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Coordination Chemistry Reviews
210 (2000) 251–277

COORDINATION
CHEMISTRY
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Recent topics in the chemistry of heavier congeners of carbenes

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Received 8 November 1999; accepted 22 December 1999

Contents

Abstract

Several recent topics in the chemistry of divalent species of heavier Group 14 elements, i.e. the heavier congeners of carbenes, are outlined. As the main topics, the synthesis, structure,

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PII: S0010-8545(00)00313-1

and properties of stable silylenes are described together with those of related divalent species of the other Group 14 elements. Also, some detailed descriptions are allotted to new aspects in the relationship between the divalent species and the corresponding double-bond species of heavier Group 14 elements. Both electronic stabilization by heteroatom-containing substituents and kinetic stabilization by bulky substituents play very important roles in the advances of the chemistry of these interesting low-coordinate species.

Keywords: Divalent species; Double-bond species; Heavier Group 14 elements; Electronic stabilization; Kinetic stabilization

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1. Introduction

In the last decade, remarkable progress has been made in the chemistry of low-coordinate compounds of heavier Group 14 elements [1]. Following the successful synthesis and isolation of the first stable silene [2] and disilene [3] in 1981, a variety of low-coordinated silicon compounds such as Si=Pn (Pn = N [4], P [5], As [6]), Si=Ch (Ch = S [7], Se [8]), 1-silaallenes [9], silabenzene [10], 2-silanaphthalene [11], and tetrasila-1,3-butadiene [12] have been synthesized as stable compounds by taking advantage of kinetic stabilization with bulky substituents (so called steric protection) and most of them are structurally well-characterized.

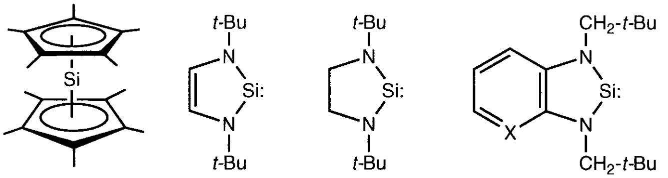
On the other hand, silylenes, one of the most interesting low-coordinated silicon compounds, had been transient species until the recent success by West and co-workers in the synthesis of the first stable silylene [13], in contrast to their heavier congeners, i.e. germylenes, stannylenes, and plumbylenes. In this article the recent progress of the chemistry of stable silylenes is outlined together with those of related divalent species of the other Group 14 elements. Another interesting topic in this field is the relationship between the divalent species and the double-bond compounds of heavier Group 14 elements. Since the latter compounds are considered to be dimers of the corresponding divalent species, much attention has been focused on the interconversion between these two systems from the standpoint of systematic studies on the stability of low-coordinated group 14 element compounds [1s].

Although some excellent reviews articles concerning the similar topics have recently been published [1,14], we present here a brief review on the latest progress in the chemistry of divalent species of Group 14 elements mainly focusing on those of kinetically stabilized systems.

2. Stabilization of silylenes

2.1. Synthesis and isolation of a stable dialkylsilylene

Divalent silicon compounds (silylenes) have been known as highly reactive, short-lived species like its carbon analogue (carbenes), and hence their structures

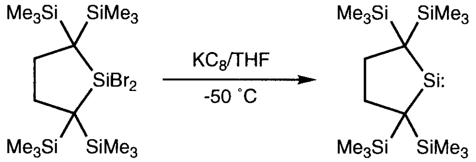


1 **2** **3** **4** (X = CH), **5** (X = N)

Scheme 1.

have been much less explored than their heavier congeners such as germylenes and stannylenes. Although decamethylsilicocene (**1**), formally also a silylene, has been known since 1986 [15], compound **1** is stabilized by η^5-coordination of pentamethylcyclopentadienyl ligands and not the congeners of a carbene. Recently, introduction of amino-substituents on the silicon atom resulted in an epoch-making breakthrough in this field, i.e. the synthesis of stable silylenes such as **2**–**5** (Scheme 1) [13,16]. Although these silylenes are all well-characterized by either X-ray crystallographic analysis or electron-diffraction analysis, the structural features of these special silylenes revealed that they are stabilized by the strong interaction between the vacant pπ-orbital at the divalent silicon and filled π-type orbitals of nitrogen atoms in the substituents. The unique structures and reactivities of these silylenes indicate that their frontier orbitals are considerably perturbed by their heteroatom substituents to such an extent that they are different from those of an intrinsic singlet carbene analogue.

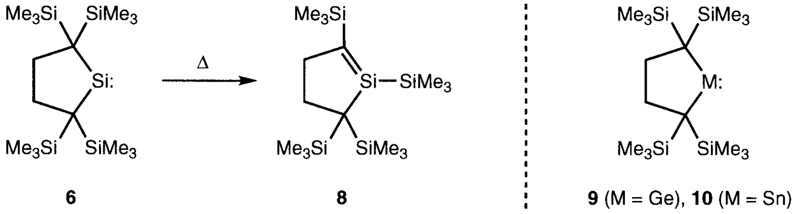
Quite recently Kira and co-workers have succeeded in the synthesis and isolation of the first stable dialkylsilylene (**6**) by taking advantage of their original cyclic ligand having four trimethylsilyl groups (Eq. (1)) [17]. Thus, the reduction of the corresponding dibromosilane (**7**) with potassium graphite resulted in the formation of silylene (**6**) as stable orange crystals, the crystallographic analysis of which revealed that the helmet-like bidentate ligand effectively protected its reactive silicon center and that the shortest distance between the divalent silicon atoms in the crystals of **6** is 7.210(1) Å. The relatively small C–Si–C angle [93.88(7)°] of **6** is indicative of the larger p-character of the silicon hybrid orbitals used in the C–Si bonds of **6**.



7 **6** (1)

Silylene **6** showed absorption maxima at 260 and 440 nm in its UV–vis spectra, the latter of which is assignable to the n(Si)–3pπ(Si) transition and close to those for observed for dimethylsilylene (453 nm) [18] and 1-silacyclopentane-1,1-diyl (436 nm) [19]. Thus, the electronic structure of silylene **6** is not so much perturbed by the substituents, and hence the successful isolation of **6** as stable crystals is again ascribed to the kinetic stabilization by the newly introduced cyclic bidentate ligand. Silylene **6** showed a ^{29}Si-NMR signal for the central divalent silicon at 567.4 ppm in C_6D_6, which is the lowest field ^{29}Si-NMR resonance reported so far [20]. Theoretical GIAO calculations revealed that the parent silylene (SiH_2) and the closely related model compounds (silacyclopentane-1,1-diyl and 2,2,5,5-tetrakis(trihydrosilyl)silacyclopentane-1,1-diyl) should have ^{29}Si-NMR resonances at 817, 754 and 602 ppm, respectively, again indicating that electronic perturbation by substituents is much smaller in **6** than that in **2**–**4**.

The most intriguing reactivity of **6** is the facile 1,2-migration of the trimethylsilyl group in the ligand to the divalent silicon atom giving the corresponding silaethene derivative **8** (Scheme 2). Such migratory insertion reaction has never been observed in the cases of stable germylene (**9**) [21] and stannylene (**10**) [22] bearing the same ligand even at 100°C. It should be noted that this is the first experimental evidence for the isomerization of silylmethylsilylene to 1-silylsilaethene, which has already been predicted by theoretical calculations [23].



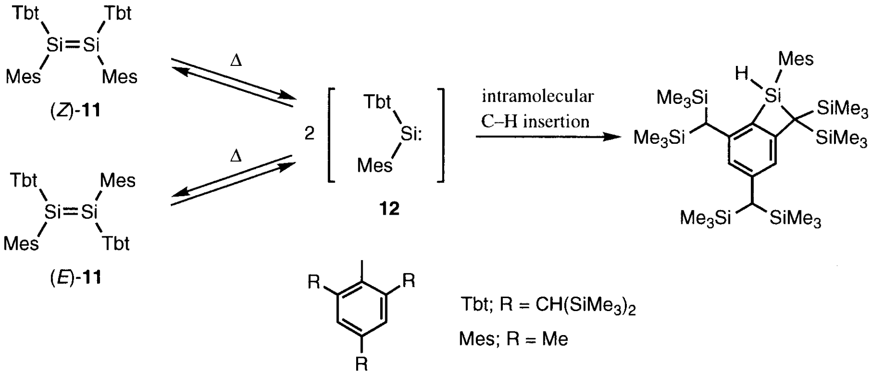
Scheme 2.

