Some Silicon, Germanium, Tin, and Lead Analogues of Carbenes, Alkenes, and Dienes

Manfred Weidenbruch[a]

The isolation and characterization of thermally stable diaminocarbenes and diaminosilylenes has reawakened interest in the low-coordinated compounds of group-14 elements. The existence of these species is presumably due to interactions between the free electron pairs on the nitrogen atoms and the carbene carbon atom or the silicon atom. The present review is mainly concerned with the heavier analogues $R_2Ge:$, $R_2Sn:$, and $R_2Pb:$, systems without intramolecular donor stabilization that owe their existence principally to steric shielding by the voluminous alkyl or aryl groups R. Dimerizations of these electron-sextet molecules give rise to the double-bond systems of the digermenes, distannenes, and diplumbenes; the latter species have for a long time been considered as being incapable of existence. The properties of these molecules are compared with the results of quantum chemical calculations. A separate section is devoted to the isomers of Si_4R_6, which include novel tetrasilacyclobutenes and the diene analogues, the tetrasilabuta-1,3-dienes.

Introduction

One of the most interesting developments in organo-element chemistry of the past few years has been the preparation and complete characterization of the diaminocarbenes **1**, which were soon supplemented by the saturated ring compounds **4** and even the corresponding acyclic compounds.[1] Shortly thereafter, the stable or marginally stable silylenes **2** and **5**,[2] as well as germylenes with the same substitution pattern,[1] were successfully prepared. The di-aminogermylenes **7**, -stannylenes **8**, and -plumbylenes **9** have been known for a longer time and have since been shown to possess an extensive chemistry.[3] A correspondingly substituted silylene has now also been detected, although it is only stable in a matrix up to 77 K.[4]

A common feature of all these compounds is the presence of a free electron pair on the nitrogen atom, or on other
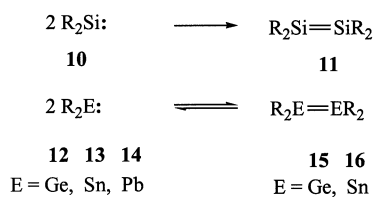

1 2 3
E = C, Si, Ge

4 5 6
E = C, Si, Ge

7 8 9
E = Ge, Sn, Pb
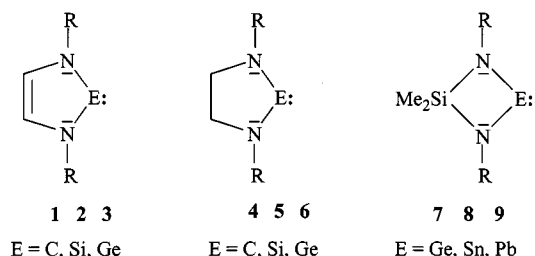
donor atoms as well, which can either allow delocalization, as in the five-membered rings of **1**−**3** or, in the case of saturated systems, can participate in π-interactions with electron-deficient centers, as in compounds **4**−**9**.[5] As a result, the tendency of these species to undergo dimerization with formation of homonuclear double bonds is rather low. The dialkyl, diaryl, or disilyl derivatives of silicon, germanium, tin, and lead behave differently: They do not experience any intramolecular donor stabilization and can thus undergo dimerization to afford the homonuclear double-bond systems of the disilenes, digermenes, and distannenes with varying degrees of ease.

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

$$2\ R_2Si: \longrightarrow R_2Si{=}SiR_2$$
$$\mathbf{10} \qquad\qquad \mathbf{11}$$

$$2\ R_2E: \rightleftharpoons R_2E{=}ER_2$$

12 13 14	**15 16**
E = Ge, Sn, Pb	E = Ge, Sn

17 R = 2,6-Et$_2$C$_6$H$_3$
     R' = tBu
18 R = R' = tBuMe$_2$Si

19 R = R' = tBuMe$_2$Si
20 R = tBu$_3$Si
     R' = I

21 R = 2,4,6-iPr$_3$C$_6$H$_2$

While most disilenes **11** are sufficiently stable towards dissociation into the silylenes **10**,[6] the tendency of the double-bond systems in **15** and **16** to undergo cleavage to the carbene analogues **12**−**14** increases on descending group 14 towards the heavier elements.[7] Thus, for example, only one distannene that retains its structural integrity in solution is known. In the case of lead, until recently merely a few dialkyl-, disilyl-, and diarylplumbylenes, but no diplumbenes R$_2$Pb=PbR$_2$, had been isolated. This behavior − which clearly deviates from that of alkenes − has been explained theoretically in terms of the varying nature of the double bond on descending the series. Thus, carbenes have either a triplet ground state (T) or a singlet ground state (S), with relatively small S → T transition energies. The familiar picture of a C−C double bond results from the approach of two triplet carbenes in the manner shown in Scheme 1.
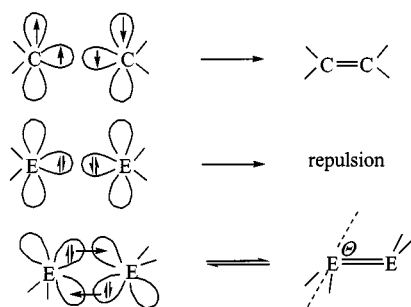
Scheme 1. Double-bond formation from two carbenes and their analogues

