The Activation of Small Molecules by Heavier Group 14 Carbene Analogues

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Abstract

Recent investigations show that low valent group 14 compounds such as stable carbenes (NHCs, CAACs), E≡E species (E=Si, Ge, Sn) and heavier stable singlet carbene analogues (e.g. germylenes Ar_2Ge: $(Ar= C_6H_3-2,6(C_6H_3-2,6-Pr^i_2)_2)$ activate small molecules such as H_2, NH_3, P_4 and olefins. Therefore, these low oxidation state compounds mimic transition metal centers and show potential for future catalytic applications. In our working group fascinating Ge and Sn compounds stabilized by 2,6-$[ArN=CH]_2(NC_5H_3)$ (Ar= Dipp) were synthesized. The activation of small molecules by this novel comlexes was investigated. The reactivity of the Sn complex stabilized by 2,6-$[ArN=CH]_2(NC_5H_3)$ (Ar= Dipp) was shown by the insertion into a P≡C triple bond resulting in a formation of a five membered ring. Furthermore a novel carbene precursor with an additional functional group was synthesized using a acetoimino pyridine ligand system 2-$[CH_3CO]$-6-$[ArN=CH](NC_5H_3)$ (Ar= Dipp). Synthesizing and investigating these species gave a new insight in low oxidation state main group compounds.

Contents

1 Introduction

"Stable singlet carbenes as mimics for transition metal centers" is the title of a recently published review by Guy Bertrand.[1] In this review, new approaches in main group element chemistry are covered due to their recently investigated, fascinating behavior to mimic transition metals. In fact main group elements, like carbon, silicon and germanium compounds, activate small molecules such as H_2, NH_3 and C_2H_4 under mild conditions and therefore show a catalytic potential for future applications.[2,3]
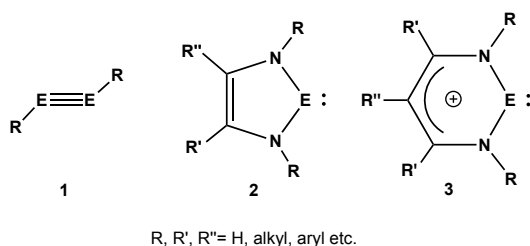

R, R', R"= H, alkyl, aryl etc.

Figure 1: The E≡E low valent compound **1** with a formal oxidation state of +1 (E= Si, Ge, Sn and Pb) and the NHCs and their heavier analogues **2** and **3** with a formal oxidation state of +2 display the possibility to activate small molecules such as H_2, NH_3 and olefins under mild conditions. (E= C, Si, Ge, Sn and Pb)

In the last 30 years fascinating compounds were synthesized, which were previously supposed to be unstable. These kinds of species are, for example, multiple bond compounds (**1**) and N-heterocyclic carbenes (NHC) and their heavier analogues **2** and **3** containing heavier group 14 elements, as shown in Figure 1. Low valent main group compounds are coordinatively unsaturated species and therefore extremely reactive. This kind of species, owing to their singlet ground state, possesses a lone pair of electrons which acts as σ donor and a vacant orbital which acts as a π acceptor.

Recently interesting Ge and Sn compounds were isolated in our working group, which could display promising activation chemistry. Investigating these Ge and Sn species and their reaction behavior, particularly the activation of small molecules, has an important impact on understanding low valent main group chemistry. Furthermore, a novel NHC with an additional functional group will be synthesized. The additional functional group modifies the electronic properties of the NHC. Novel NHCs with an additional functional group display an interesting target for complexing transition metals and their application as catalysts.

2 Literature

2.1 N-heterocyclic carbenes and their heavier analogues

Since the isolation of the first stable imidazol-2-ylidene in 1991 by Arduengo *et al.*,[4] N-heterocyclic carbenes (NHCs) have gained immense attention. NHCs display unique properties due to their reactive carbon center and their excellent σ donating properties. Therefore, they are very useful in complexing transition metals.[5,6] This led to the formation of various organometallic catalysts, which are very effective in, for example, olefin metathesis, Heck and Suzuki coupling, aryl amination reactions, hydrosilylation reactions, and many more.[5,6] Due to that enormous and outstanding applications a large number of different NHCs were synthesized, the synthetic methods were optimized and applied in industry. In contrast to the large number of NHCs, carbenes with an additional functional donating group are rare. An additional donor would influence the coordination to metals and possibly also have an effect on their catalytic properties.[7] The ligand system $2,6\text{-}[\text{ArN-C(H)}_2]_2(\text{NC}_5\text{H}_3)$ $(\text{Ar}= \text{C}_6\text{H}_3\text{-}2,6\text{-}\text{Pr}^i_2)$ is a reasonable precursor for the synthesis of a NHC with an additional funtional imino group. Diimino pyridine (DIMPY) ligands were already established for the stabilization of transition metals.[8] Fe, Co and Pd complexes stabilized by this ligand display promising catalytic properties.[9] In the literature the synthesis of imidazolium salts starting from the mono armed iminopyridine ligand (MIMPY) $2\text{-}[\text{ArN=C(H)}](\text{NC}_5\text{H}_3)$ $(\text{Ar}= \text{C}_6\text{H}_3\text{-}2,4,6\text{-Me})$ are known.[10] Lassaletta and his working group established an alternative route obtaining imidazo[1,5a]pyridines[11] and further similar carbenes were synthesized bearing a pyridine ring building block.[12–14]
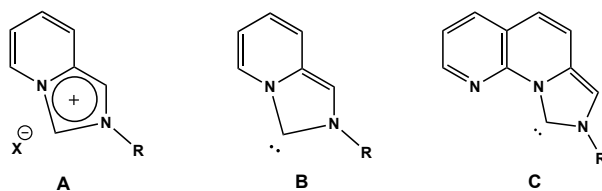

Figure 2: Selected types of an imidazolium salt **A**[10] and carbenes **B**[11,13,14] and **C**[12] containing pyridine building blocks.

