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Tetryliumylidene ions in synthesis and catalysis

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Tetryliumylidene ions ($[R{-}E:]^+$), recognised for their intriguing electronic properties, have attracted considerable interest. These positively charged species, with two vacant p-orbitals and a lone pair at the E(II) centre (E = Si, Ge, Sn, Pb), can be viewed as the combination of tetrylenes ($R_2E:$) and tetrylium ions ($[R_3E]^+$), which makes them potent Lewis ambiphiles. Such electronic features highlight the potential of tetryliumylidenes for single-site small molecule activation and transition metal-free catalysis. The effective utilisation of the electrophilicity and nucleophilicity of tetryliumylidenes is expected to stem from appropriate ligand choice. For most of the isolated tetryliumylidenes, electron donor- and/or kinetic stabilisation is necessary. This minireview highlights the developments in tetryliumylidene syntheses and the progress of research towards their reactivity and applications in catalytic reactions.

Introduction

Recent developments in the chemistry of low-valent/oxidation state main-group compounds have revealed their inherent electronic properties. These allow them to mimic the behaviour of transition-metal complexes, with regard to their ability to form coordination complexes, engage in multiple bonding, undergo redox reactions, and exhibit catalytic activity.[1–5] An important class of low-valent main group species capable of such behaviour are tetrylenes $[R_2E:]$ (E = Si, Ge, Sn, Pb) – the heavier analogues of carbenes ($R_2C:$). Numerous representatives of these species are able to activate small molecules under mild conditions and can be used as ligands in catalytic organic reactions due to their ambiphilic nature.[6–12] The heavier congeners of carbonium ions, namely tetrylium cations $[R_3E]^+$ (E = Si, Ge, Sn, Pb), have also garnered significant interest in recent decades attributed to their pronounced electrophilic nature, leading to various applications in catalysis and bond activation chemistry.[13–16] A related and less explored class of compounds are the tetryliumylidene ions (E = Si, Ge, Sn, Pb), which exhibit distinctive electronic properties, merging the strong electrophilicity observed in tetrylium cations with the Lewis ambiphilic character found in tetrylenes. In their idealised form, these mono-substituted cations have two vacant degenerate p orbitals and a lone pair at the E(II) centre (Fig. 1).[17]

The bonding situation in parent tetryliumylidenes can be examined from the point of view of the valent ns and np orbitals and their proclivity to hybridise. The inert s-pair effect, which reflects the situation where the diminishing hybridisation

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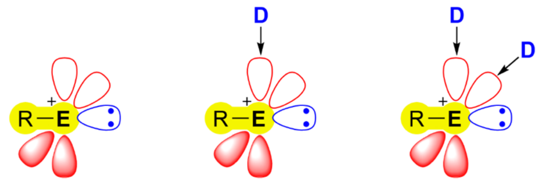
Sebastian Stigler

Sebastian Stigler received his MSc degree in chemistry in 2021 from the Technical University of Munich under the supervision of Prof. Shigeyoshi Inoue on the application of NHC-stabilised silyliumylidene ions in hydroboration and hydrosilylation catalysis. Since then he has continued his stay in the group of Prof. Shigeyoshi Inoue at the Technical University of Munich as a PhD student. His current research interests focus on the reactivity of silyliumylidene ions and their utilisation in catalytic reactions.

Shiori Fujimori

Shiori Fujimori obtained her MSc and PhD degrees in chemistry in 2019 at Kyoto University under the supervision of Prof. Norihiro Tokitoh on the synthesis of novel aromatic compounds containing heavier group 14 elements. In October 2019, she was awarded a Eurotech-Marie Curie Fellowship and joined the group of Prof. Inoue at the Technical University of Munich. She continued her stay at the TUM as an Alexander von Humboldt Fellow where she pursued her interest in low-valent silicon chemistry.



E = Si, Ge, Sn, and Pb

Fig. 1 Frontier orbitals of free (left) and donor-stabilised tetryliumylidene ions (centre, right) (D = Lewis base).

between ns and np orbitals makes only np orbitals available for bonding, has a great influence on the electronic structure of p-block element species. Consideration of the relative roles of s and p orbitals can be done using Weinhold's natural bond orbital (NBO) scheme,[18] through which natural atomic orbital (NAO) hybridisations of natural localised molecular orbitals (NLMOs) can be obtained.[19] It is known that tetrylenes exhibit higher tendency to the inert pair effect as we go down the period – the heavier elements tend to retain a low oxidation state, and forming [R_2E:] species becomes easier – thus, lead, for example, prefers $Pb^{II}R_2$ species over $Pb^{IV}R_4$. Calculations (at the B3LYP[20–23]/def2-TZVP[24] level of theory using Gaussian 16 (ref. 25) and NBO7 (ref. 26) software) show that the inert s-pair effect is significantly more pronounced in tetryliumylidenes in comparison with tetrylenes, even for lighter elements. In [H_2E:] series, there is a high p character of the lone pair in the parent carbene (0.68), and a significant drop in the p/s ratio in the silylene (0.30) (Fig. 2, top). The ratio gradually decreases when going down the period, and is 0.13 in [H_2Pb:]. In the case of [H–E:]$^+$, even the methylidyne ion lone pair has a s/p ratio (0.13) similar to that of [H_2Pb:]. The decrease is less significant in [H–Si:]$^+$, and only a slight change is observed when going down the period.

An analogous situation is observed when comparing the E–H bonds in tetrylenes and tetryliumylidenes (Fig. 2, bottom). The C–H bond in [H_2C:] has a low p/s ratio of 3.67 which increases to 13.61 in plumbylene. In contrast, in the tetryliumylidene series, the methylidyne ion already has a high p/s ratio of 7.68, which is comparable with that of [H_2Ge:]. Overall, when going down the period the p composition of the hybrid orbital increases from 87.8% in [H–C:]$^+$ to 95.4% in [H–Pb:]$^+$. These results indicate that while hybridisation is increasingly more difficult in the case of tetrylenes when going down the periodic table, in tetryliumylidenes the effect is less dramatic, since sp hybridisation is difficult to begin with.

[R–E:]$^+$ have the potential for versatile synthetic applicability due to their unique electronic structure with multiple reactive sites, originating from the two electrophilic vacant p-orbitals and one nucleophilic lone pair. Such arrangement should in principle allow the formation of up to three new bonds in a single reaction.[27] Thus, tetryliumylidene ions are expected to be highly reactive, and in general, electron donor stabilisation by inter- or intramolecular coordination of Lewis bases is required to isolate these species as stable compounds.[28]

In the pioneering studies, Jutzi and co-workers reported tetryliumylidene ions [Cp*E:]$^+$ (E = Ge, Sn, Pb; Cp* = η^5-C_5Me_5) stabilised by the hyper-coordinating cyclopentadienyl group.[29,30] Following these discoveries, researchers have successfully isolated a range of tetryliumylidene ions.[31] This was made possible by employing sterically demanding ligands for kinetic stabilisation, including bulky amide groups,[32] β-diketiminato,[33] aminotroponiminate,[34] and cyclophane groups.[35] Alternatively, Lewis basic ligands, such as carbenes,[36,37] imines,[38] or weakly coordinating arenes,[39] have been utilised for the enhancement of the thermodynamic stability. Several decades after the discovery of Jutzi's heavier tetryliumylidene ions [Cp*E:]$^+$ (E = Ge, Sn, Pb), in 2004, the same group succeeded in the synthesis of the first isolable silyliumylidene ion, the pentamethylcyclopentadienyl-silicon(II) cation [Cp*Si:][$B(C_6F_5)_4$].[40]

Arseni Kostenko

Arseni Kostenko obtained his bachelor's degree in Molecular Biochemistry at the Technion Israel Institute of Technology, subsequently pursuing a Master's degree and a PhD in the field of silicon chemistry under the supervision of Prof. Yitzhak Apeloig. In 2016, he received the Alexander von Humboldt fellowship and joined the group of Prof. Matthias Driess at the Technical University of Berlin. Since 2021, Dr Kostenko has been working in the group of Prof. Shigeyoshi Inoue at the Technical University of Munich, computationally studying the structure and reactivity of low-valent main group element-based compounds.

Shigeyoshi Inoue

Shigeyoshi Inoue obtained his PhD from the University of Tsukuba in 2008 supervised by Prof. Akira Sekiguchi. Following postdoctoral study at the TU Berlin with Prof. Matthias Driess, he established an independent research group within the framework of the Sofja Kovalevskaja program in 2010. Since 2015 he has been on the faculty at the Technical University of Munich (TUM). His research interests include the synthesis and reactivity of main-group compounds with unusual structures and unique electronic properties, with the goal of finding novel applications in synthesis, catalysis and materials science.

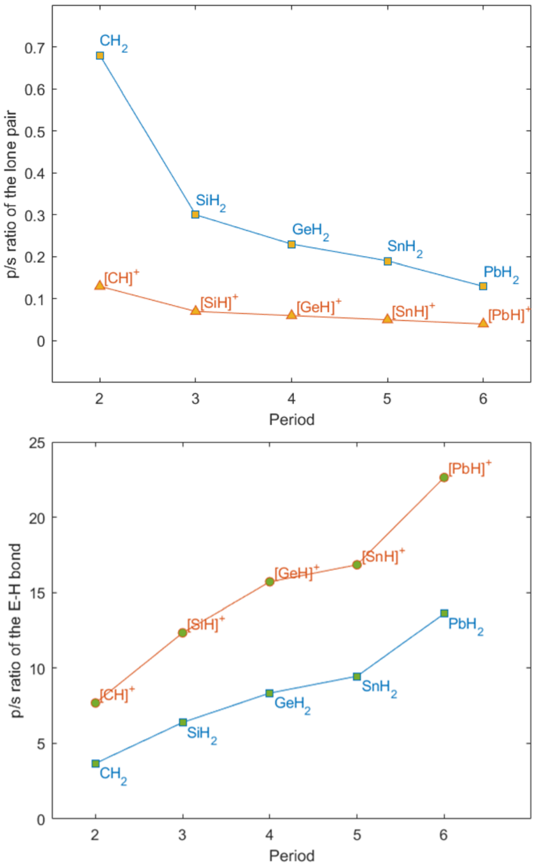


Fig. 2 Lone pair (top) and E–H bond (bottom) NAO/NLMO p/s hybridisation ratios in tetrylenes and tetryliumylidenes at the B3LYP/def2-TZVP level of theory.

