Stable Heavier Carbene Analogues

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Contents

1. Introduction

In recent decades, it has generally been recognized that carbenes play an important role as transient intermediates. As a result of a number of stable carbenes having been isolated and investigated in detail, it is not an exaggeration to say that the chemistry of carbenes has been thoroughly investigated and is now well-understood.[1] In addition, much attention has also been paid to the heavier analogues of carbenes, i.e., silylenes (R_2Si:), germylenes (R_2Ge:), stannylenes (R_2Sn:), and plumbylenes (R_2Pb:). These so-called metallylenes are monomeric species of the polymetallanes. This is especially true of the silylenes, which are believed to be monomers of polysilane. The metallylenes could be expected to be of great importance in fundamental and applied chemistry as a result of their many differences and similarities to carbenes.

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The valency of the central atom of the heavier carbene analogues (R_2M:, M = Si, Ge, Sn, Pb) is two. That is, its oxidation state is M^{II} and its stability increases as the principal quantum number (n) increases. In fact, dichloroplumbylene and dichlorostannylene, $PbCl_2$ and $SnCl_2$, respectively, are very stable ionic compounds. However, these dihalides exist as polymers or ion pairs both in solution and in the solid state. The dichlorogermylene complex $GeCl_2 \cdot$(dioxane)[3] is also known to be stable and isolable, whereas the dihalosilylenes are barely isolable compounds.[2] The early silylene research was concerned largely with comparing the chemistry of the dihalosilylenes with that of carbenes. Hence, the chemistry of the metallylenes has been considered mainly from the molecular chemistry point of view.[4]

In contrast to the carbon atom, the heavier group 14 atoms have a low ability to form hybrid orbitals. They therefore prefer the $(ns)^2(np)^2$ valence electron configurations in their divalent species.[5] Since two electrons remain as a singlet pair in the ns orbital, the ground state of H_2M: (M = Si, Ge, Sn, Pb) is a singlet, unlike the case of H_2C:, where the ground state is a triplet (Figure 1).[1a] On the basis of theoretical calculations, the singlet−triplet energy differences ΔE_{ST} for H_2M, [$\Delta E_{ST} = E$(triplet) − E(singlet)], are found to be 16.7 (M = Si), 21.8 (M = Ge), 24.8 (M = Sn), and 34.8 (M = Pb) kcal/mol, respectively. That of H_2C: is estimated as −14.0 kcal/mol.[6] Furthermore, the relative stabilities of the singlet species of R_2M: (M = C, Si, Ge, Sn, Pb; R = alkyl or aryl) compared to the corresponding dimer, $R_2M=MR_2$, are estimated to increase as the element row descends, C < Si < Ge < Sn < Pb. It follows, therefore, that one can expect that a divalent organolead compound such as plumbylene should be isolable as a stable compound. However, some plumbylenes, without any electronic or steric stabilization effects, are known to be thermally unstable and undergo facile disproportionation reactions, giving rise to elemental lead and the corresponding tetravalent organolead compounds.[7] On this basis, it could be concluded that it might be difficult to isolate metallylenes as stable compounds under ambient conditions, since they generally exhibit extremely high reactivity toward other molecules as well as themselves. Metallylenes have a singlet ground state with a vacant p-orbital and a lone pair of valence orbitals. This extremely high reactivity must be due to their vacant p-orbitals, since 6 valence electrons is less than the 8 electrons of the "octet rule". Their lone pair is expected to be inert due to its high s-character. In order to stabilize metallylenes enough to be isolated, either some thermodynamic and/or kinetic stabilization of the reactive vacant p-orbital is required (Figure 2). A range of "isolable" metallylenes have been synthesized through the thermodynamic stabilization of coordinating Cp* ligands, the inclusion of heteroatoms such as N, O, and P,

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"isolable" under ambient conditions in an inert atmosphere. Since several excellent review articles are already available on the history of the synthesis and properties of these stable metallylenes,[7,10,11] we are limiting our review to more recent reports and the current chemistry of stable metallylenes.
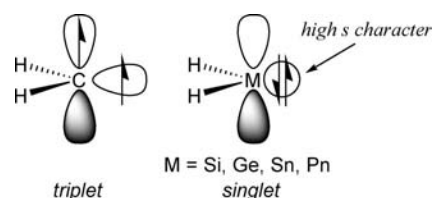