2.2. Generation and reactions of an overcrowded diarylsilylene

Since it became easy to synthesize stable disilenes by taking advantage of kinetic stabilization, impressive progress has been made in ascertaining the nature of a silicon–silicon double bond and it has been revealed that the silicon–silicon double bond is very reactive compared to the carbon–carbon double bond. However, the intrinsic nature of a silicon–silicon double bond has not been fully disclosed. For example, there had been no report concerning the thermal dissociation of disilenes into the corresponding silylenes in contrast to the facile thermal dissociation for the germanium and tin analogues [24]. The high thermodynamic stability of the C=C and Si=Si double bonds to relative to those for the Ge=Ge and Sn=Sn double bonds is in good agreement with the computed dissociation energies for the process $H_2E=EH_2 \rightarrow 2H_2E$: (ca. 140 kcal mol^{-1} for E = C [25], 52–58 kcal mol^{-1} for E = Si [26], 30–45 kcal mol^{-1} for E = Ge [27], and 22–28 kcal mol^{-1} for E = Sn [27a, 28]).

Meanwhile, Okazaki et al. has recently reported the first example of thermal dissociation of extremely hindered disilenes [Tbt(Mes)Si=Si(Mes)Tbt; Tbt = 2,4,6-

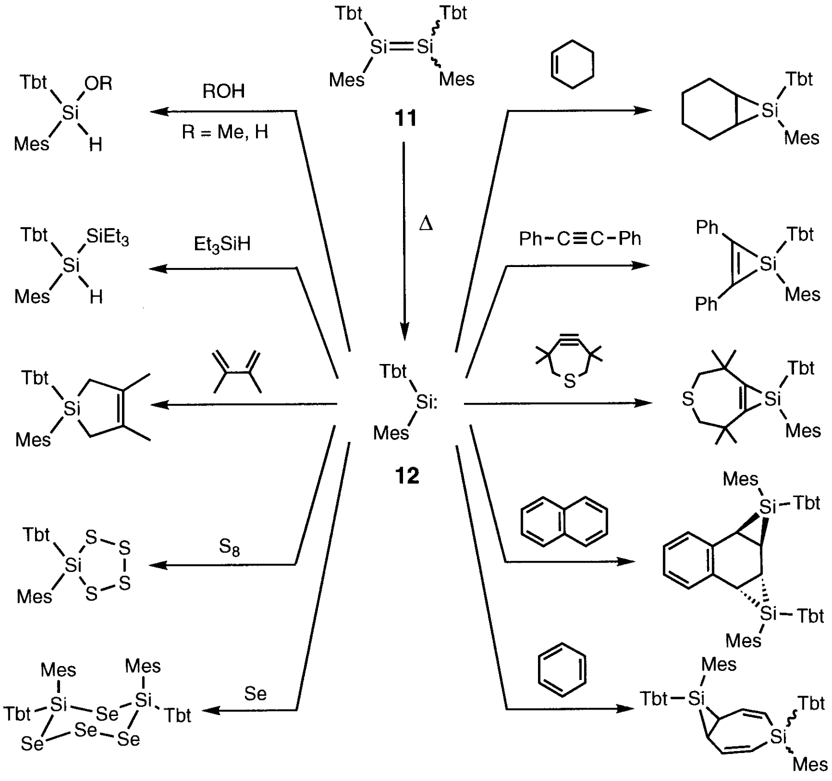
tris[bis(trimethylsilyl)methyl]phenyl, Mes = 2,4,6-trimethylphenyl (mesityl); (*Z*)-**11**: *cis*-isomer, (*E*)-**11**: *trans*-isomer] into the corresponding silylene [Tbt(Mes)Si: **12**] under very mild conditions (ca. 70°C) as shown in Scheme 3 [29].



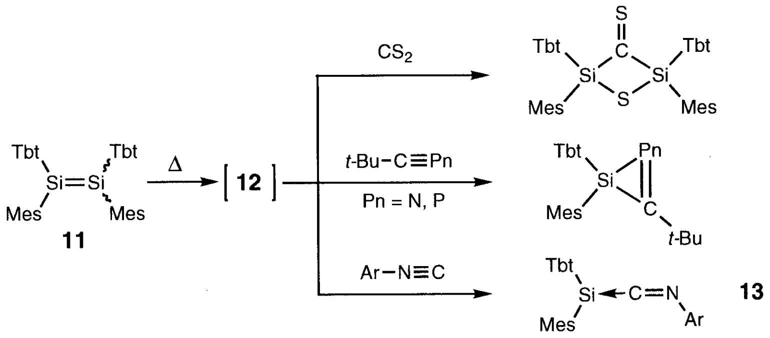
Scheme 3.

Kinetic studies on the thermal dissociation of **11** revealed that the unusual behaviour of **11** in contrast to the precedent stable disilenes obviously results from the presence of extremely bulky Tbt groups which weaken the Si=Si double bond [29]. The overcrowded diarylsilylene **12** thus generated was found to undergo facile reactions with methanol, triethylsilane, 2,3-dimethyl-1,3-butadiene, and elemental chalcogens such as sulfur and selenium (Scheme 4) [29]. Silylene **12** readily reacted also with olefins and acetylenes to afford the corresponding [1 + 2]cycloaddition products (Scheme 4) [29]. Furthermore, **12** was found to undergo addition reactions with aromatic hydrocarbons such as naphthalene and benzene to give the corresponding cycloadducts (Scheme 4), the formation of which should be noted as the first examples of [1 + 2]cycloaddition reactions of silylene to the carbon–carbon double bond in aromatic π-conjugated systems [29,30]. The successful isolation of these silylene adducts with aromatic hydrocarbons is obviously due to the much milder reaction conditions than those used in the conventional methods for generating silylenes (e.g. photolysis of cyclic or linear oligosilanes, pyrolysis of sinanorbornadiene derivatives, thermolysis of silacyclopropane derivatives).

The very mild generating conditions and the extreme bulkiness of the silylene **12** enabled us to obtain a variety of unique and important addition products with heteroatom-containing multiple bond compounds such as carbon disulfide [31], nitrile [32], phosphaalkyne [32], and isonitrile (Scheme 5) [33]. It is especially interesting that the reaction of **12** with isonitriles bearing a bulky aromatic substituent afforded the corresponding silylene–isonitrile complexes **13**, the first stable silylene–Lewis base complexes. The ^{13}C- and ^{29}Si-NMR spectroscopic data and theoretical calculations on the triphenyl-substituted model compound lead to the conclusion that the silylene–isonitrile adducts **13** have not a cumulene structure (silaketenimine) but a zwitter-ionic structure (i.e. silylene–isonitrile complex).



Scheme 4.



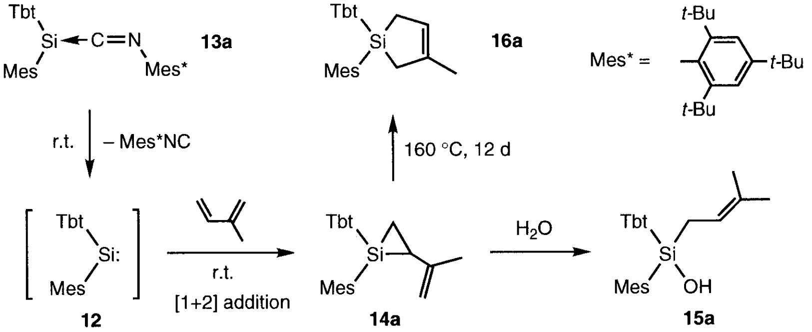
Scheme 5.

Since West et al. have also reported recently similar pyrolysis of tetraalkyldisilene $[(Me_3Si)_2CH]_2Si{=}Si[CH(SiMe_3)_2]_2$ leading to the generation of corresponding dialkylsilylene $[(Me_3Si)_2CH]_2Si$: though at somewhat higher temperature (ca. 100°C) [34], thermal dissociation of disilenes into silylenes may be a more general phenomenon than has previously been thought.

2.3. Reactions of a silylene–isonitrile complex as a masked silylene

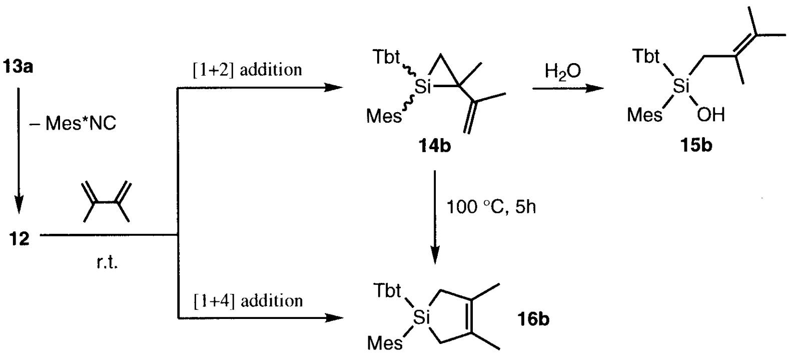
As mentioned in the previous section, there have been no examples of stable diarylsilylene while dialkyl- or diamino-substituted silylenes are now available as stable crystalline compounds. However, Okazaki et al. have recently found that the overcrowded diarylsilylene–isonitrile complexes **13** act as a free silylene **12** in solution even at room temperature (r.t.) [33]. Since there is a severe limitation in a study concerning the reactivities of silylenes under the conventional generating conditions, the reactivity of silylene–isonitrile complexes **13** as a masked silylene is of great interest.