In the last decade working groups were also interested in stabilizing very reactive heavier Group 14 species by N,N-bidentate ligands.[1,2] This led to the formation of fascinating types of compounds, some examples are shown in Figure 3. The cationic species of type **D** and **E** also exist coordinating the corresponding halogenide as anion.
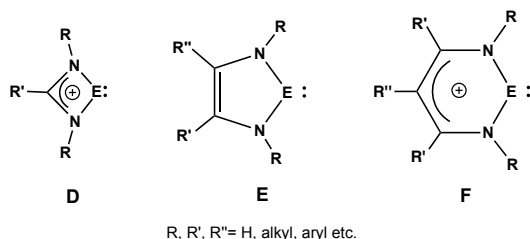
Figure 3: General types of heavier NHC analogues. E= Si, Ge, Sn and Pb.[2]

The heavier NHC type compounds, as shown in Figure 3, have an oxidation state of +2 and display fascinating reaction behavior due to the bifunctionality at the element center, E. This leads to promising properties of heavier NHC carbenes in activating small molecules. Typical synthetic methods to obtain heavier NHC analogues are salt elimination reactions followed by reduction of the mostly halogenated intermediate. The heavier NHC analogues, above all the low valent silicon species, show a fascinating reactivity and undergo numerous reactions with reactants like dienes, ketones, nitriles, transition metal complexes and chalcogens. Another very interesting behavior was investigated by the working group of Gudat, where a direct transfer of a Sn atom, from a diazastannole to a diazadiene group occurs.[15] Therefore, the coordinating ligand can be displayed as a donor molecule which is not directly bonded to the Sn atom. Consequently, this compound can also be seen as a species with a formal oxidation state of zero, as shown in Figure 4.
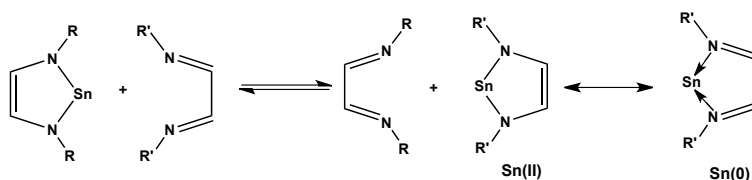

Figure 4: Sn-transfer reaction between diazastannoles and diazadienes. This indicates a certain degree of Sn(0) character. (acc. Gudat *et al.*[15])

2.2   Multiple bond compounds of the heavier carbon analogues

Research on multiple bond formation of heavier carbon analogues led to various spectacular low oxidation state compounds after intensive investigations. Very interesting reviews on multiple bond formation of main group compounds were published by Y.

Wang and G. H. Robinson,[16] P. P. Power and R. C. Fischer,[17] a profound book was written by V. Lee and A. Sekiguchi.[18] Recently, an astonishing novel type of group 14 compounds was developed, where the group 14 elements are in the formal oxidation state of zero.[16,19] For main group elements this is a completely new approach. In general, group 14 compounds with multiple bonds in an oxidation state of two, one or zero, can be classified by a simple generalization of four neutral types shown in Figure 5.
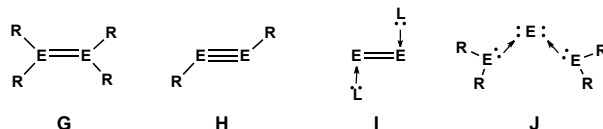

Figure 5: Generalization of neutral types of low oxidation state heavier group 14 compounds containing multiple bonds. Type G: Oxidation state 2 for E= Si, Ge, Sn and Pb, type H: Oxidation state 1 for E= Si, Ge, Sn and Pb, type I: Oxidation state 0 for E= Si and type J: Centered element with an oxidation state 0 for E= Si, Ge and Sn.[16]

For type **G**, the so called *dimetallenes* with an oxidation state of $+2$, species for all heavier carbon analogues were synthesized.[20,21] In solution however, these compounds frequently dissociate into monomers.

The formal oxidation state of type **H**, the E≡E triple bond, is $+1$. In 2000, Power *et al.* isolated the first RPb≡PbR structure, a spectacular breakthrough in multiple bond chemistry of heavier main group elements.[22] Other discoveries involving E≡E triple bonds of heavier congeners followed.[23,24] In 2004, Sekiguchi *et al.* synthesized the corresponding RSi≡SiR (R= $Si(Pr^i)$ $[CH(SiMe_3)_2]_2$) compound.

Recently the working group of Wang and Robinson investigated a fascinating novel type of group 14 compounds (type **I**), where the silicon atoms have a formal oxidation state of zero.[16,19] The Si=Si core is coordinated by two Lewis base ligands (L:), namley very bulky carbene ligands (L:= :$C[N(2,6-Pr^i_2C_6H_3)CH]_2$). The corresponding Ge=Ge species was isolated by Jones *et al.*[25] Another example of multiple bond analogues of group 14 elements and an example of E(0) and E(II) species in one molecule is type **J**, the allenes.[17] In 2003, Kira *et al.* synthesized the trisila-allene via reacting a silylene (:$Si[C(SiMe_3)_2CH_2]_2$) with $SiCl_4$ and than reducing the halogenated intermediate.[26] The analogue systems 1,3-disila-2-germa-, 1,3-digerma-2-sila-, trigerma-allenes[17] and tristanna-allene[27] were also synthesized. In addition, Frenking and coworkers studied the C(0) allene species theoretically.[28]