Since these seminal discoveries, the reactivity of tetryliumylidene ions has been studied to some extent. It has been demonstrated that these species can be used as synthons for the isolation of novel low-valent compounds containing a heavier group 14 element. For example, a new class of fascinating main-group compounds, tetrylones, which are two-coordinate E^0 species (L:→E←:L; E = Si,[41] Ge[42]), were synthesised from the reduction of the corresponding chloro-tetryliumylidenes. In addition, the ambiphilic character of tetryliumylidene ions, which mimics the frontier d-orbitals found in transition metals, enables them to activate small molecules (*e.g.*, CO_2, N_2O, H_2S, H_2O, and heavier chalcogens).[43–47] Furthermore, they have been successfully applied in several catalytic transformations without transition metals.[48–51] Various sterically bulky electron donor ligands have been developed in the last few decades, allowing the preparation of donor-stabilised hydro-tetryliumylidenes $[H–E:]^+$ with superior potency for widespread applications. For instance, hydrosilylation and hydroboration reactions were catalysed by $[H–E:]^+$.[52–54] In this minireview, we have summarised the recent developments in the chemistry of tetryliumylidene ions, including their reactivity towards small molecules, as precursors to a variety of additional low-valent species and catalytic applications. While some tetryliumylidene ions were isolated and employed in catalysis by taking advantage of cooperative effects between transition metals and group 14 elements,[55–66] this review highlights only the main-group examples.

Silyliumylidenes

The first synthesis of a silyliumylidene ions in 2004 by Jutzi *et al.* was achieved by the reaction of decamethylsilicocene, $(Cp^*)_2Si$, with the proton transfer reagent $[Cp^*H_2][B(C_6F_5)_4]$ to form $[Cp^*Si:][B(C_6F_5)_4]$ **1a** – the first isolable silyliumyidene ion.[40] In a similar fashion, in 2018, the group of Filippou showed the successful synthesis of **1a** by protonation of $(Cp^*)_2Si$ with one equivalent of $[H(Et_2O)_2][B(C_6F_5)_4]$.[57] Another procedure to form this compound was reported more recently, in 2019, by Fritz-Langhals with the hydride abstraction of $[Cp^*_2Si:]$ by a tritylium salt, resulting in tetramethylfulvene and **1a** on a technical scale.[48] Jutzi *et al.* also reported the formation of penta-isopropylcyclopentadienylsilicon(II) cation $iPr_5C_5Si^+$ **1b** by reacting the mixed silicocene $(^iPr_5C_5)(Me_5C_5)Si$ with $H(OEt_2)_2{}^{+}$·$Al(O^tBu^F)_4{}^-$ (Fig. 3).[67]

Cyclopentadienyls and their derivatives are 2σ, 4π electron donor ligands and are routinely used for stabilisation of electron-deficient species. Their proclivity to afford hyper-coordinated centres allowed, in this case, for stabilisation of highly reactive silyliumylidene ions. Due to this, **1a** and **1b** cannot be considered true mono-substituted silyliumylidene ion complexes. It took almost two decades after the isolation of **1a**, when Hinz reported the first achievements towards the mono-substituted silicon(II) cation $[RSi:]^+$ (R = bulky carbazolyl substituent) **2** by halide abstraction from a base-free halosilylene with $Ag[Al(O^tBu^F)_4]$. Even though there are arene interactions between the Si atom and the carbazolyl scaffold, this silyliumylidene bears no other σ-donors except for the carbazolyl substituent.[68]

The first two-coordinated silyliumylidene ion **3a** was reported by Driess *et al.* in 2006. Here, the authors protonated the sterically demanding β-diketiminate ligand backbone of the corresponding zwitterionic *N*-heterocyclic silylene with Jutzi's oxonium acid $[H(Et_2O)_2][B(C_6F_5)_4]$.[69] More recently, the group of Aldridge reported the silyliumylidene ion **3b** stabilised by a β-diketiminate ligand featuring a backbone with NMe_2 groups.[70] In 2014, Filippou *et al.* reacted a chromium silylidyne complex salt, containing the first Cr–Si triple bond, with CO to achieve the four-legged piano–stool complex cation **4**.[43] Very recently, in 2022, Kato *et al.* showed the formation of the Ni(0)-stabilised Si(II) species **5**. The dative Ni → Si σ-interaction and π-donations from the amino- and Ni-moieties stabilise the highly electrophilic Si centre.[71]

Most of the known silyliumylidene ions are three-coordinated, stabilised kinetically, *via* sterically demanding ligands, and electronically, *via* donation to the silicon centre by Lewis bases. A majority of reported silyliumylidene ions use stabilisation by *N*-heterocyclic carbenes (NHCs). The first example of this class of compounds was reported by the group of Filippou in 2013.[72] Here, the NHC stabilised silicon(II) diiodide was reacted with a sterically more demanding *N*-heterocyclic carbene to get to the silyliumylidene ion **6**. At essentially the same

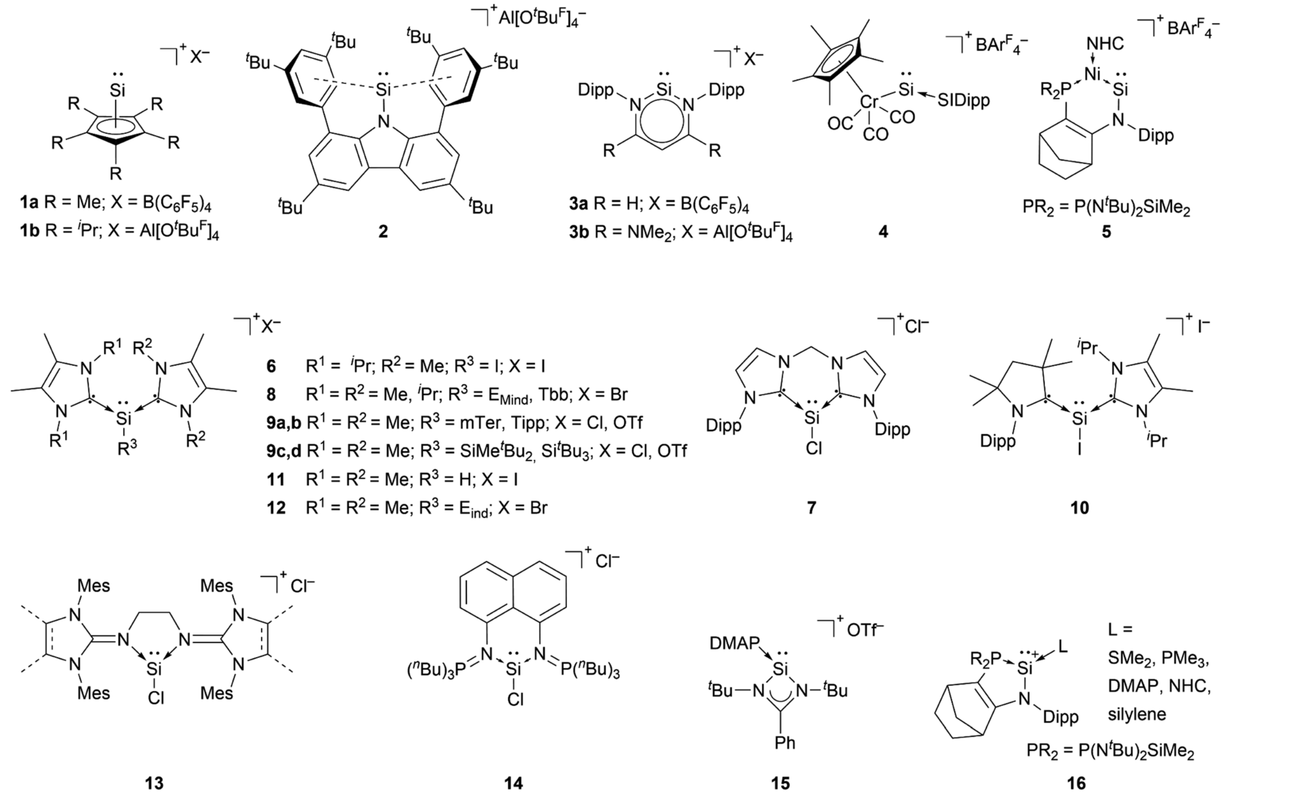
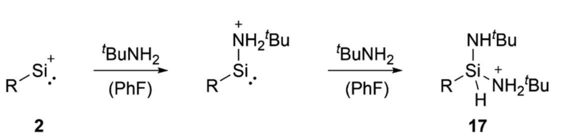
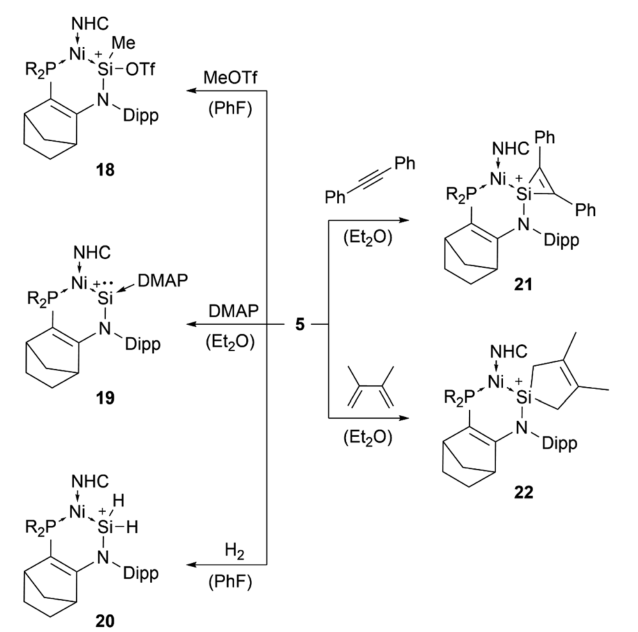


Fig. 3 Reported silyliumylidene ions. ($O^tBu^F = OC(CF)_3$; Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$; SIDipp = 1,3-bis(Dipp)imidazolidin-2-ylidene; $BAr_4{}^F = B[C_6H_3\text{-}3,5\text{-}(CF_3)_2]_4$; NHC = 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene; E_{Mind} = 1,1,7,7-tetraethyl-3,3,5,5-tetramethyl-*s*-hydrindacen-4-yl; Tbb = ((5-(*tert*-butyl)-1,3-phenylene)bis(methanetriyl))tetrakis(trimethylsilane); mTer = 2,6-Mes$_2$C$_6$H$_3$; Mes = 2,4,6-Me$_3$C$_6$H$_2$; Tipp = 2,4,6-^{i}Pr$_3$C$_6$H$_2$; E_{ind} = 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl; DMAP = 4-(*N*,*N*-dimethylamino)pyridine).

