



Final Research Paper

Reactivity and Addition Reactions to metalloid Tin Clusters

Beate G. Steller, BSc MSc

Scholarship at University of California, Davis

Supervisors:

Prof. Philip P. Power (UC Davis)

Assoc. Prof. Roland C. Fischer (Graz University of Technology)

04 March – 05 July 2019



Abstract

Utilizing two different synthetic strategies, tin clusters were isolated and studied on their reactivity towards e.g. PhTeTePh and gaseous reactants like H₂ and ethylene. From the reactions of a tin cluster Sn₁₁tBu₁₂ the oxidation compound Sn(TePh)₄ was isolated and characterized by X-ray crystallography and heteronuclear NMR.

Furthermore, reactivity of distannyne (Dipp*Sn)₂ towards tin and gallium metal was examined for its applicability in cluster synthesis.

Abstract.....	2
1 Acknowledgment.....	4
2 Literature.....	5
2.1 Synthesis of metalloid tin clusters.....	6
2.1.1 Derivatisation of ZINTL ions	7
2.1.2 Thermolysis, dehydrogenative coupling and reduction of organoelement compounds	8
2.2 Small molecule activation by low oxidation state main group element compounds	10
2.2.1 Activation of (small) molecules and unsaturated compounds	10
3 Short description of research agenda	12
4 Results, Discussion and Outlook	13
4.1 Synthesis of Clusters	13
4.1.1 From low valent tin amides	13
4.1.2 From Distannyne.....	13
4.2 Follow up Chemistry of isolated Cluster compounds.....	15
4.3 Synthesis of low valent tin compounds featuring a novel bulky arly ligand.....	17
5 Experimental.....	20
5.1 General considerations and methods	20
5.2 Synthesis of Starting material	20
5.3 Cluster syntheses	22
5.4 Follow up Chemistry.....	23
5.5 Aryl* tin compounds (Aryl* = 2,6-[C(H)Ph ₂]-4-iPr-C ₆ H ₂)	24
6 References.....	25

I Acknowledgment

It is a pleasure to take this opportunity and acknowledge the ones, who contributed to this work and made my research stay at the UC Davis so unique.

First of all, I would like to thank Prof. Philip P. Power for accepting my application to UC Davis. It was a special honor to work in the lab of “an icon of organometallic chemistry”, who contributed so significantly to the understanding of Main Group and Transition Metal Chemistry. His advice and guidance supported the work achieved during my research stay tremendously.

Furthermore, I am very grateful for the financial support of the Austrian Marshall Plan foundation for this work. Also special thanks to the Austrian Academy of Sciences, which supports my PhD with the DOC scholarship. Without these two supporting institutions this stay would not have been possible.

I also would like to thank my PhD supervisor Roland Fischer, who constantly encouraged me during my stay in the United States although being far away.

Last but not least, special thanks to the whole Power group for their help and guidance during my stay. You all made me feel welcome and as a part of the group. In particular I want to mention Cary Stennett, Josh Queen and Alice Phung. Thank you for everything!

2 Literature

In the last decades, stunning progress has been made in the isolation of low oxidation state heavier Main group element compounds. These include low valent heavier carbene analogues R_2E ($E = Si, Ge, Sn, Pb$) (**I**)^[1] and their group 13 derivatives RE ($E = Al, Ga, In, Tl$)^[2], dimeric compounds $RE=ER$, $R_2E=ER_2$ and $RE\equiv ER$ featuring formal multiple bonding (**II**)^[3] as well as the polyhedral elementoid clusters R_xE_n and cages of p-block elements (**III**).^[4] More recently, synthetic efforts focused on the reaction chemistry of these classes of compounds towards (small) molecules. In the case of heavier carbene analogues (**I**), i.e. compounds featuring an electron sextet in combination with an empty orbital at the heavier main group element, their addition chemistry towards a variety of molecules was examined. Moreover, the reversibility of the addition reaction and the ability of such compounds to function as catalyst in e.g. hydrogenation reactions was demonstrated.^[5,6] The respective chemistry of dinuclear compounds of type **II** is currently much less developed. Nevertheless, already reversible addition of alkenes, isonitriles and other species has been observed.^[7-9]

Polyhedral compounds of p-block elements exhibiting unsubstituted element atoms, R_xE_n , $x \leq n$, (**III**) contain ligand-bound atoms next to unsubstituted metal centers, which solely contribute to element-element (metal-metal) bonds. Compounds of this type feature a non-classical, i.e. delocalized, bonding situation and cannot be described by explicit 2-centre/2-electron bonds. Therefore, elementoid (metalloid) clusters appear to be highly reactive and therefore follow up chemistry of these compounds is plausible. Yet, only a few examples exemplifying the reactivity of these compounds can be found in literature^[10-12] not including the further substitution of anionic polyhedral like e.g. Zintl ions respectively.^[13]

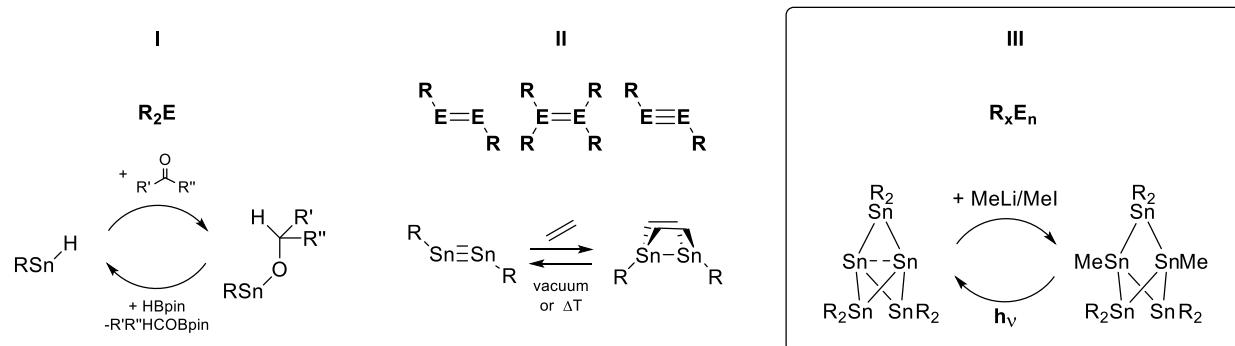


Figure 2-1 Examples for reactivities of low oxidation state tin compounds.^[6,7,10]

Compounds of classes (**I-III**) have a small energy separation of their frontier orbitals, which possess donating as well as accepting features, in common with an energy gap of typically less than 4 eV.^[14] These electronic properties are unusual in main group element compounds and rather resemble the situation observed in e.g. 16 electron transition metal compounds. Consequently, many of the low coordinate main group element compounds readily react with substrate molecules in what is equivalent to an oxidative addition in transition metal chemistry. Hence, the addition of H_2 , H_2O , NH_3 , alkenes, alkynes, CO_2 , sulfur, thiols or disulfides as well as P_4 but also transition metal dimers such as Fp_2 to heavier group 14 carbene homologues was demonstrated.^[5] But also the reversibility of the addition reaction and - even more striking – the ability of such compounds to function as catalysts in e.g. hydrogenation reactions was shown.^[6,7,15] Although most examples originate from the heavier carbene analogues, reversible addition to dimeric compounds $R_{(2)}E=ER_{(2)}$ and $RE\equiv ER$ has been observed.^[16] Due to these

characteristics, analogies have been drawn between low oxidation state heavier main group element compounds and transition metals. A thriving field in main group chemistry is currently investigating these similarities. Within the context of activating small molecules, also elementoid clusters have recently gained interest as POWER and coworkers demonstrated the addition of ethylene and hydrogen to a metalloid tin cluster Sn_8Aryl_4 ($\text{Aryl} = 2,6\text{-}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3$).^[12]

2.1 Synthesis of metalloid tin clusters

Elementoid clusters¹ contain ligand-bound atoms next to unsubstituted element centers. Although the formula R_xE_n with $n > x$ is a widely accepted guideline to categorize metalloid clusters, a more accurate phrasing was verbalized by SCHNÖCKEL and coworkers: “*Metalloid (metal-like) clusters should be epitomized by the property that the number of metal-metal contacts exceeds the number of metal-ligand contacts and by the presence of metal atoms, which participate exclusively in metal-metal interactions.*”^[17] As indicated in this quote, these clusters are described as metalloid or more general elementoid, since their structural motifs often resemble parts of the solid structure of the bulk element. Additionally, “naked” atoms only bonded to other elements of the same kind possess a formal oxidation number of zero and exhibit similar bond lengths in analogy to the metal. Therefore, they are considered as a metastable bridge between molecular and solid state chemistry. Due to their metastability, sterically demanding ligands are necessary for kinetic stabilization of this compound class to avoid bulk element formation.^[18] Structural similarities of elementoid clusters to their bulk phase may qualify them as molecular models to study characteristics of surfaces and surface reactions.^[19,20]

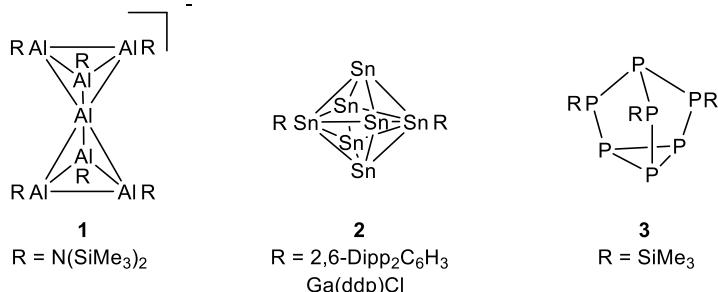


Figure 2-2 Polyhedral species of group 13-15. The aluminium cluster **1** was accessed using disproportionation of $\text{Al}(\text{l})$ halides. Compound **2** was yielded from thermolysis of RSnH as well as the co-reduction of RSnCl and SnCl_2 with KC_8 . **3** was gained from derivatization of the corresponding ZINTL ion.^[17,21-24] ($\text{Dipp} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$, $\text{ddp} = \text{HC}(\text{CMeN}(2,6\text{-iPr}_2\text{C}_6\text{H}_3))_2$)

Amount of examples and structural variety for this kind of compounds is strongly dependent on the group. In contrast to gallium and aluminum clusters, polyhedral compounds of group 14 elements are still rare despite the advances in the last years.^[20,25] The variety of (uncharged,) molecular homonuclear group 15 clusters is even smaller apart from polycyclic phosphorus compounds.^[26] Nevertheless, synthesis approaches for these compounds are similar for each group and the following categories cover most of them:

- By utilization of the so-called *cryochemistry* one of the most successful strategies was developed. Within this procedure, metastable solutions of the $\text{E}(\text{l})$ ($\text{E} = \text{Al}, \text{Ga}, \text{Ge}, \text{Sn}$) halides are generated, which will disproportionate under controlled conditions in the presence of stabilizing ligands and

¹ In contrast to cages, which are best described as localized 2e2c bonds, bonding within clusters is electron deficient and totally delocalized.^[26]

form eventually elementoid clusters. This synthesis strategy was mainly established by SCHNÖCKEL and SCHNEPF and requires high preparative effort as well as specialized equipment.^[17,25,27]

- As ZINTL ions show structural similarities to elementoid clusters, but in the absence of any organic ligands, derivatisation of these has proven to be an appealing route towards organo substituted elementoid clusters. In the case of group 14 elements, mostly (oligo)anionic derivatives $[R_nE_m]^{x-}$ were isolated, with the exception of some germanium compounds e.g. $Ge_9[Si(SiMe_3)_3]_3Et$.^[4,13,23,28,29]
- Similar to multiple bonded heavier main-group elements, also thermolysis of main group element compounds e.g. oligo-element fragments can lead to elementoid clusters. This approach has been particularly successful for corresponding group 14 compounds.^[21,30]
- Reduction of organoelement compounds represents one of the most widely applied strategies for the synthesis of elementoid clusters.^[31–33]
- Synthesis of elementoid clusters and cages via dihydrogen elimination from organotin(II)- and (IV)hydrides, where ligand migration/elimination is responsible for the presence of unsubstituted metal atoms in elementoid clusters.^[34,35]

In the following, selected examples of these strategies, which are related to the planned syntheses, will be depicted in more detail.

2.1.1 Derivatisation of ZINTL ions

After JOANNIS observed the formation of intensively coloured solutions in the reaction of lead with alkaline metals in liquid ammonia in 1890, also KRAUSS, SMYTH and especially ZINTL contributed greatly to the investigation of these binary alloys of p-block elements with alkaline metals.^[36–41] In solid state of alloys with certain stoichiometric ratio of alkali metal (A) to p-block element (E), anionic clusters E_nA_m ($m < n$) are formed. In Figure 2-3 representative ZINTL cluster ions of group 13–15 are depicted.