Figure 1. Difference between the ground states of carbenes and metallylenes.
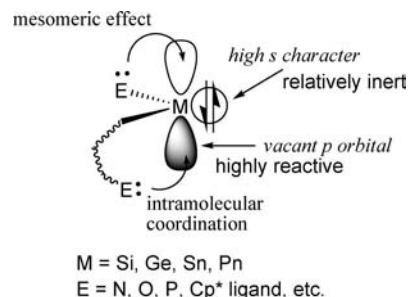
Figure 2. Thermodynamic stabilization of metallylenes.

etc. (see below), and/or the introduction of kinetic stabilization using bulky substituents (Scheme 1).

The parent silylene (H_2Si:) and derivatives having relatively simple substituents such as Me_2Si:, Cl_2Si:, and Ph_2Si: have all been investigated using gas-phase kinetic studies and/or spectroscopic detection in matrices at very low temperatures.[8,9] In particular, Leigh et al. studied the properties of simple silylenes, germylenes, and stannylenes using laser flash photolysis of suitable precursors.[9] So far, the generation of other transient and metastable metallylenes species under special conditions, as well as their reactions with trapping reagents, have all been actively investigated and reported.[8–10] Although these studies are of great importance in metallylene chemistry, this review will focus mainly on the chemistry of those compounds that are "stable" and

Scheme 1. Examples of Thermodynamically Stabilized Metallylenes
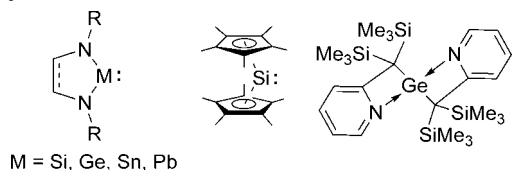
M = Si, Ge, Sn, Pb

Scheme 2. Synthetic Methods for Metallylenes

X = Cl, Br, I, etc.
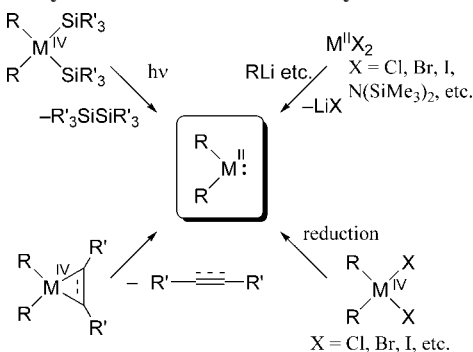
2. Carbon-Substituted (Aryl or Alkyl Substituted) Metallylenes

2.1. Synthesis

Since metallylenes have lower oxidation states, i.e., they are M^{II} species (M = Si, Ge, Sn, Pb), their synthesis is best approached as follows: (i) the reduction of an M^{IV} species as the precursor or (ii) a substitution reaction of M^{II} halides, such as $SnCl_2$, as the starting material with an organometallic species such as RLi or ArLi as the nucleophile (Scheme 2). In case (i), there are several possible reduction reactions of the R_4M species, leading to the formation of the R_2M: species: (a) the photochemical reductive elimination of a disilene from $R_2M(SiR'_3)_2$, (b) the thermal and/or photochemical reductive elimination of an olefin or an alkyne from the three-membered ring systems metalliranes or metallirenes, and finally (c) the reduction of the corresponding dihalides, R_2MX_2 (X = Cl, Br, I), using reagents such as lithium naphthalenide, KC_8. On the other hand, method (ii) is applicable only in the case of germanium, tin, and lead, since there is no suitable Si^{II} (i.e., easily handled) starting material. It should also be noted that the choice of the substituent "R" is of great importance in determining the isolability of "stable" metallylenes.[12]

Carbon substituents should lead to less electronic perturbation compared to heteroatom substituents such as N, O, and P (see below). The intrinsic nature of the metallylenes will be obscured in the cases of heteroatom-substitution due to the electronic effects of the heteroatoms i.e., intramolecular coordination of the heteroatom, and hapticity of the ligands as shown in Figure 2. The result is that steric bulkiness of the carbon substituents is necessary in order to prevent the vacant p-orbital of the carbon-substituted metallylene from undergoing both intra- and intermolecular reactions (Figure 3). When this steric hindrance is insufficient, the metallylene will undergo self-oligomerization, leading to the corresponding polymer, oligomer, or dimer.

