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REVIEW ARTICLE

Reactivity in the periphery of functionalised multiple bonds of heavier Group 14 elements

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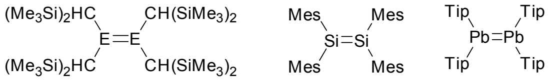
Heavier Group 14 multiple bonds have intrigued chemists since more than a century. The synthesis of stable compounds with double and triple bonds with silicon, germanium, tin and lead had considerable impact on modern ideas of chemical bonding. These developments were made possible by the use of bulky substituents that provide kinetic and thermodynamic protection. Since about a decade the compatibility of heavier multiple bonds with various functional groups has moved in to focus. This review covers multiply bonded Group 14 species with at least one additional reactive site. The vinylic functionalities of Groups 1 and 17, resulting in nucleophilic and electrophilic disila vinyl groups, respectively, are the most prevalent and well-studied. They have been employed repeatedly for the transfer of heavier multiple bonds to yield low-valent Group 14 compounds with novel structural motifs. Vinylic functionalities of Groups 2 to 16 and a few σ-bonded transition metal complexes are experimentally known, but their reactivity has been studied to a lesser extent. Donor-coordinated multiple bonds are a relatively new field of research, but the large degree of unsaturation as isomers of alkynes (as well as residual functionality in some cases) offers considerable possibility for further manipulation, e.g. for the incorporation into more extended systems. Heavier allyl halides constitute the major part of heavier multiple bonds with a functional group in allylic position and some examples of successful transformations are given. At present, remote functionalities are basically limited to *para*-phenylene functionalised disilenes. The reported use of the latter for further derivatisation might encourage investigations in this direction. In summary, the study of peripherally functionalised multiple bonds with heavier Group 14 elements is already well beyond its infancy and may be an instrumental factor in awakening the potential of Group 14 chemistry for applications in polymers and other materials.

1. Introduction

Compounds with homo- and heteronuclear multiple bonds of carbon play a pivotal role in virtually all areas of chemistry as versatile precursors and functional products. The tolerance of these unsaturated moieties for functional groups[1,2] is the key to the feasibility of elaborate synthetic protocols. Despite many attempts dating back more than one hundred years,[3,4] it took until 1976 before Lappert *et al.* isolated the first heavier analogues of alkenes, digermene **1** and distannene **2** (Chart 1).[5] The series was completed by the synthesis of stable disilene **3**[6] by West, Michl and Fink in 1981 and diplumbene **4**[7] by Weidenbruch *et al.* in 1999. Reports on the first homonuclear heavier triple bonds are even more recent.[8a-e] The quest for additional "heavier functional groups"[9] with multiple bond character goes on.

Unsaturated systems of carbons's heavier homologues generally require kinetic protection by sterically demanding substituents (aryl, alkyl or silyl) to suppress the thermodynamically favoured formation of saturated dimers or oligomers. Such substituents, however, offer little functionality and therefore the study of these derivatives is essentially limited to the reactivity (and thus usually consumption) of the heavier multiple bonds themselves, which indeed has been a major focus during the first 25 years or so after the first disclosure of stable derivatives.[10a-f]



1: E = Ge, **2**: E = Sn **3** **4**

Chart 1. The first heavier alkene analogues of Si, Ge, Sn and Pb (Mes = 2,4,6-$Me_3C_6H_2$; Tip = 2,4,6-$^iPr_3C_6H_2$).

Since the turn of the millennium, however, numerous Group 14 compounds with heavier double bonds *and* residual functionality have been reported, which exhibit at least the principal possibility of being manipulated while maintaining the integrity of the unsaturated moiety. It should be noted that hydrogen atoms bonded to heavier Group 14 elements are considered as a functional group in view of their hydridic aspect and corresponding high reactivity.

This review is a first attempt to provide a comprehensive account of the developments described above. The heavier

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alkenes in question can be categorised into derivatives with (A) vinylic functionality (E=E–X, E = group 14 element, X = atom or functional group), (B) allylic functionality (E=E–E–X,) and (C) a functional group in a remote position. The vinylic functionality is by far the most prevalent, which is likely due to the geometric impossibility of rearrangement to a saturated cyclic isomer. The large number of functionalized heavier aromatics is outside the scope of this review. The interested reader is referred instead to the excellent and comprehensive overviews by Sekiguchi and Lee et al.[10g-j]

2. Vinylic functionalities

Many heavier alkenes of Group 14 with functional groups in vinylic position have been reported. The elements directly bonded to the heavier double bond are predominantly from the s- and p-block, but a few η^1-transition metal complexes are also known. While most of these compounds have not been applied in synthesis as yet (and are therefore primarily of fundamental interest at this stage), especially vinylic halides and hydrides as well as metallated derivatives have found widespread application in the synthesis of unsaturated Group 14 compounds.

E=E–H, hydrido functionalities

The addition of E–H (E = Group 14 element) bonds to unsaturated substrates (hydrosilylation, hydrogermylation, hydrostannylation and hydroplumbylation) are established synthetic methods with many applications on the laboratory scale and in case of hydrosilylation also with examples in industrial processes.[11] Therefore, a high potential of hydrido functionalities for the introduction of heavier Group 14 multiple bonds to various substrates can be anticipated.

The isolation of the parent heavier group 14 ethylene analogues $H_2E{=}EH_2$ (E = Si, Ge, Sn, Pb) under ambient conditions is precluded by their high reactivity due to the absence of any kinetically or thermodynamically stabilising substituent. Nevertheless, they can be characterised in ultracold matrices and detected by laser flash photolytic experiments.[12] The high polarisability of the E=E bond, however, renders these molecules predisposed for coordination by Lewis acids and Lewis bases. Although the multiple bond character of the resulting species is limited, the concept of donor-acceptor stabilisation allowed for the isolation of one homonuclear **5**[13] and two heteronuclear derivatives **6a,b** (Chart 2).[14]

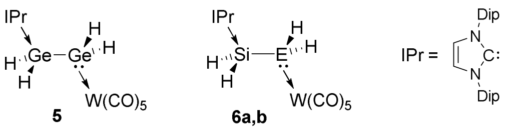
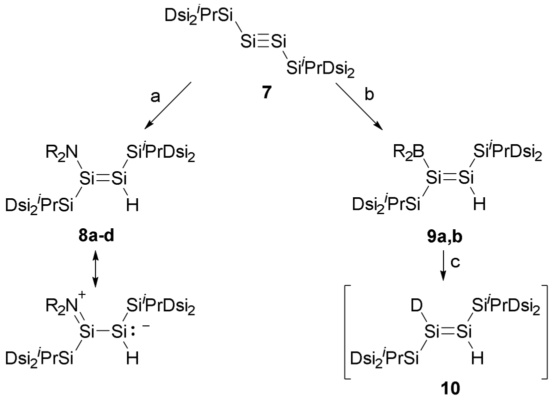


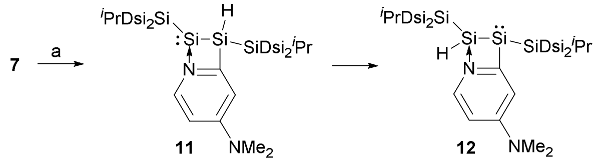
Chart 2. Donor-acceptor stabilised parent ditetrelenes **5** and **6a,b**; **6a**: E = Ge, **6b**: E = Sn, Dip = 2,6-^{i}Pr$_2$C$_6$H$_3$.

Several isolable hydrido disilenes[15] are obtained by the addition of E-H bonds to Sekiguchi's disilyne **7**.[9a] Hydroamination of disilyne **7** with one primary and three secondary amines gave access to 1-amino-2-hydrido disilenes **8a-d** that exhibit a significant contribution of a zwitterionic resonance structure and thus considerable allylic delocalisation (Scheme 1).[16, 17] In contrast to the fast addition of two equivalents of simple alcohols to disilyne **7**,[18] addition of a second equivalent of amine is only possible in the case of sterically least hindered **8d**. Hydroboration of **7** with 9-BBN or catecholborane yields 1-boryl-2-hydrido disilenes **9a,b**, respectively.[16, 19] Interestingly, the B–Si bond in **8a-d** appears to be more labile than the Si=Si moiety. As proven by deuterium labelling studies, methanolysis of disilene **9a** proceeds via initial substitution of the boryl substituent and the proposed intermediate **10**.



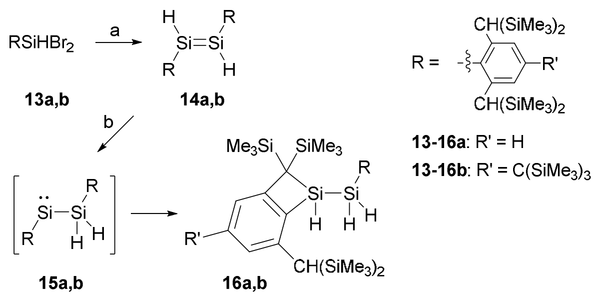
Scheme 1. Synthesis of hydridodisilenes **8a-d**. **9a,b**; **8a**: R = Et, **8b**: R = Ph, **8c**: NR$_2$ = NH^{t}Bu, **8d**: NR$_2$ = *N*-pyrrolidino, **9a**, **10**: BR$_2$ = 9-borabicyclo[3.3.1]nonan-9-yl, **9b**: BR$_2$ = catecholboryl; a: + R$_2$NH, b: + R$_2$BH, c: + MeOD, Dsi = (Me$_3$Si)$_2$CH.

The ability of disilyne **7** to activate C–H bonds allowed for the isolation of donor-stabilised silylene **11** by addition of a C–H bond of DMAP (4-dimethylaminopyridine) to one silicon centre of **7**. Rearrangement of **11** at ambient temperature gave access to ylidic hydrido disilene **12** (Scheme 2).[20]



Scheme 2. Reaction of disilyne **7** with DMAP to yield donor-stabilised silylene **11** and formation of hydrido disilene **12**; a: + DMAP (DMAP = 4-(Me$_2$N)C$_5$NH$_4$; Dsi = (Me$_3$Si)$_2$CH.

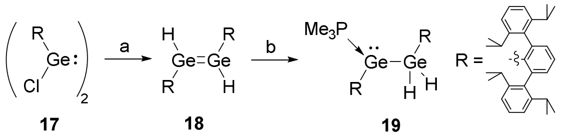
The first and to the best of our knowledge so far sole examples of stable 1,2-dihydro disilenes **14a,b** were reported in 2012.[21] Treatment of dibromosilanes **13a,b** with lithium/naphthalene gave access to the corresponding disilenes in moderate to good yield (Scheme 3). Silylsilylenes **15a,b** were suggested as intermediates in the thermal isomerisation of **14a,b** in solution to yield C–H insertion products **16a,b**.



Scheme 3. Synthesis of 1,2-dihydrido disilenes **14a,b** by reductive coupling of dibromosilanes **13a,b** and thermal isomerisation to disilanes **16a,b** via silylsilylenes **15a,b**. a: + Li/$C_{10}H_8$, b: C_6D_6, 80 °C.

Another example of a hydrido disilene, 1-lithio-2-hydrido disilene **47b**, is generated by formal addition of LiH to disilyne **7**, but will be discussed in the subsequent section due to the presence of the more reactive lithio functionality (see Scheme 14).[22] In neither of these cases any reaction of the Si–H bond of hydrido disilenes under preservation of the Si=Si moiety has been reported as yet.

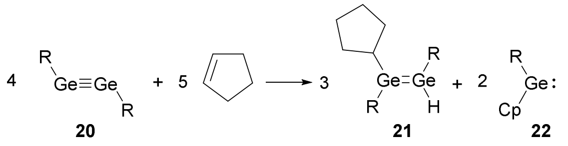
In case of germanium, the readily available Ge(II) monohalides provide an alternative access to hydrido digermenes. The first hydrido digermene, **18**, was obtained by reduction of terphenyl germanium(II) chloride **17**[9c] with $Li[BH^{s}Bu_3]$ (Scheme 4).[23]



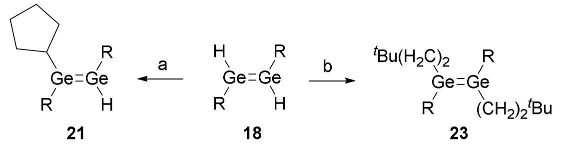
Scheme 4. Synthesis of 1,2-dihydrido digermene **18** by reaction of terphenylgermanium(II) chloride **17** with $Li[HB^{s}Bu_3]$ and isomerisation to donor-coordinated germylgermylene **19**. a: + $Li[HB^{s}Bu_3]$, b: + PMe_3.

Even though digermene **18** is thermally stable, the isomeric germylgermylene is apparently thermodynamically competitive as the reaction with trimethylphosphine yields the donor-coordinated germylgermylene **19**.[23] Digermyne **20**,[9c, 24] accessible from germanium(II) chloride **17** by reduction, has also been utilised for the synthesis of hydrido digermenes. Reaction of digermyne **20** (Scheme 5) with dihydrogen[25] or BH_3-THF[26] results in dihydrogen activation as indicated by the formation of mixtures of several germanium hydrides containing $(RGeH)_2$ (**18**), $(RGeH_2)_2$ and $RGeH_3$. The highest content of **18** according to ^1H NMR spectroscopy (21%) was obtained with one equivalent dihydrogen. 1,2-Dihydrido digermene **18** was also observed as a minor side product of the unexpected C–H activation of cyclic olefins by digermyne **20**.[27, 28] Upon optimisation of the reaction conditions, 1-cyclopentyl-2-hydrido digermene **21** was isolated as the main product of the reaction of digermyne with cyclopentene (Scheme 5).

The role of cyclopentene as formal dihydrogen donor in this reaction has been confirmed by the isolation of the cyclopentadienyl-substituted germylene **22**. In isolated form, the apparent intermediate **18** can be employed for the hydrogermylation of cyclopentene or 3,3-dimethylbut-1-ene under preservation of the double bond to yield **18** or 1,2-dialkyl digermene **23**, respectively (Scheme 6). In a trapping experiment, addition of an excess of the 3,3-dimethylbut-1-ene to the reaction of digermyne **20** and cyclopentene (Scheme 5) yields digermene **23** instead of **21**, proving the intermediacy of dihydro digermene **18** in this reaction beyond reasonable doubt.