2.3 Activation of small molecules

E≡E triple bond compounds are highly reactive. Numerous investigations display their behavior to activate small molecules. Wiberg *et al.* added ethylene and butadiene to the relatively stable disilyne RSi≡SiR (R= SiMe(SiBu$^t_3$)$_2$) to obtain the [2+2] and [2+4] addition products in 2004.[29] Further discoveries of Sekiguchi *et al.* showed addition products of their stable disilyne RSi≡SiR (R= SiPr^i[CH(SiMe$_3$)$_2$]$_2$) with cis and trans but-2-ene.[30]
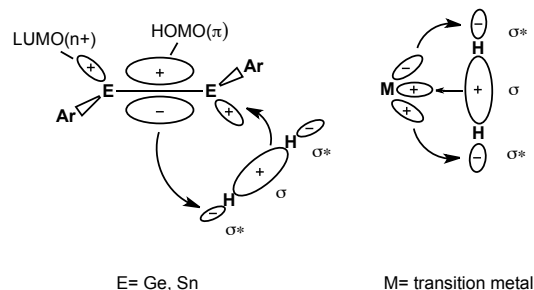

E= Ge, Sn   M= transition metal

Figure 6: The interaction of the frontier orbital of triple bond main group compounds Ar E≡EAr(Ar= C$_6$H$_3$-2,6(C$_6$H$_3$-2,6-Pr$^i_2$)$_2$(Dipp)) (E= Ge, Sn) with H$_2$ (left) and the comparison with a transition metal (right). The activation of H$_2$ by main group element compounds are very similar to the activation by transition metals. (acc. Power *et al.*[3])

In 2005 Power *et al.* were the first to react H$_2$ with the Ge and Sn alkyne ArE≡EAr (Ar= C$_6$H$_3$-2,6(C$_6$H$_3$-2,6-Pr$^i_2$)$_2$). For the Ge congener the hydrogenated products Ar(H)GeGe(H)Ar, Ar(H)$_2$GeGe(H)$_2$Ar and Ge(H)$_3$Ar were isolated.[31] The ArSn≡SnAr compound exclusively gives ArSn(µ-H$_2$)SnAr. Power *et al.* explain this phenomenon by the interaction of frontier orbitals with H$_2$, as shown in Figure 6. The π HOMO orbital of the E≡E species donates electrons into the σ* orbital of H$_2$ and then a electron donation of the σ orbital of H$_2$ follows into the LUMO of ArE≡EAr. This interaction enables the oxidative addition of H$_2$ due to the weakening of the H-H bond. More recently the same research group reacted ArSn≡SnAr (Ar= C$_6$H$_3$-2,6(C$_6$H$_3$-2,6-Pr$^i_2$)$_2$ or C$_6$H-2,6-(C$_6$H$_2$-2,4,6Pr$^i_3$)-3,5Pr$^i_2$) reversibly with ethylene at room temperture and one atmosphere pressure to obtain a double cycloadduct. This is the first example of a reversible interaction between a very reactive group 14 species and a relatively unreactive substrate molecule under mild conditions.

Recently, Bertand *et al.* published a review covering the behavior of singlet carbenes miming the reactivity of transition metal centers.[1] In this review, the activation of CO, H$_2$, NH$_3$ and P$_4$ is discussed as well as the ability of carbene analogues to stabilize highly reactive species as is possible for transition metal complexes. The ac-

tivation of H_2 was accomplished with the germylenes $Ar_2Ge:$ and stannylenes $Ar_2Sn:$ ($Ar= C_6H_3$-2,6(C_6H_3-2,6-Pr^i_2)$_2$ or C_6H_3-2,6-(C_6H_2-2,4,6-Me_3)$_2$) under relatively mild conditions. However, sometimes arene elimination of the bulky aryl substituent occurs.[1,32] Power *et al.*, reported also on the activation of ammonia by these heavier
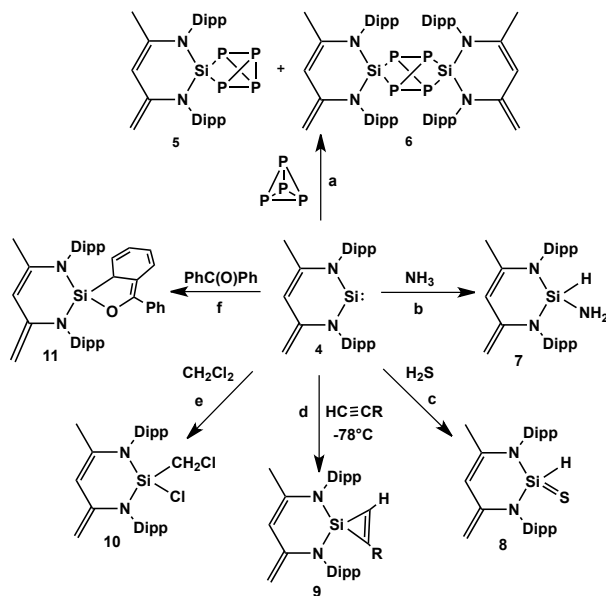

Figure 7: The silylene **4** reacts with various inorganic and organic compounds to yield the corresponding products. Reactions with: a) white phosphorus, b) ammoniac, c) hydrogen sulfide, d) multiple bonds, e) organohalides and f) benzophenone. (acc. Driess *et al.*[33])

carbene analogue species.[32] Furthermore they investigated the first example of a germaketene reacting a diaryl germylene with CO.[1,3]

In 1998, West *et al.* performed the conversion of white phosphorus to the red allotrope by a stable silylene. Recent developments by Driess *et al.* display the reactivity of silylene **4**, which inserts into P_4 to yield the strained polycyclic silaphosphanes **5** and **6**.[1] Furthermore, Driess *et al.* reported reactions of silylene **4**[33] with small molecules in a recently published review (Figure 7). These transformation led to spectacular synthetic results as the first examples of sila-ketones, sila-esters etc. were isolated. The diversity of the reaction behavior of the low oxidation state compounds can be seen by this fascinating activation of small molecules. The heavier carbene analogues also react with small molecules as shown for the Si homologue **4**. However, the reaction behavior of Ge and Sn congeners are not that well investigated as those of the silylenes. Ma *et al.* calculated the activation of H_2 by germylenes and stannylenes at density functional level.[34]

