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Highlight Review

Heteronuclear Double Bonds E=E′ (E = Heavy Group 14 Element, E′ = Group 13–16 Element)

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Abstract

A number of compounds with heteronuclear double bonds between heavy elements of groups 13, 14, 15, and 16 have been isolated and characterized in the last three decades; they are kinetically stabilized by the use of bulky substituents or thermodynamically stabilized by intra- or intermolecular coordination. They are fascinating compounds in respect of their unusual chemical properties, being very useful building blocks in organometallic chemistry.

◆ Introduction

Compounds featuring a double bond between heavy main group elements were considered for a long time to be non-isolable. This was due to the so-called double bond rule, which postulated that the elements with a principal quantum number equal to or greater than 3 (that is, elements of period 3 and below) cannot form multiple bonds, because of the significant Pauli repulsion of the electrons in the inner shells. After decades of unsuccessful attempts, great progress was made in 1981 with the synthesis of the first bulky-substituted silene $(Me_3Si)_2Si{=}C(OSiMe_3)Ad$ (Ad = 1-adamantyl) by Brook,[1a] disilene $Mes_2Si{=}SiMes_2$ (Mes = 2,4,6-trimethylphenyl) by West,[1b] and diphosphene Mes*P=PMes* (Mes* = 2,4,6-tri-*tert*-butylphenyl) by Yoshifuji.[1c] Since then, many doubly bonded compounds of group 13, 14, 15, and 16 elements have been isolated and characterized. Despite the large steric hindrance, the double bond in such compounds is generally very reactive, and many addition and cycloaddition reactions have been reported. Thermodynamic stabilization by the intra- or intermolecular coordination, mainly by nitrogen or oxygen atoms, has also been successfully used. However, in this case, the reactivity and the physicochemical properties are remarkably perturbed by complexation, resulting in a partial (or full) loss of their doubly bonded character. In the present paper, we focus our discussion on the recent progress in the synthesis and physicochemical studies (NMR, UV, and X-ray) of stable heteronuclear compounds of the types $E_{14}{=}E'_{14}$ and $E_{14}{=}E_{13/15/16}$ (E_{13}, E_{14} and E'_{14}, E_{15}, E_{16} = elements of the groups 13, 14, 15, and 16, respectively).

Heteronuclear $>E_{14}{=}E'_{14}<$ derivatives have been recently reviewed by Lee and Sekiguchi,[2] silanimines >Si=N– by Klingebiel,[3a] germanimines >Ge=N– by Baines[3b] and Escudié,[3c,3d] stannanimines >Sn=N– by Baines,[3b] phosphasilenes >Si=P– and arsasilenes >Si=As– by Driess,[4] phosphagermenes >Ge=P– by Baines[3b] and Escudié,[3c,3d] phosphastannenes >Sn=P– by Baines[3b] and heavy ketones $>E_{14}{=}E_{16}$ by Tokitoh.[5] In addition to the first successful attempts to prepare doubly bonded derivatives in each category, this review focuses on the most recent results.

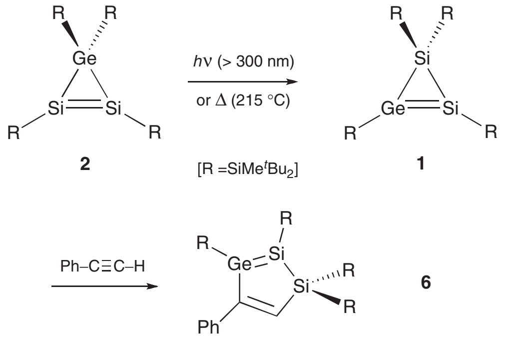
◆ $>E_{14}{=}E'_{14}<$ Derivatives

Silagermenes >Si=Ge<

Stable silagermenes (otherwise known as germasilenes) became synthetically accessible only during the last decade. The first isolable silagermene, 1*H*-disilagermirene **1**, with an endocyclic Si=Ge bond in a three-membered ring Si_2Ge-skeleton, was synthesized in 2000.[6] This cyclic silagermene **1** was readily accessible by isomerization (either thermal or photochemical) of the 3*H*-disilagermirene **2** with a skeletal Si=Si bond (Scheme 1). **1** revealed a low-field resonance of the skeletal Si atom at 100.7 ppm.

The nearest homolog of **1**, 1*H*-disilagermirene **3**, was prepared from 3*H*-disilagermirene **2** (Scheme 2).[7] At first, the ring expansion reaction of **2** with CH_2Cl_2 produced cyclic **4**, which was subsequently reduced with KC_8 yielding an isolable disilagermabicyclo[1.1.0]butane **5**, thermal isomerization of which resulted in the formation of **3**. The doubly-bonded Si atom of **3** was more deshielded than that of **1**: 126.6 ppm vs. 100.7 ppm.

The five-membered ring 1,2-disila-3-germacyclopenta-2,4-diene **6**, in which the Si=Ge double bond was structurally



Scheme 1.

