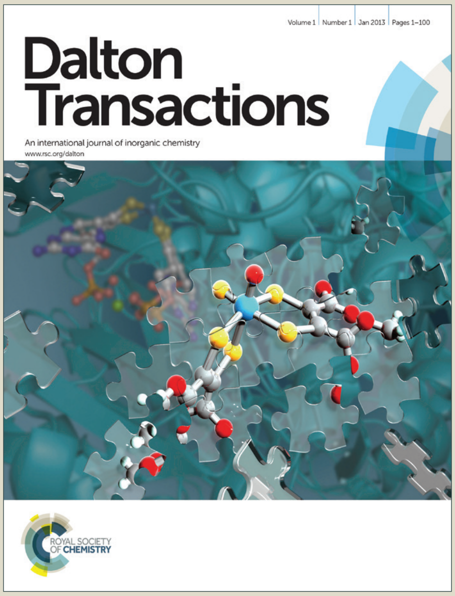
Dalton Transactions

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Cations and dications of heavier group 14 elements in low oxidation state†

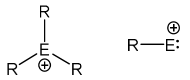
V. S. V. S. N. Swamy,[a] Shiv Pal,[b] Shabana Khan,[b]* and Sakya S. Sen[a]*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Cations and dications of heavier group 14 elements in their low oxidation state have received widespread interest in recent years. The journey started with the isolation of a series of cations of composition $[(C_5Me_5)E:]^+$ [E=Si–Pb], followed by the more recent isolation of a Ge(II) dication encapsulated within a cryptand, a carbodiphosphorane stabilized $[GeCl]^+$ monocation with a two coordinate Ge atom, Si(II) cations and dications stabilized by N-heterocyclic carbenes (NHCs), which highlights the ongoing growth and intensity in the chemistry of tetrel(II) cations. This is presumably because the central atom (E) in these compounds contains two or three unoccupied valence orbitals as well as holds a lone pair of electrons. Such an electronic description represents ambiphilicity, which is of great interest for catalysis. The successful synthesis of divalent group 14 cations has required new synthetic strategies based on the sterically demanding neutral or monoanionic ligands, utilization of counter anions, and solvents with low nucleophilicity in order to minimize the degree of interactions with the cations. An alternative approach for the realization of divalent cations of Group 14 elements is their coordination to the transition metals. This synthetic approach was successfully applied for the isolation of a range of transition metal coordinated divalent cations of Group 14 elements. Apart from academic interest some of these cations have found application as activators in Ziegler-Nata polymerization of alkenes.

Introduction

At the beginning of the 20th century, J. F. Norris and F. Kehrmann independently discovered that when triphenylmethanol and triphenylmethyl chloride were dissolved in concentrated H_2SO_4, the color of the solution was changed from colorless to deep yellow.[1] These observations along with von Bayer's subsequent interpretation that the intense color was due to the ionization of the triphenylmethanol[2] eventually paved the way for the first stable "carbocation" in chemistry, commonly known as the trityl cation. Following a series of debates over the nomenclature of this class of compounds, chemists finally accepted Olah's categorization of carbocations based on the valency of the charged carbon: carbenium ions (CR_3^+) and carbonium ions (CR_5^+).[3] The last century has witnessed a remarkable progress in the isolation of various stable carbenium ions, understanding their structural and bonding properties, and investigating their reaction chemistry.



I II

Scheme 1 Classes of cations featuring heavier group 14 elements.

Considering the rich chemistry displayed by carbenium ions, the realization of their heavier analogs i.e. $[R_3E^+$ (E = Si−Pb)] has become one of the important areas of modern inorganic chemistry and is still an area of continuous investigation. However, in contrast to the thoroughly studied chemistry of carbenium ions, only little is known about the chemistry of heavier group 14 cations. The cations of heavier group 14 elements can be classified into two distinct groups, based on the oxidation state of the atom (Scheme 1). The most common class of the cations are tetrylium ions (**I**) (group 14 is called tetrel group), which possess six valence electrons and are considered as heavier analogue of carbenium ions (R_3C^+). The generation of such a cation is easier in the gas phase, which provides an environment devoid of possible interfering solvents. However, their generation in the condensed phase is very difficult due to highly electrophilic nature of R_3E^+ and their propensity to react with any donor moiety, even with arenes. Therefore, bulky donor substituents are required to quench the electrophilicity of the cation as well as to shield the cationic center from any nucleophilic attack. With these new synthetic strategies as well as taking advantages of the low nucleophilicty of borates and carboranes as counter anions and toluene as a solvent, Lambert and Reed et al. independently isolated the first silylium ions $[Et_3Si(toluene)]^+[B(C_6F_5)_4]^-$ and $[iPr_3Si]^+[CB_{11}H_6Br_6]^-$, respectively.[4] However, the Si centers in these silylium cations adopted markedly pyramidal geometry instead of expected planar geometry and resonated at δ=92.3 and

102.8 ppm in their respective ^{29}Si NMR spectrum. The calculated gas phase chemical shift of Et_3Si^+ was of 354.6 ppm,[5] which was considerably downfield than the experimentally observed values. Consequently, the cationic character of Si atoms in these compounds was heavily questioned and eventually both Lambert and Reed agreed that neither $[Et_3Si(toluene)]^+$ nor $[iPr_3Si]^+$ were "*bona fide*" silylium cations.[6] The state of affairs was similar with those of germanium and tin. The groups of Lambert and Kira independently reported the isolation of $[nBu_3Sn]^+X^-$ [X=$B(C_6F_5)_3H$ and $B\{(3,5\text{-}CF_3)_2C_6H_3\}_4$] featuring tri-coordinate Sn atom with ^{119}Sn NMR of δ=360 and 356 ppm.[7] However, Edlund et al. proposed that the NMR data of aforementioned tin cations corresponded to the arene bound Sn atoms as three-coordinate trigonal-planar R_3Sn^+ was computationally predicted to resonate at δ=1500-2000 ppm.[8] Thus, a lot of controversies were sparked and simultaneously a huge effort was dedicated for the isolation of three-coordinate trigonal planar tetrylium ions. This was finally accomplished in 2000s with the isolation of "*bona fide*" three coordinate trigonal planar silylium $[\{Mes_3Si\}^+\{CB_{11}HMe_5Br_6\}^-$, Mes=2,4,6-$Me_3$-$C_6H_2$],[9] germylium $[\{(tBu_2MeSi)_3Ge^+\}\{B(C_6F_5)_4\}^-]$, and stannylium $[\{(tBu_2MeSi)_3Sn^+\}\{B(C_6F_5)_4\}^-]$,[10] $[\{Tipp_3Sn^+\}\{B(C_6F_5)_4\}^-]$, (Tipp=2,4,6-$iPr_3$-$C_6H_2$) cations (Chart 1).[11] Subsequently, the advances in the syntheses of novel condensed-phase cations as well as the reactivity studies have become an important research area with mainly two fold objectives: (i) to study these exotic compounds in the solid state due to the paucity of previous reports of structurally characterized heavier analogues of carbenium ions and (ii) to explore these species as efficient Lewis acid catalysts. Hallmark studies by Lambert, Reed, Müller, Corriu, Belzner, Oestreich, and others not only led to the isolation of many more such derivatives but revealed them as potential Lewis acids in homogeneous catalysis.[12] Their enhanced electrophilicity has already been exploited in Diels-Alder reactions,[13] C–C bond formation,[14] and C–F activation reactions,[15] as well as in small molecule activation e.g. dihydrogen.[16]

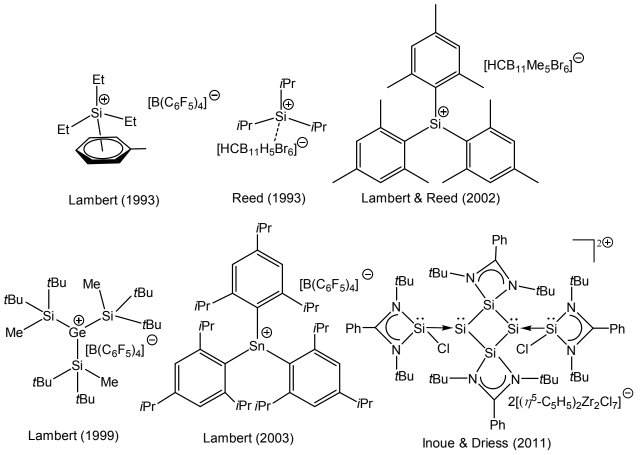


Chart 1 Selected examples of silylium, germylium, and stannylium cations.

Another distinctly different class of group 14 cations are tetrylium-ylidenes (**II**) (Scheme 1), which features a group 14 element with a lone pair. It can be imagined that a species of composition (RE:$^+$), which combines the nucleophilic nature of carbene as well as the high electrophilicity of cations is of high synthetic importance as potential noninnocent ligands in catalysis. However, the number of valence electrons in type **II** cations is only four, while there are six valence electrons in the type **I** cations. Thus, further loss of two electrons from the closed shell might imply even greater reactivity and more difficulty in isolation. It was obvious that like R_3Si^+, the laboratory realization of RSi^+ (a derivative of HSi^+) can only be accomplished through kinetic stabilization, but neither steric protection nor electronic stabilization may be adequate if only one substituent is attached to the Si center.

Increasing the coordination number of Si in RSi^+ without perturbing the formal oxidation state can be achieved mainly by two ways: (i) take advantage of cyclopentadienyl type of ligands, which can undergo haptotropic shift depending on electronic requirement of the system; (ii) attach a neutral donor ligand to the cation. The donor moiety occupies the empty coordination site of the cation and thereby reduces its electrophilicty. Both these synthetic tricks have been successfully implemented. The elegant use of pentamethylcyclopentadienyl (Cp*) ligand by Jutzi et al. allowed the isolation and characterization of the first Si(II) cation, $[(\eta^5\text{-}C_5Me_5)Si:]^+$.[17] The concept of donor-stabilization has recently been used for the isolation of a series of highly reactive compounds which were otherwise inaccessible. For example, the groups of Roesky and Filippou showed that the reactivity of silylenes like $SiCl_2$ or $SiBr_2$ can be tamed when they are attached to a N-heterocyclic carbene.[18] The N-donor stabilized amidinato chlorosilylene [PhC(NtBu)$_2$SiCl] from the Roesky group, also enjoyed substantial attention in recent years.[19] Similar N-donor stabilization afforded an unique cationic silyliumylidene ([LSi][B(C$_6$F$_5$)$_4$] (L=CH[C(MeNAr)$_2$], Ar=2,6-iPr$_2$-C$_6$H$_3$)) through protonation of the Si(II) center of the corresponding silylene, L^{1}Si (L^1=CH[C(Me)(C=CH$_2$)(NAr)$_2$]).[20] These results kick-started the chemistry of low-valent Si(II) cations although the existence of a mono-coordinated Si(II) cations has yet to be demonstrated.

In contrast to carbon and silicon atom, germanium, tin, and lead are more stable in their M^{II} oxidation state as the stability increases with the increase of the principal quantum number. Going down the periodic table, the *s*–*p* separation increases with increasing nuclear charge. As a result *s*/*p* hybridization becomes more and more difficult, leading to the "inert *s*-pair effect," in which only the *p* electrons are used in the bonding. Therefore, the isolation of LE:$^+$ (E=Ge–Pb) is relatively simpler. To the best of our knowledge, the first mention of LE:$^+$ (E=Ge-Pb) came from the group of Jutzi, who reported a series of *nido*-cluster type cations of composition $[(C_5Me_5)E:]^+$.[21] Since then a number of germanium(II), tin(II), and lead(II) mono- and dications have been reported. A few of these compounds have been cited in recent review articles[22,23] as well as in an excellent book by Lee and Sekiguchi, which primarily dealt with "*carbenium derivatives of heavier group 14 elements* (R_3E^+)".[24] However, to our knowledge no efforts have been dedicated to compile only the cations of composition RE:$^+$, where E is a heavier group 14 element in +2 oxidation state. Moreover, several important accomplishments like $[\text{Cl-Si:}]^+$, Si(II) dication, polyether ligated Ge(II) and Sn(II) mono- and dications etc. that deserve mentioning have been recently reported. However, the chemistry of cations and dications of heavier group 14 elements in low oxidation state is very far from being complete; there are still many challenges left. The practical application of these classes of compounds is still awaited. Recent studies showed that heavier carbenes have the potential to compete with transition metal complexes for single site small molecule activation, which is of significant importance in order to find cheap and green alternatives to transition metal complexes for this important class of reactions.[25] Therefore, the utilization of the cations and dications of heavier group 14 elements in various catalytic transformation and small molecule activation seems to be attractive and promising. These arguments justifies the requirement for a review at this juncture dedicated solely to tetrel(II) cations, which will extensively kindle further interest, directed towards its development. This present review will deal with the available synthetic routes for the preparation of cations of heavier group 14 elements in low oxidation states, starting from the compounds of composition Cp*E^+, which were the first to be prepared. We shall mainly concentrate on the cations stabilized by using bulky ligands. We shall also cover the transition metal supported E^{II} (E=Si–Pb) cations. The literature coverage of this review is up to 2014. Because it is difficult to definitively conclude the formation of the cations by spectroscopy alone, we have chosen to cover mainly compounds which were structurally characterized by single crystal X-ray diffraction studies.

2. The Ligands

The isolation of the aforesaid compounds and various other remarkable subvalent compounds of silicon, germanium, tin, and lead would not have been feasible without the appropriate choice of ligands that afford thermodynamic stabilization through the donor sites and kinetic stabilization through bulky substituents. For decades, organometallic chemistry and to a lesser degree the study of main group elements, has focused on the study of complexes bearing the cyclopentadienyl ligand and its ring-substituted derivatives. A current trend in main group chemistry is the search for alternative ligand sets which are able to attenuate the reactivity of subvalent main group compounds and allow their isolation. Among them, *β*-diketiminato ligands have emerged as very versatile ligands in recent years.[26] A major advantage of the *β*-diketiminato ligands is that the steric and the electronic environment of these ligands can be fine-tuned with minimum synthetic effort. This flexibility allows a degree of control over the chemistry at the metal center and can be attributed for the widespread use of *β*-diketiminato ligands for stabilizing the highly reactive species etc.

In an effort to explore the feasibility of isolating dications of heavier group 14 elements in the +2 oxidation state, synthetic chemists moved from the formally anionic ligands and focused on neutral ligands like N-heterocyclic carbenes (NHCs). Baines and coworkers introduced NHC in this chemistry and isolated the first Ge(II) dication coordinated by three I*i*Pr (1,3-$i\text{Pr}_2$-imidazol-2-ylidene) groups (*vide infra*).[27] Similar to *β*-diketiminato ligands, NHCs also offer high synthetic flexibility by varying the "wingtip" substituents (substituent at the nitrogen atom), which led them as one of the most sought after ligands in main group chemistry.[28] Another leading motif over the last few years has been the linking of two NHCs by several bridging spacers to generate discrete multitopic bis-NHCs, which exhibit high affinities toward a broad range of metals.[29] Complexes featuring such ligand are stabilized by chelate effect and offer various possibilities for tuning their geometric and electronic properties.

The enormous success of NHCs prompted the investigation of other carbon-based neutral ligands. The groups of Alcarazo and Vidovic used a divalent C(0) compound, commonly known as carbodiphosphorane $[(\text{PPh}_3)_2\text{C}]$, for the realization of B,[30a] Ge,[30b] and P[31] centered cations. The main advantage of these C(0) ligands over NHCs is that they are capable of acting as σ- as well as π-donors. A recent computational paper by Toner and Frenking proposed that the substitution of an NHC by a carbodiphosphorane in the Grubbs' catalyst for alkene metathesis might lead to an enhanced reactivity.[32]

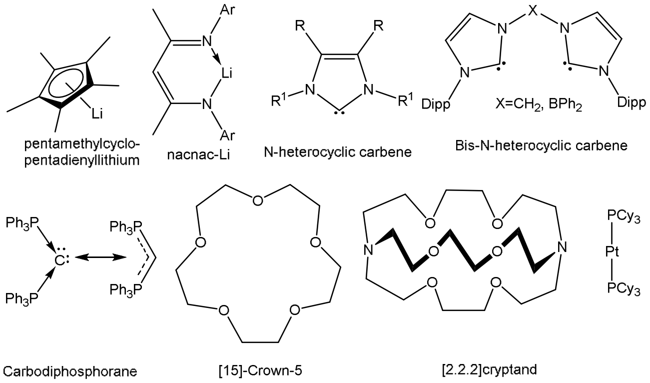


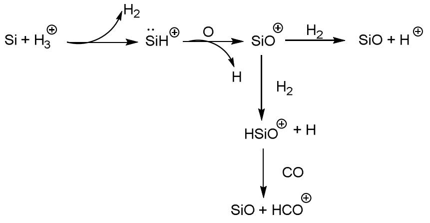
Chart 2 Selective ligands used for stabilizing cations of heavier group 14 elements in low oxidation state.