In the case of silicon, it is known that the photolysis of trisilane and cyclotrisilane derivatives leads to the generation of the corresponding silylenes.[10,11,13] When 2,2-diaryltrisilanes **1** bearing relatively bulky substituents such as Mes, Xyl, Tip,
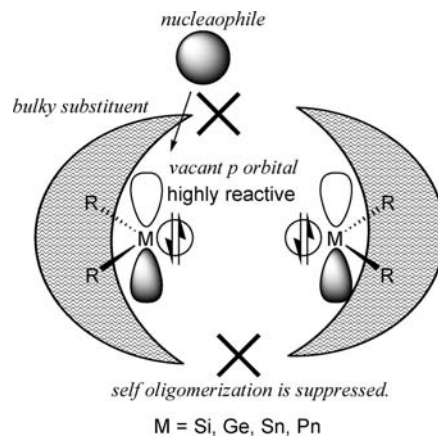

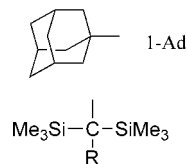**Figure 3.** Role of bulky substituents for stabilization of metallylenes.

Mes:	R = R' = CH₃

Mes: R = R' = CH_3
Dep: R = C_2H_5, R' = H
Tep: R = R' = C_2H_5
Dip: R = $CHMe_2$, R' = H
Tip: R = R' = $CH(CH_3)_2$
Xyl: R = Me, R' = H
Dmt: R = Me, R' = t-Bu
Mes*: R = R' = t-Bu
R_f: R = R' = CF_3
Tbt: R = R' = $CH(SiMe_3)_2$
Bbt: R = $CH(SiMe_3)_2$, R' = $C(SiMe_3)_3$
Titp: R = 2,4'-(i-Pr)₂-C_6H_3, R' = H
Ditp: R = 2'-(i-Pr)-C_6H_4, R' = H
Tpp: R = R' = Ph
Ar_{tip}: R = Tip, R' = H
Ar_{dip}: R = Dip, R' = H
Ar_{np}: R = 1-naphtyl, R' = H
Ar_{mes}: R = Mes, R' = H
Arph: R = Ph, R' = H
Arcy: R = cyclohexyl, R' = H

1-Ad

$Me_3Si-\overset{R}{\underset{|}{C}}-SiMe_3$ Dis: R = H
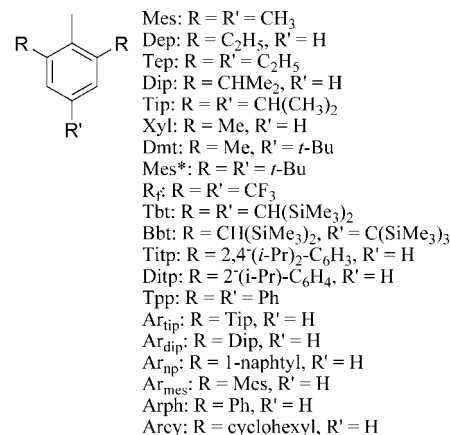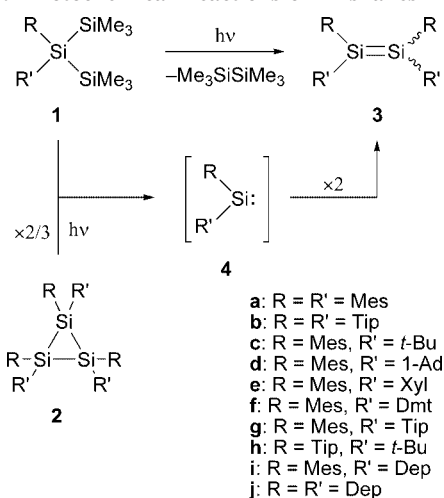Tsi: R = $SiMe_3$

Figure 4. Aryl and alkyl bulky substituents.