3 Results and Discussion

3.1 Synthesis of a Novel N-Heterocyclic Carbene

In the last decades several different synthetic routes leading to NHCs were developed.[5,6] A very important step in the design of NHCs is the synthesis of the NHC precursors. Depending on the NHC precursor, various synthetic routes were created.[35] Starting from a diimino starting material, as in the case of the ligand system 2,6-[ArN-C(H)$_2$]$_2$(NC$_5$H$_3$) (Ar= C$_6$H$_3$-2,6-Pr$^i_2$), a method is necessary to form the imidazolium salt, which is a typical precursor for NHCs. After obtaining the imidazolium salt, a reduction can take place to isolate the desired carbene. A general method to form the imidazolium salt is using paraformaldehyde as a precarbenic unit, as shown in Figure 8.
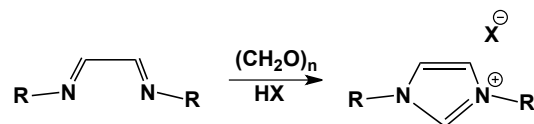

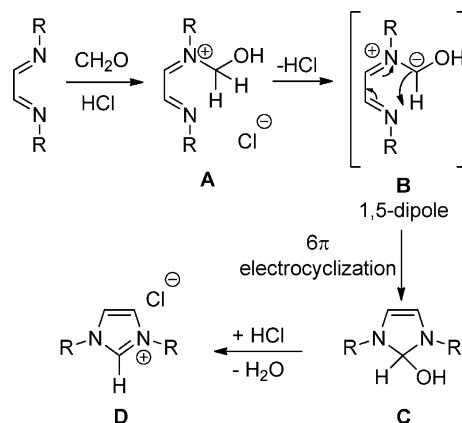Figure 8: A general method of the imidazolium salt is using paraformaldehyde as the precarbenic unit.[35]

Figure 9: A plausible mechanism to form an imidazolium salt using formaldehyde in the presence of an acid.[35]

As shown in the mechanism in Figure 9 one equivalent of 1,2 diimines reacts with formaldehyde in the presence of an acid to form the desired imidazolium salt. These route seems also applicable for the ligand system 2,6-[ArN-C(H)$_2$]$_2$(NC$_5$H$_3$) (Ar= C$_6$H$_3$-2,6-Pr$^i_2$) (Figure 10).

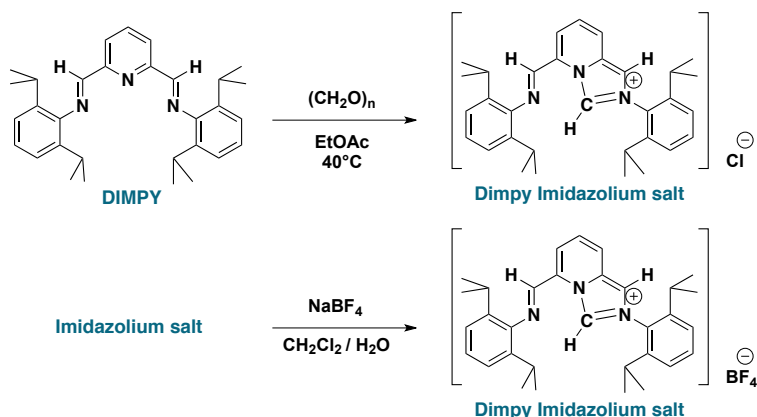The main difference is the presence of a second imino functionality, which could be

Figure 10: The synthesis of the imidazolium salt reacting the DIMPY ligand with paraformaldehyde and trimethylsilylchloride. In a second step an anion exchange takes place.

problematic due to the fact that it reacts with either the TMSCl or the paraformalde-hyde leading to several byproducts. Furthermore, it is necessary to break the aro-maticity of the pyridine ring to form the imidazolium salt, which is in general not favored.

The paraformaldehyde and the DIMPY ligand were added into a solution of ethyl acetate and the suspension was heated to 70°C. Then TMSCl was added drop wise and the reactants dissolved in the reaction solution. After 2 hours heating, a slightly yellow precipitate was formed, filtrated and washed with hexane. The ^{1}H and ^{13}C NMRs indicate a compound with an imidazolium structure. In the ^{1}H NMR a low shifted peak at 10.2 ppm was observed and also the ^{13}C correlates, but still there is also a low shifted peak found at 185 ppm in the ^{13}C NMR, which cannot be assimilated with the desired product. The precipitate was badly crystallizing and therefore an anion exchange was performed, as shown in Figure 10. After crystallizing in a mixture of dichloromethane and Et_2O a suitable crystal for X-Ray diffraction was obtained of which the crystal structure is shown in Figure 11.

An imidazolium salt is formed, but instead of having a second imino functionality an aldehyde functionality is formed. The TMSCl reacts with the second imino func-tionality and due to traces of water an elimination reaction takes place and forms the imidazolium salt with an aldehyde functionality. In this case other synthetic routes have to be found to synthesize the target molecule. In Figure 12, alternative routes are presented.

