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Reviews

From a Cyclotrisilane to a Cyclotriplumbane: Low Coordination and Multiple Bonding in Group 14 Chemistry

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In less than three decades the chemistry of low-coordinated compounds of the heavier elements of group 14 has made unforeseen and unprecedented advances. In the meantime not only have homonuclear double bonds been realized between all elements of this group but also the first examples of compounds analogous to the alkynes have been isolated. Similarly, syntheses of molecules containing heteronuclear bonds have been achieved. Analogues of the allenes as well as the first example of a spiropentasiladiene are of particular interest. The present short review covers mainly work done in the author's laboratories together with other relevant reports from the literature. It begins with the synthesis of hexa-*tert*-butylcyclotrisilane, which is cleaved photochemically into a short-lived silylene and a marginally stable disilene; in subsequent reactions both of these species can undergo cycloadditions to furnish a broad palette of mostly novel ring systems. Furthermore, the first molecules with conjugated Si═Si, Ge═C, and Ge═Ge double bonds have been obtained and their reactivities examined. The isolation of the first diplumbenes and a cyclotriplumbane exhibiting an unusual bonding situation as the first homocyclic compound of lead constitute a provisional end of these developments.

Introduction

As little as a few decades ago the molecular chemistry of the main-group elements seemed to be governed by two simple rules: the octet rule and the multiple-bond rule, often simply referred to as the double-bond rule. Many well-known molecules such as SF_6, PF_5, and also the sulfate ion appeared to speak against the octet rule, so that clear octet excesses were tacitly accepted for a long time. However, in 1984 Kutzelnigg[1] summarized the many theoretical arguments that even today continue to support the validity of this rule. Later studies confirmed these assumptions and clearly showed that the often proposed d orbital participation in hypercoordinated compounds is very small and the formal excess over the electron octet is better described by negative hyperconjugation or, more simply, by ionic−covalent resonance.[2,3]

The situation with the multiple-bond rule is different: according to this rule elements of the first eight-element period but not those of the higher periods are able to participate in multiple bonding. Although the origins of this rule are not clear, it probably goes back to papers by Pitzer[4] and Mulliken,[5] who more than 50 years ago attributed the increasing instability of multiple bonds between the heavier main-group elements to the repulsive forces between the fully occupied inner electron shells. The extraordinarily stable N_2 molecule, with its very high bond dissociation energy, and the P_2 molecule, which only exists at high temperature, were chosen as illustrative examples. Whereas in the N_2 molecule there are only repulsive forces of the first shells occupied by two electrons, in the P_2 molecule there are additionally the fully occupied second shells with their eight electrons each. These repulsive forces should become stronger as the element becomes heavier, because the number of fully occupied inner shells increases accordingly.

Thus, it was even more surprising that the first homonuclear bond was realized with tin. Lappert et al. isolated the distannene **1**—which is stable in the solid state—as early as 1976 and characterized it by X-ray crystallography.[6] However, the determined structural parameters, namely a double bond with a length hardly different from that of a single bond and the previously unknown trans bending of the substituents, were hardly understood at that time and were rationalized only after

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(1) Kutzelnigg, W. *Angew. Chem.* **1984**, *96*, 262; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

(2) Reed, A. E.; Weinhold, F. *J. Am. Chem. Soc.* **1986**, *108*, 3586.

(3) (a) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434. (b) Cooper, D. L.; Cunningham, T. P.; Geratt, J.; Karadokov, P. B.; Raimudi, M. *J. Am. Chem. Soc.* **1994**, *116*, 4414.

(4) Pitzer, K. S. *J. Am. Chem. Soc.* **1948**, *70*, 2140.

(5) Mulliken, R. S. *J. Am. Chem. Soc.* **1950**, *72*, 4493.

(6) Goldberg, D. E.; Harris, D. H.; Lappert, M. F.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* **1976**, 261.

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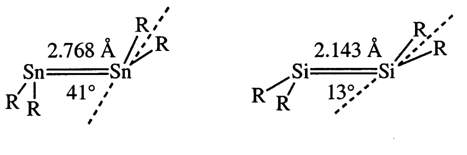
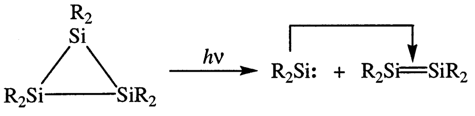
Chart 1



1, R = $CH(SiMe_3)_2$ **2**, R = 2,4,6-$Me_3C_6H_2$

Scheme 1



3 **4** **5**

R = 2,6-$Et_2C_6H_3$

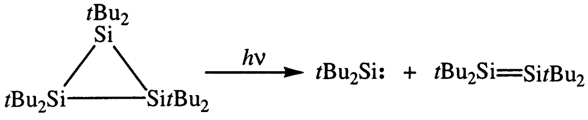
later, comprehensive theoretical calculations[7] together with the plethora of experimental data[8] collected since then.

More in line with contemporary expectations was the first disilene **2**, prepared in 1981 by West, Fink, and Michl,[9] because, in analogy to the alkenes, its double bond was shortened in comparison to the Si−Si single-bond length and the trans bending of the substituents was appreciably less pronounced than in the distannene **1** (Chart 1).

In a personal note Michl[10] has acknowledged the pivotal role that Professor West played in the development of disilene chemistry. However, the time then seemed ripe for homonuclear double bonds in group 14, because shortly thereafter Masamune et al. reported not only on the first examples of the cyclotrisilanes, cyclotrigermanes, and cyclotristannanes but also on their photochemical or thermal ring cleavage to afford disilenes, digermenes, and one, albeit not isolable, distannene.[11−13] The ring opening shown here for the example of the hexaarylcyclotrisilane **3** proceeds through simultaneous cleavage of two Si−Si bonds to afford the silylene **4** and the disilene **5**, whereby **4** dimerizes to further afford **5** (Scheme 1).

I have gladly accepted the kind invitation from the Editor of *Organometallics* to describe our progress in the field of low-coordinated and multiply bonded molecules of group 14 elements, as well as relevant reports from other research groups. The following survey begins with the photolysis of a highly strained cyclotrisilane, passes through molecules with conjugated Si═Si, Ge═Ge, and Ge═C double bonds, and comes to a provisional conclusion with the formation and structural characterization of an unusual cyclotriplumbane.

Scheme 2



6 **7** **8**

Hexa-*tert*-butylcyclotrisilane and Its Cleavage into Di-*tert*-butylsilylene and Tetra-*tert*-butyldisilene

The long sought hexa-*tert*-butylcyclotrisilane (**6**), the three-membered silicon ring compound with probably the highest ring strain, is smoothly formed by the reductive elimination of halogen from di-*tert*-butyldiiodosilane or, more simply, from dibromodi-*tert*-butylsilane.[14] Compound **6** on photolysis furnishes the silylene **7** and the disilene **8**,[15] which, in contrast to the products from **3**, remain together in the form of a cage[16] and can only be separated when suitable trapping reagents are present (Scheme 2).

This opens the possibility to trap the reactive species **7** and **8** either separately or together depending on the nature of the reaction partner. Some typical reaction modalities of **7** are summarized in Scheme 3; these include both addition and cycloaddition reactions.[17]

Nitriles probably react with the silylene **7** through an initial [2 + 1] cycloaddition to furnish three-membered-ring species which possess a very high ring strain on account of the very short C═N double bond and accordingly undergo σ dimerization to afford the six-membered-ring compounds **9** and **10**. While sterically benign molecules such as acetonitrile and benzonitrile lead to compounds of the type **9**, with sterically demanding cyanides such as *tert*-butyl cyanide and 1-adamantyl cyanide compounds of the type **10** are isolated, despite the endocyclic Si−C bond lengths in excess of 2 Å.[18] Since P═C double bonds are markedly longer than C═N bonds, cycloaddition reactions of **7** with phosphaalkynes afford the stable phosphasilirenes **11** as the first three-membered-ring compounds containing a P═C double bond.[19] Silylene **7** also reacts with ethenes and 1,3-dienes through a [2 + 1] cycloaddition process to furnish, for example, the compound **12**.[20] With 1,4-diheterodienes, e.g., 1,4-diazabutadienes, on the other hand, [4 + 1] cycloadditions occur and the five-membered-ring products **13** are isolated.[21] The [4 + 1] cycloadditions of

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(7) For a recent review, see: Karni, M.; Apeloig, Y.; Kapp, J.; Schleyer, P. v. R. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 2001; Vol. 3, p 1.

(8) For recent reviews, see: (a) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463. (b) Weidenbruch, M. *J. Organomet. Chem.* **2002**, *646*, 39.

(9) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343.

(10) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

(11) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150.

(12) (a) Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 6163. (b) See also: Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268.

(13) Masamune, S.; Sita, L. R. *J. Am. Chem. Soc.* **1985**, *107*, 6390.

(14) Schäfer, A.; Weidenbruch, M.; Peters, K.; von Schnering, H. G. *Angew. Chem.* **1984**, *23*, 311; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 302.

(15) (a) Schäfer, A.; Weidenbruch, M.; Pohl, S. *J. Organomet. Chem.* **1985**, *282*, 305. (b) For a review, see: Weidenbruch, M. *Chem. Rev.* **1995**, *95*, 1479.

(16) Michl, J. Personal communication.

(17) For reviews, see: (a) Weidenbruch, M. *Coord. Chem. Rev.* **1994**, *130*, 275. (b) Gaspar, P. P.; West, R. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, p 2463.