Macrocyclic ligands like cryptands, crown ethers, azamacrocycles etc. have been noted for their remarkable metal complexation properties through numerous weak donor sites. There are many examples of cryptands and crown ethers coordinated *s*-block and *d*-block elements in literature.[33] Schmidbaur et al. found that such a macrocyclic ligand (cyclophane) can also stabilize germanium and tin cations.[34] However, the use of macrocyclic ligands for realizing *p*-block cations was extensively increased since Baines' report of a germanium(II) dication encapsulated in [2.2.2]cryptand.[35] In the following years, a range of macrocyclic ligands like crown ethers, cryptands, azamacrocycles etc. were used to give rise an array of cations and dications of germanium(II) and tin(II), which revealed an interrelation between the cavity size of the macrocycles and the stability of the E(II) dication or the $[\text{EX}]^+$ (E=Ge and Sn) monocation (*vide infra* section 4.1.4).

It was only recently that the various research groups started to exploit the coordination sphere of the electron rich coordinatively unsaturated late transition metals such as W, Pt, Pd to stabilize germanium(II), tin(II), and lead(II) cations (*vide infra*). Precedent for this approach came from the isolation of an array of complexes featuring B≡E (E=N and O),[36] B=C,[37] Si≡Mo,[38] Ge≡Re,[39] Si=O[40] bonds, which are thus far otherwise inaccessible. However, interpretation of the bonding situation in transition metal supported tetrel(II) cationic complexes are not very straight forward taking into consideration of other possible canonical forms.

3. Si(II) Cations: Synthesis, Spectroscopic and Structural Elucidation, and Reactivity

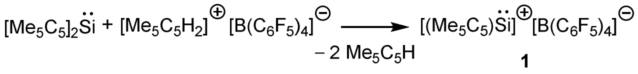
Silicon (II) cations have long been considered as a challenging target in synthetic inorganic chemistry. The laboratory identification on HSi^+, the smallest possible Si(II) cation, was carried out by Douglas and Lutz,[41] who observed five bands of the system in the emission spectrum. Following this, Grevesse and Sauval identified the presence of HSi^+ in the solar photospheric spectrum through absorption spectroscopy.[42] It is also now recognized that HSi^+ is present in the interstellar space down to large optical depth (the optical depth is just the amount of interstellar dust that the light must pass through), where it is rapidly converted to SiO by reacting with oxygen by the following sequence (Scheme 2).[43]



Scheme 2 Reactions of HSi^+ in the interstellar medium leading to SiO.

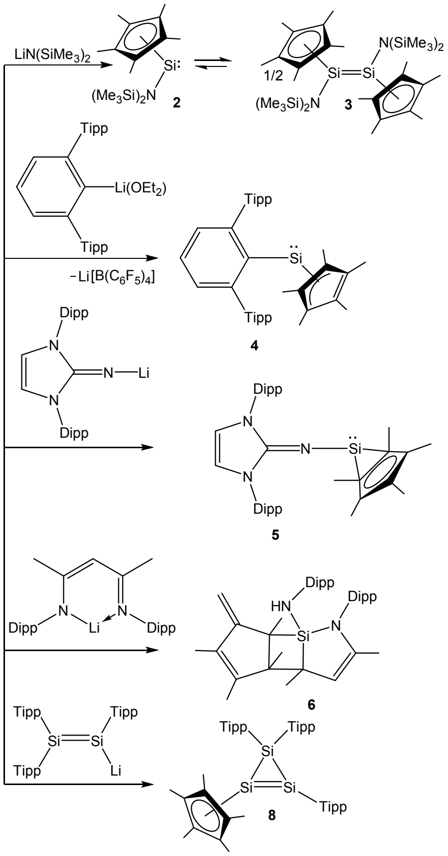
3.1. Cyclic π-conjugated Si(II) cations

Kinetic stabilization of the labile $RSi:^+$ core using the sterically demanding substituents and utilizing weakly coordinating counter-anions and solvents of low nucleophilicity was found to be a feasible strategy to furnish the Si(II) cations. Jutzi et al. employed mono-anionic pentamethylcyclopentadienyl (Cp*) ligand for the isolation of the first Si(II) compound, decamethylsilicocene (Cp^*_2Si).[44] Cp^*_2Si was initially treated with HBF_4, which apparently led to the formation of the salt $Me_5C_5Si^+$ BF_4^-. However, the latter was instantly decomposed even at low temperatures under the liberation of BF_3 and a polymeric product was obtained. Subsequently, Cp^*_2Si was reacted with $[Me_5C_5H_2]^+[B(C_6F_5)_4]^-$ which gave rise to $[\eta^5\text{-}Me_5C_5Si]^+[B(C_6F_5)_4]^-$ (**1**) with simultaneous formation of two equivalents of Me_5C_5H (Scheme 3).[17] So, it is apparent that the selection of the proton source was very critical. The η^5-coordination mode of Cp* ring was reflected in the ^1H NMR spectrum as five Me groups showed only one sharp singlet at δ=2.23 ppm. The markedly upfield signal in the ^{29}Si NMR (δ = –400.2 ppm) indicated the "π-complex" of a Si(II) atom. In the solid state structure, $[\eta^5\text{-}Me_5C_5Si]^+$ showed a weak interaction with the borate anion leading to a quasi pentagonal-pyramidal geometry at silicon atom. *Ab initio* calculations showed that the HOMO in **1** was formed by a π-interaction between Cp* moiety and silicon whereas the lone-pair corresponded to HOMO-1. The HOMO-LUMO energy gap in **1** is 12.34 eV (MP2/TZVPP) indicating strong acidic character of the cation. Such half-sandwich compounds like **1** possess six interstitial electrons (four electrons from $C_5Me_5^+$ ring and Si^+ cap donates two more electron to complete the set of six interstitial electrons) and according to Jemmis and Schleyer, they can be best regarded as three dimensional aromatic compounds.[45]


$$[Me_5C_5]_2\ddot{Si} + [Me_5C_5H_2]^{\oplus}[B(C_6F_5)_4]^{\ominus} \xrightarrow[-\,2\,Me_5C_5H]{} [(Me_5C_5)\ddot{Si}]^{\oplus}[B(C_6F_5)_4]^{\ominus}$$

1

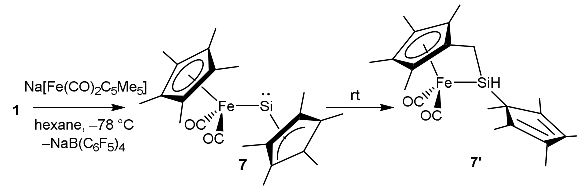
Scheme 3 Synthesis of $[Cp^*Si]^+$.



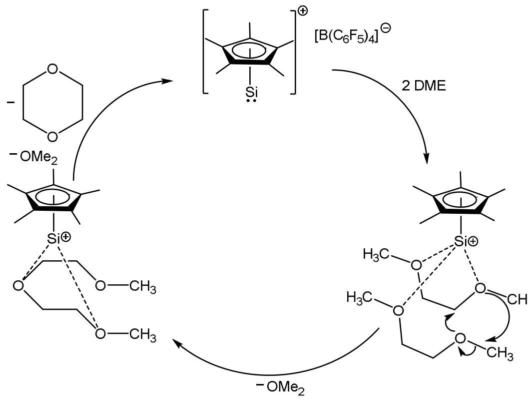
Scheme 4 Reactivity of $[Cp^*Si]^+$ towards various lithium containing reagents.

Following the synthesis of the $[Cp^*Si]^+$ cation, Jutzi, Scheschkewitz, and others reported many reactions taking advantage of **1** as a starting material, which are outlined in Scheme 4. The reaction of **1** with $LiN(SiMe_3)_2$ afforded silylene $(Me_5C_5)SiN(SiMe_3)_2$ (**2**) as a reactive intermediate, which dimerizes to give the disilene *E*-$\{(\eta^1\text{-}Me_5C_5)[N(SiMe_3)_2]Si\}_2$ (**3**).[17] Later Jutzi et al. found that a rare reversible phase dependent dynamic equilibrium exists between silylene **2** and disilene **3**.[46] During crystallization colorless silylene **2** dimerized to yellow colored disilene **3**. Again when **3** was dissolved in solvents, a colorless solution of **2** was obtained. This unusual behavior could be rationalized by steric strain in the solid disilene, flexibility in bonding modes of Cp* groups, low activation energy for the equilibrium process, small energy difference between **2** and **3**. It should be noted here that dehydrochlorination of $[(\eta^1\text{-}Me_5C_5)SiHCl_2]$ with $KN(SiMe_3)_2$ also led to disilene **3** in higher yield.[47] **1** was further reacted with various lithium containing anions like $Li(2,6\text{-}Tipp_2\text{-}C_6H_3)$ (Tipp=2,4,6-iPr$_3$-C_6H_2) and $Li[NC\{N(Dipp)CH\}_2]$ (Dipp=2,6-iPr$_2$-C_6H_3) to obtain $[(\eta^3\text{-}C_5Me_5)(2,6\text{-}Tipp_2\text{-}C_6H_3)]Si$: (**4**) and

$[(C_5Me_5)(NC\{N(Dipp)CH\}_2)]Si$: (**5**), respectively under salt elimination reaction.[48] The former features a silylene with one σ-donor and one π-donor substituent attached to Si(II) center. On the contrary, the reaction of **1** with $Li[HC(CMeNDipp)_2]$ did not result in the putative $Cp^*[HC(CMeNDipp)_2]Si$: but a constitutional isomer **6**.[49] **1** was also utilized as a stoichiometric source of silicon in reaction with $Na[Fe(\eta^5\text{-}C_5Me_5)(CO)_2]$, which gave rise to a ferrio-substituted silylene $[Fe(\eta^5\text{-}C_5Me_5)(CO)_2\{Si(\eta^3\text{-}C_5Me_5)\}]$ (**7**) at low temperature (Scheme 5).[50] However, at ambient condition, the silylene fragment was inserted into one of the C–H bonds of the Cp* ring leading to a rearranged product **7′**. The substitution reaction with the lithium disilenide $[Tipp_2Si{=}Si(Trip)(Li\{dme\}_2)]$ led to a straightforward access to the first cyclotrisilene with only carbon-based substituents (**8**) (Scheme 4).[51]



Scheme 5 Synthesis of iron-substituted silylene (**7**) from **1** and its rearrangement.



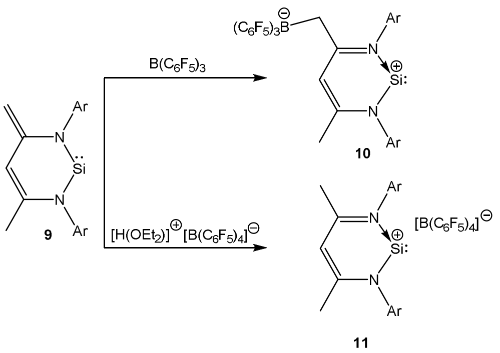
Scheme 6 Metal free catalytic cycle for conversion of DME to 1,4-dioxane.

The study of compounds featuring low valent main group elements continues to be a worthwhile subject due to their anticipated application in metal free catalysis. Recently, **1** has been found to catalytically convert 1,2-dimethoxyethane (DME) to 1,4-dioxane and dimethyl ether (Scheme 6), which is a rare example of a metal free catalytic transformation.[52] *Ab initio* calculation suggests that the O→Si dative bond in DME→**1** complex is electrostatic in nature and the subsequent enhancement of positive charge at silicon center facilitates the attack of another equivalent of DME. This catalytic process is found to be useful for a range of oligo(ethylene glycol)diethers, leading to 1,4-dioxane and dimethyl ether in each case.

3.2. Donor stabilized Si(II) cation

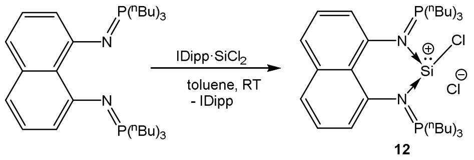
Stabilization of Si(II) cations can be achieved intra-molecularly by using N-donor ligands. Among various N-donor ligands, β-diketiminates with 2,6-disubsituted aryl groups on the nitrogen atoms has been recognized by many groups as a means of stabilizing low coordinate complexes. The journey of the β-diketiminato ligand in silicon chemistry began on 2006 with the synthesis of a unique zwitter-ionic N-heterocyclic silylene $[CH\{C(Me)(C{=}CH_2)(NAr)_2\}]Si$: (Ar=2,6-*i*$Pr_2$-$C_6H_3$) (**9**).[53] Treatment of silylene **9** with $B(C_6F_5)_3$ resulted in zwitter-ionic compound **10**, whereas the same reaction with $[H(OEt_2)_2]^+[B(C_6F_5)_4]^-$ led to the formation of separated ion pair $([LSi][B(C_6F_5)_4]$ (L=CH(CMeNAr)$_2$ (**11**) (Scheme 7).[20] It is of note here that **10** readily decomposes when dissolved in CH_2Cl_2, whereas **11** showed no sign of decomposition in CH_2Cl_2.

Presented in *Table 1* are selected NMR data for the related silicon(II) compounds. In general, more cationic charge density on the silicon center results in a more downfield shifted ^{29}Si resonance. However, both **10** (δ=40.5 ppm) and **11** (δ=69.3 ppm) exhibit upfield shifted resonances compared to that of **9** (δ=88.4 ppm) although the Si centers in **10** and **11** are higher Lewis acidic in nature. This was presumably a consequence of p_π–p_π interaction between the π-electron system of the β-diketiminate ligand and the Si atom. Moreover, the γ-H resonances of **10** (δ=6.79 ppm) and **11** (δ=6.92 ppm) also indicated the existence of aromatic ring current in the systems. X-ray studies on **10** and **11** showed that the six-membered SiC_3N_2 rings were planar and the endocyclic N–C bond lengths was shortened by 0.05 Å compared to those in **9**. Such features were in accord with the aromatic nature of these systems, which was further confirmed by Nuclear independent chemical shift (NICS) calculations (NICS (1): –3.9 ppm).

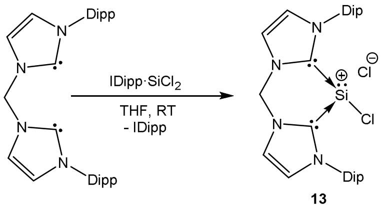


Scheme 7 Synthesis of β-diketiminato ligand supported Si(II) cations, **10** and **11**.

A chelating bis(iminophosphorane)ligand has been recently used by Driess et al. to obtain a chlorosilyliumylidene complex **12** through ligand exchange of the $SiCl_2$ unit.[54] NHC·$SiCl_2$[18a] was used as a stoichiometric source of $SiCl_2$ and its reaction with bis(iminophosphorane) ligand resulted in the ion pair with concomitant liberation of one equivalent NHC (Scheme 8). Utilizing the same synthetic strategy, Driess et al. prepared another remarkable chlorosilyliumylidene derivative **13** by the reaction of bidentate bis-NHC ligand with NHC·$SiCl_2$ (Scheme 9).[55] The ^{29}Si NMR resonances due to the three-coordinate Si nuclei in **12**$^+$ and **13**$^+$ were observed at δ= –3.3 and –58.4 ppm, respectively. The upfield shift can also be attributed to the stronger electron donation from bis-NHC and iminophosphorane ligands. Alternatively, such shifts to higher field may also indicate the decrease of cationic character. Inspection of the frontier MOs revealed that the HOMO in **12**$^+$ is associated with the ten π-electrons and the nitrogen lone pair of the P-N ylide bonds and the lone pair on the silicon atom is depicted by HOMO-1 orbital. This is in contrast to **13**$^+$ where the lone-pair of silicon constitutes the HOMO and the difference may be attributed to the stabilization of the Si lone pair by the π-system in **12**$^+$.