The reactions of silylenes with 1,3-dienes giving the corresponding 3-silolenes are one of the typical cycloaddition reactions of silylenes [35]. The mechanism of these reactions has been investigated in detail [36], and it has been proposed that the reactions of silylenes with 1,3-dienes proceed via initial [1 + 2] addition followed by the isomerization of the resulting 2-vinylsiliranes to the corresponding 3-silolenes. However, the observation and isolation of the intermediary 2-vinylsiliranes have been limited to only a few examples [37] because they readily isomerize to 3-silolenes under the conditions for the generation of the silylenes such as photolysis or thermolysis at high temperature. Okazaki et al. have tried the synthesis and isolation of a 2-vinylsilirane intermediate by using silylene–isonitrile complex **13a** as a silylene source (Scheme 6) [38].



Scheme 6.

Thus, complex **13a** reacted with isoprene at r.t. to give the corresponding 2-vinylsilirane **14a** (84%). 2-Vinylsilirane **14a** was also isolated in 89% yield by the reaction of disilene **11** with isoprene at 70°C, which indicates that these reactions proceeded via silylene **12** as an intermediate. The exclusive formation of **14a** is probably due to the steric repulsion between bulky substituents on the silicon atom and the methyl group of isoprene. Although 2-vinylsilirane **14a** was stable in the solid state even on exposure to the air, it underwent hydrolysis on silica gel to give the corresponding alcohol **15a**. Thermolysis of **14a** in C_6D_6 at 160°C for 12 days resulted in the formation of a formal [1 + 4] adduct **16a** in 88% yield. This is the first observation and isolation of the initial intermediate in the reaction of thermally generated silylene with a 1,3-diene, i.e. 2-vinylsilirane derivative, although the



Scheme 7.

intermediacy of this type of [1 + 2] adducts in the reactions of photochemically generated silylenes has been already evidenced by NMR spectroscopy [37a].

On the other hand, when complex **13a** was allowed to react with 2,3-dimethyl-1,3-butadiene in C_6D_6 in a sealed tube at r.t., the formation of both [1 + 2] adducts **14b** and [1 + 4] adduct **16b** was observed by the ^{29}Si-NMR spectrum (Scheme 7; **14b**: $\delta_{Si} = -76.3$, -72.9, **16b**: $\delta_{Si} = -5.3$). Since heating the reaction mixture at 50°C for 7 h resulted in no isomerization of **14b** into **16b**, silylene **12** seems to undergo both [1 + 2] and [1 + 4] addition reactions with 2,3-dimethyl-1,3-butadiene, competitively. This is the first clear evidence for the occurrence of direct [1 + 4] addition of a silylene to a 1,3-diene. This phenomenon is most likely due to the suppression of [1 + 2] addition by steric repulsion between the methyl groups of the butadiene and the bulky substituents on the silicon atom of **12**. This interpretation may also be supported by the exclusive production of **14a** in the reaction with isoprene. Thus, the results obtained here suggest that silylenes bearing very bulky substituents may undergo direct [1 + 4] addition to dienes. Vinylsilirane **14b** completely isomerized into **16b** by heating at 100°C for 5 h and underwent hydrolysis on silica gel to give silanol **15b** as well as **14a** (Scheme 7).

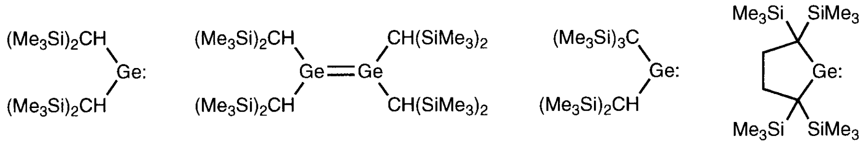
Consequently, the reactivity of silylene–isonitrile complexes **13** as a masked silylene may provide us with not only a new and useful synthetic building block for a variety of a novel class of organosilicon compounds but also a new research field of the silylene chemistry.

3. Stabilization of germylenes

3.1. Synthesis of stable dialkylgermylenes

Although it has been recognized theoretically that germylenes should be much more stable than silylenes, examples of stable germylenes become known only in recent years. In 1976, Lappert et al. have reported the synthesis and characterization of the first stable germylene, $[(Me_3Si)_2CH]_2Ge$: (**17**), and **17** was found to be in a monomeric form in solution but exist as the corresponding dimer, $[(Me_3Si)_2CH]_2Ge{=}Ge[CH(SiMe_3)_2]_2$ (**18**) in the solid state (Scheme 8) [39]. In 1991, the more sterically hindered dialkylgermylene, $[(Me_3Si)_3C][(Me_3Si)_2CH]Ge$: (**19**) was synthesized by Jutzi et al. and its monomeric structure in the solid state was established by X-ray crystallographic analysis (Scheme 8) [40]. Furthermore, quite recently Kira et al. have applied their original helmet-like bidentate ligand to the kinetic stabilization of a germylene and succeeded in the synthesis and isolation of very stable dialkylgermylene (**9**) (Scheme 8) [21]. In this case, germylene **9** was found to show an identical UV–vis spectrum in THF or hexane, indicating that this cyclic germylene **9** does not form a complex with THF because of severe steric hindrance around the central germanium atom. This is in sharp contrast to the other germylenes which are known to form complexes with bases such as ethers and amines and to cause significant blue shift of the n–p transition of the germylenes.

These results clearly show that the bulkiness of the ligand used is responsible for the nature of germylenes, and additional stable examples are likely to be reported in the future. However, the intrinsic reactivity of dialkylgermylenes still remains to be elucidated.

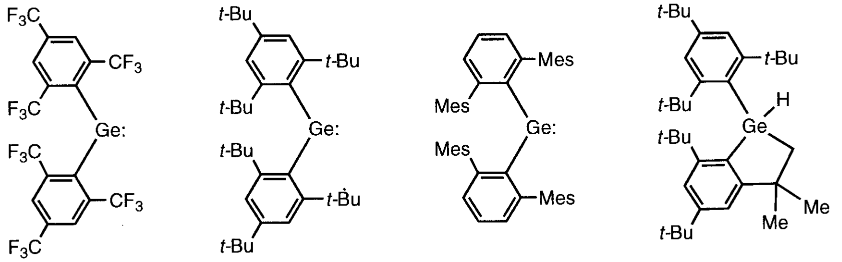


17 **18** **19** **9**

Scheme 8.

3.2. Synthesis of stable diarylgermylenes

As for stable diarylgermylenes, three examples (**20** [41], **21** [42], and **22** [43]; Scheme 9) have been structurally analyzed by X-ray crystallographic analysis. The solid state structure of germylene **20** indicated that the remarkable stability of **20** is mainly due to the intramolecular coordination of the fluorine atoms of the

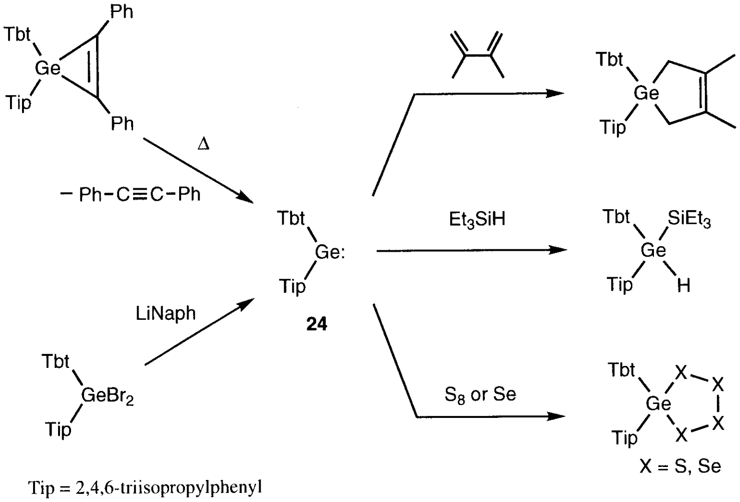


20 **21** **22** **23**

Scheme 9.

