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**SYNTHESIS, CHARACTERIZATION, AND REACTIVITY OF HEAVIER
GROUP 13 AND 14 METALLYLENES AND METALLOID CLUSTERS:
SMALL MOLECULE ACTIVATION AND MORE**

BY

PETRA VASKO

Academic Dissertation for the Degree of
Doctor of Philosophy

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ABSTRACT

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Synthesis, Characterization, and Reactivity of Heavier Group 13 and 14 Metallylenes and Metalloid Clusters: Small Molecule Activation and More

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The understanding of bonding between atoms forms the foundation of chemistry. Although modern quantum theory has helped to clarify the details of the formation of molecules with great accuracy, less is still known about what the molecules can do with their bonds. The reactivity of low-valent main group compounds is a primary example: at first, these species were thought to be inert in reactions toward small molecules, such as hydrogen and olefins, at mild conditions, but recent examples have shown that their chemistry can in fact mimic that of transition metal complexes. Breakthrough discoveries include reversible addition of dihydrogen, ethylene, or carbon dioxide to main group molecules, all of which bear a resemblance to fundamental steps in transition metal catalysis.

The work reported in this thesis describes the synthesis, characterization, and reactivity studies of new group 13 and 14 molecules. The thesis is divided into two main chapters, of which the first reviews recent advances in the chemistry of neutral group 13 and 14 monomeric, dimeric, and cage-like compounds stabilized by sterically bulky monodentate ligands. The emphasis of the discussion is on the characteristics of these compounds that allow reactivity mimicking transition metal complexes. The second main chapter outlines the most important findings described in detail in the five publications associated with this thesis. Specifically, the results shed light on the electronic structures of germylene-isocyanide adducts and their connection to the observed C-H activation as well as rationalize the different reaction behavior of germylenes and stannylenes toward water and methanol. Furthermore, the influence of reaction conditions on the formation of metalloid main group clusters is discussed, and, for the first time, these cage-like species were observed to react with small molecules under mild conditions. On the whole, the reported results not only advance our understanding of the chemistry of heavier main group elements but also lead to hitherto unexplored reactivity that could be exploited in practical applications in the future.

Keywords: main group chemistry, metallylenes, metalloid clusters, small molecule activation, synthesis, computational chemistry, X-ray crystallography.

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PREFACE

The work presented in this thesis was conducted at the Department of Chemistry at the University of Jyväskylä and the University of California, Davis between 2011 and 2015. My journey as a doctoral student began when I sent an e-mail to Heikki asking whether he had “some small and fun” experimental project in mind for me to do. He suggested a four year commitment that would culminate in a doctoral degree. Little did I know what was ahead of me when I said “yes.” These years have been demanding, frustrating, and stressful but overall extremely educational, rewarding, and fun.

First of all, I would like to express my deepest gratitude to my principal supervisor Dr. Heikki M. Tuononen, who has always been there to help and guide me as well as to push me to do better. My other supervisor, Professor Philip P. Power in UC Davis, thank you for hosting me and teaching me so much during my stay in California. I will strive to publish all my future papers in Jackass, ChemComics, or Angewankie! Furthermore, thank you to my co-supervisor Dr. Jari Konu for your guidance throughout my work and especially in the beginning, when you taught me the basics of Schlenk chemistry.

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Finally, my family and friends: thank you for putting up with me all these years; I know I’m a handful! To my parents: thank you for always believing in me, supporting me, and loving me. My sisters: you offer me a welcomed break from chemistry every time we see; thank you for that! And all my dear friends: thank you for brightening my day, making me laugh, and helping me get through the hard times.

Jyväskylä, October, 2015

Petra Vasko

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the original research papers listed below which are hereafter referred to by their Roman numerals.

- I** Brown, Z. D.; Vasko, P.; Fettinger, J. C.; Tuononen, H. M. and Power, P. P. **A Germanium Isocyanide Complex Featuring ($n \rightarrow \pi^*$) Back-Bonding and Its Conversion to a Hydride/Cyanide Product via C-H Bond Activation under Mild Conditions**, *J. Am. Chem. Soc.*, **2012**, *134*, 4045–4048.
- II** Brown, Z. D.; Vasko, P.; Erickson, J. D.; Fettinger, J. C.; Tuononen, H. M. and Power, P. P. **Mechanistic Study of Stepwise Methylisocyanide Coupling and C-H Activation Mediated by Low-Valent Main Group Molecule**, *J. Am. Chem. Soc.*, **2013**, *135*, 6257–6261.
- III** Erickson, J. D.; Vasko, P.; Riparetti, R. D.; Fettinger, J. C.; Tuononen, H. M. and Power, P. P. **Reactions of *m*-Terphenyl Stabilized Germylene and Stannylene with Water and Methanol: Oxidative Addition versus Arene Elimination and Different Reaction Pathways for Alkyl and Aryl Substituted Species**, *Manuscript submitted to Organometallics*.
- IV** Vasko, P.; Wang, S.; Tuononen, H. M. and Power, P. P. **Addition of Ethylene or Hydrogen to a Main-Group Metal Cluster under Mild Conditions**, *Angew. Chem. Int. Ed.*, **2015**, *54*, 3802–3805.
- V** Vasko, P.; Mansikkamäki, A.; Fettinger, J. C.; Tuononen, H. M. and Power, P. P. **Reaction of $\text{LiAr}^{\text{Me}_6}$ ($\text{Ar}^{\text{Me}_6} = \text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_2\text{-2,4,6-Me}_3\text{)}_2$) with Indium(I)chloride Yields Three *m*-Terphenyl Stabilized Mixed-Valent Organoindium Subhalides**, *Polyhedron*, **2015**, *in press*. doi: 10.1016/j.poly.2015.09.052.

Author's contribution

The author of the present thesis has done all computational work in the original research Papers I–V, excluding the bonding analysis of In_8H_4 in Paper V. She has also performed all synthetic work in Papers IV and V, apart from the alternative synthesis and characterization of $\{\text{Sn}(\text{H})\text{Ar}\}_4$ in Paper IV. The author is the principal writer of Papers IV and V, whereas for Papers II and III she wrote the sections discussing the computational results.

Other contributions

A list of author's other contributions not included in this thesis.

- VI** Vasko, P.; Kinnunen, V.; Moilanen, J. O.; Roemmele, T. L.; Boéré, R. T.; Konu, J. and Tuononen, H. M. **Group 13 Complexes of Dipyridylmethane, a Forgotten Ligand in Coordination Chemistry**, *Dalton Trans.*, **2015**, *44*, 18247–18259.
- VII** Faust, M.; Bryan, A. M.; Mansikkamäki, A.; Vasko, P.; Olmstead, M. M.; Tuononen, H. M.; Grandjean, F.; Long, G. J. and Power, P. P. **The Instability of Ni{N(SiMe₃)₂}₂: A Fifty Year Old Transition Metal Silylamide Mystery**, *Angew. Chem. Int. Ed.*, **2015**, *54*, 12914–12917.

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ABSTRACT

PREFACE

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ABBREVIATIONS

CGMT	the Carter-Goddard-Malrieu-Trinquier model
DFT	density functional theory
Dipp	2,6-diisopropylphenyl
EDA	energy decomposition analysis
Et ₂ O	diethyl ether
HOMO	highest occupied molecular orbital
ⁱ Bu	isobutyl
ⁱ Pr	isopropyl
IR	infrared
LUMO	lowest unoccupied molecular orbital
Me	methyl
Mes	mesityl, 1,3,5-trimethylphenyl
ⁿ BuLi	<i>n</i> -butyllithium
NMR	nuclear magnetic resonance
Ph	phenyl
^t Bu	<i>tert</i> -butyl
THF	tetrahydrofuran
Trip	1,3,5-triisopropylphenyl

1 INTRODUCTION

Chemistry is all about the ability of elements to bind together and form different compounds. Hence, understanding the rules governing the formation of chemical bonds has been a priority for chemists for hundreds of years. The modern description of chemical bonding is based on quantum theory and the atomic shell structure, which easily rationalize why bonding is typically far simpler for *s*- and *p*-block elements than for their *d*- and *f*-block counterparts. It was also long thought that chemical bonding and covalent bonding in particular are fundamentally different for elements from the first two periods as compared to the rest. This was known as the double bond rule, which was summarized by Cotton in his classic inorganic chemistry textbook: "*Si, Ge, Sn and Pb do not form $p\pi$ multiple bonds under any circumstances.*"¹ The best evidence in support of this statement was the lack of known compounds with multiple bonds between heavier main group elements. However, a growing number of studies published since the beginning of the 1980s has ultimately led to the abandonment of the double bond rule and to the realization that the chemistry of heavier main group elements is far more complex than initially thought.

The renaissance of main group chemistry that began more than 30 years ago is still going strong. A plethora of novel *s*- and *p*-block compounds are introduced every year, and many molecules that were previously considered impossible to synthesize are now used as examples in undergraduate teaching. The study of main group chemistry has certainly evolved from curiosity-driven science to a mature research field making important contributions, even at the industry level. Main group compounds exhibiting multiple bonding, low oxidation states, and low coordination numbers are nowadays considered the norm rather than the exception, and current endeavors in the field concentrate on charting the reactivity of these fascinating species. Of particular interest are reactions characteristic to transition metals and their complexes, which is the reason that small molecule activation, hydrogen storage, and catalysis are on the lips of most *p*-block chemists. It can be safely said that the bonding between main group elements is now reasonably well-known, but what the bonds and molecules can do and how they do it, we still know relatively little of.

1.1 Aim of the work

The aim of this work was to investigate the bonding and reactivity of heavier group 13 and 14 molecules, especially in the context of small molecule activation.

The first subproject focused on *m*-terphenyl stabilized heavier group 14 carbene analogues, metallylenes, and their neutral Lewis adducts with isocyanides, water, or methanol. First, a sterically protected germylene was reacted with *tert*-butyl and methyl isocyanides to investigate the nature of donor-acceptor bonding and its implications to the reactivity of these adducts. Second, the reactivity of the germylene and its tin analogue with water and methanol was probed to rationalize the differences observed in the chemistry of these metallylenes.

The aim of the second subproject was to explore the reactivity of group 13 and 14 metalloid clusters toward small molecules. In particular, the *m*-terphenyl stabilized indium and tin cubanes were of interest because they contain low-valent metal centers, a known prerequisite for the reactivity of many main group species with molecules like dihydrogen, ammonia, carbon monoxide, and ethylene. In addition to the reactivity of these cubane clusters, the influence of the employed reaction conditions, such as stoichiometry and temperature, on their synthesis were also examined.

The research in both subprojects was conducted using a variety of synthetic and characterization techniques. A significant part of the performed work relied on the manipulation of air-sensitive compounds, X-ray crystallography, and computational chemistry. With the help of these and other methods, the molecular structures and reactivity of the novel compounds prepared in this work were elucidated. A synopsis of the results thus obtained is presented in Chapter 3 of this thesis.

2 LIGAND-STABILIZED GROUP 13 AND 14 COMPOUNDS

This chapter presents a literature review on ligand-stabilized group 13 and 14 compounds. Of particular interest are metallylenes, dimetallenes, and dimetallynes as well as metalloid clusters incorporating *m*-terphenyl substituents. The purpose of the review is to introduce the reader to the themes of this thesis rather than to give a comprehensive account of the vast research field in question. The chapter begins with a brief overview of synthesis and bonding of the discussed molecules, followed by a description of their reactivity with small molecules. Unless otherwise noted, E denotes a group 13 or 14 element, while R designates any suitable monodentate ligand.

2.1 Group 13 and 14 analogues of carbenes

Stable singlet carbenes :CR₂ have been exhaustively studied since their discovery, and their properties and reactivity are well understood and utilized in various applications.²⁻⁴ Therefore, it is surprising that the chemistry of metallylenes :ER and :ER₂, the heavier group 13 and 14 analogues of carbenes, was largely overlooked until recently.

In contrast to carbon, the heavier group 13 and 14 elements prefer the $(ns)^2(np)^x$ (n = principal quantum number, x = 1 or 2) valence configuration and are reluctant to use their *s*-orbitals for bonding. This arises from Pauli repulsion associated with the inner $(n-1)p$ electrons, which spatially separates the valence *ns* and *np* electrons for $n > 2$.^{5,6} As a result, elements from the third row and below prefer to form strong σ -bonds and weaker π -bonds, whereas the opposite is true for the lighter second period elements such as carbon. The separation of *ns* and *np* levels for the heavier main group elements is also the reason that parent metallylenes have singlet ground states and singlet-triplet gaps that increase with the atomic number of the element E (Figure 1).⁵

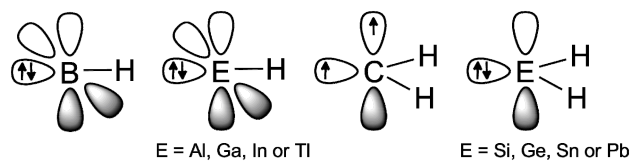


FIGURE 1 The different ground states of group 13 and 14 carbene analogues, collectively known as metallylenes.

Due to their lone pair of electrons and unoccupied p -orbital(s), metallylenes are usually very reactive and can act as both Lewis acids and bases. Thus, it is vital for their isolation to stabilize the compounds either thermodynamically or kinetically, or by using a combination thereof.⁷ Thermodynamic stabilization takes use of π -donor ligands that reduce the electron deficiency at the group 13 or 14 element E by donating electron density to its unoccupied p -orbital(s). Classic π -donor ligands are fluoride (F^-), oxide (O^{2-}), alkoxides (RO^-), imides (RN^{2-}), and amides (R_2N^-). Kinetic stabilization of metallylenes is achieved by using sufficiently large substituents, for example, *m*-terphenyls, that sterically shield the element E and prevent dimerization or other reactivity.

2.1.1 Group 13 metallylenes

Monomeric, one-coordinate group 13 metallylenes ER are relatively rare chemical species since they require the group 13 (triel) element to have a formal oxidation state of +I along with a lone pair of electrons.⁵ This leaves the group 13 element with two unoccupied p -orbitals, making the lighter metallylenes unstable and reactive, especially toward oxidation. For the heaviest triels indium and thallium, the contraction of both core and valence s -orbitals due to relativistic effects stabilizes the +I oxidation state to the extent that it becomes the preferred one for thallium (inert-pair effect).⁸ However, despite the increased lone pair character in the +I oxidation state, all group 13 metallylenes show a preference for dimerization in the solid state unless prevented by the steric bulk of the employed ligand (see section 2.2.1).

The first *m*-terphenyl stabilized InR and TlR ($R = C_6H_3-2,6-Trip_2$; Trip = $C_6H_2-2,4,6-^iPr_3$; iPr = isopropyl) species were published by Power *et al.* in 1998 (Figure 2).^{9,10} The monomeric structures of the compounds in the solid state were attributed to the steric bulk of the *m*-terphenyl ligand. The use of sterically crowded ligands proved to be vital also for the isolation and characterization of gallylenes GaR ($R = C_6H-(2,6-(2,6-Dipp_2)-3,5-^iPr_2)$ or $C_6H-(2,6-(2,4,6-Trip_2)-3,5-^iPr_2)$; Dipp = $C_6H_3-2,6-^iPr_2$).¹¹ Analogous amide-stabilized group 13 metallylenes ER (E = Ga, In or Tl; $R = N(SiMe_3)(C_6H_3-2,6-Mes_2)$; Mes = $C_6H_2-2,4,6-Me_3$, Me = methyl) have also been synthesized and characterized (Figure 2).^{12,13}

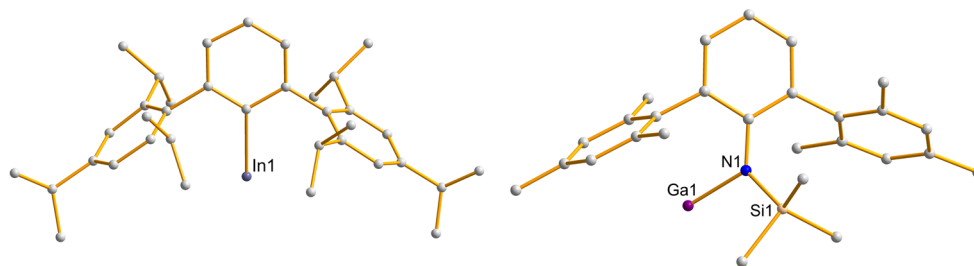


FIGURE 2 Illustrations of the solid state structures of InR (left; R = C₆H₃-2,6-Trip₂) and GaR (right; R = N(SiMe₃)(C₆H₃-2,6-Mes₂)).^{10,13} Hydrogen atoms have been omitted for clarity.

Monomeric, one-coordinate compounds of the formula AIR have yet to be identified, reflecting the preference of aluminum to adopt oxidation states other than +I. However, a metal-stabilized terminal arylaluminum AIR (R = C₆H₃-2,6-(CH(SiMe₃)₂)₂) has been isolated and structurally characterized in the solid state.¹⁴ Similar borylene complexes BR, even some with a terphenyl ligand (R = C₆H₃-2,6-Trip₂), have also been known since 2001.¹⁵⁻¹⁷ The borylene complexes were recently shown to react with CO, affording the first multicarbonyl complex of a main group element that shows π -backbonding effects similar to transition metal carbonyls.

2.1.2 Group 14 metallylenes

The heavier group 14 carbene analogues ER₂ have a singlet ground state with the two-coordinate group 14 (tetrel) element in a formal oxidation state of +II (Figure 1).^{2,5} As with group 13 metallylenes, the *s*-character of the lone pair increases descending the group, and relativistic effects render the +II oxidation state favored for lead.^{18,19} Hence, it is not surprising that the first group 14 metallylenes ER₂ (E = Sn or Pb; R = CH(SiMe₃)₂) reported by Lappert *et al.* employed tin and lead rather than their lighter congeners.²⁰⁻²³ Although monomeric in solution, Ge{CH(SiMe₃)₂}₂ and Sn{CH(SiMe₃)₂}₂ were found to dimerize in the solid state (see section 2.2.2); crystallographic data for Pb{CH(SiMe₃)₂}₂ is not available. If the size of the alkyl ligand was increased slightly, the heteroleptic compound GeRR' (R = CH(SiMe₃)₂; R' = C(SiMe₃)₃) could be isolated and characterized as a monomer also in the solid state (Figure 3).²⁴ Thus, a difference of only one trimethylsilyl group was enough to prevent Ge{CH(SiMe₃)₂}{C(SiMe₃)₃} from dimerizing, which highlights the importance of careful ligand design.

