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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 H_2, NH_3, 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 diphosphene 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.[13] A challenge, nonetheless, is still the flexible interchange between several oxidation states displayed by d-block complexes. Group 14 multiply bonded species tend to form very stable oxidative addition products, making reductive elimination, the next key step in a typical catalytic cycle for transition metals, very difficult.[14,15] There is, however, significant progress being made in that regard, so much so that recently the first catalytic cyclotrimerization of terminal alkynes by a digermyne could be realized.[16] This minireview aims to provide insight into the recent developments towards small 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 bismetallylenes.

Bonding nature

Dimetallenes and dimetallynes are compounds of the form $R_2E{=}ER_2$ and $RE{\equiv}ER$, where E is a heavier group 14 element (E = Si, Ge, Sn, Pb). In their formula, they are the direct descendants of alkenes and alkynes. 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

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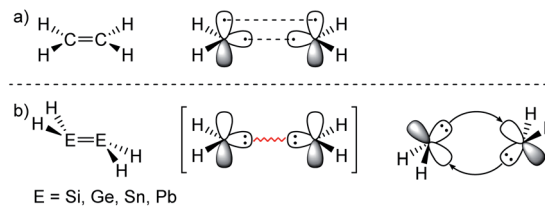
Fig. 1 (a) Ethylene with a covalent bonding description. (b) CGMT model of dimetallenes with a bonding description.

difference stems from an increased size difference of the valence orbitals leading to a less effective hybridization of the heavier elements.[17,18] To illustrate the resulting deviation in bonding, parent group 14 multiple bonds can be seen as an interaction of two monomeric 'H$_2$E:' or 'HE:·' units, respectively. While methylene (H$_2$C:) 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$_2$E:) 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)).[19] In triply bonded compounds in consequence, alkynes 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.[13,20–23] 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).

The Carter–Goddard–Malrieu–Trinquier (CGMT) model that describes the bonding of main-group multiple bonds was initially proposed for Lappert's distannene and is probably the most intuitive approach, since the principle of a classical multiple bond is retained.[5,21,22] The increasing deviation from a planar double bond of dimetallenes with the descend down group 14 can be interpreted by an increasing stability of the singlet ground state, leading to more pronounced *trans*-bending and weakening of the E=E bond.[24,25] For dimetallynes, the same effect can be seen in the orbital scheme in Fig. 3. It can be used to describe the severeness of the bending and shows the orbital mixing of HE≡EH in linear, *trans*-bent and H:E–E:H structures in the right-angled form according to the Jahn–Teller
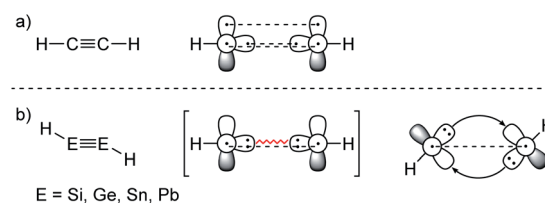

Fig. 2 (a) Acetylene with a covalent bonding description. (b) CGMT model of dimetallynes with a bonding description.
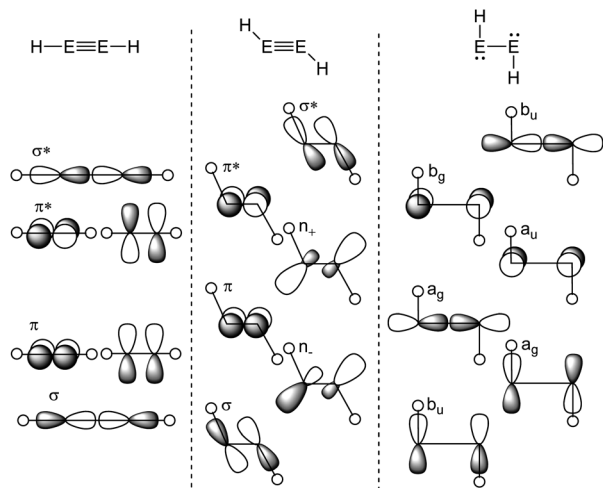
Fig. 3 Orbital scheme of the second order Jahn–Teller distortion in HEEH (E = Si, Ge, Sn, Pb).[17,28,29]

distortion model. The mixing of σ and π 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_2H_2, $Si–Si_{calc.} = 2.1$ Å[31]) and relatively big H–Si–Si angles ($Si_2H_{2calc.} \sim 125°$ [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_2H_2, $Pb–Pb_{calc.} = 3.2$ Å [34]) and high *trans*-bent angles near 90°.[34] 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.[26,30,35] 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. Like all multiple bonds, the E–E bonds also show high electron densities that result in a pronounced nucleophilicity. Nevertheless, unlike organic bonds, donor–acceptor type interactions in dimetallenes and dimetallynes allow further reactivities due to lower E–E bond energies and two lone pairs of electrons that are embedded into the multiple bond (see Fig. 1b
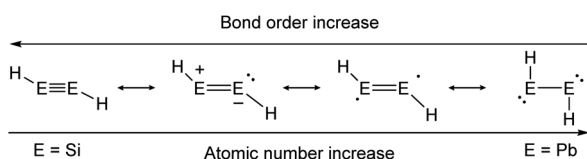

Fig. 4 Trends in bonding of heavier triple bonds, illustrated by mesomeric structures of HEEH (E = Si, Ge, Sn, Pb).[26,30]