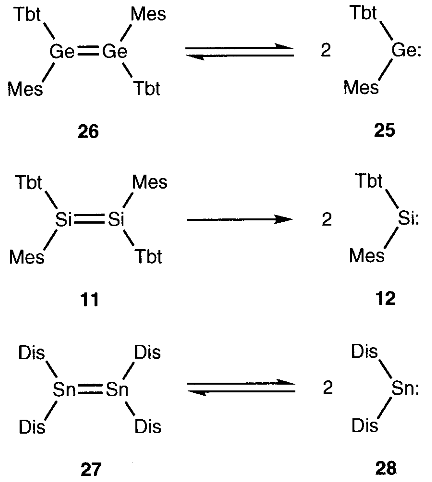
ortho-CF_3 substituents to its electron-poor germanium center, while the latter two germylenes **21** and **22** were found to be only kinetically stabilized by their extremely bulky aromatic substituents. However, the stability of germylene **22** was marginal, and in solution **21** underwent intramolecular insertion of the germanium atom into one of the methyl groups in the substituents in the presence of a Lewis acid or at high temperature to give a germaindane derivative **23** (Scheme 9) [44].

There has been reported another stable diarylgermylene **24** [45] bearing an extremely bulky aromatic substituent (Tbt group) together with 2,4,6-triisopropylphenyl group (Tip group). No color change on concentration of the blue solution of **24** in hexane ($\lambda_{max} = 581$ nm) giving the same colored crystals strongly suggest that germylene **24** is stable as a monomeric species both in solution and in the solid state, although the solid state structure of **24** was not established yet. Germylene **24** was readily synthesized by either the reductive debromination of the corresponding dibromogermane, Tbt(Tip)$GeBr_2$ [45a–c], or the thermal retrocycloadditon of the 2,3-dipheylgermirene bearing Tbt and Tip groups on the germanium atom (Scheme 10) [45d]. The latter reaction was found to be a useful synthetic method for germylene **24** under neutral conditions. In spite of the presence of such bulky substituents, germylene **24** showed versatile reactivity towards a variety of reagents such as alcohols, butadienes, acetylenes, hydrosilanes, and elemental chalcogens (sulfur and selenium) (Scheme 10). This effective combination of bulky aromatic ligands were successfully applied to the synthesis and isolation of a series of stable germanium–chalcogen double bond species Tbt(Tip)Ge=X (X = S [45a,46], Se [46,47], Te [47,48]).



Scheme 10.

On the other hand, when a slight modification from Tip to Mes was made in the ligand attached to the germanium center in Tbt-substituted diarylgermylene, the stability of the germylene drastically changed [49]. Thus, the less hindered di arylgermylene Tbt(Mes)Ge: (**25**) was found to be in equilibrium with its dimer, i.e. digermene **26** (Scheme 11). Germylene **25** showed interesting thermochromism in hexane [blue at 295 K vs. yellow at 190 K], which is in sharp contrast to that of the temperature independence of the UV–vis spectra observed for **24** [45a,46]. The absorptions observed at 190 K ($\lambda_{max} = 439$ nm, ε 2.0×10^4) and 295 K ($\lambda_{max} = 575$ nm, ε 1.6×10^3) are assignable to the π–π* transition of digermene **26** and the n-p transition of germylene **25**, respectively. The isosbestic points observed at 335, 390, and 509 nm indicate the quantitative interconversion between **26** and **25**.



26 **25**

$\Delta H = 14.7 \pm 0.2$ kcal mol^{-1}
$\Delta S = 42.4 \pm 0.8$ cal mol^{-1} K^{-1}

11 **12**

$\Delta H^{\neq} = 25.0 \pm 0.6$ kcal mol^{-1}
$\Delta S^{\neq} = 1.3 \pm 1.7$ cal mol^{-1} K^{-1}

27 **28**

$\Delta H = 11.2 \pm 0.3$ kcal mol^{-1}
$\Delta S = 28.0 \pm 1.3$ cal mol^{-1} K^{-1}
Dis = $CH(SiMe_3)_2$

Scheme 11.

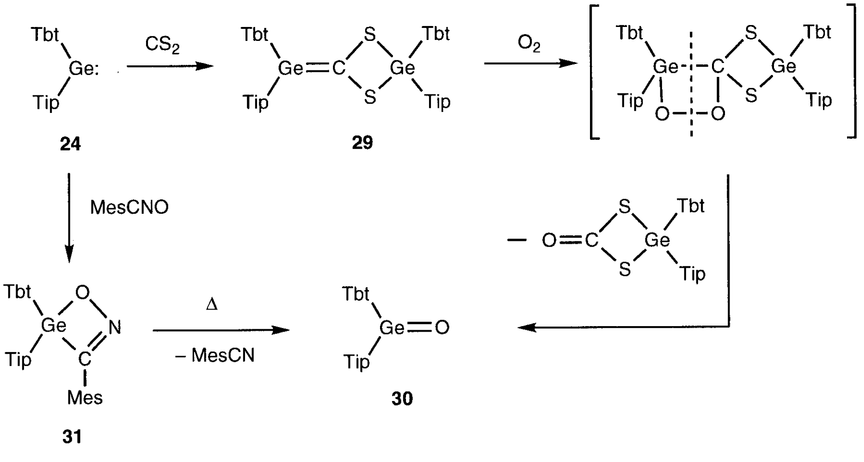
The thermodynamic parameters ($\Delta H = 14.7 \pm 0.2$ kcal mol^{-1} and $\Delta S = 42.4 \pm 0.8$ cal mol^{-1} K^{-1}) for the dissociation of digermene **26** to germylene **25** were obtained from the temperature dependence of the absorptions. This bond dissociation energy (14.7 kcal mol^{-1}) of **26** into **25** is much smaller than that of the calculated value (30–45 kcal mol^{-1} [27]) for the parent system ($H_2Ge{=}GeH_2$), indicating that the germanium–germanium double bond in **26** is considerably weakened due to the severe steric repulsion between the bulky substituents. Indeed, X-ray crystallographic analysis of the orange crystal of *(E)*-**26** revealed that it has a considerably elongated Ge=Ge double bond of (*E*)-**26** upto 2.416(4) Å in the solid state [50], which is in good agreement with the ready dissociation into germylene **25** in solution.

Meanwhile, when the orange solid of (*E*)-disilene **11** bearing the same substituents as **26** was dissolved in pentane, the generation of the corresponding silylene **12** was not observed as judged by UV–vis spectra [29]. Thus, the fact that the disilene **11** exists essentially as a dimer of **12** and dissociates into **12** in solution only to a minor at ambient temperature is also noteworthy, although a similar phenomenon is known for the bis(trimethylsilyl])methyl-substituted disilene–digermene pairs: $[(Me_3Si)_2CH]_2M{=}M[CH(SiMe_3)_2]_2$ (M = Si [51], Ge [39]). On the other hand, (*E*)-disilene **11** dissociates into the corresponding silylene **12** upon heating and the activation parameters ($\Delta H^{\neq} = 25.0 \pm 0.6$ kcal mol^{-1} and $\Delta S^{\neq} = 1.3 \pm 1.7$ cal mol^{-1} K^{-1}) of the dissociation reaction of **11** into **12** were found, although ΔH of the equilibrium between **11** and **12** was not determined because of the low concentration of **12** (Scheme 11). The most reasonable explanation for the difference between disilene **11** and digermene **26** is that the bond dissociation energy of **11** into **12** is larger than that of **26** into **25**. In the case of tin analogues, the equilibrium between distannene **27** and the corresponding stannylene **28** was reported and the thermodynamic parameters ($\Delta H = 11.2 \pm 0.3$ kcal mol^{-1} and $\Delta S = 28.0 \pm 1.3$ cal mol^{-1} K^{-1}) for the equilibrium were obtained from the temperature dependence of the NMR chemical shifts (Scheme 11) [24d]. The bond dissociation energy of distannene **27** is smaller than those of digermene **26** and disilene **11**, and the bond dissociation energy of the double bond species of heavier Group 14 elements were found to decrease on going from Si to Sn as the theoretical calculations predicted.

