REVIEW

Low Valent N-coordinated Cations and Dications of Heavier Group 14 Elements: Lewis Acids or Bases?

Roman Jambor,*[b] and Miroslav Novák*[a]

Abstract: Low-valent N-coordinated cations and dications of heavier group 14 elements are of great interest in recent years. Their unique electronic structure gives them an ambiphilic character, as they contain both a lone electron pair and an empty p-orbital on the central metal atom. Thanks to their nucleophilic character, these compounds can act as ligands in transition metal chemistry, and conversely, their electrophilic character allows them to interact with a wide range of organic substrates and thus replace catalysts based on transition metal complexes in many chemical transformations. The aim of this article is to summarize the synthesis of N-coordinated ionic compounds of heavier group 14 elements with their subsequent reactivity towards various nucleophiles and electrophiles.

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1. Introduction

Neutral compounds containing Si, Ge, Sn and Pb atoms in the +II oxidation state, known as heavier tetrylenes, are compounds that have recently attracted much interest in the chemistry of the main-group elements. The species of general formula ER_2 (E = Si, Ge, Sn, Pb; R = anionic ligand) represent the simplest class of heavier tetrylenes. They can be acyclic, with two terminal R groups, or cyclic, in which R groups chelate the central E atom. Another group consists of intra- and intermolecularly-coordinated tetrylenes with two-electron donor atom D implemented in the anionic ligand structure or in a separate supporting ligand (Figure 1).

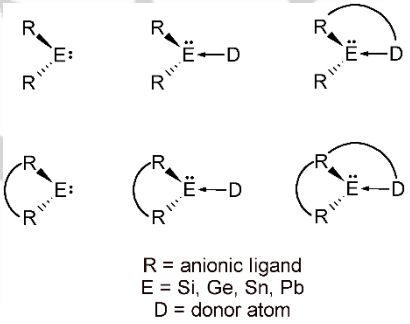

Figure 1. Structural motifs of heavier tetrylenes.

Heavier tetrylenes are unique in their rich and often unexpected reactivity, which is due to several aspects based on their nature. They possess an empty p-orbital on the central E atom together with a lone electron pair, resulting in their dual Lewis acid-base character. Further, the electrophilic character can be influenced by the choice of central E atom or anionic ligand R. The overall electrophilicity can be further increased by an applying a positive charge to E atom These monocationic analogues, referred in the literature as tetryliumylidenes, contain a lone electron pair and two empty p-orbitals (Figure 2A). In addition, the dicationic analogues exhibit three empty p-orbitals (Figure 2B), making them highly electrophilic species.

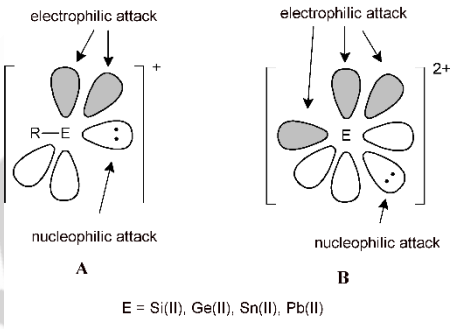

Figure 2. Electronic situation in cationic analogues of heavier tetrylenes.

On the other hand, inter- and intramolecularly-coordinated tetrylenes show a weaker Lewis acidity, since they do not possess an empty p-orbital.

The electrophilic character and thus the strong interaction of active centre with organic substrates make these E(II) cations suitable alternatives of TM-complexes for small molecule activation, cycloaddition reactions, redox processes, or insertion into inorganic or organic bonds.

To date, several reviews have been reported dealing with the synthesis, characterization, and reactivity of cations of heavier group 14 elements.[1] There are two synthetic methods to stabilize these cationic species described in the literature. The first, kinetic stabilization, is based on shielding the electrophilic center using sterically demanding ligands, while the second method, thermodynamic stabilization, involves the using of neutral or anionic donor ligands. Donor atoms included in the structure of these ligands are capable of coordination interaction with empty p-orbitals and thus reduce the electrophilic character of the mentioned compounds. Many types of donor ligands have been utilized in the preparation of E(II) cations such as carbenes[2], weak coordinating arenes[3], polyethers[4], but the largest group consists of N-donor ligands, especially amidinates, β-diketiminates, N-heterocyclic imines, cryptands, bipyridines, imine-substituted pyridines or other substituted imines. The purpose of this review is to summarize the progress of N-coordinated cations of heavier group 14 elements. Concerning N-donor ligands, the appropriate references will be given for specific examples described within this review

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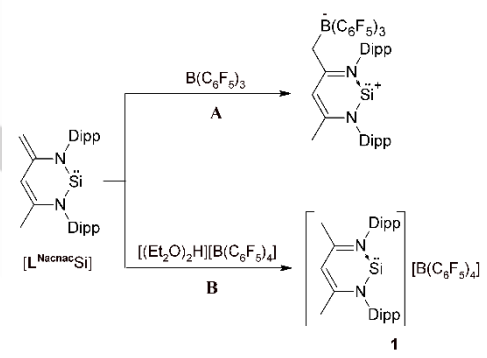
2. N-Coordinated Silyliumylidenes

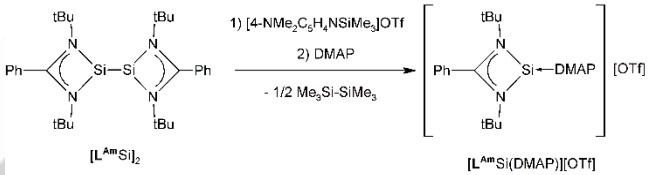
The synthesis of silyliumylidenes has long seemed to be a dream goal in the field of Si(II) cations. The simplest representative of this class of compounds is HSi^+, but due to its high reactivity it is impossible to isolate it. However, the presence of HSi^+ was demonstrated by Douglas and Lutz in the gas phase[5] and then also in the solar photosphere[6] and interstellar space[7]. The problem of isolating stable silyliumylidenes has been broken by the kinetic and thermodynamic stabilization. Pioneering works by Jutzi et. al. reported stabilization and successful isolation of $[Cp^*Si][B(C_6F_5)_4]$, which was the first kinetically stabilized silyliumylidene.[8] This finding encouraged the chemists for the utilization of intramolecularly coordinating ligands to thermodynamically stabilize these Si(II) cations, especially by the N-donor ligands. Among various N-donor ligands β-diketiminatesand amidinates have been found to be very effective in stabilizing low-valent complexes[9] and were therefore the first of choice.

In 2006, Driess et. al reported the treatment of β-diketiminate-stabilized silylene [$\mathbf{L^{Nacnac}}$]Si ($\mathbf{L^{Nacnac}}$ = CH{C(Me)(C=CH_2)(NDipp)$_2$}; Dipp = 2,6-iPr_2-C_6H_3) with $B(C_6F_5)_3$ and $[(Et_2O)_2H][B(C_6F_5)_4]$, respectively. While the reaction with $B(C_6F_5)_3$ yielded zwitter-ionic complex (Scheme 1A), the silyliumylidene [$\mathbf{L^{Nacnac}}$Si][$B(C_6F_5)_4$] (**1**) was isolated in the second case (Scheme 1B).[10]



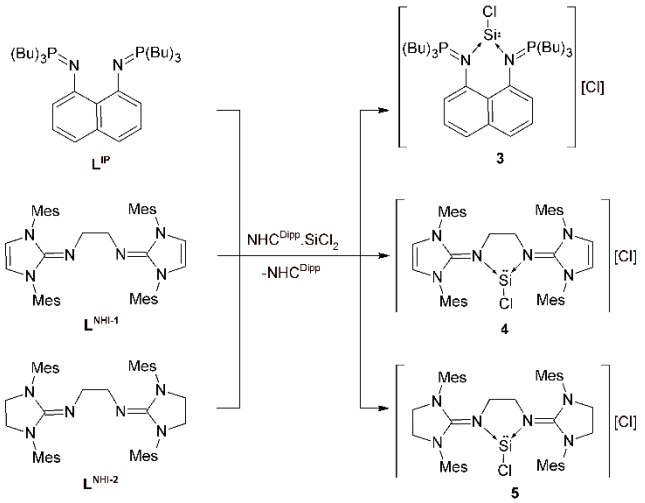
Scheme 1. Synthesis of β-diketaminite-stabilized Si(II) cations.

Later on, the cleavage of silicon-silicon bond in amidinate-substituted silicon(I) dimer [$^{L^{Am}}$Si]$_2$ ($\mathbf{L^{Am}}$ = PhC(NtBu)$_2$) by N-trimethylsilyl-4-dimethylaminopyridinium triflate [4-$NMe_2C_5H_4NSiMe_3$]OTf provided Si(II) cationic specie [$\mathbf{L^{Am}}$Si(DMAP)][OTf] (**2**) (DMAP = 4-Me_2N-C_6H_4N) (Scheme 2).[11]



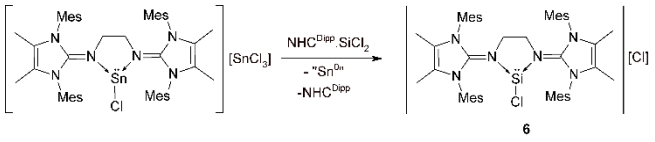
Scheme 2. Synthesis of [$\mathbf{L^{Am}}$Si(DMAP)][OTf] (**2**).