In contrast to the carbenes, all silylenes, germylenes, stannylenes, and plumbylenes characterized to date have exclusively singlet ground states, with the energy of the S → T separation increasing with increasing atomic mass of the group-14 element.[8] Thus, approach of two such singlet species in the manner shown in Scheme 1 should result in repulsion rather than in bond formation. However, if the two electron-sextet species are rotated with respect to one another, interactions between the doubly-occupied s orbitals and the vacant p orbitals can also lead to the creation of a double bond, which, in contrast to that in alkenes, arises by way of a double donor−acceptor adduct formation. This is accompanied by a *trans* bending of the substituents about the E=E vector, with the *trans*-bending angle Θ increasing appreciably on going to heavier elements.[9−12]

Since the results obtained up to 1994/1995 in the field of multiple bonding of group-14 elements have been covered in numerous review articles,[6,7] only some more recent developments, including the first diplumbene, the first tetrasilabutadiene, and some other isomers with the composition Si$_4$R$_6$, are included in the present survey.
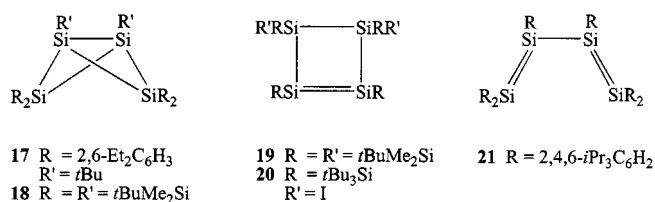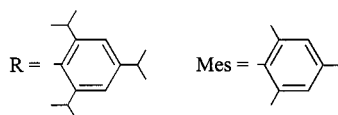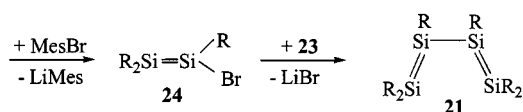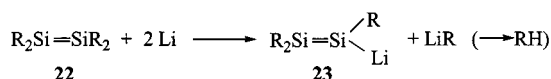
The Si$_4$R$_6$ Isomers

Since the isolation of tetramesityldisilene as the first molecule containing an Si−Si double bond in 1981,[13] numerous other compounds belonging to this class have been reported, although fundamentally new bonding systems are still rare. Recently, Kira et al. described the isolation of the first thermally stable cyclooligosilene **19** incorporating an Si=Si bond in the ring, albeit in very low yield, which was obtained by coupling of two oligosilanes.[14] Although compound **19** was found to be stable in the dark for an indefinite period, the action of visible light resulted in conversion to the tetrasilabicyclo[1.1.0]butane derivative, the butterfly-like skeleton of which had been described about 15 years earlier by Masamune et al. in relation to compound **17**.[15] Trapping experiments at low temperature indicated that the primary product of the coupling reaction was not the tetrasilacyclobutene **19**, but rather the tetrasilabicyclobutane **18**, which underwent conversion to **19** by 1,2-silyl group migration during work-up.[16] Although ring systems of this type are relatively new in molecular chemistry, the corresponding butterfly anions have long been known in solid-state chemistry. Thus, addition of two electrons to the tetrahedral anion [Si$_4$]$^{4-}$ leads smoothly to the tetrasilabicyclobutane system [Si$_4$]$^{6-}$ through cleavage of one bond, as is realized in the compound Ba$_3$Si$_4$.[17] By way of the same principle, Wiberg et al. recently obtained the tetrasilacyclobutene **20** in almost quantitative yield by reaction of the *tetrahedro*-tetrasilane (tBu$_3$SiSi)$_4$[18] with iodine.[19]

The isomer formed seemingly depends strongly not only on the nature of the substituents but also on the chosen synthetic route. The missing link in the series of simple compounds with the composition Si$_4$R$_6$, i.e. the tetrasilabuta-1,3-diene **21**, has been prepared in this laboratory in the following way. The action of excess lithium on the disilene **22**,[20] prepared photolytically from the trisilane R$_2$Si-(SiMe$_3$)$_2$ by the method of West and co-workers,[21] presumably furnishes the disilenyllithium compound **23**. Half of the formed **23** is converted by reaction with mesityl bromide to the bromodisilene **24**, which spontaneously reacts with the remainder of the formed **23** through intermolecular cleavage of LiBr to afford the tetrasilabutadiene **21** in 60% yield.[22,23]

Interestingly, a crystal structure analysis of the brownish-red compound **21** revealed that it adopts the *s-cis* arrangement in the solid state, which is rather less favorable[24] than the *s-trans* form, with a dihedral angle of 51° within the Si$_4$ skeleton. The Si−Si double bonds are slightly lengthened in comparison with the corresponding bonds in disilenes, while the formal single bond is markedly shortened in spite

$$R_2Si=SiR_2 + 2\,Li \longrightarrow R_2Si=Si\underset{Li}{\overset{R}{\diagdown}} + LiR\;(\longrightarrow RH)$$

22   **23**

$$\xrightarrow[-\,LiMes]{+\,MesBr} R_2Si=Si\underset{Br}{\overset{R}{\diagdown}} \xrightarrow[-\,LiBr]{+\,23}$$

24

21

R = (3,5-diisopropylphenyl)   Mes = (2,4,6-trimethylphenyl/mesityl)

of the bulky substituents. These data, together with the electronic spectrum in solution, which reveals a bathochromic shift of the longest wavelength absorption of 100 nm compared with that of the tetraaryldisilenes, indicate that a conjugation between the Si−Si double bonds is present in both phases.