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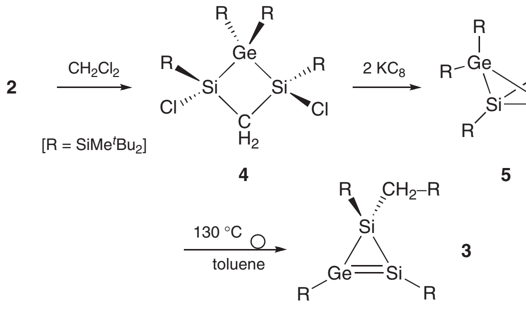


Scheme 2.

authenticated for the first time, was prepared by the reaction of 1*H*-disilagermirene **1** with phenylacetylene (Scheme 1).[8] The doubly bonded silicon atom in **6** resonated in a low-field region at 124.2 ppm. The Si=Ge bond was twisted by 38.6° and its length of 2.250(1) Å was intermediate between those of typical Si=Si and Ge=Ge bonds.

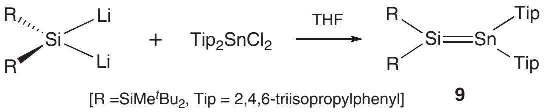
The other two stable silagermenes, $(^t\mathrm{Bu_2MeSi})_2\mathrm{Si{=}GeMes_2}$ **7**[9a] and $(^t\mathrm{Bu_3Si})_2\mathrm{Si{=}GeMes_2}$ **8**,[9b] were synthesized by the coupling of 1,1-dilithiosilane derivatives $\mathrm{R_2SiLi_2}$ ($\mathrm{R = SiMe}^t\mathrm{Bu_2}$ and $\mathrm{Si}^t\mathrm{Bu_3}$) with dichlorodimesitylgermane $\mathrm{Mes_2GeCl_2}$. Both **7** and **8** exhibited unusually shielded sp^2-Si centers, (δ^{29}Si 22.4 and 18.7 ppm), respectively, because of the electronic effects of the substituents: donating silyl groups at Si and accepting groups at Ge, altering the bond polarity from a natural $\mathrm{Si}^{\delta+}{=}\mathrm{Ge}^{\delta-}$ (expected on the basis of higher electronegativity of germanium vs. silicon: 2.01 vs. 1.90) to a reversed $\mathrm{Si}^{\delta-}{=}\mathrm{Ge}^{\delta+}$. The Si=Ge bond in **8** was longer than that of the cyclic silagermene **6**, 2.2769(8) Å vs. 2.250(1) Å, apparently due to the stronger steric interactions in the former.[9b]

Remarkable 2-germadisilaallene $\mathrm{R_2Si{=}Ge{=}SiR_2}$ ($\mathrm{R_2Si{=}}$: 2,2,5,5-tetrakis(trimethylsilyl)-1-silacyclopentylidene)[10a] and 1,3-digermasilaallene $\mathrm{R_2Ge{=}Si{=}GeR_2}$ [$\mathrm{R_2Ge{=}}$: 2,2,5,5-tetrakis(trimethylsilyl)-1-germacyclopentylidene],[10b] both containing Si=Ge bonds, were recently reported by Kira and co-workers. However, these Si=Ge double bonds are incorporated into the allenic fragments, therefore we do not discuss such compounds in detail, because cumulative doubly bonded derivatives are outside the scope of our review.

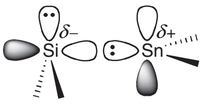
Silastannenes >Si=Sn<

The first (and still the sole) isolable silastannene $(^t\mathrm{Bu_2MeSi})_2\mathrm{Si{=}SnTip_2}$ **9** was prepared in 2002 by the coupling of 1,1-dilithiosilane derivative $(^t\mathrm{Bu_2MeSi})_2\mathrm{SiLi_2}$ with the diaryldichlorostannane $\mathrm{Tip_2SnCl_2}$ (Scheme 3).[11]

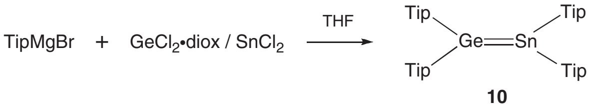
Silastannene **9** also featured an inversely polarized $\mathrm{Si}^{\delta-}{=}\mathrm{Sn}^{\delta+}$ double bond due to the electronic effects of its substituents (typically, such bonds are polarized as $\mathrm{Si}^{\delta+}{=}\mathrm{Sn}^{\delta-}$ because of the silicon and tin electronegativity difference). This was manifested in the appreciable deshielding of the sp^2-Sn nucleus (δ^{119}Sn 516.7 ppm) and significant shielding of the sp^2-Si nucleus ($\delta^{29}\mathrm{Si} = 27.4$ ppm). The Si=Sn bond of 2.4188(14) Å in **9** was intermediate between the typical values of Si=Si (2.138–2.289 Å) and Sn=Sn (2.590–3.087 Å) bonds, being ca. 7% shorter than the standard Si–Sn bond length of 2.60 Å.[11] As expected, the Si=Sn bond in **9** was *trans*-bent but the bending pattern was quite unusual, being greater (26.2°) at Si and smaller (9.6°) at Sn. These nontrivial structural features of silastannene **9** were rationalized in terms of the unconventional unsymmetrical donor–acceptor interaction mode (Scheme 4), promoted by the reversed $>\mathrm{Si}^{\delta-}{=}\mathrm{Sn}^{\delta+}<$ double bond polarization discussed above.