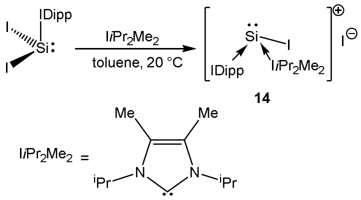
Scheme 8 Synthesis of [Cl-Si:]$^+$derivative, **12**.



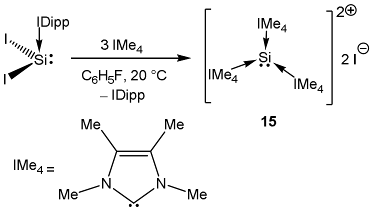
Scheme 9 Synthesis of [Cl-Si:]$^+$derivative, **13**.

Unlike NHC stabilized $SiCl_2$ and $SiBr_2$, which was reported back in 2009,[18] the synthesis of the first stable NHC stabilized diiodosilylene (IDipp·SiI_2)[56] (IDipp=1,3-(2,6-*i*Pr_2-$C_6H_3)_2$-imidazol-2-ylidene) was recently accomplished by following the same synthetic protocol used for the isolation of IDipp·$SiBr_2$.[18b] Following this, Filippou et al. have found that the reaction of IDipp·SiI_2 with I*i*Pr_2Me_2 (1,3-*i*Pr_2-4,5-Me_2-imidazol-2-ylidene) resulted in the displacement of one iodide ligand leading to [(IDipp)(I*i*Pr_2Me_2)·SiI]$^+$I$^-$ (**14**) (Scheme 10), the first formal derivative of [I-Si:]$^+$. The structure of **14** revealed a fixed orientation of the one isopropyl C–H group pointing towards Si(II) atom to maximize a Si····H–C anagostic interaction, as also supported by ^{29}Si-^{1}H coupling constant (J=10.4 Hz) and subsequent DFT calculations.

Addition of a less bulky NHC (IMe_4=1,3,4,5-Me_4-imidazol-2-ylidene) to IDipp·SiI_2 led to the first Si(II) dication $[(IMe_4)_3\rightarrow Si:]^{2+}I^{2-}$ (**15**) (Scheme 11).[56] The removal of the iodide anions from the Si center can be attributed to the steric bulk exerted by three NHCs. The Si center adopts a pyramidal propeller like conformation (Fig. 1), akin to the analogous Ge(II) dication (**49**$^{2+}$) published before by Baines and coworkers (*vide infra*).[27] However, interpretation of the ionocity of **15**$^{2+}$ as well as other donor stabilized Si(II) cations (**12**$^+$–**14**$^+$) is complicated by the fact that such stabilization takes place at the cost of the cationic character of the Si atom. Three possible canonical forms of **12**$^+$–**14**$^+$ are outlined in Scheme 12. Two of the resonating structures oppose and diminish the cationic nature of the Si atom and indicate the positive charge is distributed over the ligands. This was further manifested in the appearance of ^{13}C NMR signal of the carbene C in the relatively high field in these cations (**13**: δ=161.6; **14**: δ=151.5 and 158.3; **15**: δ=150.7 ppm), which is more close to that of the imidazolium salt (IMe_4H)Cl (δ=136.9 ppm) than that in IMe_4 (δ=212.7 ppm). However, various charge calculations indicate the accumulation of positive charge on silicon. Therefore, perhaps it is safe to comment that all three resonating structures contribute to the overall bonding of these cations.



Scheme 10 Synthesis of [I-Si:]$^+$ derivative, **14**.



Scheme 11 Synthesis of Si dication derivative, **15**.

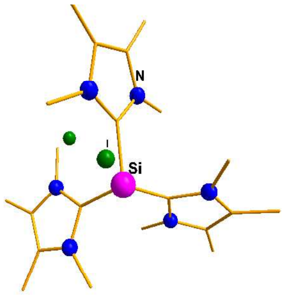
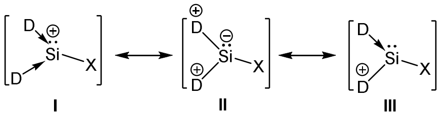


Fig 1 Molecular structure of Si dication, **15**.



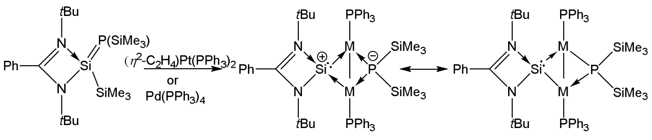
Scheme 12 Canonical forms of donor stabilized Si cations.

Table 1 ^{29}Si NMR value for related silylium ylidenes

Compound	Solvent	^{29}Si NMR (ppm)	Ref
1	CD_2Cl_2	–400.2	17
10	THF-d_8	40.5	20
11	CD_2Cl_2	69.3	20
12	CD_2Cl_2	–3.3	52
13	CD_2Cl_2	–58.4	53
14	CD_3CN	–89.9	54
15	CD_3CN	–55.3	54
16a	C_6D_6	8.3 (d, $^1J_{P\text{–}Si}$ 7.4 Hz; *Si*Me_3), 234.5 (dt, $^2J_{P\text{–}Si}$ 219.4Hz, 48.5 Hz, SiPt_2)	56
16b	THF-d_8	0.01 (d, $^1J_{P\text{–}Si}$ 6.0 Hz, *Si*Me_3), 187.8 (dt, $^2J_{P\text{–}Si}$ 43.4 Hz, 184.3 Hz, SiPd_2)	56

3.3. Transition metal supported Si(II) cation

Driess and coworkers proposed that the reaction of [PhC(N*t*Bu)$_2$SiCl] with (η^5-C_5H_5)$ZrCl_3$ led to the formation of [PhC(N*t*Bu)$_2$Si]$^+$[(η^5-$C_5H_5)_2Zr_2Cl_7$]$^-$[57] which spontaneously underwent a disproportionation reaction to afford the tetrasilacyclobutadiene dication (*vide supra* Chart 1) along with various side products. All attempts to prepare [PhC(N*t*Bu)$_2$Si]$^+$ have not been successful thus far except So and coworkers obtained 4-DMAP (4-DMAP= 4-dimethylaminopyridine) coordinated [PhC(N*t*Bu)$_2$Si]$^+$ with a triflate anion.[58] Recently, Inoue and coworkers isolated $[PhC(N\textit{t}Bu)_2Si]^+$ in the coordination sphere of Pd and Pt. Cationic transition metal complex, $[LSi\{M\text{-}(PPh_3)\}_2P(SiMe_3)_2]$ (M=Pd (**16a**) and Pt (**16b**)) was prepared from the reaction of $[PhC(N\textit{t}Bu)_2Si(SiMe_3){=}P(SiMe_3)]$ with $Pd(PPh_3)_4$ or $[(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2]$ (Scheme 13).[59] Determining the nature of the Pt–Si bonds is rather difficult. Two possible resonating structures are presented in Scheme 12. Natural population analysis (NPA) revealed a high fraction (+1.219) of overall positive charge to be accommodated on Si center. NBO analysis also indicated to the preference of charge separated structure over neutral one. However, it would not be erroneous to imagine that the real nature of this cation is somewhere between the two resonance extremes.



Scheme 13 Si(II) cation in the coordination sphere of late transition metal.

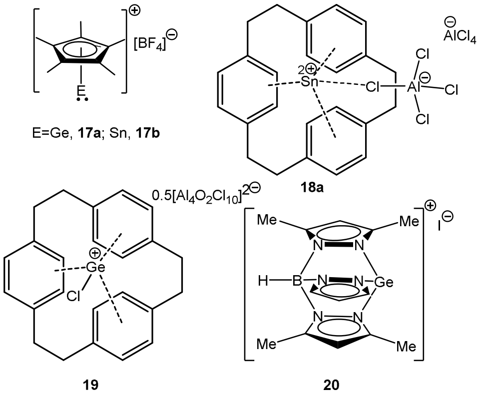
4. Ge(II) and Sn(II) Cations and Dications

In contrast to silylenes, the germylenes and stannylenes are less reactive due to the larger energy gap between their *s*- and *p*-orbitals. Therefore, the chemistry of Ge(II) and Sn(II) cations was developed rather much ahead of Si(II) cations. The major synthetic route leading to E(II) [E=Ge and Sn] cations is the dehalogenation of the corresponding germylenes and stannylenes. Of late, Reid, Driess, Roesky, Stalke, and their respective coworkers reported a series of Lewis base mediated ionization of $GeCl_2$ and $SnCl_2$ to access Ge(II) and Sn(II) cations (*vide infra*). It should be emphasized at this point that the majority of the Ge(II) and Sn(II) cations were stabilized using the same ligand sets and therefore we have decided to discuss the Ge(II) and Sn(II) cations together for the convenience of the readers. We shall divide the Ge(II) and Sn(II) cations in five different categories: (a) $[LE:]^+$ (L=mono-anionic ligand), (b) $[D{\rightarrow}E{-}X]^+$ (D=Lewis bases except macrocycles, X=halide), (c) $[D{\rightarrow}E]^{2+}$, (d) cationic polyether complexes of germanium(II) and tin(II), and (e) transition metal based germanium(II) and tin(II) cations.

4.1 Stable $[LE:]^+$

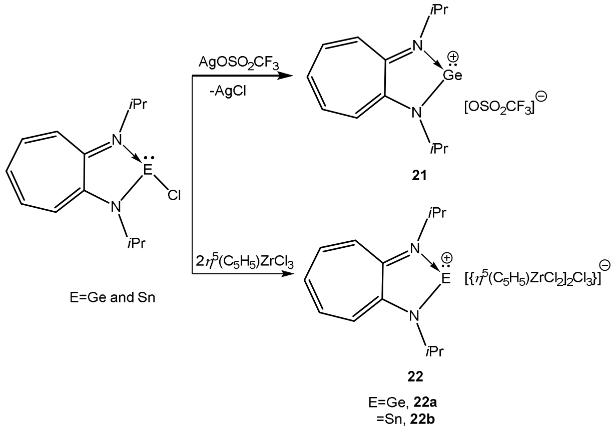
4.1.1. Cations of Ge and Sn embedded within cyclic system

The first representative example of this type of cation, $[(\eta^5\text{-}C_5Me_5)E]^+BF_4^-$ (E=Ge, **17a**; Sn, **17b**) (Scheme 14), was synthesized by Jutzi et al. by reacting the corresponding germylenes and stannylenes with HBF_4. An X-ray crystal structure of $[(\eta^5\text{-}C_5Me_5)Sn]^+BF_4^-$ revealed η^5 coordination mode of the Cp* ligand.[21a] As expected, compound **17** functioned as a Lewis acid instead of a Lewis base, which was manifested in its adduct formation with pyridine and bipyridine.[21a] A few years later, Schmidbaur and coworkers reported two Sn(II) cations of composition $[\{(C_{24}H_{24})Sn(AlCl_4)\}][AlCl_4^-]$ (**18a**) and $[\{(C_{24}H_{24})Sn(AlCl_4)\}][Al_2Cl_7^-]$ (**18b**).[34,60] The corresponding Ge(II) cation was found to have a Ge–Cl bond and during crystallization it reacted with H_2O, leading to $[(C_{24}H_{24})GeCl]_2(Al_4O_2Cl_{10})$ (**19**) (Scheme 14).[34]



Scheme 14 Ge(II) and Sn(II) cation stabilzed by pentamethylcyclopentadienyl, cyclophane, and pyrazole ligands.

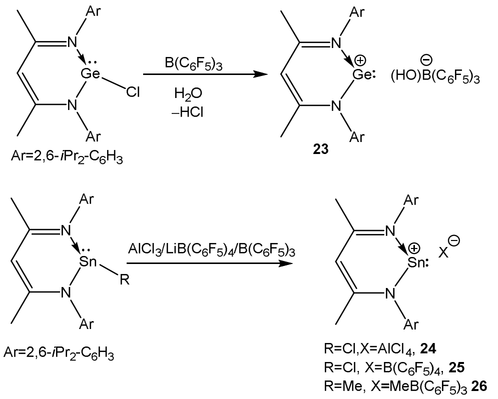
Regar and Coan reported the synthesis and structural elucidation of $[HB(3,5\text{-}Me_2pz)_3Ge]^+$ ($\mathbf{20}^+$) with an iodide counter ion (Scheme 14).[61] The shortest Ge····I distance is over 4 Å, clearly indicating the lack of a substantial covalent interaction between these atoms. The Ge(II) center adopted a pyramidal geometry with three neighboring nitrogen atoms coordinated to the Ge center. This result kick-started the use of N-donor ligands for the isolation of *p*-block cations. Following this, Dias et al. used bi-dentate, monoanionic amino-troponiminate (ATI) with a distinct 10π electron backbone for the isolation of Ge(II) and Sn(II) monocations. Substitution of the corresponding chloro precursor $[(\textit{i}Pr_2ATI)GeCl]$ with $AgOSO_2CF_3$ resulted in $[(\textit{i}Pr_2ATI)Ge][OSO_2CF_3]$ (**21**) (Scheme 15).[62a] The germanium atom was weakly bound to the oxygen atom of the triflate anion (Ge–O: 2.255(2) Å). In order to prepare a "free" Ge(II) cation, $(\textit{i}Pr_2ATI)GeCl$ was reacted with $(\eta^5\text{-}C_5H_5)ZrCl_3$, which serves as a chloride scavenger to result in $[(\textit{i}Pr_2ATI)Ge][(\eta^5\text{-}C_5H_5)ZrCl_2(\mu\text{-}Cl)_3ZrCl_2(\eta^5\text{-}C_5H_5)]$ (**22a**).[62a] A related Sn(II) cation, $[(\textit{i}Pr_2ATI)Sn][(\eta^5\text{-}C_5H_5)ZrCl_2(\mu\text{-}Cl)_3ZrCl_2(\eta^5\text{-}C_5H_5)]$ (**22b**) was earlier reported by the same group.[62b] However, the weak interactions between the cations and the terminal chloride atoms were found in the solid state structures of **22a,b**.



Scheme 15 Synthesis of Ge(II) and Sn(II) cations using aminotroponiminate ligand.

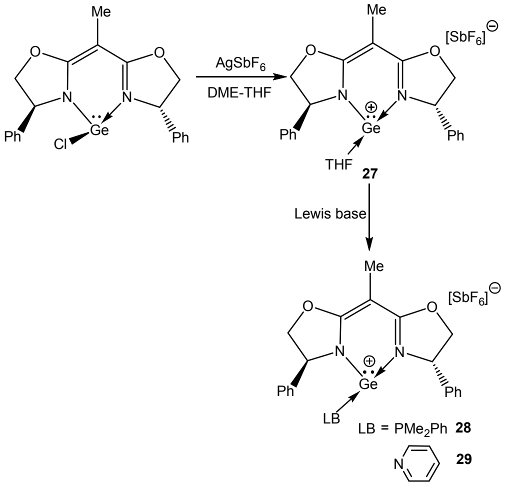
Following the synthesis of germylenemonochloride[LGeCl

[L=CH(CMeNAr)$_2$; Ar=2,6-*i*Pr$_2$C$_6$H$_3$] using the versatile mono-anionic bidentate *β*-diketiminate ligands,[63] Power group prepared a cyclic Ge(II) mono-cation [LGe][(HO)B(C$_6$F$_5$)$_3$] (**23**) by reacting LGeCl and B(C$_6$F$_5$)$_3$ in the presence of water (Scheme 15).[64] The geometrical parameters of **23**$^+$ like the decrease of C–N bond lengths (1.34$_{av}$ Å) with concomitant increase of Ge–N bond length (1.91$_{av}$ Å) and NICS(1) values (–2.4 ppm) were evocative of those observed for its silicon analogue **11**, indicating the presence of slight aromatic character in **23**$^+$.[65] However, one must note here that the *γ*-H signal of **23**$^+$ appeared at significantly higher field (*δ*=4.23 ppm), than that of **11** (*δ*=6.92 ppm).



Scheme 16 *β*-diketiminato ligand stabilzed Ge(II) and Sn(II) cations.