and 2b). Like in multiply bonded transition-metal M–M and M–C compounds,[36–38] cycloaddition is an often-observed reaction for dimetallenes and dimetallynes.[16,39–53] Moreover, when going down the group these effects get even stronger, with more exposed lone pairs and decreasing E–E bond energies. For dimetallynes, singlet diradical character can be seen as a mesomeric structure and in reaction, respectively. In a recent study Britt and Power could indeed show the dissociation of the distannyne Ar′SnSnAr′ (**5b**) into Sn(I)-radicals :ṠnAr′ in toluene solution that could be detected *via* EPR spectroscopy. These findings also strongly support the concept of charge-shift bonds being present in dimetallynes.[54] Not ending at this point, dimetallenes and dimetallynes are dinuclear complexes, in which two E atoms build the reactive core within the complex. Taking nature as a benchmark for efficient and low energy consuming activation and conversion of relatively inert small molecules, one strategy that could be mimicked by chemists is the use of two or more metal centers within the active site of a catalyst. These catalysts benefit from cooperative and synergetic effects between the metal centers that lower activation barriers and improve selectivity.[55] In dimetallenes and dimetallynes cooperative effects can take place between two neighboring tetrel elements. Due to the multiple bond character, addition of small molecules would not necessarily break the E–E bond and with that bond still intact, conversion, insertion, or addition of another molecule is rendered possible. Additionally, the release of a product molecule could be accompanied by restoration of the multiple bond. All these steps are crucial for performing 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_2EX_2) or trihalometallanes (REX_3), dimetallanes (X_2REERX_2), dimetallenes (XREERX), or metallylenes (XRE:) using reductive agents (red.) such as KC_8,[45,47,56–58] metal naphthalenides,[59,60] and $[(^{Mes}Nacnac)Mg]_2$ ($^{Mes}Nacnac = (MesNCMe)_2CH$)[61] is the central motif in isolation of these compounds.
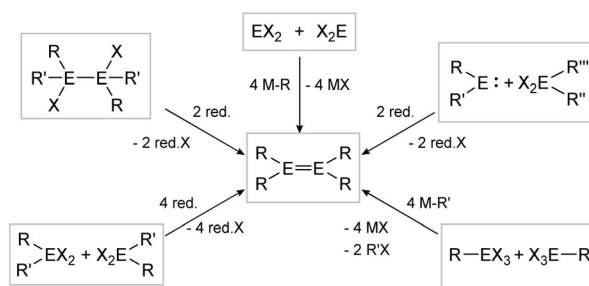
Scheme 1 Possible synthesis routes for the isolation of dimetallenes. E = Si, Ge, Sn, Pb; R = stabilizing ligand; X = halogen; red. = reductive agent.
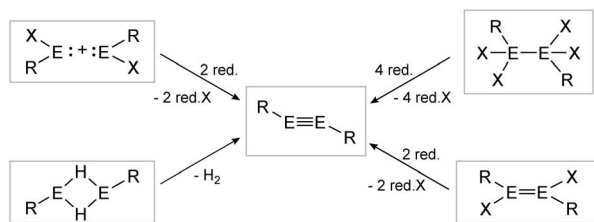
Scheme 2 Possible synthesis routes for the isolation of dimetallynes. E = Si, Ge, Sn, Pb; R = stabilizing ligand; X = halogen; red. = reductive agent. Note: Hydrogen elimination route (bottom left) is only known for E = Sn, Pb.

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–SiBr$_3$ and KSi(SiMe$_3$)$_3$, transferring the silyl ligand.[62] In dimetallyne chemistry the elimination of H$_2$ is also known to form triply bonded tin[56] and lead[9,29,63] compounds, starting from halogenated XRE *via* an X/H exchange using hydride sources like LiAlH$_4$ or DIBAL-H. Since it can be seen as the reverse of H$_2$ activation, this synthetic route towards dimetallynes of 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.[64,65] The steric demand of the ligand system is crucial to achieve kinetic stabilization of E–E multiple bonds.[31,66] 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 Si$_2$H$_2$ (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.[31]

That said, recent accounts have highlighted the importance of London dispersion force (LDF) energies that contribute *via* dispersion forces between hydrocarbon groups.[67,68] 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.[25,69] Fig. 6 shows selected examples of dimetallenes and dimetallynes that are stabilized by sterically encumbered aryl ligands that achieve primarily kinetic stabilization.
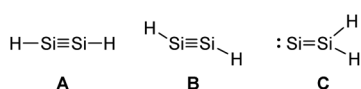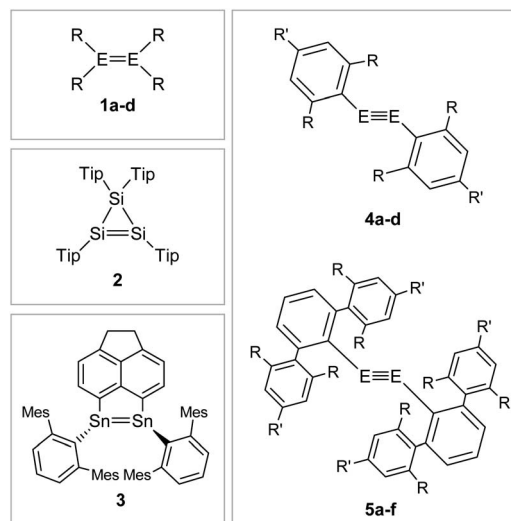

Fig. 6 Selected examples of aryl-type stabilized dimetallenes and dimetallynes. 1: **1a**[6]: E = Si, R = Mes (Mes = 2,4,6-trimethylphenyl) **1b**[70,71]: E = Ge, R = Mes **1c**[72]: E = Si, R = Tip (Tip = 2,4,6-triisopropylphenyl) **1d**[73]: E = Ge, R = 2,5-tBu$_2$C$_6$H$_3$; **2**;[74] **3**;[75] 4: **4a**[60]: E = Si, Bbt: R = CH(SiMe$_3$)$_2$ R′ = C(SiMe$_3$)$_3$ **4b**[76]: E = Ge, Bbt: R = CH(SiMe$_3$)$_2$ R′ = C(SiMe$_3$)$_3$ **4c**[47]: E = Si, Tbb: R = CH(SiMe$_3$)$_2$ R′ = t-Bu **4d**[45]: E = Ge, Tbb: R = CH(SiMe$_3$)$_2$ R′ = t-Bu; 5: **5a**[12]: E = Ge, Ar′: R = i-Pr R′ = H **5b**[11]: E = Sn, Ar′: R = i-Pr R′ = H **5c**[29]: E = Pb, Ar′: R = i-Pr R′ = H **5d**[77,78]: E = Ge, Ar*: R = i-Pr R′ = i-Pr **5e**[56]: E = Sn, Ar*: R = i-Pr R′ = i-Pr **5f**[9]: E = Pb, Ar*: R = i-Pr R′ = i-Pr.

