Account

Some recent advances in the chemistry of silicon and its homologues in low coordination states

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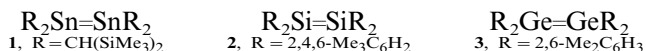Dedicated to Professor Edmunds Lukevics on the occasion of his 65th birthday

Abstract

This review summarises some recent results on synthesis, structures, and reactivity of the heavier analogues of carbenes, alkenes, and dienes. With the isolation of the first diplumbenes, the series $R_2E=ER_2$, E = C–Pb, has been completed. These double bond systems show enormous variations in the E=E bond lengths, E = Si–Pb, and the *trans*-bent angles. Furthermore, new families of multiple-bonded species have been discovered, such as a spiropentasiladiene, molecules with conjugated Si=Si, Ge=Ge, and Ge=C double bonds, and a diplumbylene RPbPbR. However, no stable compounds featuring homonuclear triple bonding between heavier Group 14 elements are known. Theoretical insights on the nature of such triple bonds as well as first attempts to achieve this target are discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Silicon; Germanium; Tin; Lead; Carbene analogues; Alkene analogues; Diene analogues; Multiple bonding

1. Introduction

Although homo- and heteronuclear multiple bonds play a dominant role in carbon chemistry, it was believed for a long time that the heavier homologues of carbon would not be able to form the corresponding bonds as a consequence of repulsive interactions of their fully occupied inner electron shells [1,2]. This dogma lost its presumed scientific basis at the latest in 1976 when Lappert et al. succeeded in synthesising the tetraalkyldistannene **1**, a compound with a homonuclear double bond between two tin atoms that is stable in the solid state [3].

$$R_2Sn=SnR_2 \qquad R_2Si=SiR_2 \qquad R_2Ge=GeR_2$$

1, R = CH(SiMe₃)₂   **2**, R = 2,4,6-Me₃C₆H₂   **3**, R = 2,6-Me₂C₆H₃

Syntheses of the first disilene **2** [4] and the first digermene **3** [5], and further compounds with homonuclear bonds, followed a short time later. In contrast, diplumbenes with a formal double bond between two lead atoms remained unknown until just a short time

ago. The question of whether triple bonds can exist between these atoms, in analogy to the acetylenes, is still unresolved. Not only calculations, but also the first successes in the formation of heteronuclear triple bonds indicate that this objective will be achieved. Nevertheless, it will probably take some time before the first compound with a homonuclear triple bond between the heavier atoms of Group 14 can be isolated and characterised.

In the case of the heavier homologues of the carbenes the situation is different, as some of these structures have been known for a very long time—not only as reactive intermediates, but also as stable molecules. Thermally stable silylenes, however, have only been known for a few years. Representative for many homologues of carbon in low coordination states, Okazaki and West stated in a review article on disilenes published in 1996, 'At this time, although details remain to be elucidated, it seems that most of the main kinds of reaction of disilenes, have been discovered' [6]. In fact, not only has a series of new bonding systems including novel Si=Si double bonds become accessible but also further unusual modes of reaction have been observed.

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And the above-mentioned authors themselves have made major contributions to these fields. Some of these new developments are presented in this account with special emphasis being placed on recent work from our laboratory.

## 2. Silicon compounds in low coordination states

2.1. Silylenes

Until recently, silylenes, R$_2$Si:, were considered—as a consequence of their outer shell electron sextets—to be extremely reactive intermediates that participate in cycloaddition, insertion, or also abstraction processes with numerous compounds. When the substituents R are small, the primarily obtained products are mostly unstable and undergo complicated rearrangements by mechanisms that have, in part, not yet been clarified [7].
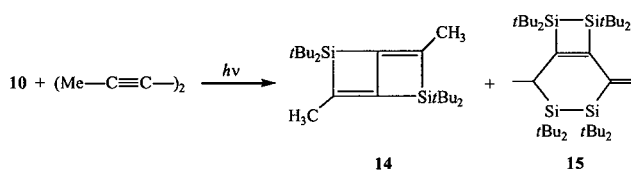
Although stable germylenes and stannylenes have long been known [8], the first stable diaminocarbene was not isolated until 1991 [9]. The first thermally
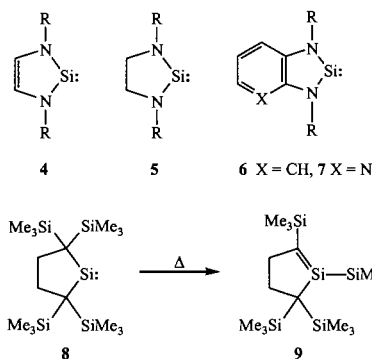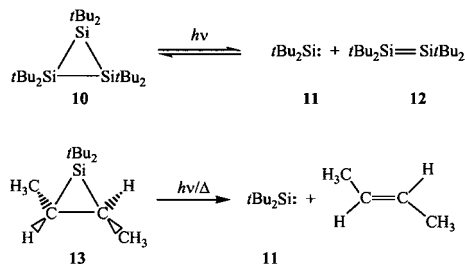
stable diaminosilylenes 4 [10], 5 [11], 6 [12], and 7 [13] as well as the dialkylsilylene 8, that is not stabilised by donor atoms [14], were synthesised a short time later. The diaminosilylenes 4, 6, and 7 exhibit remarkable thermal stabilities. In contrast, the saturated, five-membered ring silylenes 5 and 8 are only marginally stable and, in the case of 5, undergo tetramerisation (vide infra) or, in the case of 8, isomerisation to the silaethene 9 possessing an endocyclic Si=C double bond (Scheme 1). In spite of their aromatic stabilisation, the silylenes 4, 6, and 7 are very reactive, participating in a series of reactions that have recently been summarised in several review articles [15].

In spite of the presence of the two *tert*-butyl groups, the silylene 11 has only a short life-time but even so enables compounds to be prepared, for example, by [2 + 1] cycloadditions to multiple bond systems, that are difficult to access by other routes. Silylene 11 can be obtained either by photolysis of the cyclotrisilane 10, where it is formed together with the marginally stable disilene 12 [16], or by thermolysis or photolysis of the silirane 13 [17] (Scheme 2).

The high reactivity of the intermediates 11 and 12 obtained photolytically from 10 is demonstrated by their reactions with di- and polyynes from which different products can be isolated in dependence on the irradiation time. For example, photolysis of 10 in the presence of hexa-1,3-diyne furnishes the bicyclic compounds 14 and 15, that are presumably formed via [2 + 1] or [2 + 2] cycloadditions of 11 and 12 to the acetylenic tripe bonds [18] (Scheme 3).