25 $\xrightarrow{H_2O}$ **26**   **27**

$\downarrow$ (?) $\xrightarrow{H_2O}$ **21** $\xrightarrow{O_2}$
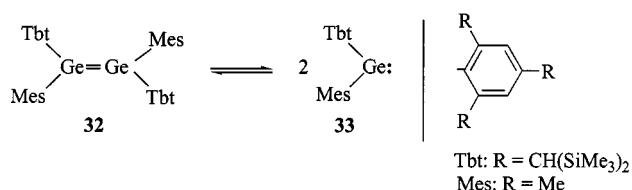
28 $\xrightarrow{mCPBA}$ **29**
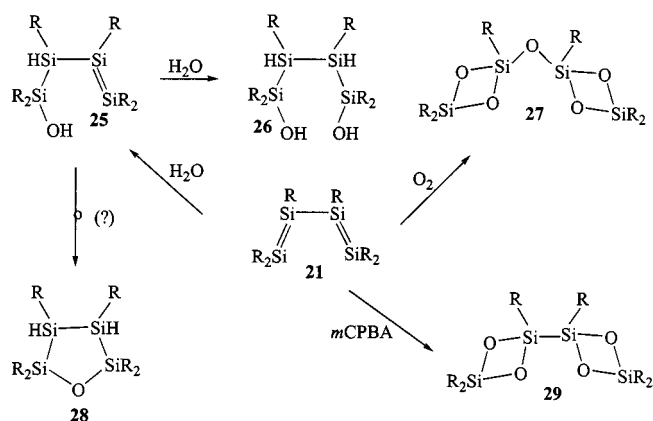
Although the *s-cis* form of compound **21** would appear to be ideally suited for Diels−Alder reactions, all attempts to achieve a [4 + 2] cycloaddition with C−C multiple bonds have failed.[25] The reason for this is probably the high steric shielding of the Si atoms in **21**, as well as the large 1,4 separation of about 540 pm. However, compound **21** does react readily with small molecules, as illustrated. For example, an initial 1,2-addition to furnish compound **25** occurs with water, which can be followed by a second 1,2-addition to afford **26**. Somewhat surprisingly, however, compound **26** does not exhibit any tendency to undergo condensation. Although the constitution of compound **28** has been confirmed by an X-ray crystal structure analysis, it cannot as yet be stated whether it is formed by rearrangement of **25** or by another route. The reaction of *meta*-chloroperbenzoic acid (*m*CPBA) with **21** proceeds through a three-membered ring intermediate [a bis(disilaoxirane)] to furnish bis(2,4-disila-1,3-dioxetane) **29** as the final product. With atmospheric oxygen, an additional insertion of oxygen into the formal Si−Si single bond with formation of **27** occurs; considering the steric shielding of this bond, this is a somewhat unexpected reaction.[23,26]

Germylenes, Digermenes

Stable dialkyl- or diarylgermylenes R_2Ge: (**30**), apart from Lappert′s compound[27] $[(Me_3Si)_2CH]_2Ge$:, have only become known in the past few years. Examples include, among others, the structurally confirmed molecules $(Me_3Si)_3C[(Me_3Si)_2CH]Ge$:[28] and $(2,4,6\text{-}tBu_3C_6H_2)_2Ge$:[29], of which the latter is converted in the presence of a Lewis acid or at high temperatures to a germaindane derivative by insertion of the germanium atom into one of the methyl groups of the *ortho-tert*-butyl substituents,[30] as well as the sterically extremely crowded $(2,6\text{-}Mes_2C_6H_3)_2Ge$: (Mes = $2,4,6\text{-}Me_3C_6H_2$).[31] The compound $[2,4,6\text{-}(CF_3)_3C_6H_2]_2Ge$: can only be mentioned with reservations since it has to be classified as an intramolecularly donor-stabilized germylene on account of the weak F···Ge contacts between the electron-poor germanium atom and the fluorine atoms of the *ortho*-CF_3 groups.[32]

$$2\,R_2Ge: \;\rightleftharpoons\; R_2Ge=GeR_2$$

30   R = alkyl, aryl, silyl   **31**
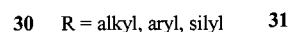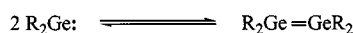
A comparatively large number of germylenes are stable in solution since some of the digermenes **31**, although stable in the solid state, dissociate to germylene molecules in solution. Whether monomeric germylenes with larger Ge···Ge separations or digermenes with a formal Ge−Ge double bond exist in the solid state probably depends on both the spatial requirements of the substituents bonded to the germanium atom and the possible donor properties of these groups. Thus, the aforementioned germylenes either bear very bulky substituent groups or, as in the case of the $2,4,6$-$(CF_3)_3C_6H_2$-substituted compound, experience a weak donor stabilization. Lappert′s germylene is an exception: It is stable in solution but exists as a digermene in the crystalline state in spite of the presence of very bulky substituents.[33]

$$Tbt\diagdown Ge=Ge\diagdown Mes \;\rightleftharpoons\; 2\;Tbt\diagdown Ge: \quad\quad$$
Mes ⁄   Tbt ⁄   Mes ⁄

32   **33**

Tbt: R = $CH(SiMe_3)_2$
Mes: R = Me

The usually facile cleavage of the Ge−Ge double bond to furnish two germylene molecules is most probably due to the low bond dissociation energy. Thus, a bond dissociation energy of merely 61.5 kJ mol^{-1} has recently been determined for the cleavage **32** → 2 **33** by variable-temperature electronic spectroscopy.[34] This is in accord with the variable Ge−Ge bond lengths in digermenes, which range from 221 to 246 pm, as well as with the *trans*-bent angles, which range from 45° to almost 0° (i.e. a planar structure). The shortest Ge−Ge bond length is observed in the digermene $Dep_2Ge=GeDep_2$ (Dep = $2,6\text{-}Et_2C_6H_3$), where the substituents have the lowest spatial requirements.[35] The *trans*-bent angle in this compound, 12°, is also small, and represents one of the lowest values yet found for a tetraaryldigermene. Even the slightest changes in the spatial require-

ments of the substituents can result in markedly different bond lengths and angles: Thus, the compound (E)-Mes-DipGe=GeMesDip (Dip = 2,6-iPr$_2$C$_6$H$_3$) has a Ge−Ge bond length of 230.1(1) pm and a bending angle of 36°.[36] These examples illustrate the difficulties in predicting the lengths and deformations of Ge−Ge double bonds, which can again be explained in terms of the flat potentials for bending angles and E=E bond lengths in homonuclear multiple bonds between the heavier elements of group 14.