Numerous other monomeric group 14 metallylenes stabilized by silyl, amido, and alkoxide ligands are nowadays known.^{2,25,26} However, more relevant to the topic of this thesis are derivatives that use aryl ligands and *m*-terphenyl in particular. Terphenyl ligands are of interest, as they are bulky enough to prevent all kinds of secondary bonding interactions between the ligand and the group 14 element that could otherwise impact further reactivity of metallylenes. At the moment, the diaryls ER₂ (E = Ge, Sn, or Pb; R = C₆H₃-2,6-Trip₂ or C₆H₃-2,6-Mes₂) have been synthesized and characterized in the solid state (Figure 3).^{27,28} In

contrast, related silylenes SiR_2 are rare not only for *m*-terphenyls but also for any ligand R, and only a few derivatives are known. The first examples were reported in 2012: a homoleptic compound employing a thiolate ligand as well as a heteroleptic complex with an amide and a cyclic boryl ligand.^{29,30}

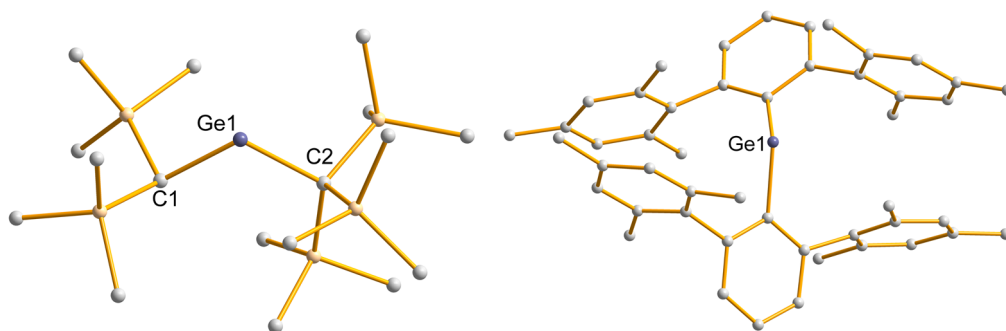


FIGURE 3 Illustrations of the solid state structures of GeRR' (left; $\text{R} = \text{CH}(\text{SiMe}_3)_2$; $\text{R}' = \text{C}(\text{SiMe}_3)_3$) and GeR_2 (right; $\text{R} = \text{C}_6\text{H}_3\text{-2,6-Mes}_2$).^{24,27} Hydrogen atoms have been omitted for clarity.

2.2 Multiply bonded homonuclear group 13 and 14 compounds

The first stable, heavier main group analogue of an alkene was structurally characterized already in 1976.²² Lappert *et al.* synthesized the ditin compound R_2SnSnR_2 ($\text{R} = \text{CH}(\text{SiMe}_3)_2$), which was found to monomerize in solution to two SnR_2 fragments (see section 2.1.2). Since then, compounds with formal multiple bonds between the heavier main group 13 and 14 elements have been studied extensively.^{31,32} At first, these systems were of fundamental interest because they contradicted the then well-established double bond rule and therefore opened new vistas in bonding.^{1,33} For example, the geometries of all heavier group 13 and 14 dimetallenes differ from their lightest boron and carbon analogues, and the differences can be rationalized with orbital mixing arguments (see sections 2.2.1 and 2.2.2).^{34,35} In addition to geometries, multiply bonded heavier main group compounds have fundamentally different chemical and physical properties than their second row analogues; for this reason, investigations on their reactivity and possible applications have been put to the fore.

2.2.1 Group 13 dimetallenes and dimetallynes

Compounds with homonuclear multiple bonds between the heavier triels are relatively scarce. This is partly due to the fact that only a few valence electrons are available for bonding and that only one substituent per element E can be used for stabilization.^{31,36,37} It is interesting that the simplest imaginable compounds with formal EE multiple bonding, the dimetallenes REER ($\text{E} = \text{Al}, \text{Ga}, \text{In}$ or Tl), were in fact the last ones to be synthesized and characterized. However, the

bonding in these systems was examined computationally already in the early 1990s.³⁸

The parent diborene HBBH was predicted to have a linear structure ($D_{\infty h}$ point group) and a triplet ground state.³⁸ In contrast, the ground state for all heavier group 13 dimetallenes HEEH was found to be a singlet with a *trans*-bent (C_{2h} point group) geometry; other isomers are also possible but they are not relevant to the topic of this thesis. The difference in geometry with respect to the parent diborene can be understood as a second-order Jahn-Teller distortion³⁹ that is common in multiply bonded heavier main group species because of their weaker bonding, which lowers the separation between σ - and π -type frontier molecular orbitals.⁴⁰ As a consequence, a change in molecular symmetry from $D_{\infty h}$ to C_{2h} allows the mixing of σ - and π -type orbitals in all heavier group 13 dimetallenes REER, thereby giving rise to a lone pair (slipped π -type) highest occupied molecular orbital (HOMO) and a σ -symmetric HOMO-1 (Figure 4). Thus, the formal bond order in REER is actually close to one.⁴¹ It should be noted, however, that the lowest unoccupied molecular orbital (LUMO) of REER is an empty π -orbital, which, if fully occupied, can possibly strengthen the EE bond to a formal double bond in the dianions $[\text{REER}]^{2-}$.

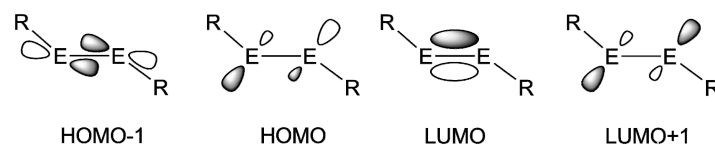


FIGURE 4 Schematic depiction of frontier molecular orbitals of *trans*-bent heavier group 13 dimetallenes REER.

An alternative view of bonding in group 13 dimetallenes can be obtained by considering their construction from monomeric metallylenes.³⁸ A linear, doubly bonded RE=ER species would require the combination of two triplet state ER fragments but, as discussed above (see section 2.1.1), the singlet-triplet gap is positive for all metallylenes and increases on descending group 13. Because π -bond energies become successively smaller for elements from the third row and below, forming an E=E double bond from two singlet state ER fragments would not bring about a net energy gain for any of the heavier triels. However, metallylenes can also bind directly from their singlet states, in which case the geometry of the resulting molecule is inevitably non-linear (Figure 5). Consequently, the bonding in heavier group 13 dimetallenes can be thought of as a weak double donor-acceptor interaction. This not only rationalizes the *trans*-bent molecular geometries but also predicts the facile dissociation of dimetallenes into the corresponding metallylenes (see section 2.2.1).

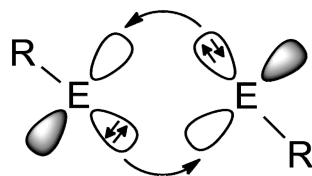


FIGURE 5 Association of two singlet state group 13 metallylenes to a *trans*-bent dimetallene via dative donor-acceptor interactions. The second set of empty *p*-orbitals has been omitted for clarity.

In 1993, the first examples of multiple bonding between triels were published by Power *et al.* and Pörschke *et al.*^{42,43} The reported compounds were salts of the radical anions $[R_2EER_2]^{*-}$ (E = Al or Ga; R = CH(SiMe₃)₂ or Trip). Both compounds were prepared by reduction of the corresponding dimetallane with lithium metal, and were shown to have a one electron π -bond between the group 13 elements. A few years later, Robinson *et al.* communicated the results of a related reduction yielding the salt Na₂[RGaGaR] (R = C₆H₃-2,6-Trip₂) which was described as containing a dianion with a Ga \equiv Ga triple bond (Figure 6).⁴⁴ The report caused much controversy and discussion, resulting in numerous experimental and computational studies aimed at investigating the nature of Ga-Ga bonding in digallynes as well as in other related species.^{11,45,46} Today, the consensus is that the bond order in digallyne dianions is close to two, whereas it is even less in the salts Na₂[RGaGaR] due to interactions between the anion and the cations. The aluminum analogue of Robinson's salt, Na₂[RAIAlR] (R = C₆H₃-2,6-Dipp₂), is also known and shares similar *trans*-bent structure with an Al-Al bond that is only marginally shorter than that in the singly reduced dialane(4) anion $[R_2AlAlR_2]^{*-}$ (R = C₆H₂-2,4,6-*i*Pr₃) with equally large *m*-terphenyl substituents and a formal bond order of 1½.⁴⁷

The first neutral digallene RGaGaR (R = C₆H₃-2,6-Dipp₂) was reported by Power *et al.* in 2002.⁴⁶ As predicted by theory almost 15 years before its characterization,³⁸ the compound was shown to have a *trans*-bent structure in the solid state with a relatively long, and presumably weak, bond between the group 13 elements. The weakness of the Ga-Ga bond was confirmed experimentally because the dimer was found to monomerize in hydrocarbon solvents (see section 2.1.1). Recently, the heaviest dimetallenes REER (E = In or Tl; R = C₆H₃-2,6-Dipp₂), have also been synthesized and structurally characterized.^{48,49} The E-E bonds in these compounds are long and weak, as evidenced by the identification of the corresponding monomers in solution. The latest theoretical work has shown that the covalent description of bonding (Figure 4) is the most significant for dialuminenes and digallenes, whereas diindenes and in particular dithallenes are held together by dispersion forces.⁴¹ Calculations have also revealed that dialuminenes have singlet diradical character that is, however, only very minor. As of now, there are no experimentally characterized examples of dialuminenes and the attempted synthesis of RAlAlR (R = C₆H₃-2,6-Dipp₂) by reduction of RAlI₂ with KC₈ afforded a [2 + 4] cycloaddition product with toluene.⁵⁰ A similar benzene adduct of RAlAlR (R = C₆H₃-2,6-{CH(SiMe₃)₂})₂

(Figure 6) has also been reported and it was found to react as a synthetic equivalent of a dialuminene, undergoing exchange reactions with naphthalene, anthracene, and bis(trimethylsilyl)acetylene.⁵¹

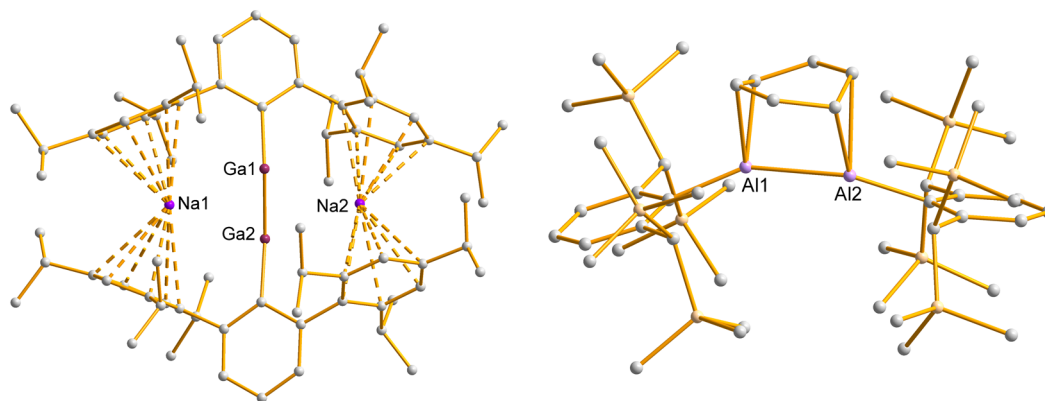


FIGURE 6 Illustrations of the solid state structures of Na₂[RGaGaR] (left; R = C₆H₃-2,6-Trip₂)⁴⁴ and benzene adduct of RAlAlR (right; R = C₆H₃-2,6-{CH(SiMe₃)₂})₂.⁵¹ Hydrogen atoms and solvent molecule have been omitted for clarity.

Although the focus of this thesis is on the chemistry of the heavier group 13 elements, some examples of multiply bonded boron species can be mentioned for comparison. The first published examples were the dianions [R₂BBR₂]²⁻ that were obtained by reducing the parent diboranes(4) with an alkali metal.^{52,53} These reports were later followed by the stabilization of a neutral diborene HB=BH with two *N*-heterocyclic carbenes, yielding the compound R→(H)BB(H)←R (R = 1,3-bis-(2,6-diisopropylphenyl)imidazole-2-ylidene).⁵⁴ Recently, the same carbene ligand was used to stabilize a formal B≡B triple bond in the diboryne R→BB←R.⁵⁵ The nature of bonding in R→BB←R has been studied by nuclear magnetic resonance (NMR) spectroscopy and computational methods, and the results of these investigations corroborate the triple bond description of its electronic structure.⁵⁶

2.2.2 Group 14 dimetallenes and dimetallynes

The dimer of two parent carbenes, an ethylene molecule, has a planar geometry due to the formation of a classic C=C double bond. In contrast, all heavier group 14 analogues of ethylene typically adopt a non-planar *trans*-bent geometry similar to that observed for group 13 dimetallenes. Hence, the bonding rules characteristic to the chemistry of carbon are actually exceptions and those observed for the heavier main group elements represent the norm.⁶ The preference for different geometries can be explained with the Carter-Goddard-Malrieu-Trinquier (CGMT) model that correlates the singlet-triplet energy gaps of ER₂ monomers to the electronic and structural characteristics of the corresponding dimers R₂EER₂.^{5,57-60}

The homolytic cleavage of an olefinic double bond in a linear R₂C=CR₂ molecule typically leads to two triplet monomers CR₂ (Figure 7). However, if the

resulting carbenes have a singlet ground state, a very good estimate of the C=C double bond energy (E_{DB}) can be obtained simply by subtracting the singlet-triplet energy gaps of the carbenes (ΔE_{S-T}) from the intrinsic C=C double bond energy (E_{INT}): $E_{DB} = E_{INT} - 2\Delta E_{S-T}$.⁶⁰ The energy E_{INT} is a reference value that, in a typical case, can be the C=C double bond energy in ethylene as it dissociates to two triplet state fragments. The simple correlation between E_{DB} and ΔE_{S-T} can also be used to assess singlet-triplet gaps of carbenes from experimental bond energy data for the corresponding alkenes.

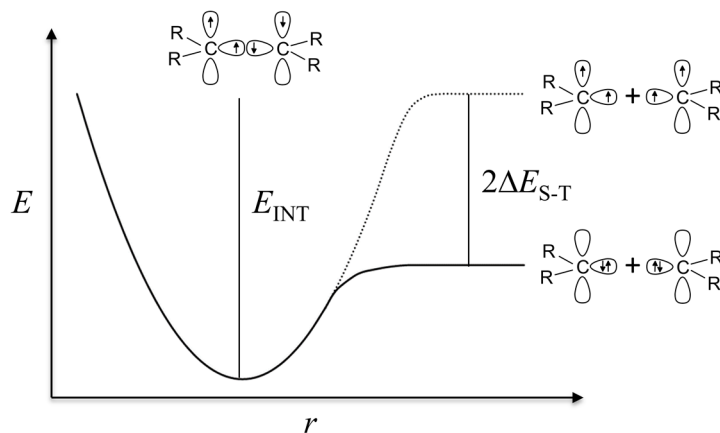


FIGURE 7 Schematic representation of the dissociation of a linear alkene into two triplet or singlet fragments. E_{INT} is the intrinsic C=C double bond energy, $2\Delta E_{S-T}$ the singlet-triplet excitation energy for two CR_2 fragments, and r the internuclear C-C distance.

The correlation between the bond energies of a substituted alkene and the singlet-triplet energy splitting of the corresponding carbene fragments was first recognized by Carter and Goddard.⁶⁰ Shortly thereafter, Malrieu and Trinquier presented how this theoretical treatment could be extended to other multiply bonded systems with heavier main group elements and non-planar geometries.⁵⁸ Specifically, they showed that for all heavier group 14 species R_2EER_2 , a non-planar *trans*-bent geometry is observed if $2\Delta E_{S-T} > \frac{1}{2}E_{DB}$. Subsequent calculations revealed that the condition is met for digermenes and in particular for distannenes but not necessarily for disilenes, which were found to have very flat potential energy surfaces (PESs) and can therefore adopt geometries similar to their carbon analogues. It should be underlined that the CGMT model rationalizes the *trans*-bent structures of group 14 dimetallenes with just one property of the monomers, the singlet-triplet gap, and completely omits the influence of steric and electronic characteristics of the ligands. The model does not, therefore, give a detailed description of the complete PES for a given molecule, as the preferred structure also depends on the bulkiness of the ligands and the nature of ER bonds.^{31,37,61}

The underlying chemical description behind the CGMT model treats the E-E bonds in group 14 dimetallenes as weak double donor-acceptor interactions (Figure 8).⁵⁸ This picture of bonding is very similar to that presented earlier for

the related group 13 systems (see section 2.2.1). It therefore comes as no surprise that *trans*-bending in group 14 dimetallenes R_2EER_2 can also be viewed as arising from second-order Jahn-Teller distortion that lowers the total energy by mixing the bonding π -orbital with the antibonding σ^* -orbital (Figure 9).⁵⁷ Consequently, the HOMO of *trans*-bent group 14 dimetallenes is mostly non-bonding in nature, as is the case for the LUMO. Because the HOMO-1 is a σ -bonding orbital, the formal bond order in R_2EER_2 should be between one and two, depending on the exact degree of *trans*-bending. For example, the geometries of many disilenes are nearly planar, which alters the orbital morphologies and increases the bond order.⁶² In contrast, the heaviest tin and lead species typically have significantly bent structures with EE distances close to, or even greater than, single bond lengths,^{63,64} indicative of low bond order and high contribution from dispersion forces to bonding. Subsequently, distannenes and diplumbenes monomerize in solution and have bond enthalpies that are only a fraction of the corresponding single bond strengths.^{37,65}

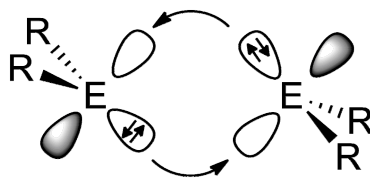


FIGURE 8 Association of two singlet state group 14 metallylenes to a *trans*-bent dimetallene via dative donor-acceptor interactions.

The discovery of Lappert's formally doubly bonded tin dimer (Figure 11)²² in 1976 led to the general realization that the isolation of heavier main group alkene analogues requires the use of bulky substituents to prevent monomerization in solution or further association of the dimers to oligomers or polymers.⁶⁶ Keeping this in mind, West *et al.* characterized the first doubly bonded silicon species, R_2SiSiR_2 ($R = \text{Mes}$), only a few years later.⁶⁷ Interestingly, the disilene did not dissociate into monomers in solution and its solid state structure showed an almost planar arrangement of atoms around the tetrels, indicative of strong Si-Si bonding. Shortly thereafter, the first digermene R_2GeGeR_2 ($R = \text{CH}(\text{SiMe}_3)_2$) was reported by Lappert *et al.*⁶⁸ This completed the series from carbon to tin, providing important experimental evidence that the nature of bonding in dimetallenes R_2EER_2 changes gradually on descending group 14. As a whole, the results of these studies also provided much of the incentive for the development of the CGMT model. Finally, the synthesis and characterization of the last missing congener, the diplumbylene, by Klinkhammer *et al.* fully exhausted the list of possible group 14 dimetallenes in 1998.⁶³ Nowadays there are more than 100 structurally characterized examples of group 14 dimetallenes that take use of a number of different ligands with widely differing electronic and steric properties. However, the number of *m*-terphenyl stabilized derivatives is limited to a single heteroleptic species, $RR'GeGeRR'$ ($R = \text{C}_6\text{H}_3\text{-2,6-Trip}_2$; $R' = \text{Ph}$), for steric reasons.⁶⁹

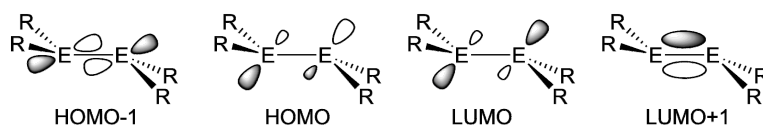


FIGURE 9 Schematic depiction of frontier molecular orbitals of *trans*-bent heavier group 14 dimetallenes R_2EER_2 .