If one goes beyond kinetic stabilization and also brings in thermodynamic influence on the system, silyl ligands like Si*t*-Bu$_3$, Sii-Pr$_2$Me, and Sii-Pr(CH(SiMe$_3$)$_2$)$_2$ 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.[62,64,79,80] 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
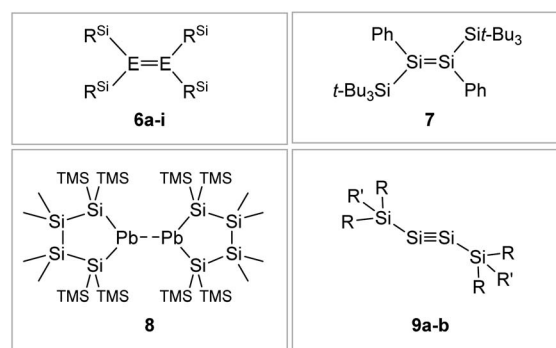

Fig. 5 Three plausible isomers of parent disilyne Si$_2$H$_2$ with A: linear, B: *trans*-bent, or C: SiSiH$_2$ structure.[31]

Fig. 7 Selected examples of silyl-type stabilized dimetallenes and dimetallynes. **6**[80–84]: **6a**: E = Si, R^{Si} = i-Pr$_2$MeSi **6b**: E = Si, R^{Si} = t-BuMe$_2$Si **6c**: E = Si, R^{Si} = i-Pr$_3$Si **6d**: E = Si, R^{Si} = t-Bu$_2$MeSi **6e**: E = Ge, R^{Si} = i-Pr$_2$MeSi **6f**: E = Ge, R^{Si} = t-BuMe$_2$Si **6g**: E = Ge, R^{Si} = i-Pr$_3$Si **6h**: E = Ge, R^{Si} = t-Bu$_2$MeSi **6i**: E = Sn, R^{Si} = t-Bu$_2$MeSi; **7**[85]; **8**[69]: TMS = SiMe$_3$; **9**: **9a**[10]: Si^1: R = CH(SiMe$_3$)$_2$ R′ = i-Pr **9b**[59]: Si^2: R = Sit-Bu$_3$ R′ = Me.
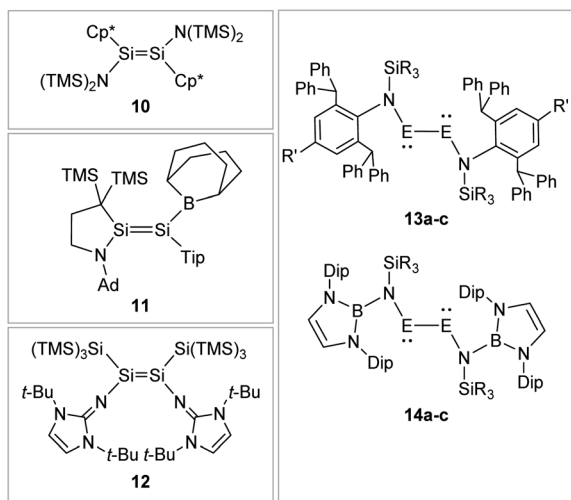
Fig. 8 Selected examples of N-type stabilized dimetallenes and dimetallynes. **10**[89,90]: Cp* = η^1-Me$_5$C$_5$; **11**[57]: TMS = SiMe$_3$, Ad = 1-adamantyl, Tip = 2,4,6-triisopropylphenyl; **12**[62,91]; **13**: **13a**[61]: E = Ge, N^1: R = Me R' = Me **13b**[92]: E = Ge, N^2: R = i-Pr R' = i-Pr **13c**[93]: E = Sn, N^2: R = i-Pr R' = i-Pr; **14**[94]: Dip = 2,6-diisopropylphenyl **14a**: E = Ge, R = Me **14b**: E = Ge, R = Ph **14c**: E = Sn, R = Ph.

Fig. 9 Selected examples of bismetallylenes, stabilized by chelating donor ligands. **15**[96]: R = Dip (Dip = 2,6-i-Pr$_2$C$_6$H$_3$) R' = t-Bu; **16**[97]: TMS = SiMe$_3$; **17**: **17a**[98]: E = Si, R = t-Bu R' = Ph **17b**[99]: E = Si, R = Dip R' = 4-t-BuC$_6$H$_4$ **17c**[100]: E = Ge, R = Dip R' = t-Bu **17d**[100]: E = Ge, R = Dip R' = Ni–Pr$_2$; **18**.[101]

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 NHI[95] 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(SiMe$_3$)$_3$, 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 p$_\pi$–p$_\pi$ orbital overlap, resulting in a decreased HOMO–LUMO energy gap. In the case of amido ligands, (SiR$_3$)ArN (dimetallynes **13**) and (SiR$_3$)BoN (dimetallynes **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 dimetallynes 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
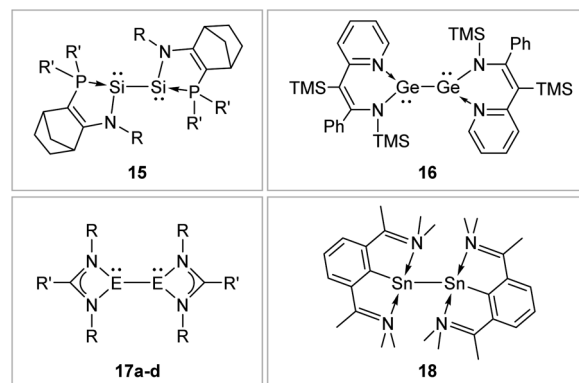
bond altogether and secondly, achieving reversibility of the reaction, *i.e.* regeneration of the multiple bond as a key step for any future catalytic application. To our knowledge, there are no examples of catalytic reactions performed by a group 14 dimetallene to date and bond activation is mostly 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.[16] 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,[14,15,102,103] 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 H$_2$, NH$_3$, CO$_2$, CO, alkenes and alkynes are discussed in further detail.

H$_2$ 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.

H$_2$ 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.
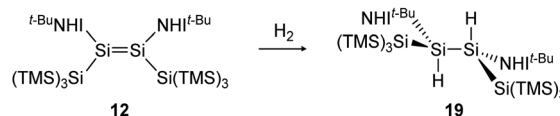
Scheme 3 Selective *trans* addition of H$_2$ by iminodisilene **12**. TMS = SiMe$_3$.[62]
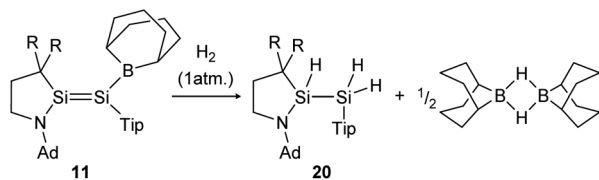
Scheme 4 Cleavage of two hydrogen molecules under formation of trihydridodisilane and hydroborane by 1-amino-2-boryldisilene **11**.[57] R = SiMe₃.