34 SiR$_3$ = iPr$_2$MeSi
35 SiR$_3$ = iPr$_3$Si

36 R = 2-tBu-4,5,6-Me$_3$C$_6$H
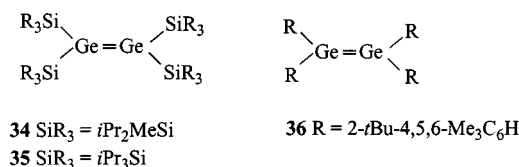
Recently, Kira et al. described some tetrasilyldigermenes, among which the structures of compounds **34** and **35** were characterized by X-ray crystallography. In agreement with theoretical calculations, which predict that electropositive substituents should favor a planar arrangement, these molecules exhibit small bending angles of 5.9° and 16.4°, while the Ge−Ge double bond lengths are surprisingly short in view of the bulky substituents, 226.8(1) pm in **34** and 229.8(1) pm in **35**.[37] However, the presence of electropositive substituents is not an essential prerequisite for such an arrangement, as demonstrated by the tetraaryldigermene **36**, which has an almost planar structure and a short Ge−Ge bond length of 225.21(8) pm.[38]
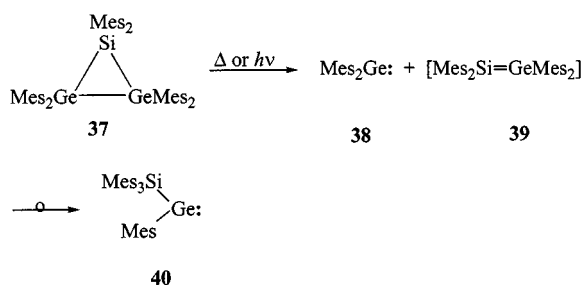

These examples further illustrate how difficult it is to correlate the substitution pattern about the Ge−Ge double bond with the molecular structure. Nevertheless, the existence of Si−Si and Ge−Ge double bonds cannot be questioned. On the other hand, stable compounds with heteronuclear double bonds between these elements are still unknown. In a series of papers, Baines et al. reported on the photolysis and thermolysis of the siladigermirane **37**, which resulted in regioselective conversion to the germylene **38** and the germasilene **39**, although the latter compound underwent rapid isomerization to the silylgermylene **40**. The presence of compounds **38**, **39**, and **40** in the reaction

mixture was confirmed by isolation of the corresponding products of trapping reactions.[39−42]
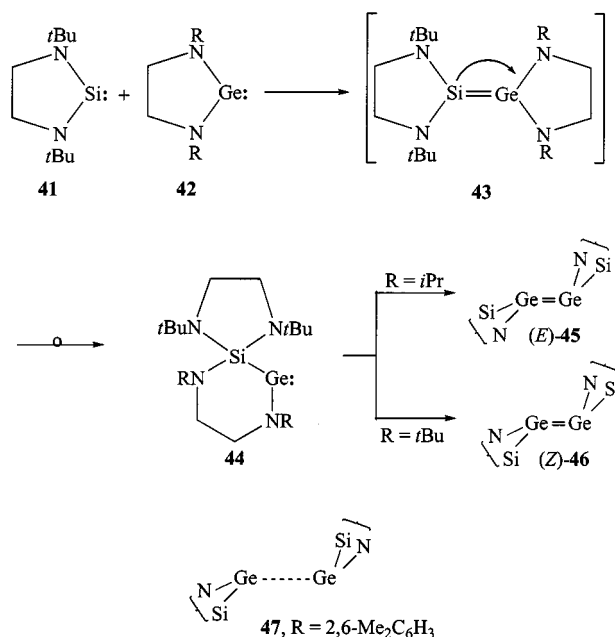
The potentially promising idea of allowing the marginally stable diaminosilylene **41**[2] to react with various diaminogermylenes **42**[1] as an approach to germasilenes yielded surprising results. It seems that in all cases an initial, loosely bound adduct **43** is formed between the electron-sextet species, which is then transformed into the novel aminosilylgermylenes **44** by insertion of the silicon atom into one of the Ge−N bonds. The conceivable subsequent reactions are again strongly influenced by the nature of the substituents R at the germanium atom. In the case of R = tBu, the digermene (Z)-**46** is formed; this compound has a very long Ge−Ge bond of 245.4(2) pm and pronounced *trans*-bent angles of 41.3° and 42.3°, which clearly exceed all previously known θ values.[43] On the other hand, with R = iPr the digermene (E)-**45** is obtained, which has an even longer Ge−Ge bond length than that in (Z)-**46**, as well as a markedly larger bending angle.[44] Finally, with the aryl substituent R = 2,6-Me$_2$C$_6$H$_3$, the germylene **47** is isolated. The Ge−Ge separation of 410 pm and the *trans*-bent angle of 14° are indicative of weak dispersive forces between neighboring germylene molecules.[44] In parallel to the investigations performed in this laboratory, Lappert et al. reported on an analogous insertion of a diaminosilylene into one of the Ge−N bonds of Ge[N(SiMe$_3$)$_2$]$_2$; the final product in this case being a germane.[45] The large Ge−Ge bond lengths in (E)-**45** and (Z)-**46**, and the only very weak interactions in **47**, are probably attributable to the substitution patterns in these compounds. Although the Ge−Si bond in the intermediate **44** promotes the formation of a Ge−Ge double bond, the Ge−N bonds also present hinder Ge−Ge contacts, with the overall result that the structural param-

eters described above represent a compromise between these opposing effects.