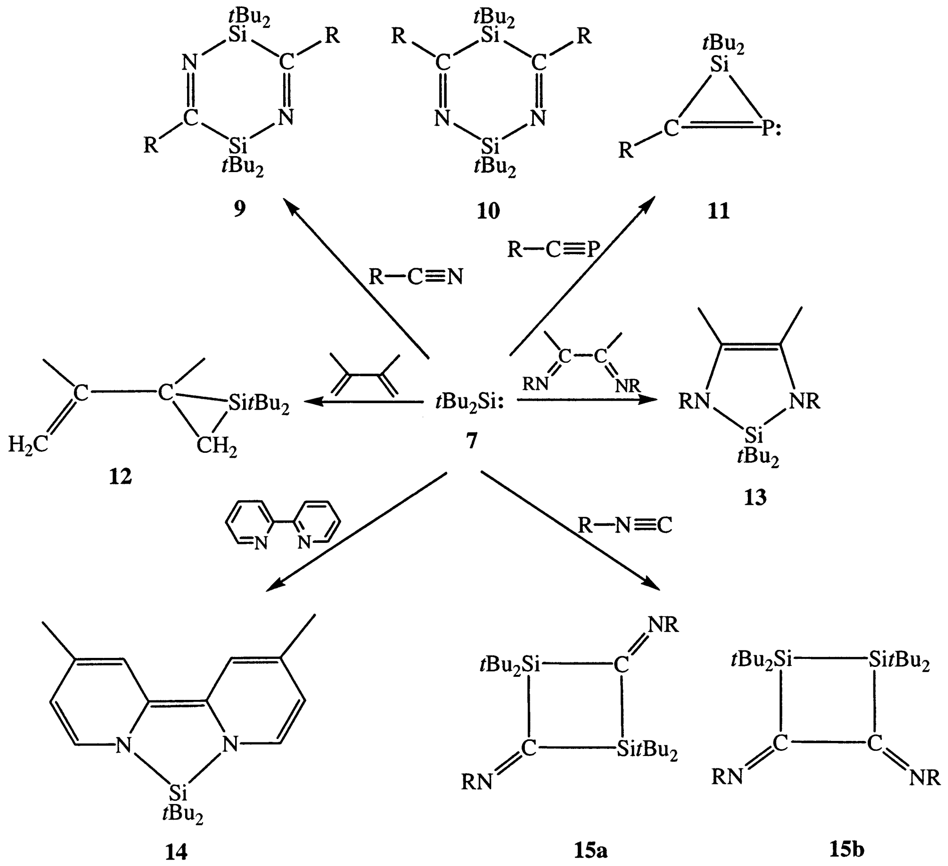
(18) (a) Weidenbruch, M.; Schäfer, A.; Peters, K.; von Schnering, H. G. *J. Organomet. Chem.* **1986**, *314*, 25. (b) Weidenbruch, M.; Meiners, F.; Saak, W. *Can. J. Chem.* **2000**, *78*, 1469.

(19) Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S. *Angew. Chem.* **1987**, *99*, 806; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 776.

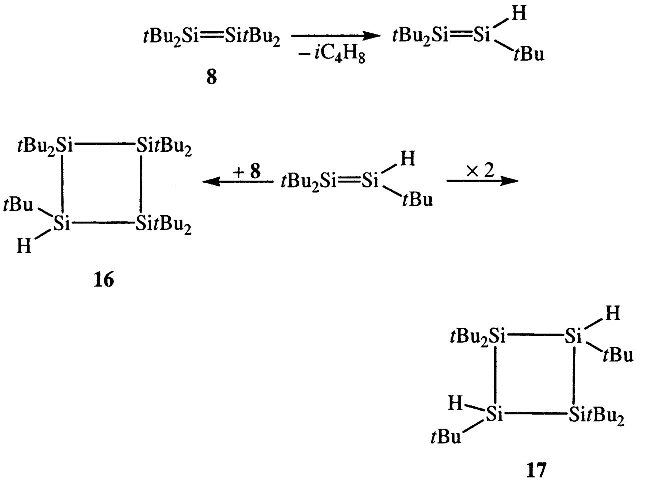
(20) (a) Weidenbruch, M.; Kroke, E.; Marsmann, H.; Pohl, S.; Saak, W. *J. Chem. Soc., Chem. Commun.* **1994**, 1233. (b) Kroke, E.; Willms, S.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Tetrahedron Lett.* **1996**, *37*, 3675.

(21) Weidenbruch, M.; Lesch, A.; Peters, K. *J. Organomet. Chem.* **1991**, *407*, 31.

Scheme 3



Scheme 4



7 to bipyridyl derivatives seem to proceed analogously to yield compounds **14**. Here it is worthy of note that the heteroaromatic system of the bipy derivative is converted into a system with nonaromatic, conjugated double bonds.[22] In contrast to these cycloadditions the reactions of **7** with isonitriles start with an addition of the silylene to the carbon atom of the isocyanide followed by a head-to-tail or head-to-head dimerization of the intermediate ketenimines to afford the isomeric four-membered-ring compounds **15a** and **15b**, which both possess an exocyclic C=N double bond.[23] Okazaki, Tokitoh, et al. provided confirmation of this assumption by using an extremely bulky diarylsilylene and thus isolated the putative intermediate silaketenimine as a stable Lewis acid–base adduct.[24]

Most of the reactions summarized in Scheme 3 involve the silylene **7** but not the disilene **8**, formed simultaneously upon photolysis of the cyclotrisilane **6**. A [2 + 2] cycloaddition of the reactive molecule **8** is probably not possible, because the resultant octa-*tert*-butylcyclotetrasilane would be most unlikely, due to the strong van der Waals repulsions between the bulky *tert*-butyl groups. However, the four-membered-ring compounds **16** and **17**, formed by cleavage of isobutene from **8** to furnish the cyclotetrasilane **16** or by [2 + 2] cycloaddition of two molecules of the cleavage product to give the four-membered-ring species **17**, have been isolated. On the basis of its structural data, **16** probably possesses a high ring strain similar to that for the cyclotrisilane **6** (Scheme 4).[25]

Similar to the classical tetramesityldisilene (**2**),[9] the only marginally stable disilene **8** also undergoes a plethora of cycloaddition reactions. Since these have recently been reviewed in two comprehensive articles,[26] only a few unusual modes of reaction of **8** that are not possible with the tetraaryldisilenes or that were discovered later will be presented here (Scheme 5).

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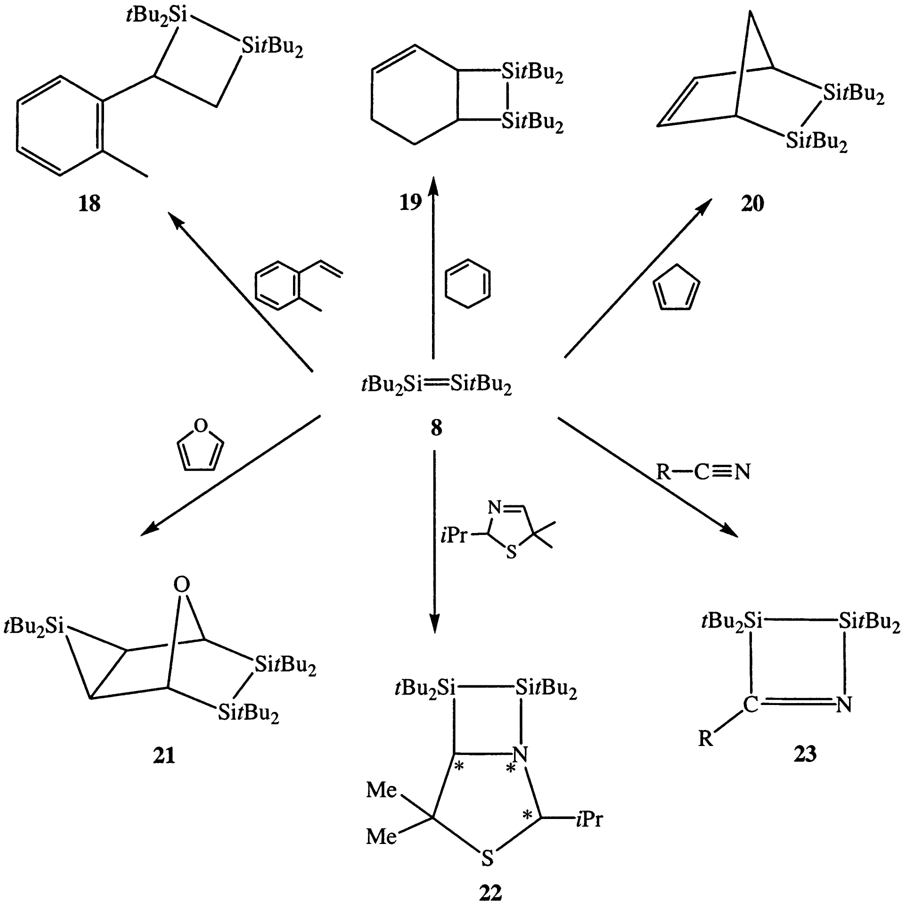
(22) Weidenbruch, M.; Lesch, A.; Marsmann, H. *J. Organomet. Chem.* **1990**, *385*, C47.

(23) (a) Weidenbruch, M.; Brand-Roth, B.; Pohl, S.; Saak, W. *Angew. Chem.* **1990**, *102*, 95; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 90. (b) Weidenbruch, M.; Brand-Roth, B.; Pohl, S.; Saak, W. *Polyhedron* **1991**, *10*, 1147.

