {^{1}H} NMR (121.54 MHz, C_6D_6): δ 332.68 ppm, ^{119}Sn {^{1}H} NMR (112.16 MHz, C_6D_6): δ 1301.06 ppm] and UV-Vis measurements. The color of the crystals and the ^{31}P NMR data suggest, that compounds **30** – **32** are structurally analogous.

Crystals of compound **31** were obtained by the same procedure as described above at room temperature. As already mentioned, the ^{31}P NMR data [^{31}P {^{1}H} NMR (121.54 MHz, thf/D_2O): δ 348.80 ppm] suggest a structural similarity to compound **30**. The structure can be described as a conjugated C-P-C-Sn-C-P-C chain, when incorporating the lone pair of the metal in the discussion. As observed in case of the germoles a 1:2 conversion of stannylene:AdaCP took place, yielding the acyclic structure bearing two adamantyl and two terphenyl moieties. A striking feature of this reaction is that an analogous insertion (of C=P into the metal-carbon bond) reaction is not included in the discussion of reactivity patterns typical for tetrylenes available in literature (compare pp. 59 – 62). The most important characteristic of the reactions toward compounds **31** – **33** is that the oxidation state of the metal center is conserved in contrast to the reactions of the germylenes with AdaCP.

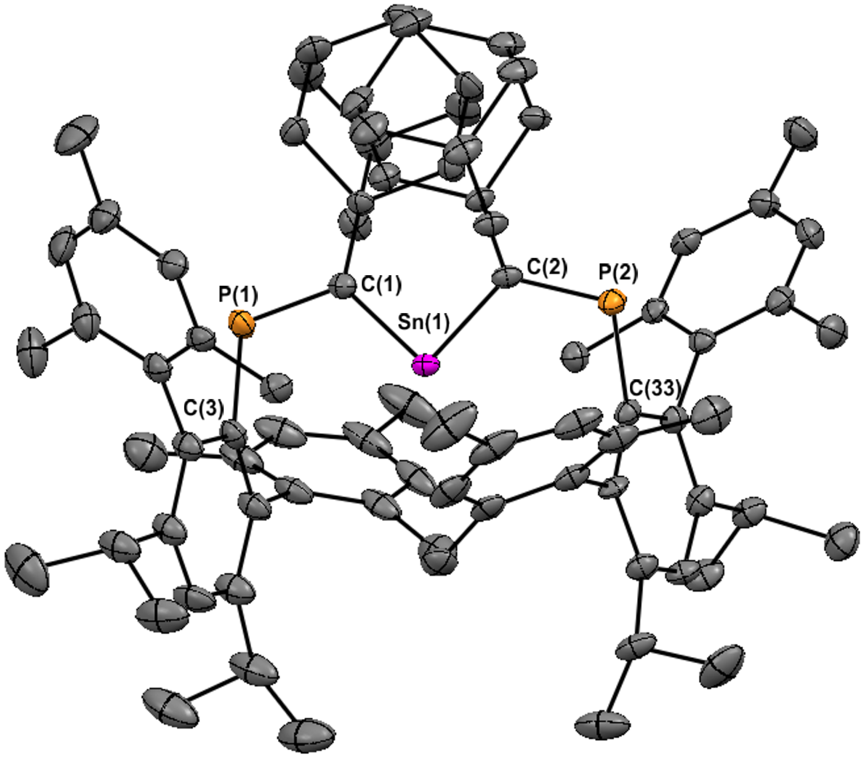


Figure 134: Thermal ellipsoid plot of compound **31** with 50% probability. Hydrogen atoms are not shown. Selected bond distances ($\AA$) and angles (°): Sn(1)-C(1) 2.202(3), Sn(1)-C(2) 2.207(3), C(1)-P(1) 1.685(3), C(2)-P(2) 1.682(3), P(1)-C(3) 1.867(3), P(2)-C(33) 1.864(3), C(1)-Sn(1)-C(2) 107.4(1), Sn(1)-C(1)-P(1) 113.9(2), Sn(1)-C(2)-P(2) 113.1(1), C(1)-P(1)-C(3) 110.3(1), C(2)-P(2)-C(33) 111.2(1).

For better recognizability, the framework of compound **31** is shown as combined wireframe and ellipsoid plot in figure 135.

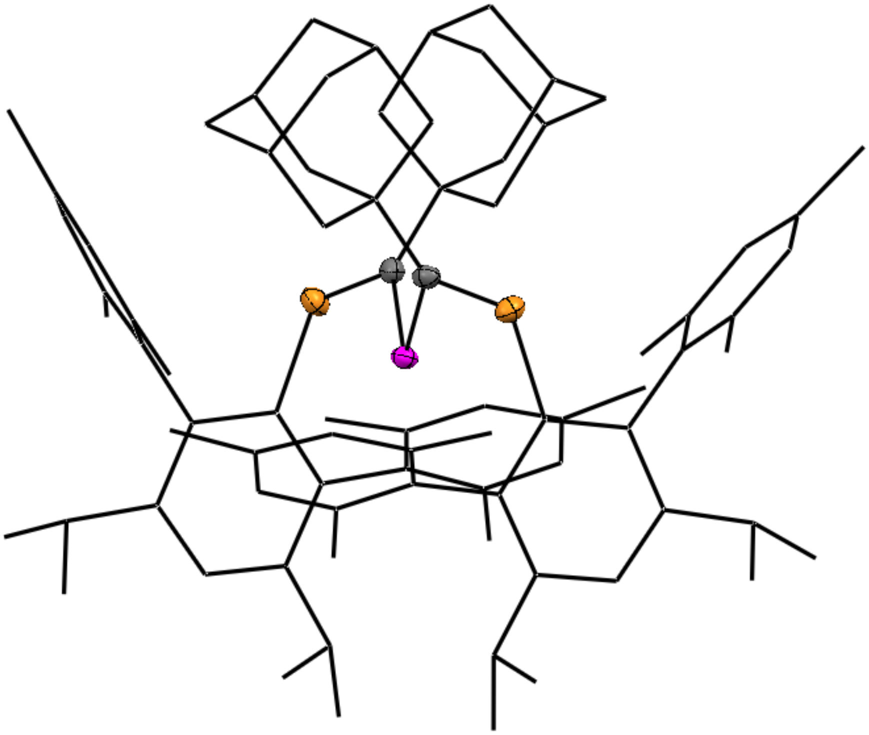


Figure 135: Wireframe and thermal ellipsoid plot of compound **31**.

One can conclude that presumably the stannylene derivatives (as well as the plumbylene derivative obtained) represent the first step of the reaction, while the germoles show the final product. The (theoretically determined) stability of the acyclic stannylene derivative is not too extensive in comparison to the cyclic analog (see discussion below), which makes the synthesis of the stannole derivatives a quite likely goal for the future.

Though, the further tin and lead derivatives found in the present work show the same structural motives as described for compound **31**. Compound **32** (obtained by the same synthesis route) shows analogy with compound **31** regarding color, structural features and ^{31}P NMR data [^{31}P {^{1}H} NMR (121.54 MHz, C_6D_6): δ 331.40 ppm].

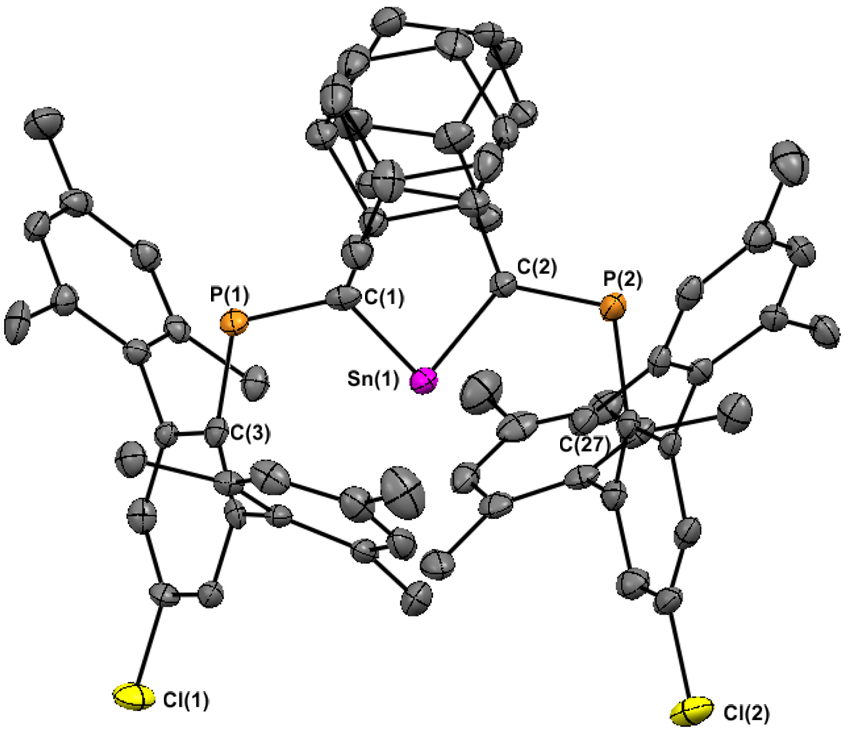


Figure 136: Thermal ellipsoid plot of compound **32** with 50% probability. Hydrogen atoms are not shown. Selected bond distances (Å) and angles (°): Sn(1)-C(1) 2.196(5), Sn(1)-C(2) 2.214(6), C(1)-P(1) 1.679(6), C(2)-P(2) 1.671(5), P(1)-C(3) 1.850(7), P(2)-C(33) 1.864(6), C(1)-Sn(1)-C(2) 104.8(2), Sn(1)-C(1)-P(1) 114.3(3), Sn(1)-C(2)-P(2) 113.4(3), C(1)-P(1)-C(3) 107.7(3), C(2)-P(2)-C(33) 109.8(3).

The only lead derivative obtained by conversion of the corresponding parent plumbylene with AdaCP is compound **33**. Unfortunately, ^{31}P NMR data was not obtained but X-ray diffraction measurements proved the structural analogy with the tin derivatives.

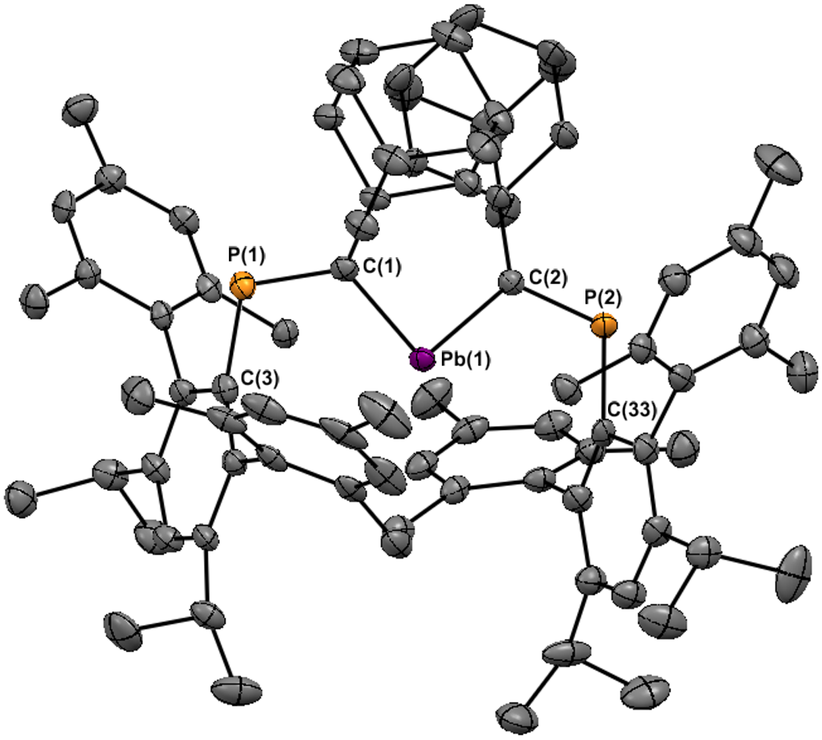


Figure 137: Thermal ellipsoid plot of compound **33** with 50% probability. Hydrogen atoms are not shown. Selected bond distances (Å) and angles (°): Pb(1)-C(1) 2.316(4), Pb(1)-C(2) 2.305(4), C(1)-P(1) 1.674(5), C(2)-P(2) 1.676(5), P(1)-C(3) 1.863(4), P(2)-C(33) 1.863(5), C(1)-Pb(1)-C(2) 107.6(2), Pb(1)-C(1)-P(1) 113.3(2), Pb(1)-C(2)-P(2) 113.8(2), C(1)-P(1)-C(3) 110.4(2), C(2)-P(2)-C(33) 108.8(2).