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.[57,87] Since theoretical calculations suggested an overpowering effect of the π-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 π*(Si=Si) orbital is essential for the reactivity. While the monoboryldisilene 2,2,5,5-(SiMe₃)₄–C₄H₄Si=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-(SiMe₃)₂C₃H₄Si=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.[87]

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 bismetallylenes 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**, digermane **22** and germane **23**, shown in Scheme 5. This account presents the first example of H_2 activation by using a molecular main-group
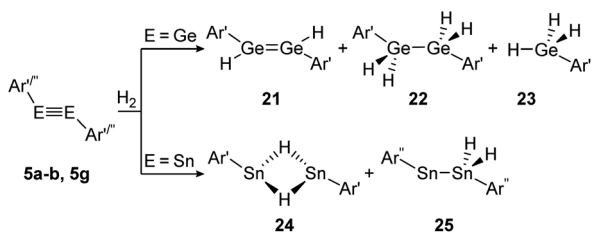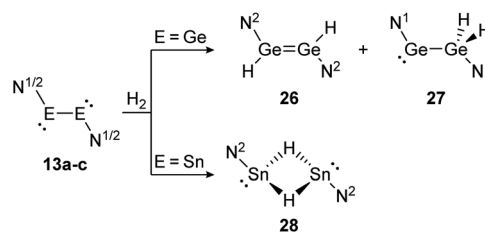
species without a catalyst that is estimated to be due to a singlet biradical character of the ground state of **5a**. The heavier analogue **5b** (Ar′SnSnAr′) was shown in 2018 to activate dihydrogen in a reversible form (Scheme 5, bottom) to produce hydrogen bridged **24**.[111] The addition of H_2 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 distannyne **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 bisstannylene **13c** each with high selectivity.[61,92,93] While **13a** reacts quantitatively with 1 bar of H_2 at ambient temperature to hydridogermane-germylene N^1GeGeH_2-N_1 (**27**), the slightly modified ligand N^2 in **13b** leads, under similar conditions, to the hydrido-digermene $N^2HGeGeHN^2$ (**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.[113–115] In 2014, the reaction of **13c** with H_2 was explored, yielding the third product motif $N^2Sn(\mu-H)_2SnN^2$ (**28**) (Scheme 6, bottom).

NH₃ 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 tetrasilabuta-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 Tipp₂Si=SiTipp₂ congener (**1c**) with only one Si=Si double bond, is inert towards NH₃, 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

Scheme 5 Reactivity of digermyne **5a** (Ar′ = C₆H₃-2,6-(C₆H₃-2,6-i-Pr₂)₂) and distannynes **5b** and **5g** (Ar″ = C₆H-2,6-(C₆H₂-2,4,6-i-Pr₃)₂-3,5-i-Pr₂) with H_2.[110–112]

Scheme 6 Reactivity of bisgermylenes **13a** and **13b** and bisstannylene **13c** with H_2. N^1 = N(Ar¹) (SiMe₃) (Ar¹ = 2,6-(CHPh₂)₂-4-MeC₆H₂), N^2 = N(Ar²) (Sii-Pr₃) (Ar² = 2,6-(CHPh₂)₂-4-i-PrC₆H₂).[61,92,93]

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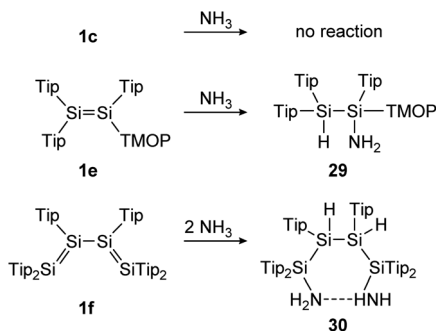
Scheme 7 Reactivity of various Tip substituted disilenes **1e**,[117] **1c**, and **1f**[116] towards NH_3. Tip = 2,4,6-triisopropylphenyl; TMOP = 2,4,6-trimethoxyphenyl.
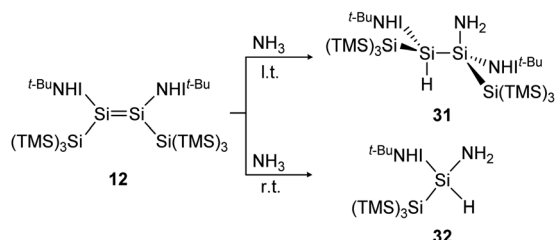
with a TMOP ligand (**1e**), resulting in a prominent polarization of the Si=Si bond and enabling a regioselective 1,2-addition of ammonia to addition product **29** (Scheme 7).[117]

In a similar manner to the 1,2-addition of hydrogen to the iminodisilene **12**, an analogous *trans*-addition product with NH_3 was reported more recently.[91] 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 NH_3 (7.7 kcal mol^{-1}) compared to that of H_2 (15.6 kcal mol^{-1}). When the reaction is performed at room temperature, the formal oxidative addition product **32** of the corresponding silylene with NH_3 is observed (Scheme 8).
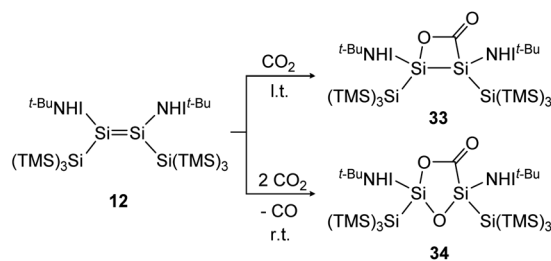
CO₂ activation

The activation and reduction of CO_2 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 CO_2 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*t*-Bu₃)PhSi=SiPh(Si*t*-Bu₃) (**7**) showed reactivity towards the molecule.