A completely different synthetic method to obtain the chlorosilyliumylidenes was reported by Driess and Inoue.[12], who take the advantage of $NHC^{Dipp}{\cdot}SiCl_2$ (NHC^{Dipp} = 1,3-bis(2,6-Dipp)imidazol-2-ylidene) as the stoichiometric source of $SiCl_2$ in the ligand exchange with bis(iminophosphorane) $\mathbf{L^{IP}}$ ($\mathbf{L^{IP}}$ = 1,8-bis(Bu_3P=N)$_2C_{10}H_6$) and bis(N-heterocyclic imine) $\mathbf{L^{NHI-1}}$ and $\mathbf{L^{NHI-2}}$ ($\mathbf{L^{NHI-1}}$ = 1,3-bis(mesityl)-imidazolin-2-imine; $\mathbf{L^{NHI-2}}$ = 1,3-bis(mesityl)-4,5-dihydroimidazolin-2-imine) ligands. These ligands are able to replace NHC^{Dipp} and initiate the ionization of $SiCl_2$ fragment forming cations [$\mathbf{L^{IP}}$SiCl][Cl] (**3**), [$\mathbf{L^{NHI-1}}$SiCl][Cl] (**4**) and [$\mathbf{L^{NHI-2}}$SiCl][Cl] (**5**), respectively (Scheme 3).



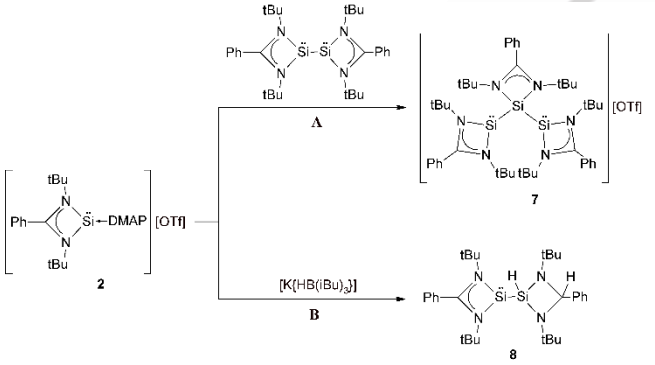
Scheme 3. Synthesis of [$\mathbf{L^{IP}}$SiCl][Cl] (**3**), [$\mathbf{L^{NHI-1}}$SiCl][Cl] (**4**) and [$\mathbf{L^{NHI-2}}$SiCl][Cl] (**5**).

On the other hand, a methylated **L^{NHI-3}** and phenylene-bridged **L^{NHI-4}** ligands as more sterically demanding ligands did not react with NHC^{Dipp}·$SiCl_2$. However, the formation of the ionic specie [**L^{NHI-3}**SiCl]Cl] (**6**) was achieved by the transmetallation reaction with chlorostannyliumylidene [**L^{NHI-3}**SnCl][$SnCl_3$] (**57**) (*vide infra*) within 3 days at 60 °C (Scheme 4)[12c], which opens new field of the usefulness of chlorostannyliumylidenes as building block in the coordination chemistry.



Scheme 4. Synthesis of [**L^{NHI-3}**SiCl][Cl] (**6**).

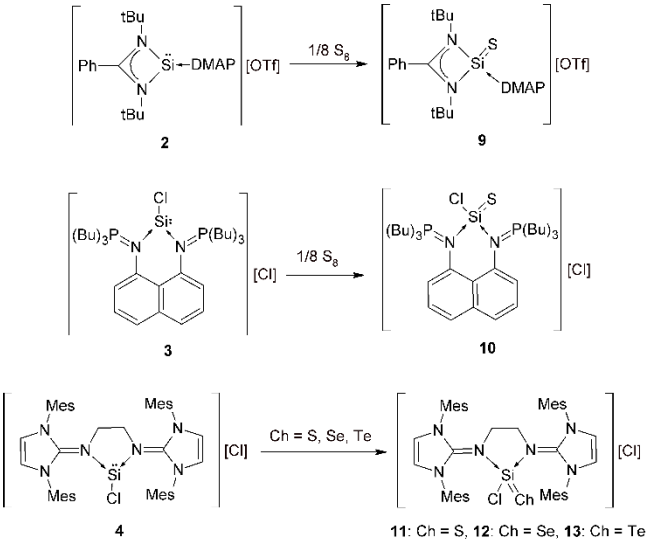
Essentially, all described silyliumylidenes should exhibit a typical ambiphilic behaviour. The electrophilicity of **2** was demonstrated by the reaction with [(**L^{Am}**)$_2$Si]$_2$ possessing a lone electron pair on each Si(I) atom. This can act as Lewis base, when one Si(I) is capable of interaction with an empty p-orbital in **2** yielding disilylenylsilylium triflate [(**L^{Am}**$_2$Si)$_2$**L^{Am}**Si][OTf] (**7**) as an example of the first stable silylium cation stabilized by the silicon substituents (Scheme 5A).[11] Further proving of high electrophilic character of **2** involves the reaction with nucleophilic reagent such as [K{HB(iBu)$_3$}]. This reaction provided silylsilylene [**L^{Am}**SiSi(H){(NtBu)$_2$C(H)Ph}] (**8**) (Scheme 5B). It is believed that the formation of hydrosilylene intermediate [**L^{Am}**SiH] takes place in the first step, which then reacts with amidinate ligand **L^{Am}** or another [**L^{Am}**SiH] affording silylsilylene.[11]



Scheme 5. Reactivity of **2** toward [(**L^{Am}**)$_2$Si]$_2$ and [K{HB(iBu)$_3$}].

The presence of a lone electron pair in silyliumylidenes as a sign of their nucleophilic character was investigated by oxidation reactions with chalcogens. It was reported that **2**, **3** and **4** are able to activate elemental sulfur to form N-stabilized silanethionium triflate [**L^{Am}**Si=S(DMAP)][OTf] (**9**) and chlorosilathiounium chlorides [**L^{IP}**Si=S(Cl)][Cl] (**10**) and [**L^{NHI-1}**Si=S(Cl)][Cl] (**11**) (Scheme 6).[11,12a]

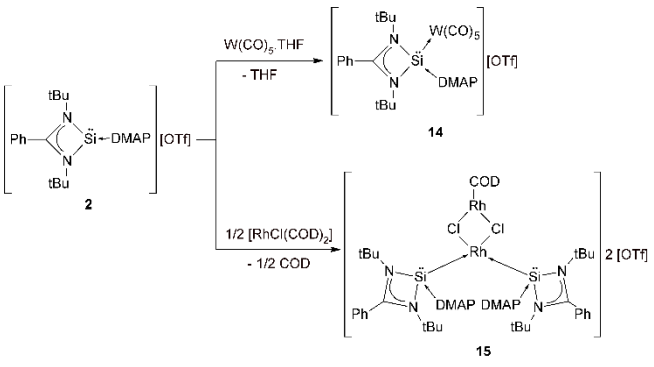
While there is no information for reactivity of **2** and **3** with heavier chalcogens, Inoue also extended the study of oxidative reactions to selenium and tellurium. The corresponding chlorosilaselenonium (**12**) and chlorosilatelluronium (**13**) salts are formed based on NMR analysis.[12b]



Scheme 6. Reactivity of **2**, **3** and **4** toward chalcogens.

Besides the oxidation reactions, a lone electron pair on the silicon atom can be employed also in the transition-metal chemistry. From this point of view, the silyliumylidenes can act as Si-based ligands and mimic well-established N-heterocyclic silylenes (NHSi). The most common route to obtain silyliumylidene-TM complexes is the formation of Si→TM interaction through a lone electron pair of Si and an empty d-orbitals of TM. The first attempts to synthesize such complexes involved the reaction of **2** with [Rh(COD)Cl]$_2$ (COD = 1,5-cyclooctadiene) and W(CO)$_5$(THF) reported by So.[13]

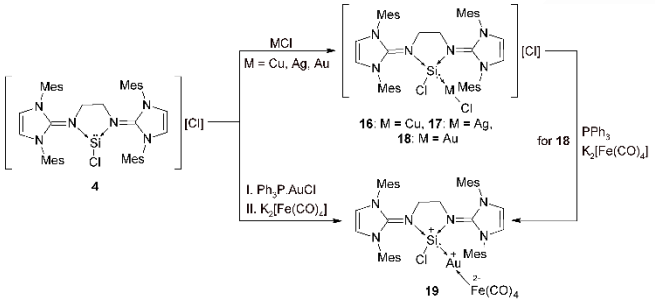
In the case of the reaction of **2** with [Rh(COD)Cl]$_2$ in a molar ratio of 2:1, the cleavage of the dimer and the formation of [{**L^{Am}**Si(DMAP)}Rh(COD)Cl][OTf] did not occur, as might be expected, but the complex [{**L^{Am}**Si(DMAP)}$_2${Rh$_2$Cl$_2$(COD)}][OTf]$_2$ (**14**) was formed indicating the ability of **2** to replace the weakly bound COD in the coordination sphere of Rh atom. In a similar vein, **2** can displace THF in W(CO)$_5$(THF), which was reflected by the synthesis of [{**L^{Am}**Si(DMAP)}W(CO)$_5$][OTf] (**15**) (Scheme 7).[13] Unfortunately, more detailed information about Si-TM bonding situation is not available.



Scheme 7. Synthesis of W- and Rh-complexes of **2**.