3.3. Reactions of a kinetically stabilized germylene

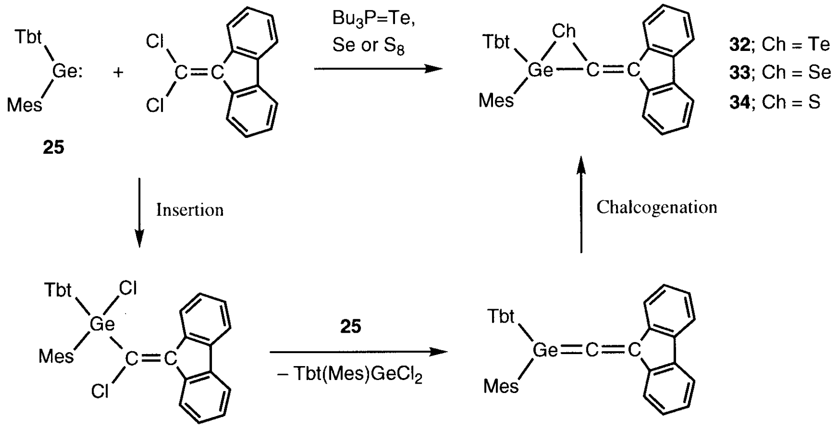
Although very little is known for the reactions of isolated germylenes **20**, **21**, and **22**, diarylgermylene **24** was found to undergo a variety of reactions with olefins, dienes, acetylenes, alcohols, isothiocyanates, elemental chalcogens, and hydrosilanes as in the cases of less hindered, transient germylenes previously reported [1e,1i].

Furthermore, germylene **24** showed a unique reactivity towards some heteroatom-containing compounds such as carbon disulfide [52], nitrile oxide [53], and gem-dihalogenated olefins [54]. Treatment of **24** with carbon disulfide resulted in a formation of a novel heteroatom-substituted germene **29** (Scheme 12) [52]. The germaketenedithioacetal structure of the core part of **29** was crystallographically established and the oxidation of **29** with molecular oxygen was found to be a novel approach to the corresponding diarylgermanone **30** (Scheme 12) [55].

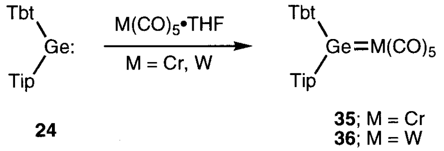


Scheme 12.

Germylene **24** was allowed to react with a bulky nitrile oxide such as mesitonitrile oxide to give the corresponding [1 + 3]cycloaddition product **31**, which is the first stable example of an oxazagermete derivative [53]. Alternative formation of germanone **30** was achieved by thermolysis of this strained germaheterocycles **31** (Scheme 12) [53]. The first stable alkylidenetelluragermirane **32** was synthesized by the reaction of **25** with 9-(dichloromethylene)fluorene, followed by addition of triphenylphosphine telluride (Scheme 13) [54]. The formation of **32** is most likely interpreted in terms of the initial insertion of germylene **25** into the C–Cl bond of 9-(dichloromethylene)fluorene followed by dechlorination with co-existing germylene **25** leading to 1-germaallene and subsequent telluration. The selenium and sulfur analogues of **32**, i.e. selena- and thiagermiranes **33** and **34**, were synthesized by a similar synthetic approach (Scheme 13) [54]. Complexation of germylene **24** with some transition metal carbonyl complexes was also examined to give the first base-free examples of a germylene-group 6 metal mononuclear complex, **35** and **36** (Scheme 14) [45b].



Scheme 13.



Scheme 14.

Thus, Tbt-substituted germylenes **24** and **25** have enough space for functionalization which enabled them to be versatile synthetic building blocks for a variety of new organogermanium compounds.

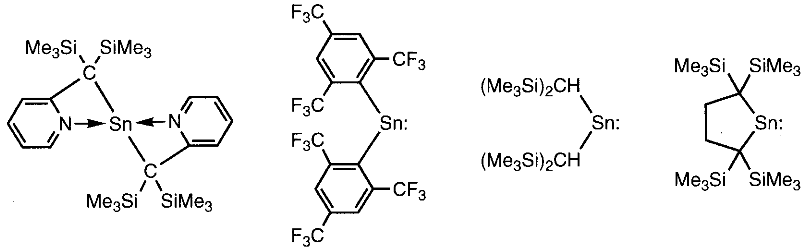
4. Stabilization of stannylenes and plumbylenes

4.1. Synthesis of stabilized stannylenes

The divalent organotin compound (stannylene) is also a fascinating synthetic target in the chemistry of Group 14 metals not only as a higher homologue of a carbene but also as a good building block for the synthesis of novel organotin species, especially tin-containing double-bond compounds. Although the reactions of transient stannylenes such as oligo- and polymerization, insertion into σ-bonds, and addition to unsaturated systems were relatively well studied [1i, 1j], there have been only a few examples of the use of a stannylene as a precursor of a novel low-coordinate organotin compound such as a transition-metal complex [24c] or a tin-containing double-bond compound [56], because a limited number of stannylenes have been available on account of their high reactivity.

The structures of some stable stannylenes, such as several amino- [57], alkoxy- [58], and arylthio-substituted [59] stannylenes, have been revealed by X-ray crystallography; they are monomeric in crystals and the tin has the coordination number 2. The divalent tin in such compounds is considered to be stabilized by the effects of electronegativity of the ligand atoms and by the donation of the lone pair electrons to the vacant 5pπ orbital of the tin. Although the first monomeric dialkyl- and diaryl stannylene in the solid state, bis[2-pyridyl-2,2-bis(trimethylsilyl)methyl]stannylene (**37**) [60] and bis[2,4,6-tris(trifluoromethyl)phenyl]stannylene (**38**) [61] were synthesized and characterized by X-ray crystallography, the stabilization of these stannylenes is considerably due to intramolecular contacts between the tin and neighboring nitrogen or fluorine atoms (Scheme 15). The chemical shift in ^{119}Sn-NMR spectrum for **37** was strongly temperature dependent, varying in the range of 120–150 ppm. The ^{119}Sn-NMR resonance of **38** is split into 13 lines by coupling with the fluorine atoms of the trifluoromethyl groups in *ortho* positions [$J(^{119}\text{Sn-F}) = 240$ Hz], clearly indicating the existence of the fluorine–tin contacts also in solution.

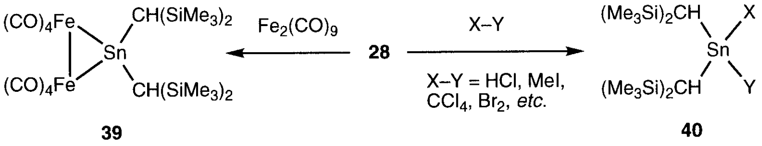
In 1976 Lappert et al. have reported the first stable dialkylstannylene **28** (Scheme 15) in solution [24c,39,62]. They found that **28** exists as a monomer in the gas phase and as a dimer **27** in the solid state, whereas it exists as a monomer–dimer



37 **38** **28** **10**

Scheme 15.

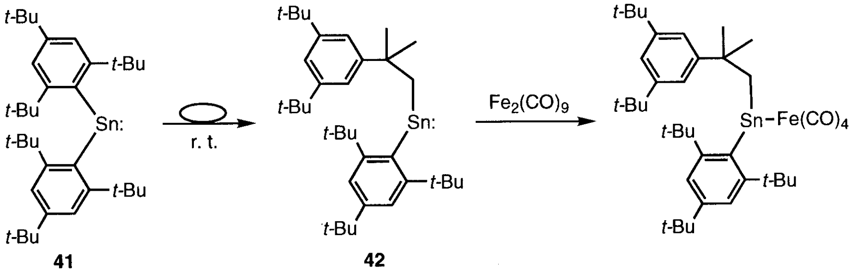
equilibrium mixture in solution. Extensive studies on the reaction of **28** were carried out, especially on oxidative addition and insertion reactions leading to a variety of new organotin compounds such as **39** and **40** (Scheme 16) [24c,39,62].



Scheme 16.

On the other hand, the first stable dialkylstannylene **10** that is monomeric in the solid state was synthesized and crystallographically characterized by Kira et al. in 1991 (Scheme 15) [22]. Their *helmet-like bidentate ligand* was useful for the stabilization of the central tin atom as in the cases of its silicon and germanium analogues (vide supra), and the protecting ability is much higher than the two bis(trimethylsilyl)methyl groups in **28**. The signal for the central tin atom in the ^{119}Sn-NMR of **10** appears at 2323 ppm as a sharp singlet which is the lowest ^{119}Sn chemical shift ever reported. In contrast to **28**, the band width and the chemical shift were almost unchanged between −40 and 80°C, clearly indicating no equilibration between monomer and dimer.