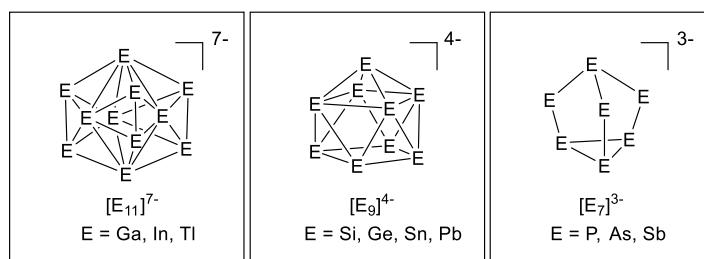


Figure 2-3 Selected structures of ZINTL ions of group 13–15.

Application of ethylenediamine as a solvent or using cryptands for complexation of counter cations overcame the solubility problem of ZINTL ions and enabled further reactions and derivatisation of these compounds.^[42] Vinylation of $[E_9]^{4-}$ ($E = Ge, Sn$) using alkynes is a well-studied reaction.^[43] Additionally, substitution of K_4Sn_9 with RCl in ethylenediamine was realized, but typically did not lead to full alkylation of group 14 ZINTL ions.^[44] Therefore, almost always charged, i.e. anionic, tin clusters are isolated from these synthetic approaches. Only a few uncharged cluster examples, directly derived from ZINTL ions are known e.g. $Ge_9[Si(SiMe_3)_3]_3Et$ and $Ge_9[Si(SiMe_3)_3]_3SnPh_3$.^[4,45] Lately, discrete group 14 element ZINTL ions were connected to more extended structures e.g. $[Ge_9=Ge_9=Ge_9]^{6-}$ as a result of oxidation steps. Examples in this context also include polymeric $[K_2Ge_9]_n$ chains.^[46–49] Linear Chains incorporating more than one parent ZINTL ion were also realized by either coordination towards transition metals or by derivatization using difunctionalized alkynes.^[50–52]

In contrast, full alkylation of $[P_7]^{3-}$ and to some extend of $[As_7]^{3-}$, both exhibiting nortricyclene constitution gives access to a number of neutral cage compounds.^[23,24,53–56] Additionally, various examples in literature show coordination of these anionic clusters towards transition metals. Even incorporation of transition metals into the structures of ZINTL ions was achieved.^[57] However, these reactions are beyond the scope of this outline. Not long ago reactivities of group 14 and 15 ZINTL ions have been reviewed.^[13,58,59]

2.1.2 Reduction of organoelement compounds, thermolysis and dehydrogenative coupling

As the synthetic strategies *thermolysis*, *dehydrogenative coupling* and *reduction of organoelement compounds* strongly overlap in their results for group 14 metal clusters, these approaches will be discussed and compared together in this section. Before the new millennium, examples of clusters of general type E_nR_m exhibiting unsubstituted group 14 element centres was very small, but spectacular advances in this field have been made in the last two decades using these synthesis strategies. (Figure 2-4)

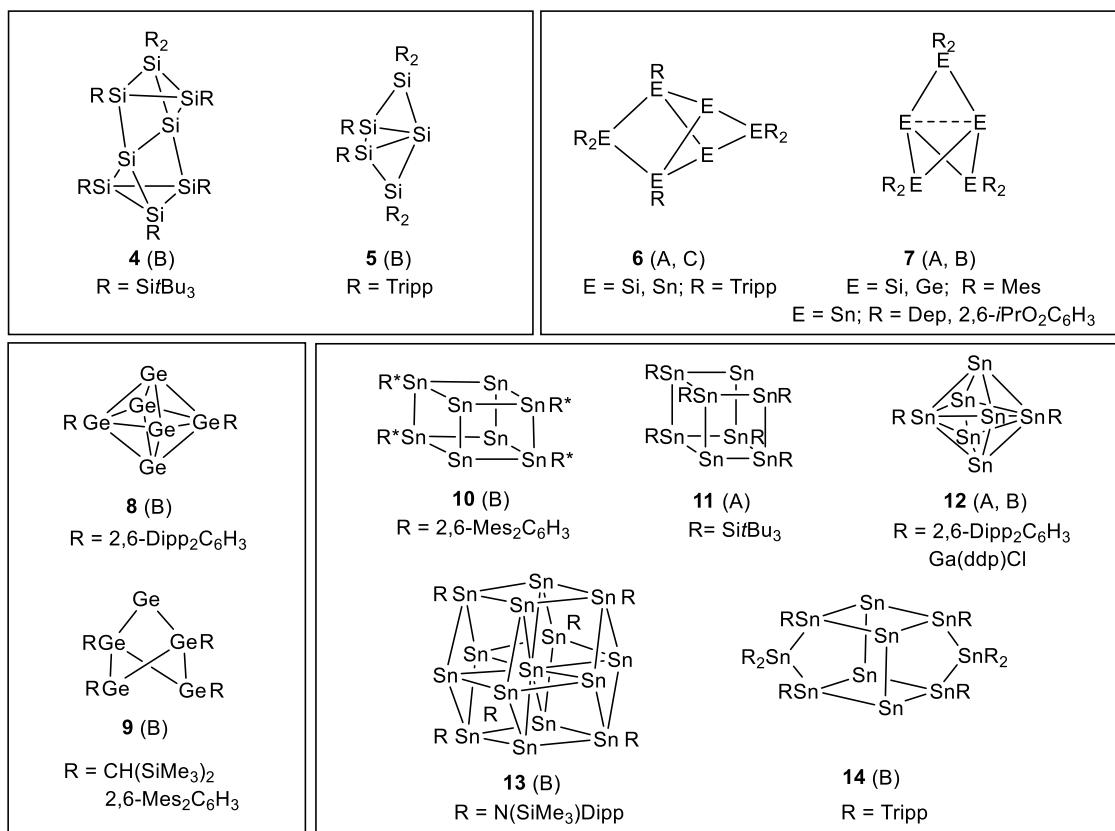
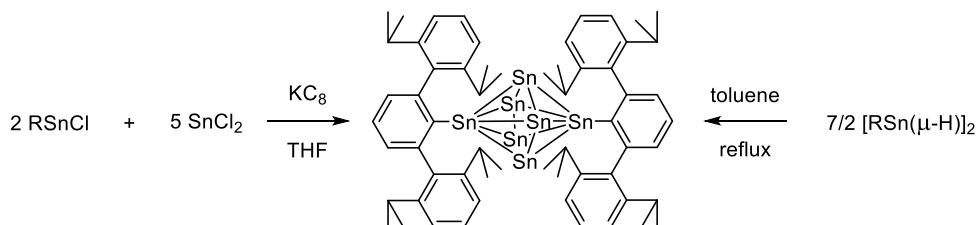


Figure 2-4 Metalloid Clusters of heavier group 14 elements. The letter next to the numbering indicates if the cluster was accessed via thermolysis (A), reduction (B) or dehydrogenative coupling (C). (Dipp = 2,6-iPr₂C₆H₃, Dep = 2,6-Et₂C₆H₃, ddp = HC(CMeN(2,6-iPr₂C₆H₃)₂, Mes = 2,4,6-Me₃C₆H₂, Tripp = 2,4,6-iPr₃C₆H₂)

In the early 1990s SITA and coworkers accomplished the first isolation of a heavy [1.1.1] propellane Sn_5Dep_6 **7** through the thermolysis of cyclic $(Dep_2Sn)_3$ (Dep = 2,6-Diethylphenyl).^[30] Indeed, a pentastanna [1.1.1]propellane does not match the general formula R_xE_n with $x < n$ as suggested for elementoid clusters. Nevertheless, heavy p-block element propellanes can be accounted to elementoid clusters since they exhibit unsubstituted group 14 element centers, where the bridgehead atoms are exclusively bonded to other heavy main group element atoms. Yet, they feature a closed shell singlet electronic ground state. Later, the same group published the improved room temperature synthesis by reduction of $(Dep_2Sn)_3$ with lithium metal and also reported a structural related

tetracyclo [4.1.0.0^{1,5}.0^{2,6}]heptastannane.^[60] Inspired by these early approaches, Drost and Breher also accomplished the synthesis of structurally related pentastanna [1.1.1]propellanes as well as homoatomic heavy propellanes of silicon and germanium.^[61–63] Noteworthy, only two more examples for group 14 element clusters featuring ligand-free silicon atoms have been reported so far.^[64–66]

WIBERG proposed the formation of a stanna-cubane Sn₈R₆ **11** with two naked tin corners in the thermolysis of tetrasupersilyl-tristannacyclopentene.² The dianionic derivative [{THF₂Na}₂Sn₈{SiBu₃}₆] was isolated from the reaction of the low valent LAPPERT's stannylene with "supersilyl sodium" [{THF₂Na}SiBu₃]. The cage compound [Sn₈{SiBu₃}₈] was obtained similarly.^[67] Shortly afterwards, POWER and coworkers isolated a cubane analogue structure **10** featuring four unsubstituted tin atoms by reduction of a organotin(II) chloride featuring a sterically demanding terphenyl substituent with potassium.^[32] Even more structural diverse group 14 metal clusters like **8** and **9** were obtained by applying the same concept, but using different and mixed E(II) species and reducing agents.^[31,68] In 2007, Sn₅(Sn(2,6-DippC₆H₃))₂ **12** was yielded from a reduction as well as a thermolysis approach.^[21] (Scheme 2-1) The structural related compound **12** (R = Ga(ddp)Cl) exhibiting the same pentagonal bipyramidal tin motif was isolated by FISCHER and coworkers, who reduced SnCl₂ with Ga(ddp). As a second product the highest nuclearity tin cluster [Sn₁₇{Ga(ddp)Cl}₄] so far was yielded in this reaction.^[22] The reduction of [Sn(NR'R)(μ-Cl)]₂ (R' = 2,6-diisopropylphenyl, R = SiMe₃ or SiMe₂Ph) using KC₈ or Li[BH₃Bu₃] gave access to body-centered tin clusters.^[19]



Scheme 2-1 Sn₅(SnR)₂ was accessed in a reduction approach as well as through thermolysis. (R = 2,6-(2,6-iPr₂C₆H₃)₂C₆H₃) WESEMANN and coworkers exploited the reductive elimination of hydrogen from organotin trihydrides using N-heterocyclic carbenes to gain **6** (E = Sn).^[34,35] The most recent contribution using reduction in the synthesis of metalloid structures was reported by SCHULZ and coworkers, where Tripp₂SnSnTripp₂ was reacted with a magnesium(I) dimer to yield **14**.^[33]

Examples for mixed group 14 element clusters are still very rare. Structures depicted in Figure 2-5 were all obtained in the reduction of corresponding element halide and organoelement chlorides RE(II)Cl.^[31,69,70] Mixed group 14/group 15 cages were isolated by MATHIASCH and DRÄGER from the reaction of HMe₂SnSnMe₂H and P₄.^[71] WRIGHT and coworkers accessed anionic mixed cages from the reaction of Sn(II) amide with RPHM (M = Li, Na, K).^[72]

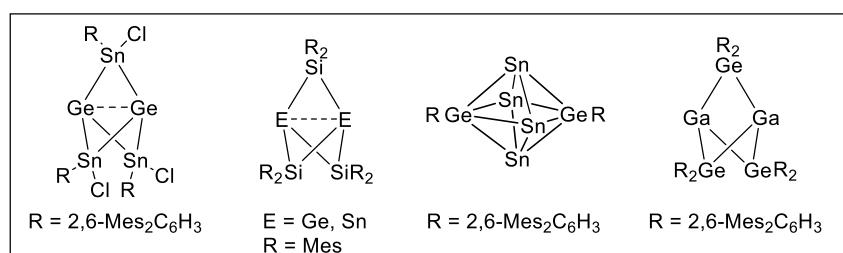


Figure 2-5 Literature known mixed group 14 element clusters.^[31,69,70] (Mes = 2,4,6-Me₃C₆H₂)

² Corresponding Germanium cluster with R = N(SiMe₃)₂ was synthesized by SCHNEPF and coworkers by the reaction of Ge(I)Br with Na[N(SiMe₃)₂.^[126]