48
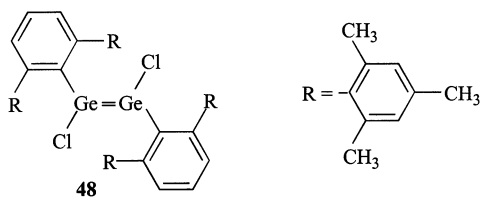
A similar situation is found in compound **48**, where each germanium atom bears an aryl group and a chlorine atom; in the solid state it exists as a dimer with a Ge−Ge bond length of 244.3(2) pm and a *trans*-bending angle of Θ = 39°.[31] A further candidate for an analogous dimer could be the germylene RGeCl (R = 2,4,6-*t*Bu$_3$C$_6$H$_2$), which is monomeric in solution but has yet to be examined in the solid state by X-ray crystallography.[46]

M = Li, Na   **49** E = Si; **50** E = Ge

49 + Ph$_3$C$^+$[BPh$_4$]$^-$ ⟶

51
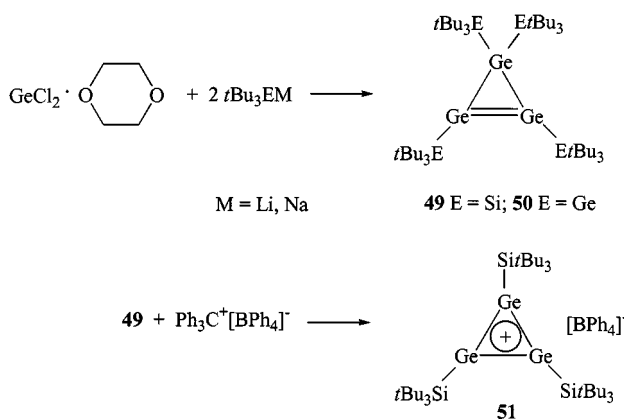
The cyclotrigermenes **49** and **50**, the first compounds with endocyclic Ge−Ge double bonds, were reported by Sekiguchi et al.,[47] who also generated and isolated the cation **51** from compound **49** by treatment with trityl tetraphenylborate.[48] An X-ray crystal structure analysis of the cyclotrigermenium salt revealed the presence of free germyl cations with a delocalized 2π-electron system, reminiscent of the cyclopropenium ion, with an equilateral triangular form.[48] The Ge−Ge bond lengths of 232.5 pm are intermediate between those of a single and a double bond.
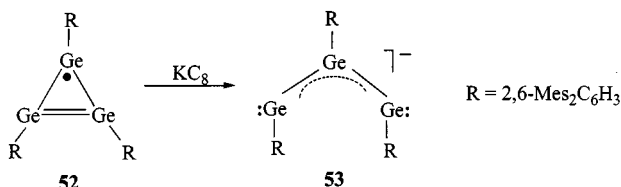

52   **53**   R = 2,6-Mes$_2$C$_6$H$_3$

Power et al. obtained another unusual compound similar to the cation **51** by dehalogenation of RGeCl (R = 2,6-Mes$_2$C$_6$H$_3$) with KC$_8$; the reaction furnished the cyclotrigermyl radical **52**. Although X-ray crystal structure analysis of **52** provided only limited details because of disorder problems, the EPR spectrum of the compound indicated the localization of the unpaired electron on one germanium atom. Further action of KC$_8$ on **52** led to the trigermyl

anion **53**, with a structure comparable to that of the allyl anion but with a very large Ge−Ge−Ge angle of 159.2°.[49]

Stannylenes, Distannenes

Lappert's distannene **54** was the first compound with a homonuclear multiple bond between two heavier atoms of group-14 elements to be prepared; however, its classification was at first difficult on account of the lack of suitable data for comparison.[9,50] The successful syntheses of stable disilenes and digermenes,[6,7] as well as the results of quantum chemical calculations,[9−12] were additionally needed to show that this molecule, with its *trans* bending of the substituents by 41° and the Sn−Sn bond length of 276.8(1) pm, a value approaching that of an Sn−Sn single bond, fits almost ideally into the series of homonuclear bonds between atoms of elements of this group.