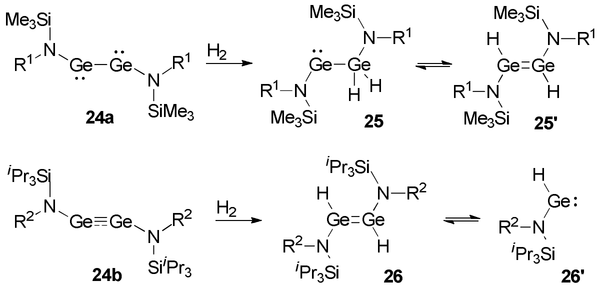


Scheme 5. Formation of hydrido digermene **21** and cyclopentadienyl germylene **22** by reaction of digermyne **20** with cyclopentene. R = 2,6-(Dip)$_2C_6H_3$, Dip = 2,6-$^iPr_2C_6H_3$.



Scheme 6. Hydrogermylation of 3,3-dimethylbut-1-ene and cyclopentene with 1,2-dihydro digermene **18** to yield alkyldigermene **21** and 1,2-dialkyl digermene **23**, respectively. a: + cyclopentene, b: + 3,3-dimethylbut-1-ene.

Germanium(II) species **24a,b** can be converted to germylgermylene **25** and 1,2-dihydrido digermene **26**, respectively, by direct dihydrogen activation in solution and the solid state (Scheme 7).[29] Spectroscopic and computational evidence suggests that in solution germylgermylene **25** is in equilibrium with 1,2-dihydrido digermene **25'**, while digermene **26** rather dissociates to the monomeric hydridogermylene **26'**.[30] No reactivity of dihydrido digermenes **25'** and **26** or their respective isomers **25** and **26'** has been reported yet.



Scheme 7. Addition of dihydrogen to digermynes **24a,b** to yield 1,2-dihydrido digermenes **25**, **26** and their equilibrium components germylgermylene **25'** and germylene, **26'**, respectively. **24a**, **25**, **25'**: R^1 = 2,6-$(CHPh_2)$-4-MeC_6H_2, **24b**, **26**, **26'**: R^2 = 2,6-$(CHPh_2)$-4-$^iPrC_6H_2$.

In general for Group 14, calculations on $(EH_2)_2$ (E = Group 14 element) show that with increasing atomic numbers the quantity of stable isomers increases. The energy difference between isomers **A**-**E** decreases and the relative order of stability is changed. As a simplified trend, hydride-bridged and mixed oxidation state species become more stable with increasing atomic number (Chart 3).[31]

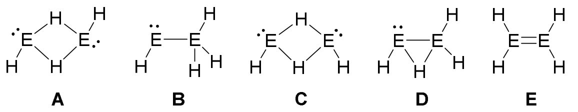
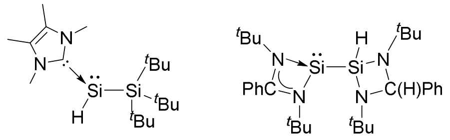


Chart 3. Calculated minima on the energy hypersurface **A-E** of $(SnH_2)_2$.

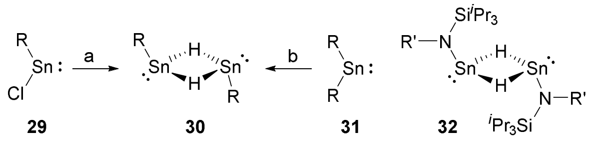
Some examples of silicon and germanium derivatives of type **B** have been discussed earlier (Schemes 2, 3, 4, 7). For stabilisation purposes, these mixed-valent species generally require either a donor substituent as in case of dihydrogen activation product **25** (Scheme 7) or an external donor as in **19** (Scheme 4), **27**,[15b] and **28**[32] (Chart 4).



27 **28**

Chart 4. Examples of donor-coordinated Si=Si double bond isomers: silylsilylenes **27**, **28**.

All known examples of donor-free, dimeric hydrido stannylenes $(RSnH)_2$, however, are representatives of either the double bridged structure **A** or the stannylstannylene **B**. Notably, no alkene-like derivative of type **E** has been reported to date.



Scheme 8. Alternate routes to hydrogen-bridged tin(II) hydride **30** from tin(II) chloride **29** and diarylstannylene **31**, H-bridged tin(II) amide **32**; a: + diisobutylaluminum hydride, b: + H_2, - RH; R = 2,6-$(Dip)_2C_6H_3$, Dip = 2,6-$^iPr_2C_6H_3$;

The first dimeric tin(II) hydride **30** was obtained by reaction of terphenyltin(II) chloride **29** with diisobutylaluminum chloride (Scheme 8).[33] The bridging hydrogen atoms were located by a single crystal X-ray diffraction study and their presence confirmed by $^1H/^2D$ NMR and IR spectroscopy. An alternate synthetic route employs diarylstannylene **31**, which was converted to tin hydride **30** by activation of H_2 (or D_2) and elimination of R–H at ambient pressure.[34] A likewise hydrogen-bridged dimeric structure was found in case of aminotin(II) hydride **32**.[26b] The lighter congeners of tin(II) hydrides **30** and **32**, germanium hydrides **18** and **26** (Scheme 4, 7), both exhibit a trans-bent 1,2-dihydrido digermene structure. The influence of the size of the terphenyl substituent on the solid state structures of terphenyltin(II) chlorides **33a-d** and **34** was also studied (Chart 5).[35]

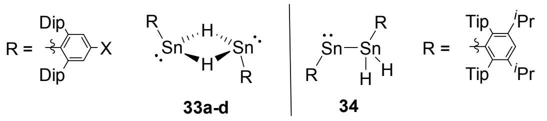
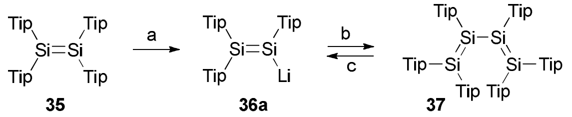


Chart 5. Terphenyl substituted tin(II) hydrides with the double hydrogen bridged (**33a-d**) and stannylstannylene (**34**) structural motifs; Dip = 2,6-$^iPr_2C_6H_3$, Tip = 2,4,6-$^iPr_3C_6H_2$, X = H, ^tBu, OMe, $SiMe_3$, F.

With exception of the tin(II) hydride with the sterically most demanding terphenyl substituent, **34**, all derivatives exhibit the double hydrogen-bridged structural motif of type **C**.

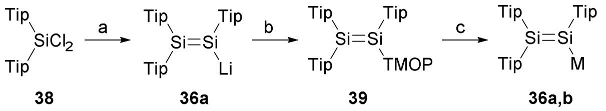
E=E–M, metallo functionalities (M = group 1 and group 2 metal)

Heavier alkenes with metallo-functionality in vinylic position have been utilised for various transformations under preservation of the heavier multiple bond, e.g. in case of disilenides.[36] Several methods for the preparation of alkaline and alkaline earth metal disilenides are available. They can be classified as reductive cleavage of a) Si–aryl bonds, b) Si–Si single bonds, c) Si–Cl bonds, d) the addition of LiR (R = H, Me) to a Si≡Si triple bond and e) transmetallation. In 1997 Weidenbruch *et al.* proposed that reduction of disilene **35**[37] leads to the non-isolated intermediate, disilenide **36a**, which is reacted with bromomesitylene to yield the stable tetrasilabutadiene **37** (Scheme 9).[38]



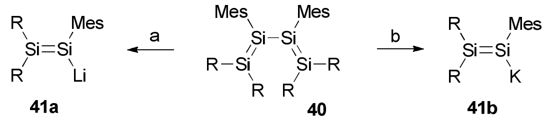
Scheme 9. Proposed generation of disilenide **36a** from disilene **35** and formation of tetrasilabutadiene **37**; a: + 2 Li, – TipLi, b: + 0.5 MesBr, – 0.5 MesLi, – 0.5 LiBr, c: + Li; Mes = 2,4,6-$Me_3C_6H_2$, Tip = 2,4,6-$^iPr_3C_6H_2$.

The first isolable disilenides, were independently reported in 2004 by Scheschkewitz[39] and the Sekiguchi group.[40] Disilenide **36a**$(dme)_2$ is synthesised directly from dichlorosilane **38** in 51 % yield (Scheme 10) without the necessity to isolate disilene **35**, a possible intermediate during the formation of **36a**$(dme)_2$ from **38**. The versatility of disilenide **36a**$(dme)_2$ prompted the authors to develop a protecting group strategy utilising the relative ease and selectivity of the reductive Si–aryl bond cleavage.[41] The coupling of disilenide **36a** with TMOP–I (TMOP = 2,4,6-trimethoxybenzene) to yield **39** and the subsequent (re-)generation of either the initial disilenide **36a** or its potassium derivative **36b** by reduction with lithium or potassium, respectively, holds a great synthetic potential.



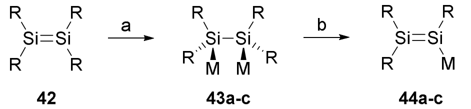
Scheme 10. Synthesis of isolable disilenide **36a**$(dme)_2$ from Tip_2SiCl_2, **38**, and functionalisation with the TMOP leaving group to yield tetraaryldisilene **39**, which was successfully employed to yield either disilenide **36a** or its potassium derivative **36b**; a: + 6 Li, – 4 LiCl, - TipLi, b: + TMOP–I, c: + Li/$C_{10}H_8$ (**a**) C_8K (**b**); Tip = 2,4,6-$^iPr_3C_6H_2$, TMOP = 2,4,6-$(MeO)_3C_6H_2$.

Reaction of tetrasilabutadiene **40** with four equivalents of ^tBuLi in thf affords disilenide **41a**$(thf)_3$ in 67% isolated yield (Scheme 11). The reaction mechanism leading to **41a** has not been fully elucidated, but does not seem to involve the scission of the Si–Si single bond by formal addition of LiH or ^tBuLi since only isobutene could be detected as a side product in NMR scale reactions. The potassium disilenide **41b**(dme,diglyme) (diglyme = diethylenglycodimethylether) was obtained by reaction of tetrasilabutadiene **40** with potassium graphite in thf.[42]

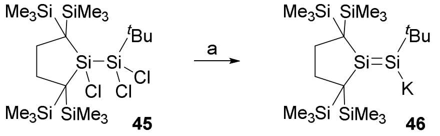


Scheme 11. Reaction of tetrasilabutadiene **40** with ^{t}BuLi and C_8K to yield disilenide **41a,b**; a: + ^{t}BuLi, − isobutene, b: + KC_8; Mes = 2,4,6-$Me_3C_6H_2$, R = $^tBu_2MeSi$

Even though a variety of 1,2-dimetallo disilanes had already been reported before 2001,[43] Sekiguchi *et al.* could show in 2005 that tetrasilyldisilene **42** can be reduced by alkaline metal/naphthalene to give the corresponding dianions **43a-c**. The dianions **43a-c** are stable in thf solution, but can be converted to disilenides **44a-c** under elimination of $^tBu_2MeSiM$ (M = Li, Na, K) by simple solvent exchange to benzene (Scheme 12).[44] A disilenide without aryl and silyl substituents **46**$(thf)_2$ was prepared by reaction of trichloro disilane **45** with potassium graphite (Scheme 13).[45]

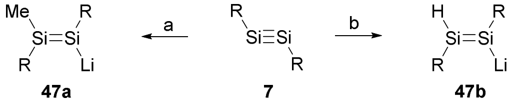


Scheme 12. Reduction of disilene **42** with alkaline metal/naphthalene to yield dianions **43a-c** and formation of disilenides **44a-c** via elimination of RM; a: + $M/C_{10}H_8$ / thf, b: benzene, − RM; **43a**, **44a**: M = Li, **43b**, **44b**: M = Na, **43c**, **44c**: M = K; R = $^tBu_2MeSi$.



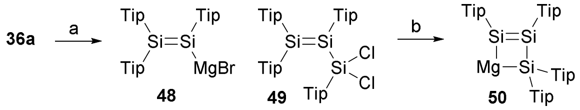
Scheme 13. Synthesis of disilenide **46**$(thf)_2$ by reductive dehalogenation of trichlordisilane **45**.

Disilyne **7**[9a] was utilised for the preparation of two different disilenides, **47a,b**. Methyllithium adds across the triple bond of **7** in thf solution at low temperature to yield methyldisilenide **47a**, which was characterised by nmr spectroscopy.[46] In the reaction of **7** with *tert*-butyllithium the hydrido disilenide **47b** is obtained.[22] In this case, however, the reaction proceeds via a single electron transfer to the triple bond followed by hydrogen radical abstraction to give the formal lithium hydride addition product **47b** (Scheme 14).



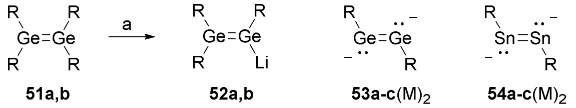
Scheme 14. Conversion of disilyne **7** to disilenides **47a,b** by addition of methyllithium and formal addition of lithium hydride, respectively; R = $Dsi_2{}^iPrSi$, Dsi = $(Me_3Si)_2CH$; a: + MeLi, b: + ^{t}BuLi.

Only two vinylic alkaline earth metal disilenes have been reported yet. Disilenylmagnesium bromide **48** is accessible from lithio disilenide **36a**$(dme)_2$ and magnesium bromide by transmetallation (Scheme 15). [47] The highly functional α,ω-dianionic trisilandiide **50**$(thf)_2$ was obtained from the reaction of (dichlorosilyl)disilene **49** and activated magnesium.[48] The reaction of dianion **50** with Me_2SnCl_2 under retention of the double bond will be described in one of the following sections.



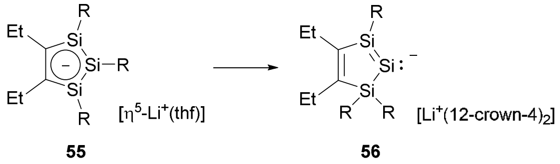
Scheme 15. Transmetallation of lithio disilenide **36a** with magnesium bromide to yield magnesio disilenide **48** and synthesis of trisilen-1,3-diide **50** from (dichlorosilyl)disilene **49**; a: + $MgBr_2$, − LiBr, b: activated magnesium; Tip = 2,4,6-$^iPr_3C_6H_2$.