Motivated by this work and with the aim of expanding the field of silyliumylidene-TM complexes, Inoue et al. investigated the coordination ability of **4** toward coinage metal salts CuCl, AgCl and Me_2S·AuCl leading to the formation of desired complexes [{**L^{NHI-1}**SiCl}CuCl][Cl] (**16**), [{**L^{NHI-1}**SiCl}AgCl][Cl] (**17**) and [{**L^{NHI-1}**SiCl}AuCl][Cl] (**18**) (Scheme 8).[12b]

These complexes were further used in a halogen abstraction reaction with $K_2[Fe(CO)_4]$ in order to obtain heterobimetallic Si-M-Fe complexes (M = Cu, Ag, Au). While [{**L**$^{NHI-1}$SiCl}CuCl][Cl] (**16**) did not react even after 16 h at 60 °C, during the reaction of [{**L**$^{NHI-1}$SiCl}AgCl][Cl] (**17**) the Si–Ag coordination bond was probably cleaved and the starting **4** was formed together with unidentified products. Finally, the treatment of [{**L**$^{NHI-1}$SiCl}AuCl][Cl] (**18**) gave the mixture of products, which could not be isolated. The belief in the successful synthesis of Si-Au-Fe complexes initiated the idea of using a supporting ligand that would be able to stabilize the empty p-orbital formed by the chlorine abstraction. Thus, the addition of Ph_3P to the reaction mixture led to the isolation of the silyliumylidene-stabilized complex [{**L**$^{NHI-1}$SiCl}Au][$Fe(CO)_4$] (**19**) possessing gold-iron bond. Furthermore, the replacement of Me_2S for Ph_3P in the starting AuCl-complex followed by the reaction with $K_2[Fe(CO)_4]$ allows the isolation of the desired complex in one step and in addition with higher purity and yield (Scheme 8). Based on structural analysis and theoretical calculations, [{**L**$^{NHI-1}$SiCl}Au][$Fe(CO)_4$] (**19**) shows a very interesting bonding situation, where the Au-atom is capable of agostic interaction with one mesityl substituent. Further, in this complex, the Si-atom behaves as a strong donor to the Au-atom with a non-negligible π-backbonding interaction. To investigate the overall electronic structure in [{**L**$^{NHI-1}$SiCl}Au][$Fe(CO)_4$] (**19**) theoretical calculations and ^{57}Fe Mössbauer spectroscopy were performed confirming the zwitterionic character with $Si^{+}\rightarrow Au^{+}\leftarrow Fe^{2-}(CO)_4$ interactions.[12b]



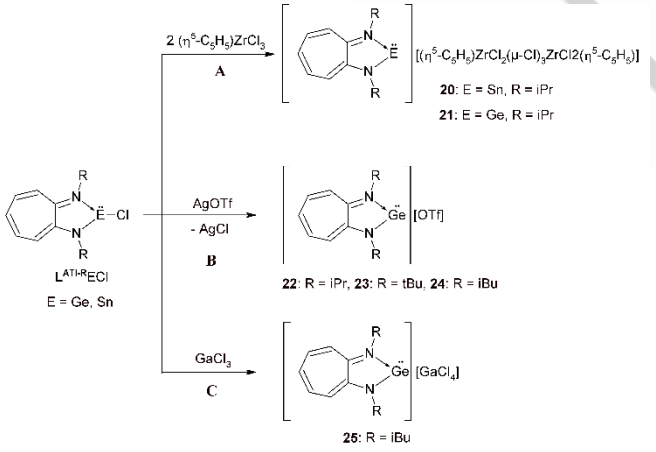
Scheme 8. Synthesis of coinage-metal complexes and novel Si-Au-Fe heterobimetallic complex of **4**.

3. N-Coordinated Ge(II) and Sn(II) cations

3.1. Synthesis of N-donor stabilized Ge(II) and Sn(II) cations

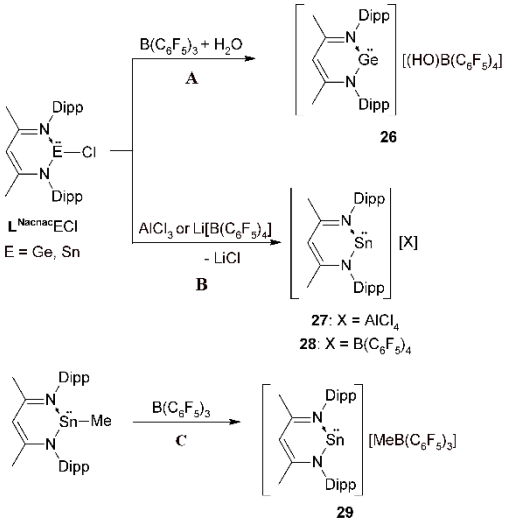
Compared to silyliumylidenes, the chemistry of Ge(II) and Sn(II) analogues is much more colorful, which is due to their lower reactivity resulting in a larger energy difference between s- and p-orbitals. For clarity, N-coordinated germylium- and stannyliumylidenes will be described in terms of their general structure, where we can divide them into three categories: 1) type of $[LE]^+$ (E = Ge, Sn; L = monoanionic ligand), 2) $[DEX]^+$ (D = Lewis base; X = halide) and 3) $[DE]^{2+}$.

In the context of $[LE]^+$ type, the first example of Sn(II) cation was published by Dias and his group, where they used tropoiminate-stabilized chlorostannylene **L**$^{ATI-iPr}$SnCl (**L**$^{ATI-iPr}$ = N-isopropyl-2-(isopropylamino)troponiminate) in the reaction with $(\eta^5\text{-}C_5H_5)ZrCl_3$ as a chloride scavenger.[14] This reaction gave the corresponding Sn(II) cation [**L**$^{ATI-iPr}$Sn][$(\eta^5\text{-}C_5H_5)ZrCl_2(\mu\text{-}Cl)_3ZrCl_2(\eta^5\text{-}C_5H_5)$] (**20**), in which the tin atom is involved in an interesting 10-π-electron C_7N_2Sn ring (Scheme 9A). An analogous Ge(II) cationic species was later prepared both by this approach but also by the chloride abstraction using AgOTf and $GaCl_3$, yielding [**L**$^{ATI-iPr}$Ge][$(\eta^5\text{-}C_5H_5)ZrCl_2(\mu\text{-}Cl)_3ZrCl_2(\eta^5\text{-}C_5H_5)$] (**21**)[15] (Scheme 9A), [**L**$^{ATI-R}$Ge][OTf] (R = iPr (**22**), tBu (**23**) and iBu (**24**))[15,16] (Scheme 9B) and [**L**$^{ATI-iBu}$Ge][$GaCl_4$] (**25**)[16] (Scheme 9C). However, the solid-state structure of these compounds did not show well-separated ion pairs, but confirmed a weak interaction of the Ge(Sn) atom with the terminal chlorine or oxygen atoms within anions.



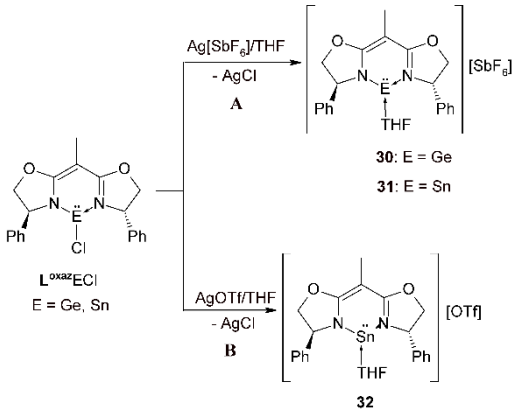
Scheme 9. Synthesis of tropoiminate-coordinated germylium- and stannyliumylidenes **20** – **25**.

As in the case of silyliumylidene **1**, the β-diketiminate ligand **L**^{Nacnac} was found to be suitable for the stabilizing its Ge and Sn versions. While [**L**^{Nacnac}Ge][$(HO)B(C_6F_5)_3$] (**26**) was prepared by the reaction of starting **L**^{Nacnac}GeCl with $B(C_6F_5)_3$ in the presence of H_2O (Scheme 10A)[17], Sn(II) cationic species [**L**^{Nacnac}Sn][$AlCl_4$] (**27**), [**L**^{Nacnac}Sn][$B(C_6F_5)_4$] (**28**) (Scheme 10B) and [**L**^{Nacnac}Sn][$MeB(C_6F_5)_3$] (**29**) (Scheme 10C) was obtained by halide abstraction with $AlCl_3$, $Li[B(C_6F_5)_4]$ and methyl abstraction with $B(C_6F_5)_3$, respectively.[18]



Scheme 10. Synthesis of β-diketiminate-coordinated germylium- and stannyliumylidenes **26** – **29**.

In order to implement a chiral ligand into the tetryliumylidene structure, which could lead to interesting results in asymmetric catalysis, Mochida et al. used the well-known bis(oxazoline) ligand **L^{oxaz}** (**L^{oxaz}** = 1,1-bis-[(4S)-4-phenyl-1,3-oxazolin-2-yl]ethane. A chloride abstraction from the corresponding chlorotetrylenes **L^{oxaz}**ECl (E = Ge and Sn) using Ag[SbF_6] and for Sn also with AgOTf in THF lead to the isolation of chiral tetryliumylidenes [**L^{oxaz}**E(THF)][SbF_6] (**30**: E = Ge, **31**: E = Sn) (Scheme 11A) and [**L^{oxaz}**Sn(THF)][OTf] (**32**) (Scheme 11B).[19] From the point of view of catalysis, it is promising that in the case of **30**, the THF molecule can be replaced by another Lewis base, which was confirmed by the reaction with pyridine or dimethylphenylphosphine.[19a] Unfortunately, no studies are known where **30** was used as a catalyst in organic synthesis.