(24) (a) Takeda, N.; Suzuki, H.; Tokitoh, N.; Okazaki, R.; Nagase, S. *J. Am. Chem. Soc.* **1997**, *119*, 1456. (b) Takeda, N.; Kajiwara, T.; Suzuki, H.; Okazaki, R.; Tokitoh, N. *Chem. Eur. J.* **2003**, 3530.

(25) Weidenbruch, M.; Kroke, E.; Pohl, S.; Saak, W.; Marsmann, H. *J. Organomet. Chem.* **1995**, *499*, 229.

Scheme 5



Reaction with *o*-methylstyrene led to the first structurally confirmed [2 + 2] cycloadduct of a disilene to a C=C double bond, namely compound **18**.[27] In the meantime the addition of the disilene **2** as well as that of a germasilene to the exocyclic double bond of styrene has been achieved.[28,29] The attempted [2 + 4] cycloaddition of **8** to cyclohexa-1,3-diene also afforded the [2 + 2] cycloadduct **19**.[30] Although Masamune et al.[31] reported in 1983 the low-yield [4 + 2] cycloaddition of **8** to 2,3-dimethylbutadiene, compound **20** was the first structurally characterized [4 + 2] cycloadduct to be isolated.[32] The 1,3-separation of the two double bonds in cyclopentadiene is apparently just right to permit a Diels–Alder type reaction with **8**. The reaction of **8** with furan presumably starts in a similar manner with, in this case, a subsequent [2 + 1] cycloaddition of the silylene **7** to the newly formed double bond which furnishes the tricyclic product **21**.[32] Worthy of note are the [2 + 2] cycloadditions of **8** to C/N double and triple bonds. For instance, reaction with a racemic 3-thiazoline proceeds diastereoselectively to afford compound **22**.[33] Also highly unusual is the cycloaddition of **8** to the cyanide $t\mathrm{Bu_3SiCN}$, giving compound **23**.[34] This reaction is of interest in that alkenes do not undergo addition to the triple bonds of cyanides.

Compounds **7** and **8**, readily accessible by photolysis of the cyclotrisilane **6**, should afford silirenes (silacyclopropenes) and disilacyclobutenes on reaction with acetylenes, both representing well-known classes of compounds. For example, the first thermally stable silirene was described by Seyferth et al. in 1976.[35] However, reactions of silylenes and disilenes with di- and oligoacetylenes were not known. Photolysis of **6** in the presence of hexa-2,4-diyne (**24**) did indeed proceed through addition of both intermediates to the 1,3-diyne, although the mode of formation of the final products **25** and **26** was at first not understood (Scheme 6).[36]

For the formation of **26** it can be assumed that initially two molecules of disilene **8** add to both triple bonds of **24**, with a subsequent 1,5-hydride shift, bond homolysis, and two cyclization steps. In spite of this complicated mechanism the bicyclic product **26** was isolated in 80% yield.[36] A better insight into the reaction process was obtained by exchanging the methyl groups

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(26) (a) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. (b) Weidenbruch, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 2001; Vol. 3, p 391.

(27) Weidenbruch, M.; Kroke, E.; Marsmann, H.; Pohl, S.; Saak, W. *J. Chem. Soc., Chem. Commun.* **1994**, 1233.

(28) Dixon, C. E.; Liu, H. W.; Van der Kant, C. M.; Baines, K. M. *Organometallics* **1996**, *15*, 5701.

(29) Dixon, C. E.; Cooke, J. E.; Baines, K. M. *Organometallics* **1997**, *16*, 5437.

(30) Weidenbruch, M.; Schäfer, A.; Thom, K. L. *Z. Naturforsch.* **1983**, *28b*, 1695.

(31) Masamune, S.; Murakami, S.; Tobita, H. *Organometallics* **1983**, *2*, 1464.

(32) Kroke, E.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Organometallics* **1995**, *14*, 5695.

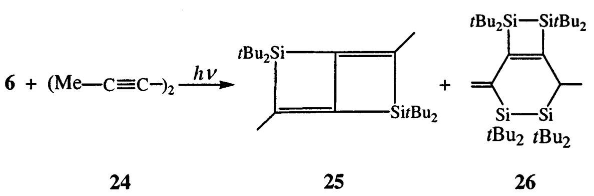
(33) Weidenbruch, M.; Flintjer, B.; Pohl, S.; Haase, D.; Martens, J. *J. Organomet. Chem.* **1988**, *328*, C1.

(34) Weidenbruch, M.; Flintjer, B.; Pohl, S.; Saak, W. *Angew. Chem.* **1989**, *101*, 89; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 95.

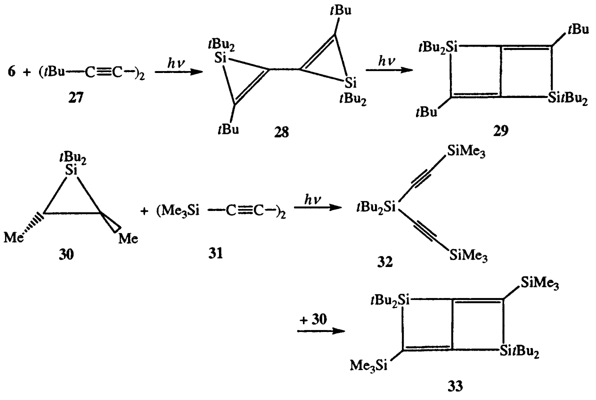
(35) Seyferth, D.; Annarelli, D. C.; Vick, S. C. *J. Am. Chem. Soc.* **1976**, *98*, 6382.

(36) Kirmaier, L.; Weidenbruch, M.; Marsmann, H.; Peters, K.; von Schnering, H. G. *Organometallics* **1998**, *17*, 1237.

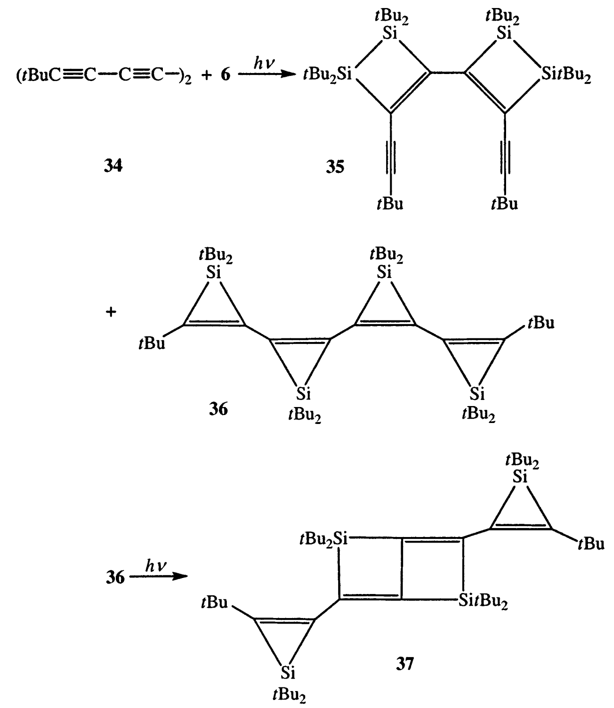
Scheme 6



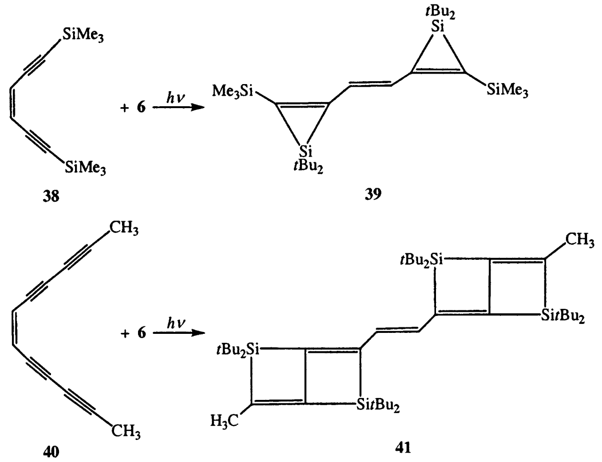
Scheme 7



Scheme 8



Scheme 9



in **24** with *tert*-butyl or trimethylsilyl groups, which should then not be able to undergo hydride shifts. Photolysis of **6** in the presence of the 1,3-diacetylene **27** gave at first the stable bis(silirene) **28**, which, upon continued irradiation, underwent rearrangement to afford the 2,5-disilabicyclohexadiene **29** (Scheme 7)[37]

Not only the nature of the end groups on the 1,3-diacetylenes but also the manner in which the silylene **7** is generated are decisive for the course of the reaction. When, instead of **6**, the silirane **30**[38] is subjected to photolysis, the thermally stable bis(ethynyl)silane **32**[39] is initially formed and furnishes the bicyclic compound **33** upon further irradiation.[37] The photolysis of **6** in the presence of the octa-1,3,5,7-tetrayne **34** is even more transparent and results in the formation of three isolable products. Addition of the disilene **8** to the two internal triple bonds of **34** affords the cycloaddition product **35** with two terminal alkynyl groups and with the double bonds adopting the s-cis form, which is unusual for butadienes. [2 + 1] cycloadditions of the four silylene molecules to the four triple bonds in **34** furnishes the teterakis(silirene) **36** that adopts the s-cis-trans-cis form to avoid steric interactions between the bulky *tert*-butyl groups. Like the bis(silirene) **28**, compound **36** is also thermally stable, whereas under photolytic conditions it undergoes rearrangement to the 2,5-disilabicyclohexadiene **37** with terminal silirene groups (Scheme 8).[40] The reaction behavior of the silylene **7** is very similar to the reactions of titanocene with oligoacetylenes investigated by Rosenthal et al., which gave rise to analogous compounds.[41]

Since not only alkynes but also alkenes undergo [2 + 1] cycloadditions, we have investigated which of these multiple bonds reacts preferentially with the silylene. Not only the photolysis of **6** in the presence of the enediyne **38** but also that of the enetetrayne **40** unequivocally show that the C≡C triple bond is more amenable to [2 + 1] cycloadditions than the also present C═C double bonds. Thus, the action of **7** on the enediyne **38** leads smoothly to the bis(silirene) **39** with a bridging C═C double bond. Similarly, the reaction of **40** with **7** probably occurs by [2 + 1] cycloadditions at all four C≡C triple bonds with subsequent rearrangement to the two 2,5-disilabicyclohexadiene units linked by a C═C double bond, namely **41**. The double bonds adopt an all-trans arrangement not only in **39** but also in **41** (Scheme 9).[42]

In analogy to the above-described reactions, the addition of **7** to the triethynylbenzene **42** furnishes the tris(silirenyl)benzene **43**. Also, photolysis of **6** in the

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[37] Ostendorf, D.; Kirmaier, L.; Saak, W.; Marsmann, H.; Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, 2301.