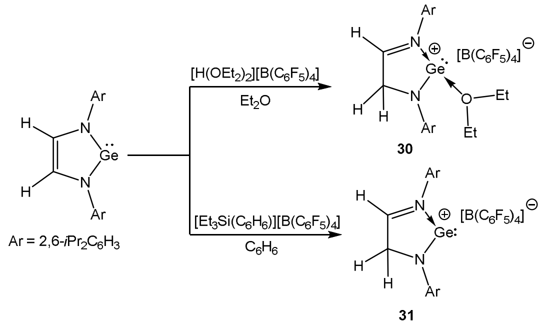
The tin versions of **23**$^+$ with the [AlCl$_4$]$^-$ (**24**), [B(C$_6$F$_5$)$_4$]$^-$ (**25**), and [B(C$_6$F$_5$)$_3$(Me)]$^-$ (**26**) counter-anions were later reported by Fulton and coworkers (Scheme 16).[66] The ^{119}Sn NMR chemical shifts for these cations are –626.7, 197.0, and –139.5 ppm, respectively (Table 2). Among them, only **25** displays a low-field ^{119}Sn NMR shift from that of its precursor (–224 ppm). Unfortunately, **24** and **25** were not characterized by X-ray crystallography. The single crystals of **26** were only grown from diethyl ether solution and in the solid-state structure of **26** one ether molecule was bound to the Sn atom, which explained the high-field chemical shift in the ^{119}Sn NMR.



Scheme 17 Synthesis of Ge(II) cation, **27** and its derivatization.

Mochida and coworkers introduced a chiral ligand, (1,1-bis[(4S)-4-phenyl-1,3-oxazolin-2-yl]ethane), popularly known as ({(*S*)-box-Ph}H) to isolate a germanium(II) cation.[67] The motivation for this work presumably came from the use of the enantiomeric carbene as a ligand for metal complexes to catalyze asymmetric reactions.[68] Abstraction of the chloride atom from the DME solution of the corresponding germylene with Ag[SbF$_6$] in presence of excess THF afforded the Ge(II) cation, [Ge((*S*)-box-Ph)(THF)](SbF$_6$) (**27**) (Scheme 17). Substitution of the THF ligand with other Lewis bases like PMe$_2$Ph and pyridine yielded [Ge((*S*)-box-Ph)(PMe$_2$Ph)](SbF$_6$) (**28**) and [Ge((*S*)-box-Ph)(py)](SbF$_6$) (**29**), respectively. Inspection of the Ge–N bond lengths in these cations revealed that the average bond length increase on going from **27**–**29** [**27**: 1.928 (2) Å, **28**: 1.933(3) Å, and **29**: 1.939(4) Å]. This lengthening was assumed to be due to increased D→Ge *π* donation from **27**–**29**, resulting in a less *σ* as well as *π* interactions, which in turn increases the Ge–N bond lengths.

By adopting the same synthetic protocol that has been used for the synthesis of **12**, Müller et al. isolated two more Ge(II) cations, **30** and **31** upon protonating 1,3-di(2,6-*i*Pr$_2$C$_6$H$_3$)-germaimidazol-2-ylidene with [H(OEt$_2$)$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ and [Et$_3$Si(C$_6$H$_6$)]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (Scheme 18).[69] The protonation took place at C-4 position instead of germanium and as a result the ligand underwent a shift from di-anionic to mono-anionic by rupturing the symmetry of the GeN$_2$ moiety. The molecular structure of **30** revealed that two ether molecules are coordinated to the Ge atom. Although exhibiting no interaction with benzene solvent, **31** was weakly bound to the borate through the fluoride atoms. A detailed theoretical calculation was carried out by Müller et al. to understand why the protonation took place in C-4 position instead of Ge. It was observed that the C-protonated product was more stable than the hypothetical Ge-protonated one by 68.3 kJ/mole (B3LYP/6-311G) and 44.8 kJ/mole (MP2), respectively. Another underlying factor responsible for this regioselective protonation is the formation of C–H bond instead of highly polarized Ge–H bond.



Scheme 18 Ge cations **30** and **31**.

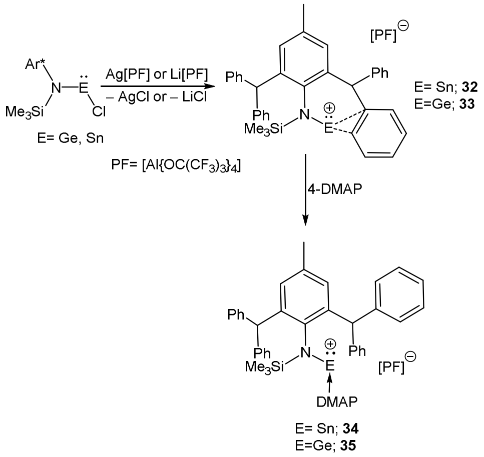
Table 2 ^{119}Sn NMR values for stannylium ylidenes and related compounds.

Compound	Solvent	^{119}Sn NMR (ppm)	Ref
18		-	21a
19		-	21a
22b	$CDCl_3$	734	60b
24	CD_2Cl_2	–626.7	64
25	CD_2Cl_2	197.0	64
26	CD_2Cl_2	–139.5	64
32	CD_2Cl_2	46.3 (solid-state: 68)	67
34	CD_2Cl_2	–30	67
39	CD_2Cl_2	249.71	28b
40	CD_2Cl_2	17.28(br)	28b
44	THF-d_8	−60.27 ($SnCl_3^-$) & −435.07	71
46	$CDCl_3$	−73.2 ($SnCl_3^-$) and −330.4	72
54	CD_3CN	–1468	76
64a-c		Solid-state: –980 (Cl), –920 (Br), –810 (I)	83b
65		Solid-state: –1533	83b
66		Solid-state: –1436	83a
67		Solid-state: –1457	83a
68		Solid-state: –840, –58	83a
69		Solid-state: –1578	83a
70		Solid-state: –1405	83a
71		Solid-state: –1721, –1706	83a
72		Not mentioned	84
74	THF-d_8	–8.4	86a
75	THF-d_8	224.0	86b
76	THF-d_8	249.9	86b
77	$CDCl_3$	70.6	83
78 & 79		Not observed	85

4.1.2. Acyclic Ge(II) and Sn(II) cations

The paucity of mono-coordinated Ge(II) and Sn(II) cations over the di-coordinated ones can be attributed to the rigorous use of mono-anionic bidentate ligands, where the additional N-donor/donors quench the electrophilicity of these cations. It was only recently that Jones and Krossing obtained the first quasi mono-coordinate Sn(II) cation, [SnN(Ar*)($SiMe_3$)][PF] (**32**) using a combination of extremely bulky amido ligand {N(Ar*)($SiMe_3$)}$^-$ [Ar*=(2,6-$CHPh_2$-4-MeC_6H_2)] and weakly coordinating anion PF=[Al{OC(CF_3)$_3$}$_4$]$^-$ (Scheme 19).[70] Synthesis of the analogous Ge(II) cation, [GeN(Ar*)($SiMe_3$)]$^+$ (**33**$^+$) was accomplished via a slightly modified synthetic route where a solution of LGeCl in DCM was slowly added to a PhF solution of Li[PF]. The molecular structures of both cations showed that there were no close contacts between anion and cation centers. However, an intramolecular η^2 arene interaction to the metal centers was present in the solid state (Ge-C: 2.65 Å (mean) and Sn-C: 2.82 Å (mean)). This interaction was further reflected in the solution-state ^{119}Sn NMR spectrum, where the signal appeared in quite high-field (δ=46.3 ppm) compared to that of the precursor, N(Ar*)($SiMe_3$)SnCl (δ=173.7 ppm). The solid-state ^{119}Sn MAS NMR spectrum (δ=68 ppm) was also in good agreement with the solution state spectrum. The low temperature ^{13}C{^{1}H} NMR spectra of **32**$^+$ and **33**$^+$ exhibited 16 aryl signals, whereas room temperature NMR spectra showed only 12 signals for aryl carbons. The appearance of four extra signals at low temperature corresponded to equivalent η^2-arene interactions with the phenyl group of both C(H)Ph_2 substituents (Fig. 2) that could not be distinguished at room temperature NMR time scale. Consistent with this, DFT calculations revealed four C····E interactions rather than two observed in the X-ray structures. The calculated WBI of the C····E contacts were of 0.423 for **32**$^+$ and 0.283 for **33**$^+$, suggesting the cations are arene stabilized. The +2 oxidation state of Sn was confirmed by Mössbauer spectroscopy, which shows a tin signal with an isomeric shift of δ=3.369(4) mm/s, a typical value for Sn(II) compounds.[71]

The electrophilic nature of **32**$^+$ and **33**$^+$ was observed upon addition of N-donor ligand, 4-DMAP, which resulted in 4-DMAP coordinated Sn(II) (**34**$^+$) and Ge(II) (**35**$^+$) cations. The 4-DMAP coordination led to the displacement of C····E interactions in the latters, which is reflected in the longer C····E distances and higher ^{119}Sn NMR resonance (δ= –30 ppm).



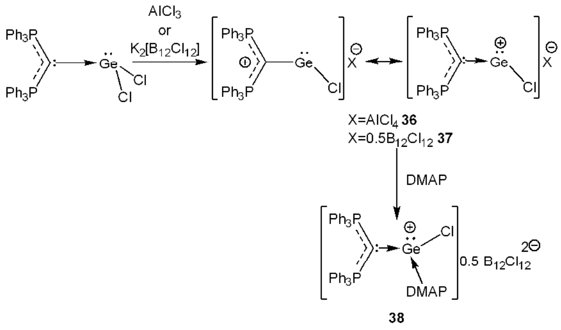
Scheme 19 Quasi-monocoordinate Ge and Sn cations, **32**$^+$ and **33**$^+$ and their adduct formation with 4-DMAP.

4.1.3. Cations featuring [E-Cl]$^+$

There has been much interest in the synthesis of cations featuring [E–X]$^+$ (E=Ge and Sn; X=halide) moiety. This can be achieved in two ways: (i) Dehalogenation from the corresponding [D→EX_2] compounds would lead to the synthesis of [D→EX]$^+$ cations; (ii) Lewis base mediated ionization of EX_2 represents an alternative synthetic route to give access to [E–X]$^+$ cations.

4.1.3.1. Dehalogenation of [D→EX_2] compounds

A starting point of our discussion on [D→EX]$^+$ cations is a report from Baines' group, who mentioned the generation of [D→Ge(Cl)←D]$^+$ [D=I*i*Pr] (**55''**$^+$) (Scheme 28, *vide infra*) with a [CF_3SO_3]$^-$ counter-anion as a side product during the reaction of I*i*Pr with [2.2.2]cryptand.[35] However, the cation was not structurally characterized. Nevertheless, the result suggested that I*i*Pr (a strong σ-donor) ligand does not provide sufficient stabilization that allows the isolation of a reactive two-coordinate [Ge–Cl]$^+$ cation. Replacement of I*i*Pr by IDipp also failed to render the two-coordinate [Ge–Cl]$^+$ moiety.[30b,72] Finally, very recently, utilizing the concomitant σ- and π-donor capabilities of sterically demanding carbodiphosphorane ligand Alcarazo et al. isolated the first two coordinate [(Ph_3P)$_2$C→GeCl]$^+$ (**36**$^+$) cation (Scheme 20).[30b]



Scheme 20 Carbodiphosphorane stabilized Ge cation and its derivatization.

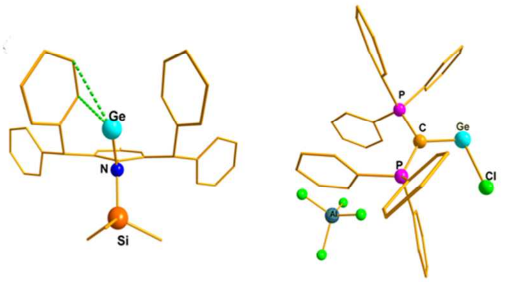


Fig 2 Molecular structures of **33**$^+$ and **36**$^+$

Interestingly, the P-C-Ge-Cl torsion angle in **36**$^+$ (Fig. 2) was of only 8.18°, a feature that facilitated good overlap between the filled *p* orbital of C and the vacant orbital of Ge, leading to the shortening of the C–Ge distance (1.954(2) Å) than that in $(Ph_3P)_2C{\cdot}GeCl_2$ (2.063(2) Å). The WBI of C–Ge bond in **36** (0.84) was considerably higher than that in $(Ph_3P)_2C{\cdot}GeCl_2$ (0.54), revealing further a significant strong π-donation from central carbon of $(Ph_3P)_2C$ to germanium atom. The HOMO of **36**$^+$ represents mainly the σ-lone-pair while the HOMO-1 corresponds to C–Ge π-bonding (Fig. 3). The LUMO of **36**$^+$ which was associated with π* (C–Ge) orbital became populated upon addition of 4-DMAP leading to increase of the C–Ge bond length (2.053(3) Å) and WBI value (0.64) in the corresponding Lewis adduct, 4-DMAP·$[(Ph_3P)_2C(GeCl)]^+$ (**38**$^+$).

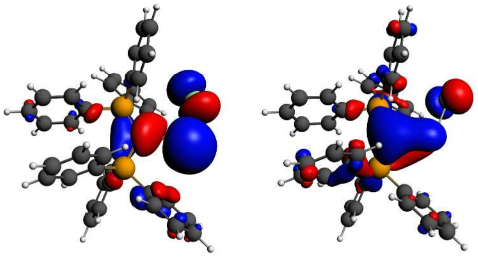
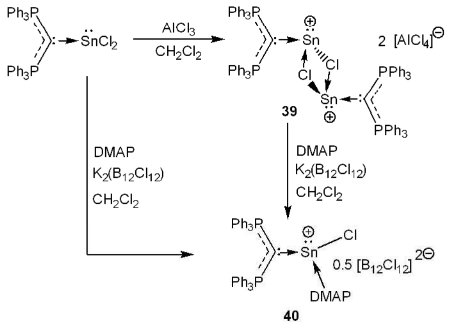


Fig 3 Frontier orbitals of **36**$^+$ (left: HOMO, right: HOMO-1). Adapted from ref. 30b.

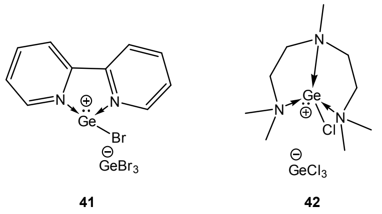


Scheme 21 Carbodiphosphorane stabilized Sn cation and its derivatization.

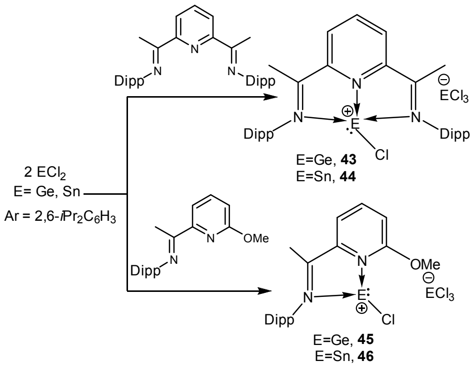
In contrast, the reaction of $(Ph_3P)_2C{\cdot}SnCl_2$ with an equivalent of $AlCl_3$ did not yield the anticipated monomeric $[(Ph_3P)_2C(SnCl)]^+$ cation and instead led to the formation of a chlorine bridged dimeric $[(Ph_3P)_2C(SnCl)]_2^{2+}$ (**39**$^+$) species (Scheme 21).[30b] This result indicates that the π(C→Sn) bond in **39**$^+$ is very weak, presumably due to less-efficient overlap between the C(2p) and Sn(5p) orbitals. The dimeric structure was stabilized by the formation of chloride bridges between the Sn atoms to provide the extra electron density to the Sn center. The reaction of 4-DMAP with **39** resulted in a monomeric 4-DMAP·$[(Ph_3P)_2C(SnCl)]^+$ adduct (**40**$^+$).