Insights into the reactivity of 11 are provided by its reaction with 2,2,7,7-tetramethylocta-3,5-diyne, from which the C–C linked bissilirene 16 can be isolated. Renewed photolysis of 16 furnishes the bicyclic analogue, 17, of 14 [19]. The reaction behaviour of the intermediates 11 and 12 is even more transparent when the photolysis of 10 in the presence of an octa-1,3,5,7-tetrayne is considered. This reaction gives three products. [2 + 2] Cycloaddition of the disilene 12 to the two inner triple bonds of the tetrayne leads to product 18 having a *cis*-butadiene unit bridged by two disilene moieties. More surprising is the addition of a silylene 11 molecule to each of the four C≡C triple bonds to afford the C–C linked quatersilirene 19 whose carbon skeleton has the *s−cis−trans−cis* configuration, apparently in order to minimise the steric interactions between the bulky *tert*-butyl groups. Similar to the case with compound 16, increasing the photolysis time here results in the formation of product 20 in which both internal silirene units have again rearranged to a bicyclic structure [20] (Scheme 4).
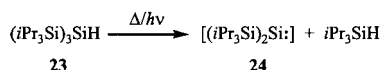
It is worthy of note that the reactions of the silylene 11 with di- and tetraynes show close similarities with the corresponding reactions of titanocene and zirconocene [21]. In contrast, although the reactions of a

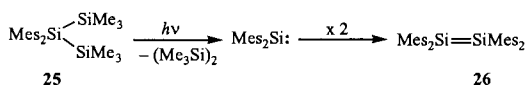

Scheme 1.
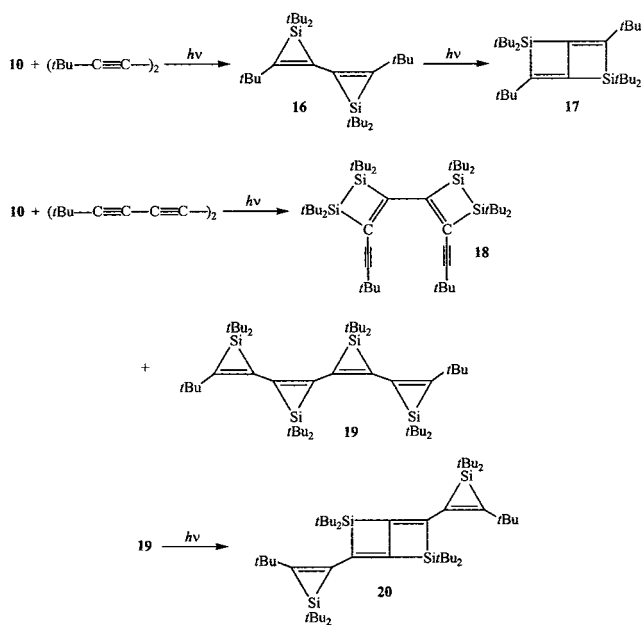
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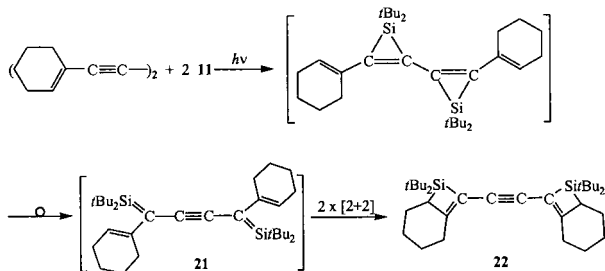
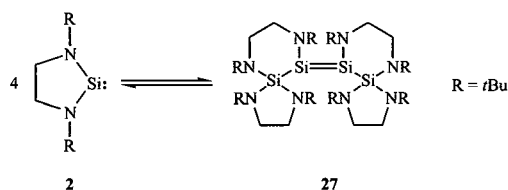Scheme 3.

Scheme 4.

Scheme 5.

Scheme 6.

Scheme 7.

Scheme 8.

diarylgermylene with dienes appear to afford primary products of the same type as **16**, the latter do not rearrange to bicyclic species of the type **14** or **17** but

rather furnish acetylene-linked bis(germaethenes) (see below). We thus addressed the question if analogous compounds with conjugated Si=C double bonds would be at least detectable indirectly. In fact, the reaction of photochemically generated **11** with the 1,4-bis(cyclohex-1-enyl)-substituted diyne did furnish compound **22**, the formation of which can be explained most simply by a twofold [2 + 2] cycloaddition of the acetylene-bridged bis(silaethene) **21** to the endocyclic double bonds of the two cyclohexene rings [22] (Scheme 5).

All previously known silylenes exist exclusively in a singlet electronic ground state. On the basis of density functional calculations, Apeloig et al. have recently predicted that the triplet state of bis(triisopropylsilyl)silylene **24** lies 1.7 kcal mol^{-1} below the lowest singlet state [23]. In an attempt to confirm this prediction experimentally, the silylene **24** was generated photochemically or thermally from the silane **23** and allowed to react with various substrates (Scheme 6). In spite of the theoretical prediction of a triplet ground state for **24**, stereospecific addition to *cis*- and *trans*-2-butene was observed [24]. With even bulkier substituents, which would make a larger opening of the RSiR angle possible, triplet silylenes should become accessible. One such suitable candidate would perhaps be the compound (*t*-Bu₃Si)₂Si:.

2.2. Novel acyclic and cyclic disilenes

The first compound with a Si=Si double bond, the classic disilene **26**, was prepared 20 years ago by dimerisation of dimesitylsilylene generated photolytically from the trisilane **25** [4] (Scheme 7).

Since then, over 40 more disilenes have been prepared and more than half of them have been structurally characterised. Most of these compounds are tetraaryldisilenes, although some examples with alkyl, silyl, or amino substituents are also known [25]. Only a few of the more recent compounds will be discussed here, either having been prepared by an unusual route or possessing a novel substitution pattern.

Four, rather than two, molecules of the marginally stable diaminosilylene **5** combine to form the diaminodisilyldisilene **27** that exists in a dynamic equilibrium with the silylene **5** (Scheme 8) [26]. The reaction sequence presumably proceeds through a loose adduct of two silylene molecules that form an aminosilylsilylene in a subsequent step. Dimerisation of two molecules of this silylene should then afford the disilene **27**. In this case, theoretical calculations support the assumption that **27** is more stable than the putative tetraaminodisilene intermediate [26] (Scheme 8).