etc. (see Figure 4) were irradiated with a low-pressure Hg lamp, the corresponding disilenes (silylene dimers) were obtained as stable compounds. This suggests that the steric bulkiness of these substituents is not enough to suppress the self-dimerization of the expected silylenes (Scheme 3).[11] However, the extremely sterically hindered disilenes **6**, (E)-Tbt(Mes)Si=Si(Mes)Tbt and (Z)-Tbt(Mes)Si=Si(Mes)Tbt, prepared by the reduction of the corresponding dibromosilane **5** using lithium naphthalenide, were found to undergo thermal dissociation, leading to the generation of the corresponding diarylsilylenes **7**. Their generation was confirmed by intra- and intermolecular trapping reactions (Scheme 4).[14] The reaction of the silylene **7**, generated by the thermolysis of (Z)-**6** at 60 °C, with aryl isocyanides was reported as affording the corresponding silylene−isocyanide complexes **8** as stable compounds.[15] In this case, the self-dimerization of silylene **7** was suppressed to some extent by the steric repulsion between the bulky aryl substituents. Similarly, extremely hindered dialkyldisilene **10** was reported to exist in solution in equilibrium between **10** and silylene **11**.[16] Thus, the introduction of extremely bulky substituents on the silylene moiety may prevent it from self-dimerization, which would lead to the formation of the corresponding disilene due to the high reactivity of the lone pair of one silylene
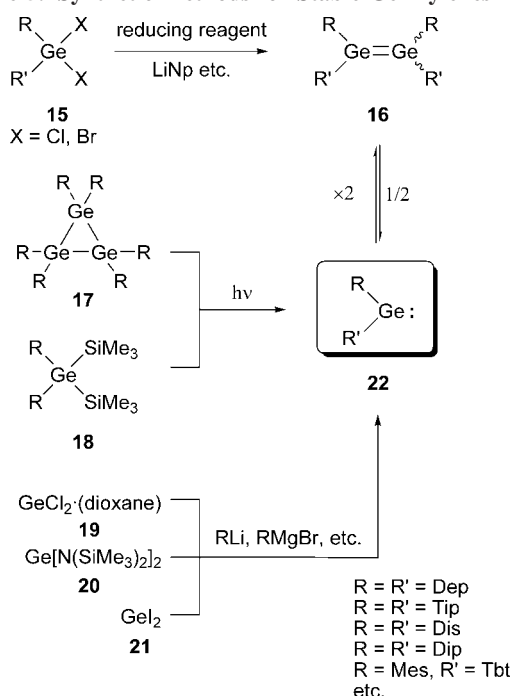
Scheme 3. Photochemical Reactions of Trisilanes

a: R = R' = Mes
b: R = R' = Tip
c: R = Mes, R' = t-Bu
d: R = Mes, R' = 1-Ad
e: R = Mes, R' = Xyl
f: R = Mes, R' = Dmt
g: R = Mes, R' = Tip
h: R = Tip, R' = t-Bu
i: R = Mes, R' = Dep
j: R = R' = Dep

Scheme 4. Thermal Generation of the Silylenes from Extremely Sterically Hindered Disilenes

Scheme 5. Synthetic Methods for Stable Germylenes
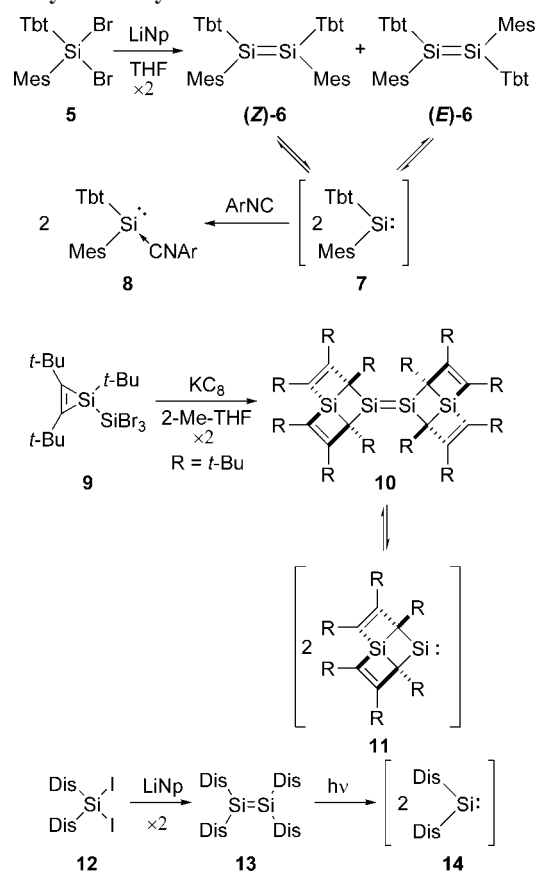
toward the vacant p-orbital of the other silylene molecule. Although the photochemical dissociation of Dis$_2$Si=SiDis$_2$ (13) to form the corresponding silylene, Dis$_2$Si: (14), has been reported,[17] the only examples of a thermal dissociation of a disilene into the corresponding silylenes are the two described here (Scheme 4).