Either a reaction solution of chloromethyl pivalate and AgOTf[10] or chloromethyl ethyl ether[36] reacts with the diimino ligand. The advantage in both cases is that no reactive species could eliminate the second imino functionality and form an aldehyde.
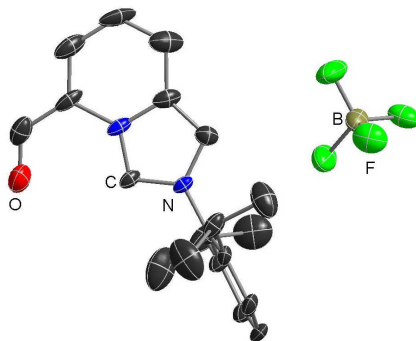
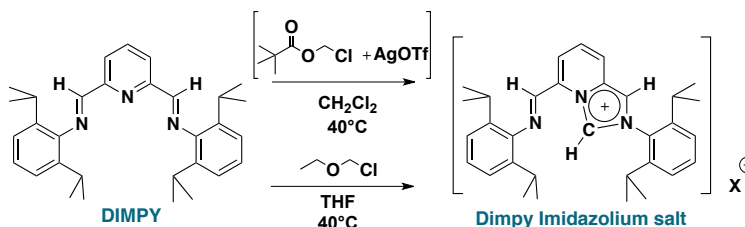Figure 11: Crystal structure of the acetpyridine imidazolium salt.

Figure 12: Alternative routes for the synthesis of the imidazolium salt. The advantage of these synthesis is the absence of reactive agents as for example TMSCl.

In both cases no main product was formed and several byproducts were obtained. Furthermore, still starting material was present in the reaction solution. This indicates that probably oligomers are formed, linking several DIMPY molecules together. This fact proves that the DIMPY ligand is not useful for the synthesis of the desired imidazolium salt.

Another synthetic route would be starting from a ketone imino pyridine ligand (acetimpy), as shown in Figure 13.
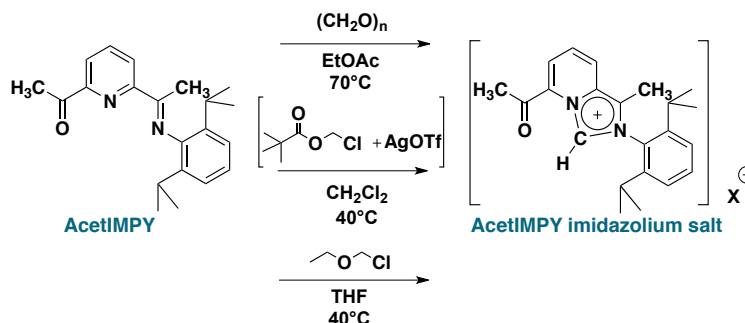

Figure 13: Synthetic routes for the isolation of the acetopyridine imidazolium salt.

The advantage is that the ketone does not react with HX or TMSCl and that only

one imino funtionality reacts and therefore byproducts as oligomers can probably be avoided. Then a condensation reaction with diisopropylaniline takes place to obtain the target molecule, the iminopyridine imidazolium salt, as shown in Figure 14.
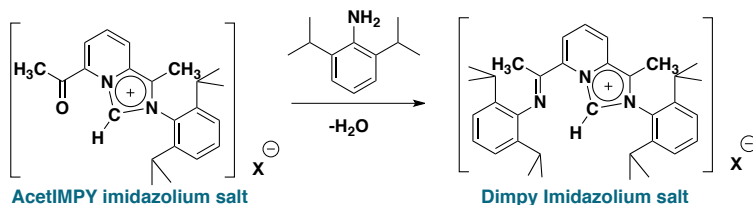

Figure 14: In a second step the acetopyridine imidazolium salt reacts with diisopropylaniline via a condensation reaction to give the target molecule the iminopyridine imidazolium salt.

In the case of the acetimpy ligand reacting with the paraformaldehyde or the chloromethyl ethyl ether the desired compound is not formed. Instead several different compounds are formed, which can also be oligomers. Although changing the reaction conditions (heating the reaction solution for several days), the target molecule could not be synthesized by these methods.

Much more efficient is the reaction with the OTf methyl pivalate species, which is formed by stirring AgOTf with chloromethyl pivalate in THF for 45 minutes. This reactive species was added to the acetimino starting material and heated at 50°C for five days. The solvent was removed and the residue was washed with hexane. The ^{1}H and ^{13}C NMRs indicate that the desired imidazolium salt is formed. There is still a byproduct after washing the residue with hexane, but via recrystallization in chloroform the target molecule can be isolated.

No time was left to perform the second step, the condensation reaction. Due to the promising properties of this carbene, this project will be continued at the home institution and in collaboration with Prof. Guy Bertrand.

3.2   Activation of Small Molecules by Heavier Group 14 Carbene Analogues

Recently working groups focus on the understanding of the reaction behavior of low oxidation state main group compounds. Especially carbenes show fascinating properties to activate small molecules. Their heavier homologues display similar properties, but there are still only a few examples known in literature, especially in the case of Ge and Sn compounds.[1–3] As mentioned, interesting low valent Ge and Sn iminopyridine complexes were synthesized in our working group. These species could display

promising activation reactions with small molecules. The reaction behavior of low oxidation state compounds depends on the central atom and the coordinating properties of the stabilizing ligands. Therefore, a different reaction behavior is expected comparing the reaction chemistry of Ge complexes and their heavier Sn homologues.