Figure 128 and the crystal structures discussed above show that the appearance of the cyclic vs. the chain-like (acyclic) structure depends on the central element of the compounds: While conversion of the germylenes leads to cyclic structures exclusively, the heavier analogs form acyclic structured compounds instead. The reversibility and stability of the two structural motives have been studied theoretically by Müller and Flock. Their calculations showed that the energetic barrier between the two structures is significantly different when varying the central metal as depicted in table 16.[307]

Derivative	ΔE
Germanium derivative	-126.1 kJ/mol
Tin derivative	-10.0 kJ/mol
Lead derivative	+44.0 kJ/mol

Table 16: Stabilization energy of the cyclic vs. the acyclic structural motive with varying central metal.[307]

As can be seen from table 16 the synthesis of the cyclic structure is very likely in case of the germylene precursors in terms of stability, while for the lead analogs the acyclic structural motive is more probable to be observed in the experiment. The stability difference of the tin compounds is not too extensive, which makes reversibility and cyclization studies on these compounds most promising. The great stabilization difference between the germanium and the lead derivative can be explained by taking into account the lone pair effect: Germanium in oxidation state +II is by far more reactive compared to the lead analog, thus tending toward oxidation state +IV. The named effect leads to a more likely conservation of oxidation state +II in tin and lead derivatives. Further experimental and theoretical studies on the stability and reversibility of the compounds will be a focus of further research of the working group.

Aromaticity of the Obtained Germoles

As discussed in the literature section, the aromaticity of germole derivatives has been a topic of research for years (see pp. 71 – 81). According to a paper by Lee and Sekiguchi from the year 2007, the aromaticity of a compound is composed by three contributors: 'The energetic criterion of aromaticity, based on the quantum chemical calculation of stabilization that is gained by the cyclic electron delocalization, the so-called resonance energy (RE), plays a major role in estimating the degree of aromaticity. The most commonly used estimate of RE is the aromatic stabilization energy (ASE) calculated by employing either isodesmic or homodesmic reactions.

The structural criterion of aromaticity deals with the geometry of the molecule: Planarity and carbon-carbon bond equalization are considered as the default prerequisites necessary for the optimum overlap of the pπ orbitals. Except for the computational estimates, such a geometric manifestation of aromaticity could be visualized by means of physicochemical methods, principially by X-ray crystallography.

The magnetic criterion of aromaticity is based on the phenomenon of the diamagnetic ring current caused by the circulation of the π electrons and exaltation of the diamagnetic susceptibility (Λ). This property can also be theoretically estimated by quantum chemical calculations, whereas the experimental assessment of aromaticity can be achieved by NMR spectroscopic measurements. Namely, deshielding of the nuclei lying in the plane of the aromatic ring and shielding of the nuclei lying inside the anisotropy cone above or below the aromatic ring are considered as a direkt evidence for induced ring current effects and, consequently, aromaticity of the compound. Such tendencies in the chemical shift changes can be quantified on the basis of quantum chemical calculations of the chemical shift at the center of the aromatic ring, the so-called nucleus independent shift (NICS) [...].'[211]

Concerning the first contributor (energetic criterion of aromaticity) it shall be mentioned (see table 16) that the germoles are significantly lower in energy than their acyclic (hypothetical) germanium bearing analogs. This fact has been discussed above.

The structural criterion of aromaticity has also been shortly mentioned in terms of the (almost) planarity of the germole rings. The equalization of bonds shall be discussed here in order to collect further evidence for the presumed aromaticity of the germole derivatives. Due to the lack of comparable experimental data in literature, comparison has to be drawn toward computational results. Two papers by Pyykkoe and Atsumi from the year 2009 give an overview on computationally calculated bond lengths of single and double bonds of nearly all the elements of the periodic table.[308,309] Selected bond lengths that are relevant for the present work are depicted in table 17.

Bond	**Bond length ($\mathring{A}$)**	**Reference compound**
Ge-C	app. 1.95	e.g. GeH_2Me_2
Ge=C	1.819	e.g. $Ar_2Ge{=}CR_2$
C-P	1.838	P_2Me_4
C=P	1.66	average for phosphaalkenes
P-P	app. 2.212	e.g. P_2Me_4
P=P	app. 2.046	e.g. HP=PH

Table 17: Selected bond lengths reported by Pyykkoe and Atsumi in 2009.[308,309]

In table 18 the bond lengths of the germoles presented in this work are summarized.

Comparison of tables 17 and 18 shows that all the bonds between carbon and germanium atoms lie in the range between a single and a double bond (referencing to the publications by Pyykkoe and Atsumi[308,309]). The same conclusion can be drawn for the bonds between carbon and phosphorus atoms and the phosphorus-phosphorus bonds. This finding supports the idea of aromaticity in

Compound	**Element 1**	**Element 2**	**Bond length ($\AA$)**
26	Ge(1)	C(1)	1.922(1)
	Ge(1)	C(2)	1.8532(9)
	C(1)	P(1)	1.713(1)
	C(2)	P(2)	1.762(1)
	P(1)	P(2)	2.1289(4)
27	Ge(1)	C(1)	1.916(2)
	Ge(1)	C(2)	1.838(2)
	C(1)	P(1)	1.716(2)
	C(2)	P(2)	1.759(2)
	P(1)	P(2)	2.1375(9)
28	Ge(1)	C(1)	1.924(2)
	Ge(1)	C(2)	1.855(2)
	C(1)	P(1)	1.717(2)
	C(2)	P(2)	1.762(2)
	P(1)	P(2)	2.1264(7)
29	Ge(1)	C(1)	1.916(3)
	Ge(1)	C(2)	1.851(3)
	C(1)	P(1)	1.706(3)
	C(2)	P(2)	1.774(3)
	P(1)	P(2)	2.133(1)

Table 18: Bond lengths of the germoles presented in this work.

the germoles since a delocalization of electrons would lead to an equalization of the bond lengths. It has to be noted, though, that there is a constant deviation of the two germanium-carbon and carbon-phosphorus bonds, respectively, present in all of the germole derivatives. Complete delocalization would be even stronger indicated by equal bond lengths.

The magnetic criterion of aromaticity was considered in the computational calculations performed by Müller and Flock cited earlier. The obtained values are shown in table 19.[307] Table 19 clearly shows that the NICS value points toward high aromaticity of the germoles and (hypothetical) stannoles. In addition to the criteria discussed above, the NICS value leads to the assumption, that aromaticity of the tetroles is not only possible but even probable. It has to be noted, though, that NICS calculations are not too reliable in the present case due to the large orbital size of germanium and tin and the small ring size of the structures investigated herein.

Compounds	**NICS**
cyclic germanium derivative	-9.3
(hypothetical) cyclic tin derivative	-9.0
benzene	-9.2
cyclohexane	-1.7

Table 19: The NICS values of cyclic derivatives and reference structures calculated by Müller and Flock.[307]

One more hint that points toward potential aromaticity of the germoles was given by Josa et al. in 2011: They discussed the effect of different locations of the phosphorus atoms in polyphosphaphospholes and found out that a direct phosphorus-phosphorus bond leads to an augmented aromaticity of the ring system. They also claimed that pyramidality of the phosphorus atom is not the only criterium to be looked at when discussing π-delocalization in this class of compounds.[255]

Further work on this interesting new class of germoles will include experiments on the potential coordination of transition metals in a sandwich-like fashion by the ring systems as illustrated in figure 138. Suchlike coordination motives would give further evidence for the aromaticity of the germoles. Literature studies (see pp. 77 – 79) show that a possible deployment as a coordinating ligand system (as shown in figure 138) of the germoles is promising.

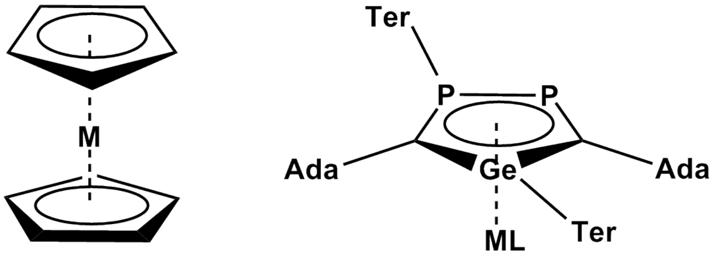


Figure 138: The general representation of metallocenes and a possible germole analog. (Coordination of two equivalents of the germole in relation to the transition metal is not very probable due to the steric hindrance of the germoles.)

To sum up, conversion of terphenyl-stabilized tetrylenes with AdaCP led to significantly varying structural motives depending on the kind of metal center. The two structures can be seen as two steps of the reaction toward tetroles. In case of tin and lead precursors only step 1 takes place and an acyclic derivative is obtained, while in case of germylenes as starting materials the cyclic 'final' product is isolated.

7.4 On the Way Toward Gallium Clusters Stabilized by Terphenyls

The gallium clusters described in the present work were obtained by conversion of 2,6-$Mes_2C_6H_3Li$ and GaI_3 (1:1) at -30°C followed by addition of PPh_3 (1 equ) and elemental sodium (2 equ). Storage of the reaction solution at - 30°C yielded black-metallic X-ray quality crystals. Compounds **34** and **35** were characterized by X-ray diffraction measurements only. The crystal structure of the clusters is composed of one equivalent of compound **34**, two equivalents of compound **35** and one toluene molecule. Attempts to separately isolate the two cluster compounds were unsuccessful, which made a further characterization via NMR difficult. The structures of the two clusters are shown in figures 139 - 142.