The heavier group 14 alkyne analogues $REER$ are another example of multiple bonding between tetrrels. Their *trans*-bent geometries can be rationalized much the same way as discussed for group 13 dimetallenes (see section 2.2.1). The ground state of a group 14 ER monomer can be either a quartet or a doublet, with all elements heavier than carbon preferring the latter. Consequently, the EE bond in dimetallynes can be viewed as a double donor-acceptor interaction between two ER monomers.⁶⁶ The two remaining electrons occupy the p -orbitals perpendicular to the molecular plane and give rise to a π -bonding contribution analogous to that in the valence isoelectronic Robinson's digallyne.⁴⁴ Consequently, the HOMO in disilynes and digermynes is a π -bonding orbital and the LUMO is mostly of lone pair type (Figure 10). However, the ordering of the HOMO and the LUMO is reversed in distannynes and diplumbynes as compared to that shown in Figure 10.⁷⁰ As a consequence, the geometries of heavier group 14 alkyne analogues become increasingly *trans*-bent on going down the group, with a concomitant decrease in the bond order and increase in the $E-E$ bond length.⁷⁰⁻⁷⁶ The unique orbital characteristics of disilynes and digermynes manifest themselves also in a singlet diradical character that the heavier congeners lack.⁷⁰

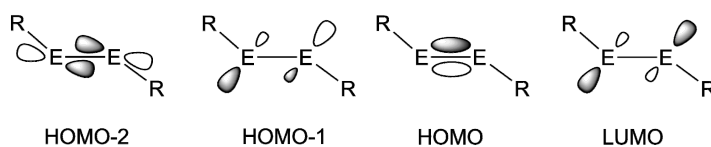


FIGURE 10 Schematic depiction of frontier orbitals of *trans*-bent heavier group 14 dimetallynes $REER$.

In 2000, Power *et al.* reported the first group 14 dimetallyne, the *m*-terphenyl stabilized diplumbyne $RPbPbR$ ($R = C_6H_3-2,6-Trip_2$).⁷⁵ This compound was obtained serendipitously during the attempted synthesis of a divalent lead(II) hydride from $RPbBr$. The diplumbyne was found to have a $Pb-Pb$ distance significantly longer than a typical single bond, along with a bending angle close to 90° (Figure 11), which indicated the presence of a highly localized lone pair at each group 14 element. The *m*-terphenyl substituted digermynes and distannynes were the next group 14 dimetallynes to be characterized.^{77,78} These compounds were found to have nearly identical bending angles at around 125° , along with $E-E$ distances that were shorter than typical single bonds and on par with bond lengths in related group 14 dimetallenes. The series of heavy alkyne analogues

was completed by the first disilyne, RSiSiR ($\text{R} = \text{Si}(\text{iPr})\{\text{CH}(\text{SiMe}_3)_2\}_2$), which was reported by Sekiguchi *et al.* in 2004.⁷³ With a bending angle close to 140° , the molecule was surprisingly *trans*-bent but it nevertheless had a Si-Si bond distance that was slightly shorter than a typical double bond. An interesting difference in the chemical behavior of group 14 dimetallynes REER as compared to the corresponding dimetallenes R_2EER_2 is that the former species do not monomerize in solution. This can be explained with the electronic ground state of the monomers: a doublet for ER and a singlet for ER_2 .

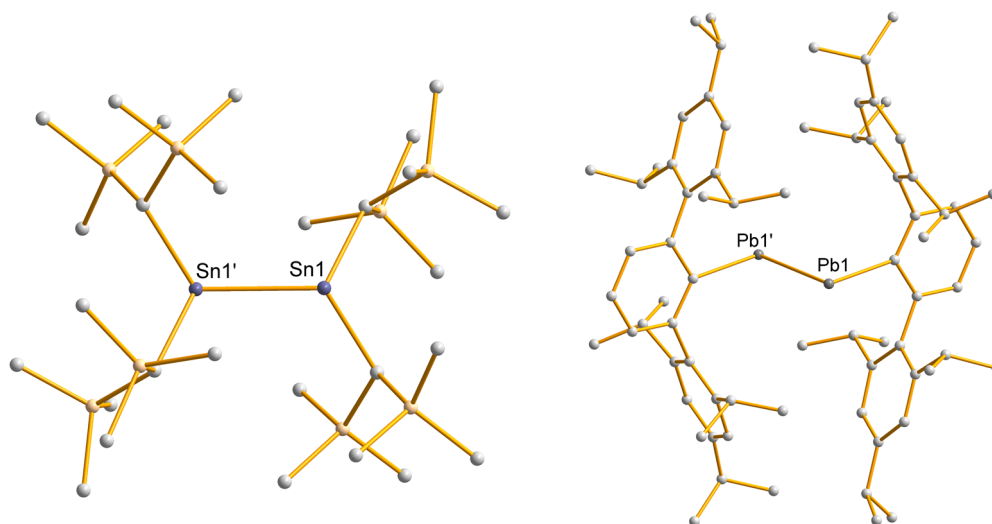


FIGURE 11 Illustrations of the solid state structures of R_2SnSnR_2 (left; $\text{R} = \text{CH}(\text{SiMe}_3)_2$) and RPbPbR (right; $\text{R} = \text{C}_6\text{H}_3\text{-2,6-Trip}_2$).^{22,75} Hydrogen atoms have been omitted for clarity.

2.3 Neutral molecular clusters of heavier group 13 and 14 elements

Ligand-stabilized clusters of heavier group 13 and 14 elements of the formula E_nR_m ($n > 2$) are an interesting group of molecules. These three dimensional cage-like species are typically stabilized by monodentate ligands and their bonding resembles that of well-known polyboranes for $n \leq m$.⁷⁹⁻⁸¹ If $n > m$, the metal-metal bonds outnumber the metal-ligand bonds and the term *metalloid cluster* is used; the term *elementoid* can also be used as silicon and germanium are semimetals.

2.3.1 Group 13 clusters E_nR_m ($n \geq m$)

Clusters of the type E_nR_m ($n = m$, $n > 2$) have the group 13 elements E in a formal oxidation state of $+I$. For aluminum and gallium, such a low oxidation state readily induces disproportionation unless prevented by bulky substituents providing kinetic stabilization. Also, the valence s -electrons in indium and, in particular, thallium are inert and do not take part in bond formation, which poses

another problem for cluster synthesis. It is therefore somewhat surprising that the smallest group 13 cluster of the type E_nR_m is the neutral trimer Tl_3R_3 ($R = C_6H_3-2,6-(C_6H_3-2,6-Me_2)_2$) reported by Power *et al.* (Figure 12).⁴⁸ The three thallium atoms are arranged in an isosceles triangle with pyramidal coordination at each metal, consistent with significant lone pair character. The cluster was found to be stable only in the solid state. In solution it dissociated into monomeric TlR units, which underlines the weakness of $Tl-Tl$ bonds in the structure. No trimers similar to Tl_3R_3 are known for aluminum, gallium, or indium, though there are characterized examples of ionic group 13 clusters with trimeric structures.⁸²⁻⁸⁴

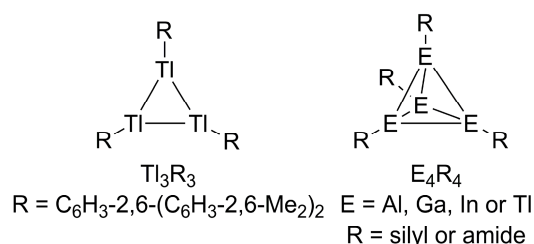


FIGURE 12 Illustrations of neutral group 13 clusters Tl_3R_3 and E_4R_4 .^{48,85-91}

All known examples of neutral clusters with the formula E_4R_4 have tetrahedral arrangement of group 13 elements (Figure 12). The extant literature includes examples for all heavier group 13 elements, though more for aluminum and gallium and only a few for indium and one for thallium. Uhl *et al.* reported the synthesis of a gallium tetrahedron Ga_4R_4 ($R = C(SiMe_3)_3$) in 1992.⁸⁵ The cluster was obtained as a disproportionation product from the reaction between $Ga_2Br_2 \cdot 2$ dioxane and $LiC(SiMe_3)_3$, and it was found to monomerize into GaR units in solution. A few years later Uhl's work, the aluminum, indium, and thallium analogues E_4R_4 ($E = Al, In \text{ or } Tl$; $R = C(SiMe_3)_3$) were also reported.⁸⁶⁻⁸⁸ Similar tetrahedra employing silyl ligands ($R = C(SiMe_2Et)_3$ or $C(SiMe_2^iPr)_3$) or amides ($R = N(SiMe_3)Dipp$) are also known,⁸⁹⁻⁹¹ but a tetrahedral structure cannot be obtained with *m*-terphenyls, possibly due to the steric bulk of the ligands.

In a tetrahedral E_4R_4 cluster, each group 13 element provides two electrons to EE bonding. This means that there are altogether eight electrons distributed among six $E-E$ interactions, resulting in a formal bond order of $2/3$.⁹² In other words, the $E-E$ interactions in E_4R_4 can be described as three-center two-electron ($3c-2e$) bonds. The electron poor nature of the clusters is in agreement with their $E-E$ bond lengths, which are typically longer than respective single bonds. Consequently, all known E_4R_4 clusters have a tendency to dissociate into metallylene monomers in solution.⁹³ Furthermore, the structure reported for the thallium cluster is significantly distorted, which indicates that the molecule does not have covalent $Tl-Tl$ bonds but is more likely dispersion-bound.⁸⁷

Bigger clusters of the type E_nR_m ($n = m$) are typically anionic, such as the icosahedral aluminum cluster $[Al_{12}R_{12}]^{2-}$ ($R = ^iBu$; $^iBu = \text{isobutyl}$) and the

antiprismatic gallium cluster $[\text{Ga}_8\text{R}_8]^{2-}$ (R = fluorenyl) reported by Uhl *et al.* and Schnöckel *et al.*^{94,95} The few neutral, structurally characterized examples (Figure 13) include molecules like Ga_6R_6 (R = $\text{SiMe}(\text{SiMe}_3)_2$),⁹⁶ Ga_9R_9 (R = ^tBu ; ^tBu = *tert*-butyl),⁹⁷ and In_8R_8 (R = SiPh_3).⁹⁸ The Ga_6 core in Ga_6R_6 has a distorted octahedral structure, whereas the gallium atoms in Ga_9R_9 are in a tricapped trigonal prism arrangement. The structure of the indium cluster In_8R_8 is a snub disphenoid, as predicted by Wade-Mingos rules. What is common to all of these clusters is that their chemistries have not been explored in great detail after their syntheses. This can be readily understood by considering the synthetic yields that range from a few crystals of In_8R_8 to 13% for Ga_6R_6 .

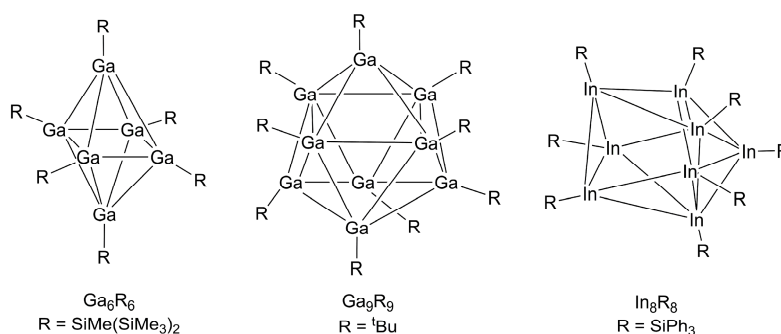


FIGURE 13 Illustrations of neutral group 13 clusters Ga_6R_6 , Ga_9R_9 , and In_8R_8 .⁹⁶⁻⁹⁸

Neutral metalloids clusters E_nR_m ($n > m$) are equally scarce for heavier group 13 elements, as are clusters with $n = m$.⁷⁹ For aluminum, the only structurally characterized example is the cluster $\text{Al}_7\text{R}_6^\bullet$ (R = $\text{N}(\text{SiMe}_2\text{Ph})_2$), reported by Schnöckel *et al.*, which is a radical species and has only one naked aluminum atom.⁹⁹ For gallium, a number of neutral metalloids clusters have been reported, where n varies from 8 to 22.^{79,100-106} Of particular emphasis is the cluster Ga_{11}R_4 (R = $\text{C}_6\text{H}_3\text{-2,6-Mes}_2$) published by Power *et al.*, as it is one of only two group 13 metalloids clusters with *m*-terphenyl ligands.¹⁰⁵ Although metalloids thallium clusters are nonexistent, a few indium species are known.¹⁰⁷⁻¹⁰⁹ These include two In_8 clusters with a distorted cubane shape, In_8R_6 (R = Si^tBu_3) and In_8R_4 (R = $\text{C}_6\text{H}_3\text{-2,6-Mes}_2$), as well as a metalloids cluster In_{12}R_8 (R = Si^tBu_3) that consists of two distorted In_6R_4 (R = Si^tBu_3) octahedra (Figure 14). The dodecaindane cluster reported by Wiberg *et al.* is a particularly interesting species because of its structure, which is similar to the slightly distorted cubic close-packing of atoms in elemental indium. Because the oxidation state of the naked metal atoms in neutral metalloids clusters is zero, the clusters should be reactive toward oxidation. However, very little is currently known of their chemistry.

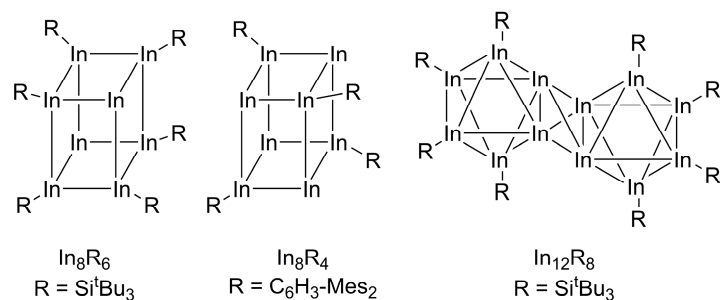


FIGURE 14 Illustrations of neutral metalloindium clusters In_8R_6 , In_8R_4 , and In_{12}R_8 .¹⁰⁷⁻¹⁰⁹

2.3.2 Group 14 clusters E_nR_m ($n \geq m$)

The smallest neutral heavier group 14 element clusters of the type E_nR_m ($n = m$, $n > 2$) are rings and tetrahedra with $n = 4$. Trimeric E_3R_3 structures have been reported in the literature but they are typically ionic with only one example of a neutral radical species, $\text{Ge}_3\text{R}_3^\bullet$ ($\text{R} = \text{C}_6\text{H}_3\text{-2,6-Mes}_2$), communicated by Power *et al.*¹¹⁰⁻¹¹⁴ For E_4R_4 , the tetrahedral shape is preferred, with a number of reported examples for both silicon and germanium,¹¹⁵⁻¹¹⁸ whereas a cyclobutane-type ring structure has been characterized only for silicon.¹¹⁹

Bigger clusters of the type E_nR_m ($n = m$) are typically more stable and isolable as the geometries around group 14 elements are less strained. Hexamers,¹²⁰⁻¹²⁴ octamers,¹²⁵⁻¹²⁷ and even decamers¹²⁸ have been reported for silicon, germanium, and tin (Figure 15). The hexamers typically adopt a prismatic array of group 14 elements, while the cubane is preferred for E_8R_8 species. The number of group 14 clusters of the type E_nR_m ($n = m$) is bigger than that of analogous group 13 systems, which can be explained by the greater number of valence electrons available for bonding. What is common between the group 13 and 14 clusters, however, is that there are no examples of neutral polyhedral E_nR_m ($n = m$, $n > 4$) compounds for either thallium or lead, the heaviest members of the groups. Furthermore, the number of *m*-terphenyl stabilized examples is limited due to the 1:1 metal:ligand ratio and the steric bulk of the ligand.

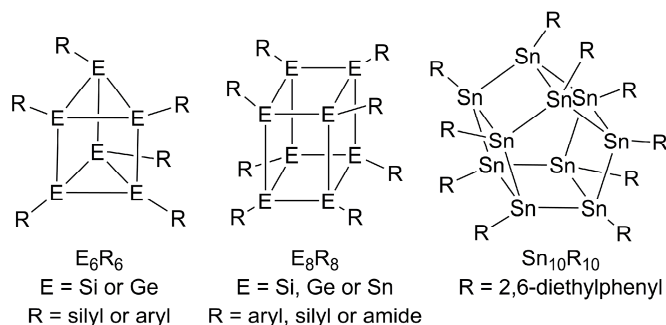


FIGURE 15 Illustrations of hexameric (prismatic, left), octameric (cubane, middle), and decameric ([5]prismane, right) group 14 clusters.¹²⁰⁻¹²⁸

In neutral metalloids clusters E_nR_m ($n > m$), the oxidation state of the group 14 element is typically either +I or 0 depending on whether the tetrel is bound to a ligand. Often n is much greater than m , in which case it is paramount to shield the naked group 14 elements to prevent any unwanted reactivity. As already mentioned, m -terphenyl ligands are aptly suited for such purpose and they have therefore been used to stabilize unusual bonding arrangements in neutral group 14 metalloids clusters. For example, Power *et al.* employed the ligand $C_6H_3-2,6-Trip_2$ in the synthesis of Sn_9R_3 , which has a structure similar to the Zintl anion $[Sn_9]^{3-}$.¹²⁹ In a similar fashion, Sn_7R_2 ($R = C_6H_3-2,6-Dipp_2$) is an example of a metal-rich cluster of tin that features a rare pentagonal bipyramidal framework.¹³⁰ The same ligand was also employed in the synthesis of $Sn_4Ge_2R_2$, the first structurally characterized polyhedral cluster with two different heavier group 14 elements,¹³¹ though such mixed-metal systems¹³¹ are beyond the scope of this thesis.