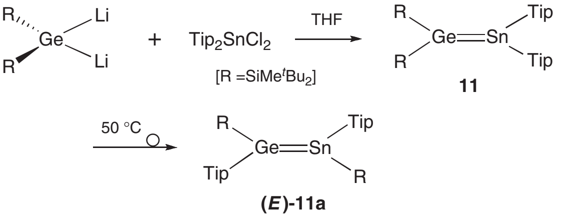
Scheme 3.



Scheme 4.



Scheme 5.



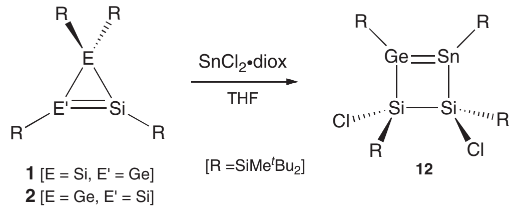
Scheme 6.

Germastannenes >Ge=Sn<

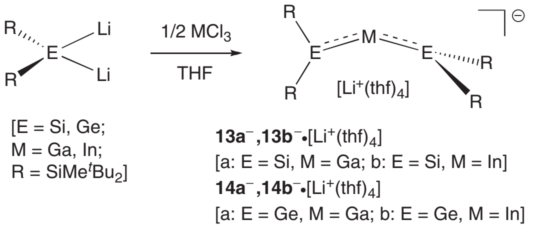
The first structurally characterized germastannene $\mathrm{Tip_2Ge{=}SnTip_2}$ **10** ($\delta^{119}\mathrm{Sn} = 268.0$ ppm) was prepared by Weidenbruch and co-workers by the one-pot reaction of TipMgBr, $\mathrm{GeCl_2{\cdot}dioxane}$ complex and $\mathrm{SnCl_2}$ (Scheme 5).[12] The Ge=Sn bond was short, 2.5065(5) Å, ca. 4.6% shorter than typical Ge–Sn bonds. As was expected, the *trans*-bending in **10** was greater at Sn (43.3°) than at Ge (30.2°).

Another stable germastannene $(^t\mathrm{Bu_2MeSi})_2\mathrm{Ge{=}SnTip_2}$ **11** ($\delta^{119}\mathrm{Sn} = 525.1$ ppm) was synthesized by the coupling of 1,1-dilithiogermane derivative $(^t\mathrm{Bu_2MeSi})_2\mathrm{GeLi_2}$ and diaryldichlorostannane $\mathrm{Tip_2SnCl_2}$ (Scheme 6).[13] Germastannene **11** readily isomerized under mild thermal conditions (50 °C) to form a symmetrically substituted isomer $(^t\mathrm{Bu_2MeSi})\mathrm{TipGe{=}Sn(SiMe}^t\mathrm{Bu_2)}$-Tip **11a** as a single *E*-isomer (Scheme 6).[13] Kinetic studies of the **11** → **11a** isomerization (negative value of $\Delta S^{\ddagger}$ of -12.0 cal K^{-1} mol^{-1}) suggested a concerted, rather than stepwise, isomerization mechanism, implying a dyotropic (that is, simultaneous intramolecular) 1,2-migration of the silyl and aryl groups in the starting **11**.

The cyclic germastannene **12**, incorporating an endocyclic Ge=Sn bond into the four-membered ring skeleton of $^3\Delta$-



Scheme 7.



Scheme 8.

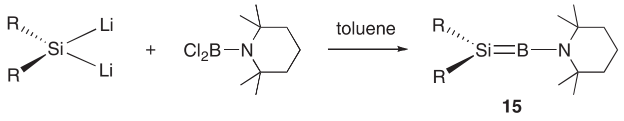
1,2,3,4-disilagermastannetene, was available by the unexpected ring expansion reaction of either 1*H*- or 3*H*-disilagermirene **1** or **2** with the SnCl$_2$•dioxane complex (Scheme 7).[14] The tin center of the Ge=Sn bond in **12** resonated in a diagnostic low field at 439.3 ppm. Cyclic germastannene **12** was indefinitely stable both in the solid state and in solution with no sign of dissociation into germylene and stannylene. Such thermal stability of the cyclic germastannene **12** was attributed to the stabilizing effect of the σ-donating silyl groups, as well as to proposed π(Ge=Sn)–σ^*(Si–Cl) orbital mixing resulting in the lowering of the π-energy level and stabilization of the HOMO.[14]