On the other hand, the diaminosilylene **29**, obtained photolytically from the silirene **28**, does not form the bridged dimer **30** expected from earlier theoretical calculations [27] but rather furnishes the disilene **31**, ac-
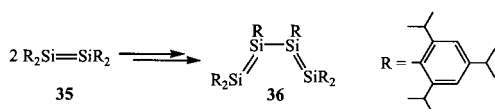
cording to the results of variable-temperature electronic spectroscopy (Scheme 9) [28]. More recent theoretical calculations show that **31** is a viable molecule although it is better described not as an Si=Si double bonded species but as a weak adduct between two silylene species with a very long Si–Si separation of 2.472 Å [29].
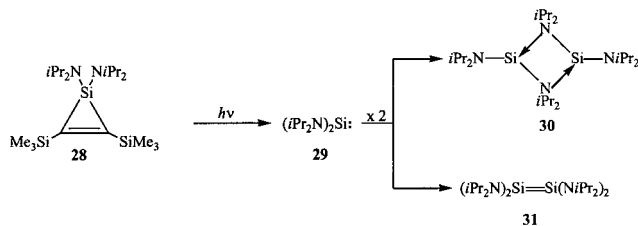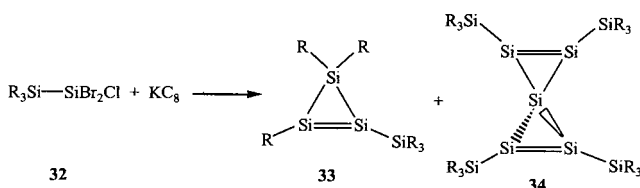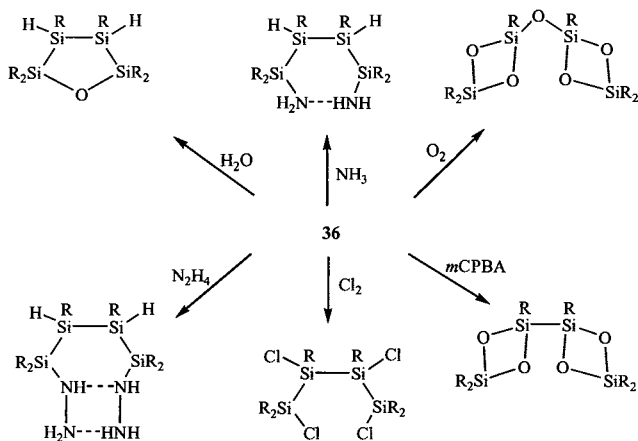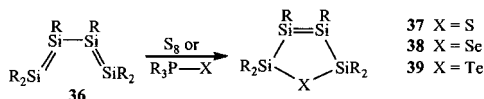
Perhaps even more unusual is the formation of the spiropentasiladiene **34**, obtained together with the main product **33** [30], by the reductive elimination of halogen from the silane **32** [31] (Scheme 10). Curiously, the corresponding, stable carbon analogues have not yet been isolated. The selection of compounds presented here holds the promise that the chemistry of the disilenes will continue to present us with more surprises in the future.

2.3. Hexaaryltetrasilabuta-1,3-diene

We recently prepared the first and, as yet, only tetrasilabuta-1,3-diene **36** from the tetraaryldisilene **35** by a sequence of metallation, halogenation, and coupling reactions [32] (Scheme 11).

In contrast to the analogous carbon compounds which mostly prefer the s–trans configuration, **36** exists in the s–cis form with a dihedral angle for the Si_4 skeleton of 51°. Conjugation between the two Si=Si double bonds has been confirmed by electronic spectroscopy; the band at longest wave length experiences a bathochromic shift of more than 100 nm in comparison to those of disilenes with analogous substitution patterns [32].

Although **36** exists in the solid state and in solution as the s–cis (s–gauche) form that should favour [4 + 2] cycloadditions of the Diels–Alder type, to date all reactions with olefins, acetylenes, and the C=O bonds of ketones have remained unsuccessful. However, compound **36** reacts readily with small molecules such as, for example, water [33], ammonia [34], hydrazine [35], chlorine [34], or oxygen [33] by twofold 1,2-addition or cycloaddition reactions (Scheme 12).

Treatment of **36** with sulphur or triphenylphosphane selenide and telluride affords five-membered heterocycles with endocyclic Si=Si double bonds. In analogy to the reaction of disilenes, the reaction sequence could be initiated by a [2 + 1] cycloaddition reaction of a chalcogen atom to one of the Si=Si double bonds, followed by rearrangement of these intermediates into the presumably less strained five-membered rings **37–39** (Scheme 13) [36].

In contrast to the attempted cycloadditions of **36** to several multiple bonds, the reaction of the tetrasilabutadiene with maleic anhydride **40** furnished the tetracyclic compound **41** in high yield. It can be assumed that the reaction sequence is initiated by the [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 **41** (Scheme 14) [37].
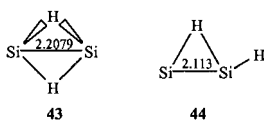
Since compound **40** apparently exhibits a high reactivity towards Si–Si multiple bonds, we also examined its reaction with the disilene **35**, and obtained the bicyclic compound **42** in high yield [37]. Such a reaction

Scheme 9.

Scheme 10.

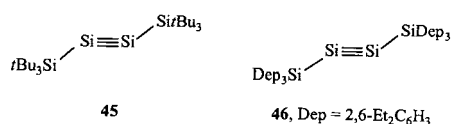Scheme 11.
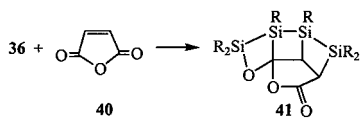
Scheme 12.
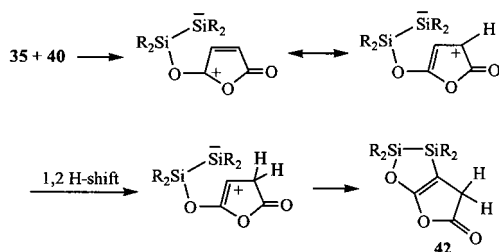
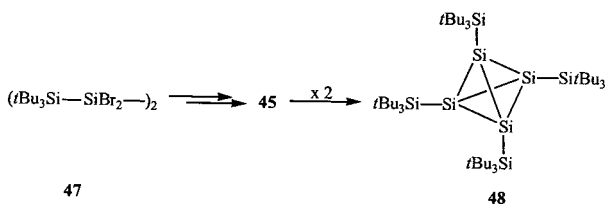Scheme 13.

Scheme 14.

Scheme 15.

Scheme 16.

Scheme 17.

Scheme 18.

mode has not previously observed in disilene chemistry. The closest precedent is the reaction of Si=Si double bonds with epoxides that proceeds through a comparable mechanism leading, among others, to the formation of similar products, albeit with saturated five-membered rings (Scheme 15) [38].

2.4. In quest of disilynes

Stable molecules containing a silicon–silicon triple bond are still unknown. Lischka and Köhler were the first to predict that the parent compound Si_2H_2 would not possess an Si≡Si triple bond like its group homo-logue acetylene C_2H_2, but should rather exist in the di-bridged $Si_2(H)_2$ form 43 [39]. In fact, the existence of the di-bridged molecule 43 could experimentally be demonstrated by submillimeter spectroscopy of a silane plasma cooled to −196 °C [40]. Later, the mono-bridged form 44 was also observed experimentally [41] (Scheme 16).

According to density functional theory calculations, electropositive silyl groups R_3Si with very voluminous R groups should be promising candidates to make disilynes synthetically available. The molecules 45 and 46 may be mentioned here as examples [42] (Scheme 17).

Both molecules 45 and 46 should be relatively stable towards attack by reactive species as well as against dimerisation. However, Wiberg et al. investigated the dehalogenation of the tetrasilane 47, which would presumably involve the disilyne 45 as an intermediate but this compound spontaneously reacts further to afford the tetrahedro-tetrasilane 48 [43] (Scheme 18).

To avoid the dimerisation, the new terphenyltrifluorosilanes 49 and 2,6-$Tip_2C_6H_3SiF_3$, Tip = 2,4,6-i-$Pr_3C_6H_2$, were synthesised and their reduction behaviour was investigated in detail. Reduction of 49 with sodium furnished a highly reactive intermediate (a disilyne?) 50 which resulted in a C–C insertion reaction and the formation of 51 as the final product [44] (Scheme 19).