The first and to date only isolable digermenides are accessible from digermenes **51a,b** and lithium/naphthalene. Although digermenides **52a,b**$(dme)_2$,[49a] had been reported fifteen years prior to the isolation of disilenides **36a** and **41a**, no information on their structure or reactivity aside from their methanolysis is available as yet (Scheme 16). A related Tip substituted digermenide was suggested as an intermediate during the formation of a tetragermabutadiene.[49b] Corresponding distannenides and diplumbenides are still unknown. Formal two-electron reduction of digermynes and distannynes gave rise to dianions **53a-c** and **54a-c**, that can be considered as digermen-1,2-diides and distannen-1,2-diides, respectively.[25, 50]



Scheme 16. Synthesis of digermenides **52a,b** from digermenes **51a,b** by elimination of RLi and experimentally known dianions of digermynes and distannynes, **53a-c**, **54a-c**; a) + $Li/C_{10}H_8$, − RLi; **51a**, **52a**: R = Dip = 2,6-$^iPr_2C_6H_3$, **51b**, **52b**: R = 2,6-$Et_2C_6H_3$, Tip = 2,4,6-$^iPr_2C_6H_2$; **53a**: R = 2,6-$Dip_2C_6H_3$, M = Li; **53b**: R = 2,6-$Tip_2C_6H_3$, M = Na; **53c**: R = 2,6-$Tip_2C_6H_3$, M = K; **54a**: R = 2,6-$Tip_2C_6H_3$, M = Na; **54b**: R = 2,6-$Dip_2C_6H_3$, M = K, **54c**: R = 2,6-$Tip_2C_6H_3$, M = K.

Trisilacyclopentadienide **55** is not only an interesting aromatic silicon compound due to its cyclic six π-electron system, it also converts to the unique cyclic β-alkenyl functionalised disilenide **56** upon addition of 12-crown-4 via migration of one silyl substituent (Scheme 17).[51]

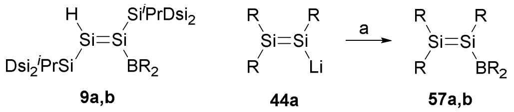


Scheme 17. Rearrangement of trisilacyclopentadienide **55** to cyclic disilenide **56**; a: + 12-crown-4; R = $^tBu_2MeSi$.

Known disilenides are excellent nucleophiles and have been utilised for the synthesis of various novel disilenes and other compounds featuring one or more Si=Si moieties. Since most of these products exhibit functionalities of their own they will be discussed in the following sections.

E=E–Tr, triel functionalities (Tr = group 13 element)

Boryl substituted disilenes are to date the only examples disilenes with Group 13-based functional groups in vinylic position. They were obtained either by hydroboration of disilyne **7** (boryldisilenes **9a,b**, Scheme 1, 18)[9a, 19] or borylation of disilenide **44a** (boryldisilenes **57a,b**, Scheme 18).[52]

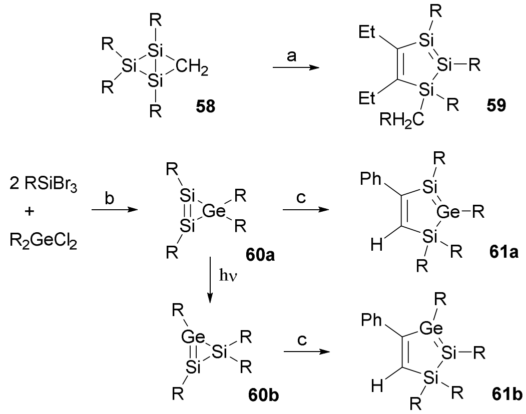


Scheme 18. Boryl disilenes **9a,b** and synthesis of boryl disilenes **57a,b** from disilenide **44a**; **9a**: BR_2 = 9-borabicyclo[3.3.1]nonan-9-yl, **9b**, **57a**: BR_2 = catecholboryl, **57b**: BR_2 = pinacolboryl; a: (**57a**) + (chloro)catecholborane, (**57b**) + (chloro)pinacolborane; R = ^{t}Bu$_2$MeSi.

No reactivity of boryldisilenes has been reported yet except for the methanolysis of compound **9a** proceeding via the proposed intermediate, dihydrido disilene **10** (see Scheme 1).

E=E–Tt, tetrel functionalities (Tt = group 14 element)

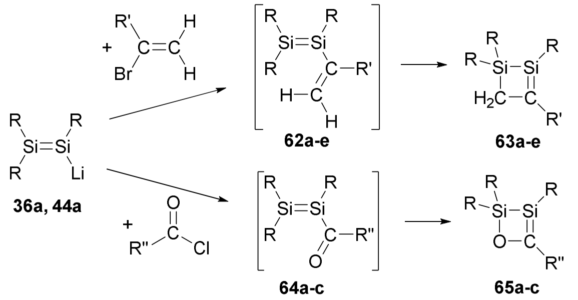
The large number of carbon and silicon based substituents that primarily serve as bulky groups for steric protection of heavier Group 14 multiple bonds will not be discussed here, even though, any aryl or silyl substituent could in principle function as a leaving group under appropriate conditions (see: metallo functionalised E=E bonds). Alkenyl substituted heavier Group 14 multiple bonds have so far only be isolated as part of cyclic systems. Disilenide **56** (Scheme 17) exhibits an endocyclic C=C double bond in addition to the negatively charged silicon atom. Neutral trisilacyclopentadiene **59** was obtained from trisilabicyclobutane **58** and 3-hexyne at elevated temperatures (Scheme 19) and was utilised as the precursor for cyclic anion **55** (see Scheme 17).[51]



Scheme 19. Synthesis of germadisilacyclopropene **60a** and its rearrangement under photolytic conditions to **60b**, ring expansion of **58**, **60a,b** with alkynes to yield heterocyclopentadienes **59**, **61a,b**; a: + 3-hexyne, b: Na, toluene, c: + phenylacetylene; R = ^{t}Bu$_2$MeSi.

Ring expansion of germadisilacyclopropenes **60a,b**[53] with phenylacetylene afforded the closely related germadisilacyclopentadienes **61a,b** (Scheme 19).[54] The heteronuclear heavier cyclopropenes **60a,b** are only the first of several examples of this substance class that have the ability to successfully deliver an E=E moiety to a substrate.

Acyclic alkenyldisilenes **62a-e** and acyldisilenes **64a-c** were suggested as intermediates in the formation of cyclic silenes **63a-e**[55] and **65a-c**,[56] respectively (Scheme 20), during the reaction of disilenides **36a** and **44a** with bromoalkenes and acyl chlorides. Spectroscopic detection of acyldisilenes **64a-c** was unsuccessful even at low temperatures.



Scheme 20. Reaction of disilenides **36a**, **44a** with bromoethanes to yield cyclic silenes **63a-e** via proposed alkenyldisilenes **62a-e** and reaction with acyl chlorides to yield oxadisiletanes **65a-c** via proposed acyldisilenes **64a-c**; **36a**, **62a,b**, **63a,b**, **64a,b**, **65a,b**: R = Tip = 2,4,6-^{i}Pr$_2$C$_6$H$_2$, **44a**, **62c-e**, **63c-e**, **64c**, **65c**: R = ^{t}Bu$_2$MeSi, **62a**, **63a**, **62d**, **63d**: R' = Ph, **62b**, **63b**, **62e**, **63e**: R' = SiMe$_3$, **62c**, **63c**: R' = H, **64a,b**, **65a,b**: R'' = 1-adamantyl, **64c**, **65c**: R'' = ^{t}Bu.

Acyldisilenes were also proposed as intermediates during the reaction of disilenide **36a** with α,β-unsaturated acyl chlorides resulting in the formation of 1,2-disilabicyclo[1,1,1]pentan-4-ones.[57] A heavier analogue of cyclobutadiene, **66**, is directly accessible from digermyne **20** and diphenylacetylene by formal [2+2]-cycloaddition (Chart 6).[58] While the presence of endocyclic C=C double and Ge–C single bonds could be established by single crystal X-ray diffraction, the Ge–Ge bond length of **66** is in the typical range of single bonds and exhibits significantly pyramidalised Ge centres.

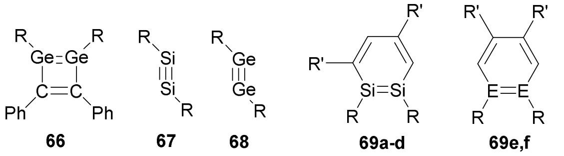
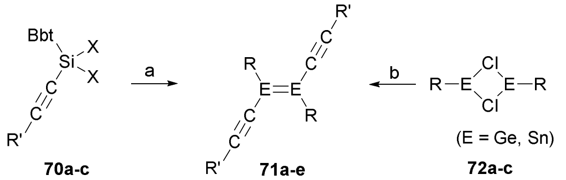


Chart 6. Digermacyclobutadiene **66** and disilyne **67**, digermyne **68**, 1,2-disilabenzenes **69a-e**, 1,2-digermabenzene **69f**; **66**: R = 2,6-(Dip)$_2$C$_6$H$_3$, Dip = 2,6-^{i}Pr$_2$C$_6$H$_3$, **67**, **68**, **69a-c**: R = Bbt = 2,4,6-(Me$_3$Si)$_2$CH)$_3$C$_6$H$_2$, **69d,e**: R = Dsi$_2$^{i}PrSi, Dsi = (Me$_3$Si)$_2$CH, **69a**: R' = H, **69b**: R' = Me$_3$Si, **69c-e**: R' = Ph, **69e**: E = Si, **69f**: E = Ge, R = Tbb = 2,6-((Me$_3$Si)CH)$_2$-4-^{t}BuC$_6$H$_2$, R' = H.

Disilabenzenes **69a-e** and 1,2-digermabenzene **69f** formally featuring a 1,3-dienyl functionality were prepared by reaction of isolable disilynes **7** and **67** and digermyne **68** with two equivalents of the corresponding alkynes.[59] Structural parameters, however, suggest the presence of delocalised π-systems. The Si–Si bond length is between those of typical single and double bonds. So far only one reaction of 1,2-disilabenzenes **69a-e** under cleavage of the Si–Si bond has been reported. Even though alkynyl derivatives of heavier double bonds of silicon, germanium and tin are experimentally known, no reactivity of any of these has been reported yet.[60] *E*-1,2-bis(alkynyl)disilenes **71a,b** are accessible from the corresponding dichloro and dibromosilanes **70a-c** by reduction with lithium/naphthalene (Scheme 21).



Scheme 21. Synthesis of bis(alkynyl) heavier double bonds of silicon, germanium and tin; a: + Li/$C_{10}H_8$, b: + R'C≡CLi; **71a,b**: R = Bbt, **71c-e**, **72a-c**: R = 2,6-$Dip_2C_6H_3$, Dip = 2,6-$^iPr_2C_6H_3$, **70a**: R' = Me_3Si, X = Cl, **70b**: R' = Me_3Si, X = Br, **70c**: R' = Ph, X = Br, **71a**: E = Si, R' = Me_3Si, **71b**: E = Si, R' = Ph, **71c**: E = Ge, R' = Me_3Si, **71d**: E = Ge, R' = ^tBu, **71e**: E = Sn, R' = Me_3Si, **72a,b**: E = Ge, **72c**: E = Sn; Bbt = 2,6-$((Me_3Si)_2CH)_2$-4-$((Me_3Si)_3C)C_6H_2$.

E-1,2-bis(alkynyl)digermenes **71c,d** and distannene **71e** were obtained directly from Ge(II) and Sn(II) chlorides **72a-c** with lithium acetylides (Scheme 21). Aside from their potential as precursors for novel heavier group 14 doubly bonded system, compounds **71a-e** are also of interest due to their optical properties resulting from electron delocalisation along the $C_2E_2C_2$ moiety. The interaction of disilene moieties with carbon based π-systems was studied in detail on phenylene bridged bis(disilenes) **73a,b**,[61] **74a,b** (Chart 7)[62] and aryl substituted disilenes **75a-c**[45] and **76a-c** (Chart 8).[63]

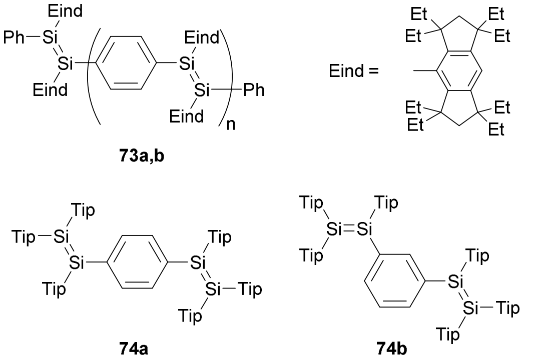


Chart 7. Phenylene bridged bis and tris(disilenes) **73a,b** and **74a,b**; **73a**: n = 1, **73b**: n = 2.

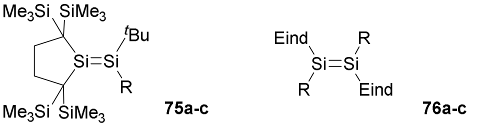
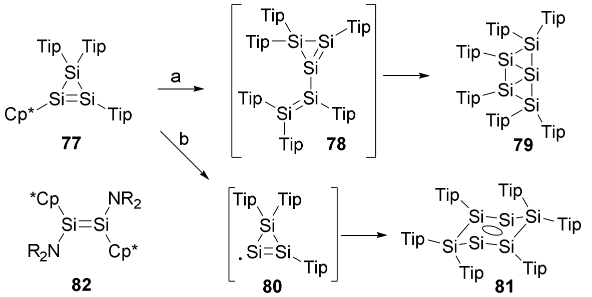


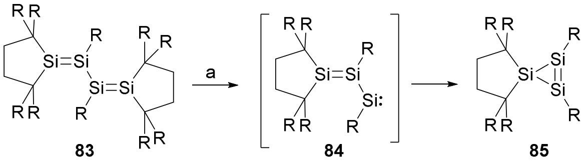
Chart 8. Aryldisilenes **75a-c**, **76a-c**, **75a**: R = 1-naphthyl, **75b**: R = 9-phenanthrenyl, **75c**: R = 9-anthracenyl, **76a**: R = phenyl, **76b**: R =2-naphthyl, **76c**: R = 2-(9,9-dimethyl-*9H*-fluorenyl).