54   **55**   **56**

R = CH(SiMe$_3$)$_2$ R = Si(SiMe$_3$)$_3$ R = 2-*t*Bu-4,5,6-Me$_3$C$_6$H
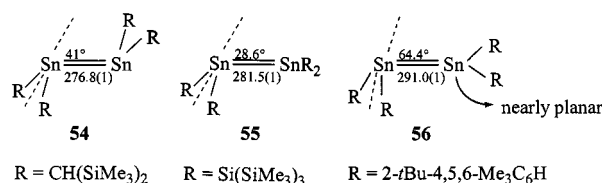
Although compound **54** was first prepared and characterized by X-ray crystallography in 1976,[50] almost twenty years passed before the isolation of **55** and **56**, two further distannenes that are also stable in the solid state. These three distannenes differ considerably in their spatial structures. While the parameters for **54** are akin to those theoretically calculated for the parent compound Sn$_2$H$_4$, the highly distorted compound **55** avoids the strain arising from the bulky substituents by means of a considerable torsion about the double bond of 63.2° and a small *trans*-bent angle of 28.6°.[51] The structure of **56** is even more unusual: The long Sn−Sn bond, the length of which even exceeds that of an Sn−Sn single bond by about 13 pm, as well as the differing environments of the substituents on the two tin atoms, are indicative of a zwitterionic character of the molecule according to R$_2$Sn$^+$→$^-$SnR$_2$, which may arise through a single donor−acceptor interaction between the fully occupied s orbital of one tin atom and the empty p orbital of the other. This hypothesis is supported by the observation that the Sn−C bond lengths at the formally negatively charged tin atom are appreciably longer than those at the tin atom bearing the positive charge.[52] However, these observations are apparently at variance with the ^{119}Sn CP-MAS NMR spectrum of crystalline **56**, which features only one signal at δ_{iso} = 819.[53]

In order to simulate the bonding situation in solid **56**, a nucleophilic carbene of the Arduengo type[1] was prepared in this laboratory according to the method of Kuhn and Kratz,[54] and was allowed to react with a diarylstannylene. In spite of the different binding partners, the resulting compound **57** exhibited great similarity to the distannene **56**.

Thus, the tin atom in **57** exhibits a strong pyramidalization, with a bending angle of 68.6°, and the molecule has

57 R = 2,4,6-*i*Pr₃C₆H₂   **58** R = 2-*t*Bu-4,5,6-Me₃C₆H
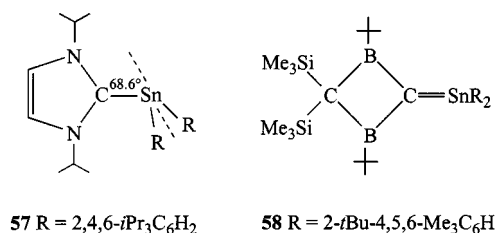
an extremely stretched Sn−C bond length of 237.9(5) pm.[55] In contrast, the stannaethene **58**, prepared for comparison purposes from an electrophilic cryptodiborylcarbene and a diarylstannylene, has completely planar environments at both the tin and the carbon atoms, with an Sn−C bond length of only 203.2(5) pm.[56]

$$R_2Sn{=}SnR_2 \rightleftharpoons 2\ R_2Sn{:}$$

59 crystal   **60** solution
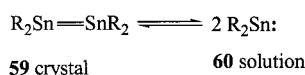
A common feature of all distannenes **59**, including the recently reported compound RR′Sn=SnRR′ [R = Si(Si-CH₃)₃, R′ = 2,4,6-(CF₃)₃C₆H₂],[57] is their stability in the crystalline state, even though they largely dissociate into stannylenes **60** in solution. An exception is the distannene **63**, first prepared by Masamune and Sita by thermolysis or photolysis of the cyclotristannane **61**, which retains its structural integrity in solution.[58]

61   R = 2,4,6-*i*Pr₃C₆H₂   **62**   **63**

63 + [X] ⟶

64 ; **65**
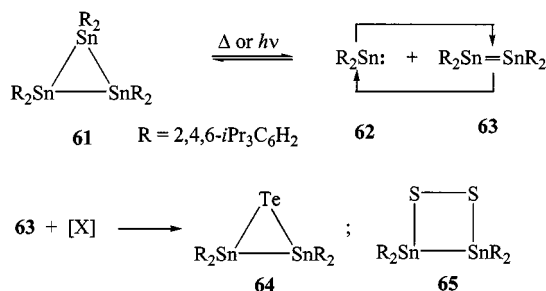
The existence of the Sn−Sn double bond in solution was demonstrated not only by variable-temperature ¹¹⁹Sn-NMR spectroscopy,[58,61] but also by trapping reactions with the heavier chalcogens to give, for example, the new ring systems of the telluradistannirane **64**,[59] or the unusual 1,2-dithiadistannetane **65**.[60] However, compound **63** cannot be isolated as a solid because at room temperature there is invariably some reversion to cyclotristannane **61** through generation of the stannylene **62** and its addition to **63**. Since the steric crowding of the aryl groups in distannene **63** is insufficient to prevent this reversion to cyclotristannane **61**, the isopropyl substituents in **63** were replaced by *tert*-butyl groups, and, after numerous unsuccessful attempts, dark-red crystals of the stannylene **66** were obtained by reaction of 2,4,6-*t*Bu₃C₆H₂Li with Sn[N(SiMe₃)₂]₂. This compound was found to exist as the monomeric stannylene both in solution and in the solid state. The spatial requirements of the substituents are apparently too great to allow a dimerization to the distannene in this case.[62]

Although the diarylstannylene **66** is stable in the crystalline state for an indefinite length of time, in solution a slow

$$R_2Sn{:} \longrightarrow RR'Sn{:} \xrightarrow{[Fe_2(CO)_9]}$$
66   **67**   **68**

R =   R' = CH₂−CMe₂−
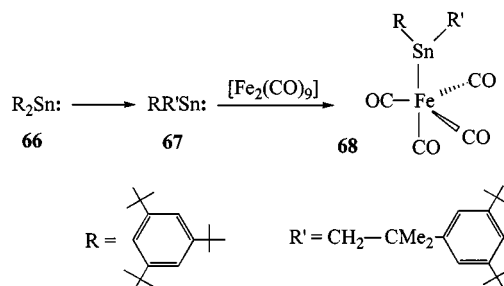
isomerization occurs, leading to the alkylarylstannylene **67**. Accordingly, all reactions with heavier chalcogens or transition metal substrates furnish exclusively products containing an aryl/alkyl-isomerized group R′.[63] One unusual result arose from the reaction of the stannylene with [Fe₂(CO)₉] or [Fe₃(CO)₁₂]: In the resulting iron complex **68** the stannylene **67** occupies an axial site, indicative of a strong σ-donor but weak π-acceptor character.[64,65]

