Reviews

Heteronuclear Heavy Alkenes E═E′ (E, E′ = Group 14 Elements): Germasilenes, Silastannenes, Germastannenes...Next Stop?

Vladimir Ya. Lee and Akira Sekiguchi*

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

Received March 2, 2004

Recent advances in the chemistry of stable heteronuclear heavy alkenes >E═E′< (E, E′ = group 14 elements) are reviewed, covering silenes (>Si═C<), germenes (>Ge═C<), stannenes (>Sn═C<), germasilenes (>Ge═Si<), silastannenes (>Si═Sn<), and germastannenes (>Ge═Sn<). Their unique structures, bonding modes, and reactivities have been shown to be different from those of the homonuclear species, primarily due to the polarity of the >E═E′< bond resulting from the difference in the electronegativities of the doubly bonded atoms.

1. Introduction

Alkenes (>C═C<) represent one of the most fundamental classes of compounds, to which organic chemistry is greatly obliged due to their diversity and richness. Carbon, the central element of organic chemistry, is the first and lightest representative of group 14, and a logical question arose: are the heavier members of the same group (i.e., Si, Ge, Sn, and Pb) also capable of forming double bonds of the type >E═E< or >E═E′< (E, E′ = group 14 elements) between themselves? The first answer to this question was given as early as 1957, and it was unambiguously negative: elements with a principal quantum number equal to or greater than 3 (that is, elements of period 3 and subsequent periods) cannot form multiple bonds, due to the significant Pauli repulsion of the electrons in the inner shells (the so-called “double-bond rule”).[1] Meanwhile, experimental chemists accumulated a vast amount of information that provided strong evidence for the real existence and participation of the doubly bonded species >E═E< in a number of organometallic reactions.[2] Nevertheless, such highly reactive and unstable species were identified only by trapping reactions and spectroscopic methods (IR matrix isolation technique, low-temperature NMR spectroscopy), which were the main experimental tools for the investigation of such reactive intermediates several decades ago.[2] Finally, the quantity of such information has been followed by its quality, and the first fundamental breakthrough was achieved in 1973 when Lappert reported the synthesis and crystal structure of the first stable compound with an Sn═Sn double bond, $[(Me_3Si)_2CH]_2Sn{=}Sn[CH(SiMe_3)_2]_2$.[3] Since then, over the last 30 years, the chemistry of stable doubly bonded compounds consisting of group 14 elements has been established. The second historical discovery came from two research groups, both of whom published their papers in 1981: West reported the synthesis of the first compound with an Si═Si double bond, tetramesityldisilene,[4] while Brook synthesized the first compound with an Si═C double bond.[5] Both compounds were absolutely stable in the solid state and in solution, thus providing a unique opportunity to study their crystal structure and reactivity. Later, the chemistry of heavy alkenes was greatly developed in all aspects, including synthetic methods, structural studies, spectroscopic properties, and reactivity. The nature of E═E double bonds in comparison with that of alkenes (C═C) was a subject of intense experimental and theoretical investigation. This topic has been thoroughly discussed in recent reviews (Power,[6k] Klinkhammer[6r]), and we shall not consider such questions in this paper.

---

[1] (a) Goubeau, J. *Angew. Chem.* **1957**, *69*, 77. (b) Jutzi, P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 232. (c) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.

[2] (a) See ref 1c. (b) Satgé, J. *Adv, Organomet. Chem.* **1982**, *21*, 241. (c) Rivieré, P.; Rivieré-Baudet, M.; Satgé, J. *Comprehensive Organometallic Chemistry*; Pergamon Press: New York, 1982; Vol. 2, Chapter 10. (d) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141. (e) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1. (f) Cowley, A. H.; Norman, N. C. *Prog. Inorg. Chem.* **1986**, *34*, 1. (g) Gordon, M. S. In *Molecular Structure and Energetics*; Leibman, J. F., Greenberg, A., Eds.; VCH: Deerfield Beach, FL, 1986; Vol. 1. (h) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (i) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Chapter 17. (j) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283.

[3] (a) Davidson, P. J.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1973**, 317. (b) Goldberg, D. E.; Harris, D. H.; Lappert, M. F.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* **1976**, 261. (c) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268. (d) Cotton, J. D.; Davidson, P. J.; Lappert, M. F.; Donaldson, J. D.; Silver, J. *J. Chem. Soc., Dalton Trans.* **1976**, 2286. (e) Goldberg, D. E.; Hitchcock, P. B.; Lappert, M. F.; Thomas, K. M.; Thorne, A. J.; Fjeldberg, T.; Haaland, A.; Schilling, B. E. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2387.

[4] West, R.; Fink, M. F.; Michl, J. *Science* **1981**, *214*, 1343.

[5] (a) Brook, A. G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R. *J. Chem. Soc., Chem. Commun.* **1981**, 191. (b) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667.

10.1021/om040027h CCC: $27.50

The homonuclear combinations $\mathrm{>E{=}E<}$ (E = a heavier group 14 element) are well-known to date, many compounds of this type have been synthesized, and the progress in this field is clearly reflected by the number of excellent reviews published in the past decade.[6] Heteronuclear combinations having two *different* doubly bonded group 14 elements $\mathrm{>E{=}E'<}$ were of particular interest, since they provide a much greater variation in the bonding modes than the symmetrical homonuclear species $\mathrm{>E{=}E<}$, depending on the nature of the two doubly bonded elements (electronegativity, polarizability, etc.). The reactivity of heteronuclear “heavy” alkenes was also expected to be different from that of the homonuclear species, primarily due to the polarity of the $\mathrm{>E{=}E'<}$ bond caused by the difference in the electronegativities of the doubly bonded atoms. The important role of heteronuclear “heavy” alkenes was recently emphasized by Driess and Grützmacher in their review published in 1996: “*Special consideration must be given to the fact that it has not yet been possible to synthesize an isolable heteronuclear* $XYE{=}E'X'Y'$ *multiply bonded system with two Group 14 E and E′ centers from the higher rows (n > 2). These compounds should have especially interesting characteristics.*”[7] However, despite such evident and undoubted interest, until very recently the chemistry of heteronuclear “heavy” alkenes was limited only to such combinations where one of the elements was carbon, that is, silenes ($\mathrm{>Si{=}C<}$), germenes ($\mathrm{>Ge{=}C<}$), and stannenes ($\mathrm{>Sn{=}C<}$). No stable combinations between the different heavier group 14 elements $\mathrm{>E{=}E'<}$ were reported in the last century. In a remarkable theoretical contribution published nearly 10 years ago, Gordon pointed out: “*...compounds containing Ge–Ge double bonds have been synthesized but compounds containing Ge–Si double bonds have not, even though these two are predicted to have approximately the same π-bond strength. The same can be said about the known Sn=Sn compounds and their as yet experimentally unknown Sn=Ge and Sn=Si analogues.*”[8] The principal progress in this field has been achieved only during the last 4 years, when the first isolable representatives of germasilenes ($\mathrm{>Ge{=}Si<}$), silastannenes ($\mathrm{>Si{=}Sn<}$), and germastannenes ($\mathrm{>Ge{=}Sn<}$) were reported in the scientific literature. To date, five silenes, eight germenes, four stannenes, four germasilenes, one silastannene, and four germastannenes have been synthesized as stable compounds, most of them being structurally characterized. Until now, no attempts to review the chemistry of such heteronuclear heavy alkenes have been undertaken, and so we are now summarizing for the first time the current state of affairs in this very new field of group 14 chemistry. The literature coverage is up to the beginning of 2004. It should be noted that in this review we will deal only with the stable representatives of heavy alkenes, and by “stable” we mean those compounds that have been isolated and unambiguously characterized in a pure form, first of all by means of X-ray crystallography. Other compounds, which undergo unavoidable changes (decomposition, dimerization, etc.) at low or room temperature, will be considered as unstable (or metastable) and will not be discussed in the present review. The few examples of the stable sila- and germaaromatic compounds reported recently by Tokitoh’s group,[9] which formally have the Si=C (or Ge=C) fragments incorporated in benzene (or naphthalene) rings, also will not be covered in this review, since they belong to the class of heavy aromatics rather than heavy alkenes. The heavy allenes (silaallenes and germaallenes) with cumulated E=C=C double bonds (E = Si, Ge) also constitute an independent class of compounds, whose chemistry was recently thoroughly reviewed by Escudié,[10,11] and therefore will be outside the framework of the present review.

2. Heteronuclear Heavy Alkenes $\mathrm{>E{=}E'<}$ (E, E′ = Group 14 Elements)

2.1. Heteronuclear Heavy Alkenes $\mathrm{>E{=}C<}$ (E = Si, Ge, Sn). 2.1.1. Silenes ($\mathrm{>Si{=}C<}$). Historically, silenes were the first representatives of heteronuclear heavy analogues of alkenes: as early as 1981 Brook published a paper on the first authenticated compound with an Si=C double bond—silene **1** having a huge adamantyl group as a substituent—and determined this double bond length for the first time (Scheme 1).[5]

---

(6) Reviews on metallenes $\mathrm{>E{=}C<}$ and dimetallenes $\mathrm{>E{=}E<}$ of group 14 elements: (a) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. (b) See ref 2i. (c) See ref 2j. (d) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (e) Escudié, J.; Couret, C.; Ranaivonjatovo, H.; Satgé, J. *Coord. Chem. Rev.* **1994**, *130*, 427. (f) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. (g) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275. (h) Kaftory, M.; Kapon, M.; Botoshansky, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Part 1, Chapter 5. (i) Escudié, J.; Couret, C.; Ranaivonjatovo, H. *Coord. Chem. Rev.* **1998**, *178–180*, 565. (j) Power, P. P. *J. Chem. Soc., Dalton Trans.* **1998**, 2939. (k) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463. (l) Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, 373. (m) Escudié, J.; Ranaivonjatovo, H. *Adv. Organomet. Chem.* **1999**, *44*, 113. (n) Kira, M.; Iwamoto, T. *J. Organomet. Chem.* **2000**, *611*, 236. (o) Weidenbruch, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 2001; Vol. 3, Chapter 5. (p) Weidenbruch, M. *J. Organomet. Chem.* **2002**, *646*, 39. (q) West, R. *Polyhedron* **2002**, *21*, 467. (r) Klinkhammer, K. W. In *The Chemistry of Organic Germanium, Tin and Lead Compounds*; Rappoport, Z., Ed.; Wiley: Chichester, U.K., 2002; Vol. 2, Part 1, Chapter 4. (s) Tokitoh, N.; Okazaki, R. In *The Chemistry of Organic Germanium, Tin and Lead Compounds*; Rappoport, Z., Ed.; Wiley: Chichester, U.K., 2002; Vol. 2, Part 1, Chapter 13. (t) Weidenbruch, M. *Organometallics* **2003**, *22*, 4348. Reviews on the cyclic trimetallenes of heavier group 14 elements (*heavy cyclopropenes*): (u) Lee, V. Ya.; Sekiguchi, A. In *The Chemistry of Organic Germanium, Tin and Lead Compounds*; Rappoport, Z., Ed.; Wiley: Chichester, U.K., 2002; Vol. 2, Part 1, Chapter 14. (v) Sekiguchi, A.; Lee, V. Ya. *Chem. Rev.* **2003**, *103*, 1429. (w) Sekiguchi, A.; Lee, V. Ya. In *Organosilicon Chemistry V: From Molecules to Materials*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, Germany, 2003; p 92.