The pentamethylcyclopentadienyl (Cp*) substituent represents one of the few Group 14 based vinylic functionalities that has been used for derivatisation of a disilene under preservation of the multiple bond. Reaction of cyclotrisilene **77** with disilenide **36a** affords a mixture containing siliconoid **79** which forms via the proposed Cp* substitution product, tetrasilabutadiene **78** (Scheme 22). The second product of this reaction is the dismutational hexasilabenzene isomer **81** accompanied by half an equivalent of tetrasilabutadiene **37** (Scheme 9), an oxidation product of disilenide **36a**. Cyclotrisilenyl radical **80** was suggested as a likely intermediate of this reaction path and indeed, treatment of cyclotrisilene **77** with one equivalent lithium/naphthalene affords dismutational hexasilabenzene **81** as sole product.[64] No reaction of Cp* substituted disilene **82**, which is in equilibrium with silylene Cp*($(Me_3Si)_2N$)Si: in solution, has been reported yet.[65]



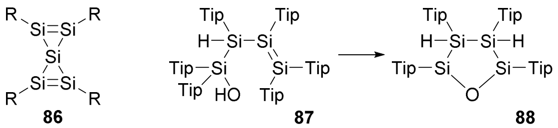
Scheme 22. Utilisation of the pentamethylcyclopentadienyl substituent in cyclotrisilene **77**: nucleophilic substitution with disilenide **36a** to yield siliconoid **79** via proposed tetrasilabutadiene intermediate **78** and formation of hexasilabenzene isomer **81** via proposed intermediate **80**; a: + **36a**, − Cp*Li, b: + Li/$C_{10}H_8$, − Cp*Li or + **36a**, − 0.5 **37** (Scheme 9), **82**: R = Me_3Si).

The generation of disilenides **36a**, **41a,b** from tetrasilabutadienes **37**, **40** has already been discussed in a previous section (Scheme 10, 12). The third isolable tetrasilabutadiene, **83**, liberates cyclotrisilene **85** upon heating in solution or photolysis (Scheme 23).[66] The likely intermediate of this reaction is disilenylsilylene **84**. A related NHC-coordinated (*N*-heterocyclic carbene) disilenylsilylene has been isolated from the equilibrium mixture of the corresponding cyclotrisilene and free NHC.[67]



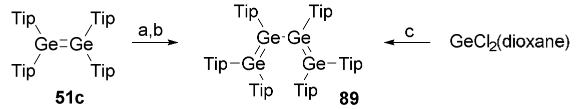
Scheme 23. Conversion of tetrasilabutadiene **83** to cyclotrisilene **85** via disilenylsilylene **84**; a: benzene, 80 °C or hν; R = Me_3Si.

The interesting spiropentasiladiene **86** was obtained as a by-product during the synthesis of a cyclotrisilene.[68] Attempted 1,2-addition to tetrasilabutadienes usually yielded the corresponding 1,4-addition products (See Section 3.). Good evidence was provided, though, that the addition of water to tetrasilabutadiene **37** yields 1,2-addition product **87** in the first step which cyclises to afford oxatetrasilolane **88** unless a second equivalent of water is available to add to the remaining Si=Si double bond (Scheme 24).[69]



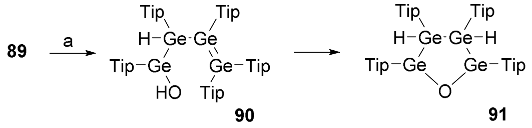
Scheme 24. Spiropentasiladiene **86** and 1,2-addition of water to tetrasilabutadiene **37** to yield disilene **87** and cyclization of **87** to afford oxatetrasilolane **88**; a: + H_2O; R = $^tBu_2MeSi$, Tip = 2,4,6-$^iPr_3C_6H_2$.

A tetrasilacyclobutadiene with a bis(ylidic) electronic structure has also been described but no reactivity has been reported yet.[70] The to date only tetragermabutadiene **89** was obtained by a synthetic route analogous to that employed for tetrasilabutadiene **37**. Alternatively, **89** can be prepared by a one-pot synthesis starting from germanium(II) chloride (Scheme 25).[49b, 71]



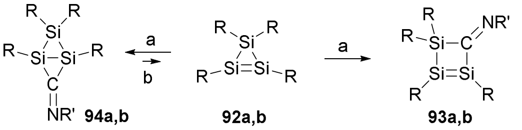
Scheme 25. Synthesis of tetragermabutadiene **89** from digermene **51c** or germanium(II) chloride; a: + 2 Li, − TipLi, b: + 0.5 MesBr, − 0.5 LiBr, − 0.5 MesLi, c: + 1.5 TipMgBr, + Mg, − $MgCl_2$, − 0.75 $MgBr_2$; Mes = 2,4,6-$Me_3C_6H_2$, Tip = 2,4,6-$^iPr_3C_6H_2$.

Similar to the case of tetrasilabutadiene **37** (see Schemes 10 and 25) the reaction of **89** with water results in the formation of a oxatetragermolane **91** via the proposed intermediate, 1,2-addition product **90** (Scheme 26).[72]



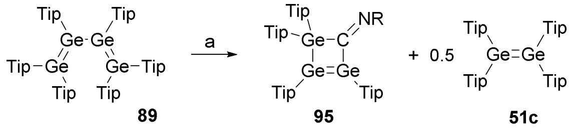
Scheme 26. Synthesis of oxatetragermolane **91** by addition of water to tetragermabutadiene **89** via proposed 1,2-addition intermediate **90**; a: + H_2O; Tip = 2,4,6-$^iPr_3C_6H_2$.

C-imino functionalised disilenes and digermenes were obtained by different routes. Cyclotrisilenes **92a,b** [73] react with aryl or alkyl isocyanides to yield iminotrisilacyclobutenes **93a,b** by insertion of the isocyanide moiety into a Si–Si single bond. The second product of this reaction, kinetically favoured trisilabicyclobutanes **94a,b**, are not direct intermediates in the formation of thermodynamically favoured iminotrisilacyclobutenes **93a,b**. The observed conversion of **94a,b** to **93a,b** most likely proceeds as a result of an equilibrium between **94a,b** and cyclotrisilenes **92a,b** (Scheme 27).[74]



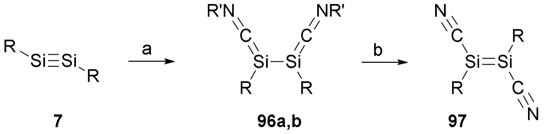
Scheme 27. Synthesis of trisilacyclobutenes **93a,b** from cyclotrisilenes **92a,b** and equilibrium between cyclotrisilenes **92a,b** and trisilabicyclobutanes **94a,b**; a: + CNR’, b: − CNR’ **92a-94a**: R = $^tBu_2MeSi$, R’ = 2,6-$Me_2C_6H_3$, **92b-94b**: R = Tip = 2,4,6-$^iPr_3C_6H_2$, R’ = ^tBu.

The related iminotrigermacyclobutene **95** was not obtained from known cyclotrigermenes[75] but by reaction of tetragermabutadiene **89** with an arylisocyanide (Scheme 28).[72] This reaction is presumably initiated by initial dissociation of one Ge=Ge double bond to afford an intermediate digermenylgermylene and Tip_2Ge:, the latter of which was identified as the dimerisation product, digermene **51c**.



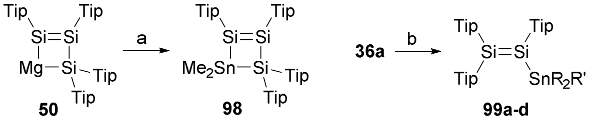
Scheme 28. Synthesis of trigermacyclobutene **95** from tetragermabutadiene **89**; a: + 2-(MeO)phenylisocyanide; R = 2-(MeO)C_6H_4, Tip = 2,4,6-$^iPr_3C_6H_2$.

The unusual disilene **97** with two π-acceptor substituents was synthesised from disilyne **7** and two equivalents alkylisonitriles. The initially formed and spectroscopically characterised isocyanide adducts **96a,b** transformed to **97** upon warming to ambient temperature by a radical mechanism (Scheme 29).[76] No reactivity of compounds **93**, **95** or **97** under retention of the double bond has been reported yet.



Scheme 29. Synthesis of 1,2-dicyanodisilene **97** via isolable disilyne-isocyanide adducts **96a,b**; a: + 2 R–N=C, b: rt.; R = $Dsi_2{}^iPrSi$, Dsi = $(Me_3Si)_2CH$, **96a**: R’ = tBu, **96b**: R’ = $^tBu(Me_2)C$.

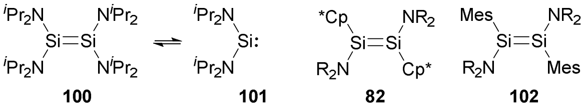
Tin-substituted disilenes have been obtained from two different metallated disilenes. Dianion **50** was reacted on NMR scale with Me_2SnCl2 to yield unsaturated four-membered ring **98** which was characterised by multinuclear NMR spectroscopy.[47] Stannyl disilenes **99a-d** were synthesised from disilenide **36a** (Scheme 11) and the corresponding diorganotin chloride or triorganotin chloride (Scheme 30).[77]



Scheme 30. Synthesis of unsaturated heterocycle **98** from dianion **50** and stannyldisilenes **99a-d**; a: + Me_2SnCl_2, b: + $R_2R'SnCl$, **99a**: R = R’ = Me, **99b**: R = R’ = Ph, **99c**: R = R’ = ^nBu, **99d**: R = ^tBu, R’ = Cl; Tip = 2,4,6-$^iPr_3C_6H_2$.

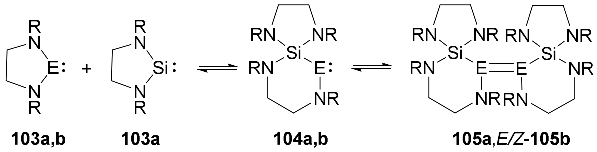
E=E–Pn, pnictogen functionalities (Pn = group 15 element)

A relatively small number of amino substituted heavier group 14 multiple bonds has been reported to date.[78] Disilene **100** is the only tetraamino substituted doubly bonded system and exists in equilibrium with diaminosilylene **101** in solution (Scheme 31).[79] A similar equilibrium was observed for 1,2-diaminodisilene **82** (Scheme 22).[65] The thermal and photochemical cis-trans isomerisation of disilene **102** was also reported.[80]



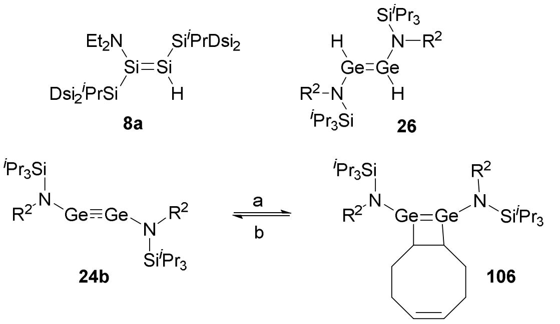
Scheme 31. Equilibrium of tetraaminodisilene **100** with silylene **101**, 1,2-diaminodisilenes **82**, **102**; R = $SiMe_3$.

Isolable diaminosilylene **103a**[81] and germylene **103b**[82] were shown to react with diaminosilylene **103a** under insertion into an E–N bond to yield silylene **104a**[83] and germylene **104b**[84], respectively. Compounds **104a,b** further dimerise to give 1,2-diaminodisilene **105a** and 1,2diaminodigermene *E/Z*-**105b**. This process is reversible in case of **103a** → **105a** (Scheme 32).



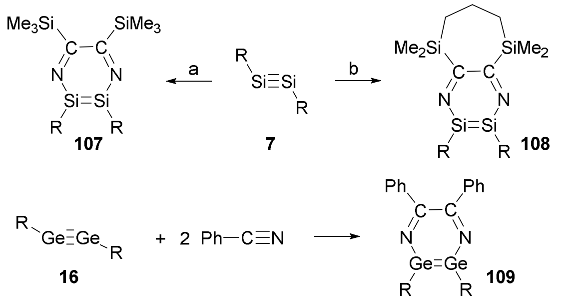
Scheme 32. Formation of disilene **105a** and digermene *E/Z*-**105b** by E–N insertion of silylene **103a** into **103a,b** followed by dimerisation; R = ^{t}Bu, **103-105a**: E = Si, **103b-105b**: E = Ge.

Further representatives of amino-substituted heavier multiple bonds have already been discussed in a previous section, namely 1-amino-2-hydridodisilenes **8a-d** obtained by hydroamination of disilyne **7** (Scheme 1) and digermynes **24a,b** together with the corresponding hydrogen activation products **25**, **26** (Scheme 7). Selected examples of these can be found in Scheme 33. Remarkably, digermyne **24b** and 1,5-cyclooctadiene form an equilibrium in solution with their [2+2] cycloaddition product **106**, thermodynamic data of this process have not been reported yet.[29c]



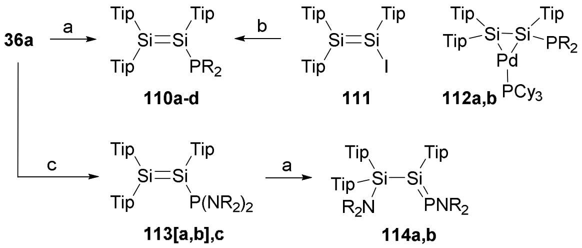
Scheme 33. 1-Amino-2-hydridodisilene **8a**, 1,2-diaminodigermene **26**; equilibrium of digermyne **24b** and 1,5-cyclooctadiene with cycloaddition product **106**; a: + 1,5-cyclooctadiene, b: − 1,5-cyclooctadiene, Dsi = $(Me_3Si)_2CH$, R^2 = 2,6-$(CHPh_2)$-4-^{i}PrC_6H_2.

Two different 1,2-bis(*N*-imino)disilenes **107**, **108** have been synthesised from disilyne **7** by reaction with nitriles. In both cases 2,3-disilapyrazine derivatives were obtained as a result of cyclisation by means of C–C bond formation (Scheme 34).[85] The endocyclic bond lengths (c-$Si_2N_2C_2$) are between typical single and double bonds indicating a delocalised electronic structure. Analogous reactivity of a nitrile towards the digermyne **16** had been reported earlier to yield 2,3-digermapyrazine derivative **109**.[85c] No reports on the reactivity of compounds **107-109** have been published yet.



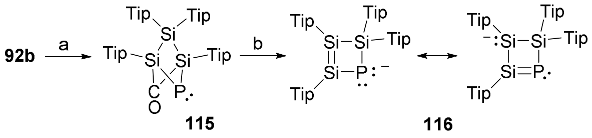
Scheme 34. Synthesis of 2,3-disilapyrazines **107**, **108** and 2,3-digermapyrazine **109** from disilyne **7** and digermyne **16**, respectively; a: + $NC(SiMe_2)(CH_2)_3(SiMe_2)CN$, b: + 2 Me_3SiCN; **7**, **107**, **108**: R = ^{i}PrDsi$_2$Si, Dsi = $(Me_3Si)_2CH$, **16**, **109**: R = 2,6-$(Dip)_2C_6H_3$, Dip = 2,6-^{i}Pr$_2C_6H_3$.