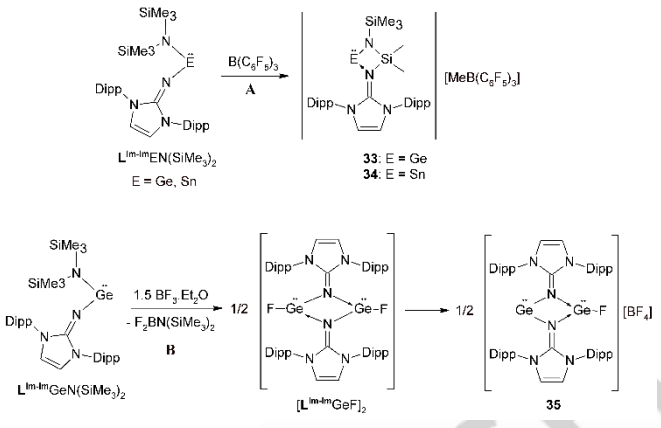


Scheme 11. Synthesis of bis(oxazoline)-coordinated germylium- and stannyliumylidenes **30** – **32**.

Another strong donor ligand that thermodynamically stabilizes Ge(II) and Sn(II) cations is the imidazoline-2-iminato

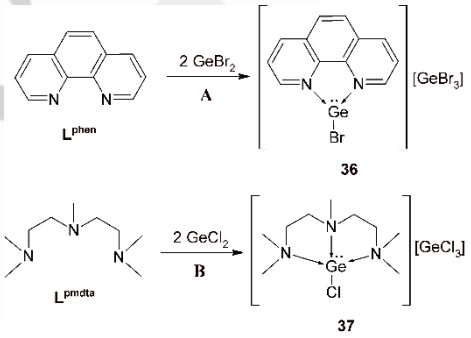
ligand. In addition, tuning of the steric hindrance of the substituents can also contribute to the kinetic stabilization of the metal center. After successful isolation of imino-aminogermylene and stannylene **L^{Im-Im}**EN($SiMe_3$)$_2$ (**L^{Im-Im}** = bis(2,6-diisopropylphenyl)imidazolin-2-imine; E = Ge and Sn), Inoue reported the reaction with B(C_6F_5)$_3$ with the aim to prepared germylene- and stannylene-borane adducts. However, the borate salts [{**L^{Im-Im}**-$SiMe_2$-N}E][MeB(C_6F_5)$_3$] (**33**: E = Ge, **34**: E = Sn) were isolated from these reactions (Scheme 12A).[20] The formation of these ionic species proceeds through a rare abstraction of silicon bound methyl followed by the ring closing providing N-Si-N-E metallacycle. In contrast, the methyl abstraction does not take place, when BF_3·Et_2O is used. In the case of **L^{Im-Im}**GeN($SiMe_3$)$_2$, BF_3·Et_2O serves as a fluorination as well as a fluoride abstraction agent. So, the treatment of **L^{Im-Im}**GeN($SiMe_3$)$_2$ with BF_3·Et_2O led, in the first step, to the formation of dimeric flurogermylene [**L^{Im-Im}**GeF]$_2$, in which one fluor atom is abstracted yielding germylene-germyliumylidene [{(**L^{Im-Im}**)$_2$Ge}GeF][BF_4] (**35**) (Scheme 12B).[21]

Regarding the synthesis of halogermylium- and halostannyliumylidenes of the general formula [DEX]$^+$, there are two main synthetic procedures of their formation: 1) Lewis base initiated ionization of $GeCl_2$ and $SnCl_2$ and 2) halide abstraction of corresponding [DEX_2].



Scheme 12. Synthesis of imidazoline-2-iminato-coordinated germylium- and stannyliumylidenes **33** – **35**.

After Reid and co-workers reported the preparation of the first stable [GeCl]$^+$ by the reaction of the Lewis bases L^{phen} (L^{phen} = 1,10-phenantroline) and L^{pmdta} (L^{pmdta} = *N*,*N*,*N'*,*N''*,*N''*-pentamethyldiethylenetriamine) with two equivalents of GeX_2 (X = Cl, Br) giving ionization products [L^{phen}GeBr][$GeBr_3$] (**36**) (Scheme 13A) and [L^{pmdta}GeCl][$GeCl_3$] (**37**) (Scheme 13B)[22], this approach became very versatile.



Scheme 13. Synthesis of [L^{phen}GeBr][$GeBr_3$] (**36**) and [L^{pmdta}GeCl][$GeCl_3$] (**37**).

Inspirited by this work, several research groups investigated various N-donor ligands such as imino- and ketiminopyridines (**38** – **48**)[23], bis(α-iminopyridines) (**49** – **51**)[24], bis(N-heterocyclic imine) (**52** – **59**)[25] or cryptands (**60** and **61**)[26] as N-Lewis bases suitable for ionization of EX_2 (Figure 3).

Very recently, we reported the synthesis of novel non-symmetric imino- (2-(CH=N(C_6H_3-2,6-iPr_2))-6-(R^2R^3P=O)C_5H_3N) and ketiminopyridine-based ligands (2-(C(Me)=N(C_6H_3-2,6-iPr_2))-6-(R^2R^3P=O)C_5H_3N) (**L^{NNPO-1}** – **L^{NNPO-6}**) possessing diphenylphosphine oxide Ph_2P=O, ethylphenylphosphinate Ph(EtO)P=O or diisopropylphosphite (iPrO)$_2$P=O group as an additional side arm. Unsurprisingly, the use of these ligands in the reaction with $SnCl_2$ led to the stabilization of the corresponding Sn(II) ionic complexes [(**L^{NNPO-1}**-**L^{NNPO-6}**)SnCl][$SnCl_3$] (**62** – **67**) (Scheme 14A). On the other hand, complexes containing OR group (R = Et, iPr) are thermally unstable and undergo to chloride anion-induced O–R bond cleavage accompanied by elimination of R-Cl and five-membered ring closure upon Sn–O bond formation (Scheme 14B). Compounds **68** – **71** can be seen as zwitterionic compounds containing each a [Sn–Cl]$^+$ moiety. The positive charge is compensated by a newly formed [O-$SnCl_2$]$^-$ anion (Scheme 14I). The negative charge is then delocalized within the [O-P-O-$SnCl_2$]$^-$ fragment.

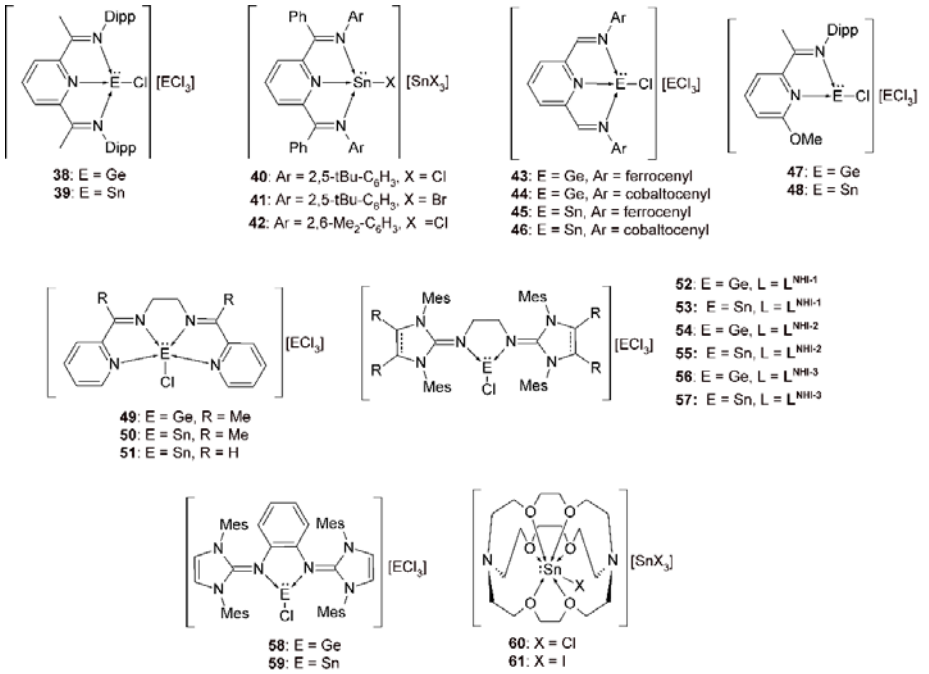
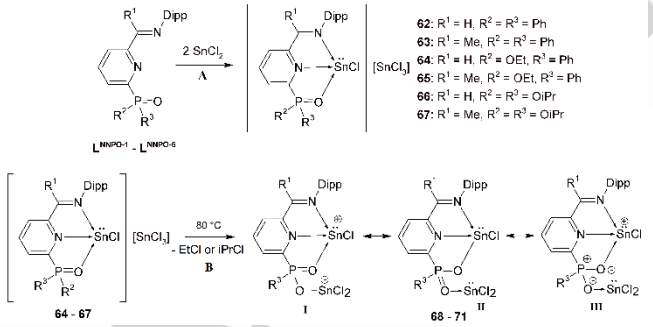


Figure 3. Examples of halogermylium- and halostannyliumylidenes of $[DECl]^+$ synthesized by N-Lewis base mediated ionization.