[38] Boudjouk, P.; Samaraweera, U.; Sooriyakumaran, R.; Chrisciel, J. *Angew. Chem.* **1988**, *100*, 1406; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1355.

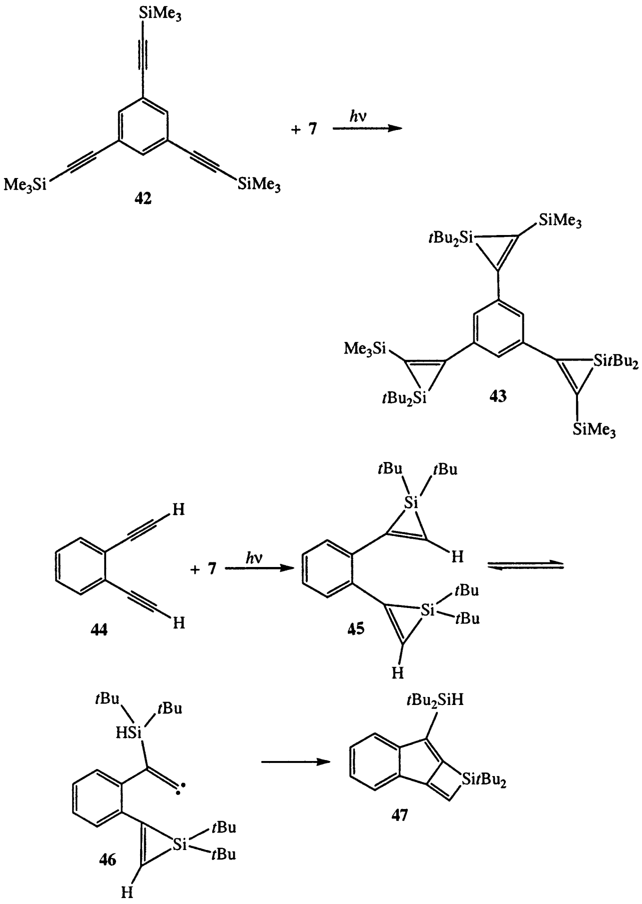
[39] Peters, K.; Peters, E.-M.; Kirmaier, L.; Ostendorf, D.; Weidenbruch, M. *Z. Kristallogr.-New Cryst. Struct.* **1999**, *214*, 2665.

[40] Ostendorf, D.; Saak, W.; Weidenbruch, M.; Marsmann, H. *Organometallics* **2000**, *29*, 4938.

[41] Review: Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spangenberg, A. *Organometallics* **2003**, *22*, 884.

[42] Ostendorf, D.; Saak, W.; Weidenbruch, M.; Marsmann, H. *Organometallics* **2002**, *21*, 636.

Scheme 10

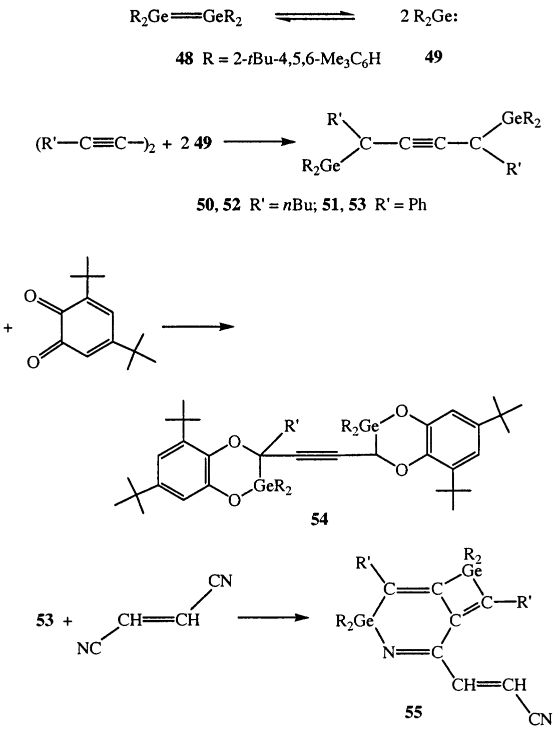


presence of 1,2-diethynylbenzene (**44**) presumably begins with the double cycloaddition of **7** to the C≡C triple bonds with formation of **45**, followed by a 1,2-hydride shift to give the intermediate **46**. Insertion of this carbene derivative into the Si−C bond should then produce the isolated tricyclic product **47** with an exocyclic $t\mathrm{Bu}_2\mathrm{SiH}$ group (Scheme 10).[42] A similar reaction pathway was recently observed for insertions into the Si−C bond of siliranes.[20]

Molecules with Conjugated Ge═C, Si═Si, and Ge═Ge Double Bonds

Similar to the silirenes, germirenes are three-membered-ring compounds containing a germanium atom and a C═C double bond and have been known for a number of years. The successful addition of silylenes to di- and oligoacetylenes opened the question of whether analogous reactions would be possible with germylenes. The compound $\mathrm{R_2Ge}$: (R = 2-tBu-4,5,6-$\mathrm{Me_3C_6H}$) was chosen as the germylene; in the solid state it exists as the digermene **48** but in solution dissociates mostly into the germylene molecules **49**.[43] Reactions of **49** with the 1,3-diacetylenes **50** and **51**, however, do not lead to the expected bis(germirenes) or their rearrangement products of the type **25**; instead the acetylene-bridged bis(germaethenes) **52** and **53**, containing systems of conjugated double bonds, are obtained (Scheme 11). The conjugation between the two Ge═C double bonds in **52** and **53** is reflected less in the bond lengths that lie in the typical range for Ge═C double bonds[44] and more in the electronic spectra of the molecules.[45,46] While the dark red dialkyl compound **52** shows its longest wavelength absorption at 518 nm, the dark blue diphenyl compound exhibits a marked red shift to furnish an absorption at 595 nm. This suggests that the two phenyl groups are also involved in the conjugation.

Scheme 11



Compound **53**, obtained in almost quantitative yield, reacts differently from the simple germaethenes.[47] Although the latter undergo smooth reactions with phosphaalkynes[48] or with 2,3-dimethylbutadiene,[49] compound **53** does not react with these partners, even under harsher conditions. In contrast, **53** participates in mostly rapid reactions with electron-poor multiple-bond systems. For example, its reaction with two molecules of a 1,2-benzoquinone proceeds through [4 + 2] cycloadditions at both Ge═C double bonds to furnish the acetylene-linked product **54**. While the Ge═C double bonds of **53** behave as ene components toward the heterodiyne, the compound reacts with one of the C≡N triple bonds of 1,2-dicyanoethene as a four-π-electron donor to form initially an unsaturated six-membered ring. However, this is not stable, on account of the

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(43) Weidenbruch, M.; Stürmann, M.; Kilian, H.; Pohl, S.; Saak, W. *Chem. Ber.* **1997**, *130*, 735.

(44) (a) Meyer, H.; Baum, G.; Massa, W.; Berndt, A. *Angew. Chem.* **1987**, *99*, 790; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 798. (b) Lazraq, M.; Escudié, J.; Couret, C.; Satgé, J.; Dräger, M.; Dammel, R. *Angew. Chem.* **1988**, *100*, 885; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 828. (c) Tokitoh, N.; Kishikawa, K.; Okazaki, R. *J. Chem. Soc., Chem. Commun.* **1995**, 1425. (d) Stürmann, M.; Saak, W.; Weidenbruch, M.; Berndt, A.; Scheschkewitz, D. *Heteroat. Chem.* **1999**, *10*, 554. (e) Meiners, F.; Saak, W.; Weidenbruch, M. *Chem. Commun.* **2001**, 215.

(45) Meiners, F.; Saak, W.; Weidenbruch, M. *Organometallics* **2000**, *19*, 2835.