Very recently, Nagase et al. reported on the results of density functional and ONIOM methods under the title 'Do bulky aryl groups make stable silicon–silicon triple bonds synthetically accessible?'. According to these calculations the molecules Ar*Si≡SiAr*, Ar* = 2,6-bis(2,4,6-tri-iso-propylphenyl)phenyl, and TbtSi≡SiTbt, Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl should be promising candidates to achieve this target. The molecules are stable towards isomerisation to the rearranged $SiSiR_2$ compounds and also to the facile dimerisation reaction. On the other hand, the dimerisation of 45 to the tetrahedrane 48 is exothermic by 80 kcal mol^{-1} [45].
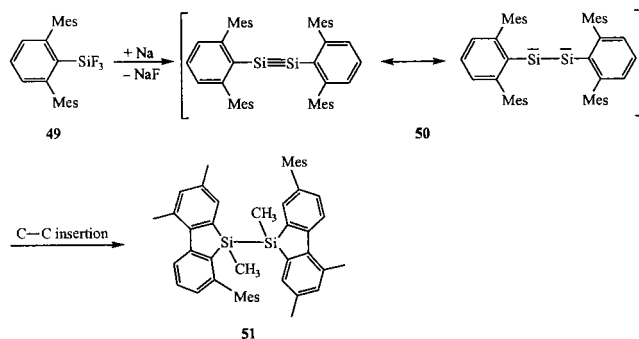
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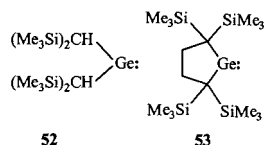
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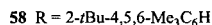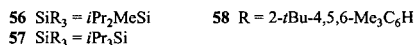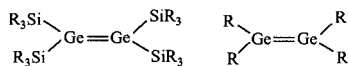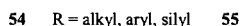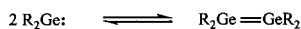
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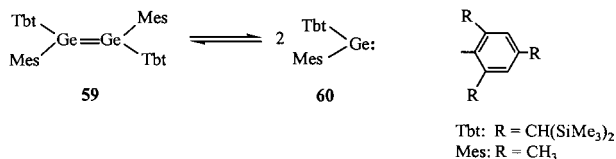
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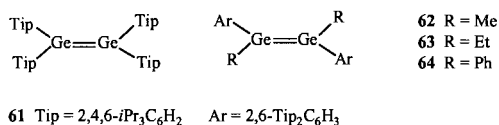
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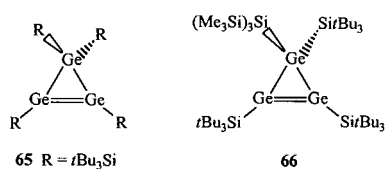
Scheme 24.
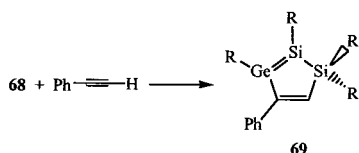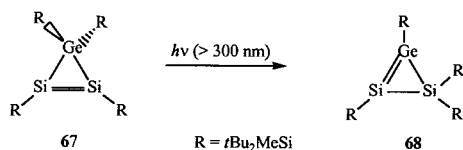
Scheme 25.

3. Germanium compounds in low coordination states

3.1. Germylenes and digermenes

Stable dialkyl- or diarylgermylenes were very rare until just recently. Although compound **52** was prepared in 1976 [46], further representatives of this class were first prepared in the past few years. These include, for example, the molecules $(Me_3Si)_3C[(Me_3Si)_2CH]Ge$: [47], $(2,4,6-t-Bu_3C_6H_2)_2Ge$: [48], $[2,4,6-(CF_3)_3C_6H_2]_2Ge$: [49], and the sterically extremely overcrowded species $(2,6-Mes_2C_6H_3)_2Ge$:, Mes $= 2,4,6-Me_3C_6H_2$ [50]. Another new example is the cyclic analogue, **53**, of **52** [51] (Scheme 20).

Although the above-mentioned substances are monomeric both in solution and in the solid state, there are some compounds that exist predominately in solution as the germylenes **54** but dimerise in the solid state to the digermenes **55** [52] (Scheme 21).
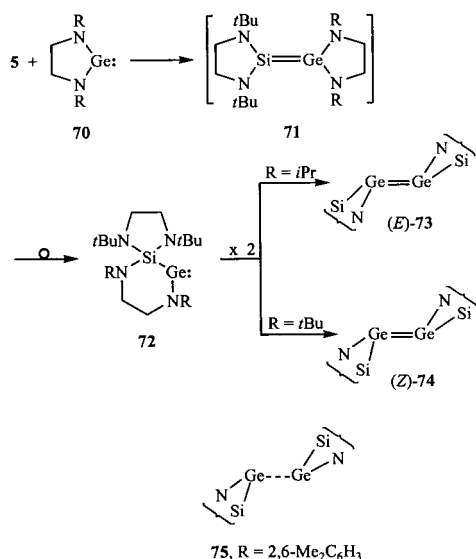
Examples of this behaviour are shown by the germylene **52** [53], compound **58** [54], and the very recently described tetrasilyldigermenes **56** and **57** [55]. A particular feature of the tetraaryldigermene **58** is its almost planar arrangements of the substituents at the two germanium atoms and the short Ge=Ge bond length of 225.21(8) pm (Scheme 21).

The generally easy cleavage of the Ge=Ge double bond in solution is attributed to the low bond dissociation energy which has been determined, for example, as merely 61.5 kJ mol^{-1} for the equilibrium **59** $\rightleftharpoons$ **60** [56] (Scheme 22).

However, it is difficult to predict whether digermenes dissociate to germylene molecules 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 in spite of similar or even higher spatial demands of the substituents. Thus, for example, the digermene **61** exists predominantly in the undissociated state at room temperature [57–59]. The terphenyl-substituted digermenes **62**–**64** are also stable in solution [60] (Scheme 23). The compound Ar(Cl)Ge: is worthy of note, since it exists in the solid not only as the V-shaped germylene molecule but also as the Ge–Ge linked dimer. This is of interest since the corresponding compounds of the heavier homologues exist as chlorine-bridged dimers [50,60]. In contrast, bis[2,6-bis(1-naphthyl)phenyl]germylene is, as expected, strictly monomeric both in solution and in the solid state [61].

Unlike the acyclic digermenes, molecules with endocyclic Ge=Ge double bonds are still rare. Two such examples are shown in Scheme 24. An unusual feature of the cyclotrigermene **66** is the *cis*-configuration of the substituents at the Ge=Ge double bond since all other known digermenes exhibit a more or less pronounced *trans*-bending [62,63] (Scheme 25).

Scheme 26.

Scheme 27.

digermenes (*E*)-**73** and (*Z*)-**74** [67,68]. Both molecules exhibit extremely long Ge=Ge bond lengths and the largest *trans*-bent angles observed to date. When the alkyl substituents on the nitrogen atoms of the germylene are replaced by aryl groups, the germylene **75** can be isolated. In spite of the large separation of 410 pm between the germanium atoms of neighbouring germylene molecules, the presence of a symmetry centre on the Ge–Ge bond axis as well as the *trans*-bending angle of 14° are suggestive of weak dispersive forces between the germanium atoms [68].