◆ >E$_{14}$=E$_{13}$– Derivatives

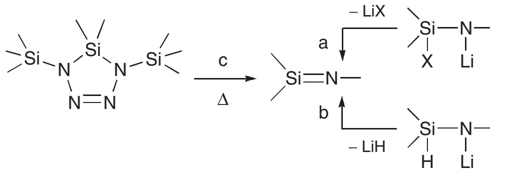
The isolation of the first stable compounds in the >E$_{14}$=E$_{13}$– series was achieved in 2004. The lithium salts of 1,3-disila-2-gallata- and -indataallenic anions $[\mathrm{R_2Si}\overset{\cdots}{-}\mathrm{M}\overset{\cdots}{-}\mathrm{SiR_2}]^-$ **13a**$^-$, **13b**$^-$•[Li$^+$(thf)$_4$] (**a**: M = Ga, R = SiMe^{t}Bu$_2$; **b**: M = In, R = SiMe^{t}Bu$_2$) were available by the reaction of R$_2$SiLi$_2$ with 0.5 equiv MCl$_3$ (Scheme 8, E = Si).[15a]

Both Si–Ga(In) bonds in **13a**$^-$ and **13b**$^-$ are ca. 6–7% shorter than the sum of the silicon and gallium (indium) covalent radii: 2.2828(9), 2.2775(9) Å in **13a**$^-$ and 2.4849(9), 2.4792(9) Å in **13b**$^-$. In contrast to linear organic allenes, the anionic $[\mathrm{R_2Si}\overset{\cdots}{-}\mathrm{M}\overset{\cdots}{-}\mathrm{SiR_2}]^-$ framework in **13a**$^-$ and **13b**$^-$ is bent and the terminal silicons are markedly pyramidalized. Accordingly, the Si atoms in the $[\mathrm{R_2Si}\overset{\cdots}{-}\mathrm{M}\overset{\cdots}{-}\mathrm{SiR_2}]^-$ unit are significantly shielded: −79.9 ppm in **13a**$^-$ and −77.6 ppm in **13b**$^-$. Overall, the structure of allenic anions $[\mathrm{R_2Si}\overset{\cdots}{-}\mathrm{M}\overset{\cdots}{-}\mathrm{SiR_2}]^-$ **13**$^-$ is best described by the major contribution of the allylic silyl anion resonance extremes R$_2$Si=M–SiR$_2$$^-$ ↔ $^-$R$_2$Si–M=SiR$_2$.

Germanium versions of **13a**$^-$ and **13b**$^-$, the lithium salts of 1,3-digerma-2-gallata- and -indataallenic anions $[\mathrm{R_2Ge}\overset{\cdots}{-}\mathrm{M}\overset{\cdots}{-}\mathrm{GeR_2}]^-$ **14a**$^-$, **14b**$^-$•[Li$^+$(thf)$_4$] (**a**: M = Ga, R = SiMe^{t}Bu$_2$; **b**: M = In, R = SiMe^{t}Bu$_2$) were prepared similarly by the reaction of R$_2$GeLi$_2$ with 0.5 equiv MCl$_3$ (Scheme 8, E = Ge).[15b] The structural characteristics of **14b**$^-$ are similar to those of **13a**$^-$ and **13b**$^-$: short Ge–In bonds of 2.5453(4) and 2.5387(4) Å (ca. 7% shorter than the sum of the germanium and indium covalent radii), bent $\mathrm{R_2Ge}\overset{\cdots}{-}\mathrm{M}\overset{\cdots}{-}\mathrm{GeR_2}$ framework, highly pyramidal germanium atoms. Similar to the case of the silicon versions **13a**$^-$ and **13b**$^-$, the constitution of 1,3-digerma-2-gallata- and -indataallenic anions **14a**$^-$ and **14b**$^-$ is best described as the hybrid of the two allylic germyl anion resonance forms R$_2$Ge=M–GeR$_2$$^-$ ↔ $^-$R$_2$Ge–M=GeR$_2$.



Scheme 9.



Scheme 10.

Synthesis of neutral heavy alkenes of >E$_{14}$=E$_{13}$– type has been achieved only in the case of boron–silicon derivatives. The isolation of the first stable silaborene **15** was achieved by the reaction of dilithiosilane (^{t}Bu$_2$MeSi)$_2$SiLi$_2$ with dichloro(2,2,6,6-tetramethylpiperidino)borane in toluene (Scheme 9).[16]

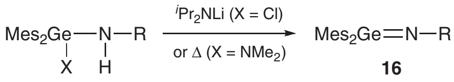
The sp^2-Si atom in **15** was remarkably shielded (δ^{29}Si −128.1 ppm), because of the reversed polarization of the double bond, >Si$^{\delta-}$=B$^{\delta+}$–. There is an important contribution of the resonance extreme >Si$^-$–B=N$^+$<. The Si–B–N framework is nearly linear (176.87(13)°) with a Si=B bond distance of 1.8379(17) Å, which is ca. 10% shorter than the typical Si–B single bonds in silylboranes (2.038–2.1249 Å).