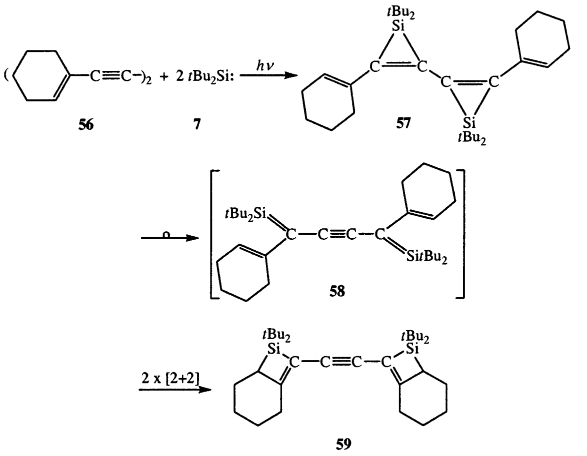
(46) Meiners, F.; Haase, D.; Koch, R.; Saak, W.; Weidenbruch, M. *Organometallics* **2002**, *21*, 3990.

(47) Baines, K. M.; Stibbs, W. G. *Coord. Chem. Rev.* **1995**, *145*, 157.

(48) Lazraq, M.; Escudié, J.; Couret, C.; Bergsträsser, U.; Regitz, M. *J. Chem. Soc., Chem. Commun.* **1993**, 569.

(49) Couret, C.; Escudié, J.; Satgé, J.; Lazraq, M. *J. Am. Chem. Soc.* **1987**, *109*, 4411.

Scheme 12

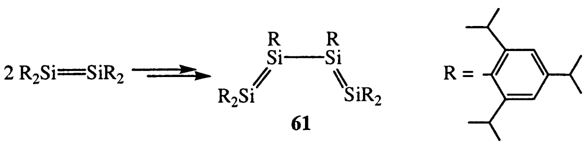


cumulated C=C double bonds, and undergoes a spontaneous [2 + 2] cycloaddition of the second Ge=C double bond to afford the bicyclic compound **55**.[46] The reaction of **53** with acrylonitrile proceeds similarly to furnish the corresponding bicyclic compound.[50]

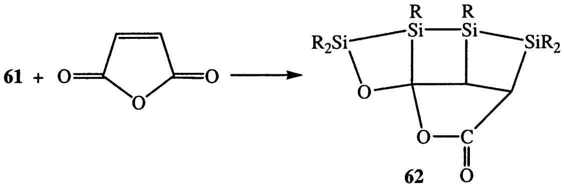
The differing reaction behaviors of silylene **7** and germylene **49** toward 1,3-diacetylenes has been confirmed by DFT calculations. The preference for bis(silirenes) over bis(silaethenes) can be explained by their significantly higher thermodynamic stability. Also, the cycloadditions of germylenes should lead preferentially to bis(germirenes). However, diarylgermylenes with sterically demanding substituents lead to a reversal of stability with formation of the experimentally confirmed acetylene-linked bis(germaethenes).[51] Despite the unambiguous theoretical results, we have attempted to obtain evidence for the at least intermediate existence of a bis(silaethene). For this purpose, the photolysis of **6** was carried out in the presence of 1,4-bis(cyclohexen-1-yl)buta-1,3-diyne (**56**). The acetylene-bridged bis(2-silacyclobutene) derivative **59**, isolated in good yield from this reaction, indicates that at least small amounts of bis(silaethene) **58** exist in equilibrium with the bis(silirene) **57** (Scheme 12).[52]

Like the molecules with conjugated Ge=C bonds, those with conjugated homonuclear double bonds of the heavier elements of group 14 were unknown until just recently. This was more surprising because, for example, to date 50 molecules with Si=Si double bonds have been prepared and, in most cases, structurally characterized.[26] In 1997, starting from the disilene **60** through a sequence of metalation, halogenation, and coupling reactions, we obtained the tetrasilabutadiene **61**,[53] which, in contrast to most of the analogous carbon compounds, exists in the s-gauche form both in the solid state and in solution (Scheme 13). Similar to the case with the bis(germaethenes), the conjugation between the Si=Si double bonds in **61** is confirmed more by the electronic spectrum than by the structural parameters. The absorption at longest wavelength of the reddish

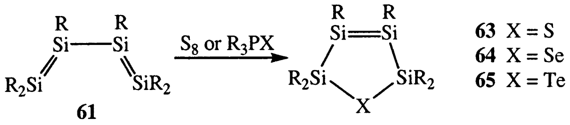
Scheme 13



Scheme 14



Scheme 15



brown crystals and solution occurs at 518 nm (ϵ = 25 800) and is bathochromically shifted by about 100 nm in comparison to those of disilenes with the corresponding substituent patterns.[53]

Although the s-gauche conformation of **61** should favor [4 + 2] cycloadditions of the Diels–Alder type, to date all reactions with olefins, acetylenes, and the C=O bond of ketones have remained unsuccessful. An exception is the reaction of **61** with maleic anhydride, which furnished the tetracyclic compound **62** in high yield. It can be assumed that the reaction sequence is initiated by a [2 + 2] cycloaddition of one of the Si=Si double bonds to the highly reactive CO group, followed by a second cycloaddition of the remaining Si=Si bond across the C=C double bond to complete the formation of **62** (Scheme 14).[54]

Since Diels–Alder products of **61** have as yet not been synthesized, probably because of the steric overcrowding and the large 1,4-separation of the terminal silicon atoms, it was surprising to find that the action of sulfur on **61** resulted in a formal [4 + 1] cycloaddition to furnish the cyclic disilene **63** in high yields. Treatment of **61** with selenium and tellurium did not lead to any reaction. However, upon addition of small amounts of triethylphosphane, the corresponding five-membered rings **64** and **65** were isolated in high yields (Scheme 15).[55]

In analogy to the reactions of acyclic disilenes with the heavier chalcogens[56] it can be assumed that an initial [2 + 1] cycloaddition of the respective chalcogen to one of the Si=Si double bonds of **61** takes place, followed by a rearrangement of the resultant three-membered ring to the less strained five-membered ring.

As opposed to the cycloaddition reaction of **61**, the 1,2-additions of small molecules were more successful.

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(51) Koch, R.; Bruhn, T.; Weidenbruch, M. Submitted for publication in *Organometallics*.

(52) Ostendorf, D.; Saak, W.; Haase, D.; Weidenbruch, M. *J. Organomet. Chem.* **2001**, *636*, 7.

(53) Weidenbruch, M.; Willms, S.; Saak, W.; Henkel, G. *Angew. Chem.* **1997**, *106*, 2612; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2503.

(54) Boomgaarden, S.; Saak, W.; Weidenbruch, M.; Marsmann, H. *Organometallics* **2001**, *20*, 2451.

(55) Grybat, A.; Boomgaarden, S.; Saak; W. Marsmann, H.; Weidenbruch, M. *Angew. Chem.* **1999**, *111*, 2161; *Angew. Chem., Int. Ed.* **1999**, *38*, 2010.

(56) (a) West, R.; DeYoung, D. J.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 4942. (b) Tan, R. P.; Gillette, G. R.; Powell, D. R.; West, R. *Organometallics* **1991**, *10*, 546.

Treatment of **61** with small amounts of water led, presumably through rearrangement of a 1,2-addition product, to the five-membered ring **66**, an analogue of tetrahydrofuran. The oxidation product **67** is formed on exposure of **61** to atmospheric oxygen. In addition to the presence of two cyclodisiloxane units, this reaction is of particular interest due to the insertion of oxygen into the sterically protected Si−Si single bond, which proceeds at room temperature with formation of a disiloxane group.[57]

When dry ammonia is passed over the solution of **61**, yellow crystals of the twofold 1,2-addition product **68** are formed in high yield. This result is somewhat surprising, because the attempted additions of ammonia to disilenes were unsuccessful. An X-ray structural analysis of the crystals of **68** revealed the existence of a conglomerate of enantiomerically pure substances.[58] Such conglomerates are still rather rare in comparison to the large number of similar molecules that crystallize as racemates.[59] A further special feature in the structure of **68** is the small separation of the nitrogen atoms of 3.00 Å, which is indicative of the dynamic hydrogen bridging system NH···N.[58] The 1,4-dihydrazinotetrasilane **69**, obtained from **61** and anhydrous hydrazine, also exists in the solid state as a conglomerate of enantiomerically pure crystals. The separations between the two pairs of nitrogen atoms are short (3.03 and 3.15 Å) and are thus suggestive of the presence of two dynamic NH···N bridges.[60]

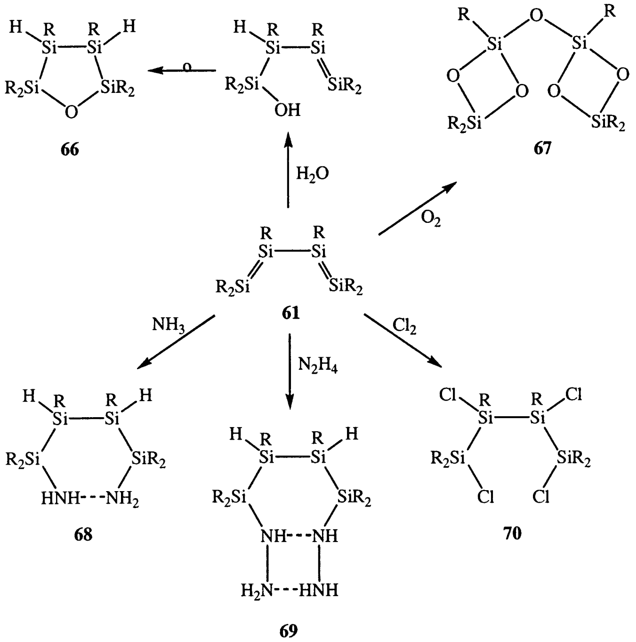
To determine whether other 1,2-addition products at the two double bonds of **61** also crystallize as conglomerates, we treated **61** with chlorine. Although the individual molecules of the tetrachlorotetrasilane **70** are also chiral, this compound crystallizes as a racemate (Scheme 16).[58]