Overall, neutral group 14 metalloids clusters are the least common for silicon and lead. Kira *et al.* have reported the sole known example of a cluster with an unsubstituted silicon atom, the spirocycle Si_5R_4 ($R = Si(tBuMe_2Si)_3$).¹³² For lead, Klinkhammer *et al.* have characterized two neutral metalloids clusters: a distorted icosahedron $Pb_{12}R_6$ and a decamer $Pb_{10}R_6$ ($R = Si(SiMe_3)_3$).¹³³ The number of germanium and tin atoms in neutral metalloids clusters varies from 5 to 15,^{129,131,134-139} with smallest clusters having only very few naked group 14 elements. The largest reported neutral metalloids cluster is the tin species $Sn_{15}R_6$ ($R = N(SiMe_3)Dipp$ or $N(SiMe_2Ph)Dipp$), published by Power *et al.* It consists of an Sn_9 body-centered distorted cube capped by six SnR units (Figure 16).¹³⁹

The synthesis of metalloids group 14 clusters can show significant variation with respect to the group 14 element. For example, octahedral Ge_6R_2 and pentagonal bipyramidal Sn_7R_2 ($R = C_6H_3-2,6-Dipp_2$) were prepared similarly, but the tin compound has one more unsubstituted metal atom in its structure.^{130,131} Naturally, the steric and electronic characteristics of the employed ligand play a role as well. For instance, cubane clusters are known for both germanium and tin, but the structures can have either four or six ligands.¹³⁵⁻¹³⁸ In a similar fashion, clusters Ge_9R_3R' ($R = Si(SiMe_3)_3$, $R' = ethyl$) and Sn_9R_3 ($R = C_6H_3-2,6-Trip_2$) have different numbers of ligands even though they share a similar square antiprismatic structure with five naked group 14 elements.^{129,140}

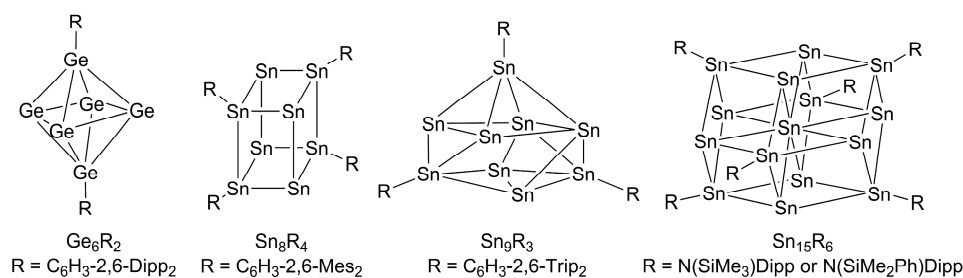


FIGURE 16 Illustrations of neutral metalloids germanium and tin clusters Ge_6R_2 , Sn_8R_4 , Sn_9R_3 , and $Sn_{15}R_6$.^{129,131,137,139}

2.4 Reactivity of heavier group 13 and 14 compounds toward small molecules

It was long thought that the chemistry of the heavier main group elements was not as rich as their transition metal congeners due to the absence of *d*-electrons.⁶⁶ However, the discoveries of multiply bonded and low-valent main group species,³¹ frustrated Lewis pairs,¹⁴¹ stable main group radicals, and singlet diradicaloid compounds¹⁴² have led to the realization that *p*-block elements can in some instances act similarly to transition metals, and interest in this new heterogeneous class of compounds has grown steadily. Today, it has been shown that compounds of the heavier group 13 and 14 elements can readily react with small molecules such as H₂, NH₃, CO, and olefins, which suggests that these systems have intrinsic potential in applications such as hydrogen storage and catalysis.

2.4.1 Reactivity of group 13 and 14 metallylenes

Although many group 13 metallylenes show monomer-dimer equilibrium in solution, their reactivity is characteristic to that of dimetallenes and will not be discussed herein (see section 2.4.2).^{13,40,143}

The combination of a lone pair of electrons (donor) and an empty *p*-orbital (acceptor) at the main group element in heavier carbene analogues is essential for their facile reactivity at low temperatures. For example, the morphologies of frontier orbitals in group 14 metallylenes match those of HOMO and LUMO in small molecules such as H₂ (Figure 17).⁴⁰ This leads to double donor-acceptor interactions and electron flow from the HOMO of H₂ to the LUMO of metallylene and *vice versa*. As a result, the orbital interactions weaken the single bond in H₂ so that oxidative addition occurs and the H-H bond is cleaved heterolytically.⁶⁶ The reactivity of heavier group 14 metallylenes with H₂ can be compared to that known for transition metal complexes (Figure 17). It is evident that the donor and acceptor orbitals in low-valent main group species play an analogous role to the *d*-orbitals in transition metal systems, which rationalizes the facile reactivity observed in both cases.

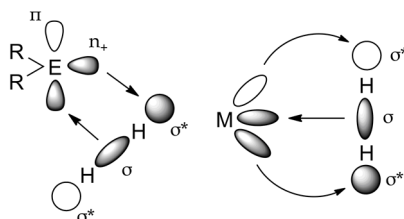


FIGURE 17 Frontier orbital interactions between group 14 metallylenes ER₂ and H₂ (left) compared to those involving transition metal (M) complexes (right).

The reactivity of neutral group 14 metallylenes can be divided into five categories: insertion, cycloaddition, reduction, oxidation, and coordination. In coordination reactions, the highly electrophilic metallylene can act as a Lewis acid toward typical Lewis bases.² However, because metallylenes exhibit both electrophilic and nucleophilic character, they can also be used as Lewis basic ligands for transition metals or other electrophilic main group compounds.^{144,145} Isocyanides are a particular group of ligands whose coordination with group 14 metallylenes can give rise to heterocumulene structures or to simple donor-acceptor complexes (Figure 18).¹⁴⁶⁻¹⁵⁰ The stannylene complex $R_2Sn \leftarrow CNMes$ ($R = C_6H_2-2,4,6-(CF_3)_3$) was originally characterized as a stannaketenimine, but further experimental studies on analogous tin and lead species confirmed that $R_2Sn \leftarrow CNMes$ is best described as a coordination compound.^{148,149} However, the experimental data for silylenes show much more variation with respect to the employed ligand, for which reason both silaketenimine and coordination compound depictions have been used.^{149,151,152} Recent theoretical work has shown that a particular bonding mode becomes adopted depending on the level of π -backbonding from the lone pair at the group 14 element to the empty π^* -orbital of the coordinating isocyanide.¹⁴⁷ Thus, in many cases, the bonding in metallylene-isocyanide adducts is somewhere between the two possible extremes (Figure 18).

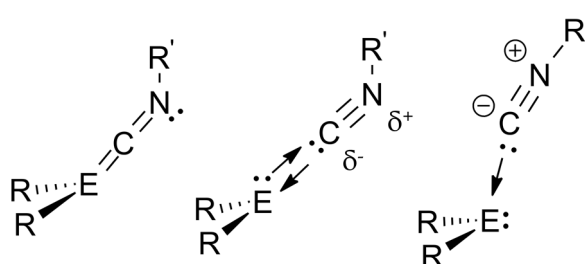


FIGURE 18 Three possible bonding descriptions for metallylene-isocyanide adducts.

Both *m*-terphenyl stabilized germlylenes and stannylenes have been shown to react with H_2 and NH_3 , giving either monomeric insertion products or bridged dimers with arene elimination.¹⁵³⁻¹⁵⁵ The obtained product depends on both the identity of the metal and the steric bulk of the employed ligand. However, the electronic structure of the ligand also plays a role, as evidenced by the outcome of the reaction of heteroleptic $SiRR'$ ($R = B(NDippCH)_2$ $R' = N(SiMe_3)Dipp$) and homoleptic SiR_2 ($R = SC_6H_3-2,6-Mes_2$) silylenes with H_2 : the former leads to the facile formation of a dihydrosilane insertion product H_2SiRR' even at $0\text{ }^\circ\text{C}$,³⁰ while the latter shows no reactivity.²⁹

Group 14 metallylenes react not only with H_2 and NH_3 but also with simple alkenes, alkynes, and related small molecules.^{146,156-162} The cycloaddition reactions of metallylenes with alkenes or alkynes produce [1 + 2] cycloadducts, whereas reactions with butadiene derivatives afford [1 + 4] cycloadducts.^{2,157,160} Insertion products $R_2E(X)R'$, $R_2E(H)R'$, and $R_2E(OH)R'$ can be obtained from reactions of metallylenes with haloalkanes $R'X$ ($X = \text{halogen}$), Brønsted acids

(HR'), or alcohols, respectively.¹⁶³⁻¹⁶⁵ Similar reactivity is also observed when treating *m*-terphenyl stabilized germylenes and stannylenes with trimethylgallium.¹⁶¹ However, the reaction of trimethylaluminum with stannylene gives a tin analogue of [1.1.1]propellane, whereas reactions involving plumbylenes lead to a diplumbene via metathesis. Lastly, the reaction between germylenes and CO has been reported to afford α -germyloxy ketones via C-C bond cleavage at room temperature.¹⁶⁶

2.4.2 Reactivity of group 13 and 14 dimetallenes and dimetallynes

Similarly to group 13 and 14 metallylenes, both dimetallenes and dimetallynes react readily with small molecules due to their favorable orbital characteristics.^{40,66} Group 13 dimetallenes have a lone pair type HOMO and a π -type LUMO, whereas group 14 dimetallynes have a π -type HOMO with a lone pair type LUMO. In group 14 dimetallenes, both the HOMO and LUMO are of lone pair type. The morphologies and energies of the orbitals are a good match with those of small molecules such as H₂ or alkenes (Figure 19). For example, the reaction of group 14 metallylenes with H₂ involves electron donation from the HOMO of the dimetallyne to the LUMO of the small molecule, along with a simultaneous electron donation from the HOMO of the small molecule to the LUMO of the dimetallyne. In case of alkenes, similar orbital interactions lead to cycloaddition and formation of a four-membered ring (Figure 19).

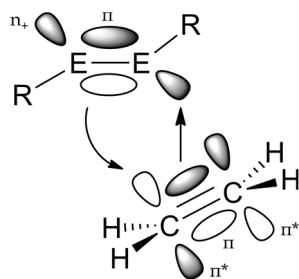
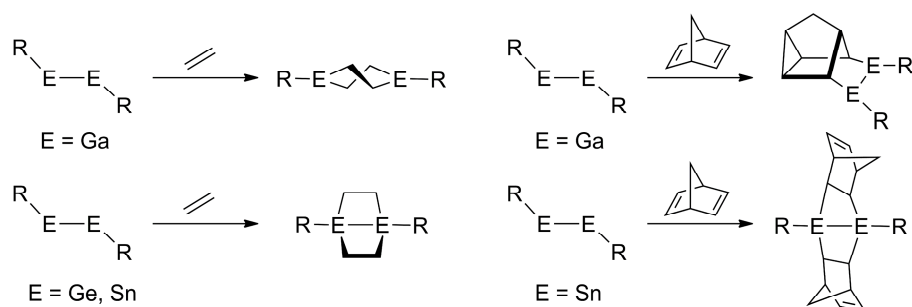


FIGURE 19 Frontier orbital interactions between group 14 dimetallynes REER and ethylene.

The reactivity of group 13 dimetallenes REER depends heavily on the metal. The isolation of dialuminenes RAlAIR is not possible due to their tendency to undergo cycloaddition with commonly used aromatic solvents (see section 2.2.1).^{50,51} For example, the benzene adduct of RAlAIR (R = C₆H₃-2,6-{CH(SiMe₃)₂}) undergoes exchange reactions with naphthalene, anthracene, and bis(trimethylsilyl)-acetylene, and therefore has the reactivity of a free dialuminene.⁵¹ The indium species RInInR (R = C₆H₃-2,6-Dipp₂) has been shown to react with N₂O and S₈ to yield dimeric aryliindium chalcogenides [RInCh]₂ (Ch = O or S).¹⁶⁷ Related indium and thallium chalcogenolates [RChIn]₂ and [RChTl]₂ (Ch = O or S) can be obtained using salt metathesis.¹⁶⁸⁻¹⁷⁰ Besides these two specific examples, very little is known of the reactivity of diindenes and dithallenes with small molecules.

Digallenes show the broadest reactivity toward small molecules of all group 13 dimetallenes. Terphenyl derivatives generally form a monomer-dimer equilibrium in solution, but their reactivity is that of the dimers, even though initial experiments suggested the involvement of monomers in the formation of a Ga_2C_8 ring from RGaGaR ($\text{R} = \text{C}_6\text{H}_2\text{-2,4,6-Trip}_3$) and 2,3-dimethyl-1,3-butadiene.¹⁰⁵ However, subsequent theoretical work has shown that the reactions of monomeric GaR species with H_2 and alkenes are energetically disfavored irrespective of the *m*-terphenyl ligand.¹⁴³ Concomitant experiments conducted with the sterically bulky, and therefore exclusively monomeric, GaR ($\text{R} = 3,5\text{-}i\text{Pr}_2\text{-C}_6\text{H}_2\text{-2,6-Trip}_3$) substantiated the computational results, as the gallylene displayed no reactivity toward ethylene or H_2 .

Digallenes such as RGaGaR ($\text{R} = \text{C}_6\text{H}_3\text{-2,6-Trip}_2$ or $4\text{-SiMe}_3\text{-C}_6\text{H}_2\text{-2,6-Trip}_2$) react with H_2 and NH_3 even at room temperature, giving the bridged insertion species $\{\text{RGa}(\mu\text{-H})\text{H}\}_2$ and $\{\text{RGa}(\mu\text{-NH}_2)\text{H}\}_2$, respectively.¹⁷¹ The slightly less sterically bulky digallene RGaGaR ($\text{R} = \text{C}_6\text{H}_3\text{-2,6-Dipp}_2$) is known to react with a range of simple acyclic alkenes such as ethylene, propene, 1-hexene, phenylacetylene, and styrene (Scheme 1).^{11,172} These reactions led to the cleavage of the Ga–Ga bond and the formation of a six-membered 1,4-digallacyclohexane ring. The reactivity of RGaGaR ($\text{R} = \text{C}_6\text{H}_3\text{-2,6-Dipp}_2$) with cyclic polyolefins like norbornadiene (Scheme 1), 1,3,5,7-cyclooctatetraene, 1,3-cyclopentadiene, and 1,3,5-cycloheptatriene is also facile, but the digallene does not react similarly with cyclic olefins such as cyclohexene and cyclopentene because of increased steric strain.¹⁷³ The reaction between RGaGaR and cyclooctatetraene is an interesting one, as it is the only example of a reaction between a digallene and a polyolefin in which the Ga–Ga bond is cleaved. In reactions with other polyolefins, the Ga–Ga bond always remains intact and polyolefin insertion gives a cyclic end product.



SCHEME 1 The reactivity of *m*-terphenyl stabilized digallenes (top) and digermynes/distannynes (bottom) with ethylene and norbornadiene.^{172,174}

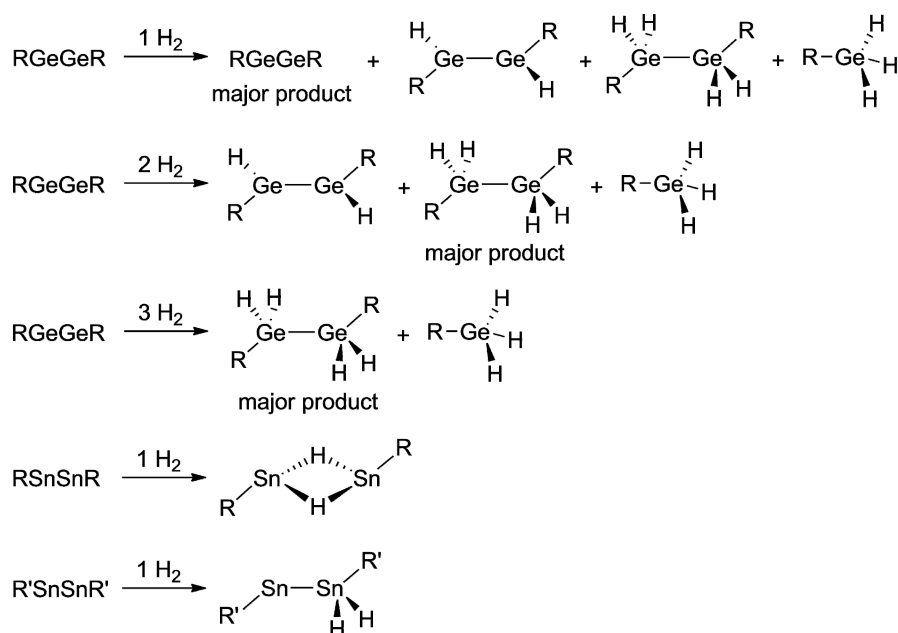
The heaviest group 14 dimetallenes, distannenes, and diplumbenes tend to dissociate in solution, for which reason the reactivity studies are virtually nonexistent. Only a few examples are reported for tin and none for lead.^{64,175} In contrast, the lighter disilenes and digermenes show more diverse reactivity. For example, disilenes R_2SiSiR_2 react with various Lewis bases, such as water, alcohols, amines, and isocyanides, and form addition products,^{176,177} whereas

digermenes are known to activate small molecules like H₂O, O₂, azides, alkenes, and alkynes.¹⁷⁸⁻¹⁸² Despite the myriad of reactions observed for disilenes and digermenes, their reactivity with small molecules is not discussed herein, as all studies have been performed for systems other than *m*-terphenyl stabilized compounds and are therefore beyond the scope of this thesis.