◆ >E$_{14}$=N– Derivatives

Silanimines >Si=N–

The first stable silanimine ^{t}Bu$_2$Si=NSi^{t}Bu$_3$ was synthesized by coupling of ^{t}Bu$_2$SiClN$_3$ and NaSi^{t}Bu$_3$ followed by elimination of N$_2$.[17] Other silanimines have been mainly prepared by the delithiofluorination of lithium fluorosilylamide derivatives, >Si(F)–N(Li)–, in which the lithium is coordinated to the fluorine atom (Scheme 10, route a).[18] Formation of the Si=N double bond is facilitated by the addition to the lithium compound of Me$_3$SiOSO$_2$CF$_3$[19a,19b] or more generally of Me$_3$SiCl (a fluorine/chlorine exchange occurs with the subsequent elimination of LiCl).[20a,20b] In some cases, the lithium fluorosilylamides >Si(F)–N(Li)– behaved like the corresponding silanimines and can therefore be considered as their synthetic equivalents. Lithium hydridosilylamides >Si(H)–N(Li)– can also serve as precursors of silanimines (route b); however, this elimination depends on the type of substituent at the Si atom.[21] Silanimines were also prepared by thermal decomposition of silatetrazolines (route c).[22]

Silanimines readily react with Lewis bases, such as tertiary amines and ethers, to form stable adducts that can sometimes be distilled without decomposition.[19a,19b,20b] ^{29}Si NMR spectra of such adducts display a remarkable high-field shift for the doubly



$$\mathrm{Mes_2Ge(X)–N(H)–R} \xrightarrow[\text{or }\Delta\ (X = NMe_2)]{{}^i\mathrm{Pr_2NLi}\ (X = Cl)} \mathrm{Mes_2Ge{=}N–R}$$

Scheme 11.

bonded silicon atom in comparison with free silanimines (for example, 2.68 ppm in the THF adduct of $^t\mathrm{Bu_2Si{=}NSi(^tBu)_2Ph}$ and −12.6 ppm in the pyridine adduct vs. 80.4 ppm for the free silanimine[19a,20b,21]). The Si=N double bond length is generally shortened by about 7–8% in relation to the corresponding single bond, for example, in $^t\mathrm{Bu_2Si{=}NSi(^tBu)_2Ph}$, 1.572 and 1.696 Å, respectively, with a trigonal-planar arrangement of the $\mathrm{C_2Si{=}N}$ unit.[19a,19b] As expected, the Si=N bond is lengthened by about 0.04 Å in the pyridine complex.[19b]

Germanimines >Ge=N–

The first isolated germanimines, $\mathrm{[(Me_3Si)_2N]_2Ge{=}NSiR_3}$ (R = Et and $\mathrm{O^tBu}$), were prepared by reaction of germylene $\mathrm{[(Me_3Si)_2N]_2Ge}$ and $\mathrm{N_3SiR_3}$ followed by elimination of $\mathrm{N_2}$.[23] This route was used for the synthesis of germanimines and stannanimines.[24] As in the case of silanimines, one of the main routes is the elimination of LiX, but also of $\mathrm{R_2NH}$, from diaminogermanes $\mathrm{>Ge(NR_2)–NHR'}$. The two stable germanimines **16** substituted by aromatic groups at nitrogen (R = $\mathrm{2\text{-}Me_2NSO_2–C_6H_4}$[25a] and $\mathrm{4\text{-}NO_2–C_6H_4}$[25b]) (Scheme 11) have been recently isolated.

Surprisingly, germanimine **16** (R = $\mathrm{4\text{-}NO_2–C_6H_4}$) is stable up to 155 °C[25a] and its dimer (digermazane) has never been formed. X-ray structures of germanimines show trigonal-planar geometry around the Ge with 8–10% shortening in relation to the Ge–N single bond.[3b,3c,3d]

◆ *>E$_{14}$=P– Derivatives*

The synthesis of the first stable phosphasilene, $\mathrm{Mes_2Si{=}PMes^*}$ ($\mathrm{Mes^* = 2,4,6\text{-}{}^tBu_3C_6H_2}$),[3b,3c,3d] by Bickelhaupt was followed by the preparation of the first phosphagermene, $\mathrm{Mes_2Ge{=}PMes^*}$,[3b,3c] and phosphastannene, $\mathrm{[(Me_3Si)_2CH]_2Sn{=}PMes^*}$.[3b,3c] A more stable phosphastannene, $\mathrm{Tip_2Sn{=}PMes^*}$ (Tip = 2,4,6-triisopropylphenyl), was prepared some years later.[26] The first doubly bonded compound with a group 15 element heavier than phosphorus, an arsasilene >Si=As–, was reported only in 1992.[4] The standard route to such derivatives involves the coupling of a group 14 dihalide with a lithium phosphide or arsenide followed by dehydrohalogenation (Scheme 12).

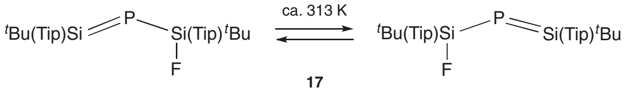
Phosphasilenes and Phosphagermenes

The new phosphasilenes $\mathrm{Mes^*HP(R)Si{=}PMes^*}$ (R = ^{t}Bu, Mes, Tip, and Cp*)[27] (δ^{31}P 142.0–169.2 ppm) and **17**[28] (δ^{31}P −33.0 ppm) (Scheme 13) have been recently prepared. In derivative **17**, the ^{1}H NMR spectrum confirms that the localized Si=P double bond is retained in solution up to 40 °C, but that a suprafacial [1,3]-sigmatropic fluorine shift with a Gibbs activation energy of about 16 kcal mol^{-1} occurs above 40 °C.[28] Phosphasilenes are very air- and moisture-sensitive compounds, but are thermally stable when the steric hindrance around the double bond is high enough; for example, derivative **17** can be recrystallized from boiling toluene.[28]