(7) Driess, M.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 828.

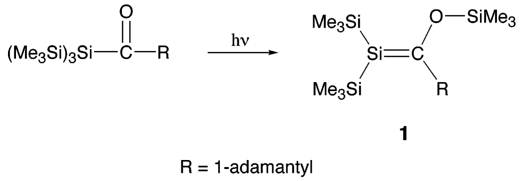
(8) Windus, T. L.; Gordon, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 9559.

(9) (a) Tokitoh, N.; Wakita, K.; Okazaki, R.; Nagase, S.; Schleyer, P. v. R.; Jiao, H. *J. Am. Chem. Soc.* **1997**, *119*, 6951. (b) Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S.; Schleyer, P. v. R.; Jiao, H. *J. Am. Chem. Soc.* **1999**, *121*, 11336. (c) Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 636. (d) Wakita, K.; Tokitoh, N.; Okazaki, R.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2000**, *122*, 5648. (e) Nakata, N.; Takeda, N.; Tokitoh, N. *Organometallics* **2001**, *20*, 5507. (f) Takeda, N.; Shinohara, A.; Tokitoh, N. *Organometallics* **2002**, *21*, 256. (g) Nakata, N.; Takeda, N.; Tokitoh, N. *J. Am. Chem. Soc.* **2002**, *124*, 6914. (h) Takeda, N.; Shinohara, A.; Tokitoh, N. *Organometallics* **2002**, *21*, 4024. (i) Nakata, N.; Takeda, N.; Tokitoh, N. *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 115. (j) Nakata, N.; Takeda, N.; Tokitoh, N. *Organometallics* **2003**, *22*, 481. Latest review: (k) Tokitoh, N. *Acc. Chem. Res.* **2004**, *34*, 86.

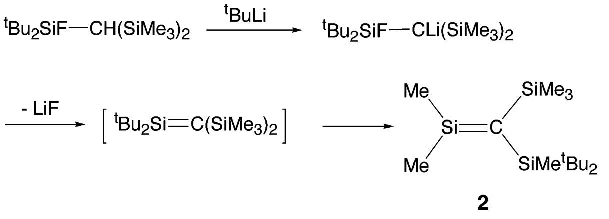
(10) Escudié, J.; Ranaivonjatovo, H.; Rigoh, L. *Chem. Rev.* **2000**, *100*, 3639.

(11) Two remarkable all-heavy-atom-containing allenes of the type $\mathrm{>E{=}E{=}E<}$, tristannaallene ($\mathrm{>Sn{=}Sn{=}Sn<}$) and trisilaallene ($\mathrm{>Si{=}Si{=}Si<}$), were recently reported by the Wiberg and Kira groups, respectively: (a) Wiberg, N.; Lerner, H.-W.; Vasisht, S.-K.; Wagner, S.; Karaghiosoff, K.; Nöth, H.; Ponikwar, W. *Eur. J. Inorg. Chem.* **1999**, 1211. (b) Ishida, S.; Iwamoto, T.; Kabuto, C.; Kira, M. *Nature* **2003**, *421*, 725.

Scheme 1



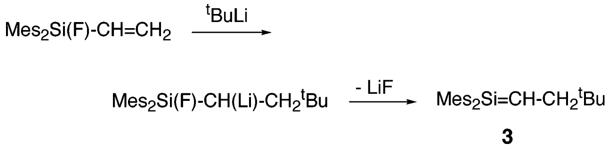
Scheme 2



Several years later, in 1985, Wiberg reported another silene, **2**, bearing the small methyl groups on the silicon atom, which nevertheless was surprisingly stable (Scheme 2).[12] The chemistry of these first two members of the stable silene family was repeatedly and comprehensively reviewed;[6] therefore, we will not be concerned with these compounds, dealing with the latest examples of stable silenes only, whose chemistry will be discussed below. These include four new silenes reported by Couret in 1994, Apeloig in 1996, and Kira in 2002.

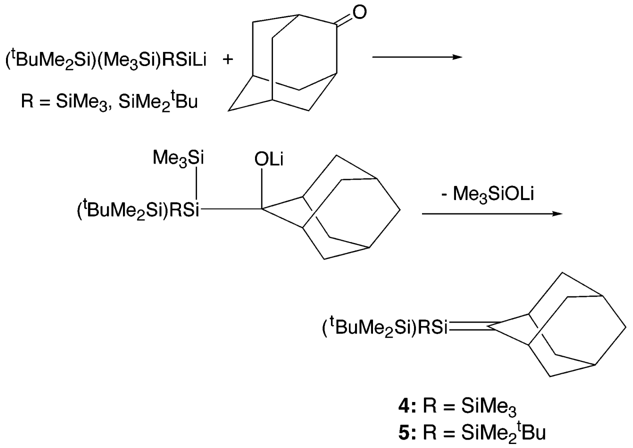
The stable silene dimesitylneopentylsilene (**3**) was synthesized by Couret's group in 1994.[13] This compound, $\mathrm{Mes_2Si{=}CHCH_2{}^{t}Bu}$, having two bulky mesityl (Mes = 2,4,6-trimethylphenyl) substituents on the silicon atom and only one bulky neopentyl group on the carbon atom (surprisingly, the other substituent was the small hydrogen atom), was nearly quantitatively obtained by the addition of *tert*-butyllithium to fluorodimesitylvinylsilane in pentane at low temperature, followed by the elimination of LiF (Scheme 3). Although lacking X-ray diffraction data, the silene **3** was isolated as an individual compound and unequivocally characterized by the downfield-shifted resonance of the doubly bonded silicon atom at +77.6 ppm. The reactivity of this new silene was exhaustively studied by the authors[13,14] and subsequently was described in detail in Escudié's recent review.[6i]

Scheme 3

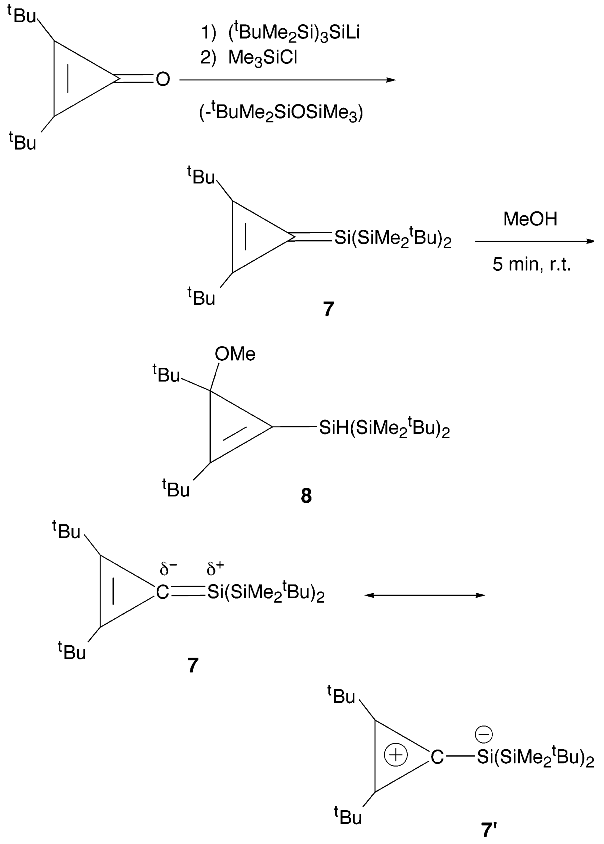


The method employed by Apeloig's group for the preparation of the stable silenes was based on the sila-Peterson reaction of silyllithium derivatives $\mathrm{R^1R^2R^3SiLi}$ ($\mathrm{R^1}$, $\mathrm{R^2}$, $\mathrm{R^3}$ = $\mathrm{SiMe_3}$, $\mathrm{SiMe_2{}^{t}Bu}$) with adamantanone in THF (Scheme 4).[15] Both stable silenes **4** and **5** displayed the downfield-shifted resonances of $\mathrm{sp^2}$ Si atoms at +51.7 and +49.7 ppm, respectively. The crystal structure analysis available for the silene **4** showed the nearly planar geometry of the Si=C double bond with a small twisting (4.6°) of the double bond. The Si=C double bond length of 1.741(2) Å was intermediate

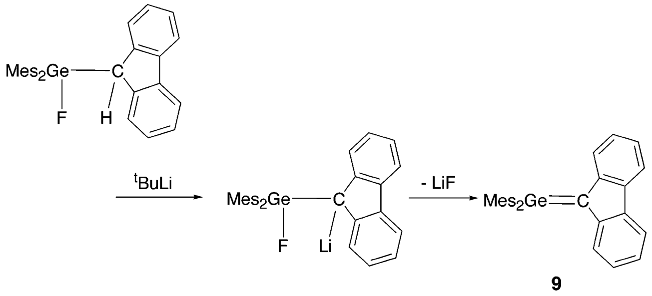
Scheme 4



Scheme 5



Scheme 6



---

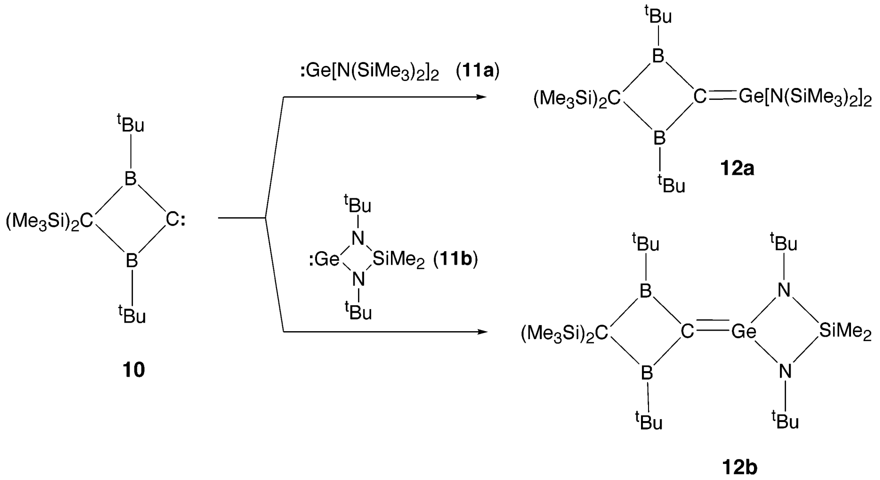
(12) Wiberg, N.; Wagner, G.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229.