2.2 Small molecule activation by low oxidation state main group element compounds

After the landmark discoveries of heavier carbene analogues, R_2E , and the formally multiply bonded heavier alkene and alkyne homologues $RE=ER$, $R_2E=ER_2$ and $RE\equiv ER$, recently the reaction chemistry of these species attracted considerable attention. These classes of compounds have a small energy separation of their frontier orbitals in common, with an energy gap of typically less than 4 eV.^[14] The HOMO is frequently a non-bonding orbital and can hence readily act as an electron donor towards anti-bonding orbitals with appropriate symmetry in substrate molecules. An energetically accessible, unoccupied orbital, on the other hand, can act as an acceptor for electron density from a bonding orbital in the substrate and thus further weaken bonds in substrate molecules. As a consequence, many of the low coordinate, low oxidation state main group element compounds readily react with substrate molecules in what is equivalent to an oxidative addition reaction and insert into bonds of the substrate molecules. Experimental evidence exists for reactions with H_2 , H_2O , NH_3 , alkenes, alkynes, CO_2 , sulfur, thiols or disulfides as well as P_4 , but also transition metal dimers such as Fp_2 . These electronic properties are quite uncommon in main group element compounds and rather resemble the situation observed in e.g. 16 electron transition metal compounds.^[5] Due to these characteristics, analogies have been drawn between the chemistry of low oxidation state heavier main group metals and that of transition metals. Indeed, a currently thriving field in main group chemistry is investigating these similarities.^[14,73,74]

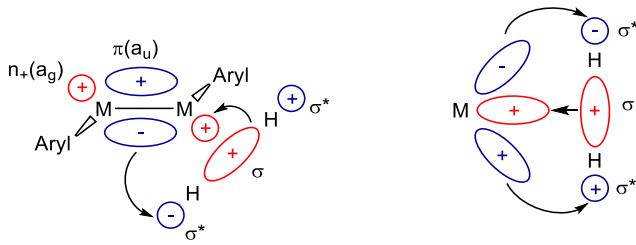
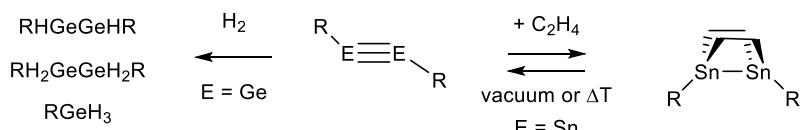


Figure 2-6 Interaction of the frontier orbital of triple bond main group compounds with H_2 (left) and the comparison with a transition metal (right). The activation of H_2 by main group element compounds is very similar to the activation by transition metals. Picture taken from [5].

In the following, some significant contributions and milestones in the activation of small molecules using heavier p-block element compounds will be presented.

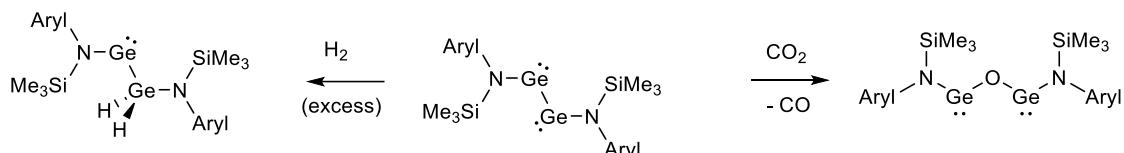
2.2.1 Activation of (small) molecules and unsaturated compounds

Already in an early stage of low oxidation state main group metal chemistry, it was shown that they readily undergo reactions with unsaturated organic molecules like aldehydes, azides and isonitriles.^[75] Yet, the activation of H_2 with the alkyne analogue $RGeGeR$ ($R=2,6-(2,6-iPr_2C_6H_3)_2C_6H_3$) yielding a mixture of hydrogenated species was accomplished decades later in 2005.^[76] Furthermore, also the first reversible addition of ethylene to a low oxidation state tin compound was observed by the same group.^[77] (Scheme 2-2) Both reactions were carried out at room temperature and 1 atmosphere pressure.



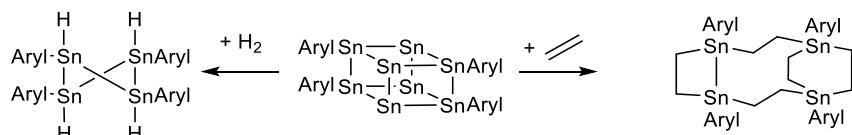
Scheme 2-2 Addition of small molecules to REER. ($R = 2,6-(2,6-iPr_2C_6H_3)_2C_6H_3$) Hydrogen reacts readily with the germanium alkaline analogue. Addition of ethylene to the corresponding tin compound is even reversible.^[7,76]

In the same way, JONES and coworkers investigated the reactivity of a digermyne featuring sterically demanding amide substituents towards selected small molecules. (Scheme 2-3) The Ge(I) dimer $[ArN(TMS)Ge]_2$ was not only shown to add hydrogen, but also was later proven to reduce CO_2 to CO at low temperature quantitatively. Its reducing properties were also investigated towards other CO_2 analogues like CS_2 and $tBuNCO$.^[77,78] Eventually, in the same group also catalytic reduction of organic carbonyls, i.e. aldehydes and ketones, was achieved by using HBpin as a hydrogen source and a low-coordinate tin (II) hydride as a catalyst.^[6] Lately, they were also able to demonstrate the catalytic reduction of CO_2 to methanol equivalents under similar conditions.^[15]



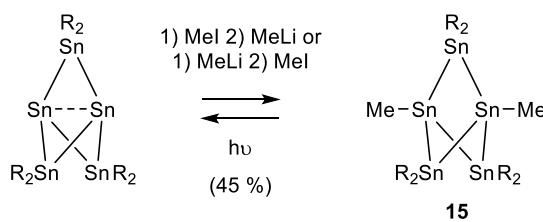
Scheme 2-3 Addition reaction of hydrogen and carbon dioxide to a single-bonded digermyne.^[77,78] (Aryl = 2,6-(Ph₂CH)₂-4-MeC₆H₃)

Within the context of activating small molecules, also elementoid clusters have recently gained interest as POWER and coworkers demonstrated the addition of ethylene and hydrogen to the tin cluster Sn_8Ar^* ($Ar^* = C_6H_3\text{-}2,6-(C_6H_3\text{-}2,4,6-Me_2)_2$) at fairly mild conditions. Noteworthy, incomplete conversion of the cluster was observed in the reaction with hydrogen.^[12] (Scheme 2-4)



Scheme 2-4 Incorporation of hydrogen and ethylene to a metalloid tin cluster.^[12] (Aryl = 2,6-(2,4,6-Me₃C₆H₃)₂C₆H₃)

While in this case the reaction with the small molecule led to degradation of the metalloid cluster, SITA and coworkers showed the reversible addition of methyl groups to pentastanna [1.1.1]propellane on two different approaches via addition of either MeI or MeLi. Photolysis of **15** restored the [1.1.1]propellane in good yields.^[10] (Scheme 2-5)



Scheme 2-5 Addition reactions to pentastanna [1.1.1]propellane and the recovery using photolysis.^[10] ($R = 2,6-Et_2C_6H_3$). The reactivity of heavier [1.1.1]propellanes towards transition metal complexes and other simple substrates was mainly studied by BREHER and coworkers.^[11,62,70,79] Also the reversible transfer of electrons was examined.^[62,63] Addition of small molecules to heavier homologues of carbenes has been reviewed by DRIESS and JONES.^[80] Additionally, next to these selected examples of addition reactions, other low coordinate/ low oxidation state compounds of heavier p-block elements were also found to incorporate (reversibly) P₄^[81-84], NH₃^[73,85], CO^[86,87], CO₂^[88], ethylene^[89], alkynes^[90,91], toluene by insertion into the benzylic C-H bond^[92], oxygen,^[87] water, silanes,^[85] azo compounds,^[93] azides,^[94] nitriles,^[95] isonitriles,^[93,96,97] nitroarenes^[98] and S₈^[99] into their structures. Recently these reactivities of Main group element centers was reviewed by CHU und NIKONOV.^[100]

3 Short description of research agenda

Metalloid tin clusters exhibiting unsubstituted element atoms appear to be highly reactive and therefore follow-up chemistry of these compounds is plausible. Yet, only a very limited number of reactions exemplifying the addition of (small) molecules is evidenced in literature.^[10–12]

During this research stay, two synthetic strategies were applied for the isolation of tin clusters including a recently developed synthetic protocol based on tin-tin bond formation from organotin hydrides $R_{4-n}SnH_n$ and low oxidation state tin diamides *via* the elimination of readily removable $H-NR_2$ as described in the preceding Master's thesis.^[101] Moreover, recent results in the Power group suggest the feasible cluster synthesis starting from $(Dipp^*Sn)_2$ and metals, which was tested in course of this stay.^[92,102]

Next to synthetic strategies, the conducted work focused on the understanding of the reaction behavior of these compounds, more particular the activation of small molecules utilizing the isolated tin clusters. More specific, cluster compounds isolated from these approaches were investigated on their reaction behavior towards compounds like $PhTeTePh$ and $Cp(CO)_3MoMo(CO)_3Cp$ and gaseous reactants like hydrogen, ethylene.

Reactions involving the activation of molecules by these novel metalloid clusters at mild conditions were supported by the extensive knowledge of experienced scientists from the POWER group. The studied working techniques were brought to Graz University of Technology, opening a new and extremely interesting field of chemistry at the home institution.

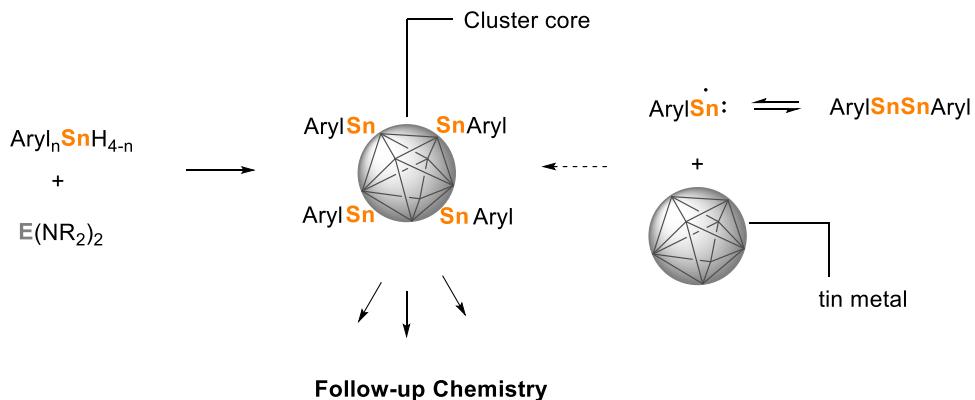


Figure 3-1 Schematic description of research agenda. Synthetic strategies and Follow-up Chemistry.

4 Results, Discussion and Outlook

4.1 Synthesis of Clusters

4.1.1 From low valent tin amides

As already described in the preceding proposal for this research stay, we developed a flexible synthetic approach to metalloid tin clusters based on tin-tin bond formation from organotin hydrides $R_{4-n}Sn_n$ and low oxidation state diamides *via* the elimination of readily removable H-NR₂.

From reactions of $(tBu_2SnH)_2$ with Sn(NEt₂)₂ in DME the cluster Sn₁₁tBu₁₂ could be isolated in moderate yields. The compound crystallizes as brown/orange needles and shows poor solubility in common organic solvents.

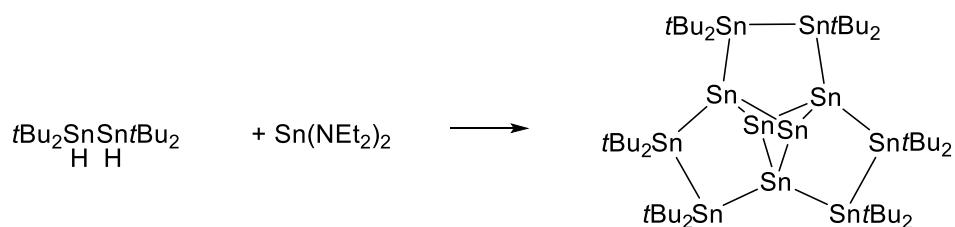
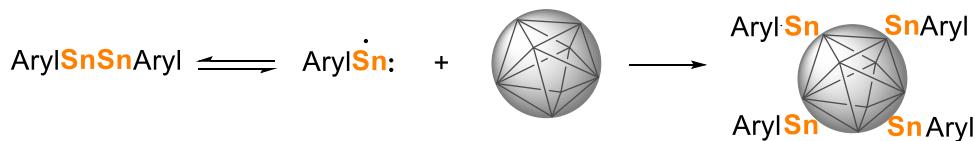


Figure 4-1 Synthesis of Sn₁₁tBu₁₂ from $(tBu_2SnH)_2$.

4.1.2 From Distannyne

In course of this research stay, a different approach for the synthesis tin or mixed tin-element clusters was tested. Recent VT-NMR and EPR investigations in the POWER group have shown that isolated Distannyne compounds ArylSnSnAryl are in equilibrium with their monomeric radical tin species [ArylSn:][·] in solution.^[92,102] The radical low coordinate species [ArylSn:][·] appears to be already present at room temperature, but is more abundant at elevated temperatures (80°C). Due to its radical nature ArylSn:[·] is likely be highly reactive and show follow-up chemistry with e.g. metals. In such a reaction, sections of the respective metal could be ‘extracted’ and solubilized from the solid state. (Scheme 4-1) Thereby, molecular clusters could be formed, which often resemble the solid state structure of the respective metal. In so far established approaches the polyhedral structure is build up from mononuclear tin precursors (bottom-up). This approach could be considered a top-down synthesis as the metal is broken down into small pieces.