Phosphino disilenes **110a-d** were obtained from disilenide **36a** and the corresponding chlorophosphanes. Structural data imply a certain allylic character of the Si_2P moiety. Phosphino disilene **110a** was also synthesised from iododisilene **111** (vide infra) and Ph_2PLi and identified by NMR spectroscopy (Scheme 35).[86] Interestingly, reaction of phoshino disilenes **110a,b** with $(Cy_3P)_2Pd$ yields metallacycles **112a,b**, which exhibit no interaction of the phosphine substituent with the metal centre. In case of reaction of disilenide **36a** with bis(dialkylamino)chlorophosphines only the phosphino disilene, **113c**, similar to **110a-d**, was isolated. If smaller substituents were employed the plausible intermediates, phosphino disilenes **113a,b**, could not be observed and phosphasilenes **114a,b** were obtained instead, presumably via 1,3-migration of a phosphorus bonded NR_2 substituent.[87]



Scheme 35. Synthesis of phosphino disilenes **110a-d**, **113a-c** from disilenide **36a** and iododisilene **111**, rearrangement of phosphino disilenes **113a,b** to phosphasilenes **114a,b**, metallacycles **112a,b**; a: + R_2PCl, − LiCl, b: + Ph_2PLi, − LiI; c: + $(R_2N)_2PCl$, − LiCl **110a**, **112a**: R = Ph, **110b**, **112b**, **113c**: R = ^{i}Pr, **110c**: R = cyclohexyl, **110d**: R = ^{t}Bu, **113a**, **114a**: R = Me, **113b**, **114b**: R = Et; Tip = 2,4,6-^{i}Pr$_3C_6H_2$.

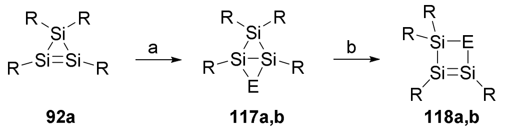
The transfer of phosphide (P^-) to cyclotrisilene **92b** by means of potassium 2-phosphaethynolate (K^+PCO^-) gave access to phosphatrisilacyclobutenide **116**[K(18-crown-6)] via the isolable bicyclo[1.1.1]pentanone-like intermediate **115**. Spectroscopic and structural data show a significant allylic character for compound **116**[K(18-crown-6)] (Scheme 36).[88]



Scheme 36. Synthesis of phosphatrisilacyclobutenide **116**[K(18-crown-6)] from cyclotrisilene **92b** via bicyclic intermediate **115**; a: + KPCO, b: hν, − CO; Tip = 2,4,6-^{i}Pr$_3C_6H_2$.

E=E–Ch, chalgogen functionalities (Ch = group 16 element)

Even though alkoxysilanes and alkoxygermanes are industrial products with various applications, oxygen functionalised heavier Group 14 multiple bonds have so far only been proposed as reactive intermediates, e.g. during the methanolysis of disilyne **7**.[9a] The only examples for chalcogenide substituted group 14 multiple bonds are thia- and selenatrisilacyclobutenes **118a,b**. They were obtained by photolysis of thia- and selenabicyclobutanes **117a,b** which are accessible from cyclotrisilene **92a** and propylene sulphide, elemental sulphur and elemental selenium, respectively (Scheme 37).[89]

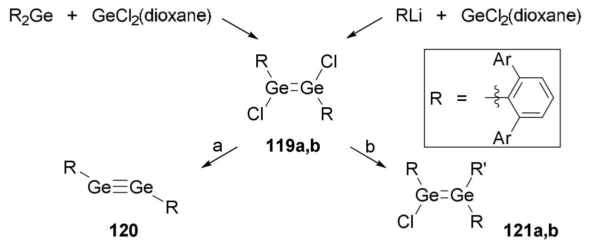


92a **117a,b** **118a,b**

Scheme 37. Synthesis of thia- and selenabicyclobutenes **118a,b** from cyclotrisilene **92a** via thia- and selenabicyclobutanes **117a,b**; a: **117a**: + propylene sulphide or S_8, **117b**: + Se, b: hν; R = ^{t}Bu$_2$MeSi.

E=E–X, halogen functionalities (X = group 17 element)

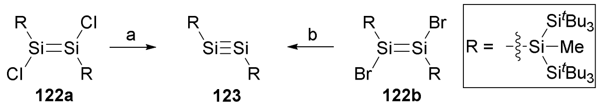
Chlorosilanes are probably the most common functional silicon compounds and they play key roles in industrial processes and laboratory scale syntheses. Halosilanes are in general very strong electrophiles and the Si–X group can be converted to many other functional groups by simple protocols. Even though organogermanium, –tin and –lead compounds are far less common if compared to their lighter homolog, the corresponding halo functionalised derivatives are still key products and intermediates of high importance. As in the case of H-substituted E(II) compounds (E = Si – Sn, vide supra) the tendency to form X_2-bridged dimers increases with increasing atomic number. To date all structurally characterised compounds $(RSiX)_2$ (X = Cl, Br, I) exhibit Si=Si multiple bonds while all compounds $(RSnX)_2$ and $(RPbX)_2$ form X_2-bridged dimers. In the case of $(RGeX)_2$ both structural motifs are known.[60, 90] Terphenyl substituted 1,2-dichlorodigermenes **119a,b** were synthesised either by reaction of R–Li with $GeCl_2$(dioxane) or comproportionation of the latter with R_2Ge (Scheme 38).



119a,b **120** **121a,b**

Scheme 38. Synthesis of 1,2-dichlorodigermenes **119a,b** by two different synthetic pathways and conversion of **119b** to digermyne **120** and monochlorodigermenes **121a,b**; a : + K, b: **121a**: + MeLi, **121b**: + EtLi; **119a**: Ar = Mes = 2,4,6-$Me_3C_6H_2$, **119b**, **120**, **121a,b**: Ar = Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$, **121a**: R' = Me, **121b**: R' = Et.

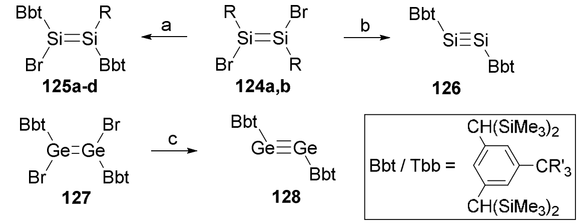
The corresponding tin compounds $(RSnCl)_2$ are Cl-bridged dimers in the solid state.[91, 92] Dichlorodigermene **119b**, which was also isolated as a monomer RGeCl in the solid state, has been converted successfully to digermyne **120**.[25] Monoalkylation of **119b** yields compounds **121a,b** while reaction with phenyllithium and dialkylation resulted in the formation of the corresponding germylenes RR'Ge.[92]



122a **123** **122b**

Scheme 39. Synthesis of disilyne **123** from disilenes **122a,b**; a, b: $M/C_{10}H_8$.

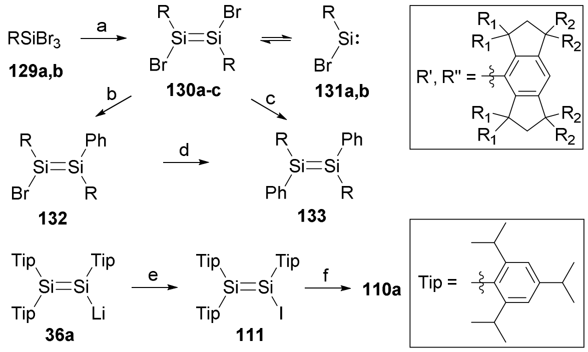
Sterically demanding silyl groups were utilised for the kinetic stabilisation of 1,2-dichlorodisilene **122a** and 1,2-dibromodisilene **122b**, which were the precursors for the first isolated disilyne **123**. (Scheme 39).[9b, 93]



125a-d **124a,b** **126** **127** **128**

Scheme 40. Reaction of dibromodisilene **124a** with RLi to yield bromodisilenes **125a-d** and disilyne **126**, Synthesis of digermyne **128** from dibromodigermene **127**; a: + RLi, b: + ^{t}BuLi, c: KC_8; **124a**: R = Bbt, **124b**: R = Tbb, **125a**: R = Me, **125b**: R = Et, **125c**: R = ^{n}Bu, **125d**: R = Ph; Bbt: R' = $SiMe_3$, Tbb: R' = Me.

The extremely bulky aryl substituents Bbt and Tbb were used for the stabilisation of 1,2-dibromodisilenes **124a,b**. Reaction of **124a** , which – in solution – exists in equilibrium with the corresponding silylene Bbt(Br)Si, with 1 equivalent of the appropriate organolithium reagent afforded monobromodisilenes **125a-d**. Reaction of **124a** with *tert*-butyllithium, however, allowed for the isolation of stable disilyne **126**.[94] The same substituent was also successfully employed for the 1,2-dibromodigermene **127** and the corresponding digermyne **128** (Scheme 40).[95]



129a,b **130a-c** **131a,b** **132** **133** **36a** **111** **110a**

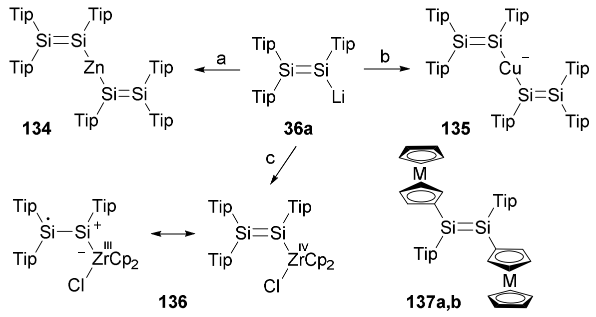
Scheme 41. Synthesis of dibromodisilenes **130a,b** from tribromosilanes **129a,b** and equilibrium with silylenes **131a,b** in solution, synthesis of disilenes **132**, **133** from **130a**, conversion of disilenide **36a**(dme)$_2$ to iododisilene **111** and reaction with $ClPPh_2$ to yield **110a**; a: + 2 Li/$C_{10}H_8$, b: + PhMgBr/Ppy, c: + excess PhLi, d: + excess PhLi, e: + I_2, f: + Ph_2PCl; R': R^1 = Me, R^2 = Et, R'': R^1 = R^2 = Et, **129a-131a**, **132**, **133**: R = R', **129b-131b**: R = R'', **130c**: R = R', R'', Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$, Ppy = 4-pyrrolidinopyridine.

The Eind and EMind groups are another example for sterically very demanding substituents that are able to stabilise 1,2-dibromodisilenes and the corresponding silylenes, which are in equilibrium in solution. Partial dehalogenation of tribromosilanes **129a,b** gave access to 1,2-dibromodisilenes **130a,b**, which were shown to be in equilibrium with silylenes **131a,b** in solution. This equilibrium is the reason for the formation of unsymmetrical disilene **130c** in a C_6D_6 solution containing initially equimolar amounts of **130a** and **130b** (Scheme 41).[96] Dibromodisilene **130a** has been converted to triaryldisilene **132** with phenylmagnesium bromide in the presence of 4-pyrrolidinopyridine (Ppy) and to tetraaryldisilene **133** with excess phenyllithium.

The very bulky aryl and silyl substituents that have been used to stabilise chloro and bromo substituted disilenes and digermenes were certainly chosen in view of their ultimate synthetic targets, stable digermynes and disilynes. The relatively small Tip-substituents turned out to be bulky enough to kinetically protect iododisilene **111** sufficiently for further derivatisation (Scheme 35, Scheme 41).[86] Iododisilene **111** was obtained by oxidation of disilenide **36a**$(dme)_2$ with iodine and successfully employed as an electrophile for the synthesis of phosphinedisilene **110a**. Donor-coordinated disilavinylidene **164** also exhibits a vinylic halogen functionality (see Scheme 48).

E=E–TM, η^1-transition metal complexes (TM = transition metal)

As in the case of carbon based transformations transition metal based silicon, germanium or tin reagents can be expected to develop into a valuable complement to e.g. alkaline metal disilenides. The latter have been shown to be the most versatile transfer reagents for the Si=Si moiety known to date. Reaction of disilenide **36a**$(dme)_2$ with half an equivalent of zinc chloride and copper iodide yielded neutral and anionic bis(disilenyl) complexes **134**, **135**$[Li^+(dme)_3]$, respectively (Scheme 42).[47] Calculation on model compounds and UV/Vis measurements reveal a significant interaction between the disilenyl moieties and the transition metal centre causing a significant red-shift of the longest wavelength absorption.

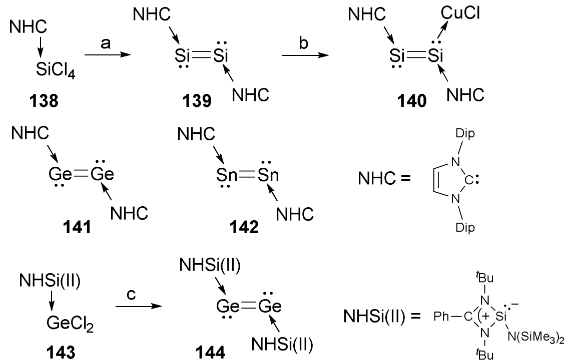


Scheme 42. Synthesis of disilenyl zinc (**134**), copper (**135**$[Li^+(dme)_3]$) and zirconium (**136**) complexes starting from disilenide **36a**$(dme)_2$; a: + 0.5 $ZnCl_2$, − LiCl, b: + 0.5 CuI, − LiI, c: + Cp_2ZrCl_2, − LiCl; **137a**: M = Fe, **137b**: R = Ru, Tip = 2,4,6-$^iPr_3C_6H_2$.

Zirconium disilenide **136** has been synthesised by reaction of disilenide **36a**$(dme)_2$ with Cp_2ZrCl_2.[97] Spectroscopic and structural data disclose a considerable contribution of the charge separated resonance structure (Scheme 42). Metallocenyl-substituted disilenes **137a,b** have been obtained from the corresponding dichlorosilanes $Tip(Cp_2M)SiCl_2$ (M = Fe, Ru) by reductive coupling with lithium/naphthalene in thf.[98] Even though reversible oxidation and reduction steps were observed by cyclic voltammetry, all known reactions of **137a,b** proceed with concomitant loss of the heavier multiple bond.