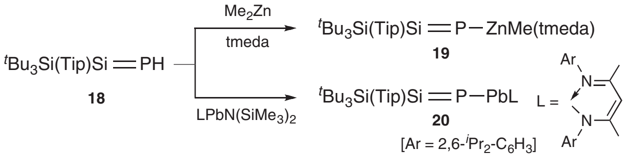
$$\mathrm{>EX_2} \xrightarrow{\mathrm{Li–E'(H)–}} \mathrm{>E(X)–E'(H)–} \xrightarrow{\text{base}} \mathrm{>E{=}E'–}$$

[E = Si, Ge, Sn; E' = P, As]

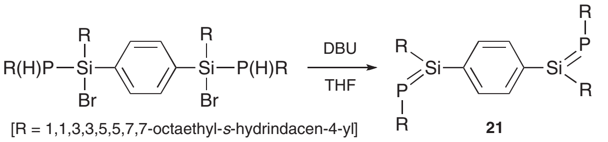
Scheme 12.



Scheme 13.



Scheme 14.

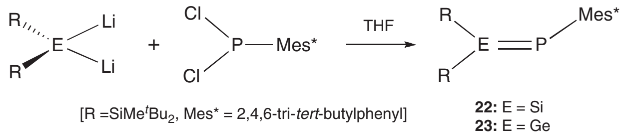


Scheme 15.

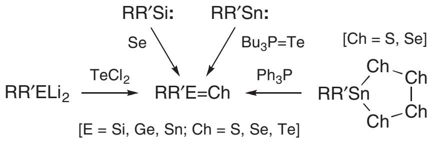
From the "half-parent" phosphasilene $^t\mathrm{Bu_3Si(Tip)Si{=}PH}$ **18** [δ^{31}P 123.1 (*E*) and 134.2 (*Z*) ppm, δ^{29}Si 249.8 (*E*), 248.9 (*Z*) ppm], *P*-zinciophosphasilene **19**[29a] (δ^{31}P 227 ppm, δ^{29}Si 203 ppm) and *P*-plumbyleniophosphasilene **20**[29b] (δ^{31}P 292.5, δ^{29}Si 227.0, δ^{207}Pb 1068 ppm), a new type of heteroleptic complex of divalent lead, have been prepared (Scheme 14). Another phosphasilene substituted at the P atom by a transition metal, the *P*-ferriophosphasilene $\mathrm{Cp(CO)_2Fe–P{=}SiTip_2}$, ($\delta^{29}$Si = 201 ppm, δ^{31}P = 57 ppm) has been obtained by delithiofluorination of the corresponding precursor.[29c]

New phosphasilenes and bis(phosphasilenes) **21** have been stabilized by huge fused-ring groups (R = substituted hydrindacene) at Si and P atoms.[30] NMR data (δ^{29}Si = 161.7–162.1 ppm, δ^{31}P = 89.2–89.7 ppm) and Si=P bond lengths (2.09–2.10 Å) are in the normal range. Strong π–π^* absorption has been observed because of the coplanar arrangement of the Si=P units and the phenylene bridge (Scheme 15).

The first "push–pull" phosphasilene **22** and phosphagermene **23** (donating Si groups at Si or Ge and accepting aryl group at P) have been synthesized very recently in one step by a novel method involving the coupling of a dilithiosilane (or -germane) with a dichlorophosphine (Scheme 16).[31] A very special feature is the deshielding of the ^{31}P nucleus (**22**: 389.3 ppm and **23**: 416 ppm), by far the most low-field shifted signals for $\mathrm{E_{14}{=}P}$ compounds [−33.0 to 292.5 ppm for the other phosphasilenes[4] (or -germenes[3b,3c,3d]) reported so far]. Such deshielding can be attributed to the σ-donating effect of the silyl groups bonded to the sp^2-silicon atom (paramagnetic effect). Remarkable red shift of the longest wavelength absorption in **22** (461 nm) was observed compared with other phosphasilenes (generally 331–343 nm). As in other Si(Ge)=P compounds, the double bond is shortened by about 7% relative to a single bond



Scheme 16.



Scheme 17.

and no pyramidalization or twisting is observed, with the Si and Ge atoms being perfectly planar.

◆ >E_{14}=E_{16} Derivatives

Heavy Thiones, Selones, and Tellones

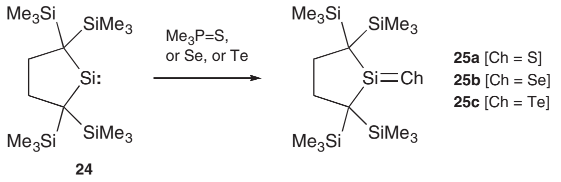
In addition to their fundamental structural and bonding situations, some of these species can be of potential industrial interest (applications in thermoelectric devices, optics, etc), for example, Sn=Te derivatives as precursors of low band gap semiconductors.[32] Kinetic stabilization is one of the most important methods to prepare isolable E_{14}=E_{16} derivatives. However, because the group 16 element bears no substituents, kinetic stabilization of the E_{14}=E_{16} double bond requires the utilization of particularly bulky ligands at the heavy group 14 element.