4.1.3.2. Ionization of EX_2 (E=Ge and Sn)

Lewis base promoted ionization of EX_2 has become an useful synthetic approach to obtain $[E\text{-}X]^+$ compounds. Parshall reported a molten alkyl ammonium salt of composition $[R_4N]^+[SnCl_3]^-$.[73] However, the first stable examples of $[Ge\text{–}X]^+$ cations, [(2,2'-bipy)GeBr][$GeBr_3$] (**41**) and [(pmdta)GeCl][$GeCl_3$] (**42**) were recently reported by Reid and coworkers upon reacting the ligand and GeX_2 in 1:2 molar ratio (Scheme 22).[74] Subsequently, a variety of different Lewis bases have been investigated to stabilize $[E\text{–}Cl]^+$ cation by this ionization route. Roesky, Stalke, and coworkers isolated two cations $[(LB)GeCl]^+[GeCl_3]^-$ (**43**) and $[(LB)SnCl]^+[SnCl_3]^-$ (**44**) from the direct reaction of substituted Schiff base 2,6-diacetylpyridinebis-(2,6-diisopropylanil) with the corresponding dihalides (Scheme 23).[75] Applying the same synthetic protocol, Jambor and coworkers obtained $[(2\text{-}[C(CH_3){=}N(2,6\text{-}i\text{Pr}_2\text{-}C_6H_3)]\text{-}6\text{-}(CH_3O)C_6H_3N)ECl]^+[ECl_3]^-$ [E=Ge (**45**) and Sn (**46**)] (Scheme 21) using the diimine ligand.[76] However, attempts to ionize $GeCl_4$ and $SnBr_4$ were so far not successful and instead simple adduct formation ($L{\cdot}EX_4$) was observed. The Ge–N bond lengths (**43**: 2.19 Å (mean); **45**: 2.06 Å (mean)) were slightly longer than the standard Ge–N bond length, thus indicating significant π-interaction between the germanium and the nitrogen.



Scheme 22 Lewis base mediated ionization of GeBr$_2$ and GeCl$_2$.



Scheme 23 Lewis base induced ionization of germanium and tin halides.

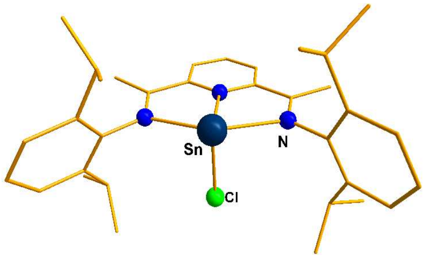
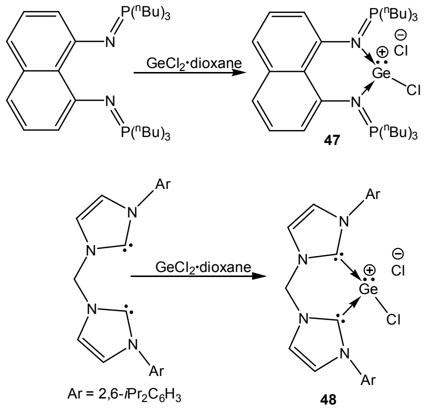


Fig 4 Molecular structure of **44**$^+$

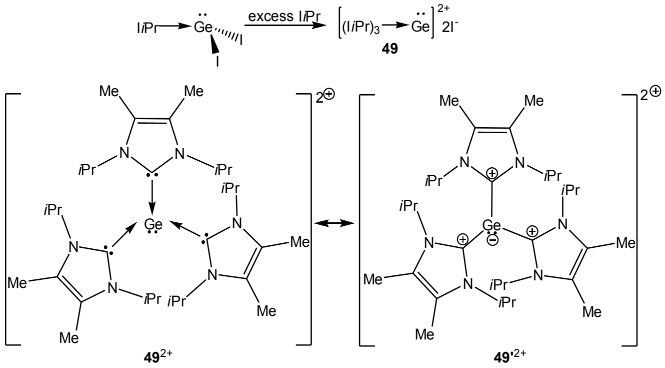


Scheme 24 Synthesis of the [Ge–Cl]$^+$ cations **47** and **48**.

The germanium variants of **12** and **13**, were reported by Driess and coworkers.[77] Apparently, the reaction of GeCl$_2$ with iminophosphorane and bis-NHC ligands led to the cleavage of one of the Ge–Cl bonds and thus afforded **47**[77a] and **48** (Scheme 24).[77b] The Ge centers were well separated from the chloride anions (**47**: 6.83 Å and **48**: 6.53 Å). The geometric features and the frontier molecular orbitals of **47**$^+$ and **48**$^+$ were almost identical to those mentioned earlier for their corresponding silicon analogs. The dative nature of the N→Ge and C→Ge bonds was further apparent from their respective WBI values (**47**$^+$: 0.436 and 0.430; **48**$^+$: 0.608 and 0.611).

4.1.4. Dications of germanium(II) and tin(II)

Significant advances have been made in the isolation of Ge(II) and Sn(II) dication which were earlier detected only by spectroscopic studies and considered as reactive intermediates. In particular, Baines and coworkers described elegant use of different neutral ligands to accomplish the synthesis of Ge(II) dication.[27] Utilizing the unique donor aptitudes of sterically demanding I*i*Pr ligands, they prepared the first Ge(II) dication, **49**$^{2+}$ (Scheme 25). All three C–Ge bond are identical and of 2.070(6) Å in length. The iodide counter-anion was located far away from the Ge center (closest Ge–I distance: 5.96 Å), but weakly bound to the CH_3 protons with I····H interaction of 3.11 Å. Like we showed in the cases of donor stabilized Si(II) cations, two canonical forms of **49**$^{2+}$ can be envisaged. No charge calculation (NPA: +0.64; Mulliken: +0.05, atomic polar tensor: +1.02) was either close to +2 or –1, so it is safe to say that the real bonding feature lies in between **49**$^{2+}$ and **49′**$^{2+}$ and the positive charge on Ge was delocalized over three I*i*Pr groups. Afterwards a Ge *κ*-edge XANES study on **49**$^{2+}$ also revealed that the Ge center receives significant electron donation from NHC in **49**$^{2+}$.[78] The white line of **49**$^{2+}$ (red line) appears as a shoulder and is broad. The decrease in intensity for the white line of **49**$^{2+}$ is likely a result of electron donation from NHC to the Ge^{2+} center (Fig. 5).



Scheme 25 Synthesis of NHC stabilized Ge(II) dication, **49**$^{2+}$.

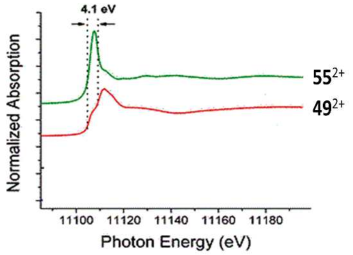
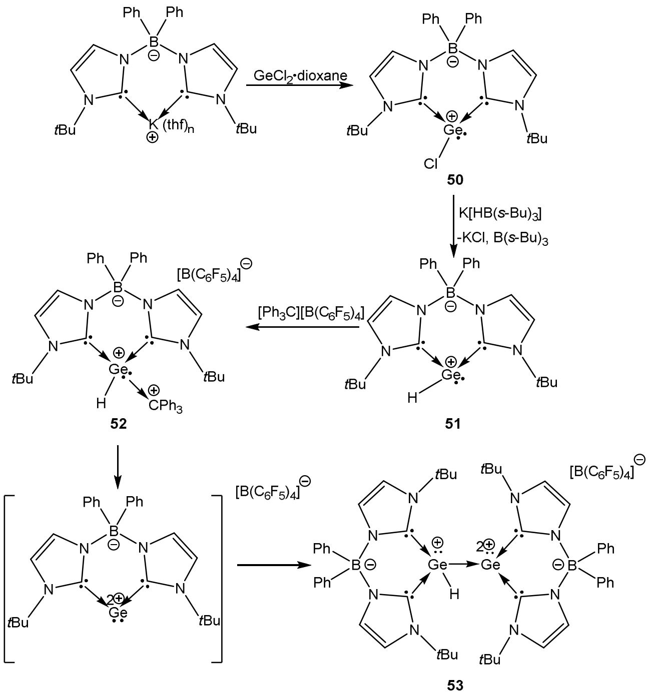


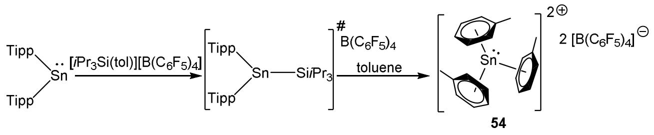
Fig 5 Germanium *κ*-edge XANES of **55**$^{2+}$ (green line) and **49**$^{2+}$ (red line). Adapted from ref. 78.

Another elegant variation of the NHCs is the linking of two NHCs using a borate spacer, which gives the ligand a certain degree of flexibility. This ligand have been recently used for the isolation of a compound featuring a Ge–Ge bond where one Ge atom is monocationic and another Ge atom is dicationic have been recently reported.[79] The preparation of **53** is unique (the reaction sequence shown in Scheme 26) and represents a tour de force in organometallic synthesis. A key step in this sequence was the generation of zwitter-ionic Ge(II) cation (**50**) from a salt metathesis route using potassium bis(NHC)-borate and $GeCl_2$·dioxane. The isolated Ge(II) cation was further derivatized to yield the zwitterionic Ge(II) cation with a [H-Ge:]$^+$ moiety, **51**, which upon reaction with $[Ph_3C]^+[B(C_6F_5)_4]^-$ generated **52**. Spontaneous elimination of the Ph_3CH from the latter apparently led to a highly reactive Ge(II) dication, which underwent donor-acceptor stabilization with unreacted **51** to form an unprecedented compound with a $[HGe:^+\rightarrow Ge:]^{2+}$ motif (**53**). A deliberate synthetic route that involved the 1:1 reaction of **51** and **52** also led to compound **53** with concomitant elimination of Ph_3CH.



Scheme 26 Synthetic steps to access **53**.

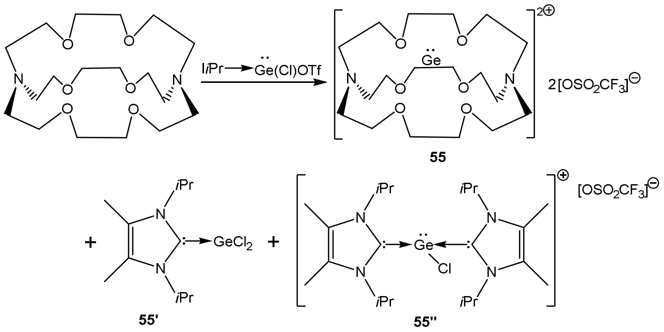
Müller and coworkers obtained a borate salt of tris toluene Sn(II) dication $[Sn(C_7H_8)_3]^{2+}$ (**54**$^{2+}$) from serendipitous decomposition of a stannylium cation during its recrystallization in toluene.[80] It was reported that the reaction of $Tipp_2Sn$ (Tipp=2,4,6-iPr$_3$-C_6H_2) with silylarenium ion $[iPr_3Si(tol)]^+[B(C_6F_5)_4]^-$ presumably generated the corresponding stannylium ion $(Tipp_2Sn(SiiPr_3))^+$ initially, which in due course decomposed to furnish $[Sn(C_7H_8)_3][B(C_6F_5)_4]_2$ (Scheme 27). No deliberate synthetic route was reported for **54**$^{2+}$. Single crystal X-ray study of **54**$^{2+}$ revealed that two toluene molecules were significantly closer to the Sn atom than the remaining third toluene molecule leading to an unsymmetrical coordination around the Sn atom. The large isomeric shift (4.14(1) mm/s) confirmed the +2 oxidation state of the Sn center and indicated that the Sn(II) valence electrons reside in orbitals that are almost exclusively of 5s character. Computations showed significant charge transfer from the arene ring to the empty p orbitals of the Sn atom leading to accumulation of high positive charge (+1.28) on Sn atom.



Scheme 27 Synthesis of Sn(II) dication, **54**$^{2+}$ from stannylene.

4.1.4. Cationic polyether complexes of germanium(II) and tin(II).

Crown ethers, cryptands, glymes etc. been renowned for their remarkable metal complexation properties with s- and d-block elements.[81] Baines and coworkers demonstrated successful implementation of polyether ligation approach to stabilize a “naked” germanium(II) dication (**55**$^{2+}$) using an electron rich [2.2.2]-cryptand (Scheme 28).[35,82] The Ge(II) center is encapsulated within the cryptand- presumably stabilized by numerous weak donor-acceptor interactions due to the presence of six oxygen and two nitrogen atoms in the cavity (Fig. 6). The anion OSO_2CF_3 exhibits no bonding interaction with Ge^{2+}. The Ge–N and Ge–O distances (2.524(3) and 2.485(2) Å) indicate very weak interactions between Ge^{2+} with O- and N-donors, which is further reflected in their WBI values (Ge–N: 0.11 and Ge–O: 0.10). NPA calculation revealed the accumulation of +1.38 residual charge on Ge center despite the donor-acceptor interaction in the cryptand. In **55**, Ge^{2+} was protected not just from anions, but also from Lewis bases such as solvent molecules. The success of the method can be attributed to the cryptand's ability to encapsulate Ge^{2+} in three dimensions. A subsequent Ge κ-edge XANES study on **55**$^{2+}$ revealed the Ge center in **55**$^{2+}$ is highly ionic (sharp intense white line) (Fig. 5).[78] and can be best described as naked Ge^{2+} encapsulated within the cryptand cage.



Scheme 28 [2.2.2]cryptand stabilized Ge(II) dication, **55**$^{2+}$.

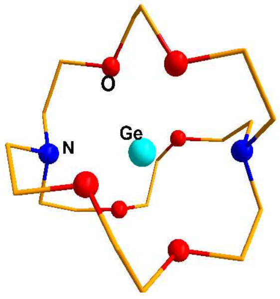
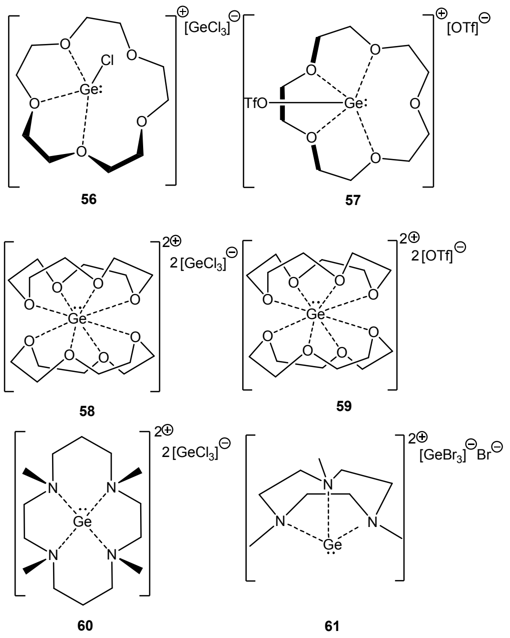
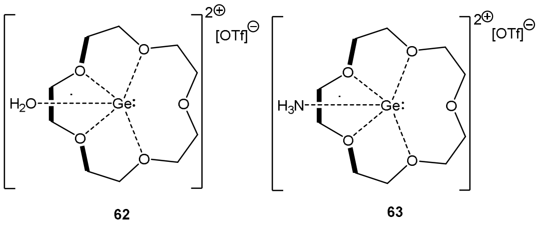


Fig 6 Molecular structure of **55**$^{2+}$.



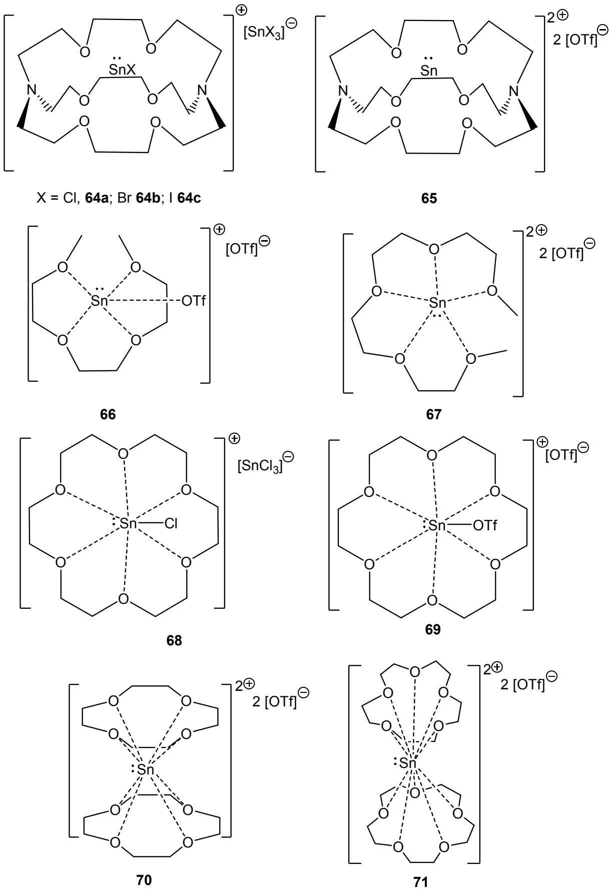
Scheme 29 Crown ether stabilized Ge cations and dications, **55–61**.