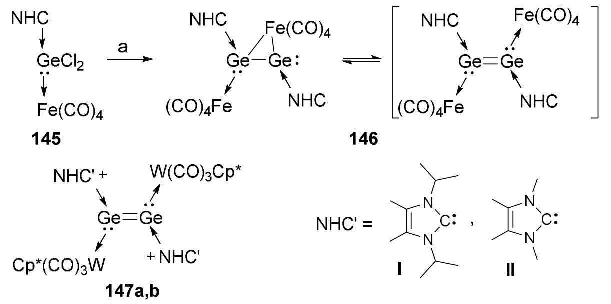
E=E←D, donor-coordinated multiply bonded systems (D = NHC)

Within the last few years donor-stabilisation of heavier group 14 multiply bonded system and many other substance classes utilising *N*-heterocyclic carbenes (NHCs) has developed rapidly and allowed for the isolation of various new compounds that were inaccessible before.[99] Some donor-coordinated species have already been discussed (Scheme 2, 4, Chart 2). In general, however, species that do not exhibit a clear-cut heavier double bond are beyond the scope of this review. The groundbreaking work in the field of NHCs coordinated to bona-fide double bonds was reported by Robinson *et al.* in 2008.[100] Reaction of NHC silicon tetrachloride complex **138** with four equivalents of potassium graphite gave access to the NHC-disilicon complex **139** (Scheme 43). Structural data and computations support an electronic structure with a Si=Si double bond and one lone pair of electrons located at each silicon centre (see also: dianions of digermenes and distannenes, Scheme 16). The heavier homologues, digermanium–NHC and ditin–NHC complexes **141**, **142**[101,102], were obtained from the corresponding NHC–ECl_2 complexes by reduction with a magnesium(I) species. Stabilisation of digermanium was also achieved by means of a donor-coordinated silicon(II) compound (NHSi(II), Scheme 43). Two-electron reduction of compound **143** gave access to digermanium-NHSi(II) **144**.[103]



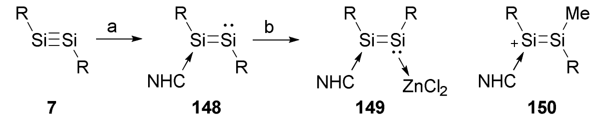
Scheme 43. Synthesis of disilicon−NHC **139** from $SiCl_4$-complex **138** and its reaction with CuCl to yield complex **140**, digermanium−NHC **141** and ditin−NHC **142**, synthesis of digermanium−NHSi(II) **144** from germanium(II) complex **143**; a: + 4 KC_8, b: + CuCl, c: + KC_8; Dip = 2,6-$^iPr_2C_6H_3$.

Disilicon–NHC **139** reacts with copper chloride to yield the η^1-bonded complex **140**, which according to computations is in equilibrium with a more symmetrical disilicon–CuCl π-complex/metallacyclopropane (Scheme 43).[104] In case of digermanium–NHC bis(irontetracarbonyl) complex **146**, which was synthesised from the donor-stabilised iron-germylene complex **145**, both coordination modes were observed in the solid state. A fast equilibrium in solution via a transient symmetrical σ/σ isomer is supported by NMR spectroscopy and DFT calculations (Scheme 44).[105]



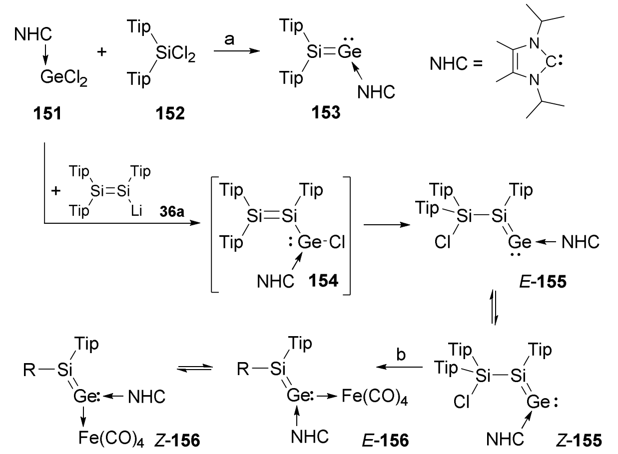
Scheme 44. Synthesis of donor-acceptor-stabilised digermanium **146** from germanium(II) complex **145** and dicationic donor-acceptor-stabilised digermanium **147a,b**(BAr$_4$)$_2$.

Donor-acceptor-stabilised dicationic digermanium complexes **147a,b**(BAr$_4$)$_2$ were synthesised from the corresponding NHC-complexes of germanium(II) chlorides by chloride abstraction. In this case in contrast to **140** and **146**, no evidence for the occurrence of an equilibrium between π- and σ-coordination was reported.[106] Disilyne **7** is capable to form the isolable donor-acceptor complex **148** with an NHC (NHC' **II**, Scheme 44) which was characterised by single crystal X-ray diffraction. The Si=Si moiety of compound **148** is valence isoelectronic with disilenides and its nucleophilic lone pair of electrons can coordinate Lewis acids as has been shown in the reaction of **148** with zinc(II) chloride to yield donor-acceptor complex **149** (Scheme 45).[107] Cationic disilene **150**(OTf) (OTf = triflate) was obtained by methylation of **148** with methyl triflate. Its positive charge resides mostly on the NHC and the adjacent silicon centre.[108]



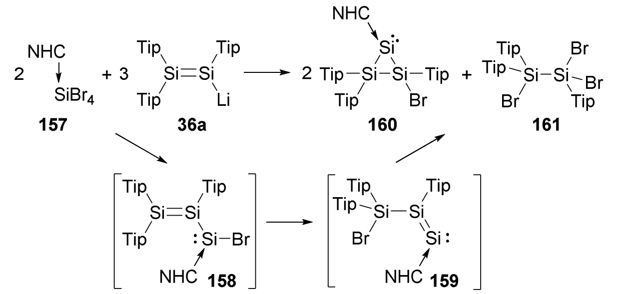
Scheme 45. Addition of a donor (NHC) to disilyne **7** to yield compound **148**, synthesis of zinc complex **149** and cationic disilene **150**; a: + NHC (tetramethylimidazol-2-ylidene), b: **149**: + ZnCl$_2$, **150**: + MeOTf; R = Dsi$_2{}^i$PrSi, Dsi = (Me$_3$Si)$_2$CH.

While heavier group 14 alkyne analogues have been known for ten to fifteen years by now, no isolable derivatives of the isomeric vinylidenes have been reported until recently. Utilising NHCs allowed for the isolation of a few donor-coordinated vinylidenes within the last two years. The first example of this substance class, silagermenylidene **153**, was obtained by treatment of a 1:1 mixture of dichlorosilane **152** and NHC–germanium(II) chloride complex **151** with four equivalents lithium/naphthalene in low yield (Scheme 46).[109] The highly functional silagermenylidene **155** was synthesised in good yield from germanium precursor **151** and disilenide **36a**(dme)$_2$ via proposed intermediate disilenylgermylene **154**. The thermodynamically favoured isomer *E*-**155** which was initially isolated from the reaction mixture equilibrates slowly with *Z*-**155** in solution.[110] A similar *E/Z*-isomerisation was reported for iron tetracarbonyl complexes *E/Z*-**156** which were obtained from *E*-**155** and diiron nonacarbonyl.



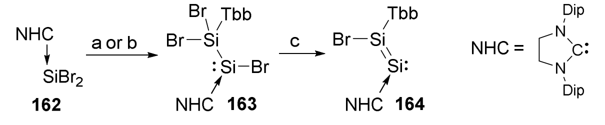
Scheme 46. Synthesis of silagermylidene **153** from NHC–GeCl$_2$ **151** and dichlorosilane **152**, synthesis of silagermylidene **155** from NHC–GeCl$_2$ **151** and disilenide **36a**(dme)$_2$ via proposed intermediate disilenylgermylene **154**, formation of iron tetracarbonyl complex **156**, *E/Z*-isomerization of **155**, **156**; a: + 4 Li/C$_{10}$H$_8$, b: + Fe$_2$(CO)$_9$; R = Tip$_2$(Cl)Si, Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$.

The attempted synthesis of disilavinylidene **159** from NHC–SiBr$_4$ **157** and disilenide **36a**(dme)$_2$ gave access to NHC-coordinated trisilacyclopropylidene **160** and tribromodisilane **161** instead (Scheme 47).[111] It can be reasonably assumed that the formation of **160** proceeds via disilenylsilylene **158** and disilavinylidene **159** in analogy to the synthesis of silagermylidene **155** (Scheme 46), even though no spectroscopic evidence for **158** or **159** was provided.



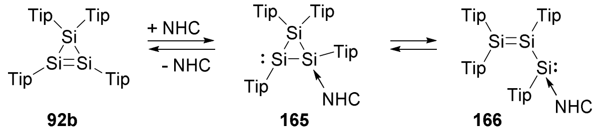
Scheme 47. Reaction of NHC–SiBr$_4$ **157** with disilenide **36a** to yield trisilacyclopropylidene **160** and tribromodisilane **161** via proposed intermediates disilenylsilylene **158** and NHC-coordinated disilavinylidene **159**; Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$.

The isolable disilavinylidene, **164**, was obtained on two different routes starting from NHC–SiBr$_2$ **162**. An NHC-complexed silylsilylene **163** can be synthesised from **162** and half an equivalent 1,2-dibromodisilene **124b** (Scheme 40). Alternatively, compound **163** was also isolated from the reaction of **162** with half an equivalent Tbb–Li. Disilavinylidene **164** was obtained in the final step by reaction of **163** with two equivalents potassium graphite (Scheme 48).[112]



Scheme 48. Syntheses of disilavinylidene **164** from NHC–SiBr$_2$ **162** via donor-coordinated silylsilylene **163**; a: + 0.5 Tbb(Br)Si=Si(Br)Tbb, b: + 0.5 TbbLi, c: + 2 KC$_8$; Tbb = 2,6-Dsi$_2$-4-^{t}BuC$_6$H$_2$, Dsi = (Me$_3$Si)$_2$CH, Dip = 2,6-^{i}Pr$_2$C$_6$H$_3$.

Donor-coordinated and free heavier vinyl carbenes (i.e. disilenylsilylenes and –germylenes) have been proposed as short-lived intermediates (see Schemes 23, 46, 48).[64b, 66, 110, 112] Donor-coordinated, isolable disilenylsilylene **166** has been prepared by reaction of cyclotrisilene **92b** with an NHC (NHC: see Scheme 46).[67] The temperature dependent equilibrium in solution between **166** and **92b**/NHC was investigated by NMR spectroscopy. Mainly due to entropic reasons, disilenylsilylene **166** is favoured at lower temperatures. The intermediate of this interconversion, cyclotrisilene-NHC complex **165**, was also observed in a flash-frozen sample at low temperature (Scheme 49).



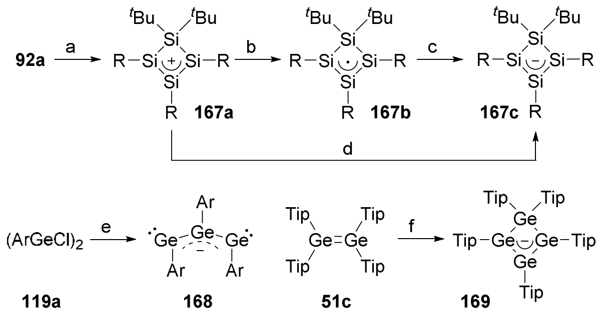
Scheme 49. Equilibrium between cyclotrisilene **92b** and donor-coordinated disilenylsilylene **166** via cyclotrisilene-NHC complex **165**; NHC = 1,3-^{i}Pr$_2$-2,4-Me$_2$imidazol-2-ylidene, Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$.

3. Allylic functionalities

A decent number of functionalised allylic heavier group 14 multiple bonds have been reported to date. In contrast to the rapidly developing documentation on reactivity of heavier vinylic functionalities, however, the chemical behaviour of functional groups in allylic position for heavier Group 14 elements remains largely unexplored. The constraint imposed by the high reactivity of heavier multiple bonds, limit the range of feasible functional groups even more severely than in the case of vinylic functional groups. In addition to intermolecular degradation pathways, intermolecular cyclisation has to be considered. Due to the comparatively small number of examples we will not organise this section according to the periodic table, but summarise the most comprehensively explored compound classes first, the allyl halides which are conceivable precursors for allyl anions.

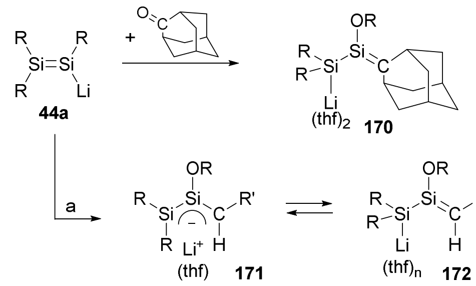
(E=E–E)$^-$M$^+$, allyl anions

Vinylically halogen-functionalised compounds of the general structure R$_2$E=E(R)–E(X)R$_2$ (E = group 14 element, X = halogen) were anticipated as ideal precursors for the synthesis of heavier allylic anions. Even though a number of cyclic and acyclic examples of such compounds have been described, none of them, however, could be converted to allyl anions yet. Instead, other interesting monoanions and dianions were obtained (*vide infra*). The first heavier allyl anion was obtained via a different route from trisilacyclopropene **92a**. In a first step methyl anion abstraction from **92a** followed by cyclisation gave access to trisilaallyl cation **167a**[B(C$_6$F$_5$)$_4$$^-$],[113a] which was converted to isolable silyl radical **167b** by one-electron reduction.[113b] Trisilaallyl anion **167c**[M$^+$] (M = Li, Na, K) was then either generated by a second one-electron reduction from radical **167b** or directly by two-electron reduction from cation **167a**[B(C$_6$F$_5$)$_4$$^-$] (Scheme 50).[114] All reactions were shown to be reversible. The unusual trigermanium anion **168**[K$^+$] was obtained by reaction of 1,2-dichlorodigermene **119a**[91] (Scheme 38) with excess potassium graphite. Structural data reveal that anion **168** is best described as a planar, delocalised germyl anion with two flanking germylenyl substituents and outwards directed lone-pairs of the germanium(II) centres.[115] A germanium analogue of trisilaallyl anion **167c** was isolated from the reaction of digermene **51c** (Scheme 25) with lithium in dme.[49b] Conditions similar to those of the synthesis of tetragermabutadiene **89** (Scheme 25) but reduced contact time with the active metal gave access to cyclic trigermaallyl anion **169**[Li$^+$(dme)$_3$] (Scheme 50).