(13) Delpon-Lacaze, G., Couret, C. *J. Organomet. Chem*. **1994**, *480*, C4.

(14) Delpon-Lacaze, G.; De Battisti, C.; Couret, C. *J. Organomet. Chem*. **1996**, *514*, 59.

(15) Apeloig, Y.; Bendikov, M.; Yuzefovich, M.; Nakash, M.; Bravo-Zhivotovskii, D. *J. Am. Chem. Soc.* **1996**, *118*, 12228.

Scheme 7

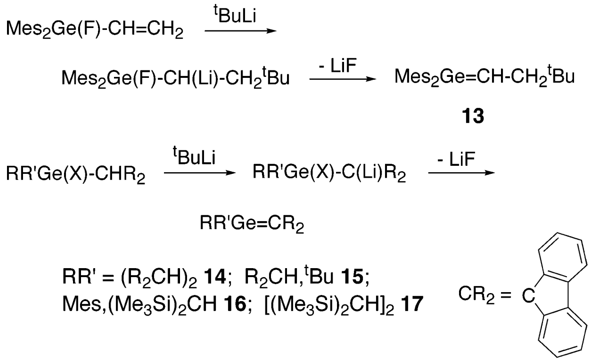


between those obtained by Wiberg (1.702(5) Å for **2**) and Brook (1.764(3) Å for **1**). The silene **4** was surprisingly inert toward dimerization, in contrast to the transient silene $(Me_3Si)_2Si{=}Ad$ (**6**), having all of the trimethylsilyl substituents on the Si atom. The authors have attributed such stability of **4** primarily to a dramatic difference in steric congestion in the dimerization transition states of **4** and **6**: the steric strain is 28.2 kcal/mol higher for the dimerization of silene **4** than for silene **6**. Despite their inertness toward dimerization, both silenes **4** and **5** are reactive toward different reagents: with water and methanol they form the corresponding 1,2-adducts, whereas with 1-methoxy-1,3-butadiene they form the expected Diels–Alder adducts.

The latest example of a stable silene was reported in 2002 by Kira's group. This compound **7**, representing a silatriafulvene derivative with an exocyclic Si=C double bond, was synthesized by the sila-Peterson reaction of di-*tert*-butylcyclopropenone with (tris(*tert*-butyldimethylsilyl)silyl)lithium followed by quenching with trimethylchlorosilane (Scheme 5).[16] The unusually high-field-shifted resonance of the doubly bonded Si atom at −71.9 ppm was reasonably explained by the inverted polarity of the Si=C double bond in **7** caused by the significant contribution of the zwitterionic resonance structure **7′** stabilized by the cyclopropenium-type contribution. Despite the theoretical calculations that predicted a preference for the bent form, the crystal structure of **7** determined by X-ray analysis exhibited a nearly planar geometry around the Si=C double bond. The Si=C double bond length was determined to be 1.755(2) Å. Similar to other silenes, the silatriafulvene **7** reacts with methanol at room temperature to form the 1,3-adduct **8** with regioselectivity corresponding to an inverted $Si^{\delta-}{=}C^{\delta+}$ double bond polarity: a methoxy group is bonded to the carbon atom, whereas H is bonded to the silicon atom.

2.1.2. Germenes (>Ge=C<). The first remarkable examples of the stable germenes were reported independently by two research groups, those of Escudié and Berndt, in the same year, 1987. Escudié synthesized dimesityl(fluorenylidene)germene (**9**) by the elimination of LiF from the corresponding precursor (Scheme 6),[17] while Berndt employed the coupling reaction of the cryptocarbene **10** with the stable germylenes **11a**,**b** to form the Ge=C doubly bonded compounds **12a**,**b** (Scheme 7).[18] Afterward, other five new stable germenes **13**–**17** were reported by Escudié's group by utilizing the same synthetic methodology—dehydrofluorination of the corresponding precursors under the action of *tert*-butyllithium (Scheme 8).[19–21]

Scheme 8



A different approach was employed by Tokitoh for the preparation of a new germene, germaketenedithioacetal **18**, by the reaction of the sterically protected diarylgermylene Tbt(Tip)Ge: (Tip = 2,4,6-triisopropylphenyl, Tbt = tris[2,4,6-bis(trimethylsilyl)methyl]phenyl) with CS_2 at room temperature in THF (Scheme 9).[22] The planar Ge=C double bond in **18** exhibited a double bond length of 1.771(16) Å—the shortest length among all structurally characterized germenes. The longest absorption band at 396 nm in the UV spectrum of **18** was attributed to a $\pi-\pi^*$ transition, responsible for the orange color of the pure germene **18**. Being effectively stabilized by the very bulky Tip and huge Tbt groups, germene **18** was surprisingly inert: it does not react with methanol, even in refluxing benzene.

---

[16] Sakamoto, K.; Ogasawara, J.; Kon, Y.; Sunagawa, T.; Kabuto, C.; Kira, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1402.

[17] Couret, C.; Escudié, J.; Satgé, J.; Lazraq, M. *J. Am. Chem. Soc.* **1987**, *109*, 4411.

[18] (a) Meyer, H.; Baum, G.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *21*, 221. (b) Berndt, A.; Meyer, H.; Baum, G.; Massa, W.; Berger, S. *Pure Appl. Chem.* **1987**, *59*, 1011.

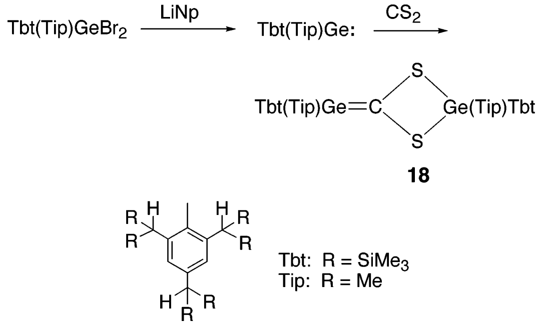
[19] Couret, C.; Escudié, J.; Delpon-Lacaze, G.; Satgé, J. *Organometallics* **1992**, *11*, 3176.

[20] Lazraq, M.; Couret, C.; Escudié, J.; Satgé, J.; Soufiaoui, M. *Polyhedron* **1991**, *10*, 1153.

[21] Anselme, G.; Escudié, J.; Couret, C.; Satgé, J. *J. Organomet. Chem.* **1991**, *403*, 93.

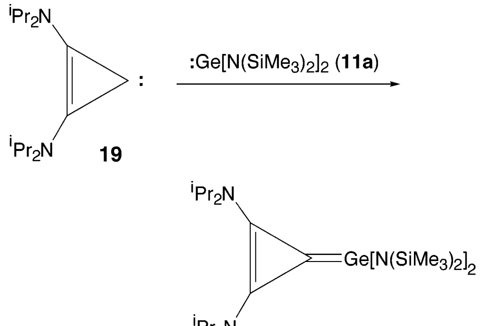
[22] Tokitoh, N.; Kishikawa, K.; Okazaki, R. *J. Chem. Soc., Chem. Commun.* **1995**, 1425.

Scheme 9



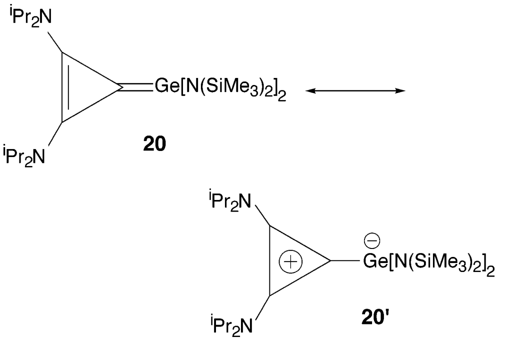
Recently, Schumann reported the coupling reaction of Lappert's stable bis(amino)germylene $[(Me_3Si)_2N]_2Ge$: (**11a**) with the transient cyclic carbene **19**, which resulted in the formation of the compound **20**, having three-coordinated Ge and C atoms (Scheme 10).[23] However, having formally doubly bonded Ge and C atoms, **20** actually exhibited the properties of the ylide structure **20′**, corresponding to a carbene–germylene complex, rather than the genuine germene structure **20** (Scheme 11). This was demonstrated by the long Ge–C bond length of 2.085(3) Å, which was longer than that expected for the Ge=C double bond and even longer than the normal Ge–C single bond, and also appreciable pyramidalization of the Ge atom. Moreover, the ^{13}C NMR resonances of the three-membered-ring carbon atoms of **20** (+145.45 and +145.62 ppm) fall in the range characteristic for cyclopropenylium compounds.

Scheme 10



20

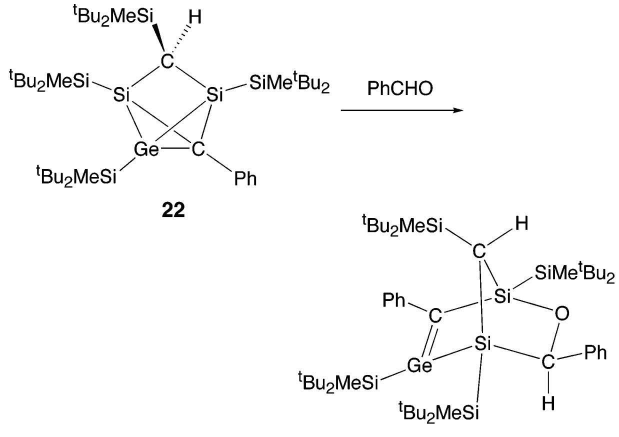
Scheme 11



The chemistry of all of the above-mentioned germenes was very carefully described in several review articles written by Escudié and co-workers in the past decade,[6e,i,m] and it was quite recently reconsidered in the latest review by Tokitoh;[6s] therefore, we feel no need to repeat their considerations in this paper. We will briefly comment only on the most recently reported compound with a Ge=C double bond (stable germene), which was synthesized and structurally characterized and whose chemistry was not covered in the preceding reviews.