In a subsequent systematic study it was demonstrated that reacting differently sized crown ethers, such as [12]-crown-4, [15]-crown-5, and [18]-crown-6 with $GeCl_2$·dioxane led to a range of Ge(II) mono- and dications (**56–61**) (Scheme 29).[83] The structural properties of these cations were governed by the size of crown ether employed. Ge^{2+} fits into the cavity of [15]crown-5 and [18]crown-6; while it formed a sandwich complex with two [12]crown-4 ligands. The structural properties can also be influenced by the substituent on Ge atom. [15]-crown-5 adopted a folded structure with the $[GeCl]^+$ fragment and a planar conformation with $[GeOTf]^+$. Related compounds with tacn (1,4,7-triazacyclononane) and cyclam (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) ligands have also been reported.[84] Like in the cases of crown ethers, the size and the denticity of the azamacrocycles strongly influence the coordination geometry of the Ge^{2+} dications and the nature of the counter anion.



Scheme 30 Water and ammonia complexes of Ge dication, **62–63**.

The reactivity of the Ge(II) crown ether cation towards H_2O and NH_3 was recently demonstrated. Instead of oxidative addition, the formation of stable adducts like [([15]-crown-5) Ge·OH_2][OTf]$_2$ (**62**) and [([15]-crown-5)Ge·NH_3][OTf]$_2$ (**63**) was observed (Scheme 30).[85] Subsequent computational studies showed that the purported oxidative addition products of water and ammonia are less stable than the adducts by 13 kJ/mol and 57 kJ/mol, respectively, which can be attributed to the preferential formation of the O–H bond rather than the Ge–H bond. The hydrogen abstraction from **62** with a suitable base like pyridine, ammonia, NHC etc. was found to be feasible, as the formation of the corresponding conjugate acids was detected in the ^{1}H NMR spectra. Such dehydrogenation would lead to multiply bound Ge–X [X=O or N] bonds, the formation of which was computationally supported with the increase of the electron density of the putative dehydrogented variants at the bond critical points.

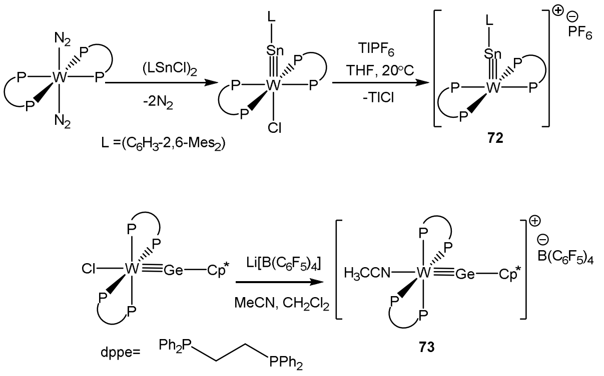


Scheme 31 Sn(II) poly ether cations, **64–71**.

The groups of Baines and Macdonald recently published the cryptand and crown ether complexes of tin (Scheme 31).[86] Unlike germanium, tin forms both mono- [Cryptand[2.2.2]SnX][SnX_3] (X = Cl; **64a**, X = Br; **64b**, X = I; **64c**) and dicationic compounds [Cryptand[2.2.2]Sn][OTf]$_2$ (**65**) with [2.2.2]-cryptand depending on the Sn(II) precursor used in the reaction. The more flexible glyme ligands are also found to be suitable in isolating Sn(II) cations, as manifested in the isolation of [TriglymeSn(OTf)]$^+$ (**66**$^+$) and [TetraglymeSn(OTf)]$^+$ (**67**$^+$) with triflate as the counter-anion. [18]-crown-6 tends to form 1:1 adducts with Sn(II) precursors leading to **68** and **69**, whereas the smaller crown ethers, [15]-crown-5 and [12]-crown-4, were not able to accommodate the tin atom within the crown ether cavity, and thereby resulted in 2:1 sandwich complexes with tin (**70** and **71**).

It was observed that crown ether, glymes form Sn(II) dication with triflate precursor whereas $[Sn–X]^+$ derivative with the halide precursors. The difference in the reaction pattern can be attributed to the greater *s*-character of the Sn valence electrons in triflate than halides. ^{119}Sn solid state NMR data revealed that ^{119}Sn nuclei are highly shielded in the triflate salt whereas considerably deshielded in the chloride salt, and thus supports the formation of resulting complexes. The +2 oxidation state of Sn(II) atoms in these polyether ligated cations was further reflected in Mössbauer spectroscopy, which revealed the pure 5s lone pair as the Sn valence orbital. The ligation of [15]crown-5 and [12]crown-4 to Sn atom hardly perturbed its electronic configuration owing to the almost symmetrical Sn bonding environment in **70** and **71**. On the contrary, the coordination geometry around the Sn(II) centers in the of [18]crown-6, triglyme, and tetraglyme complexes of Sn(II) are less symmetrical, leading to more perturbation in the valence electron as indicated by the increase of the quadrupolar splitting of the resonance in the respective Mössbauer spectrum. The effect of the poly-ether ligand and the substituent on Sn was also illustrated through cyclic voltammetry, where complexes in which the valence electrons of tin have more *s*-character need more energy to become oxidized. Besides, it also depends on the steric properties of the ligands around the tin atom as cyclic voltametry data of **70** and **71** show no oxidation current.[86a]

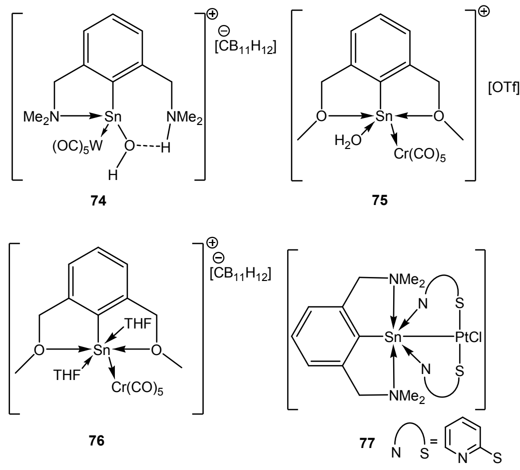
4.1.5. Transition metal supported cations of germanium(II) and tin(II).



Scheme 32 Tungsten supported Sn and Ge cations.

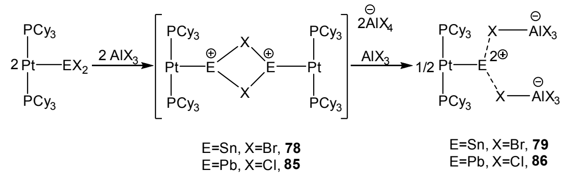
Now, we turn our discussion to another synthetic approach, where instead of a bulky organic ligand, an electron rich coordinatively unsaturated transition metal fragment was employed to stabilize Ge(II) and Sn(II) cations. Traditionally the construction of tetrel(II) cationic complexes follows two steps: (i) the oxidative addition/the adduct formation of the E-X bond to the transition metal and (ii) abstraction of the halides from the resulting transition metal -germanium/tin complexes. The idea of using transition metal fragments to stabilize *p*-block cations was put into practice by Filippou et al., who reported the isolation of *trans*-[(dppe)$_2$WSn-C$_6$H$_3$-2,6-Mes$_2$]$^+$ (**72**) (dppe=1,2-bis(diphenylphosphino)ethane).[87] A sterically demanding and electron donating substituent was used to stabilize the cationic fragment. Since then a range of cationic complexes of germanium and tin incorporating various transition metals have been synthesized (*vide infra*). Their preparation and isolation still depends on the use of stabilizing substituents. So far, mainly Cp*, Mes*, pincer based moieties have been applied.

The oxidative addition of Sn–Cl bond in 2,6-Mes$_2$-C$_6$H$_3$SnCl to *trans*-[dppe]$_2$W(N$_2$)$_2$, followed by salt elimination afforded the cation, **72** (Scheme 32). Replacing the 2,6-Mes$_2$-C$_6$H$_3$ substituent by a Cp* moiety, the same group isolated the germanium variant, **73**.[88] Both Sn and Ge atoms adopt a nearly linear geometry with W≡E triple bond distances of 2.4641(7) and 2.303(1) Å, respectively. Subsequent theoretical calculations suggested that the π-back donation from W to germanium/tin may indeed contribute to the stability of these cations. One may raise the question here that the formal oxidation state of Sn in **72** and **73** are not +2, so they are not "true" germylium and stannylium ylidenes. Although we do not completely disagree with this tenet, but such a classification for transition metal supported *p*-block cations is always questionable taking into account of other resonance contributor manifesting germylium or stannylium character. Therefore, for the sake of completion we incorporated these cations in the review.



Scheme 33 Various transition metal supported Sn and Ge cations.

The metathetical reaction between bulky pincer based ligands with (THF)W(CO)$_5$·SnCl$_2$ or (THF)Cr(CO)$_5$·SnCl$_2$, followed by the abstraction of the halides resulted in several Sn(II) cations, such as [2,6-(Me$_2$-NCH$_2$)$_2$C$_6$H$_3$Sn{W(CO)$_5$}]$^+$ (**74**$^+$), [{(2,6-MeOCH$_2$)$_2$C$_6$H$_3$}Sn(OH$_2$){Cr(CO)$_5$}]$^+$ (**75**$^+$) and [{(2,6-MeOCH$_2$)$_2$C$_6$H$_3$}Sn(THF)$_2${Cr(CO)$_5$}]$^+$ (**76**$^+$) with various counter anions (Scheme 33).[89] Another pincer based stannylene, **77** was recently reported by Jambor et al. featuring a Sn–Pt bond.[90] Although one might be tempted to assign the tin atom in +2 oxidation state, NBO analysis revealed that there was no lone pair at the tin atom. A plausible explanation is that the lone pair was shared by both Sn and Pt atoms and used up for the formation of a Sn–Pt bond, leading to some, by no means full, stannylium ion character. Low-field ^{119}Sn NMR (70.6 ppm) resonance indicated accumulation of negative charge on Pt atom. DFT calculations on this complex indicated that there is significant charge donation from the [N→Sn]$^+$ fragment to [Pt(pyt)$_2$Cl]$^-$ moiety. This finding was in accord with the NPA analysis disclosed a significant fraction of positive charge at the Sn atom (+1.709) and negative charge on the Pt (–0.486). The decrease of Sn–Pt bond length (2.466(1) Å) with respect to the other reported Sn–Pt bond lengths (*vide infra*) reflects an increased contribution of backbonding from the metal.



Scheme 34 Formation of Sn(II) & Pb(II) mono and pseudo dications in the coordination sphere of platinum.

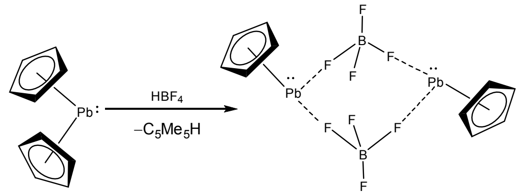
Very recently, Braunschweig et al. showed the latent *σ*-donor ability of the Pt(PCy$_3$)$_2$ to coordinate with Ge(II), Sn(II), and Pb(II) dihalides, which resulted in the formation of respective Metal Only Lewis Pairs (MOLPs).[91] The mono stannylene complex, [(Cy$_3$P)$_2$Pt–SnBr$_2$] was found to be an excellent starting material for realizing the low-coordinate Sn(II) mono- and dications via halide abstraction reaction, as manifested by the formation of [(Cy$_3$P)$_2$Pt–SnBr]$_2^{2+}$ (**78**$^+$) and [(Cy$_3$P)$_2$Pt(Sn)] (**79**$^{2+}$).[92] The Sn–Pt bond lengths in these cations [**78**$^+$: 2.524(1) and **79**$^{2+}$: 2.502(1) Å] are significantly shorter than the Sn–Pt bond present in their precursor complex [(Cy$_3$P)$_2$Pt–SnBr$_2$] (2.605(2) Å) (Scheme 34). Although exhibiting no interaction with the solvent molecule, these cations were not totally free, being weakly bound to the counter anion through their bromide atoms. No ^{119}Sn NMR signals were detected presumably due to the broadening of resonance to undetectable level caused by the increased electric field gradient and large chemical shift anisotropies induced by tin environment.

4.2 Application of Sn(II) cation in alkene polymerization

Rhodes, Chien and Rausch prepared [(η^5-C$_5$Me$_5$)Sn]$^+$ (**17**$^+$) derivative as its (B(C$_6$F$_5$)$_4$)$^-$ salt[93] which was earlier reported by Jutzi et al. with BF$_4$ counter-anion (*vide supra*). The compound was found to be effective co-catalyst in Zieglar-Nata polymerization of ethylene and propylene. The co-catalyst had an important role in the initiation step as well as in propagation step. Alkene polymerization using various Zr complexes such as Cp$_2$ZrMe$_2$, *rac*-Et(Ind)$_2$ZrMe$_2$, *rac*-Et(Ind)$_2$ZrCl$_2$, and Cp$_2$ZrCl$_2$ as catalyst precursors were carried out at variable temperature (–20 °C to 70 °C). It was found that as the polymerization temperature was increased, the activity of the alkene polymerization was also increased. However, a direct comparison of **17**$^+\cdot$B(C$_6$F$_5$)$_4$ with Ph$_3$C$^+\cdot$B(C$_6$F$_5$)$_4$ as the co-catalyst for ethylene and propylene polymerization indicated that the activities were substantially higher when Ph$_3$C$^+$ were used as co-catalyst. For example, the activity was dropped from 1.2 x 10^6 to 4.2 x 10^5 for ethylene polymerization when Ph$_3$C$^+\cdot$B(C$_6$F$_5$)$_4$ was replaced with **17**$^+\cdot$B(C$_6$F$_5$)$_4$ as the co-catalyst.

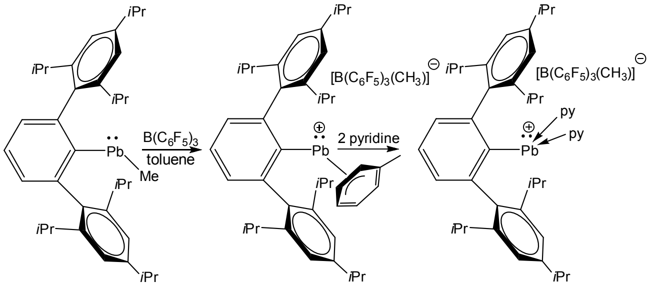
5. Pb(II) cations and dications

Low coordinate Pb(II) cations are by far the least ubiquitous among the classes of tetrel(II) cations. The isolation of low coordinate Pb(II) cations at ambient condition was plagued by the highly electrophilic nature of these species. Like in all previous cases, the first isolation of a low coordinate Pb(II) cation came from the lab of Jutzi, who obtained half-sandwich complexes [Me$_5$C$_5$Pb][BF$_4$] (**80a**) and [Me$_5$C$_5$Pb][OSO$_2$CF$_3$] (**80b**) as dimers from the reaction of [Me$_5$C$_5$]$_2$Pb with tetrafluoroboric acid and trifluoromethanesulfonic acid, respectively (Scheme 35).[21b] The high field resonance of the cationic Pb center in **80a** (–5041 ppm) and **80b** (–4961 ppm) was observed presumably due to η^5 coordination of the cyclopentadienyl ligand to the metal center. **80a** was structurally characterized which revealed pentagonal-pyramidal geometry around the Pb atom. The shortest Pb–F bond length in **80a** was of 2.831(9) Å, which was relatively long and can be classified as weak interaction, but still sufficient for the preferred formation of the dimeric units. The Lewis acidic nature of **80a** was confirmed through their reactions with 2,2′-Bipyridine and 1,8-naphthyridine, which formed 1:1 adducts.[21b]



80a

Scheme 35 PentamethylcyclopentadienylPb(II) cations **80a**.



81 **82**

Scheme 36 Quasi-mono coordinate Pb(II) monocation, **81** and donor supported monocation, **82**.