Scheme 4-1 Schematic illustration of the possible Cluster formation from ArylSnSnAryl and a metal.

The use of tin metal as a reactant seemed convenient for first attempts, since plenty of terphenyl substituted tin clusters are already known and therefore spectral data could be easily compared to known structures. In discussion prior the conducted experiments, it was considered crucial to ensure a clean surface free from contaminations as e.g. metal oxides of deployed metal. Commercially available nanoparticles were ruled out as

starting material as they are usually exposed to ambient conditions for an unknown period of time and therefore are likely to be covered with tin oxide on their surface. Since – among the well-crystallizing terphenyl compounds – Dipp* substituted compounds (Dipp* = 2,6-Dipp₂-C₆H₃) show an exceptional ability to crystalize and previous investigations of the radical nature were conducted on Dipp*SnSnDipp*, the Dipp* substituted distannyne was the compound of choice for our approach.

For first attempts, tin metal was molten under inert conditions in a Schlenk (using a gas flame) and again solidified on the glass wall of the Schlenk under swirling of the Schlenk. A green solution of distannyne Dipp*SnSnDipp* in benzene was added to the freshly melted tin shaving and gently heated to 75°C. A twenty-fold molar excess of tin was used in this reaction. After 3 days at elevated temperatures a change of color to brownish-red was observed and the solvent was removed. ¹H NMR analysis of the crude product showed the promising formation of the Sn₅(SnDipp*)₂ cluster with distinctive aromatic signals at 6.19 (triplet), 6.27 (duplet) and 7.65 (triplet) ppm next to a large quantity of protonated ligand Dipp*H. The cluster Sn₅(SnDipp*)₂ was already isolated from thermolysis of tin (II) hydrides species [Dipp*Sn(μ-H)]₂ or the co-reduction of Dipp*SnCl and SnCl₂ using KC₈ in THF.^[21] As a control experiment on NMR scale, (Dipp*Sn)₂ dissolved in C₆D₆ was heated to 75°C for 3 days. Unfortunately, NMR spectroscopic investigation of this control experiment showed likewise the formation of Sn₅(SnDipp*)₂ in same amounts as in the experiment using additional tin metal. Noteworthy, it was just recently observed that the formation of the cluster Sn₅(SnDipp*)₂ in the thermolysis of [Dipp*Sn(μ-H)]₂ at 100°C in toluene proceeds through the formation of the corresponding distannyne.^[103]

Since we assumed the surface of the applied metal was not sufficiently large enough, for following experiments tin metal with a higher surface was targeted. Reduction of SnCl₂ using DIBAL-H in Et₂O led only to partial reduction and therefore formed tin metal solely coated the surface of still unreduced, insoluble SnCl₂ chunks. In this case solubility of the Sn(II) precursor seemed to be reason for only partial reduction. Therefore, SnCl₂ was substituted by Sn(NEt₂)₂ which is soluble in common organic solvent. In this case tin (nano)particles were readily formed using again DIBAL-H as a reducing agent. The resulting tin particles were washed with Et₂O repeatedly to ensure removal of excessive DIBAL-H. Nevertheless, no higher amount in cluster formation was observed when heating the so-gained tin metal particles with precursor distannyne again in benzene. Whereas color change and therefore consumption of the distannyne seemed to occur earlier than in previous experiments.

Alternatively, the coating of finely milled sodium chloride with tin metal was tested following a recent approach by JONES and coworkers in the case of Na/NaCl. In their case, the increased surface area of the reducing agent led to higher yields in the synthesis of Mg(I) dimers.^[104] Nevertheless, the approach was not successful owing the higher melting point of tin metal.^[104]

Following these unsuccessful attempts using tin metal, alternative elements were taken in to consideration. Elemental gallium seemed to be a logical choice due to its low melting point and therefore high surface when liquid. Reactions were conducted similar to the approaches with tin metal in benzene at 70°C with a 20-fold excess of metal. ¹H NMR analysis of the crude product after removal of all volatiles under reduced pressure showed only a minor formation of Sn₅(SnDipp*)₂ and additional peaks at 0.83 (duplet), 4.26-4.35 (multiplet, presumably overlay of two septets), 6.92 (triplet) and 7.63 (tr). (Figure 4-2) These peaks could indicate the formation of an unknown Dipp* substituted species. Attempts to crystalize this compound were unsuccessful so far.

Alternatively, elemental mercury seems to be a promising starting material in this reaction as it is liquid already at rt in contrast to so far applied metals tin and gallium.

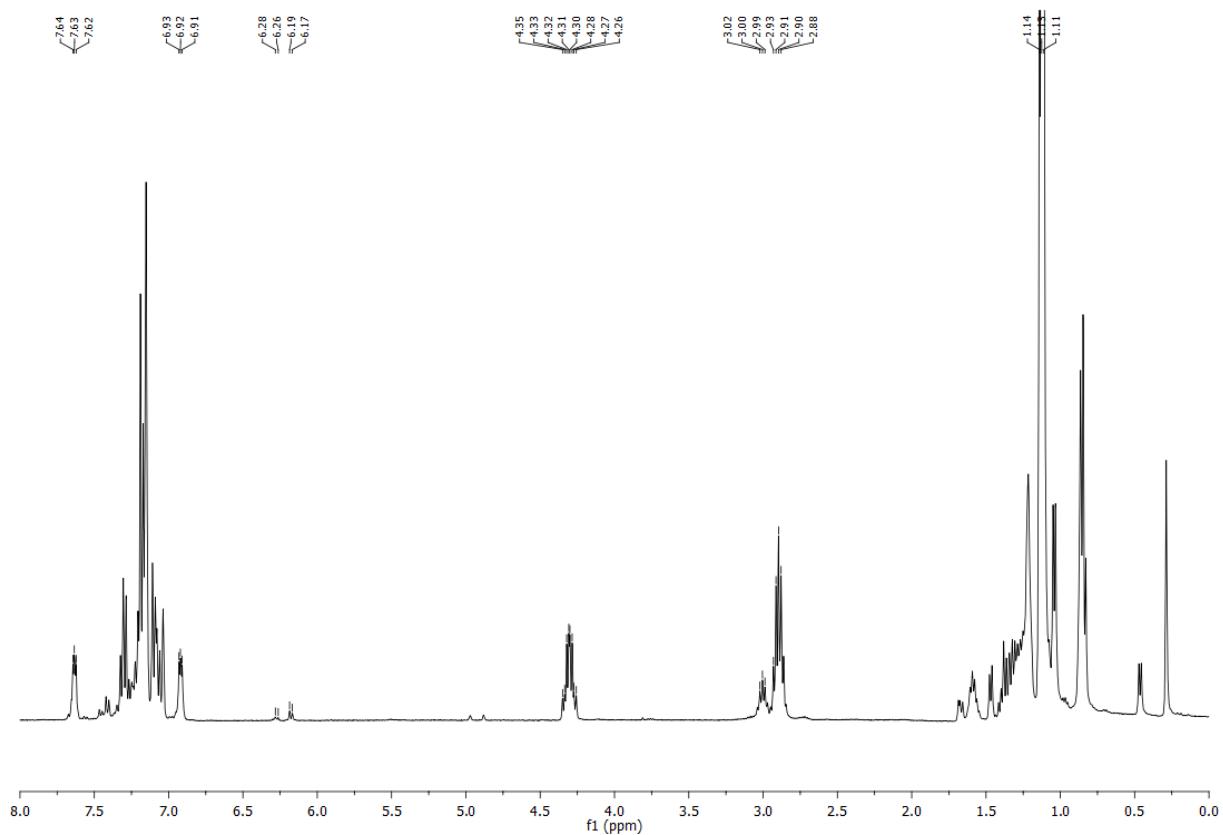


Figure 4-2 Crude ^1H NMR spectra in the reaction of Dipp $^*\text{SnSnDipp}^*$ with Gallium. The signals at 1.13 (triplet) and 2.90 (septet) ppm corresponds to the signal of isopropyl groups in Dipp $^*\text{H}$. A multiplett signal at 4.26-4.35 ppm may indicate the formation of an unknown Dipp * substituted compound.

4.2 Follow up Chemistry of isolated Cluster compounds

Follow-up chemistry of isolated cluster and low oxidation state compounds was supported by the extensive knowledge of experienced scientists from the POWER group. More particularly the handling of gaseous reactants was studied espoused by the expertise of Prof. Power's employees.

First reactivity studies were done using the cluster $\text{Sn}_{11}\text{tBu}_{12}$ isolated from reactions of $(\text{tBu}_2\text{SnH})_2$ with $\text{Sn}(\text{NEt})_2$. Noteworthy, the Sn_{11} cluster shows poor solubility in most common organic solvents. The most promising, but still not good solvent, was found to be tBuOMe . Therefore, reactivity investigations for Sn_{11} were carried out in tBuOMe .

In the conversion of $\text{Sn}_{11}\text{tBu}_{12}$ suspended in tBuOMe with an excess of PhTeTePh red/orange crystals suitable for X-Ray crystallography were found - next to crystals of the telluride starting material. Single crystal X-Ray

diffraction revealed the formation of $\text{Sn}(\text{TePh})_4$ as one of the products in this reaction. The compound crystallizes in the orthorhombic space group Fdd2.

In this structure, the tin atom is found in a nearly ideal tetrahedral environment with Te-Sn-Te angles between $107.36\text{--}110.31^\circ$, which is slightly widened compared to $\text{Ar}_2\text{Sn}(\text{TePh})_2$ with an Te-Sn-Te angle of $102.69(2)$.^[105] Sn-Te bond distances in $\text{Sn}(\text{TePh})_4$ are 2.761 and 2.7535 Å respectively. Sn-Te-C angles reach nearly a right angle with values of 93.7 and 93.5° . These values fit to distances and angles observed in comparable compounds in literature: $\text{Ar}_2\text{Sn}(\text{TePh})_2$ ($\text{Ar} = \text{C}_6\text{H}_3\text{-2,6-NMe}_2$)^[105] with Sn-Te $2.7373(4)\text{/}2.7476(5)$ Å and Sn-Te-C angles of $95.0(2)\text{/}93.8(2)^\circ$ and Ph_3SnTePh ^[106] with Sn-Te $2.732(1)$ Å and Sn-Te-C $90.2(1)^\circ$. In the extended structure the $\text{Sn}(\text{TePh})_4$ is arranged in layers and short contacts between the tellurium atoms are evident (Te-Te contacts: 3.876 and 3.882 Å respectively).

For $\text{Sn}(\text{TePh})_4$ in C_6D_6 a ^{119}Sn NMR shift at -574.38 ppm with a coupling constant $^1J_{119\text{Sn},125\text{Te}}$ of 3370 Hz was found agreeing with values observed for $\text{Ar}_2\text{Sn}(\text{TePh})_2$ ($\text{Ar} = \text{C}_6\text{H}_3\text{-2,6-NMe}_2$) ^{125}Te NMR analysis revealed a shift at 265.68 ppm with evident impurities of PhTeTePh (414.67 ppm; NMR PhTeTePh (408 ppm)).^[107]

Presumably the central tin of $\text{Sn}(\text{TePh})_4$ originates from the “naked” tin atoms in the core of the cluster. Attempts to identify other products, more specific the products of the tert-butyl substituted tin atoms, of this reaction were unsuccessful so far.

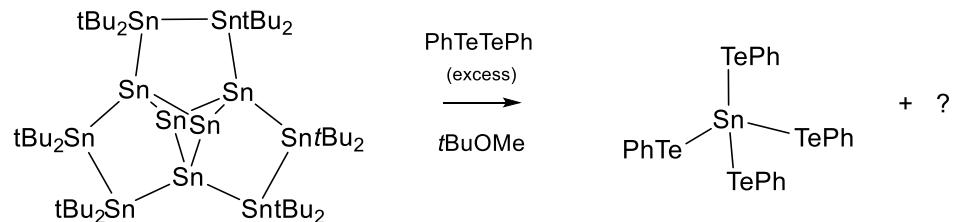


Figure 4-3 Reaction of SnI4tBu12 with excess of PhTeTePh .