It is known from organic chemistry that butadienes can participate not only in cycloaddition and 1,2-addition reactions but also in 1,4-additions. Indeed, we recently uncovered the first example of the corresponding reaction of **61**. Addition of trichlorosilane to a solution of **61** resulted in the formation of bright orange crystals of the unsymmetrically substituted disilene **71**. Also, the action of hydrogen bromide, generated slowly by the reaction of trifluoroacetic acid with lithium bromide, on **61** furnishes intensely orange crystals of the disilene **72** (Scheme 17).[61]

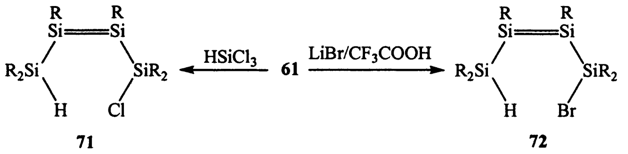
It is not clear why no 1,2-additions of the hydrogen halides to the double bonds of **61** occur in these reactions or why instead the previously unobserved 1,4-additions with formation of new double bonds take place. The closest precedent involves the action of small amounts of water on **61**, which is presumably initiated by a 1,2-addition and subsequent 1,3-hydrogen shift to form compound **66**.[57]

Little success resulted from attempts to obtain the molecule **73** with an extended system of conjugated double bonds by repeating the reaction sequence that had led to **61**. The action of lithium on **61** did not give rise to the hoped-for lithium compound by cleavage of a terminal aryl group; instead, the central Si−Si single bond was cleaved to afford the disilenyllithium compound **74**, which subsequently reacted with an aryl bromide to regenerate **61** (Scheme 18).[62]

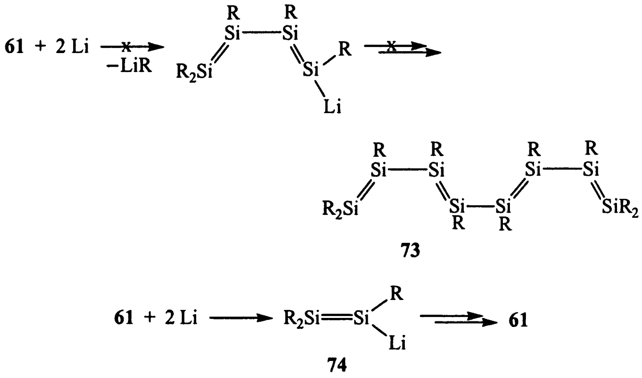
Scheme 16



Scheme 17



Scheme 18



In the meantime a second compound that probably contains conjugated Si═Si double bonds has been reported. Dehalogenation of the oligosilane compound **75** gave rise to a surprising result: in addition to the main product, the cyclotrisilene **76**,[63] red crystals of the spiropentasiladiene **77** were isolated in 3.5% yield (Scheme 19).[64]

The most striking feature of the structure of **77** is the twisting of the halves of the molecule by 72.26°. This

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(59) Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994.

(60) Boomgaarden, S.; Saak, W.; Marsmann, H.; Weidenbruch, M. *Z. Anorg. Allg. Chem.* **2001**, *627*, 805.

(61) Boomgaarden, S.; Saak, W.; Marsmann, H.; Weidenbruch, M. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1745.

(62) Boomgaarden, S.; Weidenbruch, M. Unpublished results.

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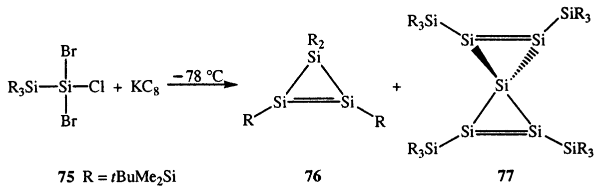
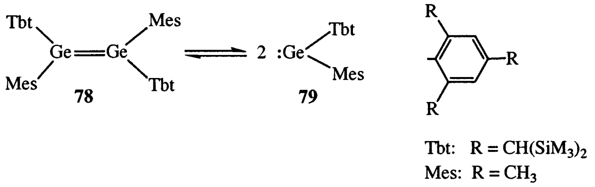
Scheme 19



Scheme 20



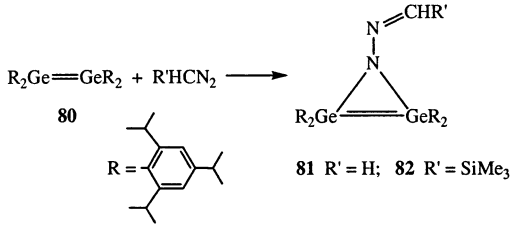
arrangement allows through-space interactions between not only the π orbitals but also the π^* orbitals of both double bonds. These interactions are reflected in the electronic spectrum of **77**, where the longest wavelength absorptions at 560 and 500 nm are shifted bathochromically compared to that of the cyclotrisilene **76** at 482 nm.[64]

The smooth formation of the tetrasilabutadiene **61** from a disilene opened the question as to whether a corresponding germanium compound could be obtained by an analogous route. The ready decomposition of digermenes to germylene molecules in solution proved to be a problem. For example, the bond dissociation for the transformation of the digermene **78** into the germylene **79** was determined to be merely 61.5 kJ mol^{-1} (Scheme 20).[65]

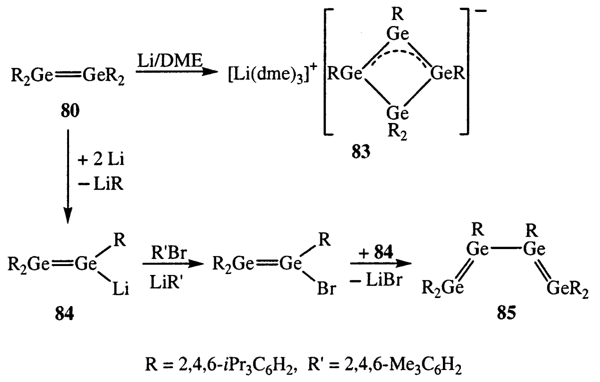
However, it is difficult to predict whether digermenes dissociate in solution. Although the spatial requirements of the substituents as well as their possible donor properties appear to play a role, there is in the meantime a series of molecules that retain their integrity in solution despite similar or even higher spatial demands of the substituents. Thus, for example, the digermene **80** exists predominantly in the undissociated state at room temperature.[66−68] This was confirmed by the reaction of **80** with diazomethane as well as with (trimethylsilyl)diazomethane to afford the [2 + 1] cycloaddition products **81** and **82** in high yields (Scheme 21).[68]

However, treatment of **80** with lithium did not afford the digermyllithium compound **84**; instead, we obtained dark red crystals of the ionic compound **83** containing an allyl-like Ge$_3$ ion as part of a four-membered ring. Precisely how **83** is formed remains unclear, since it involves not only the cleavage of Ge−C bonds in **80** but also the formation of Ge−Ge bonds. To eliminate all subsequent reactions of the primarily expected compound **84**, the reaction time of **80** with lithium was shortened to such an extent that most of the digermene

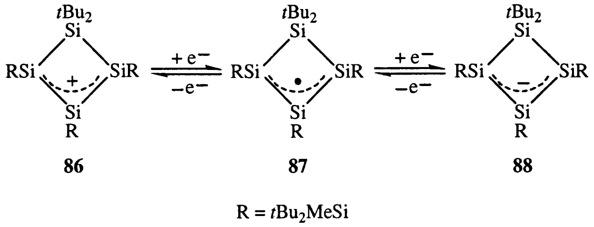
Scheme 21



Scheme 22



Scheme 23



80 had reacted before the formation of **83** could become the main reaction. This approach did indeed lead to compound **84**, which, after a series of halogenation and coupling reactions, furnished the tetragermabutadiene **85**, albeit in low yield (Scheme 22).[69]

The conjugation between the two double bonds of **85** is confirmed by the electronic spectrum of the dark blue solution in *n*-hexane, which shows a longest wavelength absorption of 560 nm; on comparison with the yellow or orange digermenes[70] this corresponds to a bathochromic shift of about 140 nm and even exceeds the absorption of tetrasilyldigermenes by almost 100 nm.[71]

Very recently, Sekiguchi et al. succeeded not only in the isolation of the silicon compound **88**, analogous to **83**, but also in the isolation and complete characterization of the cyclotetrasilylenium ion **86** and the silyl radical **87** (Scheme 23).[72−74]

We have now found that the tetragermabutadiene **85** is easily accessible by the reaction of the Grignard

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(64) (a) Iwamoto, T.; Tamura, M.; Kabuto, C.; Kira, M. *Science* **2000**, *290*, 504. (b) See also: Koch, R.; Weidenbruch, M. *Angew. Chem.* **2002**, *114*, 1941; *Angew. Chem., Int. Ed.* **2002**, *41*, 1861.

(65) Kishikawa, K.; Tokitoh, N.; Okazaki, R. *Chem. Lett.* **1998**, 239.

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(67) Ando, W.; Itoh, H.; Tsumuraya, T. *Organometallics* **1989**, *8*, 2759.

(68) Schäfer, H.; Saak, W.; Weidenbruch, M. *Organometallics* **1999**, *18*, 3159.

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(70) For a review, see: Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275.

