Recent advances of group 14 dimetallenes and dimetallynes in bond activation and catalysis

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Since the first heavy alkene analogues of germanium and tin were isolated in 1976, followed by West’s disilene in 1981, the chemistry of stable group 14 dimetallenes and dimetallynes has advanced immensely. Recent developments in this field veered the focus from the isolation of novel bonding motifs to mimicking transition metals in their ability to activate small molecules and perform catalysis. The potential of these homonuclear multiply bonded compounds has been demonstrated numerous times in the activation of \( \text{H}_2, \text{NH}_3, \text{CO}_2 \) and other small molecules. Hereby, the strong relationship between structure and reactivity warrants close attention towards rational ligand design. This minireview provides an overview on recent developments in regard to bond activation with group 14 dimetallenes and dimetallynes with the perspective of potential catalytic applications of these compounds.

Introduction

Much of the early advances in heavier group 14 chemistry stem from the vast richness of organic compounds and the motivation of mimicking those with the heavier congeners of carbon. Due to their ubiquity in hydrocarbons and simultaneous scarcity in heavier homologs, double and triple bonds are highly sought-after bonding motifs in Si, Ge, Sn and Pb chemistry. In the infancy of this chemistry, isolation of heavy group 14 multiple bonds proved to be a challenging endeavor. The consensus went even so far that the so-called “double bond rule”, according to which heavy homologues of carbon (and heavy p block elements in general) cannot form stable multiple bonds, was widely accepted.\(^1\)\(^-\)\(^3\) This rule was, however, unequivocally disproved with the first heavy alkene analogues of germanium and tin by Lappert in 1976, followed by West’s disilene as well as Brook’s silaethene and Yoshifuji’s diphasphene only 5 years later.\(^4\)\(^-\)\(^8\) With this, the search for novel, previously labeled “non-existent”, compounds sparked off. But it took almost two decades until the first heavy acetylene analogue, a diplumbyne\(^9\) by Power, was realized, followed by the completion of the series in subsequent years.\(^10\)\(^-\)\(^12\) With the isolation of more and more stable compounds, the motivation for novel bonding motifs was expanded by the incentive to mimic transition metals in their ability to activate small molecules and perform catalysis.\(^13\) Up until recently, this kind of reactivity was thought to be reserved almost exclusively for d-block elements. Low valent main-group species do, however,

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allow comparison to open-shell transition-metal complexes due to possession of donor/acceptor valence orbitals with small energy gaps. Dimetallenes and dimetallynes combine the reactivity of electron rich multiple bonds and the unique electronic properties of low valent group 14 compounds. Moreover, as dinuclear complexes they could possibly benefit from cooperative effects of two tetrel atoms. This combination makes them promising candidates for the activation of enthalpically strong small molecules. Power’s seminal review in 2010 highlighted at first the great potential of main-group compounds in that regard. There is, however, significant progress being made in that regard, so much so that aluminium compounds.

A particular emphasis is placed on low-valent silicon and bismetallyenes. Heavy alkene and alkyne analogues as well as interconnected molecule activation, bond activation and catalytic applications of group 14 compounds with homonuclear multiple bonds, i.e. heavy alkene and alkyne analogues as well as interconnected bismetallyenes.

**Bonding nature**

Dimetallenes and dimetallynes are compounds of the form $R_2E=ER_2$ and $RE=ER$, where $E$ is a heavier group 14 element ($E = Si, Ge, Sn, Pb$). In their formula, they are the direct descendants of alkenes and alkydes. However, they manifest not as planar $E_2H_4$ (like ethylene) or linear $E_2H_2$ (like acetylene), but as a trans-bent structure. The reason for this drastic structural difference stems from an increased size difference of the valence orbitals leading to a less effective hybridization of the heavier elements. To illustrate the resulting deviation in bonding, parent group 14 multiple bonds can be seen as an interaction of two monomeric ‘$H_2E$’ or ‘$HE$’ units, respectively. While methylene ($H_2C$) is a ground state triplet ($\Delta E_{ST} = -14.0$ kcal mol$^{-1}$) and therefore is capable of forming a classical planar double bond (Fig. 1a), heavier tetrylenes ($H_2E$) almost exclusively occupy a singlet ground state ($\Delta E_{ST} = 16.7$ kcal mol$^{-1}$ (Si), 21.8 kcal mol$^{-1}$ (Ge), 24.8 kcal mol$^{-1}$ (Sn), 34.8 kcal mol$^{-1}$ (Pb)). In triply bonded compounds in consequence, alkydes possess sp-hybridized carbon atoms in the quartet ground state that result in three covalent bonds and a linear structure (Fig. 2a). In dimetallynes the doublet ‘$HE$’ moieties are not capable of forming covalent triple bonds. In both cases, significant Pauli repulsion between the occupied orbitals or the excitation into the singlet or quartet state, respectively, would need to be overcome in order to form a standard E–E multiple bond. Therefore a double donor–acceptor interaction is energetically favored in which each partner of the multiple bond donates from their lone pair of electrons into the vacant p orbital of the other (Fig. 1b and 2b).