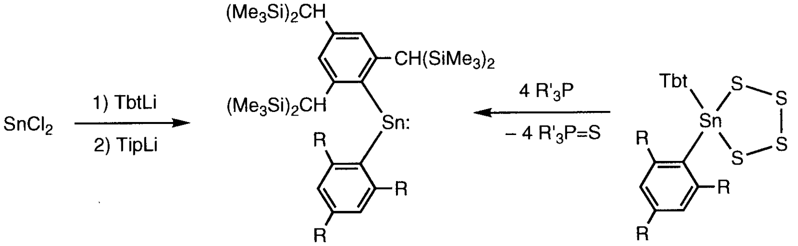
Very recently, introduction of two 2,4,6-tri-*t*-butylphenyl groups onto the tin atom has led to the successful isolation of **41**, which is the first example of kinetically stabilized monomeric diarylstannylene characterized in the solid state [63]. It is noted that ^{119}Sn-NMR spectrum of **41** shows two signals at 961 and 1105 ppm instead of a singlet expected at r.t. in solution. The striking feature of **41** is its partial isomerization into a sterically less encumbered stannylene **42** in solution (Scheme 17). The two signals of **41** coalesce upon heating to 50°C into a singlet at 980 ppm due to **42**, which persists even after cooling. The reason is still obscure why **41** and **42** show such drastically shielded ^{119}Sn-NMR signals, which are similar to those for heteroatom-substituted stannylenes, in view of the fact that the signal of **10** appears at 2323 ppm. The newly obtained alkylaryl-substituted stannylene **42** formed a unique stannylene–iron complex with the stannylene unit occupying an axial position (Scheme 17).



Scheme 17.

Soon after the isolation of **10**, Okazaki et al. described the synthesis of the first kinetically stabilized diarylstannylene stable in solution, i.e. Tbt(Tip)Sn: (**43**), by treatment of TbtLi with stannous chloride followed by addition of TipLi (Scheme 18) [64]. Under an inert atmosphere, stannylene **43** was found to be quite stable even at 60°C in solution, and it showed a deep purple color ($\lambda_{max} = 561$ nm) in hexane. ^{119}Sn-NMR spectrum of **43** showed only one signal at 2208 ppm, the chemical shift of which is characteristic of a divalent organotin compound as in the case of a monomeric dialkylstannylene **10**. The bandwidth and the chemical shift of **43** were almost unchanged between − 30 and 60°C, indicating the absence of a monomer–dimer equilibrium.

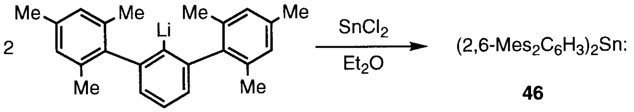
Okazaki et al. also succeeded in the synthesis of overcrowded diarylstannylenes, Tbt(Tcp)Sn: (**44**; Tcp = 2,4,6-tricyclohexylphenyl) and Tbt(Tpp)Sn: (**45**; Tpp = 2,4,6-tris(1-ethylpropyl)phenyl), by the exhaustive desulfurization of the corresponding tetrathiastannolanes with a trivalent phosphine reagent (Scheme 18) [65]. Since only few convenient precursors have been available for the generation of stannylenes so far, this new method will provide us with a useful synthetic route for a variety of overcrowded stannylenes. The successful synthesis of a series of Tbt-substituted diarylstannylenes enabled the systematic comparison of their electronic absorptions with those of the previously reported overcrowded diarylstannylenes, which led to the elucidation of the substituent effect on the n → p transition of stannylenes.



43 (R = *i*-Pr)
44 (R = cyclohexyl)
45 (R = 1-ethylpropyl)

Scheme 18.

Quite recently, Power et al. also reported the synthesis and characterization of a new type of sterically crowded diarylstannylene (**46**) [43], which bears two bulky *m*-terphenyl type ligand (2,6-$Mes_2C_6H_3$) and exists as a monomer even in the solid state (Scheme 19).

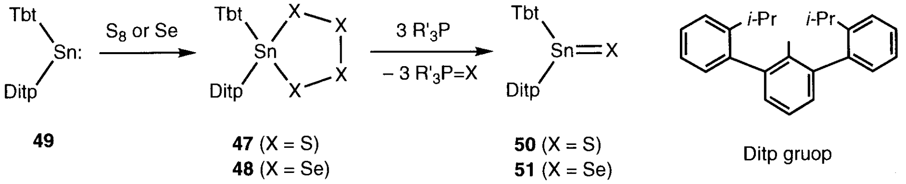


Scheme 19.

4.2. Reactions of stable stannylenes

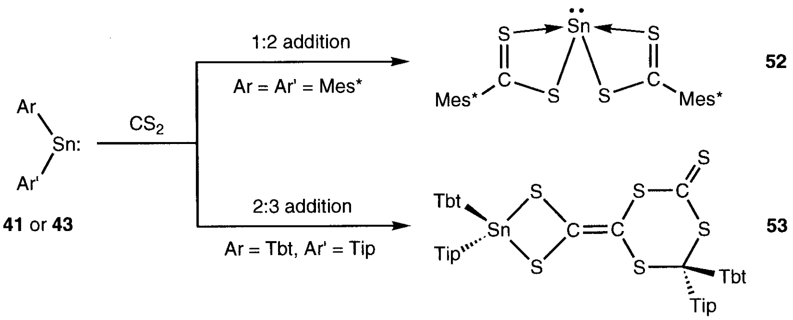
The synthesis of a variety of stable stannylenes described above is noteworthy from the standpoints of not only the elucidation of the intrinsic nature of stannylenes but also the synthetic application of a novel class of low-coordinate organotin compounds. Thus, the fine tuning of the bulkiness of the ligands on tin atom in stannylenes revealed the unique interatomic Sn–Sn bonding character of their dimeric form, i.e. the relationship between the stannylenes and distannenes, the details of which have been compiled in the recent reviews [1j,1s].

Another impressive application of stable stannylenes is the synthesis of stable double-bond species between tin and heavier chalcogen atoms. Okazaki et al. have succeeded in the synthesis of extremely hindered tetrachalcogenastannolanes Tbt(Ditp)$SnCh_4$ [**47** (Ch = S) and **48** (Ch = Se)] bearing a Tbt group together with another bulky substituent, Ditp (2,2″-diisopropyl-*m*-terphenyl-2′-yl), by the reaction of the corresponding diarylstannylene **49** with elemental sulfur and selenium, respectively (Scheme 20) [66]. The dechalcogenation of the overcrowded tetrachalcogenastannolanes **47** and **48** with a phosphine reagent led them to the first isolation of stable tin–sulfur and tin–selenium double-bond species, i.e. stannanethione (**50**) and stannaneselone (**51**), the latter of which was successfully characterized by X-ray crystallographic analysis (Scheme 20) [8,66].



Scheme 20.

In the reaction of carbon disulfide with stannylenes **41** and **43**, the difference of ligands considerably altered the structure of reaction products; **41** afforded a new type of tetracoordinated stannylene **52** via the migration of an aryl group [67], whereas **43** gave the corresponding 2:3 adduct (**53**) with carbon disulfide as shown in Scheme 21 [68].

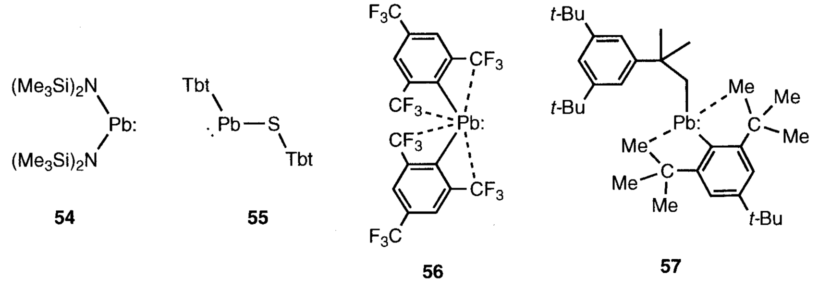


Scheme 21.

4.3. Synthesis of stable plumbylenes

In contrast to the remarkable progress in the chemistry of divalent organic compounds of silicon, germanium, and tin, the heaviest conger of this series, i.e. divalent organolead compounds (plumbylenes), are less well-known. They usually occur as reactive intermediates in the preparation of plumbanes R_4Pb and undergo polymerization and/or disproportionation in the absence of suitable stabilizing groups on the lead atom [69].

Although dicyclopentadienyllead(II) compounds, formally also plumbylenes, have been known since 1956 [70], they are not the congeners of carbenes since they are stabilized by η^5-coordination of cyclopentadienyl ligands. In 1974 the first stable diaminoplumbylene, $[(Me_3Si)_2N]_2Pb$: (**54**) was synthesized by Lappert et al. [71], and since then other stable plumbylenes with heteroatom substituents have also been reported. Recently, Okazaki et al. have reported the synthesis and characterization of a stable aryl(arylthio)plumbylene (**55**), which is one of the rare examples of heteroleptic plumbylenes (Scheme 22) [72].