The second possible explanation for the structure of **68** – **71** is the presence of Sn–O and Sn–Cl single bonds and the P=O→$SnCl_2$ Lewis base – Lewis acid interactions (Scheme 14II). However, based on the theoretical calculation, the bonding in **68** – **71** would be best described as a negatively charged ligand $\mathbf{L^{NNPO3}}$ **–** $\mathbf{L^{NNPO6}}$ coordinating $[SnCl]^+$ and $SnCl_2$ via strong O→Sn and N→Sn donor-acceptor interactions (Scheme 5C).

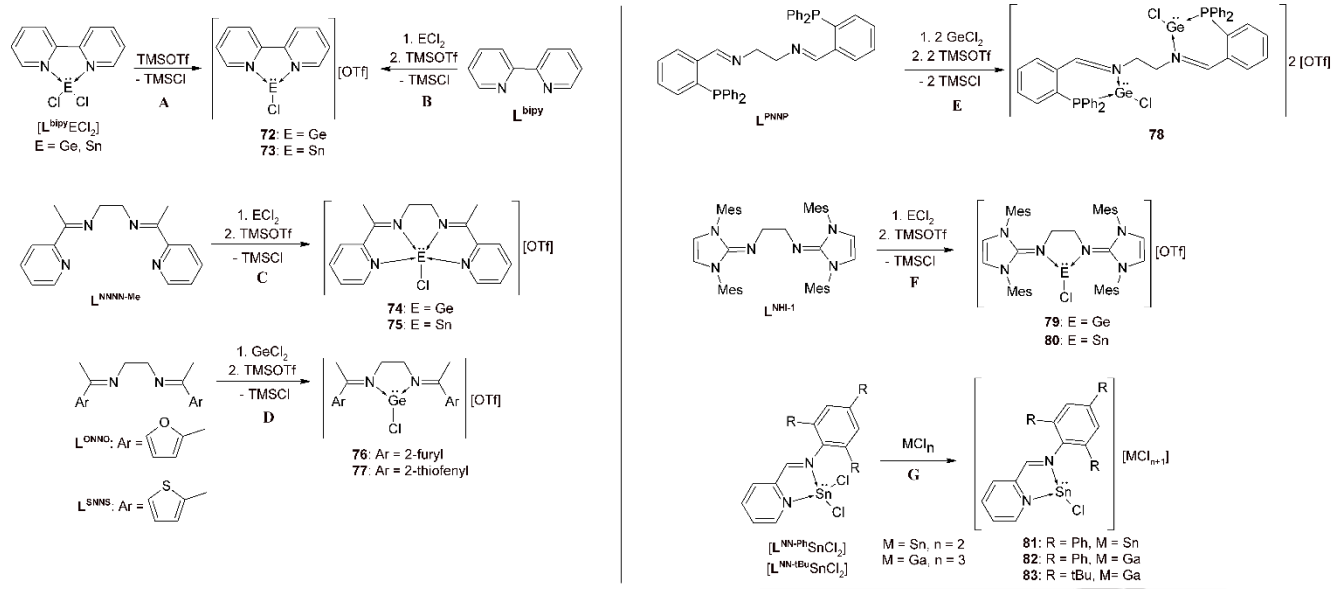


Scheme 14. Synthesis of [($\mathbf{L^{NNPO-1}}$-$\mathbf{L^{NNPO-6}}$)SnCl][$SnCl_3$] (**62** – **67**) and its thermal stability.

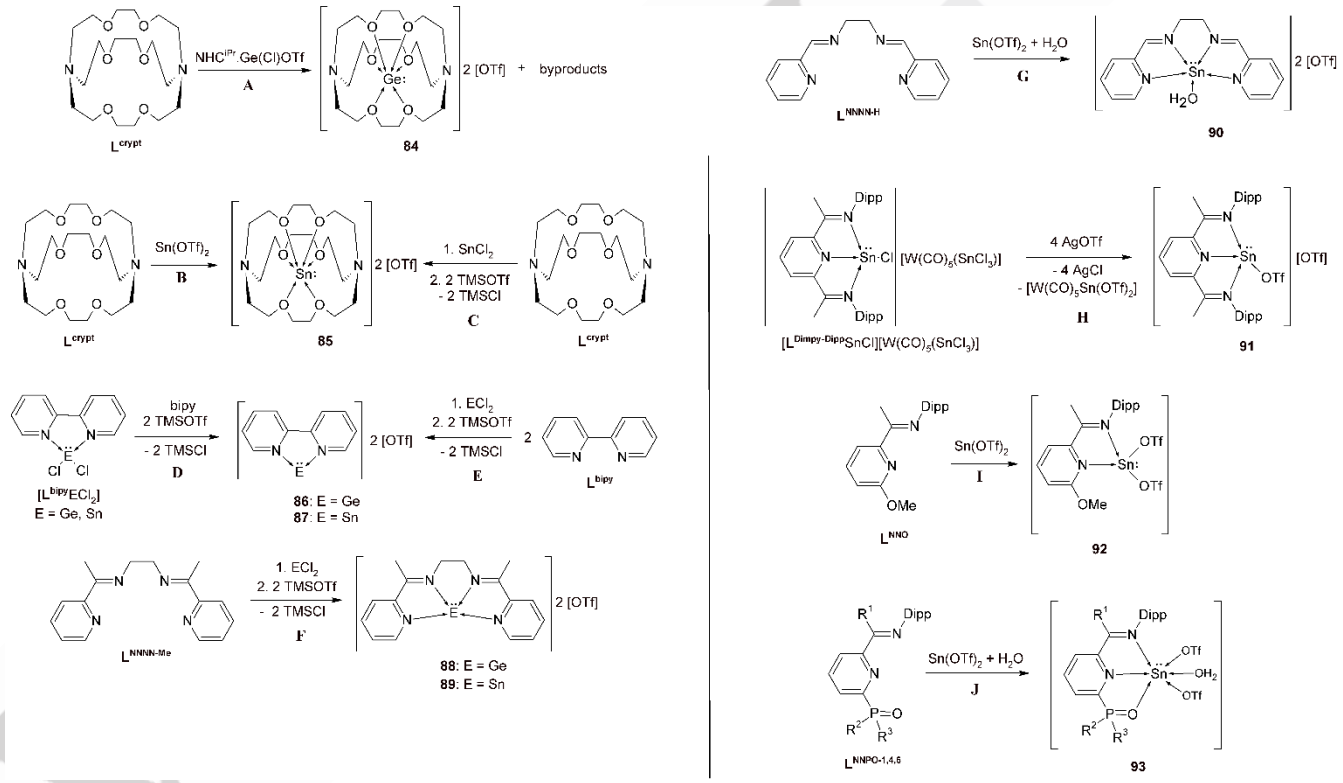
As already stated, the second synthetic approach for the synthesis of $[DGeX]^+$ and $[DSnX]^+$ cations is a halide abstraction of starting neutral complexes $[DGeX_2]$ and $[DSnX_2]$, respectively. For this purpose, previously prepared neutral adducts [$\mathbf{L^{bipy}}$$GeCl_2$][22] and [$\mathbf{L^{bipy}}$$SnCl_2$][28] served as the starting compounds, in which the chloride atom was abstracted by the addition of one equivalent of TMSOTf (TMS = trimethylsilyl) providing [$\mathbf{L^{bipy}}$GeCl][OTf] (**72**) and [$\mathbf{L^{bipy}}$SnCl][OTf] (**73**), respectively (Scheme 15A).[29] Furthermore, it was found that these complexes can also be obtained by a mixing of $\mathbf{L^{bipy}}$ with $GeCl_2$·dioxan or $SnCl_2$ and TMSOTf in a molar ratio of 1:1:1 in one step, which can greatly to facilitate and speed up the synthesis (Scheme 15B).

Almost at the same time, an analogous reaction was performed using the bis(α-iminopyridine) ligand $\mathbf{L^{NNNN-Me}}$ with $GeCl_2$·dioxane to give the [$\mathbf{L^{NNNN-Me}}$GeCl][OTf] (**74**) (Scheme 15C).[24a] Following this result, Sn(II) analogue [$\mathbf{L^{NNNN-Me}}$SnCl][OTf] (**75**) was later successfully synthesized (Scheme 15C).[24b] This group extended the study to other bis(imine)-based ligands $\mathbf{L^{ONNO}}$, $\mathbf{L^{SNNS}}$ and $\mathbf{L^{PNNP}}$, in which the pyridine units are replaced by furyl, thienyl and diphenylphosphinophenyl groups.[30] While ligands $\mathbf{L^{ONNO}}$ and $\mathbf{L^{SNNS}}$ react with $GeCl_2$·dioxane in the same manner as their pyridine analogue giving [$\mathbf{L^{ONNO}}$GeCl][OTf] (**76**) and [$\mathbf{L^{SNNS}}$GeCl][OTf] (**77**) (Scheme 15D), the reaction of $\mathbf{L^{PNNP}}$ with $GeCl_2$·dioxane and TMSOTf in molar ratio of 1:2:2 provided complex $[(\mathbf{L^{PNNP}}GeCl)_2][OTf]_2$ (**78**) containing two *N*,*P*-chelated Ge-Cl^+ unit (Scheme 15E). Interestingly, O and S atoms in [$\mathbf{L^{ONNO}}$GeCl][OTf] (**76**) and [$\mathbf{L^{SNNS}}$GeCl][OTf] (**77**) do not participate in the interaction with Ge center and can therefore be further used for the coordination of other electrophiles or metals. Inoue et. al employed bis(N-heterocyclic imine) $\mathbf{L^{NHI-1}}$, besides for the synthesis of Lewis base-ionized products, also for the [$\mathbf{L^{NHI-1}}$ECl][OTf] (**79**: E = Ge, **80**: E = Sn) preparation (Scheme 15F).[25]