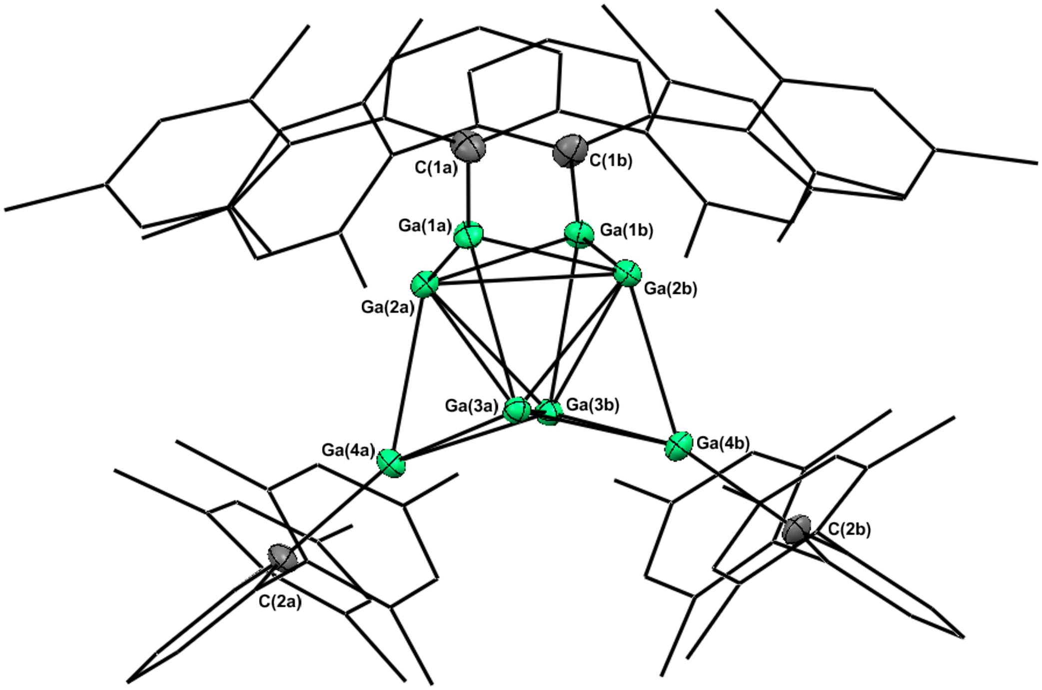


Figure 139: Wireframe and thermal ellipsoid plot of **34** with 50% probability. Hydrogen atoms are not shown. Selected bond distances ($\AA$): Ga(1)-Ga(1) 4.3136(8), Ga(1)-Ga(2) 2.4097(8)/2.9033(8), Ga(1)-Ga(3) 2.6165(9), Ga(2)-Ga(2) 2.8856(8), Ga(2)-Ga(3) 2.7634(8)/2.7644(8), Ga(2)-Ga(4) 2.6144(9), Ga(3)-Ga(3) 2.8761(8), Ga(3)-Ga(4) 2.4153(8)/2.9235(8), Ga(1)-C(1) 2.000(6), Ga(4)-C(2) 2.032(6).

While four gallium atoms are connected to carbon atoms in compound **34**, the remaining four gallium atoms are 'metalloid' in terms of only being bound to further gallium atoms (see definitions on page 84). The central core of these four atoms is depicted in figure 140 for better visualization.

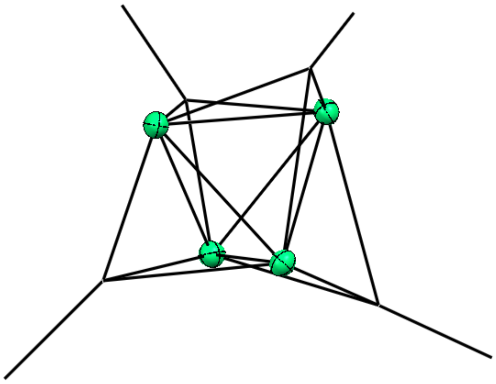


Figure 140: Wireframe and thermal ellipsoid plot of the core of compound **34** with 50% probability. Only the four core atoms of the cluster are shown as ellipsoids.

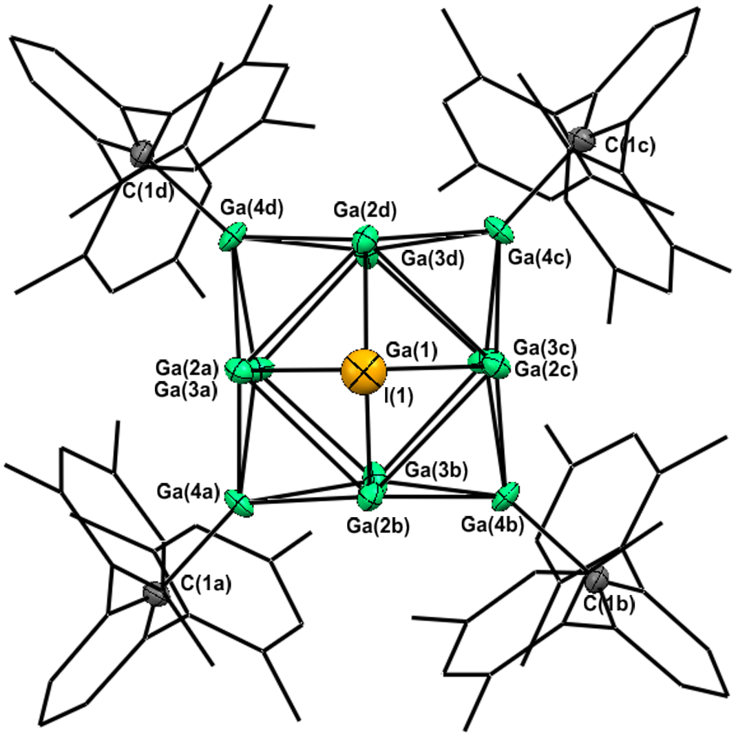


Figure 141: Wireframe and thermal ellipsoid plot of **35** with 50% probability. Hydrogen atoms are not shown. Selected bond distances ($\AA$): Ga(1)-I(1) 2.551(2), Ga(1)-Ga(2) 2.574(1), Ga(2)-Ga(2) 2.920(1), Ga(2)-Ga(3) 3.038(1), Ga(2)-Ga(4) 2.613(1)/2.634(1), Ga(3)-Ga(3) 2.617(1), Ga(3)-Ga(4) 2.622(1)/2.667(1), Ga(4)-C(1) 1.979(5).

Similar to compound **34**, only five gallium atoms are connected to either a carbon or an iodine atom in compound **35**, while eight gallium atoms are 'naked' and contribute to the metalloid character of the Ga_{13} cluster, exclusively being bound to other gallium atoms. For better visualization the core of compound **35** is presented in figure 142.

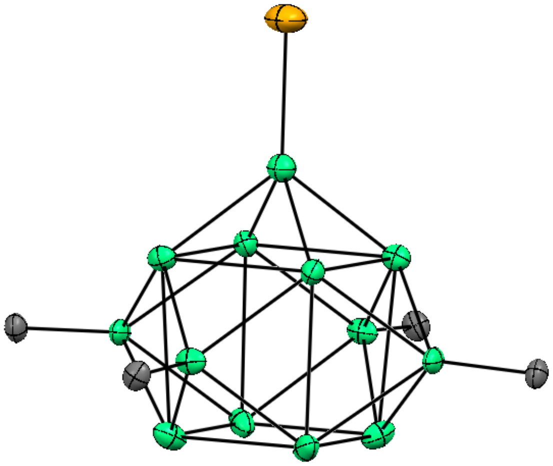


Figure 142: Thermal ellipsoid plot of the core of compound **35** with 50% probability.

As discussed in the literature section of the present work , a main focus of research on gallium clusters has been set on the structural relation of clusters and solid state modifications in the past years. (Examples of structural analogies are given on pp. 85 – 89.)

Compound **34** best resembles the 2+2+2+2 ladder structure of the normal pressure modification β-gallium as depicted in figure 143. (The structure can alternatively also be described as a gallium tetrahedron, each surface of which is bridged by a gallium-aryl moiety.) The mean oxidation number of the gallium atoms in compound **34** is 0.5, which also contributes to the 'metalloidity' of the cluster as described by a statement by Schnepf and Schnöckel from the year 2002: 'Mit steigender Gesamtzahl insbesondere nackter Ga-Atome sollte sich die Atomanordnung im Cluster der einer Elementmodifikation annähern. Dies und der damit verbundene allmähliche Übergang der mittleren Oxidationszahlen der Ga-Atome von +1 nach 0 sollte zu metalloiden oder – oft treffender – elementoiden Ga-Clustern führen.'[289,290]

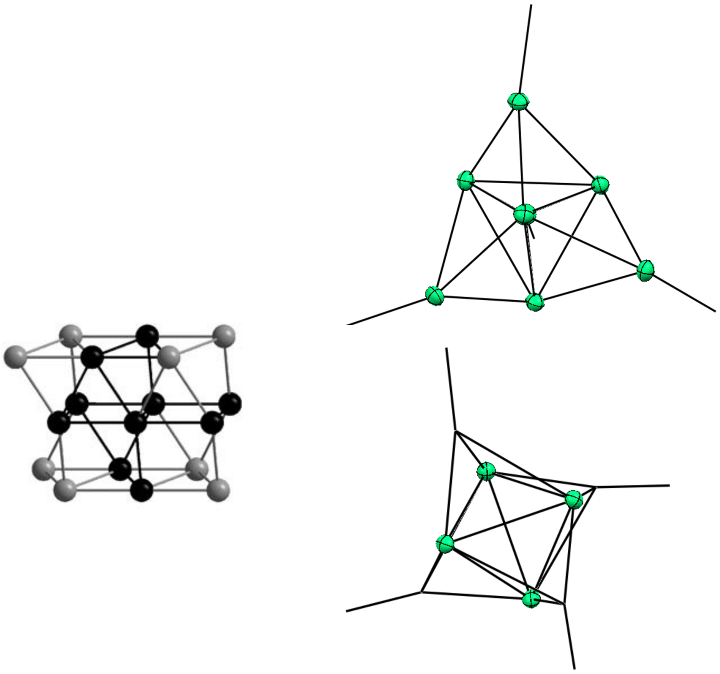


Figure 143: Structural relation of β-Ga (figure from reference 302) and compound **34**.

The structural similarity of compound **35** and the high pressure modification Ga^{III} is shown in figure 144. The mean oxidation number of the gallium atoms in compound **35** of 0.38 describes the Ga_{13} cluster als even ’more’ metalloid (in addition to the greater number of ’naked’ gallium atoms) than compound **34**.

To further characterize compounds **34** and **35** Single Point SCF calculations would be helpful in order to capture the transition of the cluster toward the metal. Schnepf and Schnöckel mentioned in their article from the year 2002, that they conducted corresponding calculations: ’Um das Atomvolumen des Ga_n-Gerüstes der Ga_{10}- und Ga_{13}-Cluster zu bestimmen und damit das Fortschreiten auf dem Weg zum Metall zu verfolgen, führten wir auf der Grundlage der experimentell ermittelten Strukturen der Clusterkerne für die Anionen [...] Single-Point-SCF-Rechnungen durch [...]. Wie erwartet, verringert sich das Atomvolumen beim Übergang vom Ga_{10}-Cluster [...] zum Ga_{13}-Cluster [...].’ Furthermore, the authors pointed out, that ’bei gleicher Ligandenhülle die größere Zahl nackter Galliumatome im Kern [...] zu einer höheren Dichte und damit zu einer weiter fortgeschrittenen Annäherung an den dreidimensionalen Festkörper führt.’[289,290] Conclusions like the cited one would make analogous calculations on compounds **34** and **35** valuable contributions toward the complete characterization of the clusters.

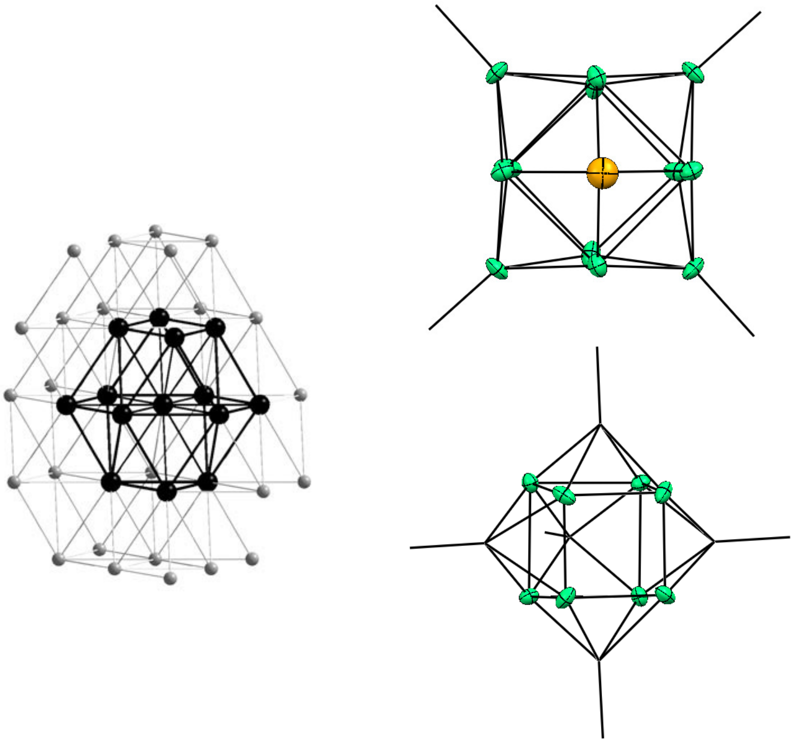


Figure 144: Structural relation of Ga^{III} (figure from reference 302) and compound **35**.