This last stable germene **21**, reported by Sekiguchi's group in 2002, was obtained in a most surprising and unpredictable way compared with all other germenes—by the reaction of the tricyclic cage compound **22** with benzaldehyde in benzene at room temperature (Scheme 12).[24] Evidently, the formation of the final germene **21** may be better interpreted as the result of the initial isomerization of the tricyclic cage compound to a monocyclic cyclopentadiene-type compound, followed by the [4 + 2] cycloaddition of benzaldehyde across the 1,3-diene system Si=Ge–C=Si to form the germene **21** as a final Diels–Alder adduct. With a Ge=C double bond being incorporated into a norbornene skeleton, the compound **21** represents the first cyclic germene. The germene **21** exhibited the longest Ge=C double bond known to date: 1.859(3) Å (Figure 1).[24]

Scheme 12



21

2.1.3. Stannenes (>Sn=C<). The first stable stannene **23** was reported by Berndt in 1987, and the synthetic route for its preparation was the same as that for Berndt's stable germene: the coupling reaction of the cryptocarbene **10** with the stannylene $[(Me_3Si)_2CH]_2$-Sn: (Scheme 13).[25] After this first report, three other representatives of stable stannenes were synthesized in Berndt's,[18b] Escudié's,[26] and Weidenbruch's[27] groups—**24**–**26**, respectively (Scheme 13), of which only **26** was structurally characterized. Thus, to date the crystallographic data on the Sn=C double bond length are limited to only two examples: 2.025(4) Å for **23** and 2.032(5) Å for **26**, which corresponds to ca. 6% shortening compared with a normal Sn–C single bond. The

---

[23] Schumann, H.; Glanz, M.; Girgsdies, F.; Ekkehardt Hahn, F.; Tamm, M.; Grzegorzewski, A. *Angew. Chem., Int. Ed.* **1997**, *36*, 2232.

[24] Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2002**, *124*, 9962.

[25] Meyer, H.; Baum, G.; Massa, W.; Berger, S.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 546.

[26] Anselme, G.; Ranaivonjatovo, H.; Escudié, J.; Couret, C.; Satgé, J. *Organometallics* **1992**, *11*, 2748.

[27] Weidenbruch, M.; Kilian, H.; Stürmann, M.; Pohl, S.; Saak, W.; Marsmann, H.; Steiner, D.; Berndt, A. *J. Organomet. Chem.* **1997**, *530*, 255.

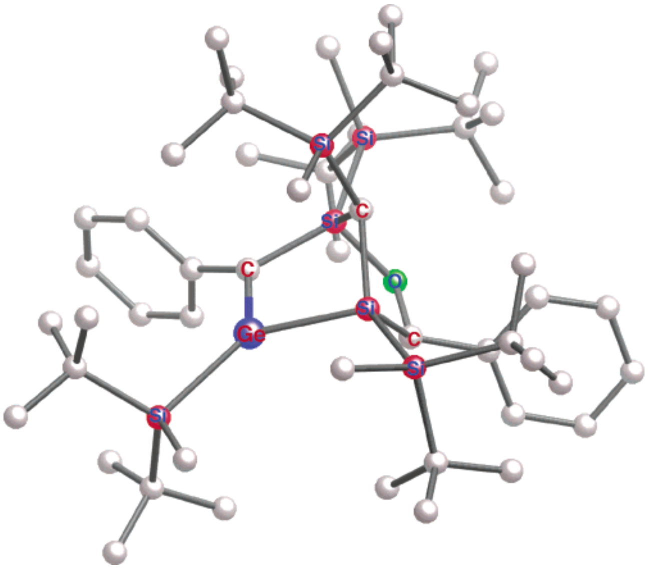
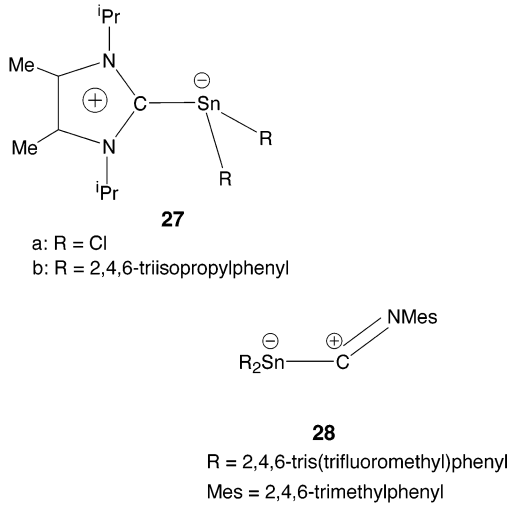


Figure 1. Molecular structure of germene **21**.

other three examples of the three-coordinate tin compounds **27a**,**b** and **28** (Chart 1)[28,29] should be better considered as zwitterionic Lewis acid–Lewis base adducts rather than the compounds with real Sn═C double bonds, on the basis of their specific geometries (very large Sn–C bond separation of 2.290(5) Å for **27a**,[28a] 2.379(5) Å for **27b**,[28b] and 2.397(3) Å for **28**,[29] which are markedly longer than the corresponding Sn–C single bond lengths and significantly pyramidalized tin atoms). The chemistry of stable stannenes (a total of four) was thoroughly discussed in recent reviews by Baines,[6g] Escudié,[6i] and Tokitoh,[6s] to which we direct our readers. No other examples of stable stannenes have been reported since then.

Chart 1



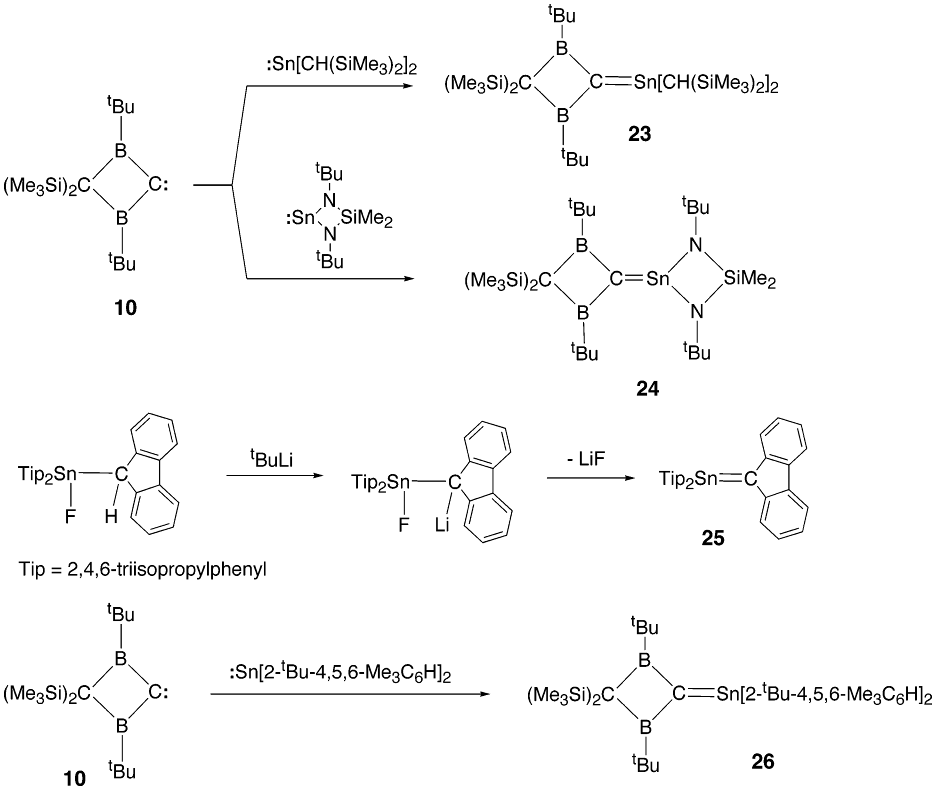
27
a: R = Cl
b: R = 2,4,6-triisopropylphenyl

28
R = 2,4,6-tris(trifluoromethyl)phenyl
Mes = 2,4,6-trimethylphenyl

2.2. Heteronuclear Heavy Alkenes >E═E′< (E, E′ = Heavier Group 14 Elements).

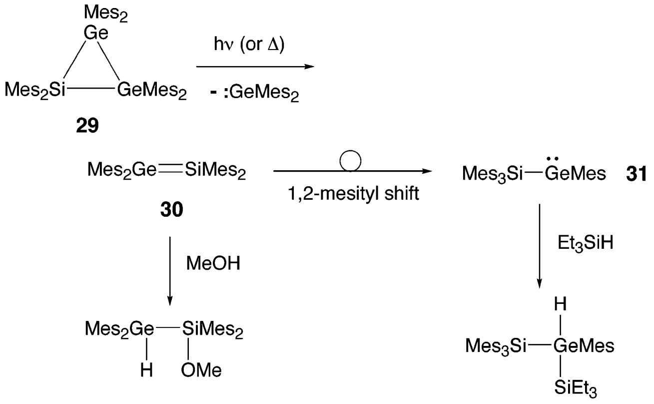
2.2.1. Germasilenes (>Ge═Si<). The formation of a double bond between group 14 elements heavier than carbon was initially attempted for their first representatives, that is, silicon and germanium. Compounds of the type >Ge═Si< were believed to be the most stable (the π-bond energy of the Ge═Si bond was calculated to be almost the same as that of the Si═Si double bond: ca. 26 kcal/mol)[8] and consequently the most synthetically accessible of all of the possible combinations of heavier group 14 elements. Therefore, the stable germasilenes have appeared to be rather attractive synthetic targets for several research groups. The first report in the germasilene story came from Baines' group in 1991:

Scheme 13



10
23
24
25
Tip = 2,4,6-triisopropylphenyl
10
26

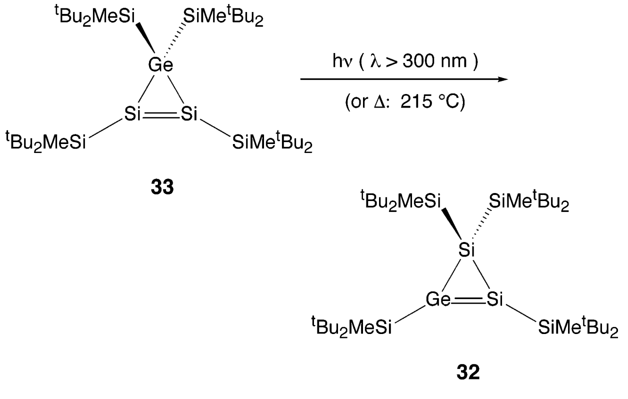
Scheme 14



they photolyzed the highly strained three-membered-ring compound hexamesitylsiladigermirane (**29**), to produce (after a cycloelimination reaction) tetramesitylgermasilene (**30**) together with dimesitylgermylene (Scheme 14).[30] Tetramesitylgermasilene, the formation of which was demonstrated by trapping reactions with methanol, was unstable under the reaction conditions and upon warming to room temperature quickly underwent isomerization to mesityl(trimesitylsilyl)germylene (**31**), which was subsequently trapped with Et_3SiH. Such an isomerization from the trans-bent germasilene $H_2Ge{=}SiH_2$ to the singlet silylgermylene H_3SiGeH was calculated to be thermodynamically favorable by 3.2 kcal/mol.[31]

Nevertheless, the tendency of such a 1,2-migration of a substituent from the Ge to the Si atom was suppressed when the first genuinely stable germasilene was reported by Sekiguchi in 2000. This compound, the three-membered unsaturated 2-disilagermirene **32**, with an Ge=Si double bond, was synthesized by isomerization (either photochemical or thermal) of 1-disilagermirene **33** with an Si=Si double bond by the formal 1,2-migration of a silyl substituent (Scheme 15).[32]