Treatment of **12** with CO_2, 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 N_2O as

well as O_2 and comparison of NMR data (Scheme 9).[91] The disilene **7** activates CO_2 in a [2 + 2] cycloaddition reaction as shown in Scheme 10 to obtain **35**.[85]

For classical dimetallynes no activation of CO_2 is known, however, examples involving interconnected bismetallylenes are reported. Upon exposure of a toluene solution of **13a** to CO_2 at -70 °C the reaction proceeds *via* the intermediate N^1GeO_2-$CGeN^1$ (**36′**) and ends with the bisgermylene oxide $N^1GeOGeN^1$ (**36**) as shown in Scheme 11.[109] Analysis of the head space gas reveals the release of CO. Theoretical analysis of the reaction profile suggests a three step mechanism, in which CO_2 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.[114] The analogue reaction with CS_2 afforded N^1GeS-GeN^1, respectively.

Another deoxygenation of CO_2 was reported by Baceiredo and Kato in 2011.[96] In detail, three molecules of CO_2 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 CO_2 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 CO_2 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

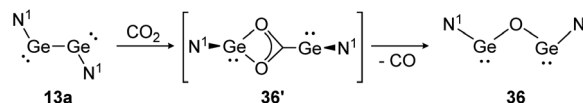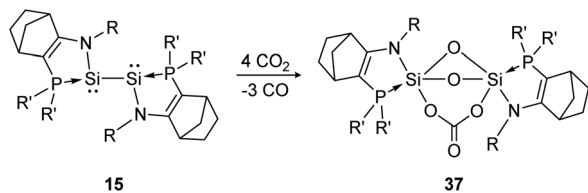**Scheme 9** Activation of CO_2 by iminodisilene **12** at l.t. = -78 °C or r.t. = room temperature. TMS = $SiMe_3$.[91]
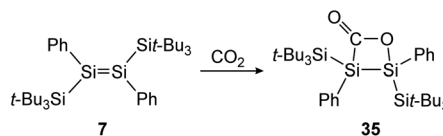
Scheme 10 [2 + 2] cycloaddition of CO_2 to supersilyl substituted disilene **7**.[85]

Scheme 11 Reactivity of bisgermylene **13a** with CO_2. N^1 = $N(Ar^1)(SiMe_3)$ (Ar^1 = 2,6-$(CHPh_2)_2$-4-MeC_6H_2).[109]

Scheme 8 Reaction of NH_3 with iminodisilene **12** at l.t. = -78 °C or r.t. = room temperature. TMS = $SiMe_3$.[91]

Scheme 12 Reactivity of bissilylene **15** with CO_2 (R = Dip, R′ = t-Bu).[96]

Scheme 15 Formation of oxadisilirane via the reaction of **12** with N_2O. TMS = $SiMe_3$.[91]

central Si-atoms, where the phosphine moiety induces a strong π donor–acceptor character of the Si^I centers.
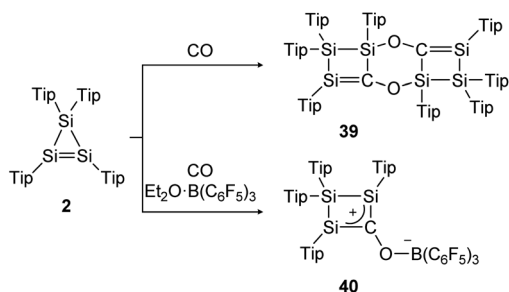
CO activation

The activation and bond cleavage of CO is in the focus of synthetic chemists mainly for the possible utilization of CO as a C1 building block as well as application in C–C bond formation in Fischer–Tropsch processes.[120] In group 14 chemistry, activations of CO are scarce but have been achieved for low valent silicon and germanium complexes, for example.[121,122] In dimetallene and dimetallyne chemistry this reactivity was mainly pioneered by the group of Scheschkewitz, who already reported in 2015 about CO cleavage and C–C bond formation using a Tip substituted disilenide (**1g**) as shown in Scheme 13.[123] Proposed reaction intermediates include the twofold addition of CO to the disilenide forming a silylenoid and a dimerization product. Overall, two molecules of disilenide are needed to activate four molecules of CO within the reaction product **38**.
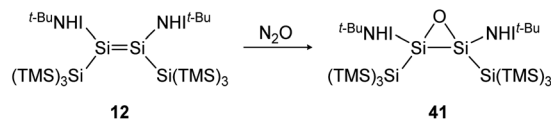
The same group could find a reactivity of a functionalized cyclic disilene – called cyclotrisilene (**2**) – towards CO. While in 2013 the 1 : 1 reaction product could only be isolated as dimer

39 (Scheme 14, top),[124] one year later the monomer **40** could be trapped using $Et_2O·B(C_6F_5)_3$ (Scheme 14, bottom).[125]
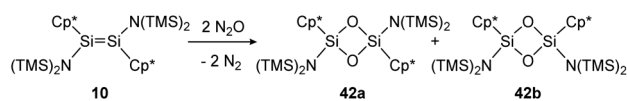
N₂O activation

Nitrous oxide is one of the classic small molecules, however, its activation is easy enough for N_2O 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 N_2 as a by-product.[126]

Reaction of iminodisilene **12** with N_2O produces three-membered ring oxadisilirane **41** in cis confirmation (Scheme 15). When exposed to oxygen, in contrast, a dioxadisiletane with a Si_2O_2-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 N_2O is trans-$[(TMS)_2N(\eta^1-Me_5C_5)Si=Si(\eta^1-Me_5C_5)N(TMS)_2]$ (**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 N_2O 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 N_2O 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 N_2O. Alternatively, N_2O reacts directly with the double bond either as a nucleophile or an electrophile. Nucleophilic N_2O leads to an end-on attack whereas electrophilic N_2O interacts with the

Scheme 13 Reactivity of disilenide **1g** with CO. Tip = 2,4,6-triisopropylphenyl, dme = dimethoxyethane.[123]

Scheme 14 Reactivity of cyclotrisilene **2** with CO and additional $Et_2O·B(C_6F_5)_3$. Tip = 2,4,6-triisopropylphenyl.[124,125]
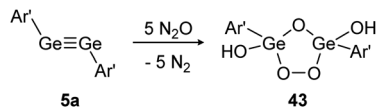

Scheme 16 Reaction of trans-disilene **10** with N_2O results in formation of both cis- (**42b**) and trans-dioxadisiletane (**42a**). TMS = $SiMe_3$.[127]
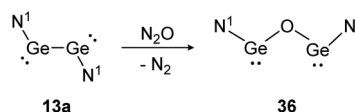
Scheme 17 Reactivity of bisgermylene **13a** with N_2O. N^1 = N(Ar¹)(SiMe₃) (Ar¹ = 2,6-$(CHPh_2)_2$-4-MeC_6H_2).[109]

Scheme 18 Reactivity of digermyne **5a** with N_2O. Ar′ = C_6H_3-2,6-(C_6H_3-2,6-i-Pr_2)$_2$.[129]

Scheme 20 [2 + 2] cycloaddition of tetramesityldisilene **1a** and *trans*-*d*-styrene gives a diastereomeric product mixture. Mes = 2,4,6-trimethylphenyl.[137]

disilene in a side-on fashion.[128] Within dimetallyne chemistry the activation of N_2O is reported with several outcomes. For bisgermylene **13a**, the reaction proceeds with a simple oxygen transfer that breaks and inserts into the Ge–Ge bond (Scheme 17).[109] In this regard, it is an alternative synthetic pathway to yield the CO_2 activation product **36**.