Only a few more recent examples of the reactions of germylenes and digermenes are described here. Ando et al. [69] had reported that the reaction of the digermene **61** with diazomethane proceeded through a [2 + 3] cycloaddition with subsequent cleavage of N_2 to furnish a digermirane that was isolated in 6% yield. Under the conditions used in our laboratory, the reactions of **61** with diazomethane as well as with trimethylsilyldiazomethane afforded the [2 + 1] cycloadducts **76** and **77** in high yields [59] (Scheme 27).

The reaction of the germylene **78**, formed from the digermene **58** in solution, with 1,3-diynes also follows a remarkable course to furnish the products **79** and **80**. The conjugation of the two Ge=C double bonds across the linking acetylene bridge is rather reflected in the UV–vis spectra than in the bond lengths. The absorptions at longest wave length of 518 nm for **79** and 595 nm for **80**, in comparison to those of the simple germaethenes [70], are bathochromically shifted by about 100 nm or more [71]. In analogy to the formation of C–C-linked bissilirenes of the type **16**, it may be assumed that the reaction is again initiated by a twofold [1 + 2] cycloaddition of the germylene **78** to the two triple bonds of the 1,3-diyne. Unlike the bissilirenes, however, the next step does not involve a rearrangement to bicyclic species of the type **17** but rather affords the acyclic molecules **79** and **80** through cleavage and reformation of bonds.

However, the conjugation between the two double bonds does not result in a higher reactivity. Thus, for example, these products do not react with acetylenes or phosphaalkynes whereas simple germaethenes furnish a palette of new compounds on reaction with these substrates [52]. Only with the *ortho*-benzoquinone **81** did a smooth, twofold [2 + 4] cycloaddition occur to afford the sterically extremely overcrowded compound **82** [72] (Scheme 28).

Similar to the reaction of the germylene **78** with diynes, the addition of this molecule to phosphaalkynes is also remarkable. While the reactions of dialkylsilylenes or dialkylgermylenes with phosphaalkynes proceed through [1 + 2] cycloadditions to afford three-membered rings systems containing a P=C double bond [73,74], the corresponding reaction of **78** furnishes a novel four-membered ring system containing a P=C

The recently synthesised disilagermirene **67** represents not only the first preparation of an unsaturated three-membered ring system containing silicon and germanium atoms in the ring but also the first example of a photochemically induced isomerisation with silyl group migration to furnish the three-membered ring system **68** [64]. The latter is the first stable compound to possess an Si=Ge double bond. Equally surprising as the isomerisation is the reaction of **68** with phenylacetylene which proceeds through several steps to give finally compound **69**. The latter contains a heterodiene skeleton within an unsaturated, five-membered ring. Unexpectedly, the electronic spectrum of **69** did not reveal any signs of conjugation between the two double bonds [65] (Scheme 26).

Another promising concept for the preparation of germasilenes appeared to be the reaction of the marginally stable diaminosilylene **5** [11] with various diaminogermylenes [66]; however, these reactions did not lead to the anticipated results. Only the action of the cyclic silylene **5** on the germylene **70** led to an unusual reaction sequence. Similar to the formation of the disilene **27**, the reaction sequence in this case is also probably initiated by a loose adduct **71** of the starting materials, followed by a rearrangement to the aminosilylgermylene **72**. Dimerisation of two of these germylenes then leads to the (*E*)- or (*Z*)-configurated

double bond with an additional *exo*-cyclic Ge=C double bond. Presumably this reaction sequence also involves an initial, unstable cycloadduct **83**, which then yields the isolated product **84** through opening of the P–Ge bond and subsequent dimerisation [75] (Scheme 29).

3.2. Hexaaryltetragermabuta-1,3-diene

Recently, we obtained the tetrasilabuta-1,3-diene **36** (see Section 2.3), the first and to date only molecule containing conjugated Si=Si double bonds [32]. We then addressed the question if an analogous compound with conjugated Ge=Ge double bonds would be accessible by following a similar synthetic approach.

As a starting compound we chose the digermene **61** whose structural integrity, according to previous investigations, is retained in solution [57–59]. Treatment of **61** with lithium did not afford the lithium compound **86** but instead we obtained the ionic compound **85** which

Scheme 28.

Scheme 29.

Scheme 30.

contains an allyl-like Ge_3 ion as part of a four-membered ring [76].

Shortening the reaction time with lithium to such an extent that most of the digermene **61** had reacted before the formation of **85** could become the main reaction. This approach did indeed lead to compound **86**. Subsequent reaction of **86** with an aryl bromide such as mesityl bromide presumably resulted in the bromine derivative **87**, from which compound **88** was formed by intermolecular coupling under elimination of LiBr. Similar to **36**, the tetragermabutadiene **88** adopts the *s−cis* (*s−gauche*) form with a dihedral angle at the Ge_4 framework of 22.5° [76] (Scheme 30). In harmony with theoretical calculations for the parent compound Ge_4H_6 [77], both Ge=Ge double bonds display a pronounced *trans*-bending of the substituents away from the respective Ge=Ge vectors.

The conjugation of the two Ge=Ge double bonds is confirmed by the electronic spectrum of the dark blue solution of **88** in *n*-hexane. It shows a longest wavelength absorption at 560 nm, which, compared with the yellow or orange digermenes, corresponds to a bathochromic shift of about 140 nm.
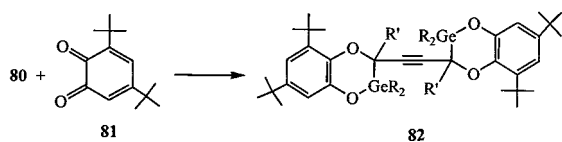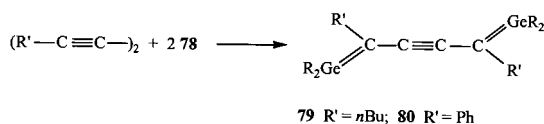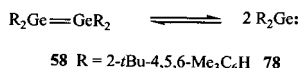
3.3. Triply bonded germanium compounds

Like the disilynes, molecules with a homonuclear Ge≡Ge triple bond are still unknown. However, the advances realised in the synthesis of compounds with heteronuclear triple bonds of germanium hold promise that the formation of such systems may indeed be possible.

Power et al. recently developed a simple access to the germylene complexes **89**–**93** containing a transition metal–germanium triple bond: reaction of the heavily substituted terphenylgermanium(II) chlorides with cyclopentadienyltricarbonylmetallates of Group 6 metals furnished red crystals of these complexes. The triple bond description is justified on consideration that a Ge≡M bond is formed from a threefold interaction of the three frontier orbitals from the 15-electron moiety $M(\eta^5\text{-}C_5H_5)(CO)_2$ and the three valence orbitals of the three-electron fragment ArGe which combine to generate a stable 18-electron complex [78,79].

Filippou et al. presented another access to transition metal–germylyne complexes, reaction of the tungsten complex *trans*-[W(dppe)$_2$(N$_2$)$_2$] [dppe = 1,2-bis(diphenylphosphenyl)ethane] with the germanium(II) halides Cp*GeX furnished the complexes **94**–**96**; the structure of **94** was characterised by X-ray crystallography. As with the compounds **89**–**92**, the pronounced shortening of the W–Ge separation is indicative for a triple bond [80,81] (Scheme 31).