The reactivity of group 14 dimetallynes REER differs from that observed for group 13 dimetallenes due to their different number of valence electrons and, hence, differing frontier orbital morphologies.⁴⁰ While a reaction between a digallene and ethylene leads to Ga–Ga bond breaking, RGeGeR and RSnSnR (R = C₆H₃-2,6-Dipp₂) give cycloaddition products with a metal–metal bond (Scheme 1).¹⁷⁴ The reactions of dimetallenes and dimetallynes with cyclic polyolefins such as norbornadiene also afford different products (Scheme 1).^{183,184} Although group 13 dimetallenes are not known to react with cyclic olefins, both *m*-terphenyl stabilized digermynes and distannynes undergo C–H activation with cyclopentene to give a cyclopentadienyl anion bound to a mononuclear group 14 element species ER.^{184,185}

Even though the reactivity of diplumbynes RPbPbR remains unexplored,¹⁸⁶ other dimetallynes react with a wide variety of small molecules including H₂,¹⁸⁷ alkenes,^{188,189} isocyanides,¹⁹⁰⁻¹⁹³ azides,¹⁹⁴ O₂,¹⁹⁵ and N₂O.¹⁹⁶ Most relevant to this thesis, however, are the reactions of *m*-terphenyl stabilized systems with H₂ and isocyanides. Concerning the latter, isocyanides form coordination complexes with *m*-terphenyl stabilized digermynes and distannynes, and both monoadducts RGeGeR(CN^{*t*}Bu) (R = C₆H₃-2,6-Dipp₂)¹⁹¹ and diadducts (R'NC)REER(CNR') (E = Ge or Sn; R = C₆H₃-2,6-Dipp₂; R' = ^{*t*}Bu or Mes) have been characterized.^{192,193} However, none of the reported adducts shows further reactivity, though the reaction of RGeGeR (R = C₆H₃-2,6-Dipp₂) with CNPh leads to cyclization and nitrile coupling via formation of a C–C bond.¹⁹¹

Both digermynes and distannynes react with H₂ by addition to the E–E bond. The reaction of RGeGeR (R = C₆H₃-2,6-Dipp₂) affords different products depending on the employed stoichiometry (Scheme 2).¹⁹⁷ For comparison, the use of an amido ligand allows the reaction to proceed even in the solid state and leads to the asymmetric monohydrogenation product RGeGe(H)₂R (R = N(SiMe₃)(4-Me-C₆H₂-2,6-{C(H)Ph₂})₂)^{197,198} or affords the symmetric hydrido-digermene R(H)GeGe(H)R (R = N(Si^{*i*}Pr₃)(4-^{*i*}Pr-C₆H₂-2,6-{C(H)Ph₂})₂).¹⁸⁷ These differences in reactivity can be correlated with the electronic structure of the ligand and how it affects the E–E bonding in the dimetallyne. The reactions of distannynes with H₂ yield hydrogen bridged products R(H)SnSn(H)R independent of stoichiometry and ligand type (amido or *m*-terphenyl).^{130,199} When using a very bulky ligand, the asymmetric mixed-valent tin dimer RSnSn(H)₂R (R = 3,5-^{*i*}Pr₂-C₆H-2,6-Trip₂) can be obtained. The different reactivity of digermynes and distannynes can be ascribed, at least in part, to relativistic effects (inert-pair effect) as well as to the ability of RGeGe(H)₂R to undergo further reactions with H₂.¹⁹⁷ Computational and theoretical evidence suggest that the diradical character of digermynes and distannynes can also play a role.²⁰⁰

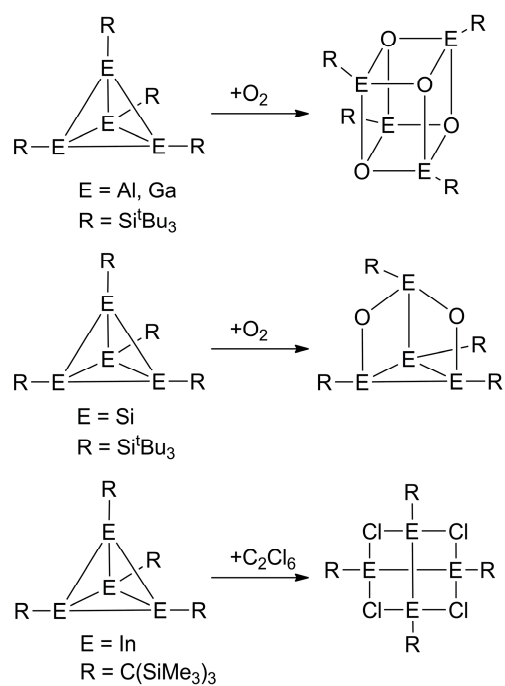


SCHEME 2 The reactivity of dimetallynes REER (E = Ge, Sn; R = C₆H₃-2,6-Dipp₂) and R'SnSnR' (R' = 3,5-ⁱPr₂-C₆H-2,6-Trip₂) with H₂.^{130,197,199}

2.4.3 Reactivity of group 13 and 14 clusters

There are virtually no reports of reactions between group 13 and 14 clusters E_nR_m (n ≥ m) and small molecules. The only well-characterized examples involve tetrahedral clusters E₄R₄ (n = m), which have been reported to react with O₂, halogens, and chalcogens.^{176,201-204} For example, the aluminum and gallium tetrahedra E₄R₄ react with O₂ by insertion. The oxygen molecules insert into the E-E bonds, resulting in a compound that has a cubane structure incorporating four oxygen atoms (Scheme 3).

The low number of reports addressing the reactivity of group 13 and 14 clusters can be understood because these species are extremely difficult to synthesize. The reactions are usually slow, and as multiple side products are also formed, the yields range from poor to mediocre.^{79,176} Furthermore, in many cases, the clusters are not readily soluble in organic solvents, which hampers both characterization and isolation. Though solubility and stability can be increased by appropriate substitution, too much steric protection can block the metallic core from further reactivity, which is of primary interest.²⁰⁵



SCHEME 3 Selected examples of the reactivity reported for tetrahedral group 13 and 14 clusters E_4R_4 with O_2 and halogen donors.²⁰¹⁻²⁰⁴

3 RESULTS AND DISCUSSION

Only a brief description of the methods used in the analysis and characterization of the synthesized compounds is given in the beginning of this chapter; a more detailed account of the work performed can be found in Papers I–V.

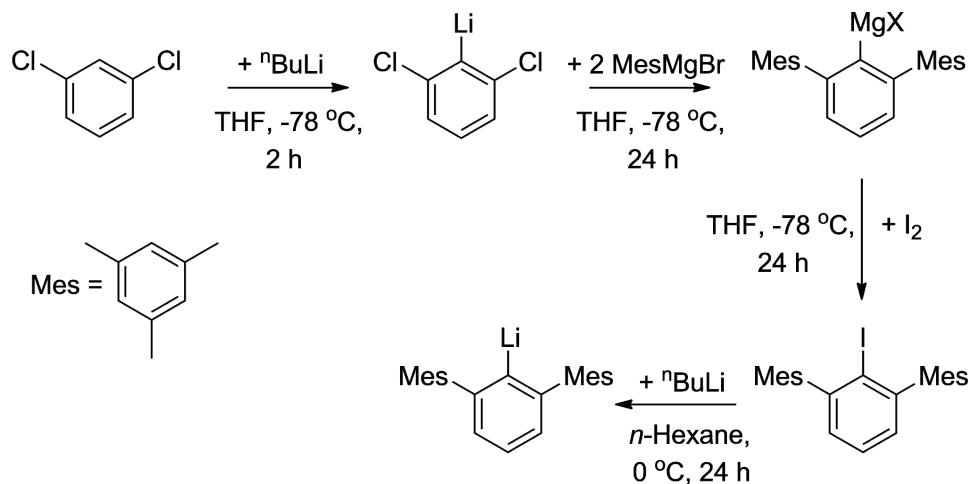
3.1 Experimental methods

All experimental manipulations and physical measurements were done under strictly anaerobic and anhydrous conditions using modified Schlenk line techniques under an inert atmosphere or in a drybox. The X-ray crystal structure determinations were done with either a Bruker APEX II diffractometer using Mo K α radiation or with a Bruker DUO diffractometer using Cu K α radiation. For well-diffracting and medium to large crystals, Mo radiation was used, whereas Cu radiation was chosen for weakly diffracting or small crystals. The graphics were produced with the program Diamond 3.²⁰⁶ The ^1H , ^{13}C , and ^{119}Sn NMR spectroscopic data were recorded as C_6D_6 or d_8 -toluene solutions on Varian Inova 400 or 600 MHz spectrometers and referenced to known standards. The solid state infrared spectroscopy (IR) measurements were done as Nujol mulls between CsI plates on a PerkinElmer 1430 ratio recording infrared spectrometer. All UV-visible spectra were recorded as dilute solutions using an Olis 17 Modernized Cary 14 UV/vis/NIR spectrophotometer. Melting points were determined on a Mel-Temp II apparatus using glass capillaries sealed with vacuum grease. Elemental analyses were performed using an Elementar Analysensysteme GmbH Vario EL III element analyzer.

3.1.1 Ligand synthesis

The ligand used in Papers IV and V was synthesized according to a published synthesis (Scheme 4).^{207,208} First, 1,3-dichlorobenzene was treated with *n*-butyllithium (*n*BuLi) in tetrahydrofuran (THF) at $-78\text{ }^\circ\text{C}$ and stirred for 2 h. The

Grignard reagent, MesMgBr, in THF was cooled to 0 °C and added dropwise to the reaction mixture. After a reaction time of 24 h, the dark solution was treated with excess I₂. Subsequent work-up and recrystallization afforded a white, air and moisture stable ArI (Ar = C₆H₃-2,6-Mes₂) as a crystalline solid. For subsequent reactions with main group element halides, the ligand was treated with ⁿBuLi to obtain the reactive aryl lithium salt ArLi.



SCHEME 4 Synthetic route to the ligand ArLi (X = Cl or Br; Ar = C₆H₃-2,6-Mes₂).

3.2 Computational methods

All computational work reported in Papers I-V was performed at the density functional theory (DFT) level with Gaussian09 (Revision C.1 or D.1),²⁰⁹ Turbomole (v6.3 or v6.6),²¹⁰ and ADF (2009.01 or 2014.01)²¹¹ program packages. Geometry optimizations were performed with the PBE1PBE exchange correlation functional²¹²⁻²¹⁵ using either def-TZVP or def2-TZVP basis sets;²¹⁶ for heavy elements In and Sn, the core electrons were treated with an effective core potential.²¹⁷ Calculations were performed for model systems (using Ph or the parent *m*-terphenyl ligand) or for experimentally characterized compounds containing the bulky Ar ligand, in which case an empirical dispersion correction was applied.^{218,219} The nature of stationary points found (minimum or saddle point) was in most cases confirmed by full frequency calculations. The bonding in metallylene-isocyanide adducts was examined within the framework of energy decomposition analysis.²²⁰⁻²²² These analyses were performed for optimized geometries at the PBE1PBE/TZ2P²²³ level of theory with scalar relativistic effects treated using the zeroth-order regular approximation.²²⁴⁻²²⁶ Graphics were created with the programs GaussView²²⁷ or gOpenMol.^{228,229}

3.3 Isocyanide adducts of a diarylgermylene

Backbonding, the release of electrons from an nd orbital of a metal into the empty π^* -antibonding orbital of a ligand, is a central concept for the description of metal–ligand interactions in transition metal complexes. Carbonyl (CO) and isocyanide (CNR) ligands are among the most widely studied π -acceptors, and the use of carbonyl stretching frequencies to quantify backbonding effects in transition metal complexes is a well-known technique.

The Lewis adducts of isocyanides with group 14 metallylenes have typically been classified either heterocumulenic species with strong double bonds ($R_2E=C=N-R'$) or simple donor–acceptor complexes with a weak coordinative interaction ($R_2E\leftarrow CNR'$) (see Section 2.4.1). Even though structural evidence had suggested that a division to two extremes might be too simplistic, the electronic structures of metallylene–isocyanide adducts had received only limited attention. It was therefore of interest to prepare and characterize the first isocyanide adduct of a germylene, as it was expected to have molecular and electronic structures in between the heterocumulenic and donor–acceptor formulations. Thus, the Ge–C bond in R_2GeCNR' could display unique backbonding effects even though the isocyanide adducts of digermynes $RGeGeR$ show all the characteristics of simple donor–acceptor complexes (see Section 2.4.2). Backbonding interactions in metallylene–isocyanide adducts are of particular interest as they would be analogous to those in transition metal complexes and could therefore enable reactivity typically unseen for main group element species.

3.3.1 Reaction of a diarylgermylene with CN^tBu

The Lewis adduct Ar_2GeCN^tBu (**1**) was obtained by reacting a pentane solution of diarylgermylene $GeAr_2$ with excess *tert*-butyl isocyanide, CN^tBu , at room temperature. The reaction was completed within 15 min and storage of a concentrated hexane solution at *ca.* 7 °C overnight afforded **1** as yellow crystals.

The solid state structural data of **1** showed that the germanium is three-coordinate, as expected (Figure 20). The asymmetric unit contains two independent molecules of **1** with nearly identical structural parameters. Of particular interest are the Ge– CN^tBu bond length (average value 2.052(3) Å) and the Ge–C– N^tBu bond angle (average value 157.0(2)°). IR spectroscopy showed that the isocyanide C–N stretching mode appears at a slightly lower frequency (2132 cm^{-1}) than that of free *tert*-butyl isocyanide (2134 cm^{-1}), which, together with the structural data, suggests that a flow of electrons from the lone pair on germanium to the π^* -orbital of *tert*-butyl isocyanide could take place.

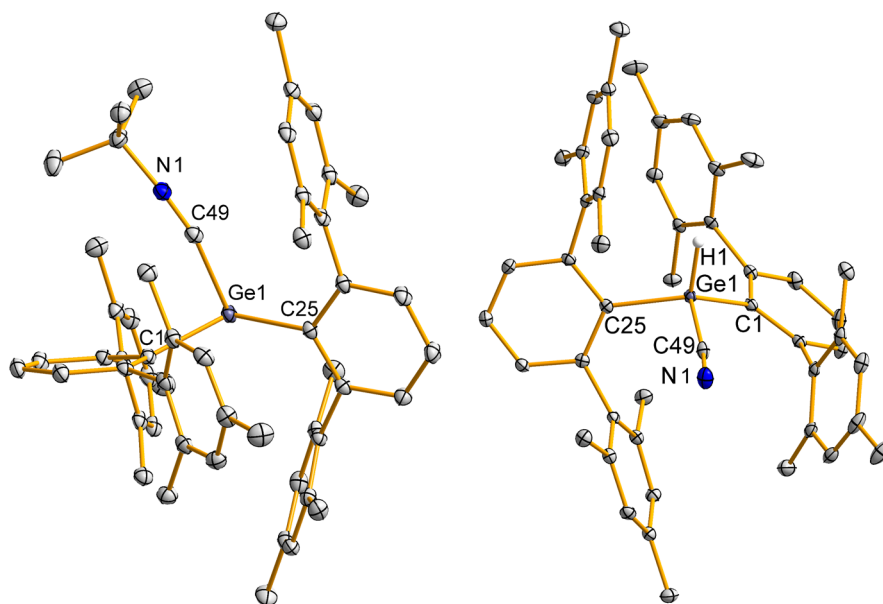


FIGURE 20 Thermal ellipsoid plot (30%) of compound **1** (left) and **2** (right). Carbon bound hydrogen atoms and solvent molecules have been omitted for clarity. Only one of the two crystallographically independent molecules of **1** is shown. Selected bond lengths (Å) and angles (°): **1**; Ge(1)-C(1): 2.063(2), Ge(1)-C(25): 2.038(2) Ge(1)-C(49); 2.077(2), C(49)-N(1); 1.154(3), C(1)-Ge(1)-C(25): 113.49(7), Ge(1)-C(49)-N(1): 157.1(2). **2**; Ge(1)-C(1): 1.973(2), Ge(1)-C(25): 1.972(2), Ge(1)-C(49): 1.952(2), C(49)-N(1): 1.145(3), Ge(1)-H(1): 1.48(3), C(1)-Ge(1)-C(25): 124.9(1), Ge(1)-C(49)-N(1): 170.1(2).

Because the nature of germanium–isocyanide bonding in **1** was of interest, the adduct was investigated computationally using DFT. The optimized structure of **1** was found to be in good agreement with the experimental data. For example, the average Ge–CN^tBu bond length was calculated to be 2.051 Å, whereas the Ge–C–N^tBu bond angle was 155.7°. The calculations also showed that the $\nu(\text{CN})$ stretching band of **1** appears at lower frequency (2234 cm⁻¹) relative to the free *tert*-butyl isocyanide (2247 cm⁻¹), even though the absolute values are not on par with the experimental data. Quantitative data of bonding in **1** was obtained with the energy decomposition analysis (EDA), which revealed that the total orbital interaction energy in the germanium–isocyanide bond is -357 kJ mol⁻¹. The division of this term to bonding and backbonding contributions was performed with the constrained space orbital variation procedure. In this methodology, the backbonding interaction can be quantified by removing all unoccupied molecular orbitals from the germylene in the EDA. In such a case, the total orbital interaction term is -148 kJ mol⁻¹. Moreover, if unoccupied orbitals are removed from the isocyanide, the backbonding interaction becomes impossible and the total orbital interaction term is -244 kJ mol⁻¹. Consequently, the backbonding interactions account for roughly one third of the total orbital interaction energy in the germanium–isocyanide bond. This interaction is clearly visible in the HOMO of **1**, which shows a bonding

combination between the lone pair of the germylene and π^* -orbital of the isocyanide (Figure 21).

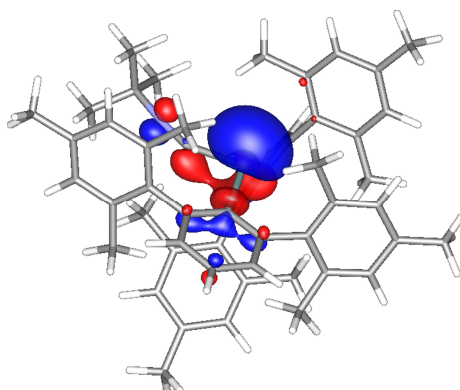


FIGURE 21 The HOMO of compound **1**.

Experimentally, it was observed that when the reaction mixture of **1** was warmed to 75 °C in hexanes and stirred under static vacuum overnight, the yellow color of the solution faded. After work-up and recrystallization from toluene/pentane, colorless crystals were harvested in quantitative yield. Subsequent X-ray diffraction studies showed that the product, $\text{Ar}_2\text{Ge}(\text{H})\text{CN}$ (**2**), contains a tetrahedral germanium bonded to two aryl substituents, a hydride and a cyanide (Figure 20); the soluble byproduct from the reaction was found to be isobutene, based on ^1H NMR spectroscopy. This data showed that the complex **1** had undergone facile C–H bond activation that leads to dealkylation of the isocyanide and formation of a germanium(IV) hydride/cyanide product. As similar reactivity is known for transition metal complexes of isocyanides, the mechanistic details of this reaction were of interest.

Computational investigations on the mechanism converting **1** to **2** and isobutene revealed that the only energetically feasible pathway involves a transition state in which C–H bond activation and proton transfer occur simultaneously with N–*t*Bu bond cleavage and elimination of isobutene (Figure 22). The overall Gibbs free energy change of the reaction was calculated to be exergonic by -101 kJ mol^{-1} (with respect to GeAr_2 and CN^tBu) with an activation barrier of 103 kJ mol^{-1} (activation enthalpy of 97 kJ mol^{-1}). The calculated activation enthalpy is slightly greater than that afforded by an Eyring plot (74 kJ mol^{-1}), which could indicate that the investigated mechanism is not the lowest energy pathway. For this reason, the possibility of a radical mechanism involving homolytic bond cleavage was tested by heating **1** with a five-fold excess of isocyanide and in the presence of excess 1,4-cyclohexadiene, an excellent hydrogen donor for alkyl radicals. Because no trace of isobutane was detected by ^1H NMR spectroscopy, both computational and experimental results support the concerted reaction mechanism and the presence of a highly activated germanium center in **1**.