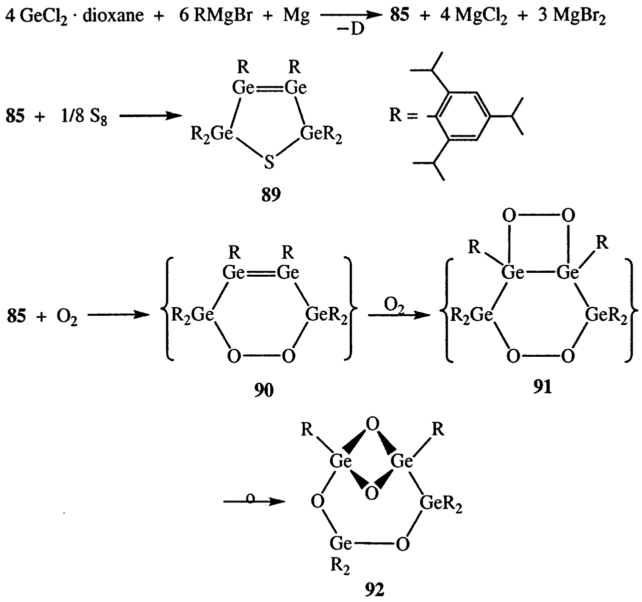
(71) Kira, M.; Iwamoto, T.; Murayama, T.; Kabuto, C.; Sakurai, H. *Organometallics* **1996**, *15*, 3767.

(72) Sekiguchi, A.; Matsumo, T.; Ichinohe, M. *J. Am. Chem. Soc.* **2000**, *122*, 11250.

(73) Sekiguchi, A.; Matsumo, T.; Ichinohe, M. *J. Am. Chem. Soc.* **2001**, *123*, 12436.

(74) Matsumo, T.; Ichinohe, M.; Sekiguchi, A. *Angew. Chem.* **2002**, *114*, 1668; *Angew. Chem., Int. Ed.* **2002**, *41*, 1559.

Scheme 24



compound RMgBr (R = 2,4,6-iPr$_3$C$_6$H$_2$) with GeCl$_2$·(dioxane) and magnesium. Although the yield of this synthetic route still only amounts to about 30%, the one-pot procedure does allow the isolation of **85** on a gram scale from readily accessible or commercially available starting materials and thus makes first investigations of the reactions of **85** possible (Scheme 24).[75]

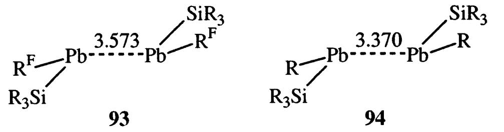
Reaction of **85** with sulfur yields the thiatetragermacyclopentene **89** as yellow needles in high yield. The reaction of **85** with dry air gave the bicyclic compound **92** in high yield. The folded cyclodigermoxane ring in the bicyclic system is presumably formed by a [2 + 4] cycloaddition of O$_2$ to the terminal germanium atoms of **85** to afford **90**, followed by a 1,2-addition of a second oxygen molecule to the newly formed double bond to give the intermediate **91**. Rearrangement reactions of the two O−O bonds of **91** should then furnish the isolated product **92** (Scheme 24).[75]

From Plumbylene Dimers to Diplumbenes and a Cyclotriplumbane

With increasing mass of the elements the number of molecules with homonuclear double bonds decreases markedly. In the case of the distannenes, besides the classical compound **1**,[6] only four further examples have been characterized; all their Sn=Sn bond lengths are in the range for typical single bonds or even longer.[8]

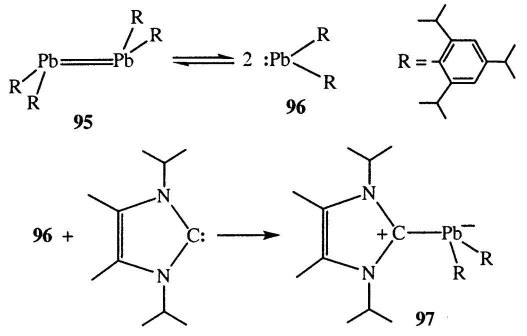
In the case of lead, in addition to :Pb[CH(SiMe$_3$)$_2$]$_2$, the first plumbylene isolated as early as 1973,[76] a series of further dialkyl- and diarylplumbylenes have been prepared over the past number of years; these new compounds also exist as V-shaped monomers in the solid state and show no tendency to dimerization.[8] The first breakthrough in the context of close Pb···Pb contacts was the isolation of the heteroleptic plumbylene dimer **93**, exhibiting a Pb−Pb separation of 3.537(1) Å and trans-bent angles of 40.8°.[77] The plumbylene dimer **94** has an even shorter Pb−Pb separation of 3.370(1) Å and trans-bent angles of 46.5°.[78] Nonetheless, the observed Pb···Pb distances of both compounds are markedly longer than the values 2.82−3.00 Å calculated for the parent compound Pb$_2$H$_4$ with a genuine Pb=Pb double bond[77,79,80] (Chart 2).

Chart 2

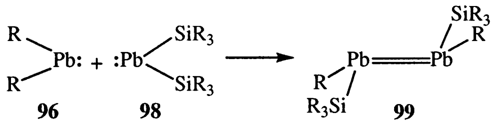


SiR$_3$ = Si(SiMe$_3$)$_3$; R^F = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$; R = 2-tBu-4,5,6-Me$_3$C$_6$H

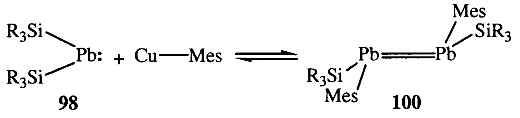
Scheme 25



Scheme 26



Scheme 27



R = SiMe$_3$; Mes = 2,4,6-Me$_3$C$_6$H$_2$

The reaction of lead(II) chloride with (2,4,6-triisopropylphenyl)magnesium bromide furnished red crystals of compound **95**, the first molecule with a short Pb=Pb double bond length of 3.0515(3) Å and trans-bent angles of 43.9 and 51.2°.[81] Compound **95** is stable in the solid state. In solution, it dissociates into the plumbylene molecules **96** that, for example, react with a nucleophilic carbene to furnish the highly labile, zwitterionic adduct **97**[82] (Scheme 25).

Substituent exchange between **96** and the plumbylene :Pb[Si(SiMe$_3$)$_3$]$_2$ (**98**)[83] leads to the heteroleptic diplum-

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(76) Davidson, D. J.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1973**, 317.

(77) Klinkhammer, K. W.; Fässler, T. F.; Grützmacher, H. *Angew. Chem.* **1998**, *110*, 114; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 124.

(78) Stürmann, M.; Weidenbruch, M.; Klinkhammer, K. W.; Lissner, F.; Marsmann, H. *Organometallics* **1998**, *17*, 4425.

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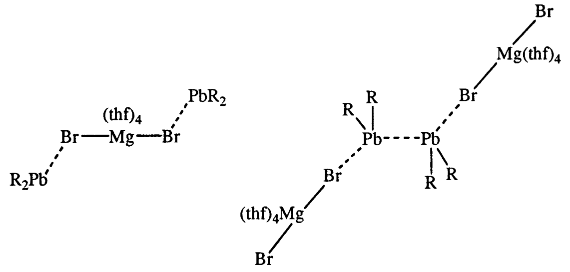
(81) Stürmann, M.; Saak, W.; Marsmann, H.; Weidenbruch, M. *Angew. Chem.* **1999**, *111*, 145; *Angew. Chem., Int. Ed.* **1999**, *38*, 187.

(82) Stabenow, F.; Saak, W.; Weidenbruch, M. *Chem. Commun.* **1999**, 1131.

Chart 3



101 R = 2,4,6-Et$_3$C$_6$H$_2$ **102** R = 2,4,6-Me$_3$C$_6$H$_2$

bene **99**, with a shorter double-bond length of 2.9899(5) Å[84] (Scheme 26).

The diplumbene **100**, with the shortest Pb═Pb bond length (2.903 Å) determined so far, was isolated from the reaction of **98** with mesitylcopper in a low yield[85] (Scheme 27).

The diplumbenes **95**, **99**, and **100** demonstrate that, in contrast to the homonuclear double bonds in disilenes, digermenes, and distannenes where increasing bond lengths require even larger substituents for shielding, lead−lead double bonds can also be realized with smaller groups. Therefore, we have replaced the above-mentioned groups by the markedly less voluminous 2,4,6-triethylphenyl group. Reaction of the corresponding Grignard compound with lead chloride furnished the compound **101**, in which two plumbylene molecules are linked by a magnesium bromide molecule.[86]

Further reduction of the steric bulk of the substituents by replacement of the triethylphenyl group by the even smaller mesityl group afforded black crystals of the plumbylene dimer **102**, that is stabilized by two magnesium bromide molecules. Worthy of note are the lead−lead separation of 3.3549(6) Å and the very large trans-bent angles of 71° at the mesityl group (Chart 3).[84]

These—in part unexpected—results prompted us to reexamine the reaction of lead(II) halides with phenylmagnesium bromide that has been known for almost 100 years to furnish tetraphenyllead and lead.[87] It was later demonstrated that hexaphenyldiplumbane is also accessible by this route in dependence on the ratio of starting materials.[88] The mechanism of the latter reaction was assumed to involve the initial formation of diphenylplumbylene, which then oligomerizes with subsequent disproportionation of the lead chain, affording the dilead compound and lead.[88,89] Repeating the reaction of phenylmagnesium bromide with PbBr$_2$ furnished yellow needles of the ionic compound **103**, the anion of which revealed some interesting features. The presence of a free electron pair at the lead atom leads to a compression of the Pb−Pb−Pb angles and to stretched Pb−Pb bond lengths (Scheme 28).[90]

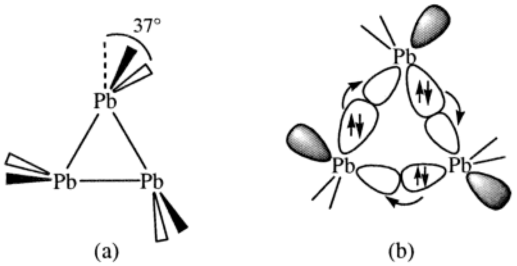


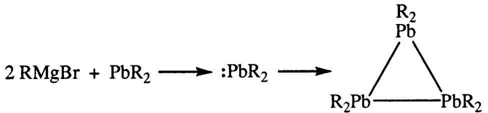
Figure 1. (a) Details of the structure of **104**. (b) Interaction of the three singlet plumbylenes R$_2$Pb:.