In contrast, reaction of N_2O with digermyne **5a** that bears significantly higher multiple bond character produces a Ge_2O_3-ring with two exocyclic hydroxo groups (**43**) (Scheme 18).[129] Theoretical calculations suggest that the reaction proceeds *via* a radical mechanism that forms a peroxo bridge, followed by subsequent deoxygenation of additional N_2O molecules. Formation of the terminal hydroxo groups in **43** could stem from dehydrogenation of solvent molecules.
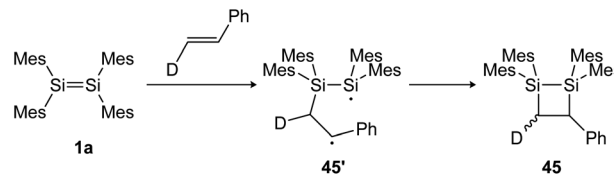
Base-stabilized bissilylene **17a** consumes three equivalents of N_2O at ambient temperature and forms the eight-membered Si_4–O_4-ring compound **44** upon dimerization of two bissilanone moieties (**44″**) induced by the polar Si=O double bonds (Scheme 19). The reaction mechanism is proposed to proceed *via* primary insertion of an oxygen atom into the Si–Si bond (**44′**) and subsequent oxygenation to **44″**. Each bissilylene unit consist of a Si(μ-O)$_2$Si core. Reaction with *t*-BuNCO affords the same product (**44**).

Cycloaddition of alkenes and alkynes

Cycloadditions of dimetallenes with unsaturated hydrocarbons and other multiple bonds are often observed. In particular, the reactivity of disilenes and digermenes with alkenes, alkynes, C=N, C=O and other heteroatom multiple bonds has been reported, resulting in otherwise difficult to obtain ring compounds.[104,105,131–135] For the reactions of disilenes with terminal alkenes and alkynes, a radical pathway with a stepwise
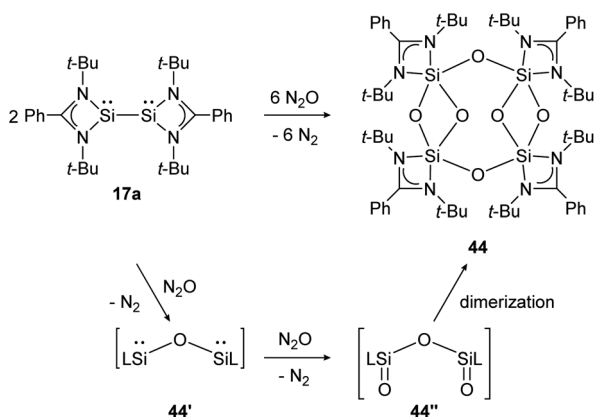
mechanism can be proposed.[134,136] Baines showed, for example, that the reaction of tetramesityldisilene (**1a**) with *trans*-*d*-styrene resulted in a 7 : 3 diastereomeric mixture of the *cis* and *trans* [2 + 2] cycloaddition products **45** (Scheme 20), indicating a bond rotation of the intermediate **45′**, yielding the *cis* isomer.[137]

Similarly, the cycloaddition reaction of tetramesityldigermene (**1b**) with a cyclopropylcarbinyl probe suggests the formation of several intermediate diradicals (**46′**, **46″**) resulting in various cyclization products of which **46a** and **46b** are shown (Scheme 21).[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_6D_6 solution, confirmed by NMR experiments (Scheme 22, top).[75] 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).[75] Cycloaddition reactions of dimetallenes are often not reversible and the reactivity of stable distannenes with terminal alkenes 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

Scheme 19 Reactivity of bissilylene **17a** with N_2O.[130]
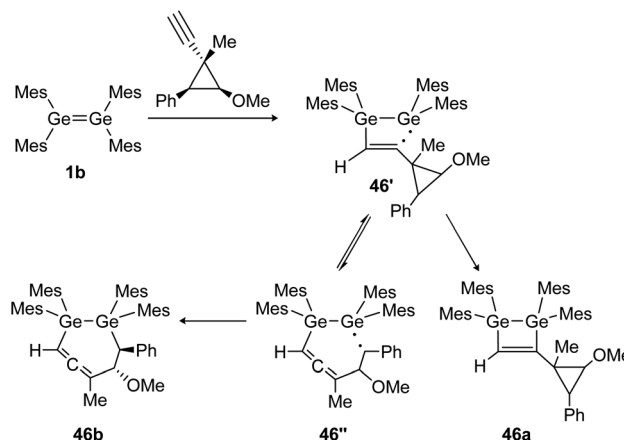
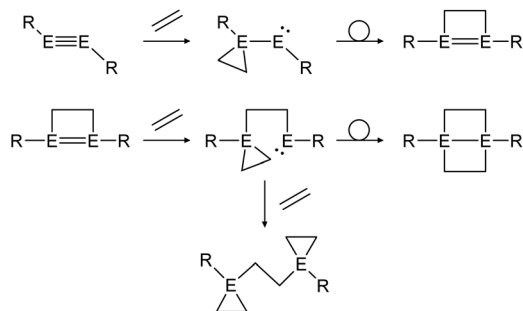Scheme 21 Reaction of tetramesityldigermene with a cyclopropyl alkyne. Mes = 2,4,6-trimethylphenyl.[134]
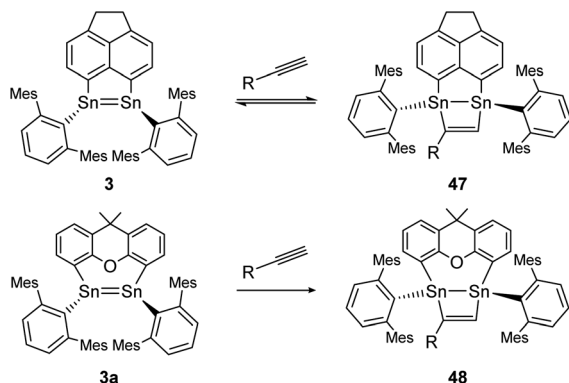
Scheme 22 [2 + 2] cycloaddition of terminal alkynes to linker bridged distannenes **3** and **3a**. Mes = 2,4,6-trimethylphenyl; **3**: R = SiMe$_3$ or Ph; **3a**: R = Ph.[75]