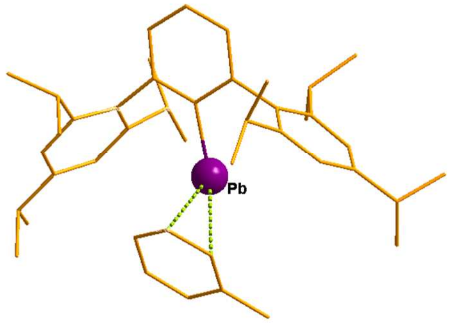
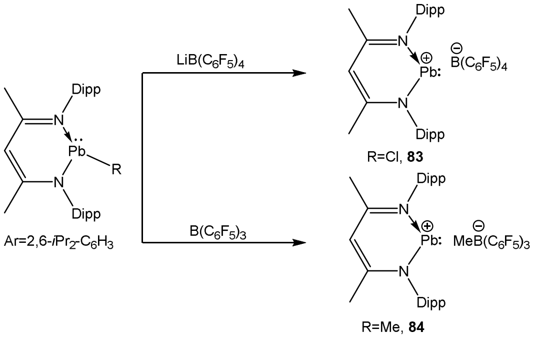


Fig 7 Molecular structure of **81**.

The next milestone contribution to the low coordinate Pb(II) cations was achieved by Power et al., who synthesized [Ar*Pb·η^2-toluene][MeB(C$_6$F$_5$)$_3$] (Ar*=2,6-(2,4,6-*i*Pr$_3$C$_6$H$_2$)$_2$-C$_6$H$_3$) (**81**) (Scheme 36) from the reaction of Ar*PbMe with B(C$_6$F$_5$)$_3$ in toluene.[94] The low coordination of the Pb center in **81** was manifested in their ^{207}Pb NMR resonances observed at δ=8974 ppm, shifted 13500 ppm downfield of these [(η^5-C$_5$Me$_5$)Pb]$^+$ salts. This very large difference is consistent with a lower effective coordination number of Pb in **81**$^+$ and weak interaction with toluene. The solid-state structure of **81** was determined by single crystal X-ray analysis. The analysis revealed that there are no close interactions (3.963(6) Å) between the lead atom and the anion in **81**. However, the Pb center interacted with the solvent toluene and Pb–toluene interaction can be best described as being of η^2 type. The weakly coordinating toluene molecule can be easily displaced by two pyridine molecules to yield [Ar*Pb(py)$_2$][MeB(C$_6$F$_5$)$_3$] (**82**). The upfield shift of ^{207}Pb NMR resonance (δ=4764 ppm) of **82** with respect to that of **81** (δ=8974 ppm) and the pyramidalization at the Pb(II) cationic center clearly reflected the decrease of cationic character in line with the increase of coordination number of the Pb atom.



Scheme 37 β-diketiminato ligand supported Pb(II) cations, **83** and **84**.

The series of tetrel(II) cations supported by the β-diketiminato ligand was recently completed by Fulton et al. with the isolation of lead(II) cations (**83**$^+$ and **84**$^+$) with the B(C$_6$F$_5$)$_4$ and MeB(C$_6$F$_5$)$_3$ counter-anions (Scheme 37). The Pb center of these compounds was well separated from its anion (the closest approach from Pb to the nearest F atom was 3.319 (4) Å), reminiscing the structural properties of their tin homologue. However, in the solid-state structure of **83**$^+$ a dichloromethane molecule was found with 64% occupancy to give a long-range lead-chlorine interaction (Pb–Cl(1) = 3.213(4) Å). Calculation points to the more stability of the solvated complexes LPb$^+$·CH$_2$Cl$_2$ over LPb$^+$ by 3 kcal/mole (L=CH(CMeNDipp)$_2$). No ^{207}Pb NMR resonances for **80** and **81** were observed, which according to the authors, may be attributed to the fast relaxation of the lead nucleus.

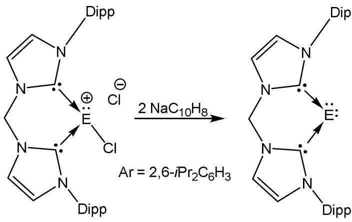
The success of stabilizing Sn(II) mono- and dication in the coordination sphere of [Pt(PCy$_3$)$_2$] led Braunschweig and co-workers to isolate the lead variants. Adopting the same synthetic protocol that was employed for **78**$^+$ and **79**$^{2+}$, they reported two Pb(II) mono-cations with AlCl$_4$ (**85a**) and [BAr$^{Cl}_4$] [Ar^{Cl}=3,5-Cl$_2$-C$_6$H$_3$] (**85b**) and a rare example of Pb(II) dication [{(Cy$_3$P)$_2$Pt(Pb)}{AlCl$_4$}$_2$ (**86**)] (Scheme 34, *vide supra*).[92] The Pb(II) cations and dication were structurally similar to the analogous Sn(II) cations upon comparison of bonding motifs and metrical parameters. The Pb centers in **85a** and **85b** revealed weak bonding interactions (3.420(1) Å) to the chloride ion in the counter-anions. In the solid-state form, **86** also exhibited a weak interaction of the Pb atom with the two chloride atoms of two aluminate counter-anions. Detailed theoretical investigations were additionally carried out to further characterize the bonding situation in these complexes. It was proposed before that the Pt(0) and Pb(II) fragments in the starting material (Pt(PCy$_3$)$_2$→PbCl$_2$) donate σ-electron density to each other, leading to the concept of "*synergic σ-donation*",[91b] which was further proposed by Su et al. in the transition metal complexes featuring multiple bonds between Group 10 and group 14 elements.[95] A recent EDA-NOCV study by Braunschweig et al. revealed that the Pt–Pb bond in (Pt(PCy$_3$)$_2$→PbCl$_2$) is a Pt→Pb dative bond whereas in **85** and **86**, they are electron sharing bonds. So, the real bonding phenomena of these complexes are not very well defined and clearly requires further theoretical investigation.

Conclusions

It is clear from the foregoing discussion that despite being a relatively new field, the chemistry of cations featuring heavier group 14 elements in low oxidation state is rich and diverse. The synthesis of [(C$_5$Me$_5$)E]$^+$ (E= Si–Pb) triggered the research in this field, which has resulted in the isolation of [Si–Cl]$^+$, Si(II), Ge(II), Sn(II) dications which were previously known only by theoretical calculation and/or in gas phase studies. A number of synthetic methods provide access to a variety of coordination environments for the cations of heavier group 14 elements. Most of the compounds were structurally characterized and understanding their bonding phenomena has become one of the most fundamental objectives in modern day main group chemistry. For instance, most of the cations were stabilized by N- or C-donor ligands and it remains a question whether the charge is localized on the central atom or delocalized over the ligand/ligands. None of the charge calculations clearly conclude about the ionocity of these cations and given by their high-field shifts especially in ^{29}Si and ^{119}Sn NMR, one would expect that the charges are not completely residing on the central atom. Recently, the group of Stalke extensively studied the charge density of various low valent silicon compounds[96] like 1,4-disilabenzene,[97] hexasilabenzene[98] etc. Perhaps experimental charge density studies of few of these cations would bring more clear pictures of their bonding situation.

The selection of ligand has turned out to be often decisive in the synthesis of these compounds because the stabilization requires the usage of sterically encumbering ligands with donor substituents. Therefore, the design of many more new ligands for stabilizing low oxidation species continue to be a central theme in this area and will remain so for many more years. For example, the emergence of carbodiphosphorane, which is simultaneous σ- and π-donor and its utilization for realizing two coordinate [Ge–Cl]$^+$ (**36**$^+$) will rival NHC for the stabilization of low coordinate group 14 cations in the coming years. In a similar way, bis-carbene already obtained a foothold in silicon (**13**$^+$) and germanium (**48**$^+$ and **53**) chemistry and many more such fascinating compounds supported by bis-carbene ligands are expected. The use of macrocycles to protect and stabilize germanium(II) and tin(II) cations and dications rendered an alternative route to the stabilization of low valent species.

Bearing in mind the infancy of cations of heavier group 14 elements in low oxidation state, there are plenty of objectives to achieve and problems to solve to develop the fundamental aspects of this field. For example, a monocoordinate silicon(II) cation, which is truly a higher homologue of HSi$^+$ is elusive. The scenario is same for other heavier group 14 elements. Similarly, a Si(II) dication encapsulated in crown ether or cryptands are yet to be realized and remains as a sought after goal. On would also notice that unlike silicon and germanium, no monomeric tin(II) cation was reported with neutral ligands like NHC or carbodiphosphorane which is due to the poor overlap between 2p (C) and 5p (Sn). The examples of Pb(II) cations and dications are still very scant and isolation of many more Pb(II) cations is highly desirable.



E= Si, **13**
E= Ge, **48**

E= Si, **87**
E= Ge, **88**

Scheme 38 Synthesis of silylone and germylone from silicon(II) and germanium(II) cations.

The reactivity of cations of low valent heavier group 14 elements has not very well studied but the seminal [Cp*Si]$^+$ (**1**) was found to be a potential workhorse for a wider range of transformations. In fact, **1** led to novel neutral silicon(II) compounds as well as a cyclotrisilene simply by the addition of appropriate anionic nucleophiles. Most of the other cations were only reacted with some Lewis bases like 4-DMAP to establish the Lewis acidic nature of the cations. However, Driess et al. recently demonstrated that bis-NHC stabilized Si(II) cation, **13** and Ge(II) cation, **48** are excellent precursors to give rise hitherto elusive cyclic silylone[55] and germylone,[77b] (heavier analogues of carbodiphosphorane) respectively (Scheme 38). These results ensure that the search for new chemistry involving heavier group 14 elements will not abate anytime soon. However, more systematic studies of the reactivities of such cations are highly desirable. The main target in this chemistry is metal-free catalysis which is yet to be realized. Nevertheless, catalytic conversion of 1,2-dimethoxyethane to 1,4-dioxane by **1** is very promising step towards metal free catalysis and it is only a matter of time before this goal will be accomplished. Besides, Rausch et al. reported $[(\eta^5\text{-Me}_5\text{C}_5)\text{Sn}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ to be an effective co-catalyst for Ziegler–Natta olefin polymerization, which manifests that low-valent group 14 cations are not only of academic interest but also have potential for application in industrial processes.

Acknowledgment

SK and SSS thank SERB (India) for financial support. SK also acknowledges the support from IISER. SSS is indebted to CSIR-NCl for the start-up grant. VSVSN thanks CSIR, India and SP thanks UGC, India for the research fellowships.

Notes and references

[a] *Inorganic Chemistry and Catalysis Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pashan, Pune 411008 (India) Fax: +9120-2590-2633;Tel: +9120-2590-2052; E-mail: ss.sen@ncl.res.in; Homepage: http://academic.ncl.res.in/ss.sen*

[b] *Department of Chemistry, Indian Institute of Science, Education, Research, Pune, Dr. Homi Bhabha Road, Pashan, Pune 411008 (India) Fax: +9120-2589-9790;Tel: +9120-2590-8137;
E-mail: shabana@iiserpune.ac.in;
Homepage: http://www.iiserpune.ac.in/~shabana*

[†] This review is dedicated to Prof. Herbert W. Roesky on the occasion of his 80th birthday

---

1. (a) J. F. Norris and W. W. Sanders, *Am. Chem. J.,* 1901, **25**, 54; (b) J. F. Norris, *Am. Chem. J.,* 1901, **25**, 117; (c) F. Kehrmann and F. Wentzel, *Chem. Ber.*, 1901, **34**, 3815.
2. A. v. Baeyer and V. Villiger, *Chem. Ber.*, 1901, **34**, 3815.
3. G. A. Olah, *J. Am. Chem. Soc.*, 1972, **94**, 808.
4. (a) J. B. Lambert, S. Zhang, C. L Stern and J. C. Huffmann, *Science*, 1993, **260**, 1917; (b) C. A. Reed, Z. Xie, R. Bau and A. Benesi, *Science*, 1993, **262**, 402.
5. G. A. Olah, G. Rasul, X. Li, H. A. Buchholz, G. Sanford and G. K. Surya Prakash, *Science*, 1994, **263**, 983.
6. (a) C. A. Reed and Z. Xie, *Science*, 1994, **263**, 985; (b) J. B. Lambert, S. Zhang and S. M. Ciro, *Organometallics*, 1994, **13**, 2430.
7. (a) J. B. Lambert and B. Kuhlmann, *J. Chem. Soc. Chem. Commun.* 1992, 931; (b) M. Kira, T. Oyamada and H. Sakurai, *J. Organomet. Chem.* 1994, **471**, C4.
8. M. Arshadi, D. Johnels and U. Edlund, *Chem. Commun.*, 1996, 1279.
9. K.-C. Kim, C. A. Reed, D. W. Elliott, L. J. Müller, F. Tham, L. Lin and J. B. Lambert, *Science*, 2002, **297**, 825.
10. J. B. Lambert, Y. Zhao, H. Wu, W. C. Tse and B. Kuhlmann, *J. Am. Chem. Soc.*, 1999, **121**, 5001.
11. J. B. Lambert, L. Lin, S. Keinan and T. Müller, *J. Am. Chem. Soc.*, 2003, **125**, 6022.
12. (a) J. B. Lambert and Y. Zhao, *Angew. Chem. Int. Ed. Engl.* 1997, **36**, 400; (b) C. Chuit, R. J. P. Corriu, A. Mehdi and C. Reyé, *Angew. Chem. Int. Ed. Engl.* 1993, **32**, 1311; (c) R. Carré, C. Chuit, R. J. P. Corriu, A. Mehdi and C. Reyé, *Angew. Chem. Int. Ed. Engl.* 1994, **33**, 1097-1099; (d) T. Müller, *Adv. Organomet. Chem.* 2005, **53**, 155; (e) T. Müller, Y. Zhao and J. B. Lambert, *Organometallics* 1998, **17**, 278; (f) J. Belzner, D. Schär, B. O. Kneisel and R. Herbst-Irmer, *Organometallics* 1995, **14**, 1840; (g) H.-U. Steinberger, C. Bauch, T. Müller and N. Auner, *Can. J. Chem.*, 2003, **81**, 1223; (h) Y. Zhang, K. Huynh, I. Manners and C. A. Reed, *Chem. Commun.*, 2008, 494; (i) H. F. T. Klare and M. Oestreich, *Dalton Trans.*, 2010, **39**, 9176; (j) K. Müther, R. Fröhlich, C. Mück-Lichtenfeld, S. Grimme and M. Oestreich, *J. Am. Chem. Soc.*, 2011, **133**, 12442; (k) S. S. Sen, J. Hey, M. Eckhardt, R. Herbst-Irmer, R. Mata, E. Maedl, H. W. Roesky, M. Scheer and D. Stalke, *Angew. Chem., Int. Ed.*, 2011, **50**, 12510.
13. (a) H. F. T. Klare, K. Bergander and M. Oestreich, *Angew. Chem. Int. Ed.*, 2009, **48**, 9077; (b) R. K. Schmidt, K. Müther, C. Muck-Lichtenfeld, S. Grimme and M. Oestreich, *J. Am. Chem. Soc.*, 2012, **134**, 4421.
14. (a) O. Allemann, S. Duttwyler, P. Romanato, K. K. Baldridge and J. S. Siegel, *Science*, 2011, **332**, 574; (b) S. Duttwyler, C. Douvris, C. D. Nathanael, L. P. Fackler, F. S. Tham, C. A. Reed, K. K. Baldrige and J. S. Siegel, *Angew. Chem. Int. Ed.* 2010, **49**, 7519; (c) N. Lühmann, R. Panisch and T. Müller, *Appl. Organomet. Chem.* 2010, **24**, 533.
15. (a) C. Douvris and O. Ozerov, *Science*, 2008, **321**, 1188; (b) R. Panisch, M. Boldte and T. Müller, *J. Am. Chem. Soc.*, 2006, **128**, 9676.
16. A. Schäfer, M. Reißmann, A. Schäfer, W. Saak, D. Haase and T. Müller, *Angew. Chem. Int. Ed.*, 2011, **50**, 12636.
17. P. Jutzi, A. Mix, B. Rummel, W. W. Schoeller, B. Neumann and H.-G. Stammler, *Science*, 2004, **305**, 849.
18. (a) R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn and D. Stalke, *Angew. Chem., Int. Ed.*, 2009, **48**, 5683; (b) A. C. Filippou, O. Chernov and G. Schnakenburg, *Angew. Chem., Int. Ed.*, 2009, **48**, 5687.
19. (a) S. S. Sen, H. W. Roesky, D. Stern, J. Henn and D. Stalke, *J. Am. Chem. Soc.* 2010, **132**, 1123; (b) S. S. Sen, J. Hey, R. Herbst-Irmer, H. W. Roesky and D. Stalke, *J. Am. Chem. Soc.* 2011, **133**, 12311; (c) S. S. Sen. S. Khan, P. P. Samuel, H. W. Roesky, *Chem. Sci.*, 2012, **2**, 659; (d) S. S. Sen, S. Khan, S. Nagendran and H. W. Roesky, *Acc. Chem. Res.*, 2012, **45**, 578.
20. M. Driess, S. Yao, M. Brym and C. van Wüllen, *Angew. Chem., Int. Ed.,* 2006, **45**, 6730.