Although still not isolated, germynes, molecules with a carbon–germanium triple bond, now seem to be within reach. Photolysis of the donor-stabilised

$$ArGeCl + Na[M(CO)_3\eta^5\text{-}C_5H_5] \xrightarrow[-CO, -NaCl]{} [ArGe\equiv M(CO)_2\eta^5\text{-}C_5H_5]$$

89 M = Mo, Ar = 2,6-Mes$_2$C$_6$H$_3$
90 M = W, Ar = 2,6-Mes$_2$C$_6$H$_3$
91 M = Cr, Ar = 2,6-Tip$_2$C$_6$H$_3$
92 M = Mo, Ar = 2,6-Tip$_2$C$_6$H$_3$
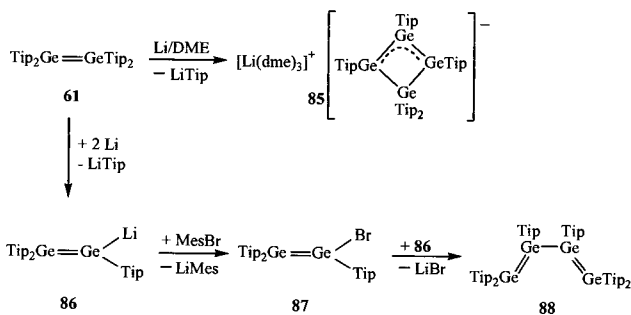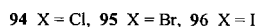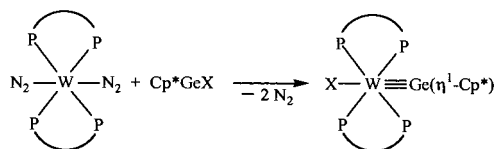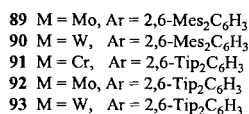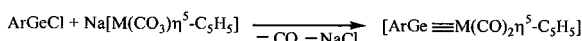**93** M = W, Ar = 2,6-Tip$_2$C$_6$H$_3$

94 X = Cl, **95** X = Br, **96** X = I

Scheme 31.

$$Ar\ddot{G}eC(N_2)SiMe_3 \xrightarrow[-N_2]{h\nu} [ArGe\equiv CSiMe_3] \leftrightarrow Ar\bar{G}e\text{---}\bar{C}SiMe_3]$$

97   **98**

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

98 + ROH ⟶ [ArGe=CHSiMe$_3$] $\xrightarrow{ROH}$ ArGe—CH$_2$SiMe$_3$

99   R = Me, tBu   **100**

Scheme 32.

101   **102**

103 Ar = 2,4,6-tBu$_3$C$_6$H$_2$
104 Ar = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$

103 ⟶   **105**   R = —CH$_2$—CMe$_2$—

Scheme 33.

106   **107** X = I; **108** X = N(SiMe$_3$)$_2$

Mes = 2,4,6-Me$_3$C$_6$H$_2$
Tip = 2,4,6-iPr$_3$C$_6$H$_2$

Scheme 34.

109 R = 2,6-Tip$_2$C$_6$H$_3$ **110**

109 + iBu$_2$AlH ⟶   **111**
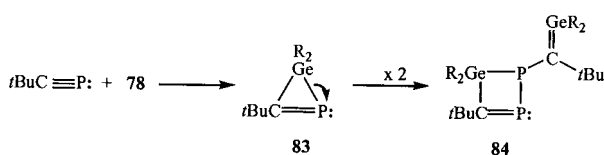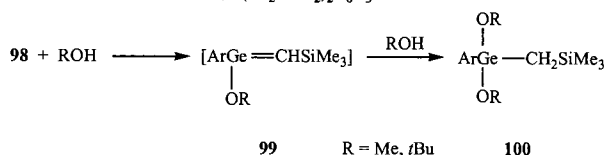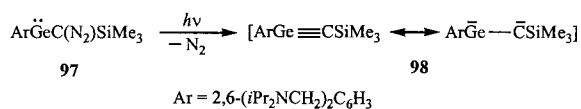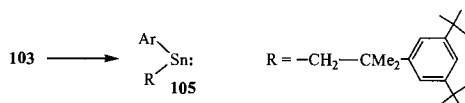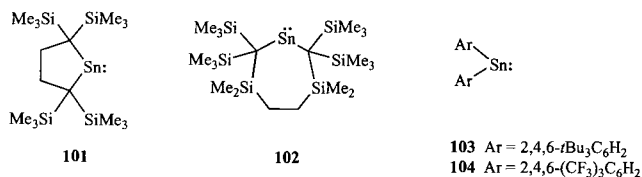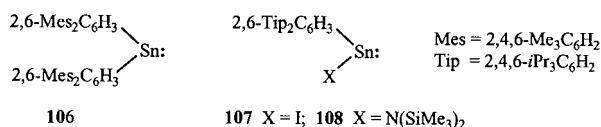
Scheme 35.

germylene **97** proceeds with cleavage of nitrogen to the intermediate **98** which, in the absence of trapping reagents, furnishes a polymer of the composition (ArGeCSiMe$_3$)$_n$. In the presence of alcohols, stepwise addition gives rise to the product **100** via the putative intermediate **99** [82] (Scheme 32).

4. Tin and lead compounds in low coordination states

4.1. Stannylenes and distannenes

Dialkyl- and diarylstannylenes that experience neither intermolecular donor stabilisation nor dimerise in the solid state are still very rare. Examples are the cyclic compounds **101** [83] and **102** [84], as well as the first diarylstannylenes **103** [85] and **104** [86], whereby the latter belongs rather to the donor-stabilised molecules on account of the weak Sn–F contacts. Although the diarylstannylene **103** is stable in the solid state, it undergoes an isomerisation in solution to the alkylarylstannylene **105** [85] (Scheme 33).

The extreme spatial requirements of terphenyl substituents offer novel possibilities for stabilising low coordination states and, in the case of the 2,6-Mes$_2$C$_6$H$_3$ group, may even make isolation of the V-shaped diarylstannylene **106** possible [87]. With the even more bulky 2,6-Tip$_2$C$_6$H$_3$ group and starting from SiI$_2$ or Sn[N(SiMe$_3$)$_2$]$_2$ it is only possible to introduce one aryl group to afford the—also V-shaped—stannylenes **107** and **108** [88] (Scheme 34).

In contrast to the strictly monomeric molecules **107** and **108**, the corresponding chlorine compounds [89] exist in the solid state both as the monomer **109** and as the dimer **110** with weak chlorine bridges [90]. Reaction of **109** with di-iso-butylaluminium hydride furnishes compound **111**, the first example of a tin(II) hydride. Interestingly, **111** does not exist in the solid state as an Sn–Sn bonded molecule but rather as the doubly hydrogen-bridged form [91] (Scheme 35).

It is also noteworthy that the reaction of **109** with methyllithium proceeds through the stage of a transalkylation product to the addition product **112** which, in turn, reacts further with **109** to give the arylstannylstannylene **113** as a valence isomer of a distannene [92] (Scheme 36).