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Shigeyoshi Inoue studied at the University of Tsukuba and carried out his doctoral studies under the supervision of Prof. Akira Sekiguchi, obtaining his PhD in 2008. As a Humboldt grantee and a JSPS grantee, he spent the academic years 2008–2010 at the Technische Universität Berlin in the group of Prof. Matthias Drieß. In 2010, he established an independent research group within the framework of the Sofia Kovalevskaja program at the Technische Universität Berlin. Since 2015 he has been on the faculty at the Technische Universität München (TUM). His current research interests focus on the synthesis, characterization, and reactivity investigation of compounds containing low-valent main group elements with unusual structures and unique electronic properties, with the goal of finding novel applications in synthesis and catalysis. A particular emphasis is placed on low-valent silicon and aluminium compounds.
distortion model. The mixing of $\sigma$ and $\pi$ orbitals of suitable symmetry leads to distorted orbitals and therefore to the observed morphed structures.\(^{17,26,27}\)

As in the case of dimetallenes, the donor–acceptor type interactions in dimetallynes show fading stability when going down the group (Fig. 4). The trend starts with disilynes, that show strong triple bond character with short Si–Si bonds (Si$_2$H$_2$, Si–Si$_\text{calc.}$ = 2.1 Å\(^*\)) and relatively big H–Si–Si angles (Si$_2$H$_2$$_\text{calc.}$ ~ 125° \(^{31,32,33}\)) and ends with diplumbynes that are almost exclusively represented in the form of bisplumbylenes – singly bonded compounds with two lone pairs of electrons, having long Pb–Pb distances (Pb$_2$H$_2$, Pb–Pb$_\text{calc.}$ = 3.2 Å\(^*\)) and high trans-bent angles near 90°\(^*\).\(^{14}\) In between, the bonding characteristics for Ge- and Sn-compounds are hard to be defined precisely and therefore need to be discussed in every case using theoretical considerations and structural characteristics.\(^{26,29,35}\)

Therefore, different resonance structures with varying weighting contribute to the bonding motifs of dimetallynes (Fig. 4). Beyond the pure understanding of bonding characters, the described effects influence strongly the reactivity that is observed and expected for heavier group 14 multiply bonded compounds that make them so attractive for small molecule activation to achieve full catalytic cycles and applications.

### Synthesis and ligand design

The synthesis of E–E multiple bonds has proven to be quite diverse. Scheme 1 and 2, however, show the main synthesis pathways for dimetallenes and dimetallynes, respectively. Reductive dehalogenation of di- (R$_2$EX$_2$) or trihalometallanes (REX$_3$), dimetallanes (X$_2$REEX$_2$), dimetallynes (XREEXR), or metallynes (XRE) using reductive agents (red.) such as KC$_8$,\(^{16,39,54-58}\) metal naphthalenides,\(^{59,60}\) and [[MesNaenac]Mg]$^+$ (MesNaenac = (MesNCMe)$_2$CH)$^{61}$ is the central motif in isolation of these compounds.

![Scheme 1](image)

**Scheme 1** Possible synthesis routes for the isolation of dimetallenes. E = Si, Ge, Sn, Pb; R = stabilizing ligand; X = halogen; red. = reductive agent.
Consecutive dimerization takes place for monomeric starting materials. Ligands are mainly applied before reduction but could also be applied throughout the reduction process. Disilene 12 (Fig. 8), for example, is synthesized from N-heterocyclic imine (NHI)-stabilized NHI-SiBr₃ and KSi(SiMe₃)₃, transferring the silyl ligand. In dimetallene chemistry the elimination of H₂ is also known to form triply bonded tin and lead compounds, starting from halogenated XRE via an X/H exchange using hydride sources like LiAlH₄ or DIBAL-H. Since it can be seen as the reverse of H₂ via nated XRE chemistry the elimination of H₂ is also known to form triply bonded tin and lead is given particular attention in this contribution although it is not yet applied for all heavier group 14 elements.

The strength and overall nature of multiply bonded group 14 compounds are not to be carved in stone, rather they can be greatly influenced by the applied ligands. The steric demand of the ligand system is crucial to achieve kinetic stabilization of E–E multiple bonds. If this stabilization is not provided, thermodynamic driving forces could lead to favored di- and oligomerization or isomerization as predicted by quantum chemical calculations.

Looking at the plausible structures of Si₂H₂ (Fig. 5, A–C), for example, reveals no minimum for A, but a non-stable minimum for B. Isomerization of B, as a consequence of a deficient kinetic stabilization, would lead to structure C or bridged structures that are thermodynamically more stable; with double H-bridging being a global minimum in this system.