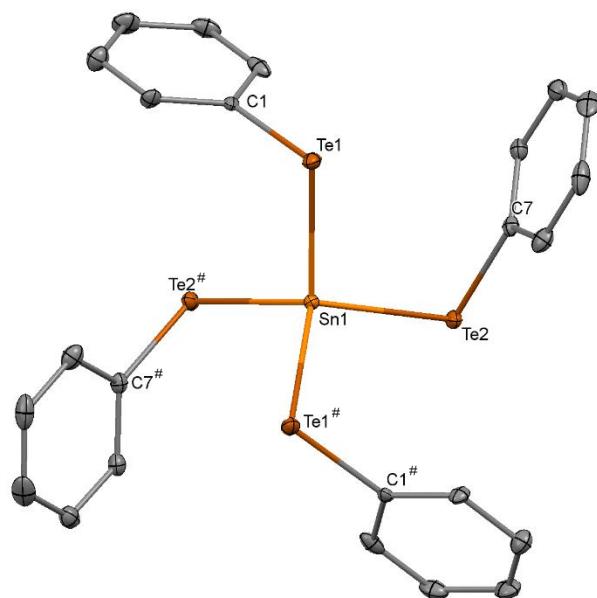


Figure 4-4 Molecular structure of $\text{Sn}(\text{TePh})_4$. Hydrogens are omitted for clarity. Ellipsoids are displayed with 30% probability. Selected bond lengths [Å] and angles [°]: Sn1-Te1 2.7535 , Sn1-Te2 2.761 , Te1-C1 $2.13(1)$, Te2-C7 $2.12(1)$, Sn1-Te1-C1 93.7 , Sn1-Te2-C7 93.5 , Te1-Sn1-Te1# 108.65 , Te1-Sn1-Te2 110.31 , Te2-Sn1-Te2# 107.36 .

In contrast to above discussed $\text{Sn}_{11}\text{tBu}_{12}$ cluster, $\text{Sn}_7\text{Dipp}^*_2$ shows increased solubility. Therefore, reactions with gaseous reactants were conducted using $\text{Sn}_7\text{Dipp}^*_2$ on NMR scale. Introduction of gaseous reactants H_2 and ethylene were done using the “freeze-pump-method”. Unfortunately, no reaction of this Sn_7 cluster was observed even after prolonged heating. The same applies to reactions of $\text{Sn}_7\text{Dipp}^*_2$ with the dimeric transition metal compound $\text{Cp}(\text{CO})_3\text{MoMo}(\text{CO})_3\text{Cp}$.

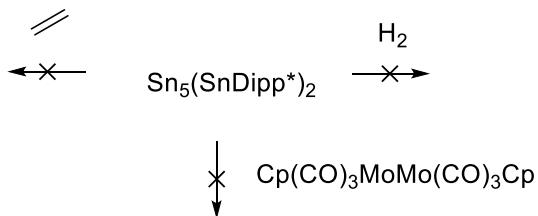


Figure 4-5 Attempted follow-up chemistry of $\text{Sn}_5(\text{SnDipp}^*)_2$.

4.3 Synthesis of low valent tin compounds featuring a novel bulky aryl ligand

Countless examples for the (reversible) addition chemistry to low group 14 element species including REER,^[103,108] R_2E ^[89,91] and REH ^[6,109,110] have proven the synthetic and catalytic potential of this compound type. As a substituent R usually bulky aryl-silyl amide ligands (e. g. $-\text{N}(\text{SiR}_3)\text{Aryl}$),^[111] m-terphenyl ligands,^[112] $(\text{Me}_3\text{Si})_2\text{CH}$ substituted aryl ligands^[113,114] and in less cases bulky thiolates of the type $-\text{S-Aryl}$ ^[115] are used. Nevertheless, these compounds show different reaction behavior depending on the nature and the substitution pattern of the ligands. Therefore, new bulky ligands could enable new and different reactivity and give more insight into the bonding situation of this compound type.

Already before terms of this research stay, the stannylenes Aryl^*Sn featuring a novel anionic aryl ligand ($\text{Aryl}^* = 2,6\text{-}[\text{C}(\text{H})\text{Ph}_2]_2\text{-}4\text{-}i\text{Pr-C}_6\text{H}_2$) could be isolated and characterized. A similar ligand system has been applied for phosphanes just recently.^[116] The expertise of researchers in the group of Prof. POWER should support the synthesis of compounds Aryl^*SnCl and $\text{Aryl}^*\text{SnSnAryl}^*$ starting from the Aryl^*Sn .

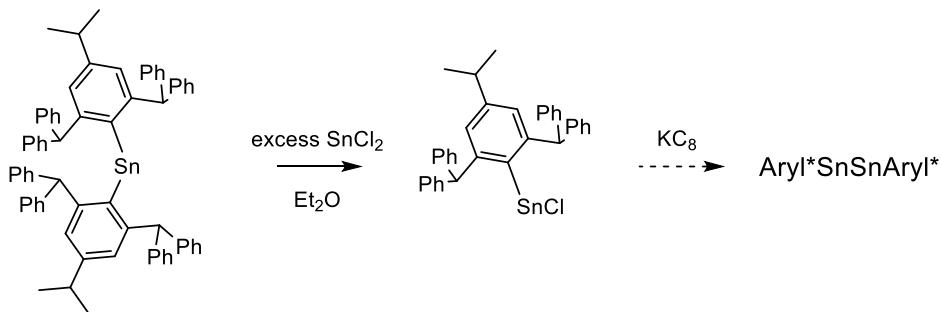


Figure 4-6 Synthesis of Aryl^*SnCl and attempted reduction to the corresponding distannyne.

Aryl^*SnCl was gained straight forward from the ligand redistribution reaction of Aryl^*Sn with an excess of SnCl_2 in Et_2O . The completion of the reaction could be easily determined as the initial red color of the starting material vanished. After work-up Aryl^*SnCl could be isolated as surprisingly colorless to beige solid. Aryltin(II) chlorides

usually exhibit an intense color. UV/VIS investigations show a λ_{max} at about 340 nm. Compound x exhibits a slightly broadened ^{119}Sn shift at 578.4 ppm, which is significantly high field shifted compared to m-terphenyl substituted compounds (Dipp* SnCl (Dipp* = 2,6-Dipp₂-C₆H₃): 817 ppm; Tripp* SnCl (Tripp*= 2,6-Dipp₂-C₆H₃): 793 ppm). Crystals suitable for X-Ray crystallography could be obtained from a mixture of toluene/Et₂O at 10°C. The compound crystallizes in the space group P2₁ with two independent Aryl* SnCl molecules in the unit cell. Since the phenyl groups of the attached ligand block the coordination sphere of the tin center, Aryl* SnCl exists as a monomeric structure. The Sn-C^{ipso} (2.231(6) and 2.249(8) Å) as well as Sn-Cl bonds (2.504(2) and 2.531(3) Å) are slightly elongated compared to bond lengths in other monomeric m-terphenyl substituted R SnCl species. (see Table 4-1) The observed C-Sn-Cl angle in Aryl* SnCl (93.0(2) and 92.1(2)°) is smaller about somewhat 7° compared to the corresponding stannylene Aryl*₂ Sn (100.76(8)°) and corresponding m-terphenyl substituted R SnCl .

Table 4-1 Structural parameters of Aryl* SnCl compared to m-therphenyl substituted R SnCl species.

	Sn-C ^{ipso} [Å]	Sn-Cl [Å]	C-Sn-Cl [°]	Ref
Aryl*SnCl	2.231(6)	2.504(2)	93.0(2)°	
	2.249(8)	2.531(3)	92.1(2)°	
B*SnCl	2.180(2)	2.4088(8)	99.67(9)	[¹¹⁷]
C*SnCl	2.176(6)	2.371(3)	98.8	[¹¹⁸]
D*SnCl	2.218(3)	2.4266(10)	100.19(3)	[¹¹⁹]

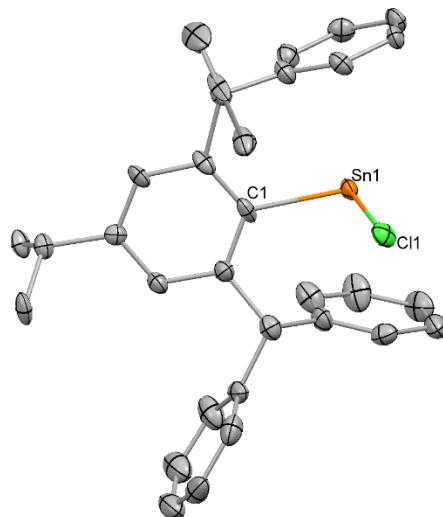


Figure 4-7 Molecular structure of Aryl* SnCl (Aryl = 2,6-[C(H)Ph₂]₂-4-iPr-C₆H₂). Hydrogens are omitted for clarity. Ellipsoids are displayed with 30% probability. Two independent monomeric Aryl* SnCl molecules exist in the unit cell. Selected bond lengths [Å] and angles [°]: Sn1-Cl1 2.231(6), Sn1-C1 2.504(2), C1-Sn1-CII 93.0(2).

Via reduction using KC₈ the isolated Aryl* SnCl was supposed to be converted into the corresponding distannyne species. Instead of Et₂O as described for m-therphenyl substituted compounds^[120] toluene was used as a solvent in this reaction, since Aryl* SnCl exhibits a considerable insolubility in ethereal solvents. ¹H NMR signals of benzylic protons of Aryl* ligand possess significantly different shifts in different but similar compounds e.g. 5.41 ppm for Aryl*H, 6.08 ppm for Aryl* SnCl and 6.25 ppm for Aryl*₂ Sn (all values in C₆D₆) and allow to easily identify

known compounds in crude mixtures. Therefore, the crude product gained from the reduction was analyzed by ^1H NMR analysis.³ Next to unconsumed Aryl $^*\text{SnCl}$ (6.08 ppm for CHPh_2) and Aryl $^*\text{H}$ (5.41 ppm) a so far unassigned signal at 6.27 ppm was observed. (Figure 4-8) This signal may indicate the formation of a distannyne species. Recrystallization of the crude product was so far unsuccessful.

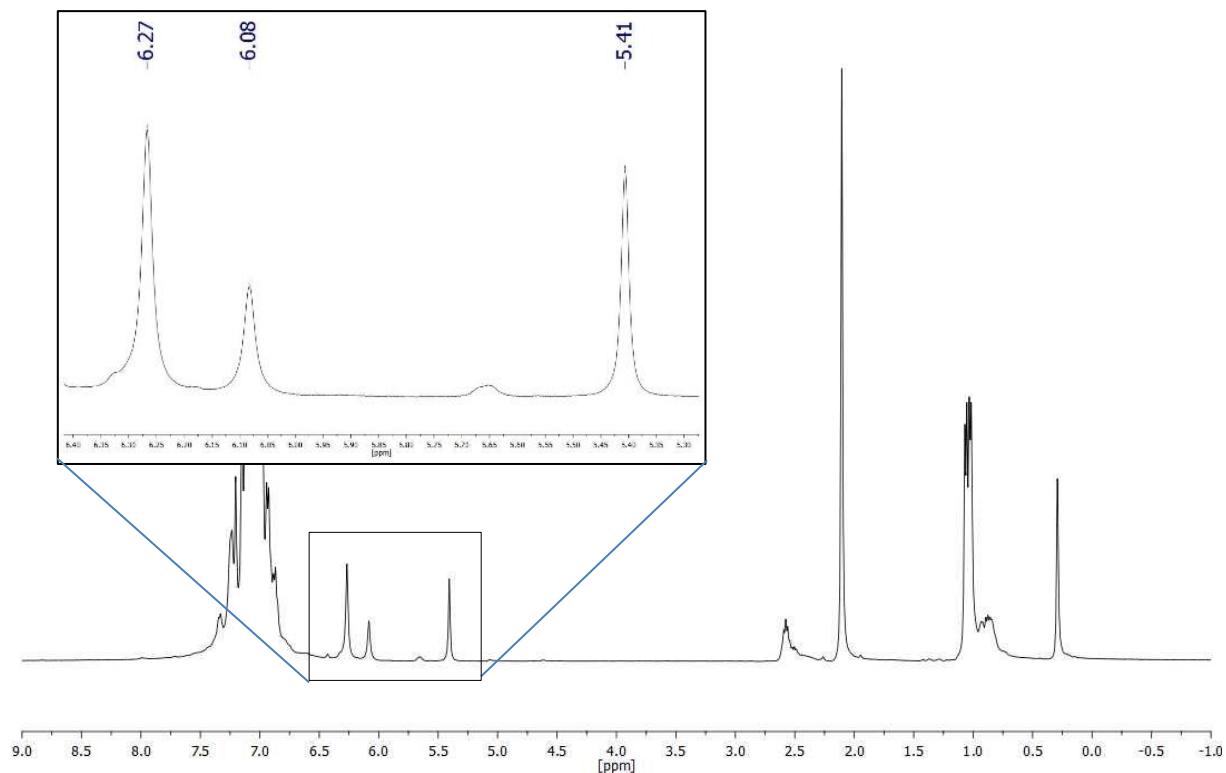


Figure 4-8 ^1H NMR of crude product in the reduction of Aryl $^*\text{SnCl}$ with KC_8 . Shifts at 5.41 and 6.08 correspond to benzylic protons of hydrolyzed ligand Aryl $^*\text{H}$ and starting material Aryl $^*\text{SnCl}$ respectively.