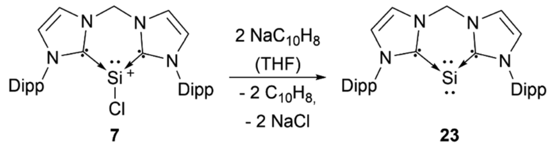
time, Driess *et al.* isolated the chloro-silyliumylidene ion **7** stabilised by a cyclic bis-NHC.[41] In 2014, Tokitoh *et al.* and our group independently used NHCs to synthesise aryl-substituted silyliumylidene ions. The group of Tokitoh treated dibromodisilenes with an excess of NHCs forming the bis-NHC adduct [ArSi(NHC)$_2$][Br] **8**.[73] Meanwhile, our group utilised dichloroarylsilanes and three equivalents of NHCs in a facile one-pot reaction to obtain the corresponding silyliumylidene ions **9a,b**.[74] In 2016, the group of So showed the formation of the silyliumylidene iodide **10**, stabilised by both an NHC and a cyclic alkyl(amino) carbene (cAAC), by reacting the corresponding cAAC stabilised silicon(II) diiodide with NHC.[75] One year later, the same group isolated the first NHC-stabilised parent-silyliumylidene ion **11** by reacting an NHC–iodosilicon(I) dimer with four equivalents of NHC.[76] Matsuo *et al.* reported a similar approach to Tokitoh in 2018. Here, they used E_{ind}-



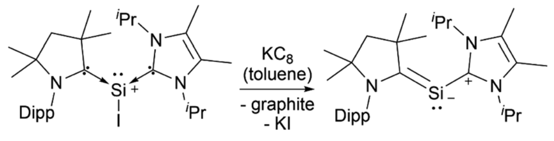
Scheme 1 Reaction of **2** with two equivalents of amines to form **17** (R = bulky carbazolyl ligand).



Scheme 2 Multiple examples for small molecule activations of **5** (R$_2$P = P(N^{t}Bu)$_2$SiMe$_2$, NHC = 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene).



Scheme 3 Reductive dechlorination of **7**.



Scheme 4 Reductive dehalogenation of **10**.

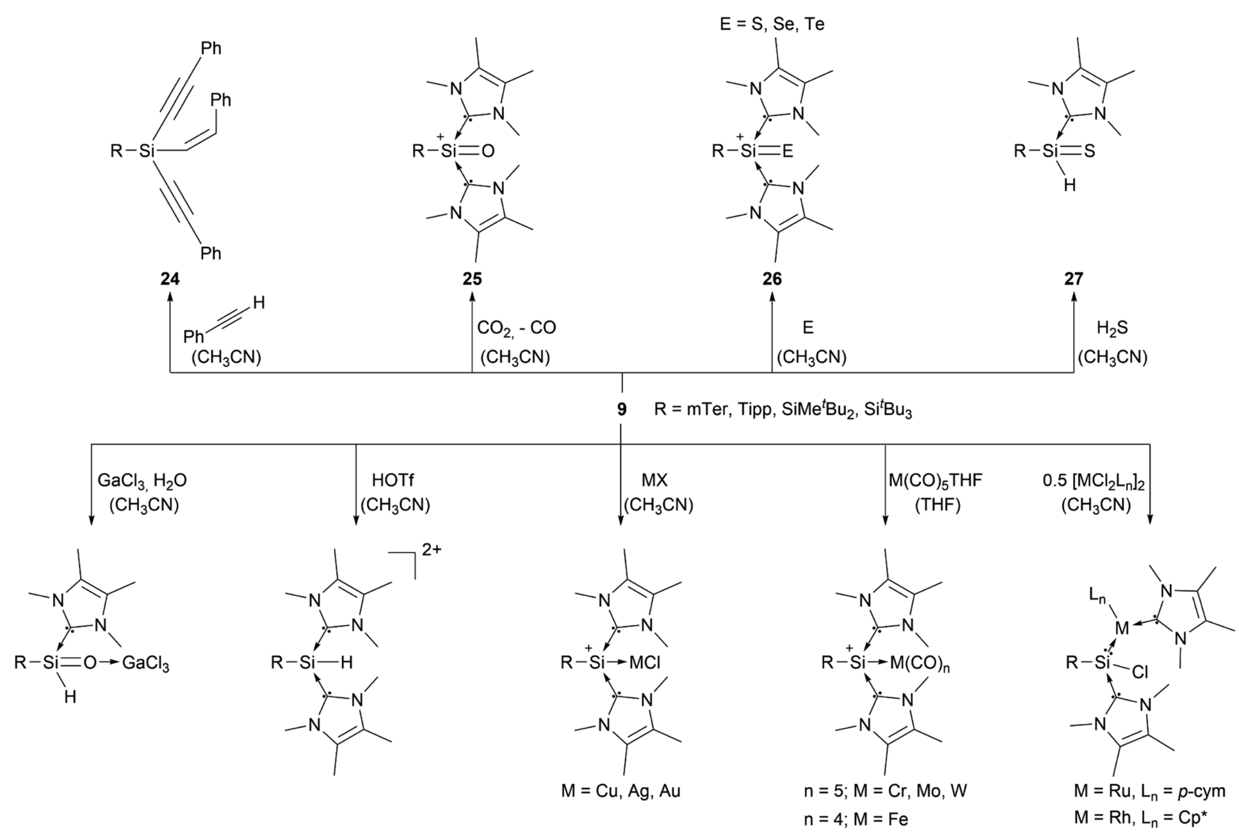
substituted 1,2-dibromodisilene to form with four equivalents of NHCs the corresponding bis-NHC adduct of the formal aryl-silyliumylidene ion **12**.[77] In 2019, utilising the already reported approach, our group could show the formation of the silyl-substituted NHC-stabilised silyliumylidene ions **9c,d**.[78] Additionally, very recently we reported the synthesis of a neutral bidentate NHI ligand (NHI = *N*-heterocyclic imine) with a saturated imidazoline backbone and the formation of the corresponding chloro-silyliumylidene ion 13.[79,80]

Apart from NHCs, the group of Driess utilised a bis(iminophosphorane) chelate ligand to form the chloro-silyliumylidene **14**. The two N=P^{n}Bu$_3$ ylide moieties can act as very strong Brønsted and Lewis bases.[81] In 2013, So *et al.* isolated the silyliumylidene ion **15** stabilised by an amidinate ligand and 4-dimethylaminopyridine (DMAP).[82] More recently, Kato *et al.* reported in 2022 the use of different Lewis bases, such as SMe_2, PMe_3, and DMAP, and even observed silylene-stabilised silyliumylidene complexes **16**.[83]

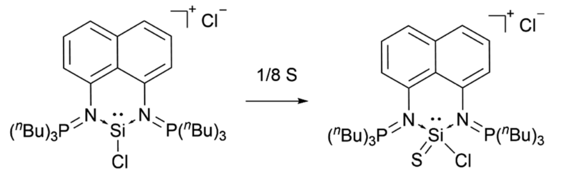
Reactivity of silyliumylidenes and their use in catalytic reactions

Among tetryliumylidenes, silyliumylidene ions show the widest diversity in reactivity reported so far. The first stable silyliumylidene **1** reacts with the metalate Na[TpMeMo(CO)$_2$(PMe$_3$)] to afford the silylidyne complex [TpMe(CO)$_2$MoSi(η^3-Cp*)] (TpMe = κ^3-*N*,*N*′,*N*″-hydridotris(3,5-dimethyl-1-pyrazolyl)borate) featuring a delocalised Mo–Si bond with a partial triple bond character.[57] Despite the high steric demand of the carbazolyl moiety, pseudo-mono-coordinated silyliumylidene ion **2** retains high reactivity and reacts with an amine to form three bonds at the silicon atom in one reaction **17** – justifying being called a "supersilylene" (Scheme 1).[27,68]

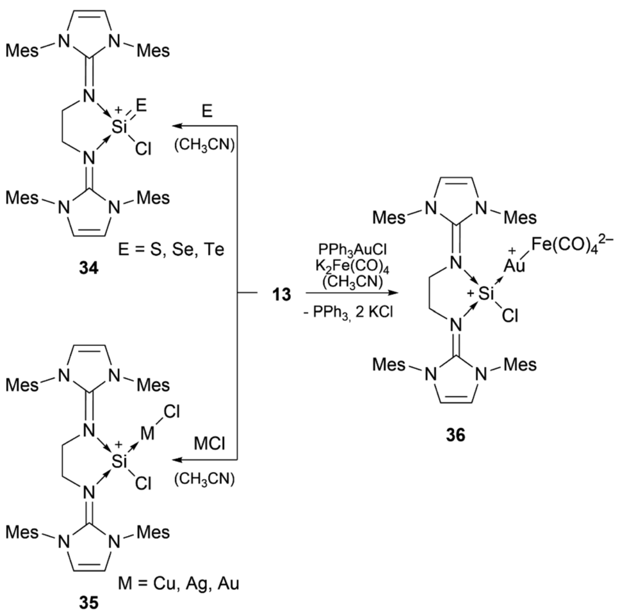
β-Diketiminate stabilised silyliumylidene **3b** can react with NH$_2$^{t}Bu *via* formal N–H oxidative addition to form a Si(H)(NH^{t}Bu) moiety.[70] When two-coordinated silyliumylidene ion **4** is exposed to an N_2O atmosphere, rapid formation of metallosilanone



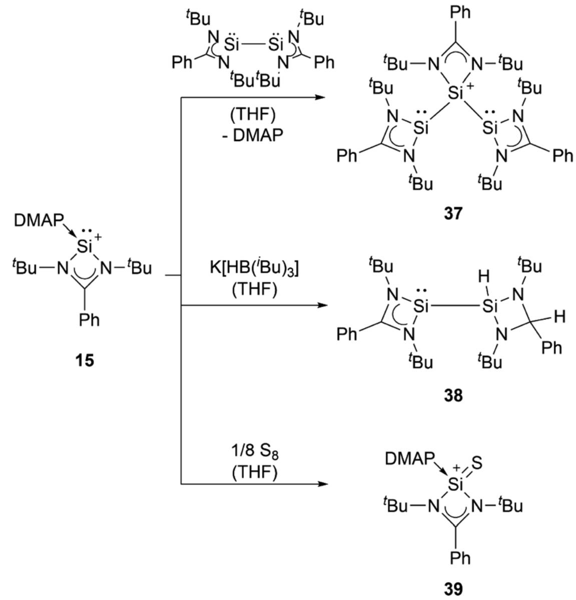
Scheme 5 Reported reactivity of **9** (X = Cl, OTf; *p*-cym = 1-Me-4-^{i}Pr-benzene).