It is of interest to note that **66** represents the first structurally characterized diarylstannylene that lacks donor stabilization. However, the stannylene [2,4,6-(CF₃)₃C₆H₂]₂Sn:, stabilized by weak F···Sn contacts, was known previously and had been observed in a second crystalline form involving weak Sn···Sn interactions.[66,67] Recently, Power et al. described the sterically crowded stannylene (2,6-Mes₂C₆H₃)₂Sn:, which, like **66**, cannot form a distannene in the solid state for steric reasons.[31] Structurally confirmed dialkylstannylenes are also rare, of which the cyclic compound SnC(SiMe₃)₂[CH₂]₂Cᵃ(SiMe₃)₂(Sn−Cᵃ) is mentioned as an example.[68]

66 + CS₂ ⟶   **69**   ⟶   **70**

R =   **71**
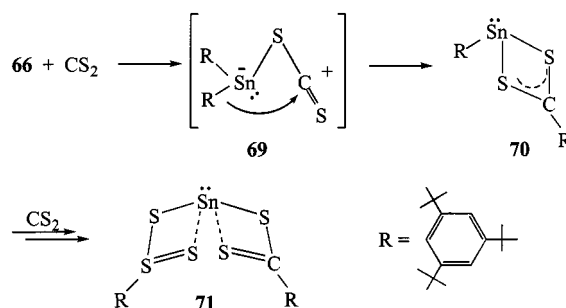
The only reaction of **66** to proceed without isomerization is that with carbon disulfide. This is probably due to the primary formation of an end-on or side-on adduct of the reacting species, **69**, followed by an aryl group migration to afford the tricoordinated stannylene **70**. A repetition of this process then leads to the final product, the tetracoordinated stannylene **71**; the structures of both compounds **70** and **71** were confirmed by X-ray crystallography.[69]

The trend towards decreasing E=E bond energies, which first becomes apparent in the digermenes, becomes more pronounced in the distannenes with the result that all distannenes, with the exception of compound **63**,[58] largely exist as the corresponding stannylenes in solution. Accordingly, the activation barrier determined for the equilibrium **59** ⇌ **60** (R = 2-*t*Bu-4,5,6-Me₃C₆H) amounts to just 34 kJ mol⁻¹.[53] As illustrated by the facile isomerization of **66**,

the Sn−C bonds are also appreciably more labile on account of their relatively large bond lengths.

72
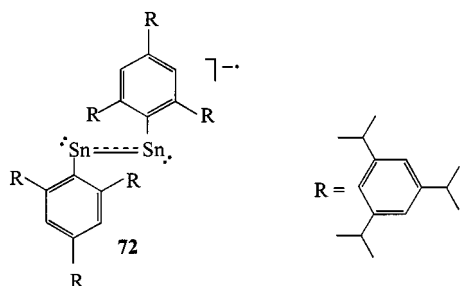
Power et al. have recently reported on a novel Sn−Sn bonding situation: Reaction of a sterically extremely crowded arylchlorostannylene with KC_8 furnished the radical anion **72**, which could be crystallized with $[K(THF)_6]^+$ or $[K(dibenzo-18-crown-6)(THF)_3]^+$ as the counterion. The anion exhibits an Sn−Sn bond length of 281.2(1) pm and a *trans*-bent angle of 95.2°. Together with the spectral data, these values are indicative of a molecular ion with an Sn−Sn bond order of 1.5 and a localization of the free electron pairs on the two tin atoms.[70]

The Elusive Diplumbenes

On account of their thermal lability and sensitivity to light, dialkyl- and diarylplumbanes were virtually unknown until recently. Although Lappert et al.[27][71] reported the isolation of the purple plumbylene **73** as early as 1973, its structure has only recently been determined.[72] In the solid state, compound **73** exists as a loosely bound dimer with a second plumbylene molecule and has a Pb⋅⋅⋅Pb separation of 412.9 pm with a *trans*-bent angle of 34.2°.


73   **74**   **75**
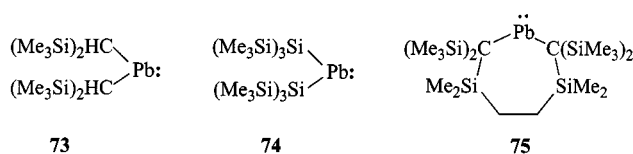
In contrast, the not too dissimilar cyclic plumbylene **75**[73] and the disilyl compound **74**[51] are strictly monomeric. The same holds for the diarylplumbylene **76**, which represents a borderline case between non-stabilized and donor-stabilized systems as a consequence of its weak Pb⋅⋅⋅F contacts,[74] and for the sterically extremely crowded diarylplumbylenes **77**[31] and **78**.[75]

The sterically less crowded diarylplumbylene **79** and the heteroleptic alkylarylplumbylene **80** do not interact with neighboring plumbylene molecules either.[76] The formation of **80** is of interest since it allows a comparison to be made with the molecules $(2,4,6-tBu_3C_6H_2)_2Ge$:[29] and **66**,[62] which were prepared by similar routes. The germanium compound is only stable at low temperature, while **66**, although stable for an indefinite length of time in the solid state, undergoes a slow isomerization in solution to furnish an alkylarylstannylene with the same substitution pattern as that in **80**. There is some evidence that the diarylplumby-