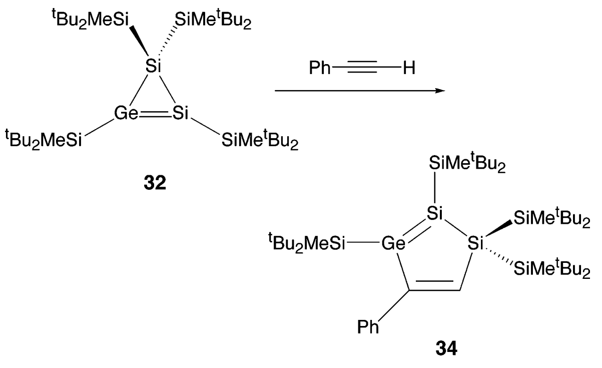
Scheme 15



The 2-disilagermirene **32** exhibited an extraordinary stability: it was absolutely stable under photolytic conditions (>300 nm, several days) and showed no sign of any decomposition under extremely intense thermolysis conditions (215 °C, 1 h).[32] Such an amazing stability for **32** is particular striking in the light of the high ring strain characteristic of cyclopropene derivatives. Definitely, the most important stabilizing factor should be ascribed to the influence of the electropositive silyl substituents, which, according to the theoretical calculations, strengthen the double bond and simultaneously significantly decrease the inherent strain of the small ring.[33] In MO terms, one can discuss the appreciable degree of π- and σ^*-orbital mixing: that is, the attractive interaction of the high-lying π-orbitals of the endocyclic Ge=Si double bond and low-lying σ^*-orbitals of the exocyclic Si−Si single bonds.[6u] The theoretical calculations showed that 2-disilagermirene (H_3Si-substituted model) is more stable than the original isomeric 1-disilagermirene (H_3Si-substituted model) by 2.3 kcal/mol, which was in fairly good agreement with the experimentally estimated value of ca. 3 kcal/mol.[32] As is typical for other compounds containing a doubly bonded silicon atom, germasilene exhibited a downfield-shifted resonance of an sp^2-Si atom at +100.7 ppm. The structure of germasilene was unambiguously proved by X-ray analysis to show the unsaturated three-membered-ring skeleton incorporating an Ge=Si double bond in the ring. The insurmountable disorder problems associated with the refinement of the positions of doubly bonded Si and Ge atoms prevented the exact determination of the Ge=Si double bond length, although the geometry of this bond was determined with sufficient accuracy as trans-bent, with bending angles of 39°.[32] Calculations on the model H_3Si-substituted 2-disilagermirene predicted an Ge=Si double bond length of 2.178 Å, close to that previously calculated for the parent trans-bent germasilene $H_2Ge{=}SiH_2$ of 2.184 Å.[34]

The reactivity of the germasilene **32** was rather interesting, in particular its reaction with phenylacetylene providing an easy and effective access to the new stable, five-membered, germasilene **34**. Such a reaction, which proceeds through the initial [2 + 2] cycloaddition of phenylacetylene across the Ge=Si double bond, after several isomerization steps finally produced a cyclopentadiene-type compound, silole **34** with Ge=Si and C=C double bonds: the first metalladiene of the type E=E′C=C (E, E′ = heavier group 14 elements) (Scheme

Scheme 16



---

(28) (a) Kuhn, N.; Kratz, T.; Bläser, D., Boese, R. *Chem. Ber.* **1995**, *128*, 245. (b) Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S. *J. Chem. Soc., Chem. Commun.* **1995**, 1157.

(29) Grützmacher, H.; Freitag, S.; Herbst-Irmer, R.; Sheldrick, G. S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 437.

(30) (a) Baines, K. M.; Cooke, J. A. *Organometallics* **1991**, *10*, 3419. (b) Baines, K. M.; Cooke, J. A. *Organometallics* **1992**, *11*, 3487.

(31) Grev, R. S.; Schaefer, H. F., III. *Organometallics* **1992**, *11*, 3489.

(32) (a) Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2000**, *122*, 9034. (b) Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A. *Phosphorus, Sulfur Silicon Relat. Elem.* **2001**, *168*, 169. (c) Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A. *J. Organomet. Chem.* **2003**, *685*, 168.

(33) (a) Nagase, S. *Pure Appl. Chem.* **1993**, *65*, 675. (b) Nagase, S. *Acc. Chem. Res.* **1995**, *28*, 469. (c) Nagase, S.; Kobayashi, K.; Nagashima, M. *J. Chem. Soc., Chem. Commun.* **1992**, 1302.

(34) Grev, R. S.; Schaefer, H. F., III; Baines, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 9458.

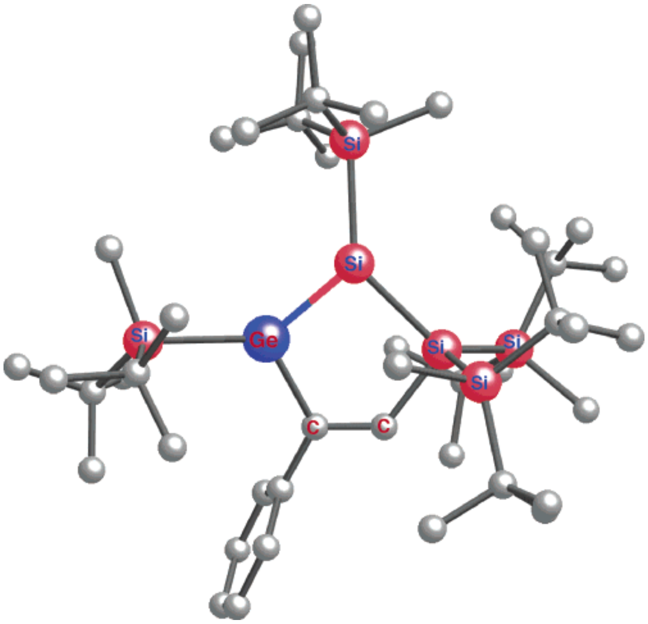


Figure 2. Molecular structure of silole **34**.

16).[35] This silole, isolated quantitatively as a bright orange crystalline material, exhibited all the features of heavy alkenes. Thus, the resonance of the doubly bonded Si atom is expectedly shifted downfield, appearing at +124.2 ppm. The crystal structure of the silole **34** was determined by X-ray diffraction analysis to show a planar five-membered-ring skeleton with two double bonds incorporated, Ge═Si and C═C (Figure 2). The Ge═Si double bond was trans-bent (bending angles of 38.6°) with a bond length, which was determined for the first time, of 2.250(1) Å,[35] this being the first structurally authenticated heteronuclear double bond between the heavier group 14 elements. This value was in excellent agreement with the latest results of DFT calculations on the parent trans-bent $H_2Ge{=}SiH_2$ (2.24 Å).[36] The Ge═Si double bond shortening compared with the Si−Ge single bond in the same molecule was ca. 7%.

The structure of the silole **34** is of special interest, since it represents the most electronically perturbed cyclopentadiene system incorporating the heavier group 14 elements (Si, Ge) in the most important diene fragment of the molecule—in contrast to all other examples of the silole and germole derivatives,[37] which have an Si (or Ge) atom in a saturated position, leaving the diene fragment C═CC═C mainly unperturbed. Such involvement of the heavy alkene fragment in the 1,3-diene system gave a unique opportunity to estimate the degree of conjugation between the energetically and geometrically very different C═C and Ge═Si double bonds. Surprisingly, the physicochemical characteristics of the silole **34** do not show any noticeable conjugation between these double bonds, which was clearly demonstrated by UV and X-ray crystal data. For example, the UV spectrum of the silole **34**[35] showed no bathochromic shift compared with that of 2-disilagermirene **32**,[32a] which has an isolated Ge═Si double bond, whereas X-ray analysis of **34** did not exhibit the shortening of the Ge−C single bond and the lengthening of the Ge═Si and C═C double bonds expected for a 1,3-conjugated system.[35] Indeed, the conjugation of the two π-orbitals of the Ge═Si and C═C double bonds is not effective because of the large energy and size differences between these MOs. In contrast, in the case of compounds containing two identical double bonds between heavier group 14 elements the conjugation is much more effective: for the 2,3-digerma-1,3-butadiene $H_2C{=}GeHGeH{=}CH_2$ the degree of conjugation was calculated as half of that of the parent 1,3-butadiene $H_2C{=}CHCH{=}CH_2$.[38] This conclusion was experimentally corroborated with the recent synthesis of tetrasila- and tetragerma-1,3-butadienes, $R_2Si{=}Si(R)Si(R){=}SiR_2$[39] and $R_2Ge{=}Ge(R)\text{-}Ge(R){=}GeR_2$[40] (R = (2,4,6-triisopropyl)phenyl), reported by Weidenbruch to be conjugated systems.

The reactivity of the silole **34** was in complete accord with its nonconjugated nature: the reactions of **34** with phenylacetylene[35] and benzaldehyde[41] or the oxidation reaction[6u] proceeded exclusively as [2 + 2] cycloaddition across the Ge═Si double bond (Scheme 17) instead of the typical route for other silole or germole derivatives of [4 + 2] cycloaddition pathways to form the corresponding cyclic and bicyclic adducts **35**−**37**.

The most striking example of the silole **34** reactivity represents its thermolysis, which amazingly produced the isomeric cage compound of a new type, **22**, having a tricyclo[2.1.0.0^{2,5}]pentane skeleton (Scheme 18).[24] This unusual compound **22** has an extremely long Ge−C bridging bond (2.242(3) Å), which greatly exceeded the normal value by 15%, an extremely short Si−Si nonbonding distance (2.558(1) Å) that was longer than the typical values of an Si−Si bond by only 9%, and an "umbrella" (inverted tetrahedral)[42] configuration of the bridgehead Ge atom.

The last two examples of stable germasilenes were reported by Sekiguchi's group, both being synthesized using very effective coupling reagents—the dilithiosilane $(^tBu_2MeSi)_2SiLi_2$ (**38**)[43,44] and dilithiogermane $(^tBu_2MeSi)_2GeLi_2$ (**39**)[45] derivatives. Thus, germasilene with mesityl groups on the Ge atom and $^tBu_2MeSi$ groups on the Si atom **40** was prepared by the coupling reaction of the dilithiosilane $(^tBu_2MeSi)_2SiLi_2$ (**38**) and dimesityldichlorogermane, Mes_2GeCl_2 (Scheme 19).[44] The ^{29}Si NMR resonance of the doubly bonded Si atom appeared at an unusually high field, +25.1 ppm, which was rationalized in terms of $Ge^{\delta+}{=}Si^{\delta-}$ double bond polarity caused by the different environments: electron-donating silyl substituents on the Si atom and electron-with-

---

[35] (a) Lee, V. Ya.; Ichinohe, M.; Sekigichi, A. *J. Am. Chem. Soc.* **2000**, *122*, 12604. (b) Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A. *J. Organomet. Chem.* **2001**, *636*, 41.