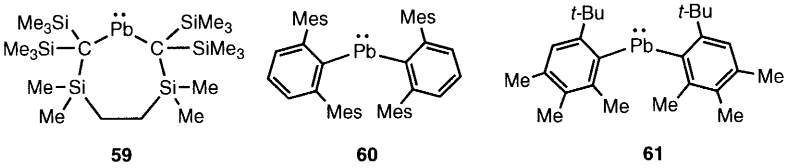


54 **55** **56** **57**

Scheme 22.

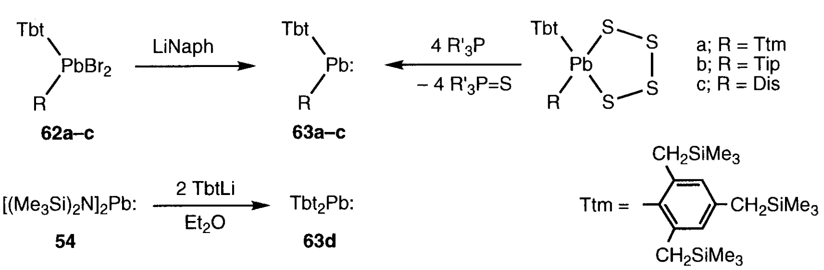
A few plumbylenes bearing only carbon substituents have also been reported. Some of them, however, are stabilized by intramolecular coordination of the lone pair of a donor group in the organic substituent, thus giving the lead a coordination number greater than 2. For example, an X-ray diffraction study of the first stable diarylplumbylene R^f_2Pb (**56**; $R^f = 2,4,6$-tris(trifluoromethyl)phenyl) showed that four CF_3 fluorine atoms were coordinated to the lead atom (Scheme 22) [73]. Four-coordinate divalent organolead compounds were also reported recently [74], in which intramolecular coordination of nitrogen atoms is responsible for their stability. Similar intramolecular interactions were also observed in the first stable alkylarylplumbylene (**57**) [75], the X-ray structural analysis of which showed the short contacts between the lead atom and the carbon atoms of the methyl groups (in *ortho*-*t*-butyl groups) indicating weak agostic interactions (Scheme 22).

On the other hand, kinetically stabilized plumbylenes bearing only organic substituents that do not contain donor groups are scarce, and their structures and reactivities are almost unexplored. The first dialkylplumbylene, Dis_2Pb [**58**; Dis = bis(trimethylsilyl)methyl)] was obtained in only 3% yield in 1973 [24c,39,76], and its structure was crystallographically determined recently [77]. Another dialkylplumbylene **59** with a lead atom in a seven-membered ring system was synthesized and characterized by X-ray diffraction (Scheme 23) [78]. Two stable diarylplumbylenes, $[2,6\text{-}Mes_2C_6H_3]_2Pb$: (**60**) [43] and R_2Pb (**61**; R = 2-*t*-butyl-4,5,6-Me_3C_6H) [75], were also structurally characterized (Scheme 23).



Scheme 23.

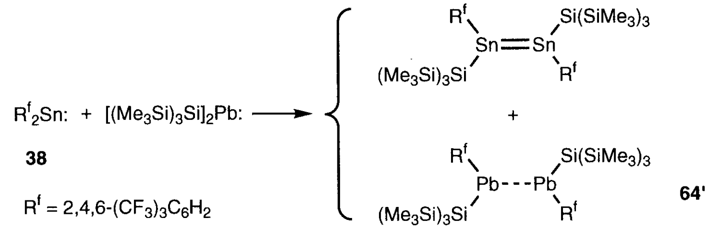
Although all of the stable plumbylenes reported to date have been synthesized by nucleophilic substitution of a lead(II) compound, Okazaki et al. recently described two kinds of new synthetic routes to a plumbylene from tetravalent organolead compounds. The first one is the reductive debromination of the overcrowded diboromoplumbanes [79], $Tbt(R)PbBr_2$ [**62a** (R = 2,4,6-tris[(trimethylsilyl)methyl]phenyl (Ttm)), **62b** (R = Tip), and **62c** (R = Dis)] with lithium naphthalenide leading to the formation of a series of hindered plumbylenes, Tbt(R)Pb: (**63a**–**c**) (Scheme 24) [80]. The other one is the exhaustive desulfurization of the corresponding overcrowded tetrathiaplumbolanes with a trivalent phosphorus reagent as in the cases of their tin analogues (vide supra). Although the more hindered diarylplumbylene, Tbt_2Pb: (**63d**) was not obtained by these synthetic methods, the conventional nucleophilic substitution reaction of $[(Me_3Si)_2N]_2Pb$: (**54**) with two molar amounts of TbtLi in ether resulted in the isolation of **63d** as stable blue crystals (Scheme 24) [80a]. The molecular structure of **63d** was definitively determined by X-ray crystallographic analysis, which showed an extremely large C–Pb–C angle of 116.3(7)°. This value largely deviates not only from the calculated one (97.3°) for Me_2Pb: [81] but also from the averaged values of those for previously reported diaryl- and dialkylplumbylenes [88.2(2) to 117.1(2)°; average = 103°], indicating the extremely large steric repulsion between the two Tbt groups. Plumbylenes **59** and **60** also showed a similar large widening of their C–Pb–C angles [117.1(2)° for **59** [78] and 114.5(6)° for **60** [43], respectively]; the widening might be mainly due to its seven-membered ring structure in the former case while



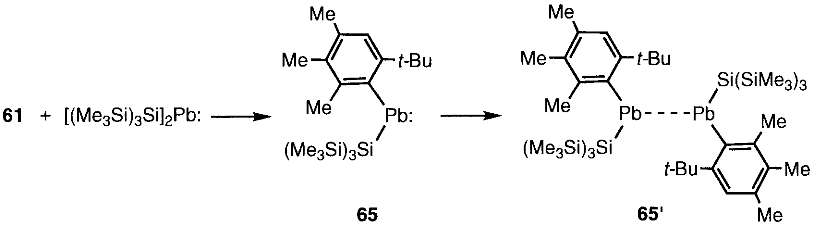
Scheme 24.

it is again due to the huge steric hindrance between the bulky terphenyl ligands in the latter case.

All the isolated plumbylenes mentioned above exists as V-shaped monomers in the solid state, Klinkhammer et al. have found a quite interesting feature for their new heteroleptic plumbylene $R^f[(Me_3Si)_3Si]Pb$: (**64**) [82]. Although plumbylene **64** was synthesized by a novel ligand disproportionation between the corresponding stannylene R^f_2Sn: (**38**) and plumbylene $[(Me_3Si)_3Si]_2Pb$:, the crystallographic analysis of the isolated lead product revealed that **64** has a dimeric form **64′** in the solid state with a considerably short Pb···Pb separation [3.537(1) Å] and a *trans*-bent angle of 40.8° (Scheme 25). Weidenbruch et al. also reported the synthesis of another heteroleptic plumbylene $R[(Me_3Si)_3Si]Pb$: (**65**; R = 2-*t*-butyl-4,5,6-trimethylphenyl), the structural analysis of which showed a dimeric structure **65′** in the solid state with a similar short Pb···Pb separation [3.370(1) Å] and a *trans*-bent angle of 46.5° (Scheme 26) [75].

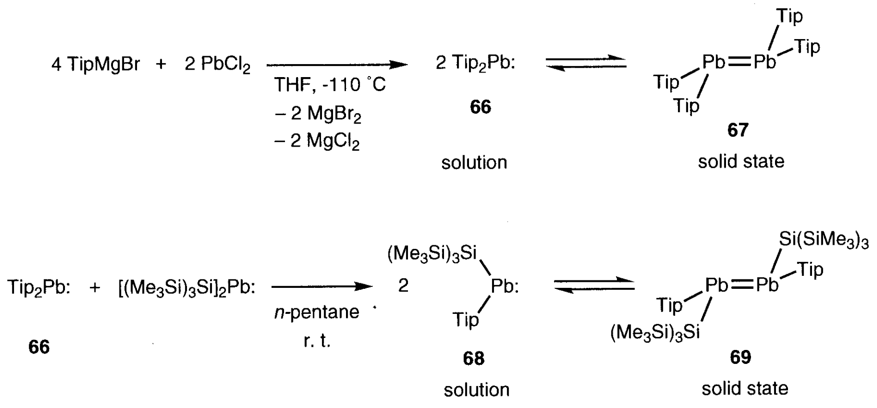


Scheme 25.



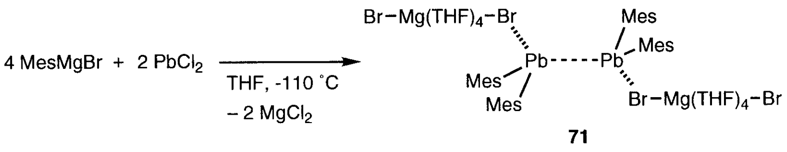
Scheme 26.