That said, recent accounts have highlighted the importance of London dispersion force (LDF) energies that contribute via dispersion forces between hydrocarbon groups. While these parts of van der Waals forces have only a minor influence on themselves, they add up in large ligands to contributions that have an observable impact on the stability of kinetically stabilized complexes. Fig. 6 shows selected examples of dimetallenes and dimetallynes that are stabilized by sterically encumbered aryl ligands that achieve primarily kinetic stabilization.

If one goes beyond kinetic stabilization and also brings in thermodynamic influence on the system, silyl ligands like SiBu₃, Si-Pr₂Me, and Si-Pr(CH(SiMe₃)₃)₂ strengthen and shorten the E–E bond in dimetallenes and dimetallynes by decreasing the singlet–triplet gap or doublet–quartet gap of the element centers, due to stabilization of the excited singlet and doublet states, respectively. Fig. 7 shows examples of silyl stabilized dimetallenes and dimetallynes.

Boryl ligands such as 9-BBN or B(NArCH)₂, in contrast (Fig. 8), incorporate electron accepting properties into the
ligand sphere, due to the vacant p orbital of the boron center. These ligands contribute π-acceptor and σ-donor capabilities, which can for example lead to π-conjugation between the disilene double bond and the boron in compound 11. 57,86–88

N-Donor ligands like amino, amide or NH2 do have a diverse influence on E–E multiple bonds. While in dimetallenes they result in a pronounced multiple bond character like for 10, in combination with silyl ligand Si(SiMe3)3, the NHI ligand in 12 causes a stretching, twisting, and trans-bending of the double bond (Fig. 8). A highly twisted and trans-bent E=E bond can lead to destabilization of the HOMO orbital due to reduced πE–πE orbital overlap, resulting in a decreased HOMO–LUMO energy gap. In the case of amido ligands, (SiR3)ArN (dimetallenes 13) and (SiR3)BoN (dimetallenes 14, Bo = boryl) reduce the multiple bond character of the resulting digermyne and distannyne tremendously, and this results in a very high bismetallylene character (Fig. 8). Utilization of additional intramolecular donors and chelating ligands has resulted in the isolation of dimetallenes in the form of interconnected bismetallylenes, as displayed in examples 15–18 in Fig. 9.

Small molecule activations of dimetallenes and dimetallynes/bismetallylenes

While the number of stable dimetallenes and dimetallynes steadily expands, accounts of reactivity towards small molecules and other bond activation reactions are relatively scarce. To date, bond activation via insertion into the multiple bond or various addition reactions with small molecules have been achieved a number of times. What seems to be challenging is firstly, the activation of a molecule without breaking the E–E bond altogether and secondly, achieving reversibility of the reaction, i.e. regeneration of the multiple bond as a key step for any future catalytic application. To our knowledge, there are no examples of catalytic reactions performed by a group 14 dimetallene to date and bond activation is mostly reserved for disilenes, whereas dimetallynes and bismetallylenes show a broader range of reactivity that peaks in the first complete catalytic cycle found for the Tbb-substituted digermyne 4d in 2018.18 The adjacent reactivity of monomeric tetrylene compounds, low valent hydrides and other low valent group 14 species have been discussed in a number of reviews,52,104–109 but are beyond the scope of this account. Although there is noteworthy progress in bond activation of functional groups as well,52,104–109 in the following paragraphs only the activation of classic small molecules such as H2, NH3, CO2, CO, alkenes and alkynes are discussed in further detail.

H2 activation

The activation of hydrogen is an important preliminary experiment on the way to industrially relevant catalytic chemical reactions like hydrogenations of unsaturated hydrocarbons, to name only one. H2 activation was achieved by only a few disilenes up till now, with the first account being the selective formation of the trans-hydrogenation product 19 under mild conditions starting from NHI-stabilized disilene 12 (Scheme 3).62 DFT calculations suggest a concerted mechanism which is enabled by the relatively easy rotation along the double bond due to the highly twisted and trans-bent structure and the staggered ligands.

![Scheme 3](image-url)
Additionally, in 2018 Iwamoto reported that the treatment of 1-amino-2-boryldisilene 11 with dihydrogen at room temperature resulted in concomitant formation of trihydridodisilane 20 and hydroborane (Scheme 4) via the initial cleavage of the Si–B bond as a first step.\(^{57,58}\) Since theoretical calculations suggested an overpowering effect of the \(\pi\)-accepting boryl moiety on the polarity and HOMO–LUMO gap (and therefore reactivity) of the Si═Si bond, similar disilenes, each with either only the boryl or amino ligand attached respectively, were also treated with H\(_2\). It turned out that the interaction of the low lying empty 2p boron orbital with the \(\pi^*\)(Si═Si) orbital is essential for the reactivity. While the monoboryldisilene 2,2,5,5-(SiMe\(_3\))\(_4\)-C\(_4\)H\(_4\)Si═Si(Bo) Tip (Bo = 9-borabicyclo[3.3.1]-nonane) (11a) reacts with H\(_2\) in a similar manner as 11, the monoaminodisilene N-(Ad)-5,5-(SiMe\(_3\))\(_2\)C\(_4\)H\(_4\)Si═Si(i-Pr)Tip (11b) is not capable of activating dihydrogen even at elevated temperatures. Interestingly, the conversion of H\(_2\) with 11a takes significantly longer compared to 11, suggesting that the amine moiety does contribute marginally to the reactivity of the compound despite an almost negligible destabilization of the HOMO energy in 11 according to computational studies.\(^{85}\)