[36] Chen, W.-C.; Su, M.-D.; Chu, S.-Y. *Organometallics* **2001**, *20*, 564.

[37] Reviews on metalloles chemistry: (a) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215. (b) Colomer, E.; Corriu, R. J. P.; Lheureux, M. *Chem. Rev.* **1990**, *90*, 265. (c) Dubac, J.; Guérin, C.; Meunier, P. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Part 3, Chapter 34.

[38] Jouany, C.; Mathieu, S.; Chaubon-Deredempt, M.-A.; Trinquier, G. *J. Am. Chem. Soc.* **1994**, *116*, 3973.

[39] Weidenbruch, M.; Willms, S.; Saak, W.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2503.

[40] Schäfer, H.; Saak, W.; Weidenbruch, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3703.

[41] Lee, V. Ya.; Sekiguchi, A. Unpublished data.

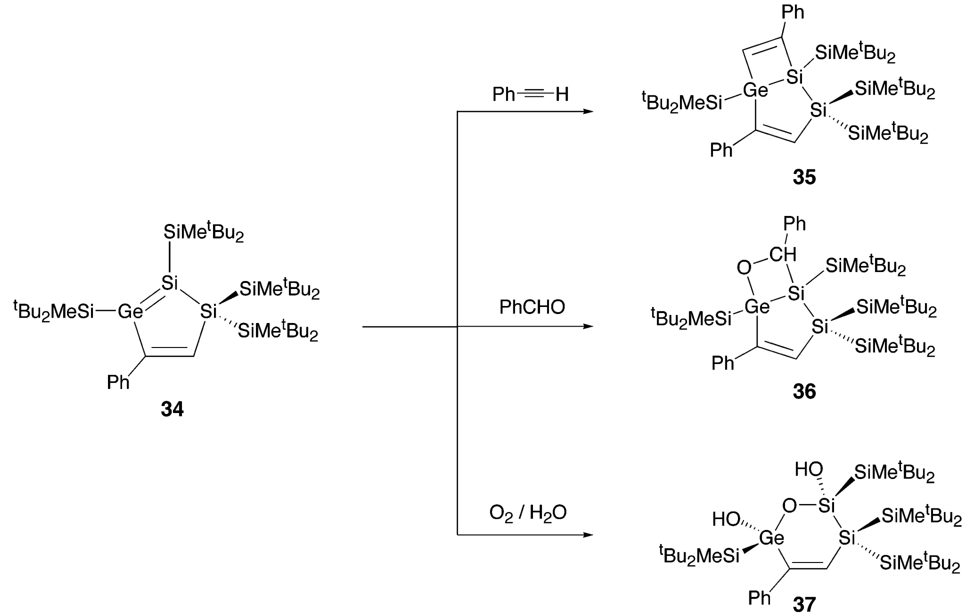
[42] Review on the inverted tetrahedral geometries at the carbon atom: Wiberg, K. B. *Acc. Chem. Res.* **1984**, *17*, 379.

[43] Sekiguchi, A.; Ichinohe, M.; Yamaguchi, S. *J. Am. Chem. Soc.* **1999**, *121*, 10231.

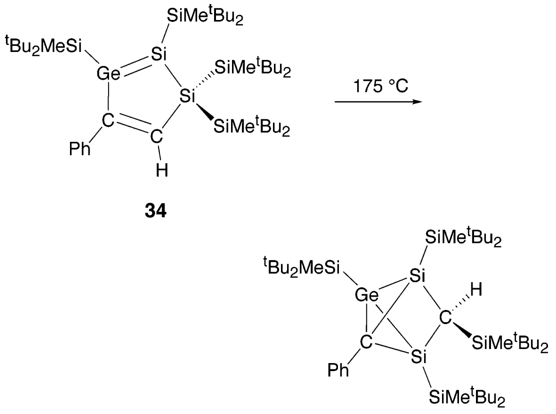
[44] Ichinohe, M.; Arai, Y.; Sekiguchi, A.; Takagi, N.; Nagase, S. *Organometallics* **2001**, *20*, 4141.

[45] Sekiguchi, A.; Izumi, R.; Ihara, S.; Ichinohe, M.; Lee, V. Ya. *Angew. Chem., Int. Ed.* **2002**, *41*, 1598.

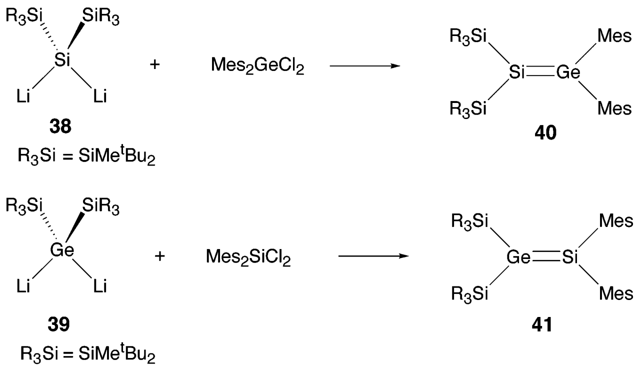
Scheme 17



Scheme 18



Scheme 19



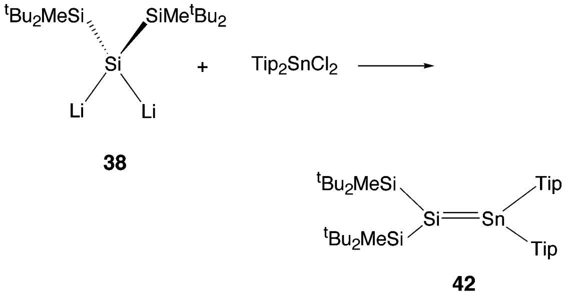
Mes = 2,4,6-trimethylphenyl

drawing aryl groups on the Ge atom. The regioselectivity of methanol addition to germasilene **40** corresponds well to such a polarity of the Ge=Si double bond: the methoxy group was bonded to the Ge atom, whereas the H atom was bonded to the Si atom.[44]

The germasilene **41** with an opposite arrangement of substituents, ^{t}Bu$_2$MeSi groups on the Ge atom and mesityl groups on the Si atom, was prepared by a coupling reaction of the dilithiogermane (^{t}Bu$_2$MeSi)$_2$GeLi$_2$ (**39**) and dimesityldichlorosilane Mes$_2$SiCl$_2$ (Scheme 19).[45] In this latter case of **41** the Ge=Si double-bond polarity meets the normal expectations, Ge$^{\delta-}$=Si$^{\delta+}$, in contrast to the above case of germasilene **40**, due to the opposite influence of the substituents. As a result, the doubly bonded Si atom of **41** is greatly deshielded (+146.9 ppm) compared with that of **40** (+25.1 ppm).

2.2.2. Silastannenes (>Si=Sn<). The silastannenes, both stable and transient, were an elusive species until 2002, when the first (and still the only known) stable representative was reported by Sekiguchi's group. The synthesis of this compound was achieved by the coupling reaction of the aforementioned dilithiosilane (^{t}Bu$_2$MeSi)$_2$SiLi$_2$ (**38**)[44] with dichlorostannane Tip$_2$SnCl$_2$ in THF (Scheme 20).[46]

Scheme 20



Tip = 2,4,6-triisopropylphenyl

The target silastannene (^{t}Bu$_2$MeSi)$_2$Si=SnTip$_2$ (**42**), which was obtained as a deep violet crystalline compound, is expectedly air- and moisture-sensitive but quite thermally stable. The ^{119}Sn NMR spectrum showed the downfield-shifted resonance of the doubly bonded Sn atom at +516.7 ppm, agreeing well with the expected range for sp^2 Sn atoms of above +400 ppm.[6g] Surprisingly, the sp^2 Si atom in **42** resonated at an unusually high field, +27.4 ppm, in sharp contrast to the vast majority of other doubly bonded Si atoms, the deshielding of which is now commonly recognized and accepted. Again, similar to the above cases of silenes and germasilenes, such a phenomenon should be definitely

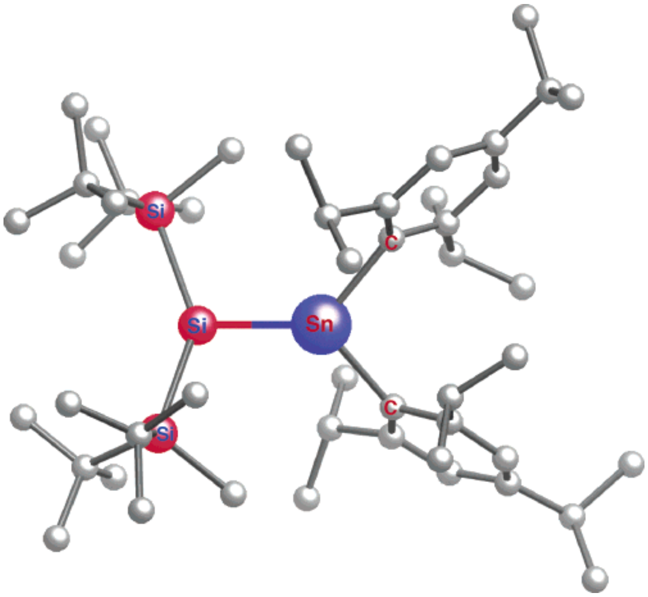
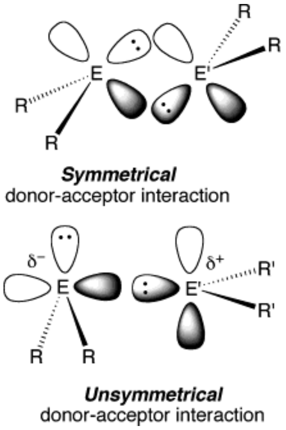


Figure 3. Molecular structure of silastannene **42**.

ascribed to the inverted polarity $Si^{\delta+}$═$Sn^{\delta-}$ of the Si═Sn double bond due to the different environments around it: electron-donating silyl substituents at the sp^2 Si atom and electron-withdrawing aryl groups at the sp^2 Sn atom cause appreciable double-bond polarization. Another striking point resulting from such bond polarization is the unusual geometry around the double bond of **42**: in contrast to expectations, the sp^2 Sn atom is nearly planar, whereas the sp^2 Si atom is significantly pyramidalized (Figure 3).