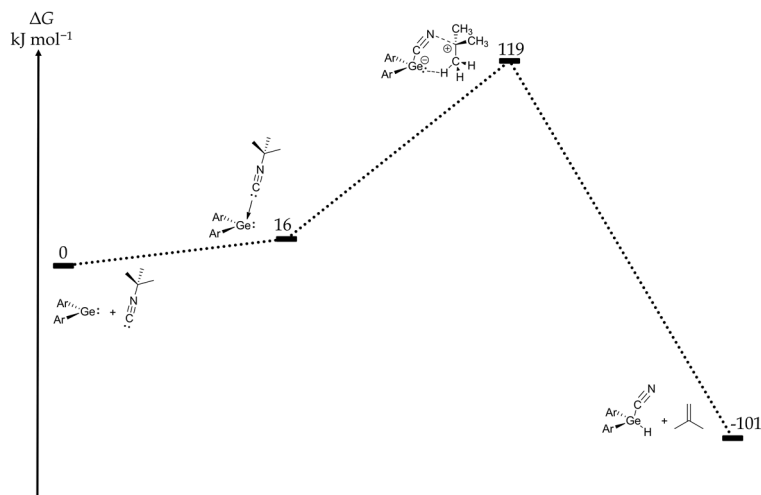


FIGURE 22 Calculated mechanism and Gibbs free energies (ΔG , kJ mol^{-1}) for the conversion of **1** to **2** and isobutene.

3.3.2 Reaction of a diarylgermylene with CNMe^{II}

The facile C-H activation observed for the *tert*-butyl isocyanide adduct of diarylgermylene gave an incentive to examine the reactivity of GeAr_2 with other isocyanides. Consequently, treating GeAr_2 with a ten-fold excess of methyl isocyanide, CNMe , in hexane afforded the adduct Ar_2GeCNMe (**3**) as yellow crystals after recrystallization. The solid state structure of **3** is similar to the adduct **1** (see section 3.3.1) with a three-coordinate germanium center bound to two aryl ligands and a molecule of methyl isocyanide (Figure 23).

When the reaction between GeAr_2 and CNMe was allowed to proceed overnight, the color of the solution changed to deep red. Subsequent work-up gave a crystalline product whose structure was determined with single crystal X-ray diffraction. Crystallography showed that the product, denoted hereafter as **5''**, contained three coupled methyl isocyanide moieties, which together with the germanium atom formed an azagermacyclopentadienyl heterocycle (Figure 24). The structure of **5''** also showed that one of the aryl ligands had migrated from germanium to the isocyanide carbon and a proton transfer had occurred from one of the isocyanide methyl groups to an imine-nitrogen atom in an adjacent isocyanide. Consequently, the product **5''** involves a three-fold insertion of methylisocyanide into the germanium-carbon bond of GeAr_2 . This reactivity is reminiscent of transition metal mediated coupling of isocyanides, for which reason the exact mechanism of the formation of **5''** was of interest.

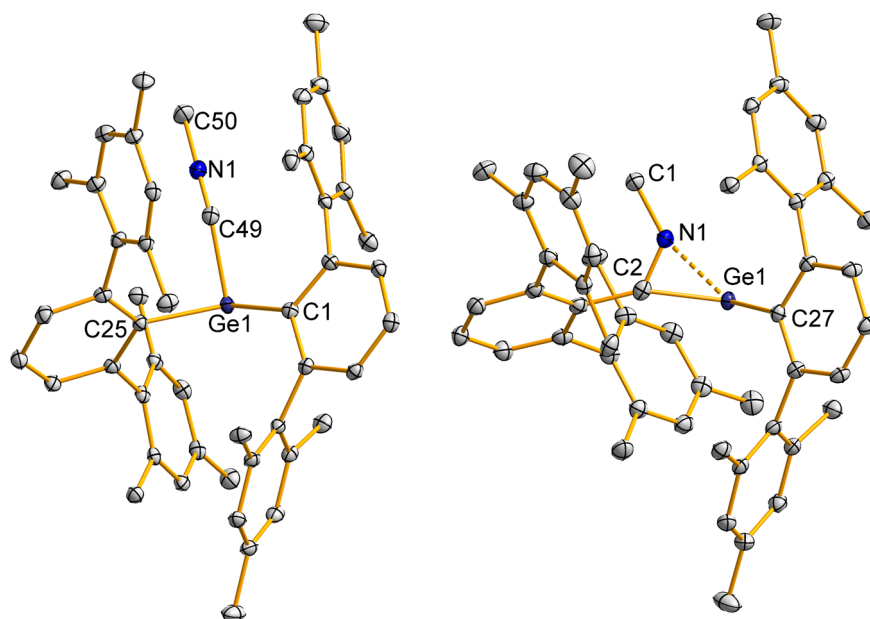


FIGURE 23 Thermal ellipsoid plot (30%) of compound **3** (left) and **3'** (right). Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°) **3**: Ge(1)-C(1): 2.057(3), Ge(1)-C(25): 2.061(3), Ge(1)-C(49): 2.028(4), C(49)-N(1): 1.164(5), C(1)-Ge(1)-C(25): 116.7(1). Ge(1)-C(49)-N(1): 156.6(3). **3'**: Ge(1)-C(27): 2.046(4), Ge(1)-C(2): 2.021(5), Ge(1)-N(1): 2.104(4), C(2)-N(1): 1.271(5), C(2)-Ge(1)-C(27): 107.4(2), Ge(1)-N(1)-C(1): 155.2(3), Ge(1)-C(2)-N(1): 75.6(3).

Because the formation of either **3** or **5''** was dictated by time, it was envisaged that by using a nearly stoichiometric amount of isocyanide, an intermediate along the reaction pathway could be trapped. For this reason, GeAr₂ was reacted with 1.5 equivalents of CNMe in hexane. After work-up and crystallization, the product **3'** could be isolated as red crystals of X-ray quality. Subsequent crystallographic structure determination (Figure 23) showed that **3'** is a one-fold insertion product in which methyl isocyanide has migrated into the Ge(1)-C(aryl) bond. The migratory insertion is accompanied by a simultaneous lengthening of the C≡N triple bond in **3** (1.164(5) Å) to what is essentially a C=N double bond in **3'** (1.271(5) Å). The structure of **3'** is also indicative of a dative Ge–N interaction, which is, however, strained, and therefore presumably weak.

Subsequent changes to the stoichiometry of the reaction between GeAr₂ and CNMe did not allow the isolation of any other intermediates than **3'** on the reaction pathway. For this reason, multiple plausible pathways leading from **3** to **5''** were examined computationally using DFT. However, only one of the many investigated routes was found to be feasible in terms of associated energy changes. These calculations were initially performed for the model germylene GePh₂, but subsequent computational work using *m*-terphenyl germylenes has confirmed that the established mechanism remains reasonable despite the significant increase in the steric bulk of the ligand.

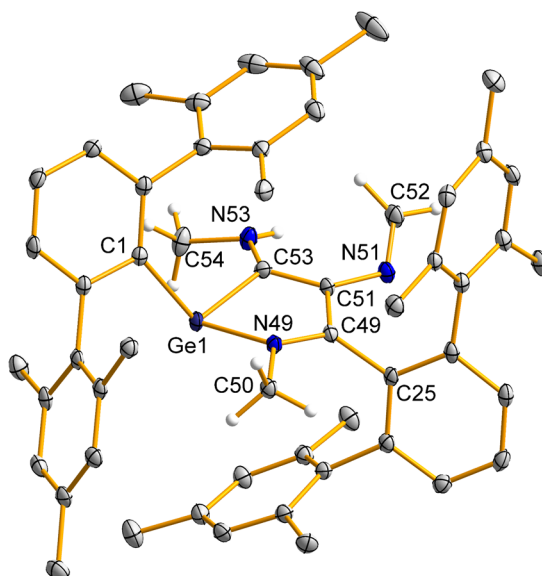


FIGURE 24 Thermal ellipsoid plot (30%) of compound **5''**. Hydrogen atoms of the aryl ligands have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)-C(53): 1.992(3), C(53)-N(3): 1.345(4), C(51)-C(53): 1.401(4), C(51)-N(2): 1.265(4), N(2)-C(52): 1.264(4), C(49)-C(51): 1.423(4), C(49)-N(1): 1.333(3), N(1)-Ge(1): 1.968(2), C(1)-Ge(1)-C(53): 107.9(1), C(1)-Ge(1)-N(1): 108.5(1), Ge(1)-N(1)-C(49): 111.4(2), Ge(1)-C(53)-C(51): 110.2(2), C(51)-N(2)-C(52): 120.1(3), C(49)-C(51)-C(53) 114.9(2).

The mechanism for the reaction between GePh_2 and CNMe begins with the formation of the adduct $\mathbf{3}_{\text{Ph}}$, which was found to be strongly favored ($\Delta G = -35 \text{ kJ mol}^{-1}$), followed by a small activation barrier (70 kJ mol^{-1} with respect to the adduct $\mathbf{3}_{\text{Ph}}$) for the formation of the migratory insertion product $\mathbf{3}'_{\text{Ph}}$ (Figure 25). Overall, the formation of the one-fold insertion product $\mathbf{3}'_{\text{Ph}}$ is a strongly favored process, with an energy difference of -67 kJ mol^{-1} with respect to GePh_2 and CNMe .

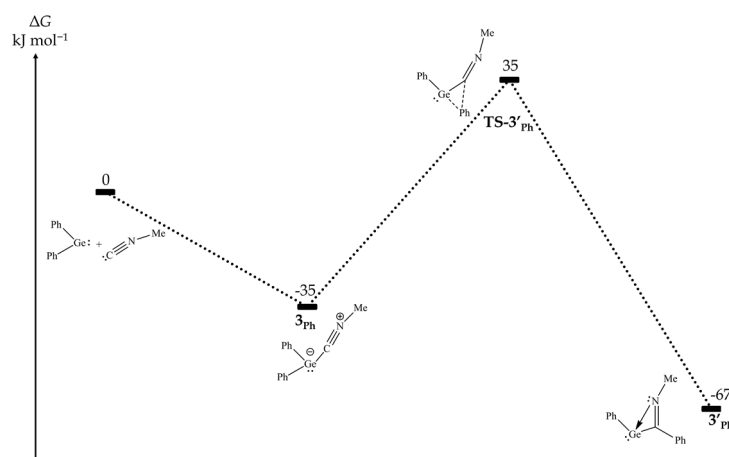


FIGURE 25 Calculated mechanism and Gibbs free energies (ΔG , kJ mol^{-1}) for the formation of $\mathbf{3}'_{\text{Ph}}$.

The dative Ge-N bond in $3'_{\text{Ph}}$ is relatively weak and easily broken in the presence of excess CNMe. The addition of a second equivalent of isocyanide to $3'_{\text{Ph}}$ gives the adduct 4_{Ph} , which can undergo a second migratory insertion with a transition state similar to $3'_{\text{Ph}}$ (Figure 26). The activation barrier of this process is comparable to the first insertion (86 kJ mol^{-1}) and the formation of the azagermacyclobutene $4'_{\text{Ph}}$ is overall a favored process, with an energy difference of -46 kJ mol^{-1} with respect to 4_{Ph} . Next, the reaction continues with a third migratory insertion, yielding the heterocycle $5'_{\text{Ph}}$ (Figure 27). This reaction step has a large energy gain (-98 kJ mol^{-1} with respect to 5_{Ph}), which can be understood in terms of the structure of $5'_{\text{Ph}}$. This structure shows less ring strain than either $3'_{\text{Ph}}$ or $4'_{\text{Ph}}$ and therefore also has the strongest Ge-N dative interaction.

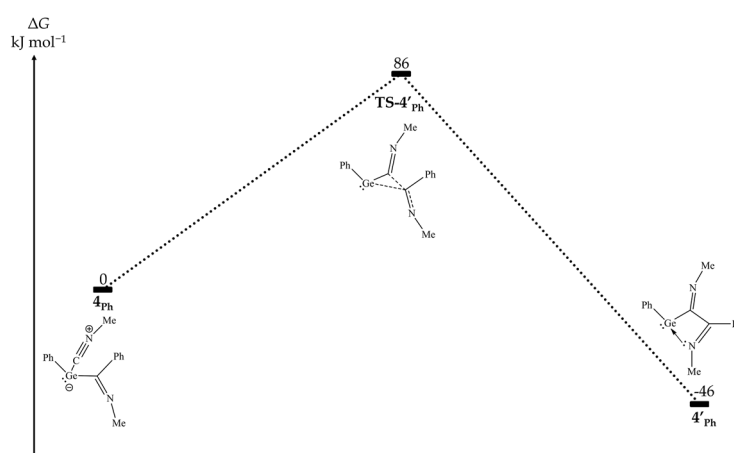


FIGURE 26 Calculated mechanism and Gibbs free energies (ΔG , kJ mol^{-1}) for the formation of $4'_{\text{Ph}}$.

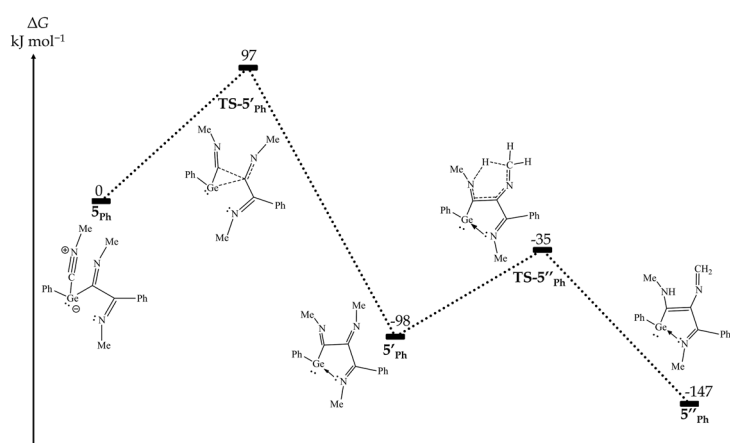


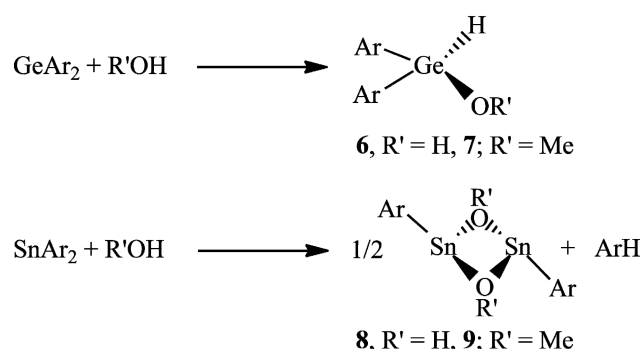
FIGURE 27 Calculated mechanism and Gibbs free energies (ΔG , kJ mol^{-1}) for the formation of $5''_{\text{Ph}}$.

Lastly, the formation of $5''_{\text{Ph}}$ from $5'_{\text{Ph}}$ involves a proton transfer from one of the methyl groups to an imine-nitrogen atom in an adjacent isocyanide (Figure 27). This reactivity is allowed by the proximity of the two coupled methylisocyanide moieties. The final product $5''_{\text{Ph}}$ is calculated to be 49 kJ mol^{-1} more stable than $5'_{\text{Ph}}$, possibly for steric reasons: there is severe steric strain associated with the two adjacent imine bonds, for which reason the five-membered ring is significantly more puckered in $5'_{\text{Ph}}$ than in $5''_{\text{Ph}}$. The transfer of hydrogen from carbon to nitrogen relieves this strain, leading to a more planar and less strained structure for the five-membered ring and, hence, to a shorter, and thereby presumably stronger, Ge–N dative bond.

3.4 Reactions of diarylmetylenes with H_2O or MeOH^{III}

Heavier group 14 metallylenes have been shown to react with various small molecules such as CO , H_2 , NH_3 , and C_2H_4 under mild conditions (see section 2.4.1).^{3,153,154,156,166,198} For example, the *m*-terphenyl stabilized germylene and stannylene EAr_2 both react with inorganic acids to give insertion products of the formula $\text{Ar}_2\text{E}(\text{H})\text{X}$ ($\text{E} = \text{Ge}$ or Sn ; $\text{X} = \text{CN}$, N_3 , or F).¹⁶⁴ However, the reactivity of these metallylenes toward NH_3 is vastly different: while the germylene gives an oxidative insertion product $\text{Ar}_2\text{Ge}(\text{H})\text{NH}_2$, the reaction between the corresponding stannylene and NH_3 leads to arene elimination and formation of a bridged $\{\text{ArSn}(\mu\text{-NH}_2)\}_2$ species.¹⁵⁴ The different reactivity of EAr_2 toward NH_3 has been probed computationally and the results unambiguously showed the dependence of the reaction mechanism on the identity of the group 14 element. In contrast, the experimental results by Pörschke *et al.*¹⁶³ showed that the acyclic germylenes and stannylenes $\text{E}\{\text{CH}(\text{SiMe}_3)_2\}_2$ ($\text{E} = \text{Ge}$ or Sn) both react with water or methanol by oxidative addition resulting in the $\{(\text{Me}_3\text{Si})_2\text{HC}\}_2\text{E}(\text{H})\text{OR}'$ ($\text{R}' = \text{H}$ or Me) insertion products.

The insertion of small molecules to transient tetrylenes, silylenes or germylenes stabilized by small alkyl (Me) or aryl (Ph) substituents, have been extensively studied both experimentally and computationally.^{230–236} These investigations have revealed that the insertion of a tetrylene to an O–H bond proceeds via the formation of a Lewis acid-base complex $\text{R}_2\text{E}-\text{OHR}'$ ($\text{E} = \text{Si}$ or Ge ; $\text{R} = \text{H}$, Me , or Ph), followed by a proton transfer from oxygen to the tetrylene. Thus, these species give rise to the oxidative addition product $\text{R}_2\text{E}(\text{H})\text{OR}'$ similarly to the acyclic tetrylenes studied by Pörschke *et al.* Another possible reaction pathway would be the elimination of H_2 from the adduct $\text{H}_2\text{E}-\text{OHR}'$ resulting in a HEOR' species, but this has not been observed experimentally. Hence, it was of interest to study the reactivity of *m*-terphenyl stabilized metallylenes EAr_2 ($\text{E} = \text{Ge}$ or Sn) toward hydroxyl compounds to see if their reactivity parallels that of other tetrylenes or whether both oxidative addition and arene elimination would be observed depending on the group 14 element (Scheme 5).



SCHEME 5 Reactions of EAr_2 ($\text{E} = \text{Ge}$ or Sn) with $\text{R}'\text{OH}$ ($\text{R}' = \text{H}$ or Me).