Scheme 6 Oxidation of **14** with elemental sulphur.



Scheme 7 Reported reactivity of **13**.



Scheme 8 Reported reactivity of **15**.

occurs.[43] **5** shows multiple examples of activation of small molecules, such as MeOTf **18**, DMAP **19**, H_2 **20**, diphenylacetylene **21**, and 2,3-dimethyl-1,3-butadiene **22** (Scheme 2).[71]

Silyliumylidenes could be used as precursors for the formation of additional exotic low-valent species. Thus, dehalogenation of chloro-silyliumylidene **7** yielded the cyclic bis-NHC stabilised silylone **23** (Scheme 3),[41] and mixed NHC–cAAC stabilised silyliumylidene **10** could be reduced with KC_8 to form the bent silaallene **33** (Scheme 4).[75]

Aryl- and silyl-substituted silyliumylidene ions **9** showed a plethora of reactivities with small molecules, such as the C–H insertion reaction with three equivalents of phenylacetylene to form 1-alkenyl-1,1-dialkynylsilane **24**.[74] **9** can activate CO_2 to form the silaacylium ion **25**,[44] as well as the NHC-stabilised heavier silaacylium ions **26** with sulphur, selenium, and tellurium *via* chalcogen-atom transfer.[45] Moreover, **9** can activate the S–H bond of hydrogen sulfide to form the thiosilaaldehyde **27**,[46] react with $GaCl_3$ and water to afford the silaaldehyde **28**,[47] and convert to the Si(IV) complex **29** by reaction with triflic acid (Scheme 5).[84] In some of these reactions, one NHC acts as a H–Cl scavenger, which is a substantial thermodynamic driving force for the reaction progress. Furthermore, compound **9** derivatives are capable of forming transition metal complexes. They can either react with coinage metals, such as copper, silver, and gold, to form the metal chloride adducts **30**,[85] or transition metal carbonyls (M = Cr, Wo, W, Fe) to form the $M(CO)_n$ (n = 4 or 5) silyliumylidene adducts **31**.[86] Additionally, **9** can undergo a facile insertion into M–Cl bonds (M = Ru, Rh), forming the chlorosilylene transition-metal complexes **32** (Scheme 5).[87]

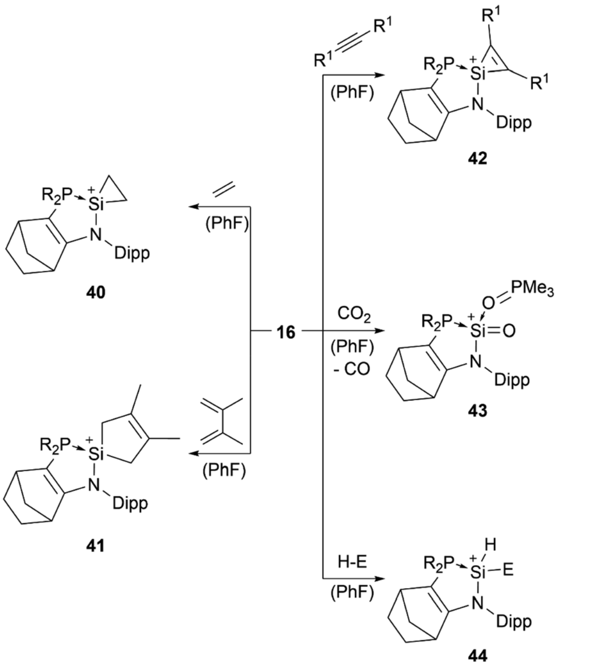
When reacted with elemental sulphur, the bis(iminophosphorane) coordinated chloro-silyliumylidene **14** is oxidised to the chlorosilathionium salt **33** (Scheme 6).[81] This reactivity is similar to the reactivity of **9** with chalcogens.

Bis-NHI stabilised silyliumylidene **13** shows the formation of the heavier silaacylium ions (E = S, Se, Te) **34** in reaction with chalcogens, coinage metal complexes **35** with CuCl, AgCl, and $(Me_2S)AuCl$, and the heterobimetallic gold–iron complex **36** in reaction with a gold–chloride complex in the presence of tetracarbonylferrate (Scheme 7).[79]

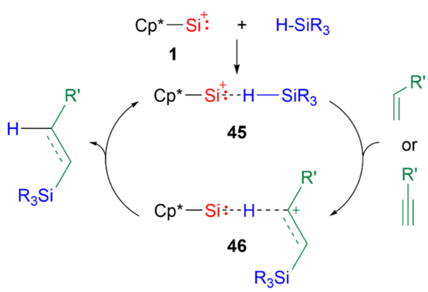
Amidinate-substituted silyliumylidene **15** can undergo oxidative addition at the silicon centre with the amidinate silicon(I) dimer to form the disilylenylsilylium triflate **37**, react with nucleophilic reagents, such as $K[HB(^iBu)_3]$, to afford the corresponding silylsilylene **38**, and form the silanethionium triflate **39** with elemental sulphur (Scheme 8).[82]

Lewis base stabilised silyliumylidene **16** is able to undergo the [1+2]-cycloaddition with ethylene at the silicon centre to form the silacyclopropyl cation **40**, [4+1]-cycloaddition with 2,3-dimethyl-1,3-butadiene (**41**), [2+1]-cycloaddition with diphenylacetylene (**42**), oxidation of the Si(II) centre with CO_2 to generate a cationic silanone **43**, and oxidative addition of triethylsilane, diphenylphosphine, or pinacolborane to give the corresponding silylium ion **44** (Scheme 9).[83,88]

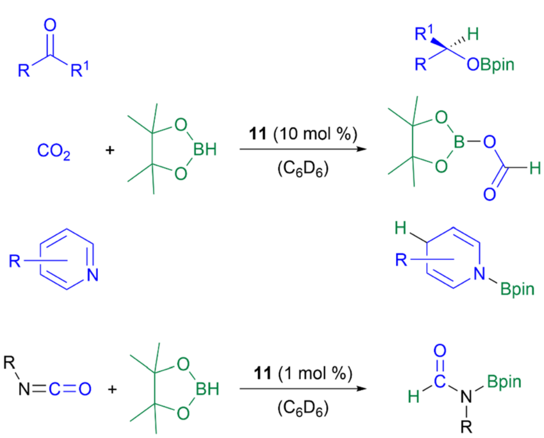
While there are a multitude of examples of silyliumylidene ion reactivities, to date there are only several examples of their use as catalysts. The first isolable silyliumylidene **1** proved to be an efficient non-metallic catalyst for the hydrosilylation of



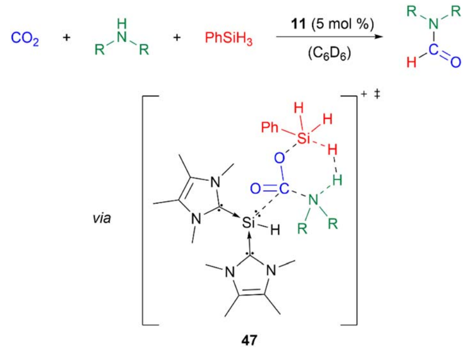
Scheme 9 Reported reactivity of **16** (R^1 = Ph, $SiMe_3$, Mes; H–E = $HSiEt_3$, $HPPh_2$, HBpin; $R_2P = P(N^tBu)_2SiMe_2$).



Scheme 10 Proposed mechanism of the hydrosilylation of carbon–carbon multiple bonds (R_3 = Me_2OTMS, $Me(OTMS)_2$, Et_3, Me_2Ph, Me_2Cl, $MeCl_2$; R′ = nC_4H_9, $SiMe_3$, Ph, cyclo-hexene, norbornene).



Scheme 11 Hydroboration of aldehydes, ketones, CO_2, pyridines, and isocyanates with pinacolborane.



Scheme 12 *N*-Formylation of amines using CO_2 and phenylsilane (HNR_2 = primary and secondary amines).

unsaturated carbon–carbon bonds at low catalyst loadings of <0.01 mol% and the Piers–Rubinsztajn reaction.[48] In the proposed mechanism for the hydrosilylation, the silyliumylidene first activates the silicon hydrogen bond to form the hydrogen-bridged complex **45**. The substrate can insert into the silicon–hydrogen bond of the silane to form **46**. Subsequent elimination of the hydrosilylated product regenerates the catalyst (Scheme 10).