In the framework of commonly recognized theory considering heavy dimetallenes as the dimers of the corresponding divalent species formed by the donor−acceptor interaction,[3b−e] one should recognize the silastannene **42** as representing a new structural motif involving an unsymmetrical donor−acceptor interaction resulting in the pyramidalization of the negatively polarized Si moiety and planarization of the positively polarized Sn moiety (Chart 2).[46]

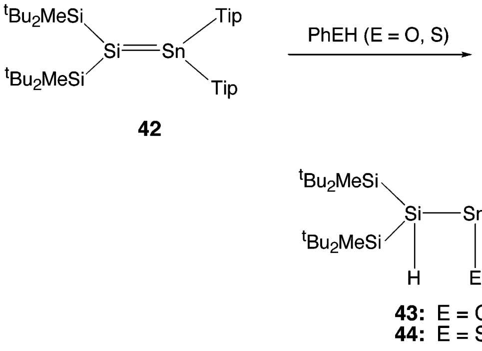
Chart 2



Such amazing results found further support from the theoretical calculations, which showed the high polarization of the Si═Sn double bond of the model compound $(H_3Si)_2Si$═$SnPh_2$ at the B3LYP/Dzd level (atomic charge values): Si (−0.536), Sn (+1.400).[46] In **42** the Si═Sn double bond length was determined for the first time as 2.4188(14) Å, which was just between the typical values of Si═Si (2.138−2.289 Å)[6h] and Sn═Sn (2.590−3.087 Å)[6k] double bond lengths. The shortening of the Si═Sn double bond compared with the Si−Sn single bond (average value 2.60 Å) was ca. 7%. The degree of such shortening is smaller than in the case of silenes (Si═C vs Si−C), which is not surprising in view of the decreasing difference between the double and single bond lengths descending group 14. The Si═Sn double bond is not only trans-bent but also twisted with a twisting angle of 34.6°.[46]

The Si═Sn double bond of **42** was surprisingly rather strong and did not dissociate in solution to silylene and stannylene, whereas all known distannenes do dissociate, behaving and reacting as stannylenes but not distannene species.[6s] The chemical reactivity of silastannene **42** in solution undoubtedly corresponds to the reactivity of the Si═Sn double bond: for example, phenol (or thiophenol) smoothly reacted with silastannene to form the corresponding 1,2-adducts **43** and **44** regioselectively according to the above-mentioned polarity of the double bond—the phenoxy (or mercapto) group being attached to a positively polarized Sn atom (Scheme 21).[46]

Scheme 21



Tip = 2,4,6-triisopropylphenyl

2.2.3. Germastannenes (>Ge═Sn<). The last class of the synthetically accessible heteronuclear dimetallenes of group 14 elements, germastannenes, is the youngest among all of the stable heavy alkenes. The first four representatives were reported in 2003 by the experimental efforts of the research groups of Weidenbruch and Sekiguchi. The increasing tendency of the double bond between the heavier group 14 elements to dissociate into the corresponding divalent species in solution on going from Si to Pb is well-known.[6k] The apparent reason for such a tendency is the increasing lone-pair character of the elements forming the double bond, which causes pyramidalization around the doubly bonded elements, elongation of the double bond, and consequently, a decrease in its strength. For this reason, one can expect that Ge and Sn would form the weakest double bond among all known heteronuclear heavy alkenes with a high tendency to dissociate into germylene and stannylene. The experimental results, however, showed that the behavior mode of germastannenes (double bond vs divalent species) is totally controlled by their structure: germastannenes reported by Escudié's (vide infra) and Weidenbruch's groups are

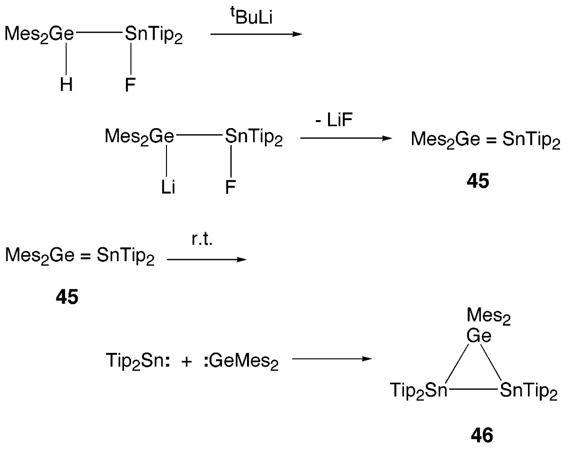
---

[46] Sekiguchi, A.; Izumi, R.; Lee, V. Ya.; Ichinohe, M. *J. Am. Chem. Soc.* **2002**, *124*, 14822.

indeed dissociated in solution, whereas all three germastannenes prepared in Sekiguchi's group were indefinitely stable, in both the solid state and solution.

The first report of a double bond between the Ge and Sn atoms appeared in 1996. $Mes_2Ge{=}SnTip_2$ (**45**) was prepared in Escudié's group by the dehydrofluorination of the corresponding precursor (Scheme 22).[47] However,

Scheme 22

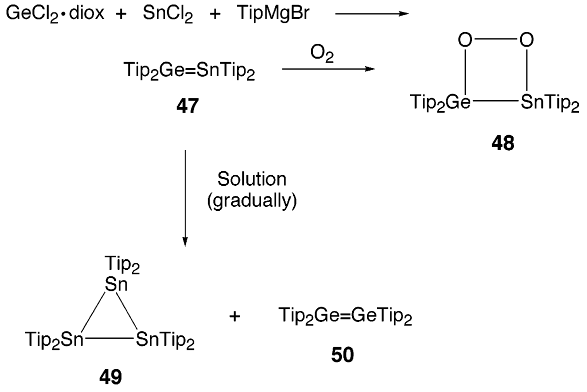


Tip = 2,4,6-triisopropylphenyl

this germastannene **45** was stable only at temperatures below −20 °C, and at room temperature it underwent unavoidable dissociation into Mes_2Ge: and Tip_2Sn: to form germadistannirane as the final isolable product **46** (Scheme 22).

The replacement of the Mes groups on Ge by the more bulky Tip groups allowed isolation of the first really stable germastannene by Weidenbruch in early 2003. $Tip_2Ge{=}SnTip_2$ (**47**) was prepared and isolated as red crystals in a surprisingly simple way by the one-pot reaction of $GeCl_2$−dioxane complex, $SnCl_2$, and TipMgBr performed at low temperature (Scheme 23).[48] The germastannene **47** was structurally characterized to show the Ge═Sn double bond length for the first time as 2.5065(5) Å, which was just 4.5% shorter than the average value for the Ge−Sn single bond. As expected, the Ge═Sn double bond was trans-bent, and the pyramidalization at the Sn atom (43.3°) was greater than that at the Ge atom (30.2°). The ^{119}Sn NMR spectrum of **47** displayed a downfield resonance at +268 ppm, which was ascribed to a doubly bonded Sn atom.

Scheme 23

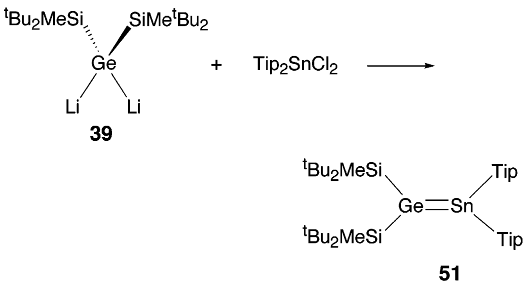


Tip = 2,4,6-triisopropylphenyl

The germastannene **47** was easily oxidized with molecular oxygen to produce the anticipated product − germastannadioxetane **48** (Scheme 23).[48] Being stable in the crystalline form, **47** slowly dissociated in solution to form the known cyclotristannane **49**[49] and digermene **50**[50] as the final products (Scheme 23). Therefore, one can conclude that the Ge═Sn double bond surrounded by the four Tip groups is sufficiently stable to survive in the solid state but not stable enough in solution to prevent dissociation into divalent species.[48]

However, further modification of germastannene by the introduction of electropositive silyl substituents on the Ge atom instead of Tip groups allowed the isolation of a compound having a Ge═Sn double bond that was stable both in the solid state and in solution. This completely stable germastannene, **51**, was prepared in Sekiguchi's group in the same year, 2003, by the coupling reaction of dilithiogermane $(^tBu_2MeSi)_2GeLi_2$ (**39**)[46] and Tip_2SnCl_2 and was isolated as a violet solid compound (Scheme 24).[51]

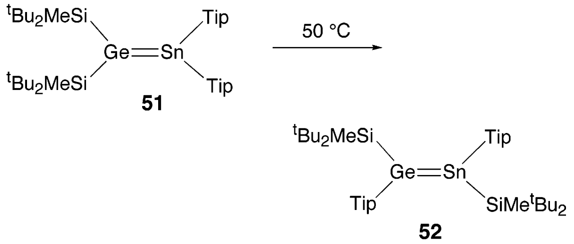
Scheme 24



Tip = 2,4,6-triisopropylphenyl

This new germastannene $(^tBu_2MeSi)_2Ge{=}SnTip_2$ (**51**) has a typically deshielded resonance of the sp^2 Sn atom at +525.1 ppm and long-wavelength absorption band at 551 nm corresponding to a $\pi-\pi^*$ electronic transition.

Scheme 25



Tip = 2,4,6-triisopropylphenyl

The most striking feature of this compound was its easy isomerization to the new, symmetrically substituted, germastannene *trans*-$(^tBu_2MeSi)TipGe{=}Sn(SiMe^tBu_2)$-Tip (**52**) under gentle heating at 50 °C of the solution of **51** (Scheme 25).[51]

---

[47] Chaubon, M.-A.; Escudié, J.; Ranaivonjatovo, H.; Satgé, J. *J. Chem. Soc., Chem. Commun.* **1996**, 2621.

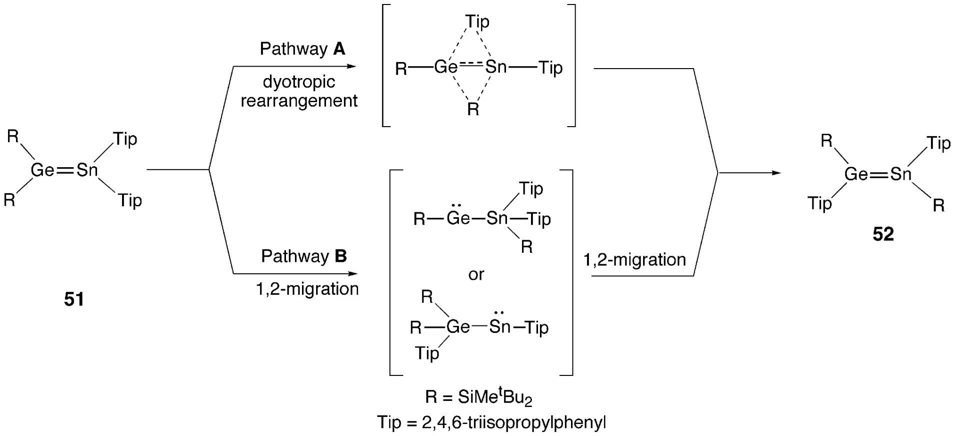
[48] Schäfer, A.; Saak, W.; Weidenbruch, M. *Organometallics* **2003**, *22*, 215.

[49] Masamune, S.; Sita, L. R. *J. Am. Chem. Soc.* **1985**, *107*, 6390.