Comparison of the obtained structural motives with literature shows that the motive of β-gallium is one of the gallium modifications frequently set in relation to molecular compounds. Ga^{III} has also been mentioned several times. E.g. Gong and Tosatti compared Ga_6 and Ga_7 clusters to β-gallium in their paper from the year 1992.[291] Yi described a distorted decahedron as preferred structural motive for Ga_{13} clusters,[293] which is not the case for compound **35**. Two gallium clusters (with a Ga_{18} and Ga_{22} core, respectively) were compared to β-gallium and Ga^{III} by Donchev et al. in 2001.[294] The same group pointed out the relation between a Ga_6 derivative and β-gallium in 2002.[295] It has to be stated, that the structures of Ga_8 and Ga_{13} clusters discussed in literature up to date, are not comparable to the structural motives determined for compounds **34** and **35** (see e.g. Song and Cao's discussion on Ga_8 and Ga_{13} clusters from 2005[297] or Nunez et al.'s paper from 2012[305]).

8 Conclusion

The deployment of two structurally completely different ligand systems led to a broad variety of structural motives of the novel low valent main group element compounds. Significantly divergent results were obtained depending on the type, size and sterical demand of the ligand as well as of the nature of the metal center.

Use of the silylamide ligands provided access to a great variety of structural motives (monomeric, dimeric, polymeric), especially of main group 1 (lithium, sodium, potassium) derivatives. These precursors were deployed in subsequent reactions yielding main group 3 (gallium, indium) derivatives in oxidation states +I and +III, depending on the back bone substitution pattern of the ligand deployed and the kind of metal center. By conversion of the lithium derivatives with main group 4 (germanium, tin, lead) precursors, products of the LECl and the EL_2 structure type were obtained, proving that conservation of oxidation state +II is possible with both silylamide ligand systems. Subsequent reactions of the tin derivatives obtained proved the high stability (and low reactivity) of these compounds compared to their terphenyl based analogs, which underlines the significance of the type of ligand system deployed.

The studies on phenyl based ligand derivatives led to the synthesis of stannide and plumbide anions as well as of a plumbylplumbylene derivative, in dependency of reaction stoichiometry, when biphenyl ligands were used. The mixed-valence lead compound was formed via ligand migration. The difference in sterical hindrance of the biphenyl and terphenyl ligands deployed in the present work becomes apparent when keeping in mind that the terphenyl ligands stabilize E(II) derivatives only as can be seen from literature. (Terphenyl ligands would not allow ligand migration as discussed above.)

Subsequent reactions of the terphenyl based low valent group 13 and 14 derivatives gave an insight in the diversity of reaction routes deploying this important substance class: Main group 4 derivatives were shown to readily react with AdaCP yielding two different structural motives depending on the metal center of the tetrylene deployed. The oxidation state of the tin and lead bearing compounds was conserved during the insertion of C=P fragments into the E-L bonds, while in case of the germanium derivatives oxidation of the metal was observed and diphosphagermoles were isolated. The reduction of the terphenyl-stabilized main group 3 element derivative covered in the present work led to the synthesis of two novel metalloid clusters, that can be seen as intermediates between molecular compounds and solid state gallium.

The broad range of structural motives of the products isolated and characterized (by multinuclear MR and single crystal X-ray diffraction measurements) shows that the central research question of the present work – studies of the effects of the ligand type deployed – is a valuable contribution to main group element chemistry in terms of deepening the understanding of reactivity and stability of the corresponding compounds.

9 Experimental Section

9.1 General Procedures

All manipulations were carried out using modified Schlenk techniques under an atmosphere of N_2 or in a mBRAUN UNIlab drybox. Solvents were dried using an Innovative Technologies column solvent purification system. Chemicals were used as received. ^{1}H, ^{13}C, ^{29}Si, ^{119}Sn spectroscopic data was recorded on a Varian Mercury 300 MHz spectrometer (operating at 300.23 MHz for ^{1}H, 75.50 MHz for ^{13}C, 59.64 MHz for ^{29}Si and 112.17 MHz for ^{119}Sn). ^{207}Pb data was recorded on a Varian Inova 300 MHz spectrometer (operating at 63.25 MHz). NMR spectra were referenced to D_2O (capillary tubes) and recorded at 25℃ . UV-Vis data was recorded on a Perkin Elmer (Lambda 35) spectrometer.

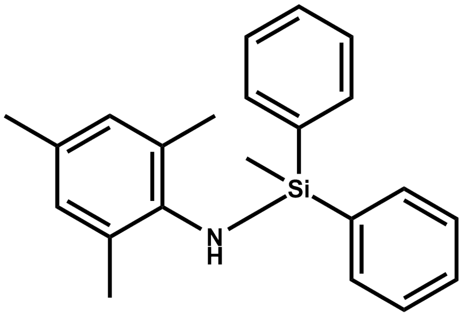
9.2 X-ray Crystallography

All crystals suitable for single crystal X-ray diffractometry were removed from a Schlenk flask under a stream of N_2 and immediately covered with a layer of silicone oil. A single crystal was selected, mounted on a glass rod on a copper pin, and placed in the cold N_2 stream provided by an Oxford Cryosystems cryometer. XRD data collection was performed on a BRUKER APEX II diffractometer with use of Mo Kα radiation (λ=0.71073 $\mathring{A}$) and a CDD area detector. Empirical absorption corrections were applied using SADABS.[310,311] The structures were solved with use of either direct methods or the Patterson option in SHELXS and refined by the full-matrix least-squares procedures in SHELXL.[312,313] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in calculated positions corresponding to standard bond lengths and angles (except for compound **1**).

9.3 Silylamide-Stabilized Derivatives

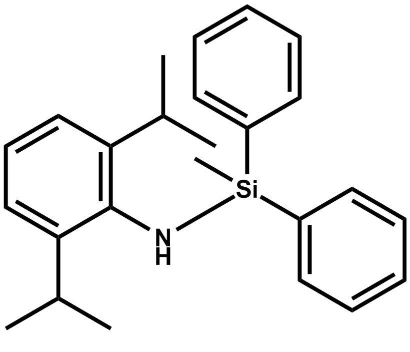
9.3.1 Ligand Synthesis

Synthesis of compound 1.



To a solution of 2,4,6-trimethylanilin (52 ml, 50 g, 369 mmol, 1 equ, ρ =0.962g/ml) in thf BuLi (155 ml, c=2.5 M, 1 equ) was added dropwise at 0 ℃. The reaction solution yielded a white precipitate. After stirring for 2 h the color changed to yellow/orange. Methyldiphenylchlorosilane (86 g, 368 mmol, 1 equ) was added dropwise at 0 ℃, the white precipitate disappeared and the reaction solution was stirred overnight. A part of the solvent was distilled off and the product was obtained in good yields as white crystals. The X-ray crystal structure of compound **1** was determined. ^{1}H NMR (300.23 MHz, Et_2O/D_2O): δ 0.64 (s, 3H, Me), 2.19 (s, 6H, ^{o}Me(Mes)), 2.25 (s, 3H, ^{p}Me(Mes)), 6.80 (s, 2H ^{m}H(Mes)), 7.41 (m, 6H, Ph), 7.71 (m, 4H, Ph) ppm. NH not found. ^{13}C {^{1}H} NMR (75.50 MHz, thf/D_2O): δ -3.06, 19.92, 20.14, 127.78, 129.01, 129.34, 130.60, 131.95, 134.55, 138.88, 140.64 ppm. ^{29}Si {^{1}H} NMR (59.64 MHz, thf/D_2O): δ -12.11 ppm.

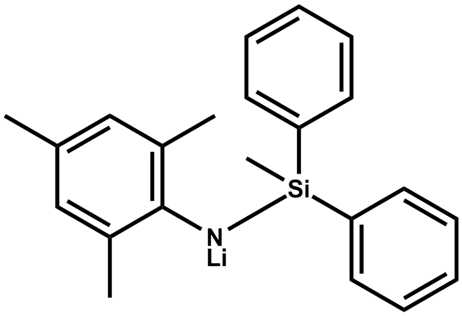
Synthesis of compound 2.



To a solution of 2,6-diisopropylaniline (50 g, 282 mmol, 1 equ) in thf BuLi (113 ml, c=2.5 M, 1 equ) was added dropwise at 0 ℃. The reaction solution was stirred for 3 h at the same temperature and the color changed to yellow-orange. Methyldiphenylchlorosilane (66 g, 283 mmol, 1 equ) was added dropwise at 0 ℃ and the reaction solution was stirred for 3 h at the same temperature. The precipitating salt was filtered off and the solvent removed in vacuo. Heptane was added in order to precipitate the remaining salt and the supernatant was separated via a filter-canula. The solvent was removed in vacuo and a dark liquid was obtained as product. ^{1}H NMR (300.23 MHz, thf/D_2O): δ 0.58 (s, 3H, Me), 1.07 (d, 12H, $CH(CH_3)_2$), 3.50 (m, 2H, $CH(CH_3)_2$), 7.04 (m, 3H, $^{p+m}$Dipp), 7.39 (m, 6H, Ph), 7.67 (m, 4H, Ph) ppm. ^{13}C {^{1}H} NMR (75.50 MHz, thf/D_2O): δ -3.38, 23.26, 28.41, 122.88, 123.66, 127.69, 129.28, 134.52, 138.49, 139.49, 144.62 ppm. ^{29}Si {^{1}H} NMR (59.64 MHz, thf/D_2O): δ -12.34 ppm.

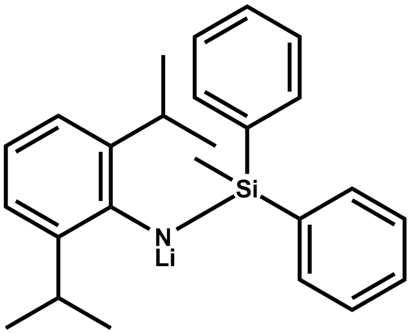
9.3.2 Synthesis of Main Group 1 Derivatives

Synthesis of compound 3.



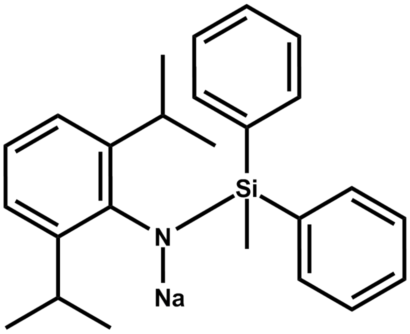
To a solution of compound **1** (7.50 g, 22.62 mmol, 1 equ) in heptane BuLi (15.6 ml, c=1.6 M, 24.88 mmol, 1.1 equ) was added dropwise at 0 ℃. Immediately, the reaction solution started to yield the product as a white precipitate. After stirring for 3 h the supernatant was removed via canula and the colorless product was dried in vacuo. ^{1}H NMR (300.23 MHz, thf/D_2O): δ 0.40 (s, 3H, Me), 2.05 (s, 6H, ^{o}Me(Mes)), 2.07 (s, 3H, ^{p}Me(Mes)), 6.56 (s, 2H, ^{m}H(Mes)), 7.07 (m, 6H, Ph), 7.50 (m, 4H, Ph) ppm. ^{13}C {^{1}H} NMR (75.50 MHz,thf/D_2O): δ 1.01, 20.10, 21.10, 121.41, 126.44, 127.10, 127.68, 132.09, 134.49, 146.96, 156.52 ppm. ^{29}Si {^{1}H} NMR (59.64 MHz, thf/D_2O): δ -34.21 ppm.