Dechalcogenation of 1,2,3,4-tetrachalcogenometallolanes with trivalent phosphorus reagents, chalcogenation of divalent species or reactions of dilithiosilanes (or -germanes) with a dihalochalcogen are the methods of choice to synthesize kinetically stabilized E_{14}=E_{16} derivatives[5] (E_{14} = Si, E_{16} = Se, Te;[33a] E_{14} = Ge, E_{16} = S,[33b] Se,[33b] Te;[33c] E_{14} = Sn, E_{16} = S,[33d,33e] Se,[33d] Te[33f]) (Scheme 17). The stabilizing groups are generally aromatic groups substituted by bulky alkyl or aryl groups. For example, the best route to stannatellone was the telluration of a stannylene by Bu_3P=Te.[33f] Such a derivative, which could be isolated owing to the bulky groups, was stable to light, in sharp contrast to its carbon analogs.

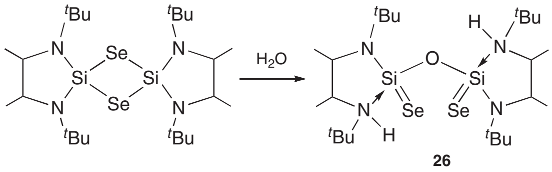
Reaction of the isolable dialkylsilylene **24** with Me_3P=S, Se, or Te afforded the first dialkyl-substituted silicon–chalcogen doubly bonded compounds **25** (Scheme 18).[34] In contrast to diaryl-substituted silachalcogenones, π–π^* transitions are distinctly observed in addition to the n–π^* transition bands.

With less bulky groups at the E_{14} elements, stabilization of E_{14}=E_{16} derivatives is possible only by an intramolecular coordination on the heavy E_{14} element, mainly by a nitrogen atom. In contrast to E_{14}=E_{15} derivatives, such coordination with N is relatively strong because of the greater polarity of the E_{14}=E_{16} bond.

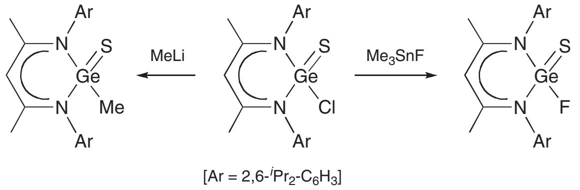
Silaselone **26** (δ^{29}Si −30.3 ppm) with two donor-stabilized Si=Se double bonds is the first example in which a direct hydrolysis reaction is successful in forming a multiple bond between heavy main group elements (Scheme 19).[35]



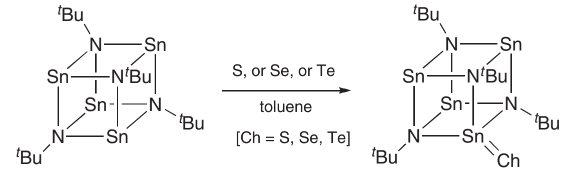
Scheme 18.



Scheme 19.



Scheme 20.



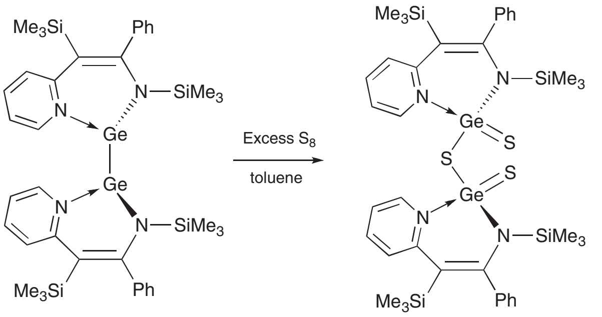
Scheme 21.

Fluorine- or methyl-substituted germanethiones were synthesized from the corresponding chlorine-substituted compound by exchange reaction with Me_3SnF or alkylation with MeLi (Scheme 20).[36] Oxidation of the system $(GeN^tBu)_4$ or $(SnN^tBu)_4$ with S, Se, or Te provides a facile route to cubic complexes containing one, two or three Ge (or Sn)=S (Se or Te) double bonds (Scheme 21).[37] The reaction of elemental sulfur with a bis(germylene) complexed with a nitrogen atom afforded a germanium analog of a dithiocarboxylic anhydride [Ge(=S)–S–Ge(=S) linkage] (Scheme 22).[38]

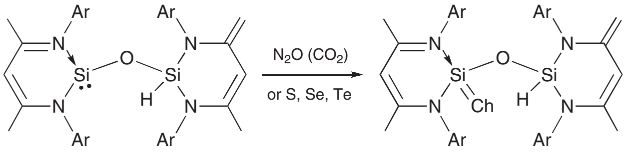
Heavy Ketones >E_{14}=O

The isolation of silanones >Si=O is particularly challenging. Because of the high polarity of the Si=O double bond [Si=O ↔ Si^+–O^-], such compounds exhibit an extraordinary high tendency to dimerize (or oligomerize), which, in contrast to their carbon analogs or other Si–heteroatom systems, proceed with no activation barriers. However, intramolecular complexation of the group 14 element with a nitrogen allowed the stabilization of silanones.