³ No ^{119}Sn NMR signal can be observed for compounds of type Aryl SnSnAryl due to large ^{119}Sn chemical shift anisotropy.^[127]

5 Experimental

5.1 General considerations and methods

All manipulations involving air or moisture sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk tube techniques or were carried out in a nitrogen or argon flushed Vacuum Atmospheres OMNI-Lab drybox under a N₂ or argon atmosphere. Solvents were dried over columns of activated alumina using a Grubbs type purification system (Glass Contour), and stored over Na or K mirrors. Bis(2-methoxyethyl)ether as well as tert-butylmethylether were dried over sodium, distilled, deoxygenated using the ‘freeze-pump-method’ and stored over 3 Å molecular sieves. Diethylamine was dried over CaH₂ and distilled. C₆D₆ was deoxygenated using the “freeze-pump-method” and dried over 3Å molecular sieves. H₂ and ethylene gas were dried via a P₄O₁₀/CaSO₄/sieves drying column prior to use. All other chemicals from commercial sources were used as purchased from chemical suppliers.

¹H, ¹³C{¹H} and ¹¹⁹Sn spectra were recorded on Varian Inova 600 MHz or Bruker Avance III HD Nanobay 400 MHz spectrometers and were referenced to the residual solvent signals in C₆D₆ or CDCl₃. Infrared spectra were collected on a Bruker Tensor 27 ATR-FTIR spectrometer. UV/Vis spectra were recorded as dilute hexanes solutions in 3.5 mL quartz cuvette using an Olis 17 Modernized Cary 14 UV/Vis/NIR Spectrophotometer.

Crystals suitable for X-Ray Crystallography were removed from a Schlenk flask under a stream of nitrogen and immediately covered with hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber on a copper pin and placed in the cold N₂ stream on the diffractometer. Data were collected at 90 K on a Bruker APEX II with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Absorption corrections were applied using SADABS.^[121,122] The crystal structures were solved by intrinsic phasing methods using SHELXT7 and refined by full matrix least-squares procedures using SHELXL.^[123,124]

5.2 Synthesis of Starting material

Lithium diethylamide

In a 400 mL Schlenk tube flask 21.5 mL diethyl amine (15.2 g, 20.8 mmol, 1.0 eq) diluted in 250 mL hexanes were cooled to 0°C. At 0°C 100.0 mL nBuLi solution (2.5 M in hexanes, 25.0 mmol, 1.2 eq) was added in portions and a colorless precipitated was formed. After complete supplementation the colorless suspension was allowed to warm up to rt. The solid was separated from the supernatant solution using a filter cannula, washed with 200 mL hexanes and dried in vacuo.

Yield: 16.27 g (99%), colorless solid. As compound was unsoluble in C₆D₆, no NMR was recorded.

Tin (II) diethylamide

In a Schlenk tube 4.80 g anhydrous SnCl₂ (25.3 mmol, 1.0 eq) and 4.00 g Lithium diethylamide (20.6 mmol, 2.0 eq) were suspended in 100 mL Et₂O at -30°C. The orange suspension was then allowed to warm up to rt overnight. The solvent was removed under reduced pressure and the remaining orange oil was extracted with 100 mL

hexanes and filtered using a filter cannula. The solvent from this so-gained red filtrate was removed under reduced pressure to give a red oil. ^1H NMR was recorded on a 400 MHz spectrometer from Bruker.

Yield: 4.59 g (69%), red oil.

^1H NMR (400 MHz, C_6D_6) δ 3.52 (q, $^3J_{\text{H,H}} = 6.9$ Hz, 8 H; 4xterm- NCH_2CH_3), 3.30 – 3.14 (m, 8 H; 4x μ 2-NCH₂), 1.20 (t, $^3J_{\text{H,H}} = 6.9$ Hz, 12 H; 4xCH₃), 0.99 (t, $^3J_{\text{H,H}} = 7.1$ Hz, 12 H; 4xCH₃) ppm.

General procedure for tin hydride compounds

In a 100 mL Schlenk tube LiAlH₄ powder was suspended in Et₂O and cooled down to 0°C. At 0°C the corresponding tin chloride species was added in portions. After the reaction was stirred for 2 h at 0°C, it was poured onto degassed H₂SO₄ (0.5 M) via a cannula at 0°C. The phases were separated, the organic layer was washed with degassed Potassium tartrate solution, dried over MgSO₄ and filtered using a filter cannula. The drying agent was again washed with Et₂O to ensure no loss of hydride species. The solvent was removed under reduced pressure to give a colorless oil or solid.

Dipp₂SnH₂

0.74 g LiAlH₄ (19.5 mmol, 1.0 eq) in 100 mL Et₂O, 10.00 g Dipp₂SnCl₂ (19.5 mmol, 1.0 eq), 50 mL degassed H₂SO₄, 1×100 mL degassed Potassium tartrate solution. The resulting colorless oil was stored at 4°C in a Schlenk flask. ^1H NMR was recorded on a 400 MHz spectrometer from Bruker.

^1H NMR (400 MHz, C_6D_6) 7.25–7.21 (m, 2 H; 2xH^{Ar}), 7.11–7.09 (m, 4 H; 4xH^{Ar}), 6.21 (s, $^1J_{\text{H,}^{119}\text{Sn}} = 1835$ Hz, $^1J_{\text{H,}^{117}\text{Sn}} = 1753$ Hz, 2 H; SnH₂), 3.27 (septett, $^3J_{\text{H,H}} = 6.6$ Hz, 4 H; 4xCH), 1.15 (d, $^3J_{\text{H,H}} = 6.6$ Hz, 24 H; 8xCH₃) ppm.

Tripp₂SnH₂

0.85 g LiAlH₄ (22.4 mmol, 0.95 eq) in 100 mL Et₂O, 14.10 g Tripp₂SnCl₂ (23.6 mmol, 1.0 eq), 50 mL degassed H₂SO₄, 1×100 mL degassed Potassium tartrate solution. The resulting brown oil was stored at 4°C in a Schlenk flask. ^1H NMR was recorded on a 400 MHz spectrometer from Bruker.

^1H NMR (400 MHz, C_6D_6) 7.14 (s, 4 H; 4xH^{Ar}), 6.23 (s, $^1J_{\text{H,}^{119}\text{Sn}} = 1820$ Hz, $^1J_{\text{H,}^{117}\text{Sn}} = 1731$ Hz, 2 H; SnH₂), 3.35 (septett, $^3J_{\text{H,H}} = 6.6$ Hz, 4 H; 4xCH), 2.78 (septett, $^3J_{\text{H,H}} = 6.9$ Hz, 2 H; 2xCH), 1.24 – 1.20 (m, 36 H; 12xCH₃) ppm.

(tBu₂SnH)₂

0.81 g LiAlH₄ (21.3 mmol, 0.95 eq) in 100 mL Et₂O, 12.00 g (tBu₂SnCl)₂ (22.4 mmol, 1.0 eq), 50 mL degassed H₂SO₄, 1×100 mL degassed Potassium tartrate solution. The resulting brownish liquid was stored at 4°C in a Schlenk. ^1H NMR was recorded on a 400 MHz spectrometer from Bruker.

^1H NMR (400 MHz, C_6D_6) δ 5.46 (s, $^1J_{\text{H,}^{119}\text{Sn}} = 1203$ Hz, $^1J_{\text{H,}^{117}\text{Sn}} = 1257$ Hz, $^3J_{\text{H,Sn}} = 85$ Hz, 2 H; 2xSnH), 1.39 (s, $^1J_{\text{H,Sn}} = 68$ Hz, 36 H; 4xC(CH₃)₃) ppm.

Terphenyl compounds (Dipp*= 2,6-Dipp₂-C₆H₃)

Dipp*Li

At 0°C 20.0 mL 2.5 M nBuLi solution in hexanes (50.0 mmol; 1.1 eq) was added in portions to 23.84 g Dipp*^I (45.5 mmol, 1.0 eq) dissolved in 250 mL hexanes while a colourless solid precipitates from the solution. After complete addition the reaction was allowed to warm up to rt overnight. The suspension was concentrated and the formed colourless solid was filtered using a filter cannula, washed with hexanes (2x75 mL) and dried in vacuo. Spectroscopic data are in agreement with values given in literature.^[125]

Yield: 16.23 g (88%), colourless powder.

¹H NMR (400 MHz, C₆D₆) δ 7.29-7.15 (m, 9 H; 9xH^{Ar}), 3.21 (sep, ³J_{H,H} = , 4 H; 4xCH(CH₃)₂), 1.14 (d, ³J_{H,H} = , 24 H; 4xCH(CH₃)₂) ppm.

Dipp*SnCl

At 0°C a solution of 6.00 g Dipp*Li (14.8 mmol, 1.0 eq) in 60 mL was added in portions to 3.99 g SnCl₂ (21.1 mmol, 1.42 eq) suspended in 15 mL Et₂O. After complete addition the greenish suspension was stirred for 30 min at 0°C and was then allowed to warm up to rt. After 18 h at rt the solvent was removed under reduced pressure. The resulting brown/greenish solid was extracted with 75 mL toluene and filtered using a filter cannula. The red solution was concentrated to 50 mL and stored at -30°C for 48 h to give the product as red and yellow crystals. Spectroscopic data are in agreement with values given in literature.^[120]

Yield: 3.65 g (44%), red or yellow crystals.

¹H NMR (400 MHz, C₆D₆) δ 7.30-7.13 (m, 9 H, overlay with solvent peak; H^{Ar}), 3.10 (sept, ³J_{H,H} = 6.7 Hz, 4 H; 4xCH(CH₃)₂), 1.33 (d, ³J_{H,H} = 6.7 Hz, 12 H; 2xCH(CH₃)₂), 1.02 (d, ³J_{H,H} = 6.7 Hz, 12 H; 2xCH(CH₃)₂) ppm.

(Dipp*Sn)₂

At rt a solution of 3.00 g Dipp*SnCl (5.44 mmol, 1.0 eq) in 75 mL Et₂O was added to potassium mirror freshly prepared from 244 mg K (6.24 mmol, 1.15 eq). The reaction was stirred for 3 days, after which the solvent was removed under reduced pressure. The resulting green solid was extracted with 100 mL toluene and filtered. The intense green solution was concentrated to 50 mL and stored at -30°C for 24 h to give the product as green and red crystals. The filtrate was again concentrated and stored at -30°C to give a second crop. Spectroscopic data are in agreement with values given in literature.^[120]

Yield: 892 mg (32%), green or red crystals.

¹H NMR (400 MHz, C₆D₆) δ 7.53 (d, ³J_{H,H} = 7.7 Hz, 2 H; m-H^{Ar} (central)), 7.20-7.18 (t, ³J_{H,H} = xx Hz, 2 H, overlay with solvent peak; 2xp-H^{Ar}(flanking)), 7.06-7.04 (d, ³J_{H,H} = 7.8 Hz, 4 H; 4xm-H^{Ar}(flanking)), 6.17 (t, ³J_{H,H} = 7.7 Hz, 1 H; p-H^{Ar}(central)), 2.86 (sept, ³J_{H,H} = 6.5 Hz, 4 H; 4xCH(CH₃)₂), 1.39 (d, ³J_{H,H} = 6.5 Hz, 12 H; 2xCH(CH₃)₂), 1.13 (d, ³J_{H,H} = 6.5 Hz, 12 H; 4xCH(CH₃)₂) ppm.

5.3 Cluster syntheses

Sn₁₁tBu₁₂

At room temperature a solution of 263 mg Sn(NEt₂)₂ (1.0 mmol, 1.0 eq) in DME was added to a solution of 468 mg (tBu₂SnH)₂ (1.0 mmol, 1.0 eq) in DME. The reaction turned yellow, orange and finally brown. After 3 days the product crystallized as orange/brown needles from the reaction solution.

*(Dipp*Sn)₂ with tin metal*

In a 100 mL Schlenk 400 mg (Dipp*Sn)₂ (0.39 mmol, 1.0 eq) and 1.01 g tin metal in 25 mL dry benzene were slowly warmed up to 75°C. After three days the reaction turned from original green to brownish red. The solvent was removed under reduced pressure and the crude product was investigated by ¹H NMR analysis, which indicated the formation of Sn₇Dipp*₂. After recrystallization of the crude product from hexanes Sn₇Dipp*₂ was isolated with 30% impurities (Dipp*H).