Synthesis of compound 4.



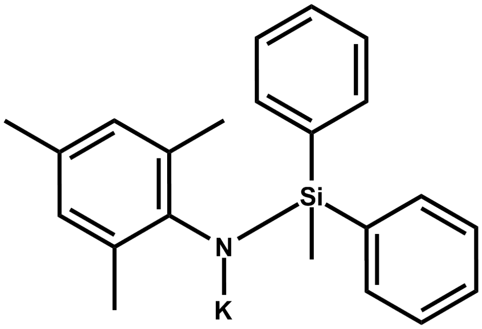
In the same manner compound **4** was synthesized from compound **2** (16.75 g, 44.83 mmol, 1 equ) and BuLi (20 ml, c=2.5 M, 49.30 mmol, 1.1 equ). The X-ray crystal structure of compound **4** was determined. ^{1}H NMR (300.23 MHz, thf/D_2O): δ 0.59 (s, 3H, Me), 1.07 (d, 12H, $CH(CH_3)_2$), 4.15 (m, 2H, $CH(CH_3)_2$), 6.58 (t, 1H, ^{p}H(Dipp)), 6.91 (d, 2H, ^{m}H(Dipp)), 7.26 (m, 6H, Ph), 7.64 (m, 4H, Ph) ppm. ^{13}C {^{1}H} NMR (75.50 MHz, thf/D_2O): δ 1.84, 24.30, 26.80, 115.00, 121.94, 126.62, 126.84, 134.80, 142.78, 146.29, 155.72 ppm. ^{29}Si {^{1}H} NMR (59.64 MHz, thf/D_2O): δ -34.24 ppm.

Synthesis of compound 5.



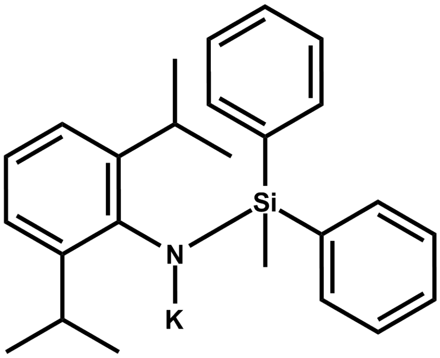
To a solution of compound **2** (500 mg, 1.34 mmol, 1 equ) in thf, sodium metal (34 mg, 1.47 mmol, 1.1 equ) was added. The metal turned black after some stirring. The grey-green reaction solution was stored at -30 ℃ and yielded pale yellow X-ray quality crystals of compound **5**.

Synthesis of compound 6.



In analogy to compound **5**, compound **6** was obtained. NMR characterization was not possible because of the low solubility of the product due to coordination polymer formation. The X-ray structure of compound **6** was determined.

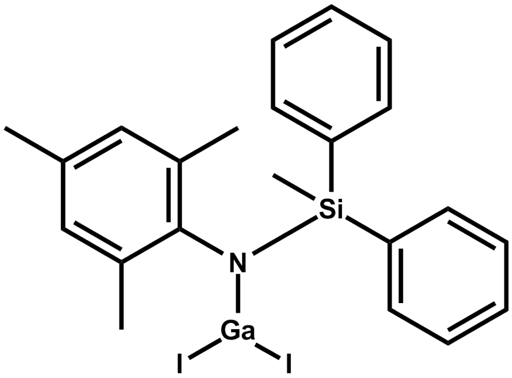
Synthesis of compound 7.



In analogy to compound **5**, compound **7** was obtained. NMR characterization was not possible because of the low solubility of the product due to coordination polymer formation. The X-ray structure of compound **7** was determined.

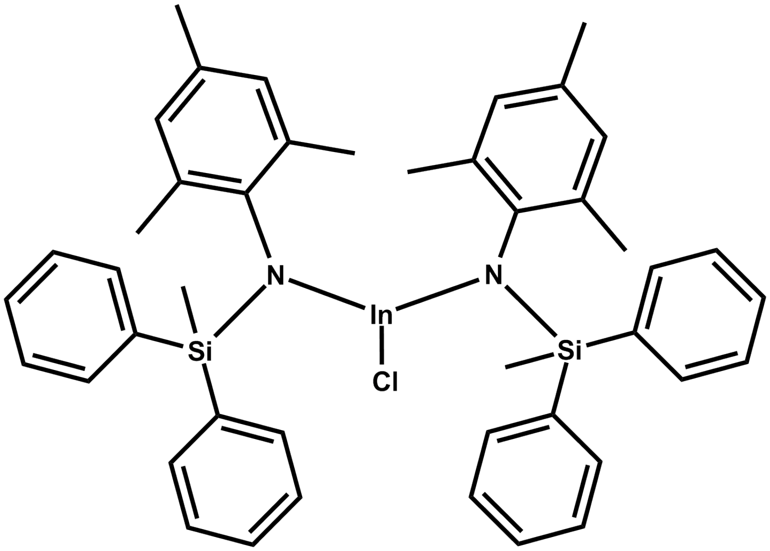
9.3.3 Synthesis of Main Group 3 Derivatives

Synthesis of compound 8.



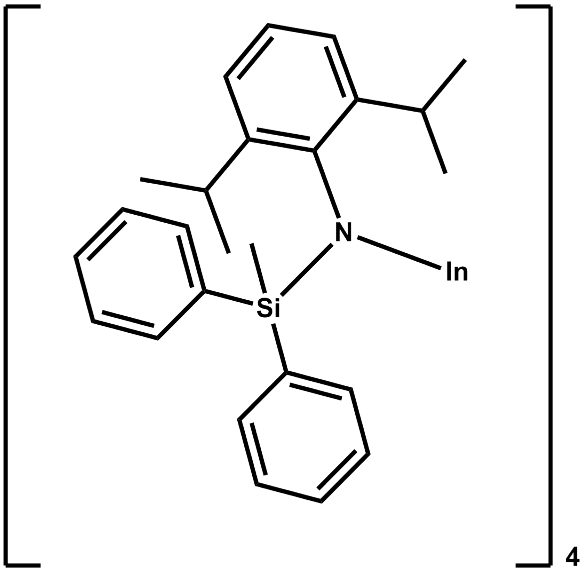
To a solution of **3** (200 mg, 0.59 mmol, 1 equ) in Et_2O, 'GaI' (117 mg, 0.59 mmol, 1 equ) was added. A small amount of elemental gallium precipitated. The solution was taken off the solid residue, an additional spatula tip of 'GaI' was added and the solution was stored at -30 °C. The X-ray crystal structure of the pale red-brown crystals of compound **8** was determined. ^{1}H NMR (300.23 MHz, Et_2O/C_6D_6): δ 1.38 (s, 3H, Me), 2.11 (s, 3H, ^{p}Me(Mes)), 2.39 (s, 6H, ^{o}Me(Mes)), 6.79 (s, 2H, ^{m}HMes), 7.12 - 7.21 (m, 8H, Ph), 7.88 (m (overlap with C_6D_6 residual peak), 2H, Ph) ppm. ^{13}C {^{1}H} NMR (75.50 MHz, Et_2O/C_6D_6): δ 1.87, 21.02, 22.01, 127.48, 129.00, 129.50, 132.59, 134.64, 136.30, 138.81, 139.22, 145.41 ppm. ^{29}Si {^{1}H} NMR (59.64 MHz, Et_2O/C_6D_6): δ -13.49 ppm.

Synthesis of compound 9.



Compound **3** (200 mg, 0.59 mmol, 1 equ) was dissolved in Et_2O and yielded a yellow solution. After adding InCl (89 mg, 0.59 mmol, 1 equ) the solution turned dark. The liquid was taken off via a pipette and the (partly metallic) residue was removed. The solution was stored at -30 ℃ and yielded X-ray quality crystals of compound **9**.

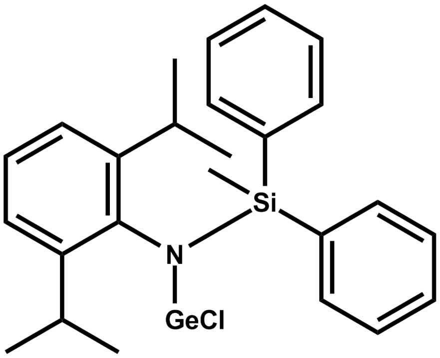
Synthesis of compound 10.



In analogy to compound **9**, compound **10** was obtained. The X-ray crystal structure of compound **10** was determined.

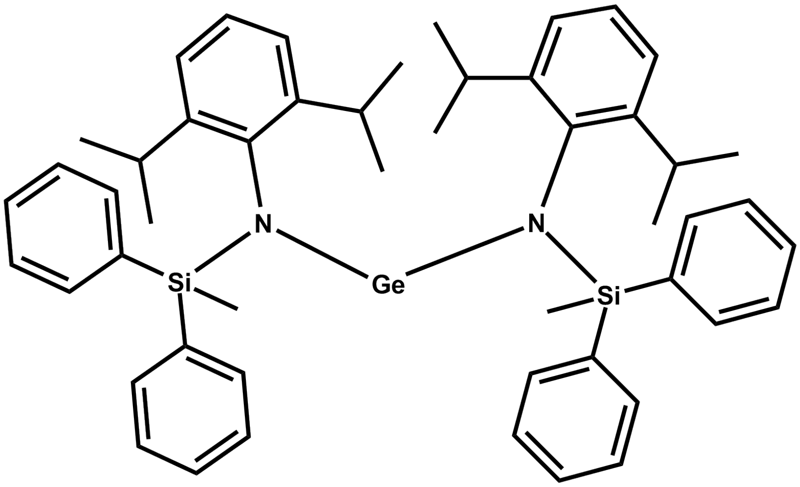
9.3.4 Synthesis of Main Group 4 Derivatives

Synthesis of compound 11.



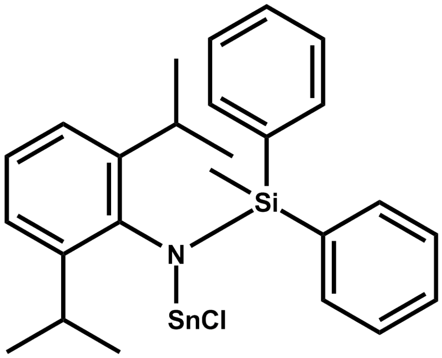
Compound **4** (200 mg, 0.53 mmol, 1 equ) was dissolved in thf and $GeCl_2$\{dioxane\} (122 mg, 0.53 mmol, 1 equ) was added. The solution was stirred overnight and afterwards stored at -30 ℃. ^{1}H NMR (300.23 MHz, thf/D_2O): δ 0.33 (d, 3H, Me), 1.01 + 1.03 + 1.07 (2d, 12H, $CH(CH_3)_2$), m, 2H, $CH(CH_3)_2$ hidden under thf residual peak at 3.59, 6.86 (m, 3H, Dipp), 7.08 - 7.18 (m, 6H, Ph), 7.49 (d, 4H, Ph) ppm. ^{13}C \{^{1}H\} NMR (75.50 MHz, thf/D_2O): δ 1.07, 22.37, 27.62 + 27.69, 122.78, 123.28, 126.58, 127.61, 136.20, 140.53, 143.59, 149.35 ppm. ^{29}Si \{^{1}H\} NMR (59.64 MHz, thf/D_2O): δ -14.04 ppm.