Not only TMSOTf can serve as a dehalogenating agent. Very recently, we reported the ability of α-iminopyridine ligands $\mathbf{L^{NN-Ph}}$ and $\mathbf{L^{NN-tBu}}$ to stabilize neutral adducts [$\mathbf{L^{NN-Ph}}$$SnCl_2$] and [$\mathbf{L^{NN-tBu}}$$SnCl_2$], which were subsequently subjected to the reactions with $SnCl_2$ and $GaCl_3$, as halogen scavengers, in an attempt to obtain the corresponding stannyliumylidenes. It was shown that the dehalogenation depends on the type of the ligand. While the reaction of [$\mathbf{L^{NN-Ph}}$$SnCl_2$] with both $SnCl_2$ and $GaCl_3$ led to the isolation of ionic compounds [$\mathbf{L^{NN-Ph}}$SnCl][$SnCl_3$] (**81**) and [$\mathbf{L^{NN-Ph}}$SnCl][$GaCl_4$] (**82**), [$\mathbf{L^{NN-tBu}}$$SnCl_2$] reacts only with $GaCl_3$ giving [$\mathbf{L^{NN-tBu}}$SnCl][$GaCl_4$] (**83**) (Scheme 15G).[24c]



Scheme 15. Synthesis of chlorogermylium- and chlorostannyliumylidenes of $[DECl]^+$ by halide abstraction.



Scheme 16. Synthesis of germylium- and stannyliumylidenes of $[DE]^{2+}$.

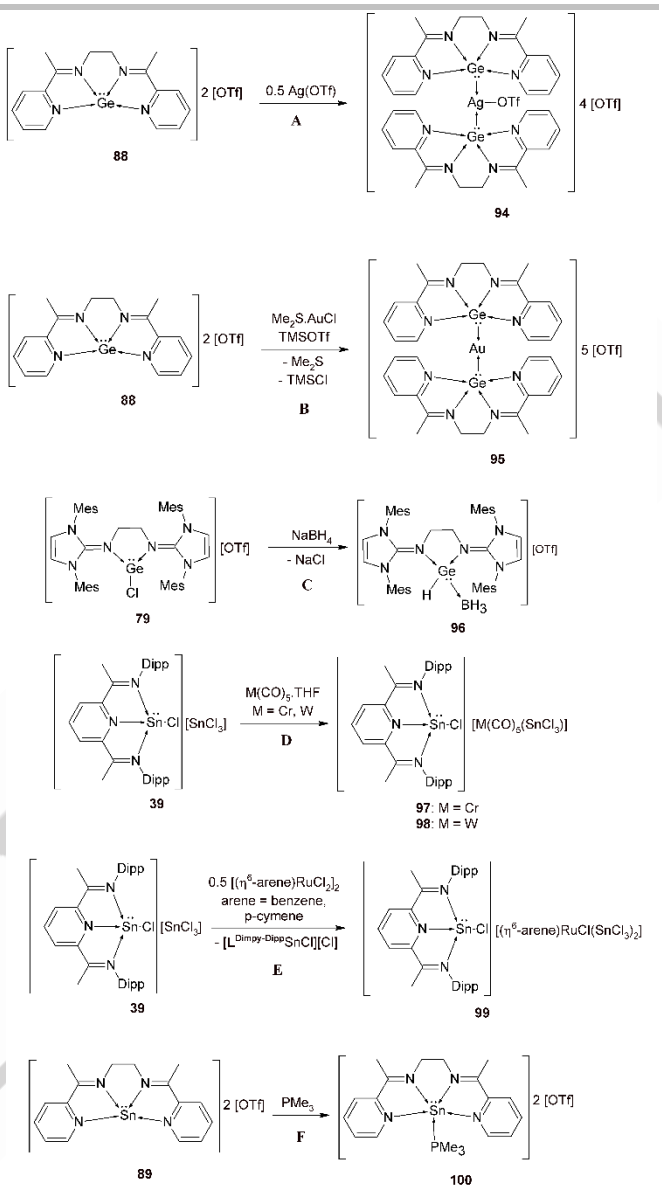
The synthesis of Ge(II) and Sn(II) dicationic species seemed unattainable for many years, but a major breakthrough in this field was reported by Müller et al., who isolated $[(\eta^6\text{-tol})_3Sn][B(C_6F_5)_4]_2$.[31] Regarding the stabilization of Ge(II) and Sn(II) dications by N-donor ligands, initial studies involve the implementation of electron-rich [2.2.2]-cryptand (**L^{cryptand}**). The reaction of **L^{cryptand}** with NHC^{iPr}·GeCl(OTf) (NHC^{iPr} = 1,3-iPr_2-imidazol-2-ylidene) provided a mixture of products from which [**L^{cryptand}**Ge][OTf]$_2$ (**84**) was successfully isolated (Scheme 16A).[32] Later on, tin analogue [**L^{cryptand}**Sn][OTf]$_2$ (**85**) was obtained by the reaction of **L^{cryptand}** with $Sn(OTf)_2$ (Scheme 16B).[26] An alternative synthetic route for the preparation of **85** was developed, which is based on the treatment of **L^{cryptand}** with $SnCl_2$ in the presence of two equivalents of TMSOTf (Scheme 16C).[26] Using these two methods, dicationic Ge(II) and Sn(II) species stabilized by various N-donor ligands were subsequently

prepared. While Burford et al. reported the synthesis of bipyridine-stabilized $[(\mathbf{L}^{bipy})_2Ge][OTf]_2$ (**86**) and $[(\mathbf{L}^{bipy})_2Sn][OTf]_2$ (**87**) (Scheme 16D,E),[29] Majumdar et al. utilized α-bis(iminopyridine) $\mathbf{L}^{NNNN\text{-}Me}$ for the synthesis of $[\mathbf{L}^{NNNN\text{-}Me}Ge][OTf]_2$ (**88**) and $[\mathbf{L}^{NNNN\text{-}Me}Sn][OTf]_2$ (**89**) (Scheme 16F).[24a,b] α-bis(iminopyridine) $\mathbf{L}^{NNNN\text{-}H}$ was also employed in the reaction with $Sn(OTf)_2$, but only an aqua complex $[\mathbf{L}^{NNNN\text{-}H}Sn(H_2O)][OTf]_2$ (**90**) was isolated (Scheme 16G). In all described complexes, the triflate anions are located outside the coordination sphere of the tetrylene atom, and therefore show the character of well-separated ion pairs. In contrast, ligands $\mathbf{L}^{Dimpy\text{-}Dipp}$, $\mathbf{L}^{NNO}$ and $\mathbf{L}^{NNPO\text{-}1,4,6}$ in the reaction with $Sn(OTf)_2$ stabilize complexes $[\mathbf{L}^{Dimpy\text{-}Dipp}Sn(OTf)][OTf]$ (**91**), $[\mathbf{L}^{NNO}Sn(OTf)_2]$ (**92**) and $[\mathbf{L}^{NNPO\text{-}1,4,6}Sn(OTf)_2(H_2O)]$ (**93**) (Scheme 16H-J), in which there is at least one triflate anion in the close coordination sphere of Sn atom.[33,27]

3.2. Reactivity of N-coordinated Ge(II) and Sn(II) cations and dications

As in the case of silyliumylidenes, Ge and Sn analogues should show an ambiphilic character due to the presence of an empty p-orbital on the central Ge and Sn atom together with a lone electron pair. Regarding the application of Ge(II) cations as σ-donors in the transition or main-group metal chemistry, and thus to confirm the nucleophilic behaviour, the first successful attempts involve the employment of **88**. Reaction of **88** with AgOTf (Scheme 17A) and $Me_2S{\cdot}AuCl$ in the presence of TMSOTf (Scheme 17B) gave bimetallic complexes $[(\mathbf{L}^{NNNN\text{-}Me}Ge)_2Ag(OTf)][OTf]_4$ (**94**) and $[(\mathbf{L}^{NNNN\text{-}Me}Ge)_2Au][OTf]_5$ (**95**), in which Ge atoms successfully coordinate Ag or Au atoms through a lone electron pair.[24a] Further, the nucleophilic character of $[DGeCl]^+$ was demonstrated by Inoue, who chose **79** for the reaction with $NaBH_4$ to form the corresponding hydride specie. Interestingly, borane adduct $[\mathbf{L}^{NHI\text{-}1}GeH(BH_3)][OTf]$ (**96**) with Ge→B interaction was isolated from this reaction (Scheme 17C).[25a] On the other hand, the use of $LiAlH_4$, as stronger reducing agent, led to the rapid transmetallation associated with the formation of $[\mathbf{L}^{NHI\text{-}1}AlH_2][OTf]$. The same transmetallation reaction was observed for **80** both by reaction with $LiAlH_4$ and also with $NaBH_4$.[25a]

The impossibility of N-coordinated stannyliumylidenes to act as σ-donors was previously demonstrated in the case of $[\mathbf{L}^{Dimpy\text{-}Dipp}SnCl][SnCl_3]$. Accordingly to the ability of $[\mathbf{L}^{Am}Si(DMAP)][OTf]$ to coordinate $W(CO)_5$ and $[Rh(COD)Cl]_2$, we studied the analogous reactions of **39** with $M(CO)_5{\cdot}THF$ (M = Cr, W) (Scheme 17D) and $[\eta^6\text{-arene})RuCl_2]_2$ (arene = benzene, p-cymene) (Scheme 17E). The complex **39** contains Sn(II) atom both in $[\mathbf{L}^{Dimpy\text{-}Dipp}SnCl]^+$ cation and $[SnCl_3]^-$ anion and therefore possesses two potential sites to coordinate transition metals. It was shown that coordination of $[SnCl_3]^-$ anion to transition metals is preferred to coordination of $[\mathbf{L}^{Dimpy\text{-}Dipp}SnCl]^+$ cation for all three complexes and compounds $[\mathbf{L}^{Dimpy\text{-}Dipp}SnCl][M(CO)_5(SnCl_3)]$ (**97**: M = Cr, **98**: M = W) and $[\mathbf{L}^{Dimpy\text{-}Dipp}SnCl][\eta^6\text{-arene})RuCl(SnCl_3)_2]$ (**99**) was formed.[33,34]



Scheme 17. Reactivity of N-coordinated Ge(II) and Sn(II) cations and dications.