*(Dipp*Sn)₂ with Gallium*

In a 100 mL Schlenk 400 mg (Dipp*Sn)₂ (0.39 mmol, 1.0 eq) and 570 mg Gallium metal in 30 mL dry benzene were slowly warmed up to 75°C. After three days the reaction turned from original green to brownish red. The solvent was removed under reduced pressure and the crude product was investigated by ¹H NMR analysis, which indicated the formation of an unknown compound. The crude product was then extracted with 40 mL toluene and filtered using a filter cannula. After concentrating this solution and cooling it to -30°C for 2 days a colorless insoluble solid precipitated. Identification of any new compound from this reaction was not successful so far.

5.4 Follow up Chemistry

Sn₁₁tBu₁₂ and PhTeTePh

At rt ca. 50 mg PhTeTePh (0.1 mmol) was added to a suspension of 100 mg Sn₁₁tBu₁₂ (0.05 mmol) in 5 mL tert-butylmethylether. Slowly the cluster reacted and went into solution. After 24 h half of the solvent was removed and cooled to -30°C. Crystals suitable for X-Ray diffraction of Sn(PhTe)₄ next to the excess PhTeTePh was found in this reaction.

¹¹⁹Sn{¹H} NMR (186.4 MHz, C₆D₆) δ -574.38 ppm.

¹²⁸Te {¹H} NMR (94.84 MHz, C₆D₆) δ 265.68 ppm.

*Sn₇Dipp*₂ and H₂/H₂CCH₂ on NMR scale*

Approximately 20 mg of Sn₇Dipp*₂ were dissolved in 0.3 mL C₆D₆. The gaseous reactant (H₂ or H₂CCH₂) was introduced using the “freeze-pump-method”. ¹H NMR investigations showed no reaction even after prolonged up to 70°C.

*Sn₇Dipp*₂ and Cp(CO)₃MoMo(CO)₃Cp on NMR scale*

Approximately 20 mg of Sn₇Dipp*₂ were dissolved in 0.3 mL C₆D₆ and 20 mg of Cp(CO)₃MoMo(CO)₃Cp were added. ¹H NMR investigations showed no reaction even after prolonged up to 70°C.

*Aryl*₂Sn and H₂/H₂CCH₂ on NMR scale*

Approximately 20 mg of Aryl*₂Sn were dissolved in 0.3 mL C₆D₆. The gaseous reactant (H₂ or H₂CCH₂) was introduced using the “freeze-pump-method”. ¹H NMR investigations showed no reaction even after prolonged up to 70°C.

5.5 Aryl* tin compounds ($\text{Aryl}^* = 2,6\text{-[C(H)Ph}_2\text{]-4-iPr-C}_6\text{H}_2$)

Aryl^*_2Sn

At -40°C a solution of Aryl*Li prepared from 4.47 g Aryl*I (7.7 mmol, 2.0 eq) and 10.0 mL 1.7 M tBuLi solution in pentane (17.0 mmol, 4.4 eq) in 80 mL Et₂O was slowly added to 732 mg SnCl₂ (3.9 mmol, 1.0 eq) suspended in 10 mL Et₂O. During the addition the reaction turns brownish red. After complete addition the reaction was allowed to warm up slowly to rt overnight. Then the solvent was removed under reduced pressure. The resulting orange solid was extracted with a 50 mL toluene, filtered using a filter cannula and the solvent was again removed under reduced pressure. The red solid was recrystallized from hexanes to give a rust-red product.

Yield: 2.84 g (72%), rust-red solid.

¹H NMR (400 MHz, C₆D₆) δ 7.20 (s, 4 H; 4x^m-H^{Ar}), 7.12-6.91 (m, 20 H; 20xH^{Ph}), 6.15 (s, 4 H; 4xCHPh₂), 2.58 (sept, ³J_{H,H} = 6.8 Hz, 2 H; 2xCH(CH₃)₂), 1.06 (d, ³J_{H,H} = 6.8 Hz, 12 H, 2xCH(CH₃)₂) ppm.

Aryl^*SnCl

A suspension of 2.88 g Aryl₂Sn (2.8 mmol, 1.0 eq) and 800 mg SnCl₂ (4.2 mmol, 1.5 eq) in 40 mL Et₂O was stirred at rt. After 42 h the solvent was removed under reduced pressure to give a brown solid. The solid was washed with 75 mL hexanes, extracted with 20 mL toluene, filtered and the solvent was removed again. The crude product was then recrystallized from toluene/Et₂O.

Yield: 343 mg (11%), beige solid.

¹H NMR (400 MHz, C₆D₆) δ 7.27 (d, ³J_{H,H} = 7.6 Hz, 8 H; 8x^o-H^{Ph}), 7.05 (t, ³J_{H,H} = 7.2 Hz, 8 H; 8x^m-H^{Ph}), 7.00 (s, 2 H; 2x^m-H^{Ar}), 6.88 (t, ³J_{H,H} = 7.3 Hz, 4 H; 4x^p-H^{Ph}), 6.08 (s, ¹J_{H,13C} = 127 Hz, 2 H; 2xCHPh₂), 2.52 (sept, ³J_{H,H} = 6.9 Hz, 1 H; CH(CH₃)₂), 1.04 (d, ³J_{H,H} = 6.9 Hz, 6 H; 2x CH(CH₃)₂) ppm.

¹³C NMR (126 MHz, C₆D₆) δ 182.41 (i-C^{Ar}), 153.65 (), 148.20(), 143.93 (), 131.33 (), 130.33 (), 129.86 (), 127.40 (), 58.61 (CHPh₂), 34.29 (CH(CH₃)₂), 24.02 (CH(CH₃)₂) ppm.

¹¹⁹Sn{¹H} NMR (186.4 MHz, C₆D₆) δ 578.4 ppm.

6 References

- [1] N. Tokitoh, R. Okazaki, *Coord. Chem. Rev.* **2000**, *210*, 251–277.
[2] R. C. Fischer, in *Compr. Inorg. Chem. II* (Ed.: T. Chivers), Elsevier, Amsterdam, **2013**, pp. 269–287.
[3] R. C. Fischer, P. P. Power, *Chem. Rev.* **2010**, *110*, 3877–3923.
[4] F. Li, S. C. Sevov, *J. Am. Chem. Soc.* **2014**, *136*, 12056–12063.
[5] P. P. Power, *Nature* **2010**, *463*, 171–177.
[6] T. J. Hadlington, M. Hermann, G. Frenking, C. Jones, *J. Am. Chem. Soc.* **2014**, *136*, 3028–3031.
[7] Y. Peng, B. D. Ellis, X. Wang, J. C. Fettinger, P. P. Power, *Science (80-.)* **2009**, *325*, 1668–1670.
[8] Y. Peng, X. Wang, J. C. Fettinger, P. P. Power, *Chem. Commun.* **2010**, *46*, 943–945.
[9] T. J. Hadlington, J. Li, M. Hermann, A. Davey, G. Frenking, C. Jones, *Organometallics* **2015**, *34*, 3175–3185.
[10] L. R. Sita, I. Kinoshita, *J. Am. Chem. Soc.* **1991**, *113*, 5070–5072.
[11] D. Nied, F. Breher, *Chem. Soc. Rev.* **2011**, *40*, 3455–3466.
[12] P. Vasko, S. Wang, H. M. Tuononen, P. P. Power, *Angew. Chemie - Int. Ed.* **2015**, *54*, 3802–3805.
[13] S. C. Sevov, J. M. Goicoechea, *Organometallics* **2006**, *25*, 5678–5692.
[14] D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.* **2011**, *2*, 389–399.
[15] T. J. Hadlington, C. E. Kefalidis, L. Maron, C. Jones, *ACS Catal.* **2017**, *7*, 1853–1859.
[16] P. P. Power, *Acc. Chem. Res.* **2011**, *44*, 627–637.
[17] A. Purath, R. Köppe, H. Schnöckel, *Angew. Chemie - Int. Ed.* **1999**, *38*, 2926–2928.
[18] C. Schrenk, A. Schnepf, *Rev. Inorg. Chem.* **2014**, *34*, 93–118.
[19] M. Brynda, R. Herber, P. B. Hitchcock, M. F. Lappert, I. Nowik, P. P. Power, A. V. Protchenko, A. Růžička, J. Steiner, *Angew. Chemie - Int. Ed.* **2006**, *45*, 4333–4337.
[20] A. Schnepf, in *Struct. Bond.* (Ed.: S. Dehnen), Springer, **2017**, pp. 135–200.
[21] E. Rivard, J. Steiner, J. C. Fettinger, J. R. Giuliani, M. P. Augustine, P. P. Power, *Chem. Commun.* **2007**, *32*, 4919–4921.
[22] G. Prabusankar, A. Kempfer, C. Gemel, M. K. Schröter, R. A. Fischer, *Angew. Chemie - Int. Ed.* **2008**, *47*, 7234–7237.
[23] M. Baudler, H. Ternberger, W. Faber, J. Hahn, *Zeitschrift für Naturforsch.* **1979**, *34b*, 1690–1697.
[24] G. Fritz, H. Schneider, *Zeitschrift für Anorg. Allg. Chemie* **1990**, *584*, 12–20.
[25] A. Schnepf, *Chem. Soc. Rev.* **2007**, *36*, 745–758.
[26] I. Krossing, in *Mol. Clust. Main Gr. Elem.* (Eds.: M. Driess, H. Nöth), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG, **2005**, pp. 209–229.
[27] C. Dohmeier, D. Loos, H. Schnöckel, *Angew. Chemie - Int. Ed.* **1996**, *35*, 129–149.
[28] G. Fritz, H.-W. Schneider, *Zeitschrift für Anorg. Allg. Chemie* **1990**, *584*, 12–20.
[29] D. J. Chapman, S. C. Sevov, *Inorg. Chem.* **2008**, *47*, 6009–6013.
[30] L. R. Sita, R. D. Bickerstaff, *J. Am. Chem. Soc.* **1989**, *111*, 6454–6456.
[31] A. F. Richards, H. Hope, P. P. Power, *Angew. Chemie - Int. Ed.* **2003**, *42*, 4071–4074.
[32] B. E. Eichler, P. P. Power, *Angew. Chemie - Int. Ed.* **2001**, *40*, 796–797.
[33] J. Wiederkehr, C. Wölper, S. Schulz, *Chem. Commun.* **2016**, *52*, 12282–12285.
[34] C. P. Sindlinger, L. Wesemann, *Chem. Sci.* **2014**, *5*, 2739–2746.
[35] J. J. Maudrich, C. P. Sindlinger, F. S. W. Aicher, K. Eichele, H. Schubert, L. Wesemann, *Chem. - A Eur. J.* **2017**, *23*, 2192–2200.
[36] A. Joannis, *Hebd. Séances Acad. Sci.* **1891**, *113*, 795.
[37] C. A. Kraus, *J. Am. Chem. Soc.* **1907**, *29*, 1907.
[38] F. H. Smyth, *J. Am. Chem. Soc.* **1917**, *39*, 1299–1312.
[39] C. A. Kraus, *J. Am. Chem. Soc.* **1922**, *44*, 1216–1239.
[40] E. Zintl, J. Goubenau, W. Dullenkopf, *Zeitschrift für Phys. Chemie A* **1931**, *154*, 1–46.
[41] E. Zintl, H. Kaiser, *Zeitschrift für Anorg. Allg. Chemie* **1933**, *211*, 113–131.
[42] C. Belin, J. Corbet, A. Cisar, *J. Am. Chem. Soc.* **1977**, *49*, 7163–7169.
[43] M. W. Hull, S. C. Sevov, *Inorg. Chem.* **2007**, *46*, 10953–10955.
[44] F. S. Kocak, P. Y. Zavalij, Y.-F. Lam, B. W. Eichhorn, *Chem. Commun.* **2009**, 4197–4199.
[45] F. Li, A. Muñoz-Castro, S. C. Sevov, *Angew. Chemie - Int. Ed.* **2012**, *51*, 8581–8584.
[46] A. Ugrinov, S. C. Sevov, *J. Am. Chem. Soc.* **2002**, *124*, 10990–10991.
[47] A. Ugrinov, S. C. Sevov, *Inorg. Chem.* **2003**, *42*, 5789–5791.
[48] C. Downie, J.-G. Mao, H. Parmar, A. M. Guloy, *Inorg. Chem.* **2004**, *43*, 1992–1997.
[49] O. Kysliak, C. Schrenk, A. Schnepf, *Angew. Chemie - Int. Ed.* **2016**, *55*, 3216–3219.
[50] F. Li, S. C. Sevov, *Inorg. Chem.* **2015**, *54*, 8121–8125.
[51] S. Frischhut, M. M. Bentlochner, W. Klein, T. F. Fässler, *Inorg. Chem.* **2017**, *56*, 10691–10698.
[52] F. Henke, C. Schenk, A. Schnepf, *Dalt. Trans.* **2009**, 9226, 9141–5.
[53] I. Kovács, G. Baum, G. Fritz, D. Fenske, N. Wiberg, H. Schuster, K. Karaghiosoff, *Zeitschrift für Anorg. Allg. Chemie* **1993**, *619*, 453–460.
[54] W. Höhle, J. Wolf, H. G. von Schnerring, *Zeitschrift für Naturforsch. B* **1988**, *43*, 219–223.
[55] E. S. S. A. G. Fritz, K. D. Hoppe, A. C. Der Universitiit, W. Hbnle, D. Weber, C. Mujica, V. Manriquez, *J. Organomet. Chem.* **1983**, *249*, 63–80.
[56] H. Siegl, W. Krumlacher, K. Hassler, *Monatshefte für Chemie* **1999**, *130*, 139–145.
[57] C. M. Knapp, C. S. Jackson, J. S. Large, A. L. Thompson, J. M. Goicoechea, *Inorg. Chem.* **2011**, *50*, 4021–4028.
[58] S. Scharfe, F. Kraus, S. Stegmaier, A. Schier, T. F. Fässler, *Angew. Chemie - Int. Ed.* **2011**, *50*, 3630–3670.
[59] R. S. P. Turbervill, J. M. Goicoechea, *Chem. Rev.* **2014**, *114*, 10807–10828.
[60] L. R. Sita, I. Kinoshita, *J. Agric. Food Chem.* **1992**, *114*, 7024–7029.
[61] C. Drost, M. Hildebrand, P. Lönnecke, *Main Gr. Met. Chem.* **2002**, *25*, 93–98.
[62] D. Nied, W. Klopper, F. Breher, *Angew. Chemie - Int. Ed.* **2009**, *48*, 1411–6.
[63] D. Nied, R. Köppe, W. Klopper, H. Schnöckel, F. Breher, *J. Am. Chem. Soc.* **2010**, *132*, 10264–10265.
[64] D. Scheschkewitz, *Angew. Chemie - Int. Ed.* **2005**, *44*, 2954–2956.
[65] G. Fischer, V. Huch, P. Mayer, S. K. Vasisht, M. Veith, N. Wiberg, *Angew. Chemie - Int. Ed.* **2005**, *44*, 7884–7887.
[66] K. Abersfelder, A. J. P. White, R. J. F. Berger, H. S. Rzepa, D. Scheschkewitz, *Angew. Chemie - Int. Ed.* **2011**, *50*, 7936–7939.