The NHC-stabilised parent-silyliumylidene ion $[NHC_2SiH]^+$ **11** shows unprecedented abilities in the catalytic hydroboration of CO_2, aldehydes, ketones, and pyridines with a catalyst loading of 10 mol%, as well as isocyanates with a catalyst loading of 1 mol% (Scheme 11).[52,54]

Furthermore, **11** catalyses the chemoselective *N*-formylation of amines using CO_2 and phenylsilane with a catalyst loading of 5 mol%. The reaction mechanism was studied using density-functional theory (DFT) calculations. The silyliumylidene sequentially activates first CO_2, then simultaneously phenylsilane and amines *via* transition state **47**. Following a dihydrogen elimination mechanism, formamides, siloxanes, dihydrogen gas, and the regenerated catalyst are formed (Scheme 12).[53]

Germyliumylidenes

The richest chemistry among tetryliumylidenes, in terms of the number of different reported examples, is that of germyliumylidenes. Over two decades before the silicon analogue, the cyclopentadienyl moiety was utilised by Jutzi's group to achieve the synthesis of the first isolable germyliumylidene ion **48** by reaction of decamethylgermanocene $(Cp^*)_2Ge$ with HBF_4.[29] Following this outstanding work, numerous germyliumylidenes have been reported. There are several synthetic strategies for the isolation of Ge(II)-derived monocations, most of them utilising neutral ancillary ligands (Fig. 4).

For example, *N*-heterocyclic carbenes (NHCs) have been used extensively to stabilise germyliumylidenes. Driess *et al.* reported the formation of bis-NHC stabilised chloro-germyliumylidene **49** by reacting $GeCl_2\cdot$dioxane with the corresponding ligand.[42] They also isolated parent-germyliumylidene hydride **50** stabilised by a bis(NHC)borate ligand.[37] By the addition of two equivalents of

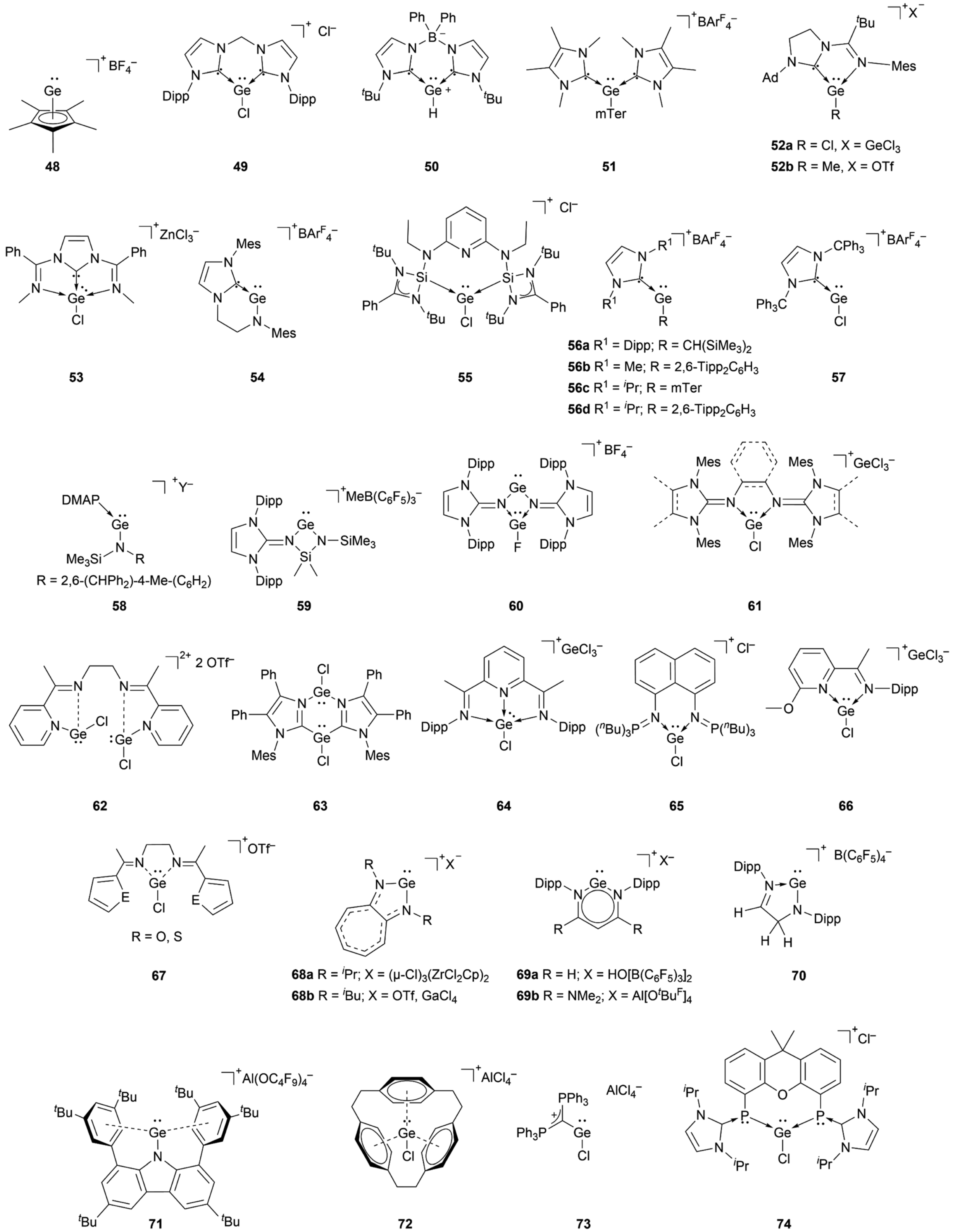


Fig. 4 Reported germyliumylidene ions.

NHC to an aryl chloro-germylene, our group could isolate the corresponding three-coordinate germanium cation **51**.[89]

Utilising an imino-*N*-heterocyclic carbene ligand, Kinjo *et al.* obtained chloro- and methyl-substituted germyliumylidene **52a,b**, respectively.[90,91] More recently, a diimino-carbene was utilised by

Nikonov *et al.* to stabilise the germyliumylidene **53**.[92] The groups of Glorius and Hahn reported the first intramolecularly NHC-stabilised germyliumylidene **54**.[93] Utilisation of a bis(*N*-heterocyclic silylenyl)pyridine pincer ligand led to the formation of chloro-germyliumylidene **55** reported by Driess *et al.*[94]

In 2016, it was demonstrated that a single NHC with adequate steric bulk together with a sterically more demanding substituent is also sufficient for germyliumylidene stabilisation. Thus, Rit, Aldridge, *et al.* isolated the two-coordinate germyliumylidene **56a** bearing a $CH(SiMe_3)_2$ substituent, stabilised by a Dipp-substituted NHC (Dipp = 2,6-diisopropylphenyl).[95] More recently, the same group reported NHC-stabilised germyliumylidenes **56b–d** with smaller NHCs, but larger substituents at the Ge centre.[96] Rivard *et al.* utilised the steric protection provided by the extremely bulky trityl (CPh_3)–NHC to prepare the chloro-germyliumylidene **57**.[97] Using a single Lewis base, Krossing, Jones, and co-workers reported the bulky amido germanium(II) monocation **58** stabilised by either weak intramolecular arene interactions or DMAP.[32]

NHIs can also be used for germyliumylidene stabilisation. By utilising Dipp–NHIs, we could isolate the four-membered amino(imino)germyliumylidene **59** and the germylene-germyliumylidene **60** borate salts, respectively.[98–100] Computational analysis indicated the latter to have a considerable bis(germyliumylidene) character. In 2020, we used bidentate bis(*N*-heterocyclic imine) ligands to stabilise the three-coordinate chloro-germyliumylidenes **61**.[80,101]

A similar approach to $[R–Ge:]^+$ stabilisation is the use of imino ligands. Recently, Majumdar *et al.* reported bis(chlorogermyliumylidene) stabilised within a flexible tetra-dentate 2,7-bis(2-pyridyl)-3,6-diazaocta-2,6-diene ligand **62** (ref. 102) and within bifunctional PNNP ligand frameworks.[103] In 2018, Kinjo *et al.* reported the bis(imidazolyl) supported chloro-germyliumylidene **63** in which the $Ge_2N_2C_2$ six-membered ring possesses two Ge–Cl units.[104] In 2012, the groups of Roesky and Stalke used the substituted Schiff base 2,6-diacetylpyridinebis(2,6-diisopropylanil) as Lewis base, which mediated the autoionisation of $GeCl_2$ to the germyliumylidene **64**.[38] The group of Driess isolated the bis(iminophosphorane) chelate stabilised chloro-germyliumylidene **65** similar to the structurally equivalent silyliumylidene **3**.[105] In 2013, Jambor *et al.* showed the synthesis of the chloro-germyliumylidene **66** by treating a neutral 2-[C(CH$_3$)=N(C$_6$H$_3$-2,6-^{i}Pr$_2$)]-6-(CH$_3$O)C$_6$H$_3$N ligand with $GeCl_2$, which spontaneously dissociates.[106] Majumdar and co-workers reported acyclic flexible diiminodi(furan) and diiminodi(thiophene) ligands in which the two imino nitrogen coordinating sites can stabilise the chloro-germyliumylidene ion **67**.[107]

Another type of germyliumylidene stabilisation is the use of monoanionic ligands that form cyclic compounds, such as the aminotroponiminate derivatives **68a,b** utilised by Dias *et al.* in 1997,[34] and, more recently, by the group of Nagendran in 2019.[49] Power *et al.* used a Dipp-substituted β-diketiminate ligand to form the two-coordinated germyliumylidene **69a**.[33] In 2020, Aldridge *et al.* utilised a β-diketiminate ligand bearing two NMe_2 groups to form the germyliumylidene **69b**.[70] The structurally similar Ge(II) cation **70** was isolated by Müller and co-workers by protonating the corresponding germylene.[108] Similar to silyliumylidene **2**, stabilised by arene coordination, Hinz showed the formation of the carbazolyl-substituted pseudo-one-coordinate germyliumylidene **71** by halide abstraction.[109]

Schmidbaur reported a related approach, for which he reacted cyclophane with one equivalent of $GeCl_2$ to form the [2.2.2]-paracyclophane chloro-germyliumylidene complex **72**.[35]