Rather than nucleophilic character, N-coordinated stannyliumylidenes exhibit electrophilicity, which was demonstrated by the ability of PMe_3 to coordinate Sn(II) atom in dicationic **89** yielding $[\mathbf{L}^{NNNN\text{-}Me}Sn(PMe_3)][OTf]_2$ (**100**) (Scheme 17F).[24b] Later on, a series of Sn(II) ionic complexes, namely $[\mathbf{L}^{NNO}SnCl][SnCl_3]$ (**48**), $[\mathbf{L}^{NN\text{-}Ph}SnCl][SnCl_3]$ (**81**), $[\mathbf{L}^{NN\text{-}Ph}SnCl][GaCl_4]$ (**82**), $[\mathbf{L}^{NN\text{-}tBu}SnCl][GaCl_4]$ (**83**), $[\mathbf{L}^{NNNN\text{-}H}SnCl][SnCl_3]$ (**51**) and $[\mathbf{L}^{NNNN\text{-}H}Sn(H_2O)][OTf]_2$ (**90**), were tested as potential catalyst in ring-opening polymerization of L-lactide (L-LA) via activated monomer mechanism.[24c] The initial and key step of this mechanism is the coordination of cyclic ester through carbonyl oxygen atom to the electrophilic site in the catalyst (Figure 4).

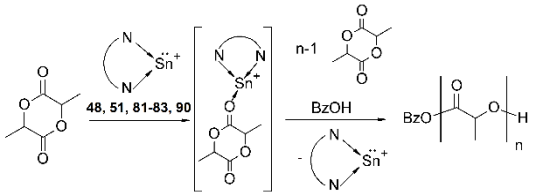


Figure 4. Schematic representation of activated monomer mechanism of ROP of L-lactide catalysed by Sn(II) cations.

For all complexes, the coordination of L-LA is exergonic (ΔG ranging from –2.7 to –9.1 kcal·mol^{-1}). However, the rate of polymerization by using studied complexes is slower compared to the industrially preferred Sn(2-ethylhexanoate)$_2$. On the hand, produced PL-LAs show, under the same reaction conditions, better uniformity in terms of dispersity $Đ$ (range of 1.23 – 1.45 vs. 2.04). Moreover, [**L**$^{\mathbf{NNNN\text{-}H}}$SnCl][SnCl$_3$] (**51**) and [**L**$^{\mathbf{NNNN\text{-}H}}$Sn(H$_2$O)][OTf]$_2$ (**90**) produce also the star-shaped PLA with a dipentaerythritol core with very good agreement of the experimental number of arms with the theoretical ones (Figure 5).

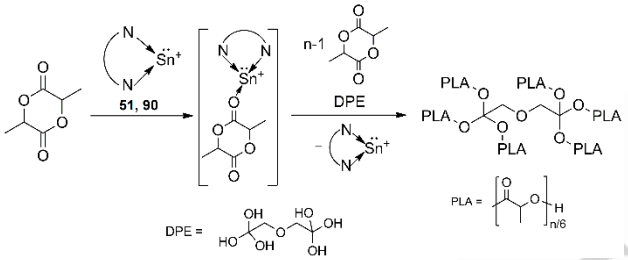
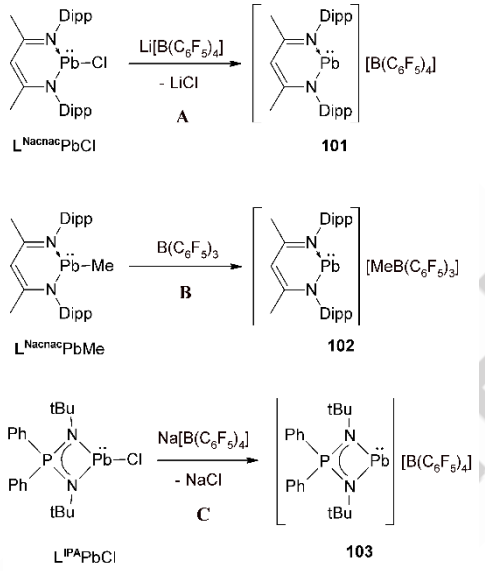


Figure 5. Synthesis of star-shaped PLAs using **51** and **90** as catalysts.

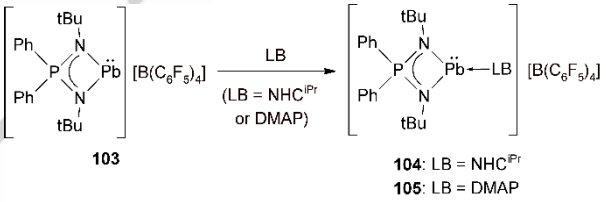
4. N-Coordinated Plumbyliumylidenes

Although a few examples of plumbyliumylidenes stabilized by bulky substituents, such as cyclopentadienyl Cp, Cp*, terphenyl 2,6-(Trip)$_2$-C$_6$H$_3$ (Trip = 2,4,6-iPr$_3$-C$_6$H$_2$), 1,8-(3,5-tBu-C$_6$H$_3$)$_2$-3,6-tBu$_2$-carbazolyl, and a rare example of chloroplumbyliumylidene donating by (Cy$_3$P)Pt(0) have been synthesized,[35] the field of N-coordinated plumbyliumylidenes, compared to lighter congeners silyliumylidenes and especially germyliumylidenes and stannyliumylidenes, is a much less explored area. Only three representatives of these cationic complexes are described in the literature.[18,36] Following the successful synthesis of the [**L**$^{\mathbf{Nacnac}}$Pb][B(C$_6$F$_5$)$_4$] (**101**) by chloride abstraction in starting chloroplumbylene **L**$^{\mathbf{Nacnac}}$PbCl (Scheme 18A) and [**L**$^{\mathbf{Nacnac}}$Pb][MeB(C$_6$F$_5$)] (**102**) by methyl abstraction in **L**$^{\mathbf{Nacnac}}$PbMe (Scheme 18B), Nakata et al. very recently implemented the first synthetic approach also for the preparation the iminophosphonamide-stabilized Pb(II) cation. With chloroplumbylene **L**$^{\mathbf{IPA}}$PbCl (**L**$^{\mathbf{IPA}}$ = Ph$_2$P(NtBu)$_2$) in hands, they treated it with Na[B(C$_6$F$_5$)$_4$] providing corresponding [**L**$^{\mathbf{IPA}}$Pb][B(C$_6$F$_5$)$_4$] (**103**) (Scheme 18C).



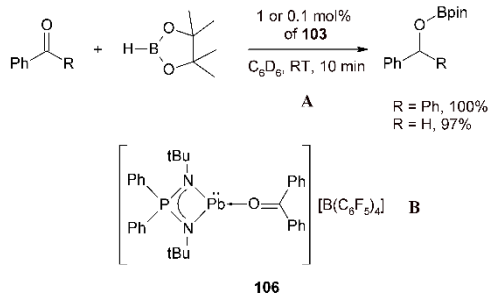
Scheme 18. Synthesis of [**L**$^{\mathbf{Nacnac}}$Pb][B(C$_6$F$_5$)$_4$] (**101**), [**L**$^{\mathbf{Nacnac}}$Pb][MeB(C$_6$F$_5$)] (**102**) and [**L**$^{\mathbf{IPA}}$Pb][B(C$_6$F$_5$)$_4$] (**103**).

The Lewis acidic character of **103** was explored by the reaction with Lewis bases such as NHC^{iPr} and DMAP. These reactions provided the corresponding adducts [**L**$^{\mathbf{IPA}}$Pb(NHC^{iPr})][B(C$_6$F$_5$)$_4$] (**104**) and [**L**$^{\mathbf{IPA}}$Pb(DMAP)][B(C$_6$F$_5$)$_4$] (**105**) in good yields (Scheme 19) proving a positive charge on Pb atom.



Scheme 19. Reactivity of [**L**$^{\mathbf{IPA}}$Pb][B(C$_6$F$_5$)$_4$] with NHC^{iPr} and DMAP as Lewis bases.