- [67] N. Wiberg, H. W. Lerner, S. Wagner, H. Nöth, T. Seifert, *Zeitschrift für Naturforsch. - Sect. B* **1999**, *54*, 877–880.
- [68] A. F. Richards, M. Brynda, M. M. Olmstead, P. P. Power, *Organometallics* **2004**, *23*, 2841–2844.
- [69] A. F. Richards, M. Brynda, P. P. Power, *Organometallics* **2004**, *23*, 4009–4011.
- [70] D. Nied, P. Ona-Burgos, W. Klopper, F. Breher, *Organometallics* **2011**, *30*, 1419–1428.
- [71] M. Dräger, B. Mathiasch, *Angew. Chemie* **1981**, *93*, 1079–1080.
- [72] F. García, J. P. Hehn, R. A. Kowenicki, M. McPartlin, C. M. Pask, A. Rothenberger, M. L. Stead, D. S. Wright, *Organometallics* **2006**, *25*, 3275–3281.
- [73] P. P. Power, *Chem. Rec.* **2012**, *12*, 238–255.
- [74] Z. D. Brown, P. P. Power, *Inorg. Chem.* **2013**, *52*, 6248–6259.
- [75] R. West, *Angew. Chemie* **1987**, *12*, 1231–1241.
- [76] V. Uni, V. Da, O. S. A. V. V. Da, G. H. Spikes, J. C. Fettinger, P. P. Power, *J. Am. Chem. Soc.* **2005**, *127*, 12232–12233.
- [77] J. Li, C. Schenck, C. Goedecke, G. Frenking, C. Jones, *J. Am. Chem. Soc.* **2011**, *133*, 18622–18625.
- [78] J. Li, M. Hermann, G. Frenking, C. Jones, *Angew. Chemie - Int. Ed.* **2012**, *51*, 8611–8614.
- [79] D. Nied, E. Matern, H. Berberich, M. Neumaier, F. Breher, *Organometallics* **2010**, *29*, 6028–6037.
- [80] M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, *111*, 354–396.
- [81] M. Haaf, A. Schmiedl, T. A. Schmedake, D. R. Powell, A. J. Millevolte, M. Denk, R. West, *J. Am. Chem. Soc.* **1998**, *120*, 12714–12719.
- [82] Y. Xiong, S. Yao, M. Brynd, M. Driess, *Angew. Chemie - Int. Ed.* **2007**, *46*, 4511–4513.
- [83] Y. Peng, H. Fan, H. Zhu, H. W. Roesky, J. Magull, C. E. Hughes, *Angew. Chemie - Int. Ed.* **2004**, *43*, 3443–3445.
- [84] J. W. Dube, C. M. E. Graham, C. L. B. Macdonald, Z. D. Brown, P. P. Power, P. J. Ragogna, *Chem. - A Eur. J.* **2014**, *20*, 6739–6744.
- [85] A. V. Protchenko, J. I. Bates, L. M. A. Saleh, M. P. Blake, A. D. Schwarz, E. L. Kolychev, A. L. Thompson, C. Jones, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2016**, *138*, 4555–4564.
- [86] M. Majumdar, I. Omlor, C. B. Yıldız, A. Azizoglu, V. Huch, D. Scheschkewitz, *Angew. Chemie - Int. Ed.* **2015**, *54*, 8746–8750.
- [87] X. Wang, Y. Peng, M. M. Olmstead, J. C. Fettinger, P. P. Power, *J. Am. Chem. Soc.* **2009**, *131*, 14164–14165.
- [88] A. V. Protchenko, P. Vasko, D. C. H. Do, J. Hicks, M. Á. Fuentes, C. Jones, S. Aldridge, *Angew. Chemie - Int. Ed.* **2019**, *58*, 1808–1812.
- [89] K. L. Gullett, T. Y. Lai, C. Y. Chen, J. C. Fettinger, P. P. Power, *Organometallics* **2019**, *38*, 1425–1428.
- [90] C. Cui, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2004**, *126*, 5062–5063.
- [91] T. Y. Lai, K. L. Gullett, C. Y. Chen, J. C. Fettinger, P. P. Power, *Organometallics* **2019**, *38*, 1421–1424.
- [92] T. Y. Lai, J. C. Fettinger, P. P. Power, *J. Am. Chem. Soc.* **2018**, *140*, 5674–5677.
- [93] C. Cui, M. M. Olmstead, J. C. Fettinger, G. H. Spikes, P. P. Power, *J. Am. Chem. Soc.* **2005**, *127*, 17530–17541.
- [94] X. Wang, C. Ni, Z. Zhu, J. C. Fettinger, P. P. Power, *Inorg. Chem.* **2009**, *48*, 2464–2470.
- [95] K. Takeuchi, M. Ichinohe, A. Sekiguchi, *J. Am. Chem. Soc.* **2008**, *130*, 16848–16849.
- [96] C. A. Caputo, P. P. Power, *Organometallics* **2013**, *32*, 2278–2286.
- [97] Z. D. Brown, P. Vasko, J. C. Fettinger, H. M. Tuononen, P. P. Power, *J. Am. Chem. Soc.* **2012**, *134*, 4045–4048.
- [98] X. Wang, Y. Peng, Z. Zhu, J. C. Fettinger, P. P. Power, J. Guo, S. Nagase, *Angew. Chemie - Int. Ed.* **2010**, *49*, 4593–4597.
- [99] N. Kano, K. Shibata, N. Tokitoh, R. Okazaki, *Organometallics* **1999**, *18*, 2999–3007.
- [100] T. Chu, G. I. Nikonorov, *Chem. Rev.* **2018**, *118*, 3608–3680.
- [101] B. G. Steller, Diorganotin Dihydrides as Building Blocks for Functionalised Oligomers and Sigma-Conjugated Materials, Graz University of Technology, **2017**.
- [102] T. Y. Lai, L. Tao, R. D. Britt, P. P. Power, *J. Am. Chem. Soc.* **2019**, *141*, 12527–12530.
- [103] S. Wang, T. J. Sherbow, L. A. Berben, P. P. Power, *J. Am. Chem. Soc.* **2018**, *140*, 590–593.
- [104] J. Hicks, M. Juckel, A. Paparo, D. Dange, C. Jones, *Organometallics* **2018**, *37*, 4810–4813.
- [105] P. B. Hitchcock, M. F. Lappert, L. J. M. Pierssens, A. V. Protchenko, P. G. H. Uiterweerd, *Dalt. Trans.* **2009**, 4578–4585.
- [106] J. Beckmann, D. Heinrich, S. Mebs, *Zeitschrift für Anorg. und Allg. Chemie* **2013**, *639*, 2129–2133.
- [107] C. Kollemann, F. Sladky, *Organometallics* **1991**, *10*, 2101–2102.
- [108] J. S. Han, T. Sasamori, Y. Mizuhata, N. Tokitoh, *Dalt. Trans.* **2010**, *39*, 9238.
- [109] O. T. Summerscales, C. A. Caputo, C. E. Knapp, J. C. Fettinger, P. P. Power, *J. Am. Chem. Soc.* **2012**, *134*, 14595–14603.
- [110] S. Wang, M. L. McCrea-Hendrick, C. M. Weinstein, C. A. Caputo, E. Hoppe, J. C. Fettinger, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2017**, *139*, 6596–6604.
- [111] D. L. Kays, *Chem. Soc. Rev.* **2016**, *45*, 1004–1018.
- [112] D. L. Kays, in *Organomet. Chem.*, Royal Society Of Chemistry, Cambridge, **2010**, pp. 56–76.
- [113] T. Agou, Y. Sugiyama, T. Sasamori, H. Sakai, Y. Furukawa, N. Takagi, J. D. Guo, S. Nagase, D. Hashizume, N. Tokitoh, *J. Am. Chem. Soc.* **2012**, *134*, 4120–4123.
- [114] T. Sasamori, Y. Sugiyama, N. Takeda, N. Tokitoh, *Organometallics* **2005**, *24*, 3309–3314.
- [115] B. D. Rekken, T. M. Brown, J. C. Fettinger, F. Lips, H. M. Tuononen, R. H. Herber, P. P. Power, *J. Am. Chem. Soc.* **2013**, *135*, 10134–10148.
- [116] J. Bresien, J. M. Goicoechea, A. Hinz, M. T. Scharnhölz, A. Schulz, T. Suhrbier, A. Villinger, *Dalt. Trans.* **2019**, *48*, 3786–3794.
- [117] B. E. Eichler, L. Pu, M. Stender, P. P. Power, *Polyhedron* **2001**, *20*, 551–556.
- [118] Y. Peng, R. C. Fischer, W. A. Merrill, J. Fischer, L. Pu, B. D. Ellis, J. C. Fettinger, R. H. Herber, P. P. Power, *Chem. Sci.* **2010**, *1*, 461–468.
- [119] L. G. Perla, J. M. Kulenkampff, J. C. Fettinger, P. P. Power, *Organometallics* **2018**, *37*, 4048–4054.
- [120] L. Pu, A. D. Phillips, A. F. Richards, M. Stender, R. S. Simons, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 11626–11636.
- [121] R. H. Blessing, *Acta Crystallogr. Sect. A* **1995**, *A51*, 33–38.
- [122] G. M. Sheldrick, SADABS Version 2.10 Siemens Area Detector Correction., Universitaet Goettingen, Goettingen, Germany, **2003**.
- [123] G. M. Sheldrick, *SHELXTL Version 6.1*. Bruker AXS, Inc., Madison, WI, **2002**.
- [124] G. M. Sheldrick, GM SHELXS97 and SHELXL97, Universitaet Goettingen, Goettingen, Germany, **2002**.
- [125] B. Schiemenz, P. P. Power, *Angew. Chemie (International Ed. English)* **1996**, *35*, 2150–2152.
- [126] A. Schnepf, R. Köppe, *Angew. Chemie - Int. Ed.* **2003**, *42*, 911–913.
- [127] G. H. Spikes, J. R. Giuliani, M. P. Augustine, I. Nowik, R. H. Herber, P. P. Power, *Inorg. Chem.* **2006**, *45*, 9132–9136.