Amongst activation products, the hydrogen binding modes have an impact on the hydrogen-transfer ability of those complexes, if a catalytic cycle is intended. In this respect, dimetallynes show a variety of hydrogen binding modes that – unfortunately – lack reliable selectivity in most cases. However, the number of H\(_2\) activating dimetallynes and bismetallynes is limited to a few examples featuring aryl and amide stabilization. In the first report from 2005, Power treated 5a (Ar'GeGeAr') with H\(_2\) at room temperature and atmospheric pressure (Scheme 5).\(^{110}\) In a product mixture they found the digermene 21, digermene 22 and germane 23, shown in Scheme 5. This account presents the first example of H\(_2\) activation by using a molecular main-group species without a catalyst that is estimated to be due to a singlet biradical character of the ground state of 5a. The heavier analogue 5b (Ar'SnSnAr') was shown in 2018 to activate dihydrogen in a reversible form (Scheme 5, bottom) to produce hydrogen bridged 24.\(^{111}\) The addition of H\(_2\) proceeds at room temperature, whereas it is released again by heating to 80 °C. A tremendous connection between ligand nature and size and reactivity could be shown by reacting slightly bigger distannynes 5g with H\(_2\) under ambient conditions. In this case the reaction brings forth the non-bridged hydrogenation product 25.\(^{111}\) For amide ligands H\(_2\)-activation has been proven possible for bisgermylene 13a and 13b and bistannylene 13c each with high selectivity.\(^{61,92,93}\) While 13a reacts quantitatively with 1 bar of H\(_2\) at ambient temperature to hydridogermylene N\(_2\)GeGeHN\(_2\) (27), the slightly modified ligand N\(_2\) in 13b leads, under similar conditions, to the hydrido-digermene N\(_2\)HGeGeHN\(_2\) (26) (Scheme 6, top). Attempts to form di- or tri-hydrogenation products by applying harsher conditions failed in both cases. In order to understand the differences in the reaction mechanism that result in the formation of the two diverging products, theoretical reaction profiles were explored, leading to the conclusion that NHGeGeHN is formed in both reactions, followed by a rearrangement in the case of 27 due to a low activation barrier and higher thermal stability.\(^{111,112}\) In 2014, the reaction of 13c with H\(_2\) was explored, yielding the third product motif N\(_2\)Sn(\(\mu\)-H)\(_2\)SnN\(_2\) (28) (Scheme 6, bottom).

NH\(_2\) activation

The splitting of N–H bonds is especially interesting in regard to the activation of ammonia in order to facilitate transfer reactions to olefins or arenes. Breaking this strong bond is still challenging, even for transition-metal complexes. Still, some group 14 dimetallene compounds have shown the ability to perform hydroamination reactions.

In the first example, a tetrasiabuta-1,3-diene (1f), each double bond reacts with ammonia in a 1,2-addition reaction, yielding six-membered ring compound 30. This is somewhat surprising, since the simpler Tipp\(_2\)Si═SiTipp\(_2\) congener (1c) with only one Si═Si double bond, is inert towards NH\(_3\), indicating the increased reactivity of the conjugated double bonds (Scheme 7).\(^{116}\)

Similarly, Scheschkewitz could demonstrate an increased reactivity of the Si═Si bond by substituting one ligand moiety...
with a TMOP ligand (1e), resulting in a prominent polarization of the Si–Si bond and enabling a regioselective 1,2-addition of ammonia to addition product 29 (Scheme 7).117

In a similar manner to the 1,2-addition of hydrogen to the iminodisilene 12, an analogous trans-addition product with NH3 was reported more recently.93 The ammonia reaction to 31 progresses at a much lower temperature (−78 °C) which can be explained by the significantly lower energy barrier of the anti-addition of NH3 (7.7 kcal mol−1) compared to that of H2 (15.6 kcal mol−1). When the reaction is performed at room temperature, the formal oxidative addition product 32 of the corresponding silylene with NH3 is observed (Scheme 8).