The DAMPY ligand system $(2,6\text{-}[ArN\text{-}CH_2]_2(NC_5H_3)$ $(Ar= C_6H_3\text{-}2,6\text{-}Pr^i_2))$ was involved in transition metal chemistry isolating DAMPY*ZrR$_2$ (R= Me, Cl, NMe$_2$, CH$_2$Ph, C$_4$H$_6$) complexes and Th complexes.[37–39] In our working group the DAMPY ligand system was employed in a transamination reaction with germanium and tin dihexamethyldisilazanides (EHMDS$_2$, E= Ge, Sn), as shown in Figure 15.[40]
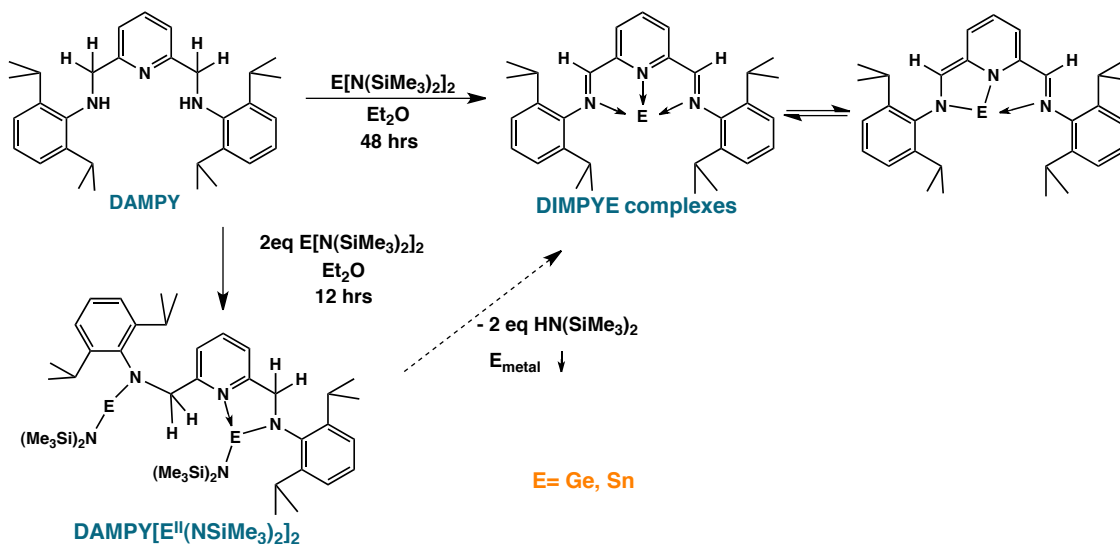

Figure 15: Possible reaction mechanism for the DIMPYE complex (E=Ge, Sn).[40]

The DAMPY ligand reacts with two equivalents of E(HMDS)$_2$ (E= Ge, Sn) and eliminates hexamethyldisilazane to form a heteroleptic bistetrylene DAMPY[E^{II}N(SiMe$_3$)$_2$]$_2$. In a second step again a transamination reaction occurs eliminating the hydrogen atoms of the ligand backbone and generates a diimino pyridine ligand system coordinating a group 14 element. There is no full conversion to the final product due to kinetically hindrance of eliminating HMDS in the second step and therefore a mixture of products is obtained. Via recrystallization in pentane the main products can be isolated.

The diimino pyridine ligand, $2,6\text{-}[ArN=C(H)]_2(NC_5H_3)$ $(Ar= C_6H_3\text{-}2,6\text{-}Pr^i_2)$, acts as a donor molecule and is highly effective in stabilizing the Ge or Sn atom. In literature this ligand system is also known as an effective donor for main group elements as the cationic compound $[GaI_2(DIMPY)][GaI4]$ $(DIMPY= 2,6\text{-}[ArN=C(Me)]_2(NC_5H_3))$.[41] In 2006 the formation of aluminum diimino pyridine complexes with interesting co-
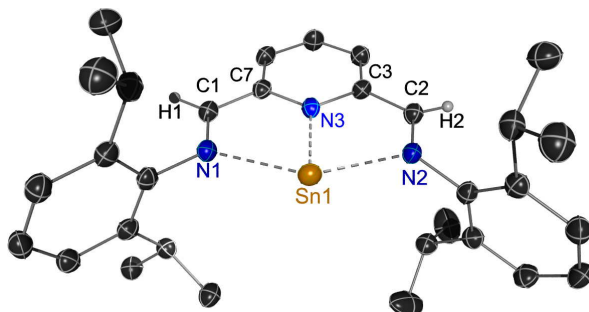
Figure 16: Crystal structure of a Sn diimino pyridine complex. Selected bond lengths ($\mathring{A}$): Sn(1)-N(1) 2.120, Sn(1)-N(2) 2.312, Sn(1)-N(3) 2.397, N(2)-C(27) 1.321, N(3)-C(28) 1.308.

ordination properties were reported.[42] In the same year Cowley *et al.* published the synthesis of cationic arsenic(I) diimino pyridine complexes[43] and in 2009 Ragogna and coworkers reported Ch^{2+} (Ch= S, Se, Te) complexes[44] which are isoelectronic to the Sn diimino pyridine species, as shown in Figure 17.
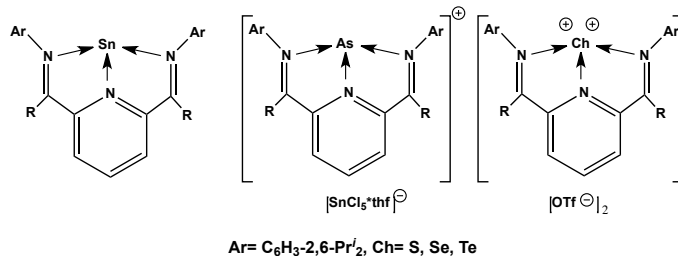

Ar= C_6H_3-2,6-Pr^i_2, Ch= S, Se, Te

Figure 17: The Sn species of Fischer and Flock is isoelectronic to the group 15 analogue of Cowley *et al.* and group 16 analogues of Ragogna *et al.*[43, 44]

The donating properties can either be explained as three donor acceptor interactions (left resonance structure in Figure 15) stabilizing a germanium or tin atom in a formal oxidation state of zero or as two covalent bonds with one donor acceptor interaction (right resonance structure). This trend is also depending on the central atom. In case of Ge the right resonance structure resembles much more the solid state structure due to the small atomic radius of the Ge atom. In case of the bigger Sn atom the left resonance structure resembles much more the solid state structure as shown in Figure 16.[40]