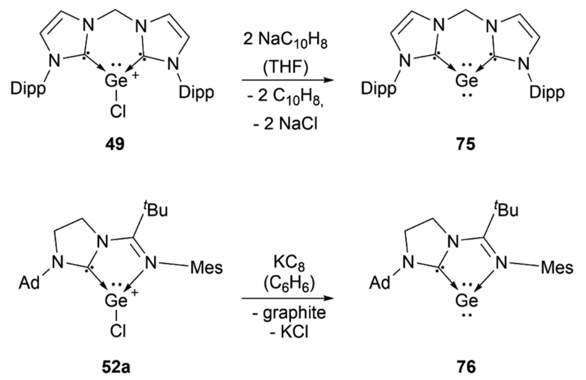
Two additional examples of methods to stabilise germyliumylidenes were provided by the groups of Alcarazo and Driess.[110,111] Alcarazo *et al.* isolated the two-coordinated chloro-germyliumylidene **73** stabilised by σ- and π-donation from a monodentate carbodiphosphorane;[110] while Hadlington, Driess *et al.* reported the bisphosphinidine stabilised chloro-germyliumylidene **74**.[111]

Reactivity of germyliumylidenes and their use in catalytic reactions

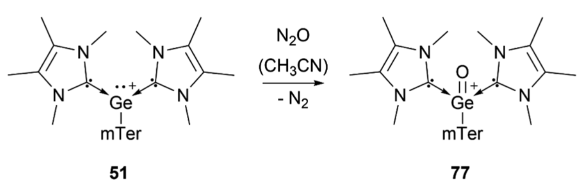
Several examples of the reactivity of germyliumylidene ions have been reported, while only a few catalytic applications are known. Similarly to the silicon analogue, the chloro-germyliumylidene **49** can be dehalogenated (by sodium naphthalenide) to form the cyclic bis(NHC) Ge(0) complex **75** (Scheme 13).[42] The reduction of **52a** with KC_8 leads to the formation of the corresponding germylone **76** (Scheme 13), similar to germyliumylidene **64**.[90,92] Germyliumylidene **51** reacts with N_2O to form the germa-acylium ion **77** (Scheme 14).[112]

By reacting it with $K_2[Fe(CO)_4]$, germyliumylidene **55** forms the germylone–iron carbonyl complex **78** stabilised by a bis(NHSi)pyridine pincer ligand (Scheme 15).[94]

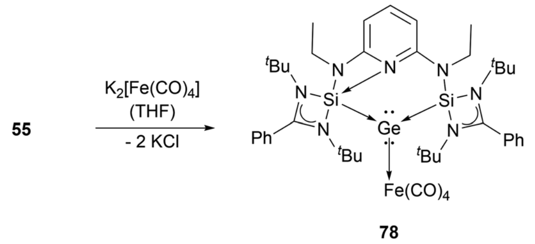
56a can undergo oxidative addition of dichloromethane (**79**), [2+1] cycloaddition with phenylacetylene (**80**), and formation of an imido complex (**81**) by reacting with Me_3SiN_3 (Scheme 16).[95]



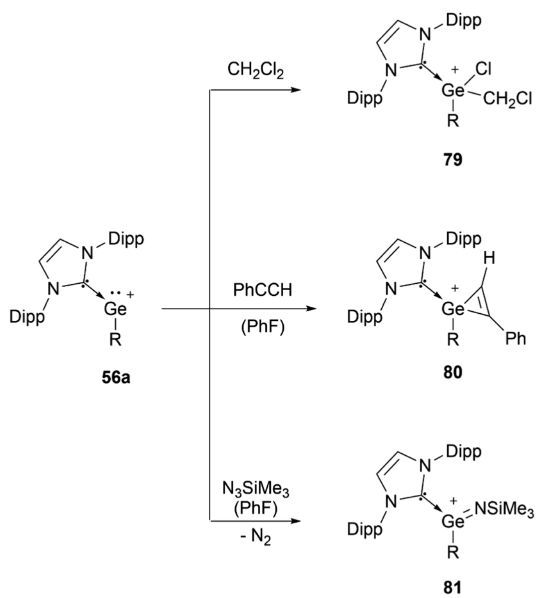
Scheme 13 Dechlorination of 49 and 52a to form the corresponding germylone.



Scheme 14 Formation of germa-acylium ion 77.



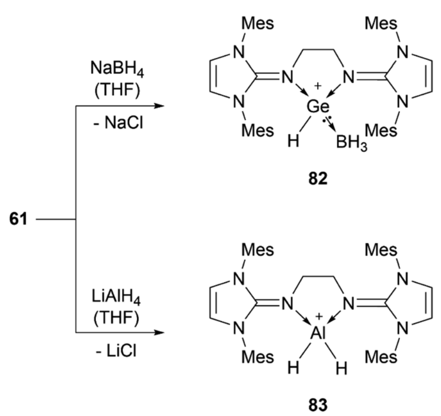
Scheme 15 Reaction of **55** with $K_2[Fe(CO)_4]$.



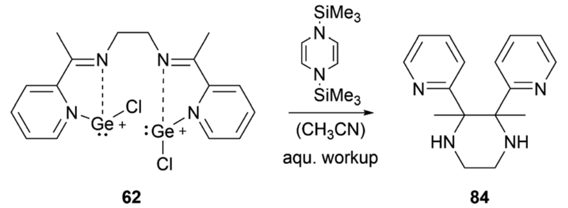
Scheme 16 Reported reactivity of **56a**.

56b can insert into the Si–H bond of phenylsilane.[96] Germylene-germyliumylidene **60** reacts with Me_3SiOTf to form a bis(triflate).[100] Bis(NHI)-stabilised chloro-germyliumylidene **61** can react with $NaBH_4$ to the hydridogermyliumylidene–BH_3 adduct **82** and with $LiAlH_4$ to the corresponding aluminium dihydride **83** (Scheme 17).[101]

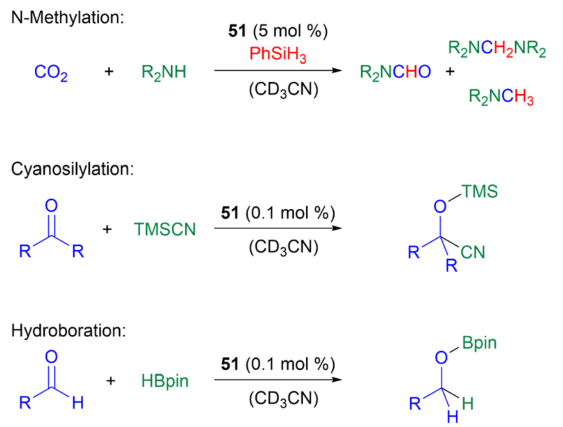
By using organosilicon reductants bis(chlorogermyliumylidene) **62** can undergo reductive cyclisation to



Scheme 17 Reactions of **61** with $NaBH_4$ and $LiAlH_4$.



Scheme 18 Reductive cyclisation of **62**.



Scheme 19 Multiple reactions catalysed by germyliumylidene **51**.

form the 2,3-di(pyridin-2-yl)-substituted piperazine **84** with high diastereoselectivity (Scheme 18).[102]

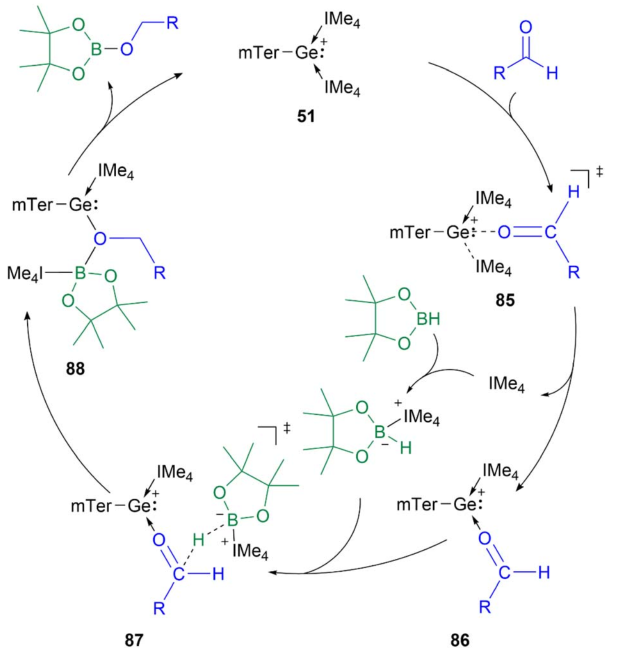
65 can undergo oxidation with elemental sulphur to form a chloro-germathionium salt.[105]

In contrast to its Si analogue, germyliumylidene **69b** does not undergo oxidative addition but reacts with $NH_2{}^tBu$ to form the simple adduct.[70] Two-coordinated chloro-germyliumylidene **73** can form a DMAP adduct and reacts with elemental sulphur to form a dimeric S=Ge double-bond species.[110]

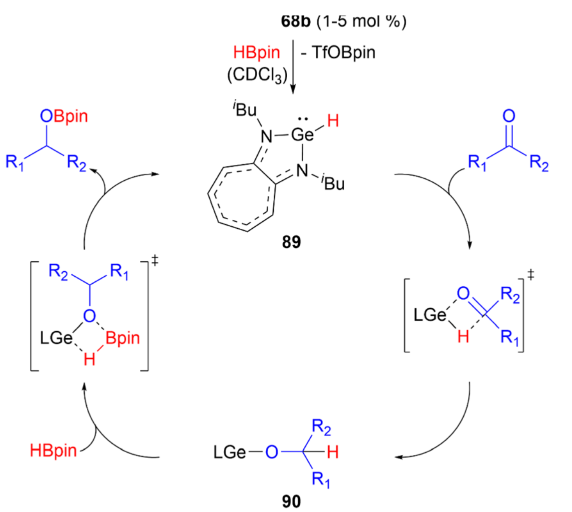
In terms of catalysis, germyliumylidenes have only rarely been applied in catalytic reactions. As already mentioned, **51** can form the germa-acylium ion **77**, which is used as a precatalyst for the germanium-catalysed *N*-functionalisation of amines with CO_2.[112] **51** can catalyse the reduction of CO_2 with amines and phenylsilane, the cyanosilylation of carbonyls with TMSCN, and the hydroboration of aldehydes with pinacolborane (HBpin) (Scheme 19).[50]

The proposed mechanism of the hydroboration catalysed by **51** shows the initial substitution of IMe_4 (IMe_4 = 1,3,4,5-tetramethyl-1*H*-imidazole-3-ium-2-ide) by an aldehyde to form **86** *via* transition state **85**. The subsequent B–H bond activation in HBpin is mediated by the previously released IMe_4. The formed adduct transfers the hydride to the carbonyl carbon in **86**, while the boron coordinates to the oxygen centre to form intermediate **88**. Subsequently, the IMe_4 re-associates with the Ge centre to regenerate the catalyst and obtain the hydroboration product (Scheme 20).