Scheme 24 General reaction pathway for cycloaddition reactions of dimetallynes with alkynes exemplified by acetylene. E = Si, Ge, Sn; R = stabilizing ligand.

elevated temperatures.[104] Dimetallynes – like many multiply bonded compounds – are also prone to cycloaddition reactions. Therefore, a broad variety of examples are known today.
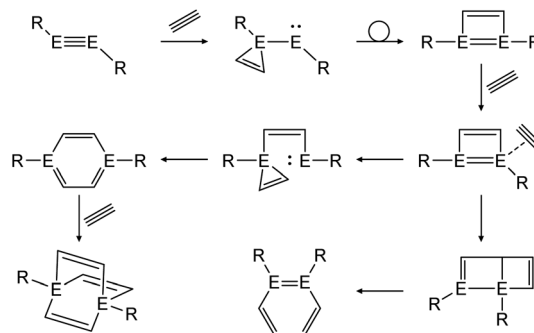
Multiple studies have shown that the cycloaddition of olefins follows a certain pathway.[43,46,48] Within two addition and rearrangement reactions dimetallynes are able to form 4-membered cycloadducts and upon addition of an extra alkene molecule, 3-membered cycloadducts also (Scheme 23). The product 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.[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.[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 Ar^{iPr8}SnSnAr^{iPr8} (Ar^{iPr8} = C$_6$H-2,6-(C$_6$H$_2$-2,4,6-i-Pr$_3$)$_2$-3,5-i-Pr$_2$), 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**.[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** (Ar′GeGeAr′) with SiMe$_3$CCH and diphenylacetylene (Scheme 26, right).[39] While for diphenylacetylene only one addition takes place forming product **52**, in case of the sterically less demanding trimethylsilylacetylene two molecules can be added and form the
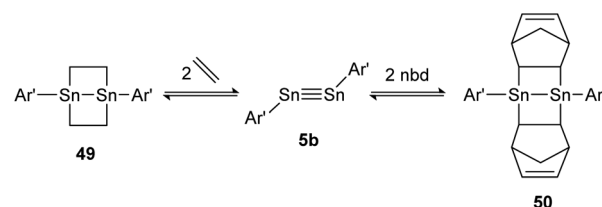
Scheme 25 Reversible cycloaddition of ethylene to distannyne **5b**. Ar′ = C$_6$H$_3$-2,6-(C$_6$H$_3$-2,6-i-Pr$_2$)$_2$, nbd = norbornadiene.[138]

Scheme 23 General reaction pathway for cycloaddition reactions of dimetallynes with olefins exemplified by ethylene. E = Si, Ge, Sn; R = stabilizing ligand.
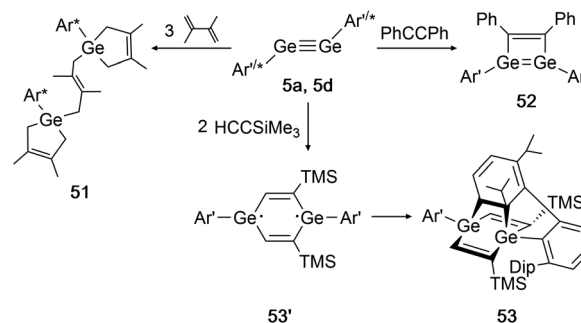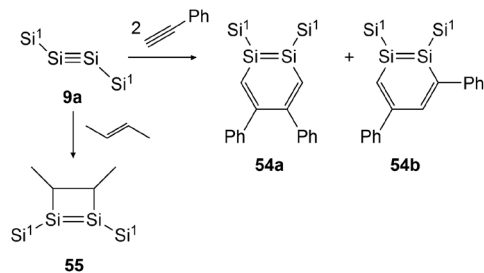

Scheme 26 Cycloaddition reactions of digermyne **5a** with diphenylacetylene, trimethylsilylacetylene, and digermyne **5d** with 2,3-dimethyl-1,3-butadiene. Ar′ = C$_6$H$_3$-2,6-(C$_6$H$_3$-2,6-i-Pr$_2$)$_2$, Ar* = C$_6$H$_3$-2,6-(C$_6$H$_2$-i-Pr$_3$)$_2$, TMS = SiMe$_3$.[39,52,139]

Scheme 27 Cycloaddition reactions of disilyne **9a** with phenyl-acetylene and 2-butene. $Si^1 = Sii$-Pr$[CH(SiMe_3)_2]_2$.[43,50]

Scheme 29 Cycloaddition reactions of digermyne **4b** with ethylene and terminal olefins R = n-C$_4$H$_9$, Ph.[46,48]
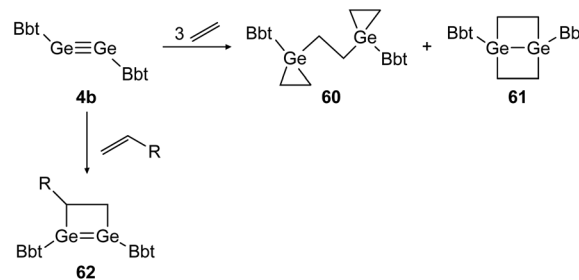
postulated diradical intermediate **53'**. A third cycloaddition process is initiated by one of the ligand's Dip-rings, finally forming the rather unusual product **53** (Scheme 26, bottom).