76 R = R' = CF₃
77 R = 2,4,6-Me₃C₆H₂, R' = H
78 R = R' = CH(SiMe₃)₂

79

80   R =   R' = CH₂−CMe₂
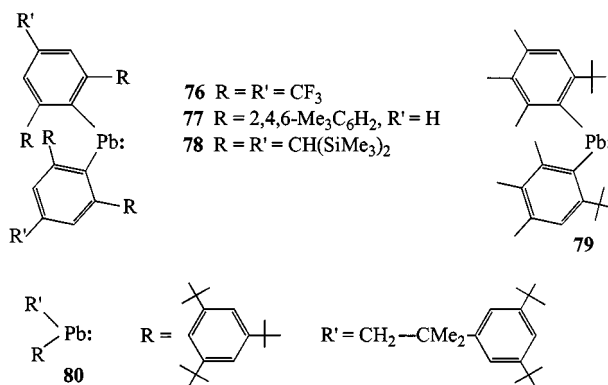
lene is formed initially in the reaction of 2,4,6-$tBu_3C_6H_2$MgBr with lead(II) chloride, but then undergoes rearrangement to compound **80** at temperatures above −30°C.[76]

81   **82**
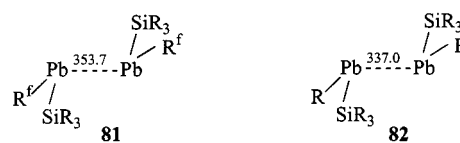
SiR₃ = Si(SiMe₃)₃; Rᶠ = 2,4,6-(CF₃)₃C₆H₂; R = 2-tBu-4,5,6-Me₃C₆H

The plumbylenes **73**−**80** all exist as V-shaped monomers in the crystal, with C−Pb−C angles ranging from 96.5° (**80**) to 117.1° (**75**). A first breakthrough with regard to lead−lead contacts between plumbylene molecules was realized with the recent isolation of the heteroleptic plumbylene dimer **81**, which has a Pb⋅⋅⋅Pb separation of 353.7(1) pm and a *trans*-bent angle of 40.8°.[57] Since intramolecular interactions between the fluorine atoms of the *ortho*-CF₃ groups and the lead atoms should weaken rather than favor a possible lead−lead interaction, another heteroleptic plumbylene has been prepared in this laboratory by reaction of the plumbylenes **74** and **79**. In the solid state, the thus formed plumbylene dimer **82** exhibits a short lead−lead separation of 337.0(1) pm and a *trans*-bent angle of 46.5°.[76] However, the observed lead−lead separations in **82**, and especially in **81**, are still markedly larger than the bond length of 295−300 pm calculated for the parent compound $H_2Pb=PbH_2$.[10,12,57]

83 solution   **84** crystal   R =
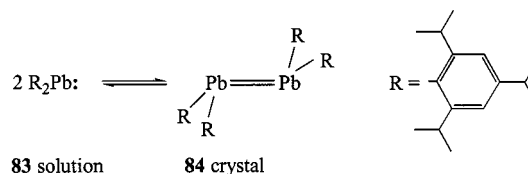
Since sterically less demanding aryl groups apparently favor lead−lead contacts between plumbylene molecules, the reaction of 2,4,6-$iPr_3C_6H_2$MgBr with lead(II) chloride at low temperature has been examined. This led to a violet solution of the plumbylene **83**, from which red crystals of the diplumbene **84** could be obtained. The existence of the first molecule with a lead−lead double bond is supported by the Pb−Pb bond length of 305.15(3) pm and the *trans*-

bent angles of 43.9° and 51.2°, which agree rather well with the calculated values.[77] Thus, with the discovery of compound **84**, homonuclear double bonds between all elements of group 14 are now known.
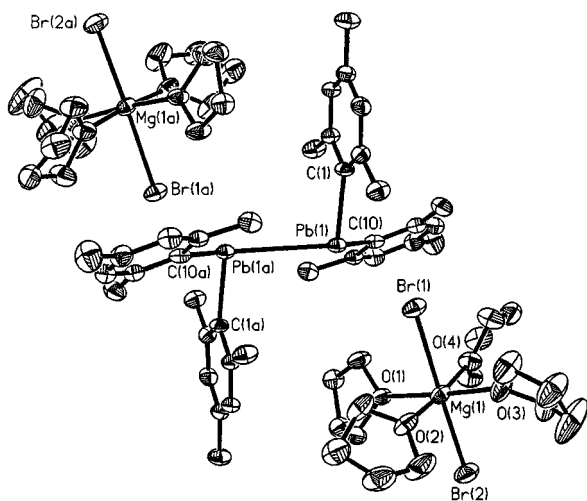

Figure 1. Molecular structure of the MgBr$_2$(thf)$_4$-stabilized plumbylene dimer (Mes$_2$Pb)$_2$

In order to examine whether even smaller aryl groups are capable of protecting a possible diplumbene from subsequent reactions, 2,4,6-Me$_3$C$_6$H$_2$MgBr was allowed to react with lead(II) chloride under otherwise identical conditions. Black crystals of compound **85** were obtained, a plumbylene dimer stabilized by MgBr$_2$(THF)$_4$, as shown in Figure 1. Although the Pb···Br contact is about 50 pm longer than a Pb−Br bond, it does have an appreciable influence on the molecular structure of **85**, as manifested in the *trans*-bent angle of 71.2° and the Pb···Pb separation of 335.49(6) pm.[78] These examples indicate that more interesting results may be expected in the field of plumbylene dimers and diplumbenes.

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