Although these two plumbylenes **64** and **65** were found to have a close intramolecular contact and exist as a dimer in the solid state, the lead–lead distances in their dimeric form are still much longer than the theoretically predicted values (2.95–3.00 Å) for the parent diplumbene, $H_2Pb{=}PbH_2$ [82,83]. Quite recently, however, Weidenbruch et al. have succeeded in the synthesis and isolation of the dimer of less hindered diarylplumbylene Tip_2Pb: (**66**), i.e. $Tip_2Pb{=}PbTip_2$ (**67**) (Scheme 27) [84]. Compound **67** showed a rather shorter Pb–Pb length [3.0515(3) Å] and much larger *trans*-bent angles (43.9 and 51.2°) than those observed for **64′** and **65′**, strongly indicating that **67** is the first molecule with a lead–lead double bond in the solid state, although **67** was found to dissociate into the monomeric plumbylene **66** in solution. Furthermore, they examined the synthesis of a heteroleptic plumbylene, Tip[(Me$_3$Si)$_3$Si]Pb: (**68**), by the treatment of diarylplumbylene Tip$_2$Pb: (**66**) and disilylplumbylene [(Me$_3$Si)$_3$Si]$_2$Pb: and found that the product exists as the diplumbene Tip[[(Me$_3$Si)$_3$Si]Pb=Pb[Si(SiMe$_3$)$_3$]Tip (**69**) in the solid state (Scheme 27) [85]. The X-ray structure analysis of **69** reveals the centrosymmetrical diplumbene structure with a *trans*-bent angle of 42.7° and a Pb–Pb bond length of 2.9899(5) Å, which is even shorter than that of **67** and very close to the theoretically predicted value for the parent diplumbene.



Scheme 27.

In order to elucidate the relationship between the structure of plumbylene dimers and the bulkiness of substituents, Weidenbruch et al. synthesized and characterized much less hindered diarylplumbylene Mes$_2$Pb: (**70**), which was isolated as a plumbylene dimer (**71**) stabilized with co-existing magnesium salt [MgBr$_2$(THF)$_4$] (Scheme 28) [85]. The large Pb···Pb separation [3.3549(6) Å] and *trans*-bent angle (71.2°) of **71** suggest that the character of the lead–lead bonding interaction in plumbylene dimers is delicate and changeable.

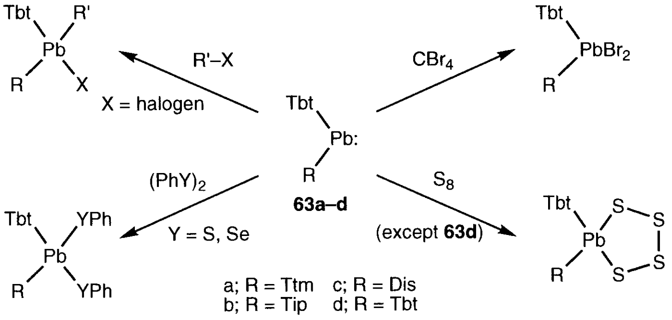


Scheme 28.

4.4. Reactions of plumbylenes

Since the progress in the chemistry of plumbylenes is far behind those of its lighter congeners (silylenes, germylenes, and stannylenes) as mentioned above, most of recent reports on plumbylenes are those for their synthesis and structural analysis and there have been very few descriptions of their reactivities.

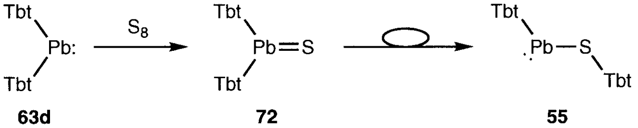
Recently, however, Okazaki et al. reported a versatile reactivity of Tbt-substituted plumbylenes **63a**–**d**, i.e. insertion reactions with alkyl halide, diphenyl dichalcogenides, bromine abstraction from carbon tetrabromide, and sulfurization with elemental sulfur as shown in Scheme 29 [72,79,80,86].



Scheme 29.

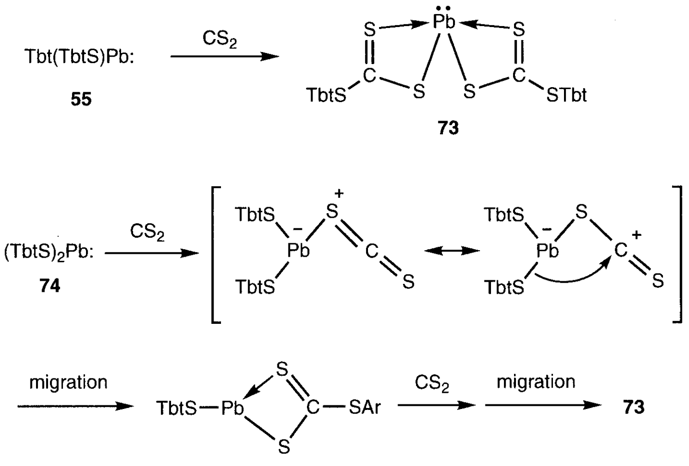
These results indicate that the reactivity of a plumbylene, the heaviest congener of a carbene, is essentially the same as those observed for its lighter congeners. The successful isolation of the reaction products in the case of plumbylenes **63** might be due to the effective steric protection not only for the starting plumbylenes but also for the reaction products, which inevitably contain weak bonds between the lead and other atoms. Among the results obtained by Okazaki et al. the sulfurization of **63d** should be noted [80b]. Treatment of the overcrowded plumbylene **63d** with one atom equivalent of elemental sulfur at low temperature (−78°C) resulted in the formation of plumbanethione $Tbt_2Pb{=}S$ (**72**), the expected sulfurized product, while similar sulfurization of **63d** at 50°C gave a new heteroleptic plumbylene Tbt(-TbtS)Pb: (**55**), i.e. the 1,2-aryl migration product of **72** (Scheme 30). These results demonstrate that R(RS)Pb: is more stable than $R_2Pb{=}S$, and this fact is in sharp contrast to the relative stabilities of their lighter congeners. The kinetically stabilized metallanethiones Tbt(R)M=S (M = Si [7], Ge [45–47], and Sn [64,66]) are isolated as stable crystalline compounds and no isomerization to heteroleptic divalent species via 1,2-migration of the ligand is observed on heating. This unique relative stabilities found for plumbanethione and its plumbylene type isomer was corroborated by ab initio calculations on those of a series of double bond compounds, [$H_2Pb{=}X$] and their isomers [*trans*-H–Pb–S–H] and [*cis*-H–Pb–S–H] (X = O, S, Se, and Te) [87,88].

The reactivity of the heteroleptic plumbylene **55** toward carbon disulfide should also be noted. Treatment of **55** with excess amount of carbon disulfide resulted in



Scheme 30.

a formation of unexpected product, lead(II) bis(aryl trithiocarbonate) (**73**), as yellow, air- and moisture stable solid (Scheme 31) [89]. The reaction must involve not only the insertion of carbon disulfide into the Pb–S bond but also the formal insertion of a sulfur atom into the Pb–C(Tbt) bond and subsequent insertion of another carbon disulfide. Compound **73** was also obtained by the reaction of bis(arylthio)plumbylene **74** with carbon disulfide, indicating the double insertion of carbon disulfide into the two Pb–S bonds (Scheme 31). Although the migratory insertion of carbon disulfide into a metal–sulfur bond is known for some transition metal complexes, such double insertion of carbon disulfide as suggested above has not been observed in the case of other heavier Group 14 element divalent species, i.e. silylenes [31], germylenes [52], and stannylenes [68].



Scheme 31.

5. Conclusions

As can be seen in this article, the chemistry of divalent species of heavier Group 14 elements is still growing with a variety of novel findings. The remarkable development of ligands for thermodynamic and kinetic stabilization provided us with a number of stable examples of heavier homologues of carbenes, whose unique chemical and physical properties will stimulate the further progress in this field. Although the progress in the chemistry of stannylenes and plumbylenes is much slower than that of silylenes and germylenes probably due to the weakness of bonds involving such heavier elements, a comparative study on the whole chemistry of divalent species of Group 14 elements including carbenes should be important to produce new concepts and applications for these low-coordinate species.

Acknowledgements

This review was written at the Universität Göttingen during the tenure of a von Humboldt Senior Research Award of one of the authors (R.O.), who is grateful to the von Humboldt Stiftung for their generosity and to Professor Herbert W. Roesky for his warm hospitality.

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