Germyliumylidene **68b** can act as a precatalyst in the catalytic hydroboration of aldehydes and ketones with



Scheme 20 Proposed mechanism for the hydroboration of aldehydes catalysed by **51**.



Scheme 21 Proposed mechanism of the hydroboration of carbonyls catalysed by **68b** (L = aminotroponiminate ligand).

pinacolborane.[49] In the proposed mechanism, **68b** reacts with HBpin to form the hydridogermylene **89** as the active catalyst. Subsequent reaction with the substrate *via* a four-membered heterocyclic transition state leads to formation of the germylene alkoxide intermediate **90**. Through σ-bond metathesis with HBpin the catalyst is regenerated and the hydroboration product is formed (Scheme 21).

Stannyliumylidenes

The chemistry of stannyliumylidenes $[R–Sn:]^+$ was commenced with the first isolation of $[Cp^*Sn:]^+[BF_4]^-$ **91**, reported by Jutzi and co-workers in 1980.[29] **91**, like the other first examples of tetryliumylidenes was stabilised by the hyper-coordinating pentamethylcyclopentadienyl. Since then, several stannyliumylidenes have been isolated by sterically demanding ligands (kinetic stabilisation) and/or electronically stabilising ligands based on heteroatom substituents. Halogen-substituted stannyliumylidenes $[X–Sn:]^+$ (X = halogen) are crucial intermediates since they have been employed as synthons for the isolation of novel low-valent tin compounds such as stannyliumylidene derivatives $[R'–Sn:]^+$ and Sn(0) through substitution reactions and halide abstraction, respectively.

Unlike germyliumylidene, where several examples of stabilisation using carbenes were reported, in the case of tin, there is only one reported mixed NHC–cAAC-substituted species **92**.[113]

Our group could isolate the *N*-heterocyclic imine (NHI) stabilised stannyliumylidenes **93**,[114] **94**,[101] and **95**.[115] Similar to germanium, neutral chelating ligands with nitrogen atoms have attracted attention for stannyliumylidene stabilisation due to the tunability of the steric and/or electronic nature by changing the substituents on the nitrogen atoms. Thus, iminopyridine **96**,[106] diiminopyridine (DIMPY) **97**,[38] and bis(α-iminopyridine) **98** (ref. 116) have been utilised.

Coordination by bisphosphinidene **99**,[111] mixed phosphine-imino **100**[117] and ferrocene-bridged *N*-heterocyclic carbene-phosphinidene (NHCP) **101** (ref. 118) ligands have been reported.

Stannyliumylidene ions stabilised by monoanionic ligands such as aminotroponiminate **102**,[119] β-diketiminate **103a,b**,[70,120] extremely hindered amide **104**,[32] bis(oxazoline) **105**,[121] organophophane oxide **106**,[122] and bulky carbazolyl **107** (ref. 109) were isolated. Schmidbaur *et al.* utilised a [2.2.2]–paracyclophane ligand to stabilise stannyliumylidene **108** (Fig. 5).[35]

Reactivity of stannyliumylidenes

The reactivity of stannyliumylidenes is scarcely studied, and only a few examples of their clearly identified transformations have been reported so far. The β-diketiminate stabilised stannyliumylidene **103b** forms, like its germanium congener, with $NH_2{}^tBu$ the simple adduct.[70] The organo-phosphane oxide substituted stannyliumylidene **106** reacts with elemental sulphur to form a heavier acylium ion intermediate, which upon head-to-tail dimerisation yields the corresponding dication **109** containing a four-membered Sn–S–Sn–S ring (Scheme 22).[122] This type of reactivity would be expected from heavy ketone derivatives. The NHI-substituted stannyliumylidene has been demonstrated to undergo transmetalation reactions. Thus, in the reaction of **94** with $NaBH_4$ in a mixture of THF and 1,2-difluorobenzene (DFB), selective transformation to form the bisNHI-stabilised dihydroboronium **110** was observed. The precipitation of elemental tin accompanied this process. Analogously, treatment of **94** with $LiAlH_4$ resulted in the formation of the aluminium dihydride **111**. In a similar fashion, transmetalation of **94** with an equivalent of $GeCl_2$·(dioxane) in acetonitrile at room temperature furnished the germyliumylidene cation **61** (Scheme 23).[101]

Like the NHI-substituted counterpart, NHCP-stabilised stannyliumylidene **101** could also be transmetalated. **101-I**

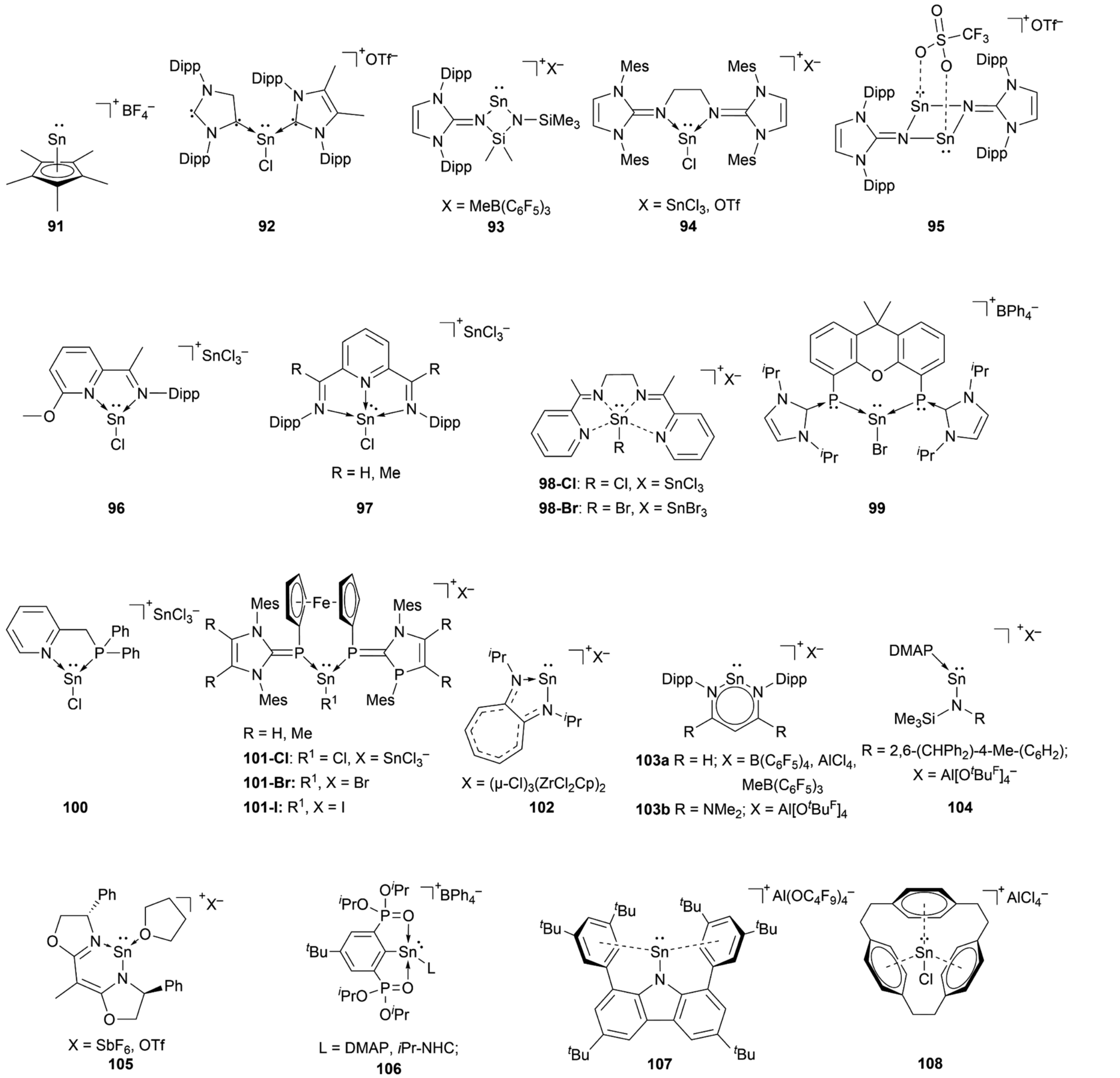
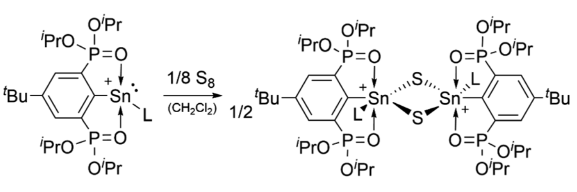


Fig. 5 Reported stannyliumylidenes.