Furthermore, the mono armed iminopyridine ligand (MIMPY) 2-[ArN=C(H)](NC_5H_3) (Ar= C_6H_3-2,6-Pr^i_2), earns special interest as the Ge containing ring displays aromatic behavior by expense of the aromaticity of the pyridine group (Figure 18).[45]

In 2009, Heinicke *et al.* synthesized the silylene and germylene stabilized by the
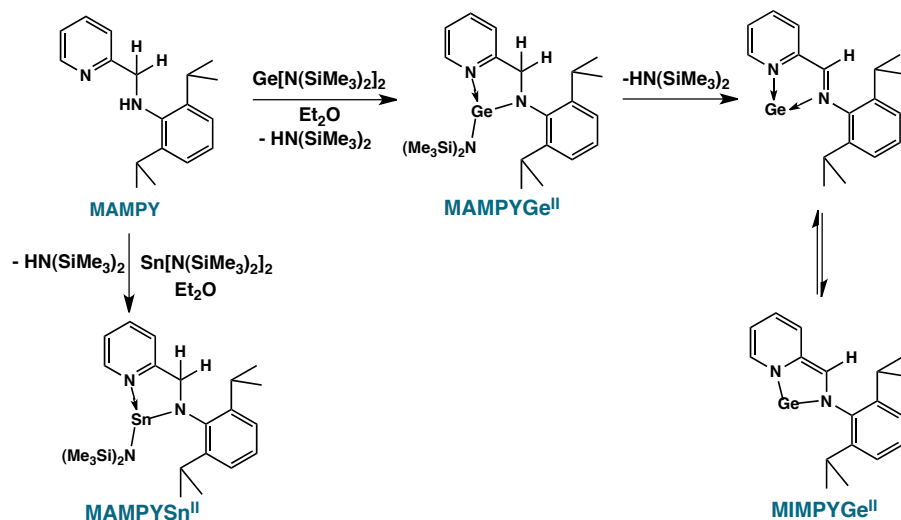
Figure 18: The transamination reaction of the MAMPY ligand system with EHMDS$_2$ (E= Ge, Sn). Depending on E, an additional transamination reaction takes place as in case of Ge to form MIMPYGe or as in case of Sn, the thermodynamical equilibrium stops with the heteroleptic Sn complex MAMPYSn^{II}.[45]

iminopyridine ligand 2-[RN=C(H)](NC$_5$H$_3$) (R= Bu^t)[46] and Gudat *et al.* synthesized the corresponding diazaphospholene.[47] The MAMPY ligand system 2-[ArN=CH$_2$](NC$_5$H$_3$) (Ar= C$_6$H$_3$-2,6-Pr$^i_2$) reacts with one equivalent of EHMDS$_2$ (E= Ge, Sn) to the heteroleptic MAMPYGe^{II} and MAMPYSn^{II} complexes, as shown in Figure 18.
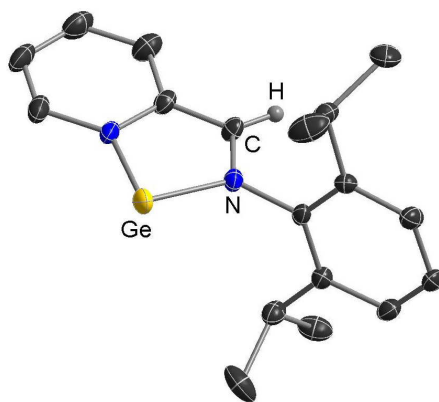

Figure 19: Crystal structure of an aromatic Ge iminopyridine complex. Selected bond lengths (Å): Ge(1)-N(1) 1.917, Ge(1)-N(2) 1.843, N(1)-C(5) 1.380, N(2)-C(6) 1.370, C(5)-C(6) 1.380.

Depending on the main group element the reaction stops as in case of the Sn complex or performs an additional transamination reaction eliminating a hydrogen atom at the ligand backbone, as in case of Ge, to form the MIMPYGe complex of which the crystal structure is shown in Figure 19.[45]

The ability to activate small molecules can be visualized by the frontier orbitals of

the Sn and Ge iminopyridine compounds (Figures 20 and 21). Theoretical calculations of these compounds were accomplished at density functional level by Flock *et al.*[40]
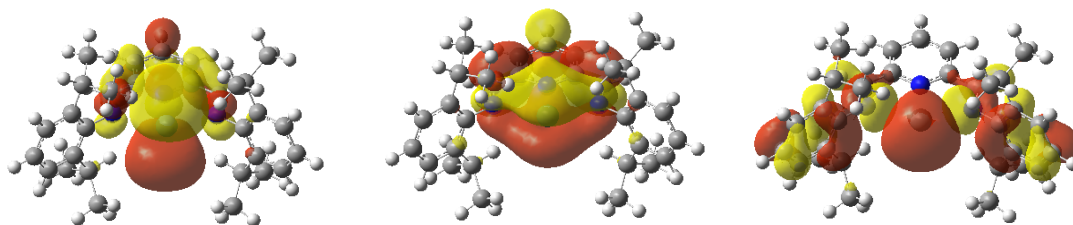

Figure 20: The frontier orbitals of the Sn diimino pyridine complex either can accept electrons with its unoccupied orbitals (left) which are π acceptors or donate electrons with the occupied orbitals which in the one hand are π donors (middle) or on the other hand σ donors (right).
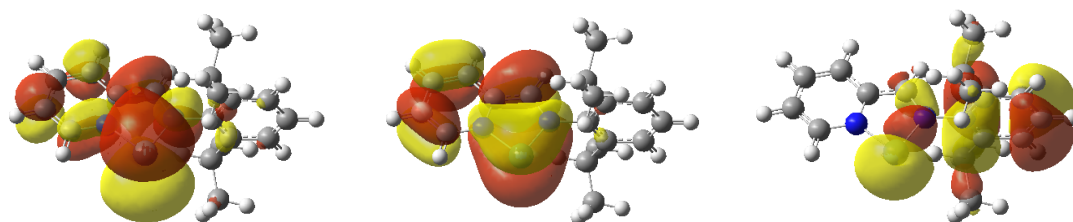

Figure 21: Calculated frontier orbitals of the Ge iminopyridine complex, unoccupied orbital (left) which can act as π acceptor and the occupied orbitals which either can act as π donor (middle) or σ donor (right).