The reaction between GeAr_2 and water or methanol was performed in Et_2O at $-78\text{ }^\circ\text{C}$. Stirring the reaction mixtures for 24 to 48 hours at room temperature led to gradual fading of the purple color of the metallylene. After concentration and storing the mother liquor at $-28\text{ }^\circ\text{C}$, colorless crystals were obtained from both reactions. Subsequent solid state X-ray diffraction studies showed the formation of oxidative insertion products $\text{Ar}_2\text{Ge}(\text{H})\text{OR}'$ (**6**, $\text{R}' = \text{H}$; **7**, $\text{R}' = \text{Me}$) with comparable structures (Figure 28). The germanium atom in **6** and **7** is tetrahedrally coordinated to two aryl ligands, an oxygen atom from the hydroxyl or methoxy group, and a hydrogen atom. Although the germanium bound hydrogen atoms were not clearly visible in the electron difference map of **6** and **7**, both IR and ^1H NMR spectroscopy confirmed their presence in the structures.

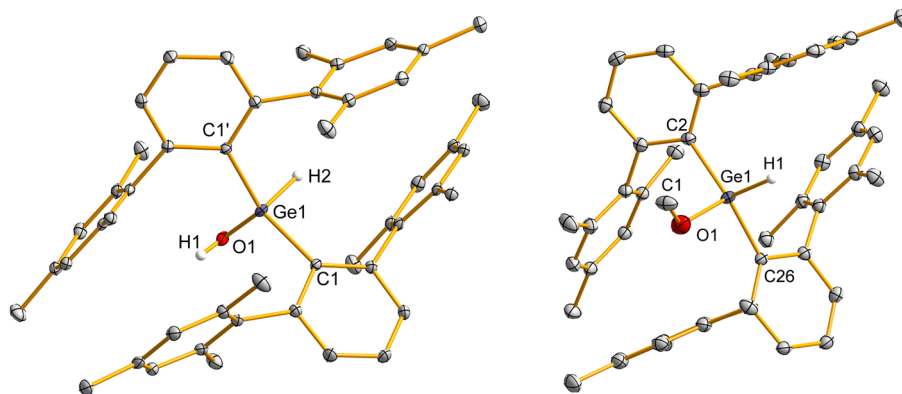


FIGURE 28 Thermal ellipsoid plot (30%) of compounds **6** (left) and **7** (right). Structural disorder and carbon bound hydrogen atoms have been omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): **6**: $\text{Ge}(1)\text{-O}(1)$: 1.770(4), $\text{C}(1)\text{-Ge}(1)\text{-O}(1)$: 109.1(8), $\text{C}(1')\text{-Ge}(1)\text{-O}(1)$: 101.7(7), $\text{C}(1)\text{-Ge}(1)\text{-C}(1')$: 129.48(19). **7**: $\text{Ge}(1)\text{-O}(1)$: 1.797(2), $\text{C}(1)\text{-O}(1)$: 1.357(6), $\text{Ge}(1)\text{-O}(1)\text{-C}(1)$: 123.9(4), $\text{C}(2)\text{-Ge}(1)\text{-O}(1)$: 101.89(8), $\text{C}(26)\text{-Ge}(1)\text{-O}(1)$: 98.81(8), $\text{C}(2)\text{-Ge}(1)\text{-C}(26)$: 136.54(7).

The reactions between SnAr_2 and water or methanol were performed similarly to those of GeAr_2 , yielding yellow solutions after stirring overnight at room temperature. Subsequent work-up, crystallization, and single crystal X-ray structure determination showed the products to be the bridged dimers $\{\text{ArSn}(\mu\text{-OR}')\}_2$ (**8**, $\text{R}' = \text{H}$; **9**, $\text{R}' = \text{Me}$) instead of insertion products similar to **6** and **7**.

(Figure 29). The structures of **8** and **9** are similar with comparable metrical parameters. Either hydroxy (**8**) or methoxy (**9**) moieties bridge two ArSn units, and only the orientation of the aryl ligands is different in **8** and **9**, probably because of different steric requirements of the bridging groups. The four-membered ring is essentially planar in both structures with the aryl ligands above and below the plane. In **8** and **9**, the tin atoms are bonded to only one *m*-terphenyl ligand due to arene elimination, which has occurred during the reaction. The formation of the ArH byproduct was confirmed by ^1H NMR spectroscopy and single crystal X-ray diffraction.

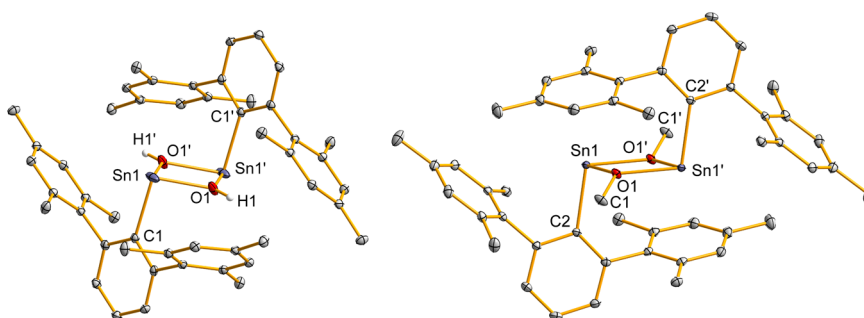


FIGURE 29 Thermal ellipsoid plot (30%) of compounds **8** (left) and **9** (right). Carbon bound hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): **8**: Sn(1)-O(1): 2.1345(14), C(1)-Sn(1): 2.208(3), C(1)-Sn(1)-O(1): 92.69(7), Sn(1)-O(1)-Sn(1'): 108.42(11), O(1)-Sn(1)-O(1'): 71.59(11). **9**: Sn(1)-O(1): 2.1682(11), C(1)-O(1): 1.4304(17), Sn(1)-C(2): 2.2557(14), C(2)-Sn(1)-O(1): 92.53(5), Sn(1)-O(1)-Sn(1'): 107.67(4), O(1)-Sn(1)-O(1'): 72.33(4).

In order to understand the different reactivity of GeAr_2 and SnAr_2 with water and methanol, the mechanisms leading to products **6–9** were probed computationally with DFT. The calculations used slightly simplified model compounds $\text{E}(\text{Ar}^{\text{Me}_4})_2$ ($\text{E} = \text{Ge}$ or Sn ; $\text{Ar}^{\text{Me}_4} = \text{C}_6\text{H}_3\text{-2,6-C}_6\text{H}_3\text{-2,6-(CH}_3)_2$), in which the mesityl substituents of the Ar ligands were replaced with *m*-xylyl to reduce the computational cost. Furthermore, the experimental results clearly showed that the outcome of the reaction depends only on the identity of the metallylene, for which reason only water was used as a reactant in the calculations.

The insertion products $(\text{Ar}^{\text{Me}_4})_2\text{E}(\text{H})\text{OH}$ were found to form via a catalytic mechanism whereby two water molecules react with the metallylene $\text{E}(\text{Ar}^{\text{Me}_4})_2$ (Figure 30). The first step along the pathway involves a formation of an adduct $(\text{Ar}^{\text{Me}_4})_2\text{E}(\text{OH}_2)$. This process is favored by enthalpy but strongly disfavored by entropy, for which reason the calculated energies are slightly endergonic or energy neutral for germanium and tin, respectively. The next step on the pathway is a transition state involving simultaneous proton transfer from a second, mediating, water molecule to the group 14 element and from the -OH group of the coordinated water molecule to the mediating one. The calculated Gibbs free energy of activation for the formation of $(\text{Ar}^{\text{Me}_4})_2\text{E}(\text{H})\text{OH}$ (with respect to $(\text{Ar}^{\text{Me}_4})_2\text{E} + 2 \text{H}_2\text{O}$) was found to be 46 and 73 kJ mol^{-1} for Ge and Sn,

respectively. All attempts to model the oxidative insertion mechanisms via direct proton transfer from the coordinated water molecule to the group 14 element led to considerably higher activation energies (above 100 kJ mol⁻¹) and were therefore deemed unlikely.

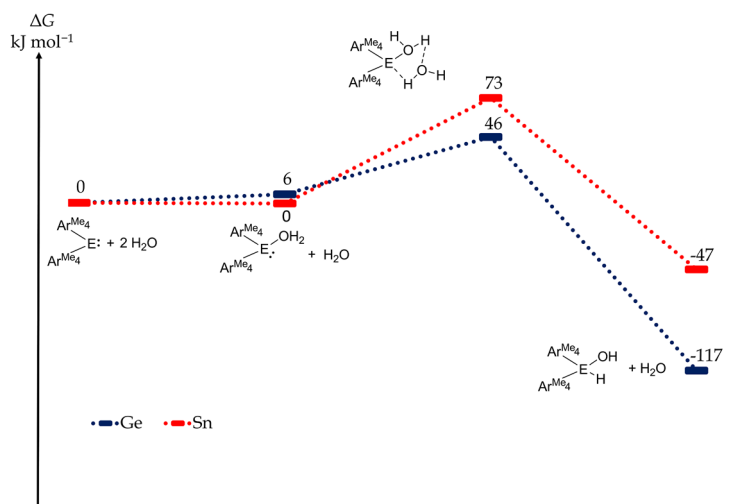


FIGURE 30 Calculated mechanism and Gibbs free energies (ΔG , kJ mol⁻¹) for the formation of the insertion products $(\text{Ar}^{\text{Me}_4})_2\text{E}(\text{H})\text{OH}$ ($\text{E} = \text{Ge}$ or Sn).

The mechanism leading to the dimers $\{\text{Ar}^{\text{Me}_4}\text{E}(\mu\text{-OH})\}_2$ involves the monomers $\text{Ar}^{\text{Me}_4}\text{EOH}$ that are formed via arene elimination from the adducts $(\text{Ar}^{\text{Me}_4})_2\text{E}(\text{OH}_2)$ by one-step sigma bond metathesis (Figure 31). The associated transition state has a four-membered ring structure formed by the group 14 element, the coordinated $-\text{OH}$ moiety and the α -carbon of the terphenyl substituent. The calculated Gibbs free energies of activation (with respect to $(\text{Ar}^{\text{Me}_4})_2\text{E} + \text{H}_2\text{O}$) were found to be 64 and 40 kJ mol⁻¹ for Ge and Sn, respectively. The monomers $\text{Ar}^{\text{Me}_4}\text{EOH}$ can dimerize without an energy barrier, leading directly to the dimers $\{\text{Ar}^{\text{Me}_4}\text{E}(\mu\text{-OH})\}_2$, along with the $\text{Ar}^{\text{Me}_4}\text{H}$ byproduct.

A comparison of the pathways depicted in Figures 30 and 31 clearly shows that the dimers $\{\text{Ar}^{\text{Me}_4}\text{E}(\mu\text{-OH})\}_2$ are the thermodynamically favored products irrespective of the group 14 element. However, for $\text{E} = \text{Ge}$ the oxidative addition pathway leading to the $(\text{Ar}^{\text{Me}_4})_2\text{Ge}(\text{H})\text{OH}$ product has a lower activation energy than the arene elimination, whereas for $\text{E} = \text{Sn}$, the dimer $\{\text{Ar}^{\text{Me}_4}\text{Sn}(\mu\text{-OH})\}_2$ is the kinetically favored product. These results fully corroborate the experimental findings for the reactivity of the tetrylenes EAr_2 ($\text{E} = \text{Ge}$ or Sn) with water and methanol, and are similar to the results obtained for the reactions of EAr_2 with ammonia.¹⁵⁴

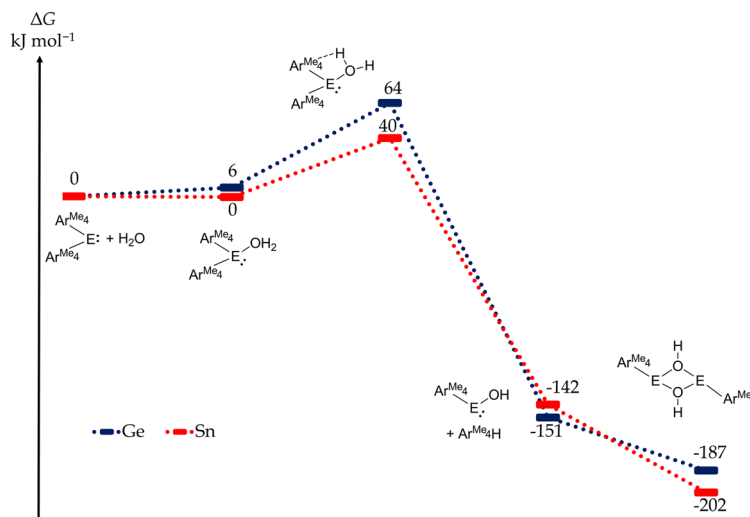


FIGURE 31 Calculated mechanism and Gibbs free energies (ΔG , kJ mol^{-1}) for the formation of the dimers $\{\text{ArMe}_4\text{E}(\mu\text{-OH})\}_2$ and ArMe_4H ($\text{E} = \text{Ge}$ or Sn).

The computational results also clarify why SnAr_2 reacts with HBF_4 by insertion. The arene elimination from $\text{Ar}_2\text{Sn}(\text{H})\text{F}$ would probably proceed via a very high energy transition state that cannot be reached under ambient conditions. However, it is less clear why $\text{Sn}\{\text{CH}(\text{SiMe}_3)_2\}_2$ reacts with water and methanol by insertion.¹⁶³ Subsequent computational work revealed that the arene elimination pathway should be the preferred one also for the reaction between $\text{Sn}\{\text{CH}(\text{SiMe}_3)_2\}_2$ and water, which is in contrast to experimental findings. However, the reaction between $\text{Sn}\{\text{CH}(\text{SiMe}_3)_2\}_2$ and water was performed in THF rather than in Et_2O and using excess H_2O . These differences in the experimental reaction conditions could well be the reason for the difference in reactivity between $\text{Sn}\{\text{CH}(\text{SiMe}_3)_2\}_2$ and SnAr_2 .

3.5 Aryl-stabilized metalloid indium and tin clusters

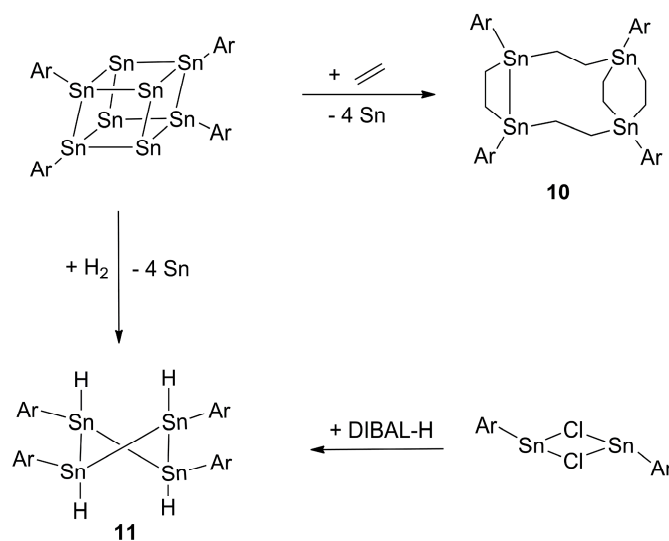
Group 13 and 14 metalloid clusters E_nR_m ($n > m$) are typically electron deficient and in many cases very reactive. Because metalloid clusters contain unsubstituted (naked) elements E , they function in the realms of both molecular and solid state chemistry. For example, when n is small, metalloid clusters behave physically and chemically like molecules. However, for sufficiently large n , the clusters can exhibit the properties of bulk materials. Thus, large metalloid clusters can be described as nanostructured element modifications. Research on metalloid clusters can help to better understand the correlation between particle size and the physical properties of metals, as well as to provide insight into important chemical and physical processes such as dissolution and precipitation.

Most small molecule activation studies involving group 13 and 14 compounds have been done with metallocenes, dimetallenes, and dimetallynes. Though all aforementioned compounds have proven to be very reactive toward

small molecules, a second approach worth investigating is to use metalloids clusters, because they contain low-valent metal centers and function as molecular mimics of metallic surfaces that can nevertheless be handled using normal synthetic techniques and characterized with methods such as NMR spectroscopy and single crystal X-ray diffraction. It is therefore interesting that there are no reports on the reactivity of group 13 and 14 metalloids clusters with small molecules. Keeping this in mind, the clusters Sn_8Ar_4 and In_8Ar_4 were synthesized to investigate their reaction behavior with ethylene and hydrogen. The two clusters were chosen because of their ease of synthesis and relatively high yields.

3.5.1 Addition of small molecules to $\text{Sn}_8\text{Ar}_4^{\text{IV}}$

The tin cluster Sn_8Ar_4 was synthesized according to a literature procedure¹³⁷ and used as a starting material for small molecule reactivity studies (Scheme 6). The dark purple cluster was dissolved in THF and the flask was flushed with ethylene gas for 45 min at room temperature, followed by stirring of the reaction mixture for 48 h. Upon stirring, the solution turned dark red, and gray powder, presumably elemental tin, started to precipitate. After filtration and extraction, colorless crystals of the product **10** were grown overnight at 6 °C.



SCHEME 6 Reactions of Sn_8Ar_4 with excess H_2 and ethylene, and a reaction of $\{\text{ArSn}(\mu\text{-Cl})_2\}_2$ with diisobutylaluminum hydride (DIBAL-H).

Single crystal X-ray diffraction studies confirmed that the cluster Sn_8Ar_4 had reacted with five equivalents of ethylene, forming the insertion compound $\text{Sn}_4\text{Ar}_4(\text{C}_2\text{H}_4)_5$ (**10**) by elimination of four tin atoms (Figure 32). Interestingly, all tin atoms in **10** are tetrahedrally coordinated, although one of the original Sn–Sn bonds has remained intact in the reaction. Even though the structure of **10** is not symmetric in the solid state, ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectroscopy indicated that the molecule is fluxional in solution with pseudo C_s symmetry.