CO2 activation

The activation and reduction of CO2 has attracted much attention over the last few decades, because it could make it possible to use this abundant gas, which is a critically discussed greenhouse gas, and transform it into value-added chemicals such as carbon monoxide or higher hydrocarbons.118 In main-group chemistry the number of examples of CO2 activations has increased over the years but is still limited compared to other reactivities.119 Up till now, the aforementioned iminodisilene (12) and the supersilyl substituted disilene, (Si(Ph3))2SiSi(Ph(Ph3)) (7) showed reactivity towards the molecule.

Treatment of 12 with CO2, again has different outcomes depending on the reaction temperature. Either selective adduct 33 is formed at −78 °C or a mixture of products including the novel five-membered silacycle 34, which could be identified by stepwise and partial oxidation of the double bond with N2O as well as O2 and comparison of NMR data (Scheme 9).94 The disilene 7 activates CO2 in a [2 + 2] cycloaddition reaction as shown in Scheme 10 to obtain 35.85

For classical dimetallynes no activation of CO2 is known, however, examples involving interconnected bismetallylenes are reported. Upon exposure of a toluene solution of 13a to CO2 at −70 °C the reaction proceeds via the intermediate N1GeO2-GeN1 (36) and ends with the bisgermylene oxide N1GeOGeN1 (36) as shown in Scheme 11.96 Analysis of the head space gas reveals the release of CO. Theoretical analysis of the reaction profile suggests a three step mechanism, in which CO2 connects through a side-on approach to one or both germanium centers. Via Ge–Ge bond rupture and rearrangement, intermediate 36 is formed, which yields product 36 after elimination of one CO molecule.119 The analogue reaction with CS2 afforded N1GeSSGeN1, respectively.

Another deoxygenation of CO2 was reported by Baceiredo and Kato in 2011.97 In detail, three molecules of CO2 are deoxygenated concomitant with the formation of three Si–O–Si units upon Si–Si bond rupture. In a subsequent step the carbonate unit is formed via insertion of one additional CO2 molecule into a previously built Si–O bond, resulting in product 37 (Scheme 12). The high reactivity of the bissilylene is clearly indicated by the rapid reaction with CO2 that is completed upon mixing of the reactants.

Apart from the singly bonded and lone pair exposed structure of the bissilylene, a peculiar ligand effect also acts on the
using a Tip substituted disilenide (Scheme 14, top). One year later the monomer 40 could be trapped using Et₂O·B(C₆F₅)₃ (Scheme 14, bottom).

**N₂O activation**

Nitrous oxide is one of the classic small molecules, however, its activation is easy enough for N₂O to find application as a mild oxidant in synthetic chemistry. Utilization of this readily available industrial waste gas as a mono oxygen transfer agent offers the advantage of producing only greenhouse-neutral and non-toxic N₂ as a by-product.¹²⁶

Reaction of iminodisilene 12 with N₂O produces three-membered ring oxadisilirane 41 in cis confirmation (Scheme 15). When exposed to oxygen, in contrast, a dioxadisiletane with a Si₂O₂-central 4-membered ring is formed via the trans analogue of 41 as an intermediate.

The first example of a disilene that produces both the cis (42b) and trans (42a) isomers of a dioxadisiletane upon reaction with N₂O is trans-[(TMS)₂N[η²-Me₅C₅]Si]=Si[η²-Me₅C₅]N(TMS)₂ (10), displayed in Scheme 16.¹²⁷ DFT calculations revealed the two isomers to be isoenergetic, with the cis counterpart 42b being slightly higher in energy by 3.3 kcal mol⁻¹.

Depending on the attached ligands, three reaction pathways of the addition of N₂O to a Si=Si bond likely take place according to a recent theoretical study.¹²⁸ The first one, starting with dissociation of the double bond into silylene monomers followed by a nucleophilic attack of N₂O and concluding with the dimerization of the resulted silanone intermediates, affords cis- and trans-products. This pathway is favored by substituents without a lone pair of electrons, leading to a more unstable disilene and therefore facilitating the subsequent attack of N₂O. Alternatively, N₂O reacts directly with the double bond either as a nucleophile or an electrophile. Nucleophilic N₂O leads to an end-on attack whereas electrophilic N₂O interacts with the...
disilene in a side-on fashion.\textsuperscript{128} Within dimetallene chemistry the activation of N\textsubscript{2}O is reported with several outcomes. For bissilylene 13a, the reaction proceeds with a simple oxygen transfer that breaks and inserts into the Ge–Ge bond (Scheme 17).\textsuperscript{109} In this regard, it is an alternative synthetic pathway to yield the CO\textsubscript{2} activation product 36.

In contrast, reaction of N\textsubscript{2}O with digermyne 5a that bears significantly higher multiple bond character produces a Ge\textsubscript{2}O\textsubscript{3} ring with two exocyclic hydroxo groups (43) (Scheme 18).\textsuperscript{129} Theoretical calculations suggest that the reaction proceeds via a radical mechanism that forms a peroxo bridge, followed by subsequent deoxygenation of additional N\textsubscript{2}O molecules. Formation of the terminal hydroxo groups in 43 could stem from dehydrogenation of solvent molecules.