The frontier orbitals shown in Figure 20 and 21 could be applicable for the activation of, for example, H_2, NH_3 or P_4. The already known multiple bond species and heavier NHC compounds which activate small molecules possess similar frontier orbitals. Compared to the NHC compounds, the iminopyridine complexes have π acceptor orbitals, which lead to a different and possible richer reaction behavior of these species. Due to the byproduct formation in the reaction of DIMPYGe, DIMPYSn and MIMPYGe the isolation of these complexes in bigger amounts is difficult. Therefore another synthetic route was accomplished by lithiating the ligand system and then adding EHMDS$_2$. This methods seemed to work, but due to the lithiation also radical byproducts were formed, which could not be detected by NMR methods. Therefore the activation chemistry could not be performed for the Ge complexes. The formation of radical species can be avoided by using other solvents, because as lithiated ligand species are not soluble in hexane. The radical pyridine species are soluble in hexane and therefore the lithiated ligands can be isolated by filtration. These methods could not be performed at the host institution, but will be continued at the home institution.

For the DIMPYSn complex an activation reaction with an adamantyl phosphaalkine was successful. As shown in Figure 22 two equivalents of the adamantyl phosphaalkine reacts with the DIMPYSn complex. Due to insertion into one P≡C triple bond a five membered ring is formed which is so reactive that a second P≡C triple bond reacts with the five membered ring. The main product crystallized out of ether to give dark red crystals of which the solid state structure is shown in Figure 23.
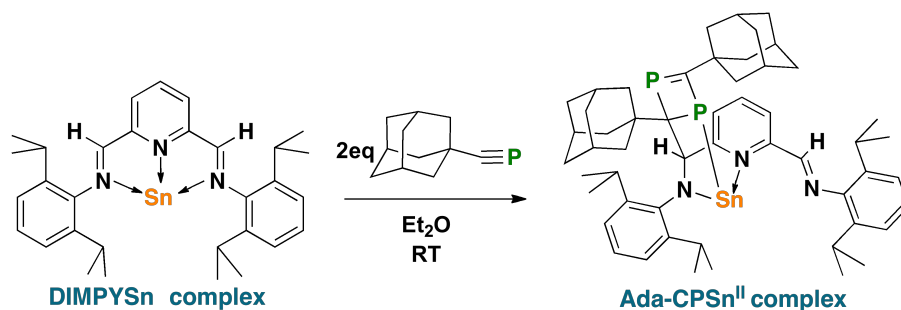

Figure 22: The activation of adamantyl phosphaalkine by the DIMPYSn complex. The DIMPYSn complex inserts into the P≡C triple bond and forms a five membered ring, which is so reactive that it immediatley reacts with a second adamantyl phosphaalkine by inserting again into the P≡C triple bond.
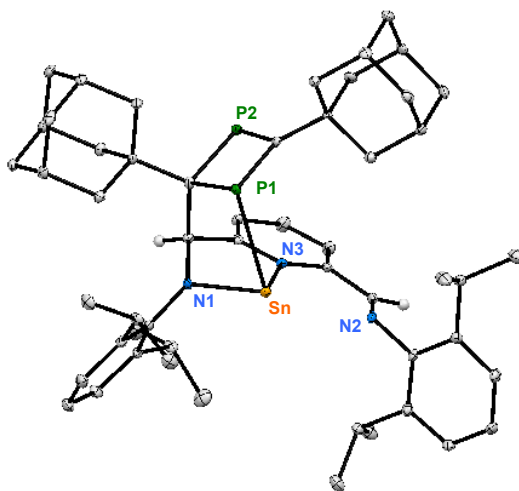

Figure 23: The solid state structure of the reaction of DIMPYSn with two equivalents of adamantyl phosphaalkine.

This reaction proves the reactivity of the DIMPYSn complex and therefore promising activation chemistry is excpected by activating H_2, NH_3 or P_4. This work will be also continued at the home university.

4 Conclusion and Outlook

The focus of this scholarship was the investigation of activating properties of the synthesized Ge and Sn iminopyridine compounds. An interesting reaction behavior is expected, considering the calculated frontier orbitals. This was shown by the reaction of the DIMPYSn complex with adamantyl phosphaalkine. An interesting compound was formed by the insertion of the DIMPYSn into the $P{\equiv}C$ triple bond forming a five membered ring, which was so reactive that a second insertion into a $P{\equiv}C$ triple bond took place. Therefore, reactions with small molecules such as H_2, NH_3, P_4, CO, CO_2, H_2O, H_2S, alkenes, alkynes and ketones will be accomplished in the future at the home university.

Furthermore during the scholarship novel precursors for a NHC with an additional functional group were successfully synthesized. This has an important impact for further investigations concerning the coordination of these novel NHCs towards transition metal complexes. In the future these transition metal complexes could perform interesting catalytic properties.

This new insights in main group chemistry will be introduced into our working group and the projects will be continued at the home university in collaboration with the Prof. Bertrand.

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