Synthesis of compound 12.



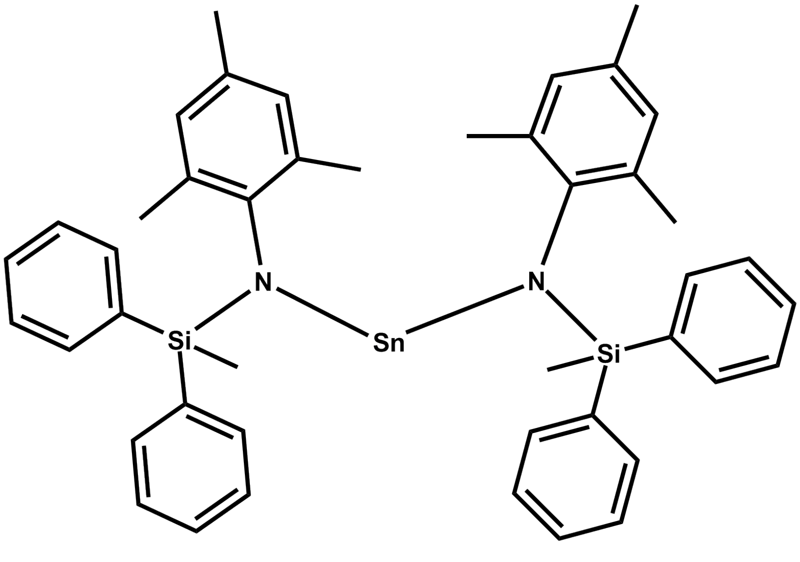
Compound **4** (500 mg, 1.32 mmol, 2 equ) was dissolved in thf and $GeCl_2$\{dioxane\} (153 mg, 0.66 mmol, 1 equ) was added. The solution turned yellow and the salt precipitated. After stirring for 48 h, the solids were removed by taking off the solution. After storage at -30 ℃ the solution yielded yellow X-ray quality crystals. ^{1}H NMR (300.23 MHz, thf/C_6D_6): δ 0.05 (s, 6H, Me), 0.82 (d, 12H, $CH(CH_3)_2$), 1.09 (d, 12H, $CH(CH_3)_2$), m, 4H, $CH(CH_3)_2$ hidden under thf residual peak at 3.53, 6.99 (m, 6H, $^{p+m}$Dipp), 7.07 (m, 12H, Ph), 7.39 (m, 8H, Ph) ppm. ^{13}C \{^{1}H\} NMR (75.50 MHz, thf/C_6D_6): δ -0.95, 23.35, 26.43, 28.05, 124.13, 125.78, 127.49, 129.12, 135.40, 138.56, 141.52, 147.65 ppm. ^{29}Si {^{1}H} NMR (59.64 MHz, thf/C_6D_6): δ 7.18 ppm.

Synthesis of compound 13.



Compound **4** (200 mg, 0.53 mmol, 1 equ) was dissolved in thf and $SnCl_2$ (100 mg, 0.53 mmol, 1 equ) was added. The solution was stirred overnight, afterwards stored at -30 ℃and yielded pale yellow X-ray quality crystals. ^{1}H NMR (300.23 MHz, thf/D_2O): δ 0.32 (d, 3H, Me), 0.98 + 1.01 (d, 12H, $CH(CH_3)_2$), m, 2H, $CH(CH_3)_2$ hidden under thf residual peak at 3.63, 6.74 - 6.82 (m, 3H, Dipp), 7.04 - 7.12 (m, 6H, Ph), 7.47 (d, 4H, Ph) ppm. ^{13}C {^{1}H} NMR (75.50 MHz, thf/D_2O): δ 1.21, 22.69, 27.26 + 27.49, 121.92, 122.57, 126.57, 127.47, 136.02, 141.37, 145.51, 148.22 ppm. ^{29}Si {^{1}H} NMR (59.64 MHz, thf/D_2O): δ -15.39 ppm. ^{119}Sn {^{1}H} NMR (112.16 MHz, thf/D_2O): δ -45.47 ppm.

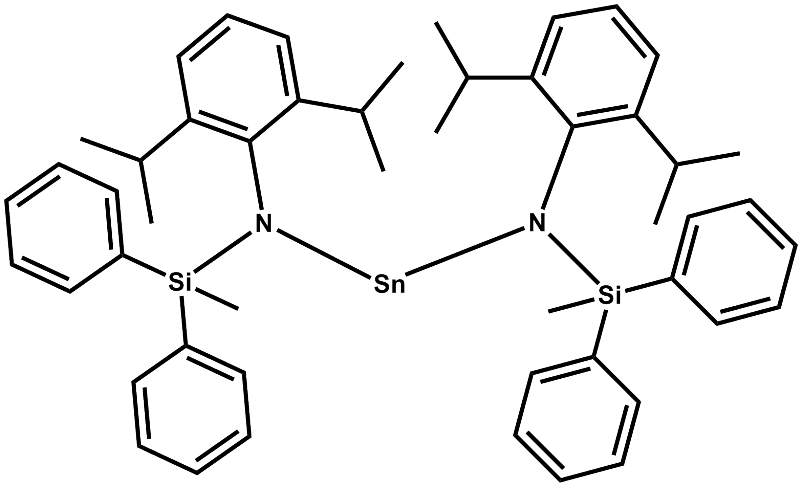
Synthesis of compound 14.



To a mixture of compound **3** (500 mg, 1.48 mmol, 2 equ) and $SnCl_2$ (140 mg, 0.74 mmol, 1 equ) Et_2O was added. The solution turned yellow and after stirring overnight the salt was removed by taking off the liquid. The solution was stored at room temperature overnight to partially evaporate the solvent, which yielded yellow good-quality crystals of compound **14**. ^{1}H NMR (300.23 MHz, C_6D_6): δ

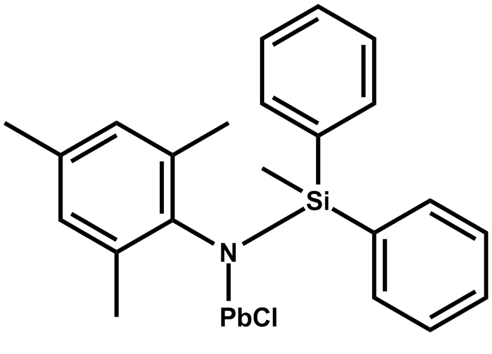
0.40 (s, 6H, Me), 1.96 (s, 12H, ^{o}Me(Mes)), 2.14 (s, 6H, ^{p}Me(Mes)), 6.48 (s, 4H, ^{m}HMes), 7.10 (m, 12H, Ph), 7.60 (m, 8H, Ph) ppm. ^{13}C {^{1}H} NMR (75.50 MHz, C_6D_6): δ 0.55 (d), 20.37 (d), 21.34 (d), 128.55, 128.85, 130.76, 133.20, 134.78, 135.18, 139.95, 145.65 ppm. ^{29}Si {^{1}H} NMR (59.64 MHz, C_6D_6): δ 1.17 ppm. ^{119}Sn {^{1}H} NMR (112.16 MHz, C_6D_6): δ 580.65 ppm.

Synthesis of compound 15.



In analogy to compound **14** (deploying C_6H_6 instead of Et_2O) compound **15** was obtained and yielded X-ray quality crystals. ^{1}H NMR (300.23 MHz, C_6D_6): δ 0.12 (s, 6H, Me), 0.82 (d, 12H, $CH(CH_3)_2$), 1.13 (d, 12H, $CH(CH_3)_2$), 3.60 (m, 4H, $CH(CH_3)_2$, 6.83 (d, 2H, ^{p}Dipp), 6.99 (d, 4H, ^{p}Ph), 7.09 (t, 8H, ^{m}Ph), 7.38 (d, 8H, ^{o}Ph), 7.48 (d, 4H, ^{m}Dipp) ppm. ^{13}C {^{1}H} NMR (75.50 MHz, C_6D_6): δ 0.05, 23.30, 27.15, 27.62, 124.00, 124.94, 129.14, 134.39, 135.10, 139.33, 141.34, 147.80 ppm. ^{29}Si {^{1}H} NMR (59.64 MHz, C_6D_6): δ -10.14 ppm. ^{119}Sn {^{1}H} NMR (112.16 MHz, C_6D_6): δ 345.1 ppm.

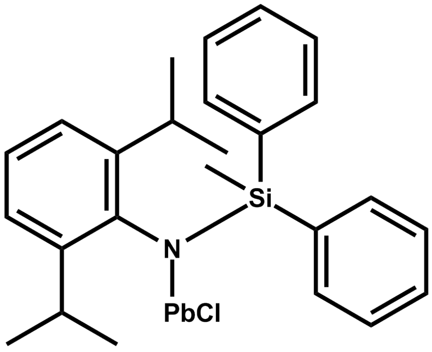
Synthesis of compound 16.



To a mixture of compound **3** (200 mg, 0.59 mmol, 1 equ) and $PbCl_2$ (165 mg, 0.59 mmol, 1 equ) Et_2O was added. The solution turned orange-red and after stirring overnight the salt was removed by taking off the liquid via a pipette. The solution was stored at room temperature overnight to partially evaporate the solvent, which yielded red good-quality crystals of compound **16**. ^{1}H NMR

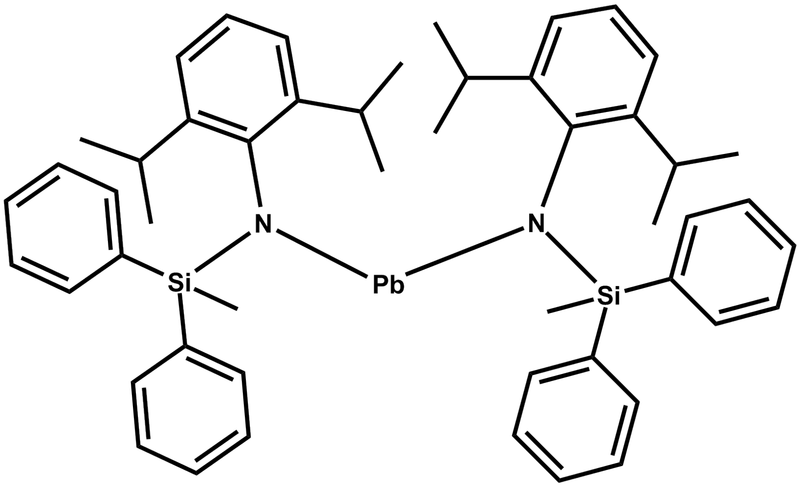
(300.23 MHz, C_6D_6): δ 0.43 (s, 3H, Me), 2.18 (s, 6H, ^{o}Me(Mes)), 2.40 (s, 3H, ^{p}Me(Mes)), 6.70 (s, 2H, ^{m}HMes), 7.09 (m, 6H, Ph), 7.51 (m, 4H, Ph) ppm. ^{13}C {^{1}H} NMR (75.50 MHz, C_6D_6): δ 0.91, 20.06, 20.39, 127.90, 128.02, 129.28, 131.36, 134.32, 134.62, 135.67, 140.63, 146.38 ppm. ^{29}Si {^{1}H} NMR (59.64 MHz, C_6D_6): δ -13.44 ppm. ^{207}Pb {^{1}H} NMR (112.16 MHz, C_6D_6): δ 2493.79 ppm.

Synthesis of compound 17.