The number of known, donor-stabilised stannylenes has increased dramatically in the past few years, however, they are not considered here on account of the formal higher coordination number of tin. When the distannenes R$_2$Sn=SnR$_2$ that exist as dimers in the solid state but dissociate almost completely to stannylene molecules in solution are included, the number of known dialkyl-, diaryl-, and silylstannylene again increases markedly. The dissociation in solution into stannylene molecules occurs not only with the classical

Left column (Schemes):

$$109 \xrightarrow[-\text{LiCl}]{+\text{MeLi}} \quad \underset{\text{Me}}{\overset{R}{}}Sn: \xrightarrow{\text{MeLi}} \quad 112$$
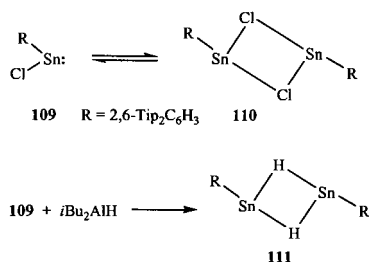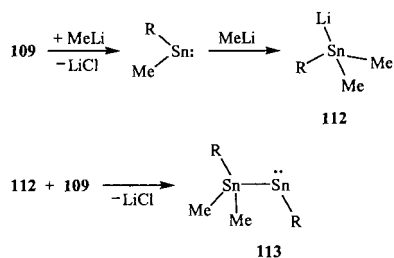
Scheme 36.

$$112 + 109 \xrightarrow{-\text{LiCl}} \quad 113$$

Scheme 36.

Scheme 37.
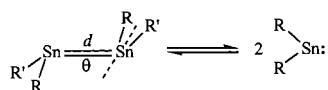
1, 104, 114–117

1	R = R' = CH(SiMe₃)₂	$d = 2.768(1)$	Å
104	R = R' = 2,4,6-(CF₃)₃C₆H₂	$d = 3.64$	Å
114	R = R' = Si(SiMe₃)₃	$d = 2.825(1)$	Å
115	R = R' = 2-tBu-4,5,6-Me₃C₆H	$d = 2.910(1)$	Å
116	R = 2-tBu-4,5,6-Me₃C₆H, R' = Si(SiMe₃)₃	$d = 2.7914(4)$	Å
117	R = 2,4,6-(CF₃)₃C₆H₂, R' = Si(SiMe₃)₃	$d = 2.833(1)$	Å

Scheme 37.

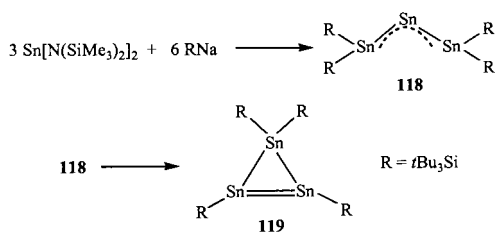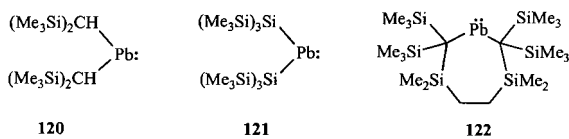$$3\ Sn[N(SiMe_3)_2]_2 + 6\ RNa \longrightarrow 118$$

$$118 \longrightarrow 119 \qquad R = tBu_3Si$$

Scheme 38.

120   **121**   **122**

Scheme 39.

123 R = 2,4,6-(CF₃)₃C₆H₂
124 R = 2,6-Mes₂C₆H₃
125 R = 2,4,6-[(SiMe₃)₂CH]₃C₆H₂
126 R = 2-tBu-4,5,6-Me₃C₆H

$$PbCl_2 + 2 \quad 127 \longrightarrow 128$$

129

Scheme 40.

Right column (body text):
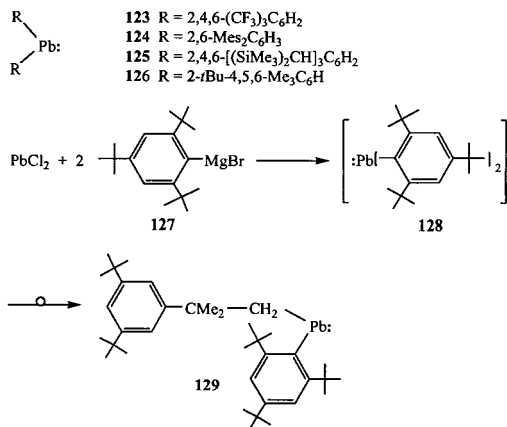
distannene **1** [3] but also with the distannenes **114** [93], **115** [94], as well as the heteroleptic distannenes **116** [95] and **117** [96]. On the other hand, the stannylene **104** exists as a weakly associated dimer in the solid state exhibiting a very large Sn–Sn separation [96] (Scheme 37).

All distannenes exhibit Sn–Sn separations in the range of, or markedly larger than, the Sn–Sn single bond length. The *trans*-bending angle varies between 0 and 64°, indicating a soft potential for this *trans*-pyramidalisation [97–99]. This is supported, for example, by the following observation, the distannene **115** exhibits not only a large Sn–Sn bond length but also highly differentiated environments at the two tin atoms with regard to the substituents. In contrast, the distannene **114** avoids interactions between the bulky silyl groups by torsion about the double bond of 63.2°. When solutions of the stannylenes derived from **114** and **115** are mixed, the heteroleptic distannene **116** results, and exists in the solid state as an undistorted, centrosymmetric molecule with a *trans*-bent angle of 44.9° [95]. Wiberg et al. recently reported another unusual reactivity mode: depending on the experimental conditions, the reaction of a tin(II) amide with NaSi*t*-Bu₃ gave either the tristannaallene **118** or the cyclotristannene **119**. It may be assumed that **119** is formed by an isomerisation of **118** [100] (Scheme 38).

The selection of results presented here clearly shows that the field of low coordinated tin compounds holds the promise of further surprises.

4.2. Plumbylenes and diplumbenes

Although Lappert et al. [101] reported on the isolation of the plumbylene **120** as long ago as 1973, structurally characterised dialkyl- and diarylplumbylenes were first described in the past few years. One reason for this may be the thermal lability and high light-sensitivity of many plumbylenes as well as diplumbenes. In the solid state, **120** forms a loose dimer with a Pb–Pb separation of 4.129 Å and a *trans*-bent angle of 34.2° [102]. As with the germylene dimer **75**, weak dispersive forces may again serve to hold the units together (Scheme 39).