Scheme 28

$$\mathrm{PbBr_2 + PhMgBr \xrightarrow{THF} [(thf)_5MgBr]^+[:Pb(PbPh_3)_3]^-}$$

103

Scheme 29



104

To suppress the formation of **101** found in the reaction between (2,4,6-triethylphenyl)magnesium bromide and lead(II) bromide in THF, the same reaction was performed in the presence of dioxane. We then obtained black crystals of the cyclotriblumbane **104**, the first compound of lead with a homocyclic ring system (Scheme 29).[91]

The structure of **104** revealed some unusual parameters. With an average value of 3.184 Å the Pb−Pb bonds are markedly longer than those of a typical diplumbane such as Ph$_3$Ph−PbPh$_3$, with a bond length of 2.844(4) Å.[92] Equally unusual is the orientation of the substituents at the lead atoms, which are twisted by 37° out of their ideal positions (Figure 1a).[91] These structural parameters are in accord with those obtained from theoretical predictions for the parent compound c-Pb$_3$H$_3$: e.g., Pb−Pb bond lengths of 3.231 Å and displacement angles of 50° for the hydrogen atoms.[93]

The observed and calculated structures clearly demonstrate that the Pb−Pb bonds in **104** are not classical single bonds but rather that the structure is held together by weak interactions between the three singlet plumbylene molecules (Figure 1b).[91,93] The weakness of the interactions is probably due to the relativistic contraction[94] of the 6s orbital of one lead atom, which then incompletely overlaps with the unoccupied 6p orbitals of the other respective lead atom.

Alkyne Analogues of the Heavier Group 14 Elements and Heteronuclear Multiple Bonds

With the recent isolation of the diplumbenes **95**, **99**, and **100**, homonuclear double bonds are now known between all elements of group 14. Very recently Power

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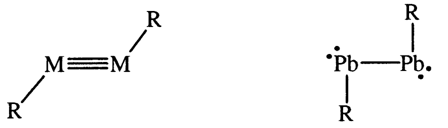
Chart 4



105 M = Ge, **106** M = Sn **107**

R = 2,6-(2,6-iPr$_2$C$_6$H$_3$)$_2$C$_6$H$_3$

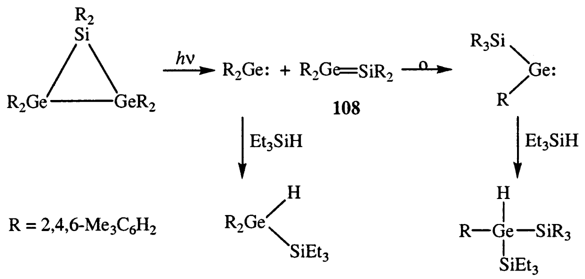
et al. have reported on the isolation of the first digermyne, **105**,[95] and distannyne, **106**.[96] In **105** the Ge−Ge bond length is significantly shorter than a Ge−Ge single bond (2.44 Å) and lies in the region typical for digermenes. As a consequence of the short Sn−Sn bond length of 2.6675 Å and trans-bent angle of 125.24°, the ditin compound **106** should have a multiple-bond system similar to that of **105** (Chart 4).

While the molecules **105** and **106** contain homonuclear multiple bonds with a bond order of 2 or higher, the corresponding lead compound **107**[97] should rather be considered as a diplumbylene with a Pb−Pb single bond and a free electron pair on each of the lead atoms. This situation is indicated by the Pb−Pb bond length of 3.1881 Å and the trans-bent angle of 94.26°. These experimental observations are supported by quantum-chemical calculations that unequivocally show the diplumbylene form **107** to be an energy minimum.[98]

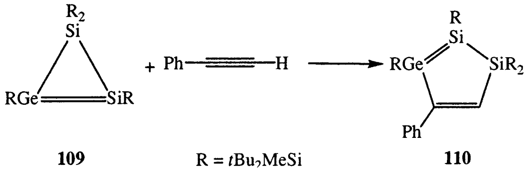
Structurally characterized disilynes, molecules containing a formal silicon−silicon triple bond, are still unknown. A promising candidate for the realization of a compound with such a bond is the molecule $R_2MeSiSi{\equiv}SiSiMeR_2$ ($R = t\mathrm{Bu}_3\mathrm{Si}$), containing two extremely bulky $(t\mathrm{Bu}_3\mathrm{Si})_2\mathrm{MeSi}$ groups. The NMR data are suggestive of the existence of this molecule.[99] Although the final structural elucidation has not yet been achieved, DFT calculations support the existence of this molecule, which should also be very stable not only to isomerization but also to dimerization.[100,101]

Just like the formal, homonuclear triple bonds between elements of group 14, heteronuclear double bonds between these elements were unknown until recently due to their ready isomerization. For example, calculations on the parent compound of the germasilenes, $H_2Si{=}GeH_2$, revealed that the silylgermylene $H_3Si(H)Ge$: is appreciably more stable than the molecule with a heteronuclear double bond.[102] In fact, the tetramesitylgermasilene **108**, for example, can indeed be generated at low temperature and detected by trapping reactions; at higher temperature it isomerizes to a correspondingly substituted silylgermylene[103] (Scheme 30).

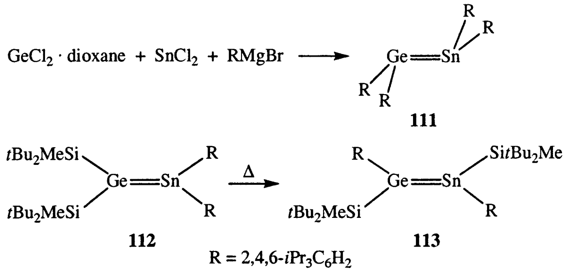
Scheme 30



Scheme 31



Scheme 32



The first examples for thermally stable germasilenes were the cyclic compounds **109** and **110**, reported by Sekiguchi et al.; the structure of the five-membered-ring compound **110** has been confirmed by X-ray crystallography.[104,105] It is noteworthy that, according to the electronic spectra, the two double bonds in **110** do not exhibit any conjugation[105] (Scheme 31).

On the basis of its spectral data, the acyclic compound $R_2Ge{=}SiMes_2$ ($R = t\mathrm{Bu}_2\mathrm{MeSi}$) also contains a germanium−silicon double bond.[106] The first stannasilene, $R_2Si{=}SnAr_2$ ($R = t\mathrm{Bu}_2\mathrm{MeSi}$, $Ar = 2,4,6\text{-}i\mathrm{Pr}_3\mathrm{C}_6\mathrm{H}_2$), possessing a short Si═Sn double-bond length of 2.4188(14) Å and remarkably small trans-bent angles at the two atoms, was also prepared by Sekiguchi et al.[107]

A heteronuclear double bond between the as yet heaviest elements of group 14 is present in the stannagermene **111**, prepared surprisingly simply by the action of the Grignard reagent RMgBr ($R = 2,4,6\text{-}i\mathrm{Pr}_3\mathrm{C}_6\mathrm{H}_2$) on an equimolar suspension of $GeCl_2$ and $SnCl_2$ in THF. The product is stable in the solid state and exhibits a Ge═Sn bond length of 2.5065(5) Å as well as a trans-bent angle of 43.3° at the tin atom and of 30.2° at the germanium atom.[108] Just a short time later a further stannagermene, namely compound **112**, which

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easily undergoes isomerization to the stannagermene **113**, was reported[109] (Scheme 32).

Conclusions and Outlook

In less than three decades the field of multiple bonds between elements of group 14 has expanded to encompass not only molecules with homonuclear double bonds but also—with the exception of lead—heteronuclear double bonds. Also, successful syntheses of compounds with conjugated Si═Si, Ge═C, and Ge═Ge double bonds as well as spiropentasiladiene, in which the conjugation between the two double bonds occurs through space, have been reported. Just recently, the first alkyne analogues containing germanium and tin were described; these compounds supposedly possess a formal triple bond. In contrast, the dilead compound RPbPbR must, despite an analogous composition, rather be considered as a diplumbylene with a Pb−Pb single bond. The peculiarities of lead are also reflected in a cyclotriplumbane structure held together by weak interactions between three plumbylene molecules.

These results appear to suggest that the chemistry of multiple bonds between the heavier elements of group 14 has been more or less completely uncovered. However, the recent successful isolation of a trisilaallene,[110] together with the longer known tristannaallene,[111] show that the potential for novel compounds is by no means exhausted. Thus, be it through targeted synthesis or by serendipity, further molecules with novel bonding situations may be expected.

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