This fact and the successful application of NHC-stabilized silylium- and germyliumylidenes in hydroboration reactions[37] evoked the idea to use **103** as the catalyst in the hydroboration of carbonyls. The treatment of an equimolar amount of benzophenone with HBpin (HBpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane) in the presence of 10 mol% of **103** showed a complete conversion (TOF > 600 h-1) of benzophenone to the hydroborated product in 10 min (Scheme 20). Moreover, in the case of the reduction of benzaldehyde only 0.1 mol % of catalyst is needed for 97% conversion (TOF 5820 h-1). To better understanding of the hydroboration mechanism using **103** as the catalyst, several experiments and theoretical calculations were carried out. It has been proved that hydroboration reaction of benzophenone (Scheme 20A) proceeds through an adduct [**L**$^{\mathbf{IPA}}$Pb(O=CPh$_2$][B(C$_6$F$_5$)$_4$] (**106**), in which carbonyl bond is, due to the interaction with Pb atom (Scheme 20B), activated and easily attacked by hydride from HBpin.

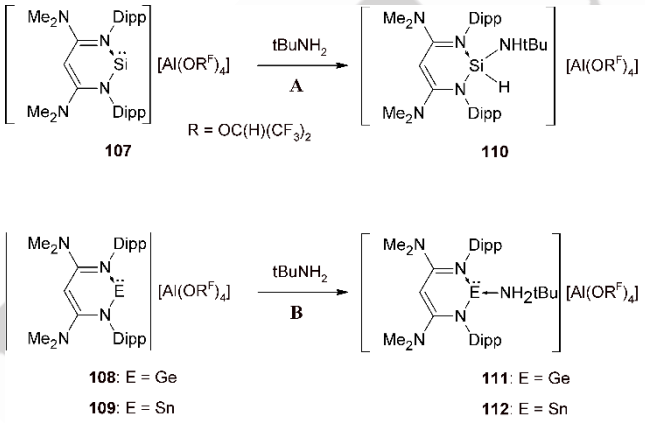


Scheme 20. Hydroboration of carbonyls using **103** as the catalyst.

5. Oxidative additions on N-coordinated tetryliumylidenes

Oxidative addition as a key step in many catalytic cycles has long been the domain of TM-complexes, in particular. However, this dogma has been broken in the last few years. Number of low-valent complexes of main group elements have been shown to be able to undergo this type of reaction, including tetrylenes.[38] The increased Lewis acidity of tetryliumylidenes could thus be an advantage in the initial reaction with an organic substrate.[39]

However, to the best of our knowledge, there is only one study dealing with the oxidative addition to N-coordinated tetryliumyledenes in the literature. In 2020, Aldridge et al. studied possible N-H bond activation with [$\mathbf{L^{NacnacNH2}}$E][Al(OR^F)$_4$)] (**107**: E = Si, **108**: E = Ge, **109**: E = Sn; R = OC(H)(CF$_3$)$_2$).[40] The reactivity of [$\mathbf{L^{NacnacNH2}}$E][Al(OR^F)$_4$)] towards tBuNH$_2$ strongly depends on the central atom E. While **107** generates [$\mathbf{L^{NacnacNH2}}$Si(H)(NHtBu)][Al(OR^F)$_4$)] (**110**) (Scheme 21A) as the product of oxidative addition, compounds **108** and **109** lead only to the amine-coordination providing [$\mathbf{L^{NacnacNH2}}$E(tBuNH$_2$)][Al(OR^F)$_4$)] (**111**: E = Ge, **112**: E = Sn), in which no N-H bond cleavage was occured.



Scheme 21. Oxidative addition vs. amine-coordination of tBuNH$_2$ on [$\mathbf{L^{NacnacNH2}}$E][Al(OR^F)$_4$)] (**107** – **108**).

6. Summary and Outlook

In conclusion, it can be stated that cations and dications of heavier group 14 elements in low oxidation state stabilized by N-donor ligands are a very attractive area in the field of coordination chemistry. In recent years, several research groups have expanded this field with many beneficial findings involving the preparation and reactivity of these ionic complexes. From the point of view of the general structure, it is possible to obtain several groups of species classified as [LE]$^+$, [DEX]$^+$ or [DE]$^{2+}$ (L = monoanionic ligand, D = neutral ligand, X = halide). The synthesis of [LE]$^+$ class of compounds consists the halide or methyl abstraction in the corresponding halo- or methyl-substituted N-coordinated tetrylenes. This synthetic protocol is universal for complexes within all heavier group 14 elements. Further, some special approaches can be applied as demonstrated by silicon-silicon bond cleavage in [$\mathbf{L^{Am}}$Si]$_2$ by [4-NMe$_2$C$_5$H$_4$NSiMe$_3$]OTf providing [$\mathbf{L^{Am}}$Si(DMAP)][OTf]. The ionization of GeCl$_2$ and GeBr$_2$ initiated by 1,10-phenanthroline and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine gave rise to ionic complexes of [DEX]$^+$ type. However, these complexes are the domain of germanium and tin chemistry only. Similarly, dicationic species of [DE]$^{2+}$ were prepared only with germanium and tin as central atom, where OTf serves as the counteranion in all cases.

Many of these N-coordinated cations and dications of heavier group 14 elements were further studied in terms of their reactivity in order to prove their ambiphilic character. It was found out that the electrophilicity is inherent independently of the central metal atom. This fact was reflected by the interaction of electrophilic metal center in specific complexes with Lewis bases such as DMAP, [($\mathbf{L^{Am}}$)$_2$Si]$_2$, PMe$_3$, L-LA, NHC^{iPr} or acetophenone. Thus, studied ionic species can act as catalysts in various chemical transformation or activate small molecules. The first examples of such use involve complexes [$\mathbf{L^{NNNN\text{-}H}}$SnCl(L-LA)][SnCl$_3$], [$\mathbf{L^{NNNN\text{-}H}}$Sn(L-LA][OTf] and [$\mathbf{L^{IPA}}$Pb(O=CPh$_2$][B(C$_6F_5$)$_4$] form essential intermediates in the catalytic cycles of ROP and hydroboration. On the other hand, the nucleophilic behavior given by the presence of a lone electron pair on metal center within the group decreases. It was proved by the oxidation reactions with chalcogens. While silyliumylidenes afford silathionium, silaselenonium or silatelluronium salts, the same study with heavier analogues is not known. The differences in the nucleophilic character of the described complexes can also be seen in the possibility of their use as ligands in transition metal chemistry. In the case of Si(II)-ionic species, there are several examples with Si(II)→TM coordination, e.g. [{$\mathbf{L^{Am}}$Si(DMAP)}$_2${Rh$_2$Cl$_2$(COD)}][OTf]$_2$,[{$\mathbf{L^{Am}}$Si(DMAP)}W(CO)$_5$][OTf], [{$\mathbf{L^{NHI\text{-}1}}$SiCl}CuCl][Cl], [{$\mathbf{L^{NHI\text{-}1}}$SiCl}AgCl][Cl], [{$\mathbf{L^{NHI\text{-}1}}$SiCl}AuCl][Cl] or [{$\mathbf{L^{NHI\text{-}1}}$SiCl}Au][Fe(CO)$_4$]. On the other hand, only two complexes of Ge(II)→TM type ([($\mathbf{L^{NNNN\text{-}Me}}$Ge)$_2$Ag(OTf)][OTf]$_4$ and [($\mathbf{L^{NNNN\text{-}Me}}$Ge)$_2$Au][OTf]$_5$) have been reported and even for tin and lead analogues, the Sn(II)→TM and Pb(II)→TM interaction is not known at all within N-coordinated ionic complexes.

Despite the fact the chemistry of low-valent N-coordinated cations and dications of heavier group 14 elements are relatively well explored, the research of this area is far from over. In the future, it is desirable to design new ionic complexes that would be versatile and highly active catalysts in many reactions, thereby replacing traditional catalysts derived from transition metals on a larger scale.

Acknowledgements

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Keywords: tetryliumylidene • N-donor ligand • ambiphilicity • catalysis

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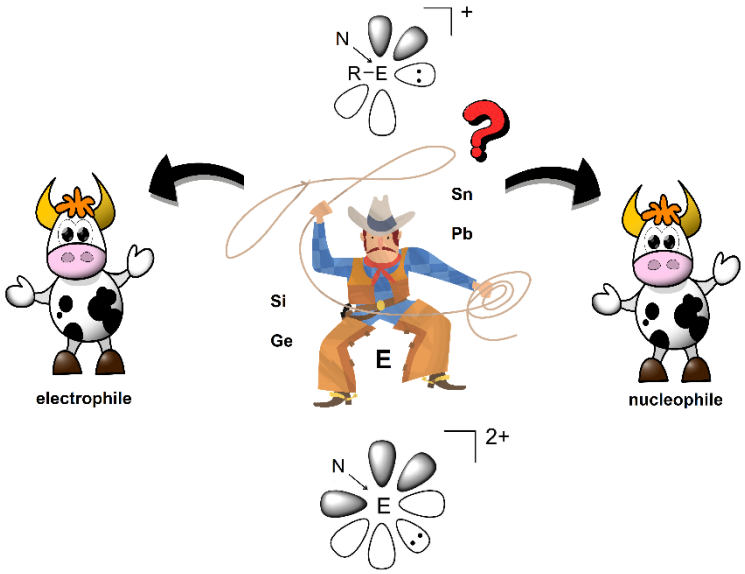

The aim of this paper is to summarize the synthesis of N-coordinated cations of heavier group 14 elements and to show their ambiphilic behavior towards Lewis acids or bases.