Base-stabilized bissilylene 17a consumes three equivalents of N\textsubscript{2}O at ambient temperature and forms the eight-membered Si\textsubscript{2}O\textsubscript{2}-ring compound 44 upon dimerization of two bissilanone moieties (44\textsuperscript{a}) induced by the polar Si=O double bonds (Scheme 19). The reaction mechanism is proposed to proceed via primary insertion of an oxygen atom into the Si–Si bond (44\textsuperscript{a}) and subsequent oxygenation to 44\textsuperscript{b}. Each bissilylene unit consist of a Si[μ-O\textsubscript{2}]Si core. Reaction with t-BuNCO affords the same product (44).

### Cycloaddition of alkenes and alkynes

Cycloadditions of dimetallenues with unsaturated hydrocarbons and other multiple bonds are often observed. In particular, the reactivity of disilenes and digermines with alkenes, alkynes, C≡N, C=O and other heteroatom multiple bonds has been reported, resulting in otherwise difficult to obtain ring compounds.\textsuperscript{130,131,132,133} For the reactions of disilenes with terminal alkenes and alkynes, a radical pathway with a stepwise mechanism can be proposed.\textsuperscript{134,135} Baines showed, for example, that the reaction of tetrasmethylsilene (1a) with trans-d-styrene resulted in a 7 : 3 diastereomeric mixture of the cis and trans [2 + 2] cycloaddition products 45 (Scheme 20), indicating a bond rotation of the intermediate 45\textsuperscript{a}, yielding the cis isomer.\textsuperscript{137}

Similarly, the cycloaddition reaction of tetrasmethylgermene (1b) with a cyclopropylcarbinyl probe suggests the formation of several intermediate diradicals (46, 46\textsuperscript{a}) resulting in various cyclization products of which 46a and 46b are shown (Scheme 21).\textsuperscript{134}

Moreover, two linker-bridged distannenes showed the ability to activate terminal alkynes at ambient temperature. The reaction of 3 with trimethylsilylacetylene and phenylacetylene occurs via a formal [2 + 2] cycloaddition reaction. The gradual reverse reaction of the isolated product 47 could be observed in a C\textsubscript{6}D\textsubscript{6} solution, confirmed by NMR experiments (Scheme 22, top).\textsuperscript{73} Other distannenes like 3a with similar backbones (Scheme 22, bottom) are also able to perform cycloaddition with alkynes to exemplified product 48, but show no reversibility or only with some alkynes with no obvious correlation with the respective ligand structures. In all cases, the Sn=Sn bond lengths do not change significantly upon cycloaddition from 2.729–2.784 Å before cycloaddition to 2.744–2.767 Å after.\textsuperscript{73} Cycloaddition reactions of dimetallenues are often not reversible and the reactivity of stable distannenes with terminal alkynes has only been observed a handful of times. To our knowledge, the only example of a reversible cycloaddition to a digermene is the [2 + 2]-cycloaddition of acetonitrile, which can be reversed at
elevated temperatures.\textsuperscript{104} Dimetallynes – like many multiply bonded compounds – are also prone to cycloaddition reactions. Therefore, a broad variety of examples are known today.

Multiple studies have shown that the cycloaddition of olefins follows a certain pathway.\textsuperscript{43,46,48} Within two addition and rearrangement reactions dimetallynes are able to form 4-membered cycloadducts and upon addition of an extra alkene molecule, 3-membered cycloadducts also (Scheme 23). The product distribution of those reactions depends on reaction conditions as well as on the central group 14 element and the choice of ligand.

In a similar fashion, reactions with alkynes show a common reaction mechanism.\textsuperscript{47,49,51} Upon addition of two alkyne molecules either 1,2-ditetrel-benzene or 1,4-ditetrel-benzene are isolated as stable products. In case of a 1,4-ditetrel-benzene a third alkyne can be added resulting in 1,4-ditetrelbicyclo[2.2.2]octa-2,5,7-triene derivatives (Scheme 24). A highly regarded report about olefin cycloaddition on tetrel triple bonds was published by Power in 2009.\textsuperscript{138} It describes the reversible ethylene addition to distannyne \(5b\) that proceeds readily at room temperature to form the cycloadduct \(49\). Under reduced pressure both ethylene molecules dissociate and distannyne \(5b\) is recovered. Theoretical calculations point out a rare combination of electronic, steric and thermodynamic effects that result in considerable weak Sn–C cycloadduct bonds. Noteworthily, the reactivity with ethylene is shared by the sterically more protected distannyne \(\text{Ar}^0\text{GeGeAr}^0\)\textsuperscript{5b} (\(\text{Ar}^0\text{Pr}^3\text{Ph} = \text{C}_9\text{H}_2\text{Cl}_{2.5.6}(\text{C}_6\text{H}_3\text{Cl}_{2.5.6}\text{Pr}^3)_{2.5.6}\)), whereas the reversible addition of norbornadiene (nbd) to \(50\) can be obtained exclusively by using \(5b\) (Scheme 25).