Chalcogenation of the siloxysilylene LSiOSiL′H **27** led to the corresponding silachalcogenones **28** (Scheme 23).[39] Such compounds with a donor–acceptor N–Si bond, which induces a N^+–Si–Ch^- (Ch = chalcogen) resonance betaine structure,

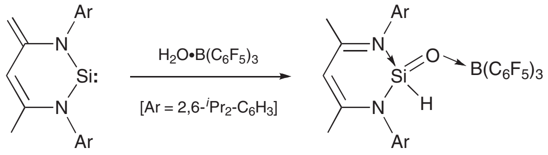


Scheme 22.



27 [Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$] **28** [Ch = O, S, Se, Te]

Scheme 23.



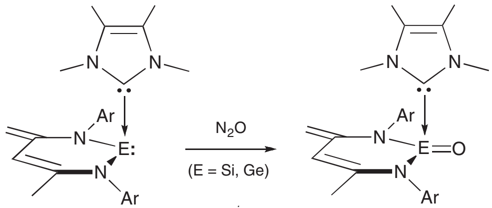
Scheme 24.

however, present a considerable Si=Ch double bond character because of a π-back-donation from the lone pair electrons of Ch into the antibonding Si–N σ^*-orbitals, which are mainly located at Si.[39] The silanone possesses an estimated Si–O bond order of 1.8 (2.0 in $H_2Si{=}O$[39a]).

A silaformyl derivative L(H)Si=O has been stabilized by the presence of an *n*-donor group on the Si atom and a π-acceptor group on O, which reduce the polarity and provides an additional steric protection for the Si=O double bond (Scheme 24).[40]

Another type of stabilization of silanones[41a] and germanones,[41b] i.e. complexation of Si and Ge atoms by an *N*-heterocyclic carbene (NHC), has been recently reported. The oxidation of an NHC–silylene adduct with N_2O leads to an NHC-stabilized silanone **29** (Scheme 25).

Low-field chemical shifts are characteristic of sp^2-hybridized E_{14} nuclei. In kinetically stabilized >Si=Ch and >Sn=Ch compounds (Ch = chalcogen), ^{29}Si and ^{119}Sn NMR signals are observed around 150–230 and 380–600 ppm, respectively. ^{77}Se and ^{125}Te NMR chemical shifts also appear at low field within the range 900–1000 (^{77}Se) and 1000–1200 ppm (^{125}Te). In the complexed derivatives **26** and **28**, the ^{29}Si, ^{119}Sn, ^{77}Se, and ^{125}Te NMR resonances appear at much higher fields than in the noncomplexed compounds **25**. For example, δ^{29}Si: **25a** 216.8,[34] **28** (Ch = S) −85.1 and −85.8 ppm;[39b] δ^{119}Sn: Bbt(Titp)Sn=Te 282,[33e] [N]$_3$Sn=Te −429.7 ppm;[32] δ^{77}Se: Tbt(Dip)Si=Se 635,[33a] **26** −344 ppm;[35] δ^{125}Te: Tbt(Dip)Si=Te 1194,[33a] **28** (Ch = Te) −1067.7 and −1105.5 ppm[39b] (Bbt, Dip, Titp, Tbt: substituted aromatic groups).



[Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$] **29**

Scheme 25.

In the UV–vis spectra of **28**, n–π^* absorptions appear at 355, 390, and 430 nm for Ch = S, Se, and Te,[39b] close to those of the unsupported **25** (336, 383, and 476 nm),[34] and are as expected red-shifted from S to Te. Whereas a shortening of 6–10% compared with the standard single bonds is observed for kinetically stabilized $E_{14}{=}E_{15/16}$ derivatives, a much smaller shortening occurs in complexed compounds; the bond length is intermediate between a single and a double bond.

Conclusion and Prospects

Many doubly bonded compounds $E_{14}{=}E'_{14}$ and $E_{14}{=}E_{13/15/16}$ have been isolated and structurally characterized. However, upon descending the periodic table within the main group elements, the stabilization becomes more and more difficult. Thus, for $E_{14}{=}E_{15}$ derivatives, there are no examples of $E_{14}{=}Sb$ (or Bi) and, with As, only arsasilenes Si=As are known. However, the reverse trend is observed for $E_{14}{=}E_{16}$ derivatives; because of their high polarity, kinetically stabilized silanones Si=O are still unknown, whereas their heavier analogs with S, Se, and Te have been reported.

After the synthesis of doubly bonded compounds, the characterization and isolation of heteronuclear triply bonded derivatives of the type $E_{14}{\equiv}E_{13/15}$ appears to be a next challenge. Some phosphaalkynes C≡P have been described;[42] however, no analogs featuring group 14 elements heavier than C are known. In such cases, the problem is the stabilization of the system with only one substituent on the group 14 and no substituents on the group 13 (or 15) element.

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