In 2007 Sekiguchi could find the first examples of cycload-dition on disilyne **9a** ($Si^1SiSiSi^1$, $Si^1 = Sii$-Pr$[CH(SiMe_3)_2]_2$) when reacting it with either 2-butene or phenylacetylene (Scheme 27).[43] For the reaction with 2-butene, a significant time dependence could be revealed. While after 30 minutes the reaction affords **55** with the methyl groups in *cis* formation, after 24 hours **55** could be obtained in *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**).[41,42] 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 *anti*-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 trime-thylsilylacetylene (Scheme 28, bottom right).

Similar reactivity was found for digermyne BbtGeGeBbt (**4b**) upon reaction with ethylene and terminal olefins (Scheme 29).[46,48] Depending on the applied conditions, both stable addition products, 3-membered and 4-membered cycloadduct **60** and **61** can be isolated separately. Theoretical calculations suggest that 1,4-digermabicyclo[2.2.0]hexane (**61**) is the ther-modynamically favored product whereas bis(germiranyl)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 **63** 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 **63**.[49] Remarkably, a transformation of **63** can be induced photochemically, yielding disilabenzvalene derivative **64** (Scheme 30).

Apart from dimetallynes with high multiple bond character, amide stabilized bisgermylene N^1GeGeN^1 (**13a**) shows a stan-dard [2 + 2] cycloaddition reaction for ethylene and cod that results in **66** and **68** (Scheme 31, left) but proceeds *via* fracture of the Ge–Ge bond in case of nbd and methylacetylene, yielding **67** and **69** (Scheme 31, right).[40,53] 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

Scheme 28 Cycloaddition reactions of disilyne **4a** with ethylene, cyclohexene, acetylene derivatives (R = H, Ph, SiMe$_3$), and 2,3-dimethyl-1,3-butadiene.[41,42]
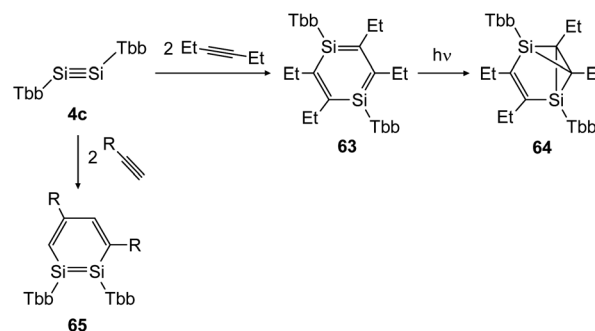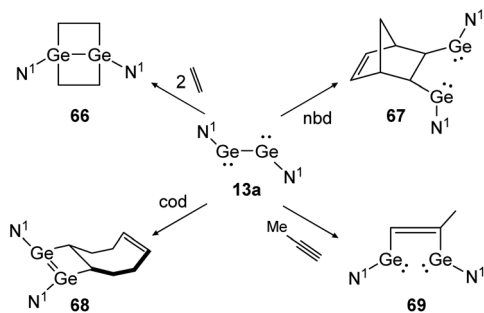

Scheme 30 Cycloaddition reactions of disilyne **4c** with mono and disubstituted acetylene derivatives R = H, Ph.[47,49]
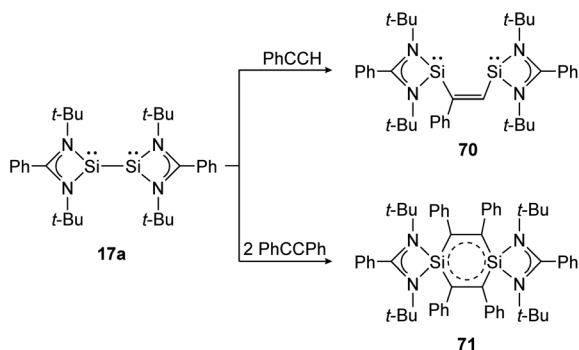
Scheme 31 Cycloaddition reactions of bisgermylene **13a** with ethylene, cyclooctadiene (cod), methylacetylene, and norbornadiene. $N^1 = N(Ar^1)(SiMe_3)$ ($Ar^1 = 2,6-(CHPh_2)_2-4-MeC_6H_2$).[40,53]

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).[140] 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 Si_2C_4-ring.

Catalytic application

Recently, Sasamori and Tokitoh reported on a cyclotrimerization of terminal alkynes (Reppe reaction) using TbbGeGeTbb (**4d**) as a pre-catalyst.[16,45] In this reaction route two equivalents of PhCCH are added to the digermyne and form 3,5-diphenyldigermabenzene (**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-triphenylbenzene 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
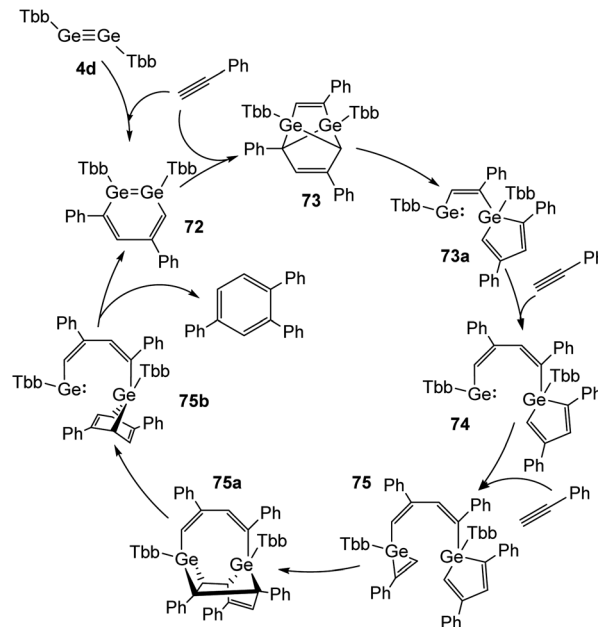
Scheme 33 Full catalytic cycle for the cyclotrimerization of phenylacetylene using digermyne **4d**.[16]

two Ge atoms act in a cooperative fashion during the redox processes between Ge(II) and Ge(IV).

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 H_2, NH_3, CO_2 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 H_2 to the distannyne Ar′SnSnAr′ 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

Scheme 32 Cycloaddition reactions of bissilylene **17a** with phenylacetylene and diphenylacetylene.[140]

interesting new concept of cooperative interactions of two tetrel 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.

Acknowledgements

Notes and references

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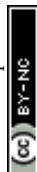
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