Compound **4** (200 mg, 0.53 mmol, 1 equ) was dissolved in thf and $PbCl_2$ (147 mg, 0.53 mmol, 1 equ) was added. The solution was stirred overnight and afterwards stored at -30 ℃. ^{1}H NMR (300.23 MHz, thf/D_2O): δ 0.58 (d, 3H, Me), 0.95 + 1.12 + 1.14 (12H, $CH(CH_3)_2$)), m, 2H, $CH(CH_3)_2$ hidden under thf residual peak at 3.69, 6.72 (t, 1H, ^{p}Dipp), 6.97 (d, 2H, ^{m}Dipp), 7.22 (m, 6H, Ph), 7.63 (m, 4H, Ph) ppm. ^{13}C {^{1}H} NMR (75.50 MHz, thf/D_2O): δ 1.28, 23.50, 26.87 + 28.03, 121.98, 122.24, 126.96, 127.92, 135.81, 141.90, 145.28, 148.09 ppm. ^{29}Si {^{1}H} NMR (59.64 MHz, thf/D_2O): δ -14.98 ppm.

Synthesis of compound 18.



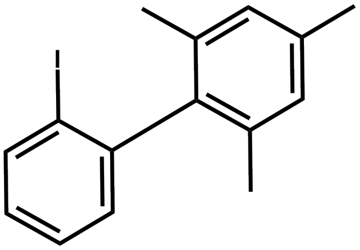
Compound **4** (500 mg, 1.32 mmol, 2 equ) was dissolved in Et_2O and $PbCl_2$ (183 mg, 0.66 mmol, 1 equ) was added. The red-brown reaction solution was stirred for 12 h and stored at -30 ℃ to yield orange good-quality crystals of compound **18**. ^{1}H NMR (300.23 MHz, C_6D_6): δ 0.51 (s, 3H, Me), 0.65 (s, 3H, Me), 0.96 - 1.02 (2d, 24H, $CH(CH_3)_2$)), 3.34 (m, 2H, $CH(CH_3)_2$)), 3.69 (m, 2H, $CH(CH_3)_2$)), 6.89 -

7.18 (m, 18H, aromat. H), 7.50 - 7.55 (m, 8H, aromat. H) ppm. ^{13}C {^{1}H} NMR (75.50 MHz, C_6D_6): δ 1.21, 25.22, 27.23, 123.40, 128.32, 129.34, 134.60, 137.73, 139.83, 143.33, 147.61 ppm. ^{29}Si {^{1}H} NMR (59.64 MHz, C_6D_6): δ 4.69 ppm.

9.4 Biphenyl-Stabilized Derivatives

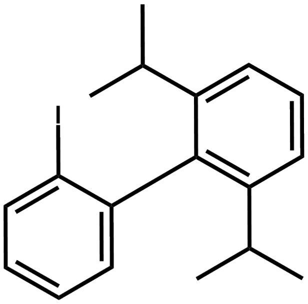
9.4.1 Ligand Synthesis

Synthesis of compound 19.



Compound **19** was synthesized according to Hartmann and Niemeyer[122] with minor changes in the synthesis procedure: Namely, the addition of MesMgBr to LiPhF was followed by addition of $FeCl_2$ and stirring for 2 days. NMR data of compound **19** is given in reference 122. Molecular structure data is available within the CCDC database.[306]

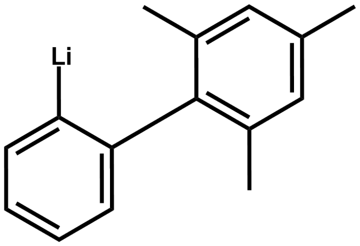
Synthesis of compound 20.



In the same manner, compound **20** was synthesized regarding the changes mentioned above for compound **19**. ^{1}H NMR (300.23 MHz, $CDCl_3$): δ 0.94 (d, 6H, $CH(CH_3)$), 1.15 (d, 6H, $CH(CH_3)$), 2.33 (m, 2H, $CH(CH_3)$), 6.97 (t, 1H, aromat. H), 7.09 - 7.14 (m, 3H, aromat. H), 7.29 - 7.36 (m, 2H, aromat. H), 7.88 (d, 1H, aromat. H) ppm. ^{13}C {^{1}H} NMR (75.50 MHz, $CDCl_3$): δ 23.39, 24.82, 30.61, 101.91, 122.82, 127.82, 128.42, 128.49, 130.26, 138.87, 141.64, 145.50, 146.20 ppm.

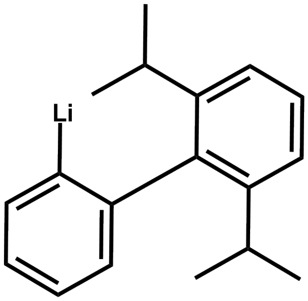
9.4.2 Synthesis of Main Group 1 Derivatives

Synthesis of compound 21.



Lithiation of compound **19** in order to yield compound **21** was performed according to Hartmann and Niemeyer[122] and Jones et al.[123] with one minor variation: Heptane was deployed as solvent. After the reaction was complete, the solvent was removed via canula. Furthermore, the remaining solvent was removed in vacuo. ^{1}H NMR (300.23 MHz, Et_2O/D_2O): δ 2.50 (s, 6H, ^{o}Me), 2.82 (s, 3H, ^{p}Me), 7.30 - 7.52 (m, 4H, aromat. H), 8.25 (d, 1H, aromat. H) ppm. ^{13}C {^{1}H} NMR (75.50 MHz, Et_2O/D_2O): δ 20.92, 21.27, 123.87, 124.74, 126.01, 128.35, 129.73, 134.09, 135.50, 141.65, 154.84, 183.49 ppm.

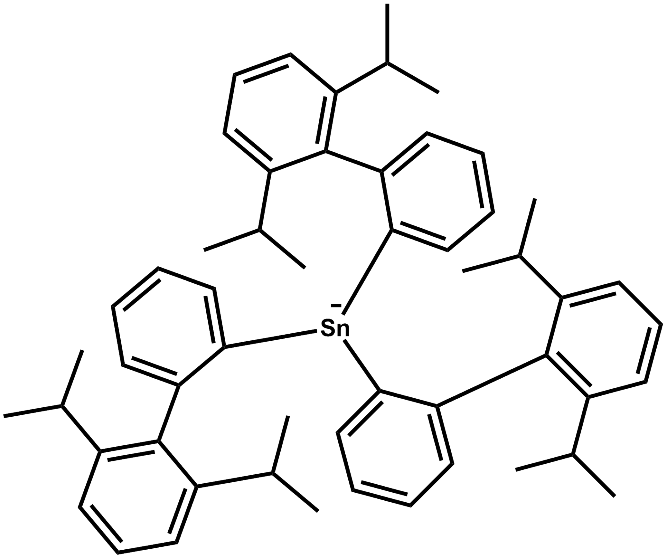
Synthesis of compound 22.



In the same manner, compound **22** was synthesized with the same minor change. ^{1}H NMR (300.23 MHz, Et_2O/D_2O): δ 1.45 (d, 12H, $CH(CH_3)$), 3.41 (m, 2H, $CH(CH_3)$), 7.26 - 7.41 (m, 3H, aromat. H), 7.55 - 7.66 (m, 3H, aromat. H), 7.99 (d, 1H, aromat. H) ppm. ^{13}C {^{1}H} NMR (75.50 MHz, Et_2O/D_2O): δ 23.35, 25.13, 29.82, 122.24, 123.70, 123.80, 126.11, 126.62, 140.98, 146.32, 148.89, 153.80, 183.91 ppm.

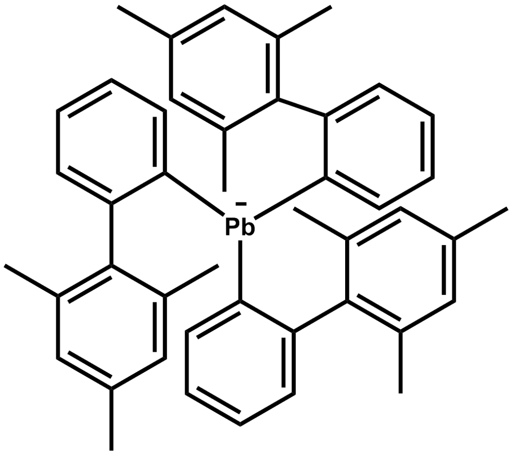
9.4.3 Synthesis of Main Group 4 Derivatives

Synthesis of compound 23.



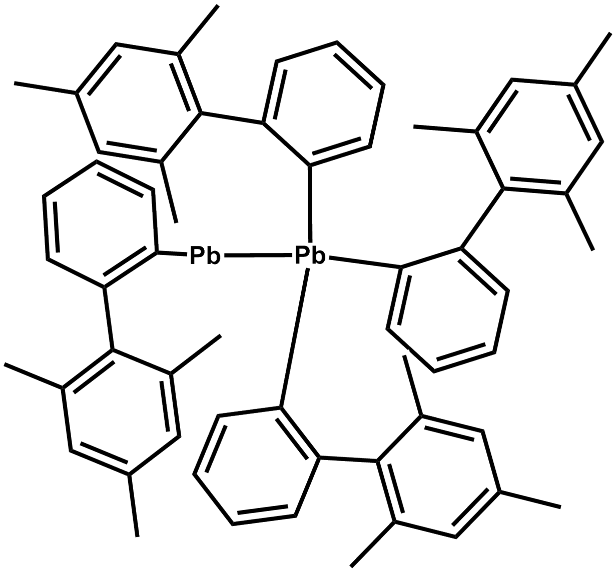
Compound **22** (1.05 g, 4.51 mmol, 3.3 equ) and $SnCl_2$ (0.26 g, 1.36 mmol, 1 equ) were provided in a Schlenk tube and Et_2O was added at -70°C (N_2/EtOH). The reaction was stirred for 12 hours at the same temperature and then warmed to room temperature. The salts were removed by filtration via filter-canula, pentane was added and the orange solution was stored at -30°C. The solution yielded yellow good-quality crystals of compound **23**. The X-ray crystal structure of compound **23** was determined. ^{1}H NMR (300.23 MHz, thf/D_2O): δ 0.45 + 0.71 + 0.79 + 1.00 (4d, 4*9H, $CH(CH_3)_2$), 2.67 + 2.83 (2m, 2*3H, $CH(CH_3)_2$), 6.72 - 6.74 (m, 3H, aromat. H), 6.90 - 6.98 (m, 12H, aromat. H), 7.08 (t, 3H, aromat. H), 7.92 (t, 3H, aromat. H) ppm. ^{13}C {^{1}H} NMR (75.50 MHz, thf/D_2O): δ 22.53 + 22.91, 29.51 + 29.97, 120.90 + 121.08, 122.24, 124.40, 125.62, 127.94, 140.43, 145.13, 146.82 + 146.98, 149.15, 168.62 ppm, ^{119}Sn {^{1}H} NMR (111.92 MHz, thf/D_2O): δ -137.23 ppm.

Synthesis of compound 24.



By the same procedure as described for compound **23**, compound **24** was obtained in form of X-ray quality crystals. The crystal structure of the compound was determined.

Synthesis of compound 25.



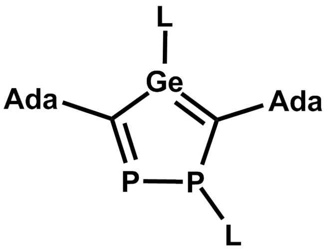
By the same procedure as described for compound **23**, compound **25** was obtained in form of X-ray quality crystals (change in stoichiometry: molar ratio of 2:1 instead of 3:1!). The crystal structure of the compound was determined.

9.5 Terphenyl-Stabilized Derivatives

AdaCP[314] and ligand systems L[166,167] were obtained as described in literature.