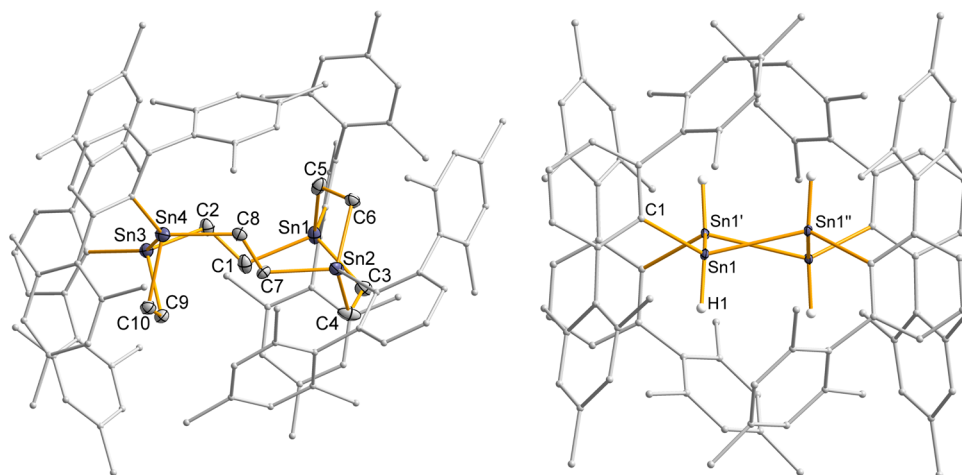


FIGURE 32 Solid state structures of compounds **10** (left) and **11** (right). Thermal ellipsoids are drawn at 30% probability level, carbon bound hydrogen atoms, solvent molecules, and disordered C7B and C8B atoms in **10** have been omitted for clarity. Selected bond lengths (Å) and angles (°): **10**: Sn(3)-Sn(4): 2.8549(5) Sn(1)-C(1): 2.181(4) C(1)-C(2): 1.538(6) Sn(3)-C(9): 2.208(4) Sn(3)-C(59): 2.205(4), C(1)-Sn(1)-C(3): 108.82(17), C(1)-Sn(1)-C(5): 106.15(17), C(2)-Sn(3)-C(9): 110.36(16). **11**: Sn(1)-Sn(1'): 2.8433(4), Sn(1)-Sn(1''): 2.8050(3), Sn(1)-C(1): 2.173(3), Sn(1)-H(1): 1.47(5), C(1)-Sn(1)-Sn(1'): 130.89(7), Sn(1)-Sn(1')-Sn(1''): 87.030(3).

Because the tin cluster exhibited interesting reactivity toward ethylene and yielded a novel insertion product, a reaction between Sn_8Ar_4 and excess H_2 was performed. The synthesis was conducted in toluene, but it required heating at 60 °C for 3.5 h. Subsequent stirring at room temperature overnight yielded gray precipitate with no significant color change. After work-up and crystallization, a few crystals of compound **11** could be isolated along with unreacted Sn_8Ar_4 . For this reason, compound **11** was synthesized in a more straightforward manner from $\{\text{ArSn}(\mu\text{-Cl})\}_2$ and diisobutylaluminum hydride (Scheme 6).

Crystallographic analyses showed that the compound **11** is a tetrameric tin hydride $\{\text{Sn}(\text{H})\text{Ar}\}_4$. Each tin atom in **11** is bonded to an aryl ligand, two other tin atoms, and a hydride, generating a puckered ring where the hydrides have an alternating orientation above or below the ring (Figure 32). The high symmetry of the molecule is retained even in solution, as only a singlet is observed for the hydrides in ^1H NMR and a doublet for the tin atoms in ^{119}Sn NMR.

Having established that the cluster Sn_8Ar_4 reacts with both ethylene and H_2 , its reactivity was examined computationally using DFT. A model compound in which all aryl groups of Sn_8Ar_4 were replaced with phenyls, Sn_8Ph_4 , was used in the calculations. The reasonably facile reactivity of Sn_8Ar_4 can be rationalized by considering the frontier orbitals of Sn_8Ph_4 , which show characteristics of both electron donors and acceptors. Gas phase calculations probing the reaction of Sn_8Ph_4 with one equivalent of ethylene and H_2 resulted in the formation of similar adducts (Figure 33), even though the associated energetics were different. For ethylene, the reaction was found to have a reasonable barrier (86 kJ mol^{-1}) and the addition is exothermic, albeit slightly disfavored by entropy ($\Delta H = -33$

kJ mol^{-1} ; $\Delta G = 22 \text{ kJ mol}^{-1}$). In contrast, the reaction between Sn_8Ph_4 and H_2 has a much larger activation barrier (134 kJ mol^{-1}) and is disfavored by both enthalpy and entropy ($\Delta H = 4 \text{ kJ mol}^{-1}$; $\Delta G = 39 \text{ kJ mol}^{-1}$). However, the entropic penalty is small in both instances and can be overcome in an experimental setting by using excess H_2 or ethylene.

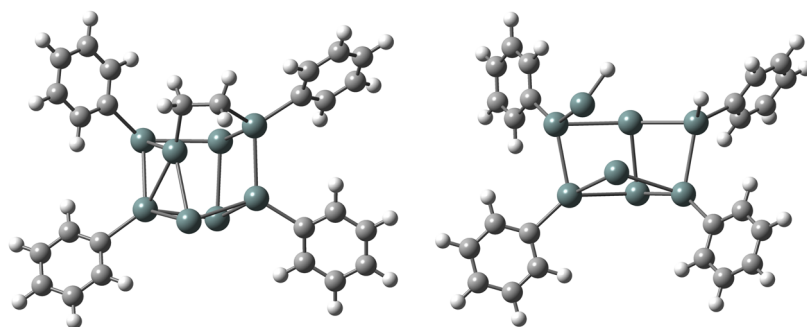
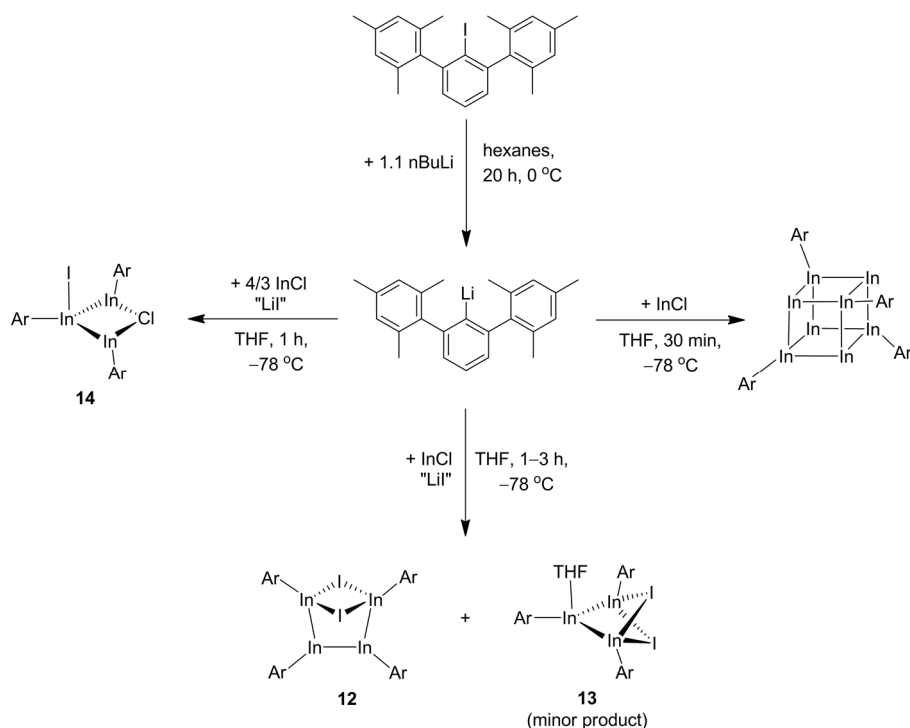


FIGURE 33 Optimized structures of $\text{Sn}_8(\text{C}_2\text{H}_4)\text{Ph}_4$ (left) and $\text{Sn}_8(\text{H}_2)\text{Ph}_4$ (right).

3.5.2 Influence of reaction conditions to the synthesis of $\text{In}_8\text{Ar}_4^{\text{V}}$

The indium cluster In_8Ar_4 has a slightly distorted cubane structure that is very similar to that of Sn_8Ar_4 .¹⁰⁷ Consequently, the metalloid cluster In_8Ar_4 is an interesting target for reactivity studies with small molecules. However, while exploring this possibility in detail, it was observed that the synthesis of In_8Ar_4 is very sensitive toward reaction conditions and can easily afford other mixed-valent indium products. As these compounds can undergo further substitution reactions or other postsynthetic modifications to their structure, it was of interest to examine their chemistry and formation in more detail.

The cluster In_8Ar_4 can be synthesized by treating a suspension of InCl in THF with a THF solution of ArLi at -78°C (Scheme 7). After a dropwise addition of ArLi to InCl and 30 min of stirring, a dark orange solution is obtained. Subsequent work-up and crystallization yield In_8Ar_4 as red crystals. However, if the ArLi solution is freshly prepared and isolated without recrystallization, and the reaction is continued for more than 30 min, a dark orange solution accompanied by an almost black precipitate, presumably elemental indium, is obtained. Subsequent work-up and crystallization from hexanes gave dark brown crystals of compound **12** (Figure 34).



SCHEME 7 Reactions of ArLi with InCl under different reaction conditions.

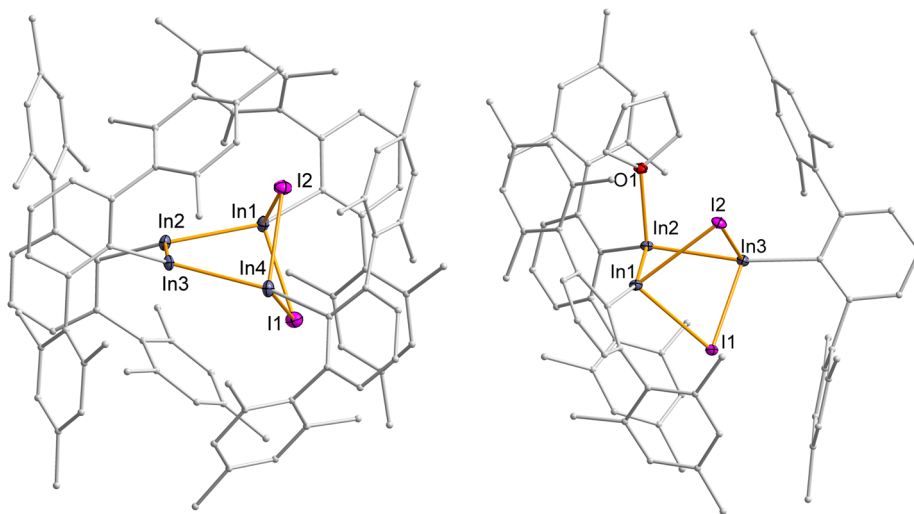


FIGURE 34 Solid state structures of compounds **12** (left) and **13** (right). Thermal ellipsoids are drawn at 30% probability level, structural disorder, hydrogen atoms, and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): **12**: In(1)-In(2): 2.7806(13), In(1)-I(1): 2.9212(14), In(1)-I(2): 2.9214(12), In(2)-In(3): 2.8565(16), In(3)-In(4): 2.8165(14), In(4)-I(1): 2.9296(14), In(4)-I(2): 2.9635(12), In(1)-In(2)-In(3): 102.26(5), In(2)-In(3)-In(4): 101.10(5), In(1)-I(1)-In(4): 89.48(3), In(1)-I(2)-In(4): 88.82(4), In(2)-In(1)-I(1): 92.36(4), In(2)-In(1)-I(2): 92.30(4), In(3)-In(4)-I(1): 101.58(7), In(3)-In(4)-I(2): 81.72(6), I(1)-In(1)-I(2): 86.05(4), I(1)-In(4)-I(2): 85.14(4). **13**: In(1)-In(2): 2.8148(7), In(2)-In(3): 2.7992(8), In(1)-I(1): 2.9393(8), In(1)-I(2): 3.0451(8), In(3)-I(1): 2.9271(7), In(3)-I(2): 3.0741(7), In(1)-In(2)-In(3): 82.24(2), In(1)-I(1)-In(3): 77.999(19), In(1)-I(2)-In(3): 74.214(18), I(1)-In(1)-I(2): 82.62(2), I(1)-In(3)-I(2): 82.316(19).

Single crystal X-ray diffraction studies of **12** showed that the compound had a bicyclo[2.1.1]hexane-type core with four stabilizing ligands (Figure 34). Though some ambiguity of the identity of the bridging atoms existed, an In_4I_2 core was considered the correct interpretation, based on both experimental and computational evidence. The iodide can be present in the reaction mixture through the precursor ArI . This has been reported before for *in situ* prepared ArLi that afforded the mixed halide product $\text{In}_4\text{Ar}_4\text{Cl}_2\text{I}_2$ upon reaction with InCl in toluene.²³⁷ The In_4I_2 core in **12** has two trigonal planar and two tetrahedral indium atoms with different formal oxidation states (+I and +II). This suggests that the remaining indium(I) centers in **12** could be oxidized to form a tetraiodo compound $\text{In}_4\text{Ar}_4\text{I}_4$. However, all attempts at its rational preparation gave mixtures of uncharacterizable products and indium metal, possibly due to the use of too strong oxidizing agents, which results in cleavage of the In-C bond and decomposition.

The synthesis of **12** also yielded a small amount of pale yellow needle-like crystals which were identified as $\text{In}_3\text{Ar}_3\text{I}_2 \cdot \text{THF}$ (**13**) by single crystal X-ray crystallography. The structure of **13** consists of three aryl indium fragments in a chain with two iodides bridging the two terminal indium centers (Figure 34). A solvent molecule (THF) coordinates to the middle indium atom and completes its coordination sphere. The mechanism for the formation of **13**, or **12**, is currently unknown. Both reactions could involve the initial formation of the cluster In_8Ar_4 , which then decomposes because of the longer reaction time used. In addition, the presence of "LiI" in the reaction mixture can favor the formation of **12** over In_8Ar_4 or In_4Ar_4 . It is also unclear why **12** and **13** both incorporate iodide, whereas the same reaction in toluene is known to give a mixture of products with chloride and iodide derivatives as well as compounds with no halides.²³⁷ Hence, it was of interest to investigate whether stoichiometric changes would lead to incorporation of chloride in the products.

The lithium aryl solution was reacted with InCl in varying stoichiometry in THF at -78°C . When a slight excess of InCl was used, the reaction mixture turned dark orange. After an organic work-up and crystallization from hexanes, crystals of **14** were harvested as intense yellow blocks. Subsequent X-ray diffraction studies showed the product to be $\text{In}_3\text{Ar}_3\text{ClI}$ with a four-membered ring formed by three indium atoms and a chloride anion (Figure 35). The middle indium center is coordinated to a terminal iodide, which is disordered above and below the In_3Cl plane. All indium atoms in **14** are bound to one aryl ligand and their formal oxidation state is either +I or +II, depending on the exact coordination. The oxidation states reveal that disproportionation of the indium(I) precursor has again occurred similarly to that in compound **12**.

The formation of compound **14** confirms that an increase in the chloride:aryl ratio results in incorporation of both halides to the product. If the amount of InCl was increased to approximately two equivalents, the reaction gave a golden yellow solution and a black precipitate, indicative of the formation of a product different from **12**, **13**, or **14**. After work-up and crystallization, significant amounts of light yellow crystals were harvested. Subsequent single crystal X-ray

structure determination revealed that the product was the mixed halide species $\text{In}_4\text{Ar}_4\text{Cl}_2\text{I}_2$, whose synthesis and characterization had been reported earlier.²³⁷ Further increasing the aryl:ligand ratio did not lead to the formation of any new products.

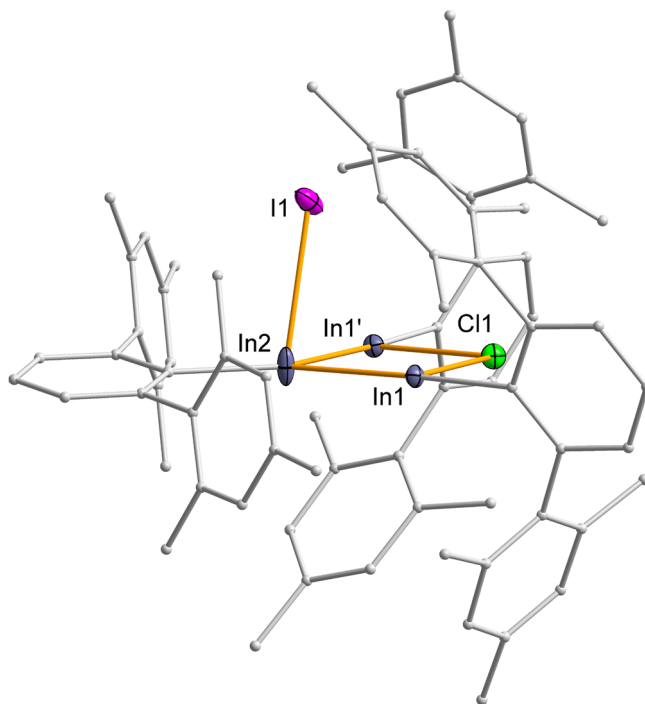


FIGURE 35 Solid state structure of compound **14**. Thermal ellipsoids are drawn at 30% probability level, disordered I(1') (50% occupancy) and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): In(1)-In(2): 2.7777(7), In(1)-Cl(1): 2.6574(13), In(2)-I(1): 2.9947(10), Cl(1)-In(1)-In(2): 88.49(4), In(1)-In(2)-In(1'): 88.91(3), In(1)-In(2)-I(1): 88.15(3), In(1')-In(2)-I(1): 76.24(3).

4 CONCLUSIONS

The primary aim of this thesis was to investigate the reactivity of group 13 and 14 metallylenes and metalloids toward small molecules. To achieve this goal, 14 new *m*-terphenyl stabilized compounds were synthesized and characterized using different spectroscopic and X-ray crystallographic techniques, both in solution and in the solid state. In addition, the electronic structures of the compounds and their formation were examined in detail by computational methods.

The diaryl germylene was shown to afford coordination complexes with methyl and *tert*-butyl isocyanides. With *tert*-butyl isocyanide, the formed adduct was found to have an activated germanium center and a unique backbonding interaction traditionally observed in transition metal complexes. Consequently, the adduct underwent further C-H addition and conversion to a hydride/cyanide product. The methyl isocyanide complex reacted similarly, but gave an azagermacyclopentadienyl heterocycle through coupling of three isocyanides. With the help of computational work, the reaction mechanisms involved in these transformations were elucidated. Computational investigations also gave important insight into the reactivity of the diaryl metallylenes toward water and methanol. While the germylene was found to form a simple insertion product, the stannylenes were observed to react via arene elimination to form a dimeric species.

The syntheses of aryl-stabilized indium and tin metalloids were performed and optimized. However, the formation of the indium cluster was found to be highly sensitive toward the employed reaction conditions and was therefore more complex than what had been reported. Three different mixed-valent indium subhalides, mainly depending on the stoichiometry of the starting materials, were obtained from the reaction. All afforded compounds had the indium elements in two different oxidation states, indicating that further reactivity such as oxidation could be feasible for these species. The synthesized metalloids tin cluster was found to react with both ethylene and dihydrogen via addition/metal elimination. The reactivity of the cluster could be attributed to the donor and acceptor capabilities of its metallic core. This has been the first time

that a main group metalloid cluster was reported to react toward small molecules.

Taken as a whole, this work has illustrated that the reactivity of main group 13 and 14 metallylenes and metalloid clusters is more diverse than previously believed. The reactivity of the prepared compounds, especially toward small molecules, can resemble that of transition metal complexes, despite the lack of *d*-electrons. Hence, the field of main group chemistry and the studies on reactivity of the aforementioned compounds deserve further investigation, which may lead to a new, inexpensive class of reagents for catalysis, hydrogen storage, and small molecule activation.

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