21. (a) P. Jutzi, F. Kohl, P. Hofmann, C. Krüger and Y. Tsay, *Chem. Ber.,* 1980, **113**, 757; (b) P. Jutzi, R. Dickbreder and H. Nöth, *Chem. Ber.,* 1989, **122**, 865.
22. Y. Mizuhata, T. Sasamori and N. Tokitoh, *Chem. Rev.* 2009, **109**, 3479.
23. M. Asay, C. Jones and M. Driess, *Chem. Rev*. 2011, **111**, 354.
24. V. Y. Lee and A. Sekiguchi, Organometallic Compounds of Low-coordinate Si, Ge, Sn and Pb: *From Phantom atom to Stable Compounds*, Wiley, 2010, Chapter 1.
25. (a) A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford and S. Aldridge, *J. Am. Chem. Soc.*, 2012, **134**, 6500; (b) A. V. Protchenko, A. D. Schwarz, M. P. Blake, C. Jones, N. Kaltsoyannis, P. Mountford and S. Aldridge, *Angew. Chem., Int. Ed.*, 2013, **52**, 568; (c) N. Kuriakose and K. Vanka, *Dalton Trans.*, 2013, **43**, 2194; (d) P. P. Power, *Nature* 2010, **463**, 171.
26. L. Bourget-Merle, M. F. Lappert and J. R. Severn, *Chem. Rev.*, 2002, **102**, 3031.
27. P. A. Rupar, V. N. Staroverov, P. J. Ragogna and K. M. Baines, *J. Am. Chem. Soc.*, 2007, **129**, 15138.
28. (a) E. Rivard, *Dalton Trans.*, 2014, **43**, 8577; (b) Y. Wang and G. H. Robinson, *Dalton Trans.*, 2012, **41**, 337; (c) G. Prabusankar, A. Sathyanarayana, P. Suresh, C. N. Babu, K. Srinivas and B. P. R. Metla, *Coord. Chem. Rev.*, 2014, **269**, 96.
29. (a) W. A. Herrmann, M. Elison, J. Fischer, C. Köcher and G. R. J. Artus, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2371; (b) J. A. Mata, M. Poyatos and E. Peris, *Coord. Chem. Rev.*, 2007, **251**, 841.
30. (a) B. Inés, M. Patil, J. Carreras, R. Goddard, W. Thiel and M. Alcarazo, *Angew., Chem. Int. Ed.*, 2011, **50**, 8400; (b) S. Khan, G. Gopakumar, W. Thiel and M. Alcarazo, *Angew. Chem., Int. Ed.*, 2013, **52**, 5644.
31. M. Q. Y. Tay, Y. Lu, R. Ganguly and D. Vidović, *Angew. Chem., Int. Ed.*, 2013, **52**, 3132.
32. R. Toner and G. Frenking, *Chem. Commun.*, 2008, 1584.
33. J. M. Lehn, *Acc. Chem. Res.* 1978, **11**, 49.
34. T. Probst, O. Steigelmann, J. Riede and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.* 1990, **29**, 1397.
35. P. A. Rupar, V. N. Staroverov and K. M. Baines, *Science*, 2008, **322**, 1360.
36. (a) H. Braunschweig, K. Radacki, D. Rais and K. Uttinger, *Angew. Chem., Int. Ed.*, 2006, **45**, 162; (b) H. Braunschweig, K. Radacki and A. Schneider, *Science*, 2010, **328**, 345; (c) J. Brand, H. Braunschweig and S. S. Sen, *Acc. Chem. Res.* **2014**, *47*, 180.
37. J. Brand, H. Braunschweig, F. Hupp, A. K. Phukan, K. Radacki and S. S. Sen, *Angew. Chem., Int. Ed.*, 2014, **53**, 2240.
38. A. C. Filippou, O. Chernov, K. W. Stumpf and G. Schnakenburg, *Angew. Chem. Int. Ed.,* 2010, **49**, 3296.
39. A. C. Filippou, U. Chakraborty and G. Schnakenburg, *Chem. Eur. J.* 2013, **19**, 5676.
40. (a) A. C. Filippou, B. Baars, O. Chernov, Y. N. Lebedev and G. Schnakenburg, *Angew. Chem. Int. Ed* 2014, **53**, 565; (b) S. S. Sen, *Angew. Chem. Int. Ed* 2014, **53**, 8820.
41. A. E. Douglas and B. L. Lutz, *Can. J. Phys.,* 1970, **48**, 247.
42. N.Grevesse and A.Sauval, *Astron. Astrophys.*,1970, **9**, 232.
43. D. Rehder, *Chemistry in Space*, Wiley-VCH, Verlag and Co., Chapter 3.
44. P. Jutzi, D. Kanne and C. Krüger, *Angew. Chem., Int. Ed. Engl.,* 1986, **25**, 164.
45. E. D. Jemmis and P . v. R. Schleyer, *J. Am. Chem. Soc.*, 1982, **104**, 4780.
46. P. Jutzi, A. Mix, B. Neumann, B. Rummel, W. W. Schoeller, H.-G. Stammler and A. B. Rozhenko, *J. Am. Chem. Soc.*, 2009, **131**, 12137.
47. S. Khan, S. S. Sen, H. W. Roesky, D. Kratzert, R. Michel and D. Stalke, *Inorg. Chem.,* 2010, **49**, 9689.
48. P. Jutzi, K. Leszczyńska, B. Neumann, W. W. Schoeller and H.-G. Stammler, *Angew. Chem., Int. Ed.* 2009, **48**, 2596.
49. P. Jutzi, K. Leszczyńska, A. Mix, B. Neumann, W. W. Schoeller and H.-G. Stammler, *Organometallics,* 2009**, 28**, 1985.
50. P. Jutzi, K. Leszczyńska, A. Mix, B. Neumann, B. Rummel, W. W. Schoeller and H.-G. Stammler, *Organometallics*, 2010, **29**, 4759.
51. K. Leszczyńska, K. Abersfelder, A. Mix, B. Neumann, H.-G. Stammler, M. J. Cowley, P. Jutzi and D. Scheschkewitz, *Angew. Chem., Int. Ed.* 2012, **51**, 6785.
52. K. Leszczyńska, A. Mix, R. J. F. Berger, B. Rummel, B. Neumann, H.-G. Stammler and P. Jutzi, *Angew. Chem., Int. Ed.,* 2011, **50**, 6843.
53. M. Driess, S. Yao, M. Brym, C. van Wüllen and D. Lentz, *J. Am. Chem. Soc.,* 2006, **128**, 9628.
54. Y. Xiong, S. Yao, S. Inoue, E. Irran and M. Driess, *Angew. Chem., Int. Ed.,* 2012, **51**, 10074.
55. Y. Xiong, S. Yao, S. Inoue, J. D. Epping and M. Driess, *Angew. Chem., Int. Ed.,* 2013, **52**, 7147.
56. A. C. Filippou, Y. N. Lebedev, O. Chernov, M. Straßmann and G. Schnakenburg, *Angew. Chem., Int. Ed.*, 2013, **52**, 6974.
57. (a) S. Inoue, J. D. Epping, E. Irran and M. Driess, *J. Am. Chem. Soc.*, 2011, **133**, 8514.
58. H.-X. Young, H.-W. Xi, Y. LI, K. H. Kim and C. -W. So, *Chem. Eur. J.*, 2013, **19**, 11786.
59. N. C. Breit, T. Szilvási, T. Suzuki, D. Gallego and S. Inoue, *J. Am. Chem. Soc.*, 2013, **135**, 17958.
60. H. Schmidbaur and A. Schier, *Organometallics*, 2008, **27**, 2361.
61. D. L. Reger and P. S. Coan, *Inorg. Chem.*, 1996, **35**, 258.
62. (a) H. V. R. Dias and Z. Wang *J. Am. Chem. Soc.* 1997**, 119***,* 4650; (b) H. V. R. Dias and W. Jin, *J. Am. Chem. Soc.*, 1996, **118**, 9123.
63. Y. Ding, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *Organometallics*, **2001**, *20*, 1190.
64. M. Stender, A. D. Philips and P. P. Power, *Inorg. Chem.*, 2001, **40**, 5314.
65. M. Driess, S. Yao, M. Brym and C. van Wüllen, *Angew. Chem. Int. Ed.*, 2006, **45**, 4349.
66. M. J. Taylor, A. J. Saunders, M. P. Coles and J. R. Fulton, *Organometallics*, 2011, **30**, 1334.
67. H. Arii, F. Nakadate, K. Mochida and T. Kawashima, *Organometallics*, 2011, **30**, 4471.
68. (a) M. P. Doyle and D. C. Forbes, *Chem. Rev.*, 1998, **98**, 911; (b) J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang and I. J. B. Lin, *Chem. Rev.*, 2009, **109**, 3561; (c) S. Díez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612.
69. A. Schäfer, W. Saak, D. Haase and T. Müller, *Chem. Eur. J.*, 2009, **15**, 3945.
70. J. Li, C. Schenk, F. Winter, H. Scherer, N. Trapp, A. Higelin, S. Keller, R. Pöttgen, I. Krossing and C. Jones, *Angew. Chem., Int. Ed.,* 2012, **51**, 9557.
71. P. E. Lippens, *Phys. Rev. B* 1999, **60**, 4576.
72. (a) A. Sidiropoulos, C. Jones, A. Stasch, S. Klein and G. Frenking, *Angew. Chem., Int. Ed.* 2009, **48**, 9701; (b) K. C. Thimer, S. M. I. Al-Rafia, M. J. Ferguson, R. McDonald and E. Rivard, *Chem. Commun.*, 2009, 7119.
73. G. W. Parshall, *J. Am. Chem. Soc.*, 1972, **94**, 8716.
74. F. Cheng, J. M. Dyke, F. Ferrante, A. L. Hector, W. Levason, G. Reid, M. Webster and W. Zhang, *Dalton Trans.*, 2010, **39**, 847.
75. A. P. Singh, H. W. Roesky, E. Carl, D. Stalke, J.-P. Demers and A. Lange, *J. Am. Chem. Soc.,* 2012, **134**, 4998.
76. M. Bouska, L. Dostal, A. Ruzicka and R. Jambor, *Organometallics,* 2013, **32**, 1995.
77. (a) Y. Xiong, S. Yao, S. Inoue, A. Berkefeld and M. Driess, *Chem. Commun*., 2012, **48**, 12198; (b) Y. Xiong, S. Yao, G. Tan, S. Inoue and M. Driess, *J. Am. Chem. Soc*., 2013, **135**, 5004.
78. M. J. Ward, P. A. Rupar, M. W. Murphy, Y.-M. Yiu, K. M. Baines and T. K. Sham, *Chem. Commun.*, 2010, **46**, 7016.
79. Y. Xiong, T. Szilvási, S. Yao, G. Tan and M. Driess, *J. Am. Chem. Soc.,* 2014, **136**, 11300.
80. A. Schäfer, F. Winter, W. Saak, D. Haase, R. Pöttgen and T. Müller, *Chem. Eur. J.*, 2011, **17**, 10979.
81. (a) N. N. Greenwood and A. Earnshaw, Chemistry of the elements, Pergamon Press, 1989; (b) B. L. Haymore, J. D. Lamb, R. M. Izatt and J. J. Christensen, *Inorg. Chem.*, 1982, **21**, 1598; (c) A. P. de

Silva, H. Q. N. Gunaratne, T. Gunnlaugsson and M. Nieuwenhuyzen, *Chem. Commun.,* 1996, 1967; (d) T. Gunnlaugsson, A. Harte, J. P. Leonard and M. Nieuwenhuyzen, *Chem. Commun.*, 2002, 2134.

82. (a) J. B. Lambert, *Science*, 2008, **322**, 1333; (b) T. Müller, *Angew. Chem., Int. Ed.,* 2009, **48**, 3740.
83. P. A. Rupar, R. Bandyopadhyay, B. F. T. Cooper, M. R. Stinchcombe, P. J. Ragogna, C. L. B. Macdonald and K. M. Baines, *Angew. Chem., Int. Ed.*, 2009, **48**, 5155.
84. (a) F. Cheng, A. L. Hector, W. Levason, G. Reid, M. Webster and W. Zhang, *Angew. Chem., Int. Ed.*, 2009, **48**, 5152; (b) W. Levason, G. Reid and W. Zhang, *Coord. Chem. Rev.*, 2011, **255**, 1319.
85. R. Bandyopadhyay, J. H. Nguyen, A. Swidan and C. L. B. Macdonald, *Angew. Chem., Int. Ed.*, 2013, **52**, 3469.
86. (a) C. L. B. Macdonald, R. Bandyopadhyay, B. F. T. Cooper, W. W. Friedl, A. J. Rossini, R. W. Schurko, S. H. Eichhorn and R. H. Herber, *J. Am. Chem. Soc.*, 2012, **134**, 4332. (b) J. C. Avery, M. A. Hanson, R. H. Herber, K. J. Bladek, P. A. Rupar, I. Nowik, Y. Huang and K. M. Baines, *Inorg. Chem.*, 2012, **51**, 7306.
87. A. C. Filippou, A. I. Philippopoulos and G. Schnakenburg, *Organometallics*, 2003, **22**, 3339.
88. A. C. Filippou, A. I. Philippopoulos, P. Portius and G. Schnakenburg, *Organometallics,* 2004**, 23***,* 4503.
89. (a) R. Jambor, B. Kašná, S. G. Koller, C. Strohmann, M. Schürmann and K. Jurkschat, *Eur. J. Inorg. Chem.*, 2010, 902; (b) R. Dostalova, L. Dostal, A. Ruzicka and R. Jambor, *Organometallics*, 2011, **30**, 2405.
90. J. Martincov, L. Dostal, S. Herres-Pawlis, A. Ruzcka and R. Jambor, *Chem. Eur. J.***,** 2011, **17**, 7423.
91. (a) J. Bauer, H. Braunschweig and R. D. Dewhurst, *Chem. Rev.*, 2012, **112**, 4329; (b) H. Braunschweig, A. Damme, R. D. Dewhurst, F. Hupp, J. O. C. Jimenez-Halla and K. Radacki, *Chem. Commun.*, 2012, **48**, 10410.
92. H. Braunschweig, M. A. Celik, R. D. Dewhurst, M. Heid, F. Hupp and S. S. Sen, *Chem. Sci.*, 2015, **6**, 425.
93. B. Rhodes, J. C. W. Chien and M. D. Rausch, *Organometallics*, 1998, **17**, 1931.
94. S. Hino, M. Brynda, A. D. Phillips and P. P. Power, *Angew. Chem., Int. Ed.*, 2004, **43**, 2655.
95. W. H. Liao, P. Y. Ho and M. D. Su, *Inorg. Chem.*, 2013, **52**, 1338.
96. (a) D. Kratzert, D. Leusser, J. J. Holstein, B. Dittrich, K. Abersfelder, D. Scheschkewitz and D. Stalke, *Angew. Chem., Int. Ed.,* 2013, **52**, 4478; (b) J. Hey, D. Leusser, D. Kratzert, H. Fliegl, J. M. Dieterich, R. A. Mata and D. Stalke, *Phys. Chem. Chem. Phys.*, 2013, **15**, 20600 and references therein.
97. S. S. Sen, H. W. Roesky, K. Meindl, D. Stern, J. Henn, A. C. Stückl and D. Stalke, *Chem. Commun.,* 2010, **46**, 5873.
98. K. Abersfelder, A. J. P. White, H. S. Rzepa and D. Scheschkewitz, *Science* 2010, **327**, 564.