The structurally similar molecules **121** [93] and **122** [103], by contrast, are strictly monomeric with large separations to the lead atoms of neighbouring plumbylene molecules. The same holds for the diarylplumbylene **123** [104] and for the sterically extremely overcrowded plumbylenes **124** [50], **125** [105] as well as **126** [106]. The reaction of PbCl₂ with the Grignard reagent **127** follows an unexpected course, probably involving the diarylplumbylene **128** that rearranges to finally afford the isolated alkylarylplumbylene **129** [106] (Scheme 40).
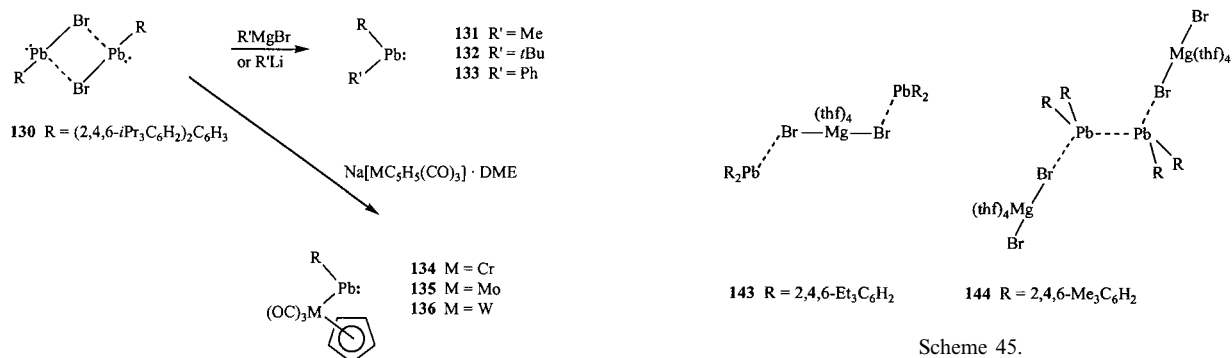
Scheme 41.
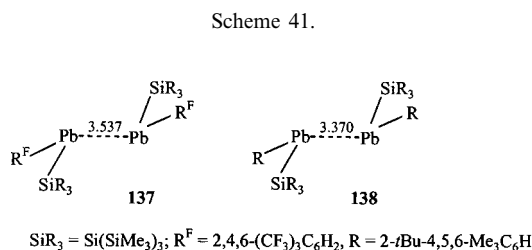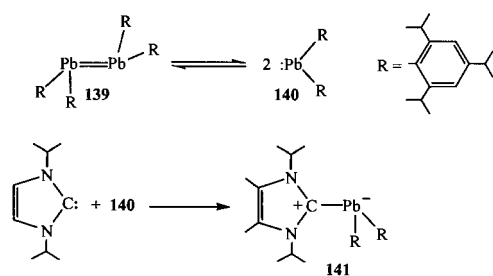
Scheme 42.

Scheme 43.
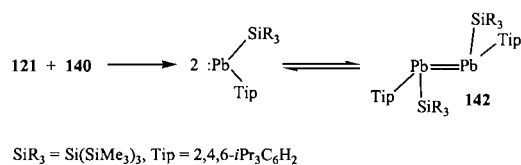
Scheme 44.

Scheme 45.

Similar to the case with tin, it is only possible to introduce one voluminous 2,6-bis(2,4,6-triisopropylphenyl)phenyl group to lead to obtain the plumbylene **130** in spite of the larger atomic radius of lead. Compound **130** exists in the solid state as the halogenbridged dimer. Starting from **130** not only the heteroleptic plumbylenes **131**–**133** [107], but also the again heteroleptic metalloplumbylenes **134**–**136** [108] can be prepared (Scheme 41).

These plumbylenes also exist as V-shaped molecules without contacts to neighbouring plumbylene molecules. A first breakthrough in the context of Pb···Pb contacts was the isolation of the heteroleptic plumbylene dimer **137** exhibiting a Pb–Pb separation of 3.537(1) Å and a *trans*-bent angle of 40.8° [97]. The plumbylene dimer **138** has a shorter Pb–Pb separation of 3.370(1) Å and a *trans*-bent angle of 46.5° [106]. Nonetheless, the observed Pb···Pb distances in both compounds are markedly longer than the value 2.82–3.00 Å calculated for the parent compound Pb_2H_4 with a genuine Pb=Pb double bond [97,109,110] (Scheme 42).

Since sterically less demanding substituents would favour the formation of lead–lead bonds, we have allowed lead(II) chloride to react with 2,4,6-tri-*iso*-propylphenylmagnesium bromide at −110 °C and obtained red crystals of compound **139**, the first molecule showing a Pb=Pb double bond length of 3.0515(3) Å and *trans*-bent angles of 43.9 and 51.2° to exist in the solid state [111]. In solution, **139** dissociates into the plumbylene molecules **140** that, for example, react with a nucleophilic carbene to furnish the highly labile, zwitterionic adduct **141** [112] (Scheme 43).

The Pb=Pb double bond length of 2.9899(5) Å in the heteroleptic diplumbene **142** is even shorter than that in **139**. Compound **142** was prepared by substituent exchange between **121** and **140** [113] (Scheme 44).

Both diplumbenes demonstrate that, in contrast to the homonuclear double bonds in the disilenes, digermenes, and distannenes where increasing bond lengths require even larger substituents for shielding, lead–lead double bonds can also be realised with smaller substituents. Therefore, we have replaced the triisopropylphenyl group by the markedly less voluminous triethylphenyl group. Reaction of the corresponding Grignard compound with lead chloride furnished the compound **143** in which two plumbylene molecules are linked by a magnesium dibromide molecule [114] (Scheme 45).

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 a plumbylene dimer **144** that is stabilised 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 the mesityl groups of 71° [113] (Scheme 45).
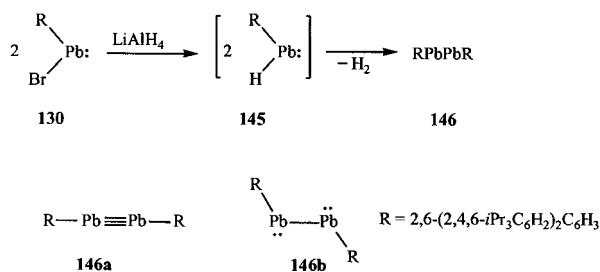
Scheme 46.
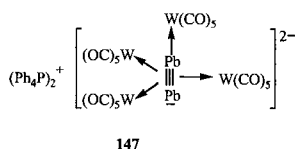
Scheme 47.

5. Does a lead–lead triple bond exist?

With the isolation of the diplumbenes **139** and **142**, homonuclear double bonds are now known between all elements of Group 14. However, experimental data on the physical properties or bonding of heavier Group 14 acetylene analogues are limited to the matrix spectroscopy of the di- or mono-bridged Si_2H_2 isomer [40,41]. Very recently Power et al. reported on the compound **146** which was synthesised by the reaction of the lead(II) bromide **130** with $LiAlH_4$, presumably via the hydride **145**. The strongly bent arrangement of **146** with a Pb–Pb–C bending angle of 94.26(4)° and the long Pb–Pb separation of 3.1881(1) Å indicate that **146** adopts the unique diplumbylene form **146b** instead of the acetylene-like diplumbyne form **146a** [115] (Scheme 46).

The suggestion of the authors [115] that molecule **146** has only a Pb–Pb single bond was corroborated by quantum chemical calculations showing that the *trans*-bent equilibrium structure **146b** is the form with the lowest lying energy minimum [116] (Scheme 47).

The description of bonding in the anion of **147** is less transparent since it may possibly exist as a complex-stabilised Pb_2^{2-} ion. This notion is supported by the short Pb–Pb separation of 2.806(8) Å, i.e. somewhat shorter than the Pb–Pb single bond length [117].

Acknowledgements

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