[50] Schäfer, H.; Saak, W.; Weidenbruch, M. *Organometallics* **1999**, *18*, 3159.

[51] Sekiguchi, A.; Izumi, R.; Lee, V. Ya.; Ichinohe, M. *Organometallics* **2003**, *22*, 1483.

Scheme 26



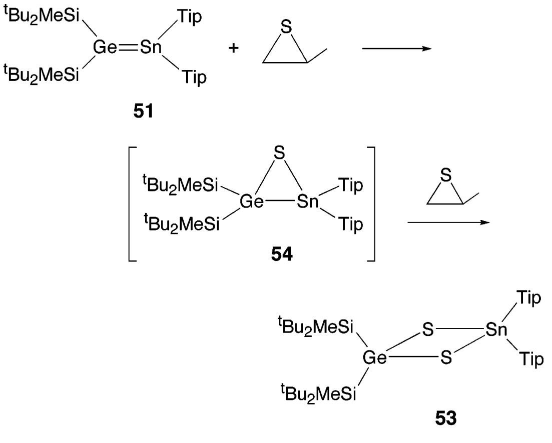
R = SiMe^{t}Bu$_2$
Tip = 2,4,6-triisopropylphenyl

This new isomeric germastannene **52**, isolated as red crystals, exhibited a ^{119}Sn NMR resonance of the sp^2 Sn atom at higher field (+373.4 ppm) compared to that of the original germastannene **51** (+525.1 ppm). This was predictable because of the different environments around the doubly bonded Sn atom in both **51** and **52**: two electron-withdrawing groups in **51** vs one electron-withdrawing and one electron-donating group in **52**. The structure of **52** was unambiguously confirmed by X-ray diffraction analysis, although the symmetrical vicinity of the Ge═Sn double bond causes unavoidable disorder problems, which did not allow the precise determination of the Ge═Sn double bond length. Similar to the above case of Weidenbruch's germastannene,[48] the Ge═Sn double bond of **52** was also trans-bent with bending angles around both Ge and Sn atoms of 28°.[51]

One may imagine the possible mechanism of such an isomerization as either a concerted one involving the dyotropic 1,2-migration of silyl and aryl groups from Ge to Sn and from Sn to Ge atoms (pathway A)[52] or a stepwise one implying the initial 1,2-migration of silyl (or aryl) group to form stannylgermylene (or germylstannylene) intermediates followed by the subsequent 1,2-migration of the aryl (or silyl) group (pathway B)[52,53] (Scheme 26).[51] The activation parameters determined for such an isomerization were more consistent with a concerted rather than a stepwise mechanism: the relatively low value of $\Delta H^{\ddagger}$ (22 kcal mol^{-1}) and the negative value of $\Delta S^{\ddagger}$ (-12 cal K^{-1} mol^{-1}) give evidence for a more ordered and rigid transition state lacking a high degree of freedom typical of the linear intermediates in pathway B.[51] An additional support for such a conclusion is provided by the stereospecificity of isomerization leading exclusively to the *E* isomer of **52**, whereas the intermediate germylene (or stannylene) species are not expected to provide such stereospecificity. Moreover, there was no evidence for the trapping products when isomerization was carried out in the presence of Et$_3$SiH, an effective trapping reagent for both germylenes and stannylenes.

As was mentioned above, both germastannenes **51** and **52** are indefinitely stable in solution at room temperature, showing no signs of dissociation to carbene-like species,[51] in sharp contrast to the germastannenes previously reported by Escudié[47] and Weidenbruch.[48] The chemical reactivity of germastannenes **51** and **52** also supports the existence of a genuine double bond between the Ge and Sn atoms. For example, **51** smoothly reacted with propylene sulfide to form the four-membered germastannadithietane **53**, formed through the intermediate formation of germastannathiirane **54** by a [2 + 1] cycloaddition reaction of sulfur across the Ge═Sn double bond, followed by insertion of the second sulfur atom into the Ge−Sn single bond of **54** (Scheme 27).[51]

Scheme 27

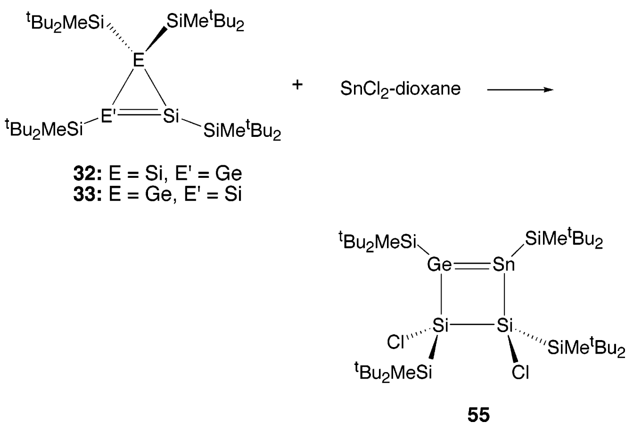


Tip = 2,4,6-triisopropylphenyl

The latest example of a stable germastannene was reported also in the same year, 2003, representing the first compound incorporating a Ge═Sn double bond in a ring—cyclic germastannene **55**.[54] If all of the stable germastannenes described above were prepared in predictable ways by the coupling reactions of lithio derivatives (or Grignard reagents) with dihalogermanes (or -stannanes), the cyclic germastannene **55** was synthesized in a totally different and unexpected method. The addition of SnCl$_2$−dioxane complex to an Si═Si double bond of 1- (or 2-) disilagermirenes **33** (or **32**) resulted in a ring expansion from a three- to a four-membered ring accompanied by the very curious formal transformation of the Si═Si double bond to a Ge═Sn double bond, to form after a sequence of steps the final $^3\Delta$-1,2,3,4-disilagermastannetene **55**, quantitatively isolated as orange crystals (Scheme 28).[54]

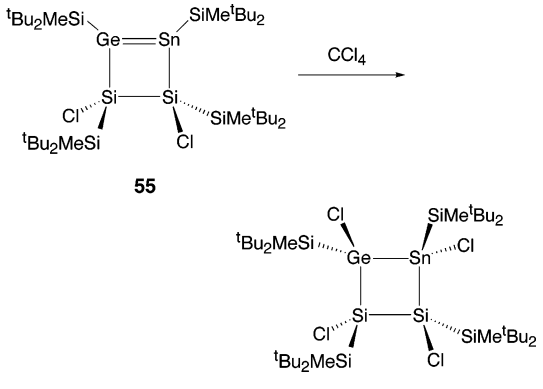
Despite the anticipated weakness of the Ge═Sn π-bond complicated with the inherent strain of the unsaturated four-membered ring, **55** was amazingly stable both in the crystalline state and in solution. Why is **55** so stable, in contrast to the usual expectations? Apparently, we should attribute part of such an abnormal stabilization of **55** as being due to the electropositive

Scheme 28


32: E = Si, E' = Ge
33: E = Ge, E' = Si
55

influence of the σ-donating silyl groups, since one can consider **55** as a tetrasilyl-substituted germastannene. Furthermore, the geometry of the molecule also favors appreciable π(Ge=Sn)$-\sigma^*$(Si$-$Cl) orbital mixing, which lowers the π-energy level and thus stabilizes the HOMO of **55**.[54] The characteristic doubly bonded Sn atom resonance was observed in the expected downfield range at +440 ppm, whereas responsibility for the orange color resulting from the absorption band at 471 nm was attributed to a $\pi-\pi^*$ electronic transition.[54] Again, the symmetry of the molecule **55** caused positional disorder between the doubly bonded Ge and Sn atoms, although the folded unsaturated four-membered-ring structure (folding angle 28°) with a trans-bent Ge=Sn double bond (bending angle 55°) was definitely determined.[54] Although it was quite stable at room temperature, **55** exhibited high reactivity toward addition and cycloaddition reactions across the Ge=Sn double bond. Thus, it can be smoothly chlorinated with CCl_4 to form quantitatively the *trans*,*trans*,*trans*-tetrachloro derivative **56** (Scheme 29).

Scheme 29


55
56

3. Summary and Outlook

As one can see, the great progress that has been made in just the last 4 years has turned the heavy alkenes of the type E=E′ (E, E′ = heavier group 14 elements) from the class of "potentially available" target molecules previously known only by theoretical calculations to the class of experimentally accessible and fully characterizable compounds. Now, after the discovery of the first stable germasilenes, silastannenes, and germastannenes, we can say that heteronuclear heavy alkenes E=E′ do really exist, constituting a new independent class of unsaturated multiply bonded organometallic compounds. Keeping all of the characteristic properties of homonuclear dimetallenes, the heteronuclear analogues undoubtedly represent novel bonding, structural, and chemical motifs, thus featuring new, often unexpected, peculiarities, which greatly distinguish them from their homonuclear counterparts. Being just in its infancy, the chemistry of heteronuclear heavy alkenes of group 14 elements looks to be a very promising field of modern organometallic chemistry, still having many synthetic challenges and problems to be solved. First, this concerns the synthesis of all Pb-containing representatives Pb=E (E = C, Si, Ge, Sn), which are still unknown. An understanding of the nature of the double bond between the different group 14 elements is also a question waiting for a proper explanation, from both experimental and theoretical chemists. The problem of the environment around the E=E′ double bond, which appears now to be of overwhelming importance for the stabilization, geometry, and properties of this double bond, also needs additional efforts to clarify this situation. This also concerns not only experimental achievements but also deeper theoretical considerations, since the latest results have shown the extreme importance of the substitution pattern (for example, electropositive silyl substituents vs electron-withdrawing aryl groups), which seems to govern the total behavior of the double bond. Until now, only calculations on the parent $H_2E{=}E'H_2$ compounds have been available in the literature. Extrapolation of the theoretically calculated results to real chemical systems should be done very carefully, since it has become clear that the differences (energetic, geometric, etc.) between the parent hydrogen-substituted and real molecules are great, which often causes significant discrepancies between the experimental and calculated results. Therefore, ideally the calculated model compounds should approximate the real systems as closely as possible; in such a case one can expect the most effective interplay between theory and experiment.

Acknowledgment. We wish to thank our co-workers Dr. Masaaki Ichinohe, Ms. Yoriko Arai, Ms. Rika Izumi, and Mr. Kazunori Takanashi for their invaluable experimental contribution to this work. We are also grateful for the permanent financial support of the Ministry of Education, Science and Culture of Japan (Nos. 13440185, 14044015, 14078204) and the COE (Center of Excellence) program.

OM040027H

---

(52) Yokelson, H. B.; Maxka, J.; Siegel, D. A.; West, R. *J. Am. Chem. Soc.* **1986**, *108*, 4239.

(53) Aryl(germyl)-substituted germylene and stannylene: Setaka, W.; Sakamoto, K.; Kira, M.; Power, P. P. *Organometallics* **2001**, *20*, 4460.

(54) Lee, V. Ya.; Takanashi, K.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2003**, *125*, 6012.