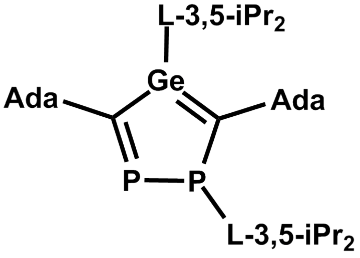
9.5.1 Conversions with AdaCP

Preparation of compound 26.



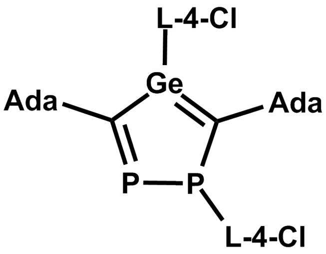
To a solution of GeL_2 (100 mg, 0.14 mmol, 1 equ) in Et_2O a solution of AdaCP (51 mg, 0.29 mmol, 2 equ) in Et_2O was added. Immediately, the color of the blue solution turned yellow. After storage at -30°C overnight, yellow good-quality crystals of **26** were obtained. The X-ray crystal structure of compound **26** was determined. ^{1}H NMR (300.23 MHz, C_6D_6): 1.45 - 1.95 (m, 30H, Ada), 1.90 (s, 6H, CH_3), 2.10 (s, 12H, CH_3), 2.21 (s, 12H, CH_3), 2.33 (s, 6H, CH_3), 6.57 (s, 2H, ^{m}Mes), 6.64 (d, 4H, $^{m}C_6H_3$), 6.76 (s, 2H, ^{m}Mes), 6.86 (s, 2H, ^{m}Mes), 6.89 (s, 2H, ^{m}Mes), 7.03 (t, 2H, $^{p}C_6H_3$) ppm. ^{13}C {^{1}H} NMR (75.50 MHz, C_6D_6): δ 20.41, 20.87, 22.10, 22.54, 24.74, 29.84, 30.36, 36.14, 36.50, 46.85 (d, $^{2}J_{13C\text{-}31P}$: 5 Hz), 47.31 (d, $^{2}J_{13C\text{-}31P}$: 12 Hz), 128.18, 128.75, 128.91, 129.04 (d, $J_{13C\text{-}31P}$: 3 Hz), 129.22, 130.01, 130.37 (d, $J_{13C\text{-}31P}$: 4 Hz), 134.97, 135.03, 135.63, 136.35, 137.06, 137.80, 140.08, 140.58, 148.09 (d, $^{1}J_{13C\text{-}31P}$: 2 Hz), 149.18 (d, $^{1}J_{13C\text{-}31P}$: 14 Hz), 153.54, 154.42 ppm. ^{31}P {^{1}H} NMR (121.54 MHz, C_6D_6): δ 12.66 (d, $^{1}J_{31P\text{-}31P}$: 420 Hz), 276.67 (d, $^{1}J_{31P\text{-}31P}$: 420 Hz) ppm.

Preparation of compound 27.



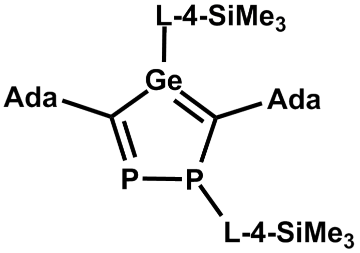
To a solution of Ge(L-3,5-iPr$_2$)$_2$ (100 mg, 0.12 mmol, 1 equ) in Et_2O or thf a solution of AdaCP (41 mg, 0.23 mmol, 2 equ) in Et_2O or thf was added dropwise. After rapid stirring for 2 h, the color of the teal solution turned yellow and yielded good-quality crystals of **27**. The X-ray crystal structure of compound **27** was determined. ^{1}H NMR (300.23 MHz, thf/D_2O): 1.11 (s, 24H, $CH(CH_3)_2$), 2.10 - 2.21 (m, 30H, Ada), 2.33 (s, 12H, Me), 2.36 (s, 12H, Me), 2.44 (s, 12H, Me), m, 4H, $CH(CH_3)_2$ hidden under thf or Et_2O solvent residual signal, 6.88 (s, 4H), 6.91 (s, 2H), 7.58 (s, 2H), 7.62 (s, 2H) ppm. ^{13}C {^{1}H} NMR (75.50 MHz, thf/D_2O): δ 20.09, 20.58, 21.79, 21.93, 23.21, 23.60, 24.28, 24.48, 29.77, 30.62, 31.01, 36.27, 36.68, 46.22 (d, $^2J_{13C\text{-}31P}$: 4 Hz), 46.73 (d, $^2J_{13C\text{-}31P}$: 11 Hz), 123.81, 124.24, 127.72, 128.34, 128.47, 135.52, 135.58, 135.72, 136.11, 137.64, 137.89, 138.51, 138.68 (d, $J_{13C\text{-}31P}$: 4 Hz), 143.62, 144.20 (d, $J_{13C\text{-}31P}$: 17 Hz), 147.24 (d, $J_{13C\text{-}31P}$: 5 Hz), 147.42, 151.95, 152.86 ppm. ^{31}P {^{1}H} NMR (121.54 MHz, thf/D_2O): δ 19.65 (d,^1J $_{31P\text{-}31P}$: 449 Hz), 259.62 (d, ^1J $_{31P\text{-}31P}$: 449 Hz) ppm.

Preparation of compound 28.



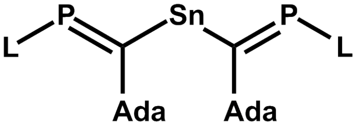
To a solution of Ge(L-4-Cl)$_2$ (100 mg, 0.13 mmol, 1 equ) in Et_2O a solution of AdaCP (46 mg, 0.26 mmol, 2 equ) in Et_2O was added dropwise. After rapid stirring for 2 h, the color of the violet solution turned yellow and yielded good-quality crystals of **28**. The X-ray crystal structure of compound **28** was determined.

Preparation of compound 29.



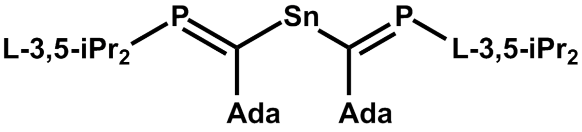
To a solution of Ge(L-4-SiMe$_3$)$_2$ (100 mg, 0.12 mmol, 1 equ) in Et_2O a solution of AdaCP (42 mg, 0.24 mmol, 2 equ) in Et_2O was added dropwise. After rapid stirring for 12 h, the color of the blue solution turned green and yielded yellow good-quality crystals of **29**. The X-ray crystal structure of compound **29** was determined. ^{1}H NMR (300.23 MHz, C_6D_6): δ 0.05 (s, 9H, SiMe$_3$), 0.07 (s, 9H, SiMe$_3$), 1.50 - 2.08 (m, 30H, Ada), 1.98 (s, 6H, CH$_3$), 2.12 (s, 6H, CH$_3$), 2.20 (s, 6H, CH$_3$), 2.22 (s, 6H, CH$_3$), 2.26 (s, 6H, CH$_3$), 2.40 (s, 6H, CH$_3$) 6.61 (s, 2H, ^{m}Mes), 6.68 (s, 4H, aromat. H), 6.82 (s, 2H, ^{m}Mes), 7.32 (s, 4H, aromat. H) ppm. ^{13}C {^{1}H} NMR (75.50 MHz, C_6D_6): δ -1.72, -1.65, 20.43, 20.88, 22.32, 22.69, 24.80, 29.88, 30.45, 36.14, 36.52, 46.89 (d, $^2J_{13C\text{-}31P}$: 6 Hz), 47.31 (d, $^2J_{13C\text{-}31P}$: 12 Hz), 128.89, 129.13, 134.72, 135.11, 135.25, 135.70, 136.38, 137.20, 137.85, 140.41, 141.46, 147.19 (d, ^1J $_{13C\text{-}31P}$: 3 Hz), 148.34 (d, ^1J $_{13C\text{-}31P}$: 10 Hz), 154.52, 155.57 ppm. ^{29}Si {^{1}H} NMR (59.64 MHz, pentane/D_2O): δ -4.33 ppm. ^{31}P {^{1}H} NMR (121.54 MHz, C_6D_6): δ 12.80 (d,^1J $_{31P\text{-}31P}$: 419 Hz), 276.98 (d, ^1J $_{31P\text{-}31P}$: 419 Hz) ppm.

Preparation of compound 30.



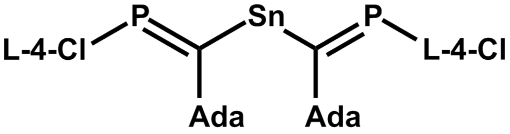
To a solution of SnL_2 (100 mg, 0.13 mmol, 1 equ) in Et_2O a solution of AdaCP (48 mg, 0.27 mmol, 2 equ) in Et_2O was added dropwise. The color of the solution started to change to green immediately. After rapid stirring for 12 h, the solution was stored at -30°C and yielded crystals of **30**. ^{31}P {^1H} NMR (121.54 MHz, C_6D_6): δ 332.68 ppm. ^{119}Sn {^1H} NMR (112.16 MHz, C_6D_6): δ 1301.06 ppm. UV-Vis: (Et_2O)/nm 636 (ϵ/dm^{3}mol^{-1}cm^{-1} 1233).

Preparation of compound 31.



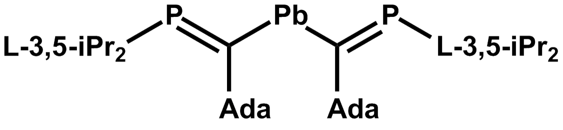
To a solution of Sn(L-3,5-iPr$_2$)$_2$ (100 mg, 0.11 mmol, 1 equ) in Et_2O a solution of AdaCP (39 mg, 0.22 mmol, 2 equ) in Et_2O was added dropwise. The color of the solution started to change from blue to green immediately. After rapid stirring for 12 h, the solution yielded good-quality crystals of **31**. The X-ray crystal structure was determined. ^{31}P {^1H} NMR (121.54 MHz, thf/D_2O): δ 348.80 ppm.

Preparation of compound 32.



To a solution of Sn(L-4-Cl)$_2$ (100 mg, 0.12 mmol, 1 equ) in Et_2O a solution of AdaCP (44 mg, 0.25 mmol, 2 equ) in Et_2O was added dropwise. After rapid stirring for 12 h, the color of the violet solution had turned green and the solution yielded good-quality crystals of **32**. The X-ray crystal structure was determined. ^{31}P {^1H} NMR (121.54 MHz, C_6D_6): δ 331.40 ppm.

Preparation of compound 33.



To a solution of Pb(L-3,5-iPr$_2$)$_2$ (100 mg, 0.10 mmol, 1 equ) in Et_2O a solution of AdaCP (36 mg, 0.20 mmol, 2 equ) in Et_2O was added dropwise. After rapid stirring for 12 h, the color of the violet solution had turned green and and the solution yielded good-quality crystals of **33**. The X-ray crystal structure was determined.

9.5.2 Gallium Clusters

Preparation of compounds 34 and 35.

A solution of LLi (200 mg, 624 mmol, 1 equ) in thf was cooled to -30℃ in the dry box, followed by addition of a solution of GaI_3 (281 mg, 624 mmol, 1 equ) (at -30℃) in thf. The reaction solution was stored at -30℃ for 12 h. Afterwards the solution was allowed to come to room temperature. To the in-situ formed $LGaI_2$ PPh_3 (164 mg, 624 mmol, 1 equ) was added, followed by addition of elemental sodium (29 mg, 1.2 mmol, 2 equ). The metal started the reaction immediately while turning black. The solution turned from yellow to green-brown. After 28 h the salts were separated by centrifugation and the solution was stored at -30℃. The product consisting of two clusters was isolated as black-metallic crystals. The crystal structure of the clusters was determined.

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