In 2002 Power had already accomplished activation of the alkene 2,3-dimethyl-1,3-butadiene with digermyne \(5d\).\textsuperscript{139} Upon addition of three diene molecules the previously unknown ‘bridged’ reaction product \(51\) was furnished. Two years later, the same group reported on a cycloaddition of \(5a\) (\(\text{Ar}^*\text{GeGeAr}^*\)) with SiMe\(_3\)CCH and diphenylacetylene (Scheme 26, right).\textsuperscript{39} While for diphenylacetylene only one addition takes place forming product \(52\), in case of the sterically less demanding trimethylysilylacetylene two molecules can be added and form the

\textbf{Scheme 23} General reaction pathway for cycloaddition reactions of dimetallynes with olefins exemplified by ethylene. \(E = \text{Si}, \text{Ge}, \text{Sn}; R = \) stabilizing ligand.

\textbf{Scheme 24} General reaction pathway for cycloaddition reactions of dimetallynes with alkynes exemplified by acetylene. \(E = \text{Si}, \text{Ge}, \text{Sn}; R = \) stabilizing ligand.

\textbf{Scheme 25} Reversible cycloaddition of ethylene to distannyne \(5b\). \(\text{Ar}^* = \text{C}_9\text{H}_3\text{Cl}_{2.5.6}(\text{C}_6\text{H}_3\text{Cl}_{2.5.6}\text{Pr}^3)_{2.5.6}\), nbd = norbornadiene.\textsuperscript{138}

\textbf{Scheme 26} Cycloaddition reactions of digermyne \(5a\) with diphenylacetylene, trimethylysilylacetylene, and digermyne \(5d\) with 2,3-dimethyl-1,3-butadiene. \(\text{Ar}^* = \text{C}_9\text{H}_3\text{Cl}_{2.5.6}(\text{C}_6\text{H}_3\text{Cl}_{2.5.6}\text{Pr}^3)_{2.5.6}\), \(\text{Ar}^*\text{Pr}^3\text{Ph} = \text{C}_9\text{H}_2\text{Cl}_{2.5.6}(\text{C}_6\text{H}_3\text{Cl}_{2.5.6}\text{Pr}^3)_{2.5.6}\), TMS = SiMe\(_3\).\textsuperscript{39,52,139}
postulated diradical intermediate \( \text{53}' \). A third cycloaddition process is initiated by one of the ligand’s Dip-rings, finally forming the rather unusual product 53 (Scheme 27). In 2007 Sekiguchi could find the first examples of cycloaddition on disilyne \( \text{9a} [\text{Si}^{\text{1}}=\text{Si}^{\text{1}} \text{Si}^{\text{1}} \text{Si}^{\text{1}}], \text{Si}^{\text{1}}=\text{Si}-\text{Pr}[\text{CH(SiMe}_{3}]_{\text{2}}] \) when reacting it with either 2-butenes or phenylacetylene (Scheme 27).\(^{43}\) For the reaction with 2-butenes, a significant time dependence could be revealed. While after 30 minutes the reaction affords 55 with the methyl groups in \( \text{cis} \) formation, after 24 hours 55 could be obtained in \( \text{trans} \) formation solely. In the course of this investigation, Sekiguchi could also find a working synthetic procedure for the isolation of stable 1,2-disilabenzene 54a and 54b that are formed in the ratio of 54a : 54b = 2 : 3.

In the following years the same strategy has led to several examples of stable ditetrelbenzenes and a rich follow up chemistry. In 2010, Tokitoh investigated the cycloaddition of olefins and alkynes to disilyne BbtSiSiBbt (4a).\(^{44,45}\) Depending on the steric demand of the olefins, the reactions result in the 3-membered cycloadduct 56 for ethylene and the \( [2 + 2] \) addition product 58 for cyclohexene (Scheme 28, left). In the addition of 2,3-dimethyl-1,3-butadiene to the disilyne, only one addition takes place affording the unusual product 57 as \( \text{anti}-\text{tricyclo}[3.1.0.0^{2,4}]_1,2\)-disilahexane (Scheme 28, top right). As mentioned before, using a similar synthetic pathway to that used by Sekiguchi, Bbt substituted 1,2-disilabenzene derivative 59 can be furnished for acetylene, phenylacetylene and trimethylsilylacetylene (Scheme 28, bottom right).