106 109

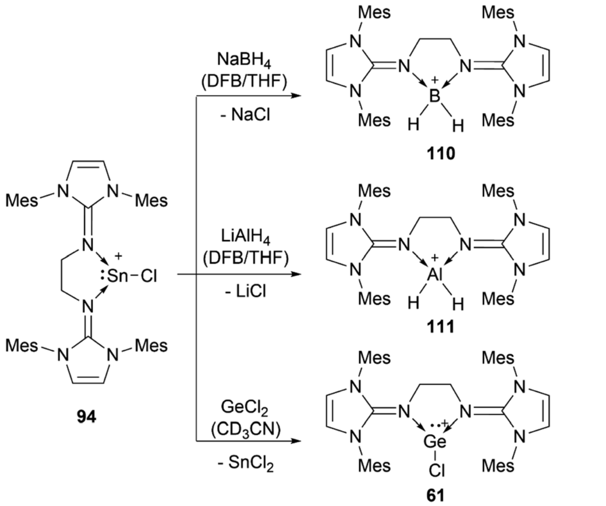
Scheme 22 Reaction of stannyliumylidene **106** with S_8 (L = DMAP).

reacts with CuCl to provide the transmetalation product **112** (Scheme 24).[118] In addition, chloro-stannyliumylidene **101-Cl** was utilised to transfer the Sn(II) synthon from the bisphosphinidene to a bisimine. Treatment of the bisNHCP-supported **101-Cl** with bisNHI in THF-d_8 gave a bisNHI-stabilised **94** and free bisNHCP (Scheme 25).[118]

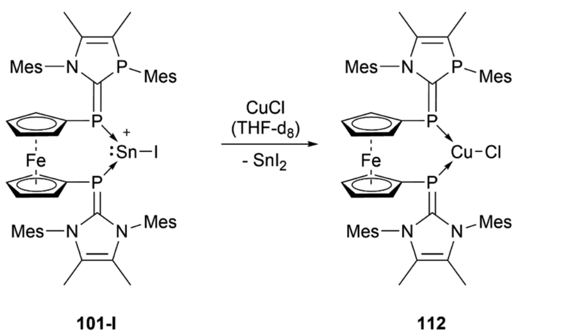
To date, to the best of our knowledge, except for the dinuclear tin complex **95** that was found to catalyze the hydroboration of aldehydes and ketones, no other examples of catalytic transformations that utilize stannyliumylidenes have been reported.[115]

Plumbyliumylidenes and catalytic reactions

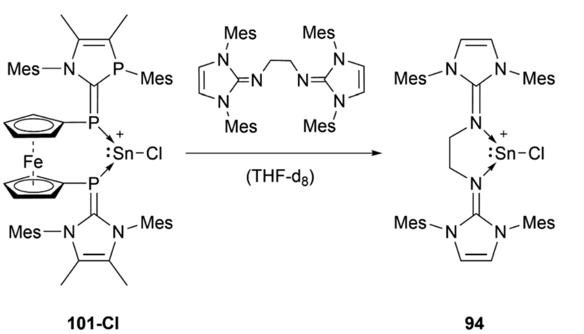
Compared to lighter congeners, the chemistry of the heaviest plumbyliumylidenes [R–Pb:]$^+$ remains underdeveloped. This can be attributed to the bad reputation of lead due to its



Scheme 23 Transmetalation reactions of stannyliumylidene **94** (DFB = 1,2-difluorobenzene).



Scheme 24 Transmetalation reaction of stannyliumylidene **101-I**.



Scheme 25 Sn(II) transfer reaction between bisNHCP and bisNHI.

toxicity. Like the lighter congeners, the first example of isolable plumbyliumylidene emerged from Jutzi's group. Accordingly, in 1989, Jutzi and Nöth reported **113**, a plumbyliumylidene stabilised by a pentamethylcyclopentadienyl ligand (Fig. 6).[30] Since then, several examples of isolable plumbyliumylidenes stabilised by bulky and strongly donating substituents have been reported. Power and co-workers succeeded in isolating the plumbyliumylidene **114**

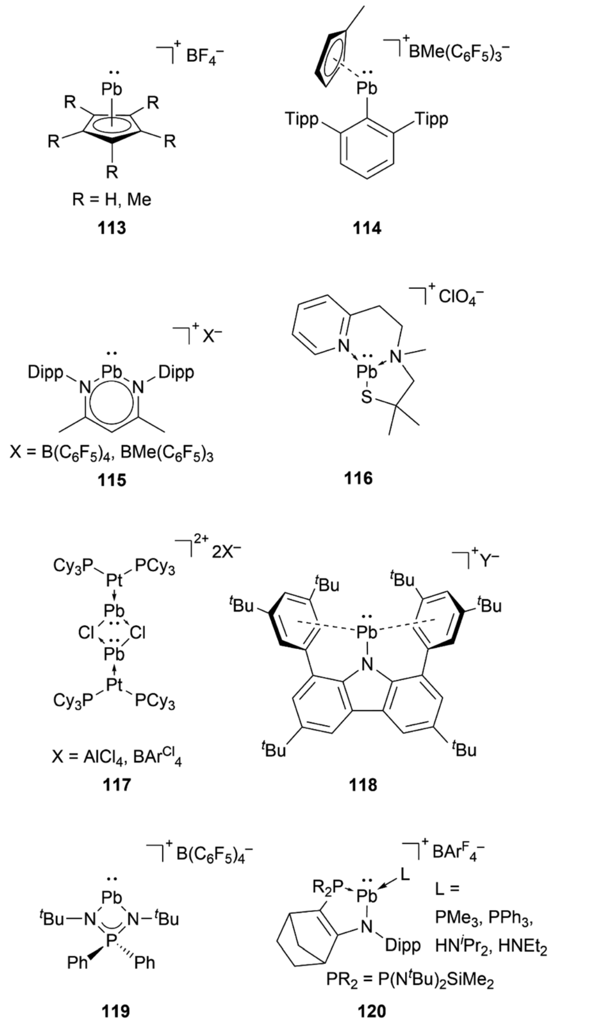
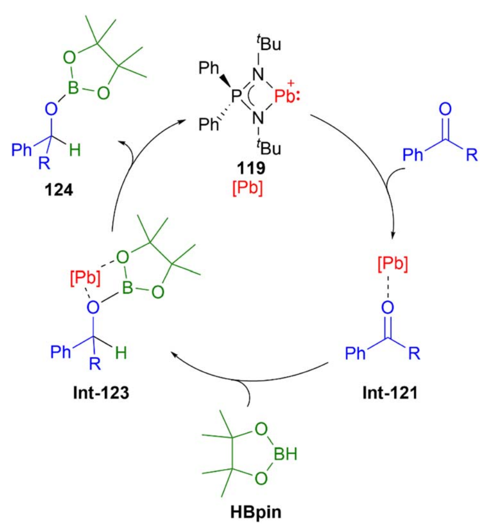
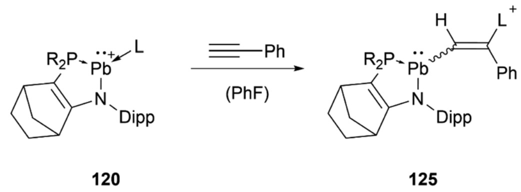


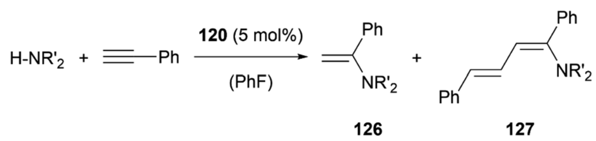
Fig. 6 Reported plumbyliumylidene ions (Cy = cyclohexyl; Y = = B(C$_6$F$_5$)$_4$ or Al(OC$_4$F$_9$)$_4$).



Scheme 26 Plumbyliumylidene-catalysed hydroboration of benzaldehyde (R = H) and benzophenone (R = Ph).



Scheme 27 Reaction of **120** with phenylacetylene (R_2P = $P(N^tBu)_2SiMe_2$, L = PMe_3, PPh_3, HN^iPr_2, $HNEt_2$).



Scheme 28 Catalytic hydroamination of phenylacetylene (R′ = ^{i}Pr, Et).

with a terphenyl group in 2004.[123] Subsequent to this, Fulton and co-workers reported the plumbyliumylidenes **115** that are stabilised by a β-diketiminate ligand.[120] In 2006, Godwin *et al.* obtained the three-coordinated N_2S(alkylthiolate) stabilised plumbyliumylidene ion **116**.[124] In addition, the coordination of platinum complex $Pt(PCy_3)_2$ (Cy = cyclohexyl) can stabilise the plumbyliumylidene **117**.[66] The carbazole-based bulky substituent that has been utilised in Si, Ge, and Sn analogues was also used to isolate the corresponding plumbyliumylidene **118**.[109]

Recently in 2022, Nakata and co-workers prepared the plumbyliumylidene **119** supported by an *N*,*N*′-di-*tert*-butyl-iminophosphonamide ligand. **119** is one of the two examples of a cationic low-coordination lead compound capable of acting as a catalyst.[51] In the proposed mechanism, which was also supported by quantum chemical calculation, the Lewis acidic **119** captures a carbonyl compound (benzophenone or benzaldehyde) to furnish the plumbyliumylidene–benzophenone complex **Int-121**-[$B(C_6F_5)_4$]. This reactive intermediate can further react with an HBpin (HBpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane) to form a four-membered intermediate **Int-123**. Subsequent reductive elimination of a boronate ester **124** regenerates the plumbyliumylidene **119**. The catalytic cycle proceeds at room temperature with a low for a main-group complex catalyst loading of 0.1 mol% (Scheme 26).

At around the same time, the group of Kato obtained the phosphine or amine stabilised plumbyliumylidene **120**, which readily reacts with phenylacetylene to the corresponding cationic vinylplumbylene **125** *via* alkyne insertion into the Pb–L bond (Scheme 27).[125]

In the case of amine stabilisation, plumbyliumylidene **120** can catalyse the hydroamination of phenylacetylene to give the corresponding enamine **126** in a regioselective manner (Scheme 28). The yield improves drastically, when using $HNEt_2$ instead of HN^iPr_2. The faster attack of amine on the activated acetylene bound to the cationic plumbylene prevents side reactions, which can deactivate the catalyst. Further reaction of **126** with Pb-activated phenylacetylene can lead to the formation of the corresponding diene **127**. The use of an excess of amine can improve the selectivity of the reaction to enamine **126**.[125]

Conclusions

Pioneering work by Jutzi and co-workers set the stage for the isolation and stabilisation of the unique E(II) cations (E = Si, Ge, Sn, Pb), which merge the electrophilicity of tetrylium cations with the ambiphilic character of tetrylenes.[29,30] The subsequent decades witnessed the isolation of various stable tetryliumylidene ions with different ligand stabilisation strategies. The following studies demonstrated promising reactivity of tetryliumylidene ions in various synthetic transformations. These developments expanded our understanding of tetryliumylidene capabilities and paved the way for their application in small molecule activation and catalysis. Despite these achievements, the chemistry of tetryliumylidenes remains largely underexplored. We hope that this review will highlight the topic and stimulate further research aimed at developing more tetryliumylidene-based systems capable of facilitating unique chemical transformations and fostering novel catalytic applications.

Author contributions

All authors discussed the concepts and contributed to the final manuscript. S. S. and S. F. performed literature reviews and wrote the original draft. A. K. carried out the quantum chemical calculations. A. K. and S. I. conceived the topic, strategised on content and information organisation, and edited the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

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