Scheme 50. Synthesis of cyclic trisilaallyl anion **167c** by methyl abstraction from trisilacyclopropene **92a** and stepwise reduction via trisilaallyl cation **167a** and radical **167b**, synthesis of trigermanium anion **168**[K$^+$] from 1,2-dichlorodigermene **119a** and preparation of cyclic trigermaallyl anion **169**[Li$^+$(dme)$_3$]; a: + [Et$_3$Si(C$_6$H$_6$)$^+$][B(C$_6$F$_5$)$_4$$^-$], − Et$_3$SiMe, b: + ^{t}Bu$_3$SiNa or KC$_8$, c: + Li, d: + Li, e: + KC$_8$, f: + Li/dme; R = ^{t}Bu$_2$MeSi, Ar = 2,6-Mes$_2$C$_6$H$_3$, Mes = 2,4,6-Me$_3$C$_6$H$_2$, Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$.

So far no other heavier allyl anions with a skeleton of three heavier group 14 elements have been reported. The versatile disilenide **44a** has been utilised for the synthesis of two different disilaallyl anions with more or less electronic delocalisation over the two silicon atoms and one carbon atom. Reaction of **44a** with 2-adamantanone yields contact ion pair **170**. Based on UV/Vis, NMR and X-ray data it is best described as a silyl anion substituted silene (Scheme 51).[116] A related reaction of disilenide **44a** with a sterically encumbered aldehyde allowed for the isolation of allyl anion **171** which exhibits a much more delocalised electronic structure in a non-polar environment.[117] An interconversion between η^3-type (**171**) and η^1-type (**172**) coordination of the lithium counter cation was achieved simply by addition and removal of thf.



Scheme 51. Reaction of disilenide **44a** with 2-adamantanone and Ar$_3$CCHO to yield disilaallyl anions **170**, **171**, respectively, interconversion of anions **171** and **172** by addition and removal of donor molecules; a: + Ar$_3$CCHO; R = ^{t}Bu$_2$MeSi, Ar = 3,5-^{t}Bu$_2$C$_6$H$_3$, R’ = Ar$_3$C.

E=E=E, heavier allenes

A few homo- and heteronuclear heavier allenes have been reported. In contrast to C_3-allenes they all deviate substantially from linearity and their electronic structure can be described by canonical forms **A** to **D** (or the corresponding zwitterionic representations). Theoretical calculations also demonstrate their close relation to the valence-isomeric cyclopropylidenes **E** (Chart 9, Scheme 47).[118] Notably, allenes are also isomeric to the aforementioned cyclopropene analogues **F**.

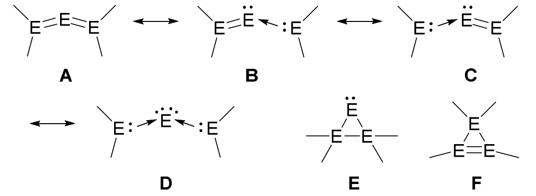
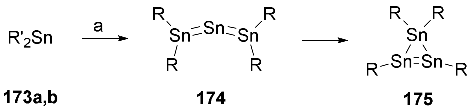


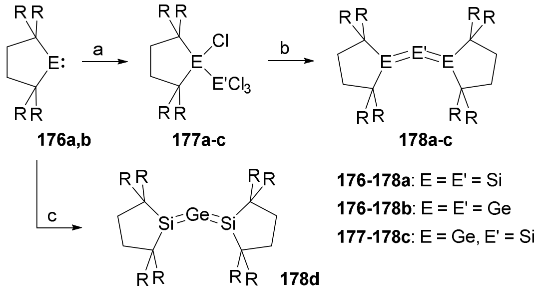
Chart 9. Canonical forms of heavier allenes **A-D**, cyclopropylidene **E** and cyclopropane **F**, E = Si, Ge, Sn, Pb.

The first heavier allene was described in 1999. Tristannaallene **174** was synthesised from tin(II) compounds **173a,b** and reported to isomerise to tristannacyclopropene **175** with a half-live of 9.8 hours as ambient temperature (Scheme 52).[119]



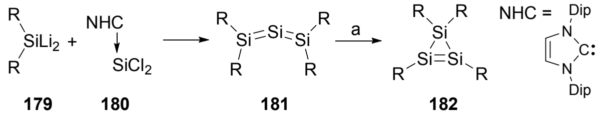
Scheme 52. Synthesis of tristannaallene **174** from tin(II) compounds **173a,b** and isomerisation to tristannacyclopropene **175**; a. + 2 RNa; R = ^{t}Bu$_3$Si, R' = O^{t}Bu, N(SiMe$_3$)$_2$.

A series a homo- and heteronuclear heavier allenes of silicon and germanium were obtained starting from stable silylene **176a** and germylene **176b**. In case of allenes **178a-c** the corresponding E–X insertion products **177a-c** were synthesised first and then treated with potassium graphite to yield the final products. Reaction of silylene **176a** with potassium graphite in the presence of approximately half an equivalent of $GeCl_2$(dioxane) allowed for the isolation of heavier allene **178d** (Scheme 53).[120] Trigermaallene **178b** was also synthesised following the second route with yields comparable to the first.[121]



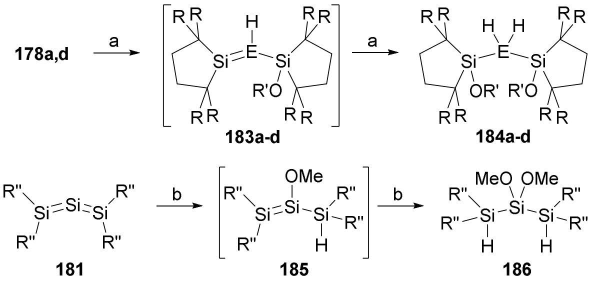
Scheme 53. Synthesis of heavier allenes **178a-c** from silylene **176a** and germylene **176b** via E–Cl insertion products **177a-c**, synthesis of allene **178d** from **176a**; a: + ECl_4, b: + KC_8, c: + 0.5 $GeCl_2$(dioxane), KC_8; R = Me_3Si.

A second trisilaallene **181** is accessible from the reaction of dilithiosilane **179** and NHC–$SiCl_2$ **180**. Similar to the case of tristannaallene **175** an isomerisation to trisilacyclopropene **182** was observed, in this case, however, heating a benzene solution to 120 °C was required (Scheme 54).[122]



Scheme 54. Synthesis of trisilaallene **181** from dilithiosilane **179** and NHC–$SiCl_2$, thermal isomerisation of **181** to yield trisilacyclopropene **182**; a: benzene, 120 °C; R = ^{t}Bu$_2$MeSi, Dip = 2,6-^{i}Pr$_2$C$_6$H$_3$.

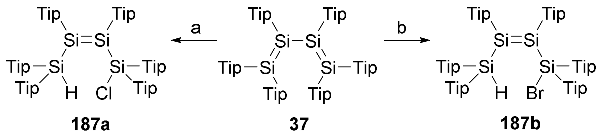
The reactivity of heavier allenes **178a,d** and **181** towards water, alcohols and other reagents has been investigated. So far, no product with a residual heavier multiple bond has been isolated from or even detected in any of these reactions.[121, 122] Compounds **183a,b**, **185** have been proposed as intermediates during the formation of bis-addition products **184a,b**, **186**. Interestingly, both oxygen atoms add to the terminal silicon atoms of the allene moiety in case **184a,b**, but to the central one in case of **186**. This was explained by the inverse polarity of heavier allene **181** compared to allenes **178a,d** (Scheme 55).



Scheme 55. Reaction of heavier allenes **178a,d** with MeOH and H_2O to yield addition products **184a-d** via proposed intermediates **183a-d**, synthesis of trisilane **186** by addition of MeOH to allene **181** via proposed intermediate **185**; a: + MeOH/H2O, b: + MeOH; **178a**, **183a,b**, **184a,b**: E = Si, **178d**, **183c,d**, **184c,d**: E = Ge, **183a,c**, **184a,c**: R' = Me, **183b,d**, **184b,d**: R' = H, R = Me_3Si, R'' = ^{t}Bu$_2$MeSi.

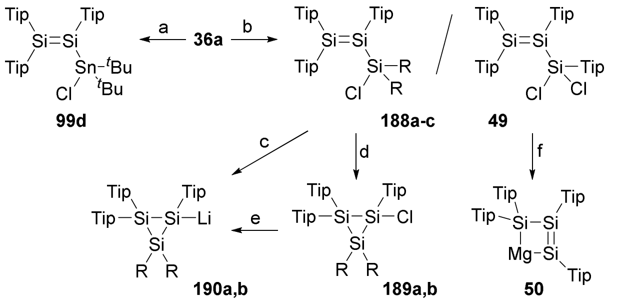
E=E– E–X, halogen functionalities (X = group 17 element)

Acyclic disilenes with halogen functionalities in allyl position have been synthesised from two different precursors. Tetrasilabutadiene **37** was utilised for the preparation of chlorosilyl- and bromosilyldisilenes **187a,b** (Scheme 56).[123] 1,4-addition of hydrogen chloride which was not used directly but transferred from excess trichlorosilane in the reaction mixture yielded chlorosilyldisilene **187a**. Reaction of tetrasilabutadiene **37** with excess hydrogen bromide gave access to bromosilyldisilene **187b**.



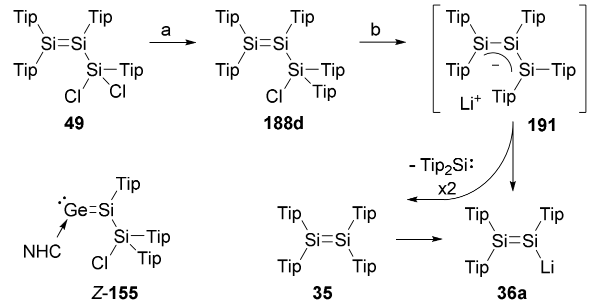
Scheme 56. 1,4-addition of hydrogen chloride and bromide to tetrasilabutadiene **37** to yield disilenes **187a,b**; a: + $HSiCl_3$, b: + HBr; Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$.

Disilenide **36a**(dme)$_2$ was allowed to react with dichloro- and trichlorosilanes and a dichlorostannane to yield stannadisila- and trisilaallyl chlorides **99d**,[77] **49**,[48] **188a-c** (Scheme 57).[39b,124] Allyl chlorides **188a,b** could be isolated but isomerise to chloro cyclotrisilanes **189a,b** in donor solvents. Reaction of **188a,b** with lithium afforded trisilacyclopropyl anions **190a,b**(Et$_2$0) instead of the anticipated trisilaallyl anions. The latter were also obtained from trisilacyclopropyl chlorides **189a,b** under similar reductive conditions.



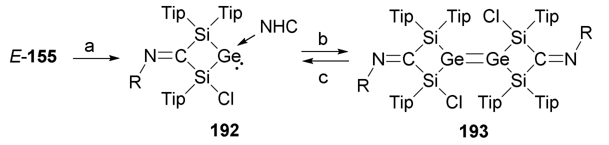
Scheme 57. Synthesis of chlorostannyl disilene **99d** and chlorosilyldisilenes **188a-c**, **49** from disilenide **36a**, cyclisation of **188a,b** to yield cyclotrisilanes **189a,b** and reaction pathways to trisilacyclopropanides **190a,b**, synthesis of **50**; a: + ^{t}Bu$_2$SnCl$_2$, b: **188a**: Me$_2$SiCl$_2$, **188b**: + Ph$_2$SiCl$_2$, **188c**: + Mes$_2$SiCl$_2$, c: + Li, d: thf, e: + Li, f: + Mg; **188-190a**: R = Me, **188-190b**: R = Ph, **188c**: R = Mes, Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$, Mes = 2,4,6-Me$_3$C$_6$H$_2$.

The conversion of allyl dichloride **49** to α,ω-dianionic trisilandiide **50** has already been discussed in a previous section. In order to decrease the tendency of allyl chlorides like **188a-c** to cyclise by increasing the steric bulk around the Si$_3$-backbone the homoleptic derivative **188d** was synthesised. Interestingly, **188d** could not be obtained directly from disilenide **36a**(dme)$_2$ and Tip$_2$SiCl$_2$, but was prepared instead by the reaction of trisilaallyl dichloride **49** and TipLi via nucleophilic substitution in the allylic position of a Si=Si double bond (Scheme 58).[39b] Reaction of **188d** with excess lithium in diethyl ether, however, led to the isolation of **36a**(Et$_2$O)$_2$. It was speculated that trisilaallyl anion **191** was initially formed, but converted to disilenide **36a** by elimination of silylene Tip$_2$Si. The latter would probably dimerise in solution and generate additional disilenide **36a** under the reaction conditions.



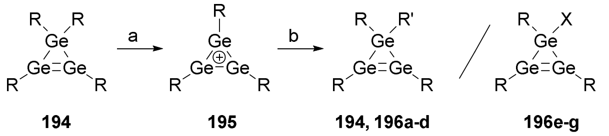
Scheme 58. Synthesis of homoleptic chlorosilyldisilene **188d** from dichlorosilyldisilene **49**, reaction of **188d** with excess lithium to yield disilenide **36a** via proposed intermediate trisilaallyl anion **191** and possible fate of eliminated silylene to give disilene **35**, chlorosilyl-substituted silagermylidene *Z*-**155**; a: + TipLi, b: excess Li; NHC: see Scheme 46, Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$.