Similar reactivity was found for digermyne BbtGeGeBbt (4b) upon reaction with ethylene and terminal olefins (Scheme 29).\(^{30,33}\) Depending on the applied conditions, both stable addition products, 3-membered and 4-membered cycloadduct 60 and 61 could be isolated separately. Theoretical calculations suggest that 1,4-digermabicyclo[2.2.0]hexane (61) is the thermodynamically favored product whereas bis(gemimiranyln)ethane (60) is stabilized kinetically. Using substituted terminal olefins, products of the form of 62 were obtained exclusively.

In 2018 Sasamori could uncover the reactivity of disilyne 4c (TbbSiSiTbb) with organic triple bonds (Scheme 30) that gave rise to the 1,2-disilabenzene 65 and 1,4-disilabenzene 66 depending on the size of the substrate.\(^{47}\) While reaction with terminal acetylene derivatives afforded 1,2-disilabenzene 65 within 10 minutes selectively, the slightly bigger 3-hexyne first formed 1,4-disilabenzene 66.\(^{48}\) Remarkably, a transformation of 63 can be induced photochemically, yielding disilazabenvalene derivative 64 (Scheme 30).

Apart from dimetallynes with high multiple bond character, amide stabilized bigermynene N¹GeGeN¹ (13a) shows a standard \([2 + 2]\) cycloaddition reaction for ethylene and cod that results in 66 and 68 (Scheme 31, left) but proceeds \( \text{via} \) fracture of the Ge–Ge bond in case of nbd and methylacetylene, yielding 67 and 69 (Scheme 31, right).\(^{46,53}\) Theoretical investigation points out an initial \([2 + 1]\) addition to one metal atom and consecutive rearrangement to the cyclic species 66 in case of ethylene. In contrast, for addition of nbd and methylacetylene, rotation around the carbon–carbon bond and thereafter, Ge–Ge
bond rupture takes place to yield compounds 67 and 69, respectively.

The same reaction motif can be found for base stabilized bissilylene 17a upon addition of substituted acetylenes (Scheme 32). This study shows, in a remarkable way, how the product structure depends on the steric demand of the utilized alkyne. For phenylacetylene, a [1 + 2] addition and insertion with Si–Si bond rupture leads to cis-1,2-disilylenylethene 70. Using the sterically more demanding diphenylacetylene, a singlet delocalized biradicaloid (71) has been synthesized that is stabilized through the donor ligand as well as delocalization within the Si2C4-ring.

Catalytic application

Recently, Sasamori and Tokitoh reported on a cyclo-trimerization of terminal alkynes (Reppe reaction) using TbbGeGeTbb (4d) as a pre-catalyst. In this reaction route two equivalents of PhCCH are added to the digermyne and form 3,5-diphenyldigermabenzen (72) within three minutes. 72 acts as the catalyst, to which three more molecules of PhCCH are added during the catalytic cycle to obtain intermediate products 73, 74, and 75 (Scheme 33) and to release 1,2,4-triphenyldibenzene from 75b with high selectivity. A range of arylic substrates was tested. The high regioselectivity remains with all tested terminal alkynes and challenges even transition-metal catalysts in its performance. The mechanism of the reaction suggests that the two Ge atoms act in a cooperative fashion during the redox processes between Ge(a) and Ge(α).

Conclusions

In 2010, Power’s seminal review highlighted the great potential of main-group compounds in regard to mimicking transition-metal behavior for the first time. Since then, the growing field of group 14 dimetallenes and dimetallynes has been more and more appreciated and their potential for bond activation and catalysis, increasingly recognized. The influence of ligand properties and central group 14 atoms on the structure and electronic nature of these multiple bonds is better understood. This allows rational design of new compounds with the intention to optimize and decrease HOMO–LUMO gaps and fine-tune the reactivity towards target molecules. Multiple accounts could show, for example, the importance of strongly donating ligands, such as sterically encumbered NHIs or silanides and certain boryl moieties, in enabling activation of H2, NH3, CO2 and other industrially relevant building blocks. A persistent challenge in activating small molecules remains the reversibility of the reaction, i.e. reductive elimination, as the key step in most catalytic reactions to close the cycle and recover the catalyst. There is, however, an increasing number of accounts that show reversibility. For example, the activation of terminal alkynes with a number of bridged distannenes, the reaction of acetonitrile with tetramesityldigermene and the addition of H2 to the distannyne ArSnSnAr have been reported. Probably the most notable stride in the reactivity of dimetallenes and dimetallynes is the catalytic cyclotrimerization of terminal alkynes with TbbGeGeTbb. This highly regioselective process can certainly compete with transition metal catalysts and represents an
interesting new concept of cooperative interactions of two tetravalent centers in discrete oxidation states.

There is no doubt that the chemistry of group 14 multiple bonds will continue to flourish and open up new alternatives to scarce, expensive and often more toxic transition-metal catalysts. Whilst germanium and tin are more promising to achieve transition-metal mimicking conversions, silicon is so abundant and environmentally benign that it has the highest potential to offer ecological and economic incentives for future application.

Conflicts of interest
There are no conflicts to declare.

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