NHC-complexes of silagermenylidenes, *E/Z*-**155,** and the corresponding iron tetracarbonyl complexes *E/Z*-**156** also exhibit a halogen functionality in allylic position of a heavier Group 14 multiple bond (Scheme 46, 58).[110] Reaction of *E*-**155** with 2,6-dimethylphenylisocyanide yields the NHC-coordinated cyclic germylene **192**, which can be reversibly converted to digermene **193** by addition of triphenylborane as an NHC-scavenger and back to **192** by additional NHC. Digermene **193** exhibits not only a chloride functionality but also a *C*-imino functionality in allylic position (Scheme 59).[125]



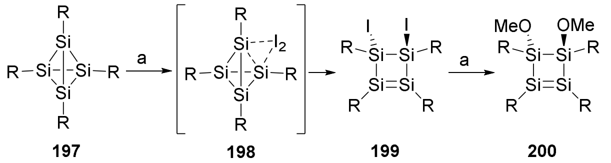
Scheme 59. Reaction of silagermylidene *E*-**155** with isocyanide to yield NHC-stabilised germylene **192** and its reversible dimerisation to chloro functionalised digermene **193**; a: + 2,6-dimethylphenylisocyanide, b: + BPh$_3$, − [NHC–BPh$_3$], c: + NHC; NHC: see Scheme 46, R = 2,6-Me$_2$C$_6$H$_3$, Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$.

Sekiguchi *et al.* demonstrated that cyclotrigermene **194** is converted to cyclotrigermenylium cations **195**[B(2,3,5,6-F$_4$C$_6$H)$_4$$^-$] and **195**[B(3,5-(CF$_3$)$_2C_6H_3$)$_4$$^-$] by abstraction of one substituent R$^-$ (R$^-$ = ^{t}Bu$_3$Si$^-$) (Scheme 60).[75a,b, 126] Reaction of **195** with carbon, silicon and germanium nucleophile yielded cyclotrigermenes **194**, **196a-d**. Interestingly, cyclotrigermenylium cation **195**[B(2,3,5,6-F$_4$C$_6$H)$_4$$^-$] can also be converted to cyclotrigermenyl chloride **196e**, bromide **196f** and iodide **196g** with the corresponding potassium halide. The halocyclotrigermenes exhibit a highly fluxional structure at ambient temperature in which the halogen rapidly exchanges its position in the three-membered ring.



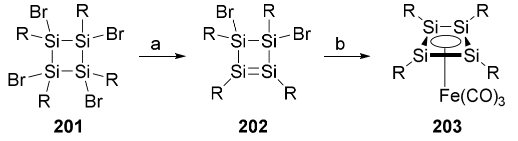
Scheme 60. Synthesis of cyclotrigermenes **194**, **196a-g** from cyclotrigermene **194** via cyclotrigermenylium cation **195**; a: + [Ph$_3$C$^+$][Ar$_4$B$^-$], – Ph$_3$C–Si^{t}Bu$_3$, b: + R’M or KX; Ar = F$_5$C$_6$, 2,3,5,6-F$_4$C$_6$H, 3,5-(CF$_3$)$_2$C$_6$H$_3$, 4-^{t}BuMe$_2$Si-2,3,5,6-F$_4$C$_6$, R’M = ^{t}Bu$_3$SiNa, (Me$_3$Si)$_3$SiLi, (Me$_3$Si)$_3$GeLi, MesLi, **196e-g**: KX = KCl, KBr, KI, R = ^{t}Bu$_3$Si, Mes = 2,4,6-Me$_3$C$_6$H$_2$.

Diiodo tetrasilacyclobutene **199** was obtained from the reaction of tetrahedral tetrasilane **197**[127] with elemental iodine.[128] Species **198** was suggested as a possible intermediate of this reaction. Methanolysis with excess methanol afforded methoxy functionalised tetrasilacyclobutene **200** (Scheme 61).



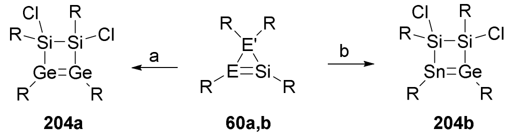
Scheme 61. Synthesis of diiodotetrasilacyclobutene **199** from tetrahedral tetrasilane **197** via proposed intermediate **198**, conversion of **199** to dimethoxyetrasilacyclobutene **200**; a: + I$_2$, b: + MeOH,

Dibromo tetrasilacyclobutene **202** was synthesised by partial dehalogenation of tetrabromo tetrasilacyclobutane **201** with potassium graphite. Compound **202** was further converted to tetrasilacyclobutadiene complex **203** (Scheme 62).[129]



Scheme 62. Synthesis of dibromotetrasilacyclobutene **202** by partial dehalogenation of cyclotetrasilane **201** and synthesis of iron complex **203**; a: + 2.1 KC_8, b: + $Na_2[Fe(CO)_4]$; R = $^tBu_2MeSi$.

An interesting ring expansion of germadisilacyclopropenes **60a,b** (Scheme 19) was discovered about a decade ago. Reaction of germadisilacyclopropenes **60a,b** with germanium(II) chloride(dioxane) and tin(II) chloride(dioxane) yielded digermadisila- and stannagermadisilacyclobutenes **204a,b**, respectively. In both cases migration of silyl and chlorine substituents at ambient temperature or even below 0 °C affords products with the double bond between the two heavier elements, germanium and tin (Scheme 63).[130]



Scheme 63. Reaction of germadisilacyclopropenes **60a,b** with $GeCl_2$(dioxane) and $SnCl_2$(dioxane) to yield chlorinated heterocyclobutenes **204a,b**; a: + $GeCl_2$(dioxane), b: + $SnCl_2$(dioxane); **60a**: E = Si, E' = Ge, **60b**: E = Ge, E' = Si, R = $^tBu_2MeSi$.

E=E–E–Ch, chalcogen functionalities (Ch = group 16 element)

Aside from methoxy-functionalised tetrasilacyclobutene **200** (Scheme 61) two more compounds with a heavier Group 14 multiple bond and oxygen functional groups in allylic positions have been described.[131] 1-Hydroxy-4-phenoxytetrasilabut-2-enes **205**, **206** were formed during the reaction of *para*- and *ortho*-quinones with tetrasilabutadiene **35** in the presence of water (Chart 10).

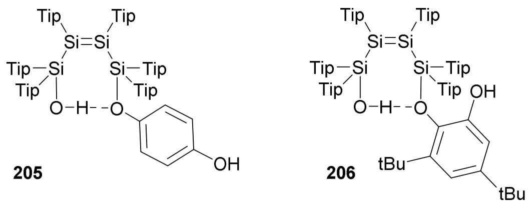
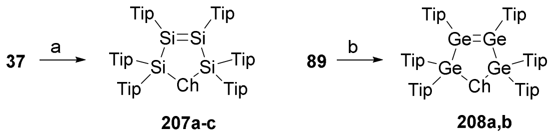


Chart 10. Products of the 1,4-addition of 1,4-benzoquinone (**205**) and 3,5-$^tBu_2$-1,2-benzoquinone (**206**) to tetrasilabutadiene **35** in the presence of water; Tip = 2,4,6-$^iPr_3C_6H_2$.

Disilenes are known to yield chalcogenadisilacyclopropanes in reaction with heavier chalcogens at ambient temperature by formal [2+1] cycloadditions.[132] In case of tetrasilabutadiene **37**, however, tetrasilacyclopentenes **207a-c** were obtained by formal [4+1] cycloaddition with elemental sulphur and selenium, tellurium in the presence of triethylphosphine, respectively (Scheme 64).[133] Similarly, tetragermabutadiene **89** was converted to tetragermacyclopentenes **208a,b** with elemental sulphur and selenium in the presence of triethylphosphine.[68, 69]



Scheme 64. Synthesis of chalcogenatetrasilacyclopentenes **207a-c** and chalcogenatetragermacyclopentenes **208a,b** from tetrasilabutadiene **37** and tetragermabutadiene **89**, respectively; a: **207a**: + 1/8 S_8, **207b**: + Se/PEt_3, **207c**: + Te/PEt_3; b: **208a**: + 1/8 S_8, **208b**: + Se/PEt_3, Tip = 2,4,6-$^iPr_3C_6H_2$.

E=E–E–Tt/Pn, tetrel/pnictogen functionalities (Tt = group 14 element, Pn = group 15 element)

Little is known about heavier Group 14 multiple bonds with tetrel and pnictogen functionalities in allylic position. Disilacyclohexadiene **209** was synthesised from disilyne **123** by [2+4] cycloaddition with 1,3-butadiene (Chart 11).[9b, 93] Disilene *Z*-**105a** and digermenes *E/Z*-**105b** (Scheme 32) exhibit six Si–N bonds in allylic position each.[84, 134] No reactivity of these compounds has been reported yet.

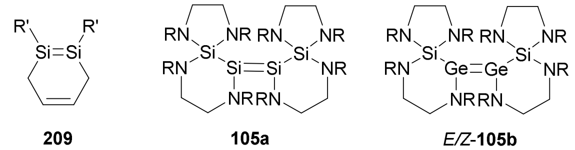
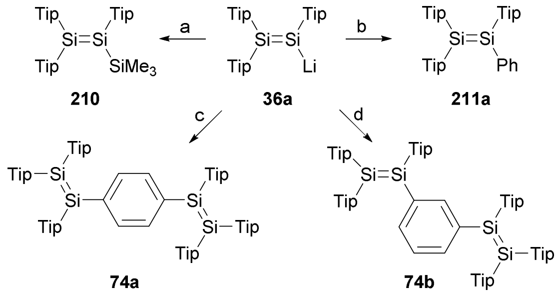


Chart 11. 1,2-disilacyclohexa-1,3-diene **209**, disilene **105a** and digermenes *E/Z*-**105b**; R' = $(^tBu_3Si)_2MeSi$, R = ^tBu.

4. Remote functionalities

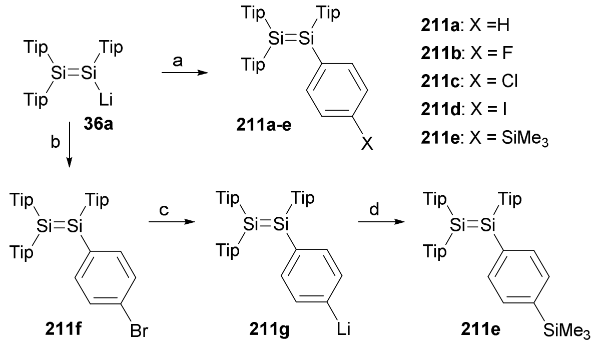
Compounds with heavier Group 14 multiple bonds that feature a functional atom or group two or more atoms away will be summarised in this section. Aside from the [2+2] cycloaddition product **106** of digermyne **24b** and 1,5-cyclooctadiene (Scheme 33), all examples are derived from disilenide **36a**$(dme)_2$ and exhibit a phenylene bridge. Disilenide **36a**$(dme)_2$ is a powerful nucleophile that can transfer the Si=Si moiety not only to good electrophiles, e.g. trimethylsilyl chloride to yield disilene **210** (Scheme 65),[39a] but also to rather awkward ones like iodobenzene and even bromobenzene for the synthesis of tetraaryldisilene **211a**.[62, 135]



Scheme 65. Reaction of disilenide **36a**$(dme)_2$ with trimethylsilyl chloride and iodo-/bromobenzene to yield disilenes **210**, **211a**, synthesis of *para*- and *meta*-

phenylene bridged bis(disilenes) **74a,b**; a: + Me_3SiCl, b: + iodobenzene/bromobenzene, c: + 0.5 1,4-$I_2C_6H_4$, d: + 0.5 1,3-$I_2C_6H_4$; Tip = 2,4,6-$^iPr_3C_6H_2$

This capability was employed for the synthesis of *para*- and *meta*-phenylene bridged bis(disilene) **74a,b** from disilenide **36a**$(dme)_2$ and 1,4-diiodo- and 1,3-diiodobenzene, respectively. UV/Vis investigations of compounds **74a,b** revealed that the Si=Si double bonds of **74a** are conjugated while those of **74b** are not.[62, 135] The successful straightforward synthesis of *para*-substituted phenyldisilenes **211b-f** from disilenide **36a**$(dme)_2$ and the corresponding *para*-iodobenzene (**211e**: *p*-bromo(trimethylsilyl)benzene) sheds some light on the functional group tolerance and selectivity of **36a**$(dme)_2$ towards halogenated benzenes. As an interesting proof of concept (*para*-bromophenyl)disilene **211f** was converted to *para*-lithio derivative **211g** at low temperature and reacted with trimethylsilyl chloride to yield disilenes **211e** / **211a** in a ratio of 8:2 to 9:1 according to NMR spectroscopy (Scheme 66).[135]



Scheme 66. Synthesis of tetraaryldisilenes **211a-f**, generation of lithiated species **211g** at low temperature and conversion to **211e**; a: **211a**: + I/BrC_6H_5, **211b**: + (4-F)IC_6H_4, **211c**: + (4-Br)IC_6H_4, **211d**: + (4-I)IC_6H_4, **211e**: + (4-Me_3Si)BrC_6H_4, b: + (4-Br(IC_6H_4), c: + 2 ^{t}BuLi, – LiBr, – C_4H_{10}, – C_4H_8, d: + Me_3SiCl

5. Conclusions and Outlook

In the past ten to fifteen years, the number of stable doubly-bonded compounds of Group 14 has substantially increased. These developments are mainly due to the emergence of functionalized derivatives such as disilenides on the one hand and multiply unsaturated species such as alkyne, allene and butadiene analogues on the other hand. In many of these species residual functionality is retained for further manipulation. The relatively recent development of NHC-stabilized derivatives, e.g. Si_2, Ge_2 as well as heavier vinylidenes provides a novel route to stable compounds with heavier multiple bonds and peripheral functional groups. Notably, the lone pair in these species is related to vinylic anions by an isoelectronic relationship. The occasionally observed reversibility of NHC-coordination can be expected to provide further momentum to this rapidly expanding field.

Although reductive approaches still appear to be the method of choice for the formation of multiply bonded compounds in many cases, dehydrogenative coupling techniques are gaining ground in particular in case of the heavier Group 14 elements, germanium and tin. In view of the overwhelming importance of similar elimination pathways during the deposition of elemental tetrels from the gas phase, the application in the molecular domain and in the condensed phase shapes up to be a viable alternative for the Wurtz-type coupling under strongly reducing conditions. Bearing in mind that thermodynamically competitive elimination pathways are also a necessary prerequisite for catalytic applications, it can be anticipated that efforts in this regard will be rewarding.

The manipulation of functional groups in the presence of highly reactive heavier double bonds has become a real synthetic option that may soon allow the selective construction of extended systems such as polymers or other interesting materials from the bottom-up. The further elaboration of the successful concept of kinetic stabilisation by steric bulk will reveal many more parallels to organic chemistry in the next few years. In all of these endeavours, however, investigators should keep their minds open for substantial – and occasionally surprising – differences to carbon chemistry.

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