On the other hand, to date a number of stable carbon-substituted germylenes, R$_2$Ge:, have been reported (Schemes 5 and 6).[11] Although the synthetic methods for the ger-mylenes are similar to those of the silylenes, in solution the former are generally in equilibrium with digermenes, the corresponding dimers, and are dimers in the solid state. This is in contrast to the silylenes, which form a strong Si=Si double bond to give disilene species both in solution and in
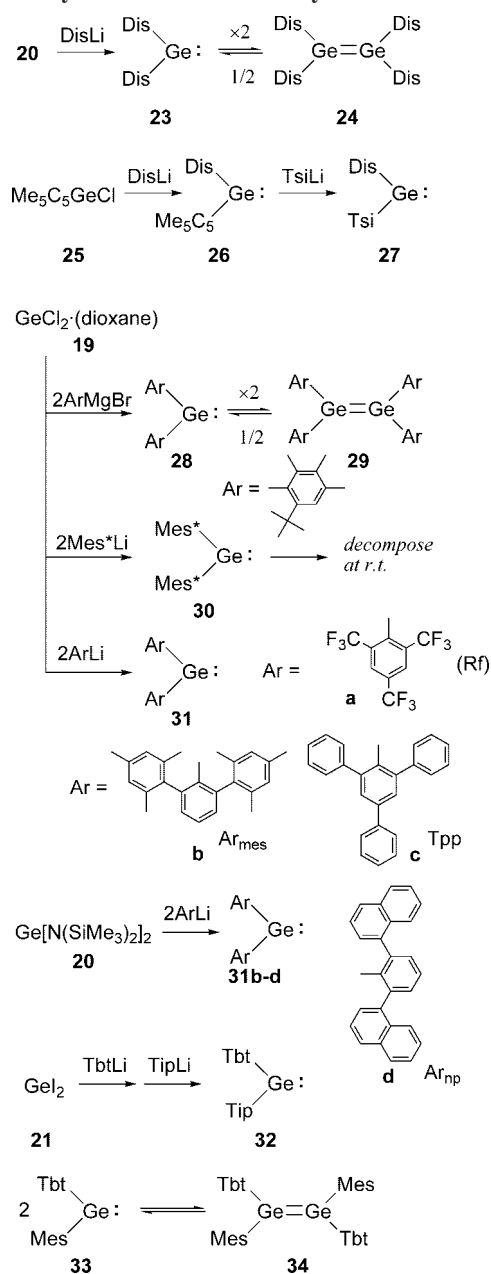
the solid state. This is the case even for silylenes with relatively bulky substituents. This means that the germylene lone pair exhibits high s-character compared to a silylene. This indicates a weaker coordinating ability of the lone pair toward the vacant p-orbital. Indeed, the reduction of the dibromogermanes 15 with reducing reagents such as lithium naphthalenide, and the photolysis of the cyclotrigermanes 17 or bis(trimethylsilyl)germanes 18 were both reported to give the corresponding germylenes 22. These exist as monomers in solution but exhibit the dimeric structure, digermenes 16, in the solid state. On the other hand, the photolysis of the cyclotrigermane, Mes$_6$Ge$_3$, afforded the corresponding digermene, Mes$_2$Ge=GeMes$_2$, which was reported as having a stable Ge=Ge double-bond structure even in solution.[18,19] In contrast to the silicons, there are a few kinds of stable divalent species available as precursors for the germylenes. The reaction of GeCl$_2$·(dioxane), GeI$_2$, and [(Me$_3$Si)$_2$N]$_2$Ge with RLi and RMgBr (R = Dis, Dip, etc.) yielded the corresponding germylenes 22 with the concomitant elimination of insoluble salts.

The first isolable monomeric dialkylgermylene 27 was synthesized by Jutzi's group.[20] Although Dis$_2$Ge: (23) exists as a monomer in both solution and in the gas phase and as a dimer in the solid state, Dis(Tsi)Ge: (27) is a monomer both in solution and in the solid state. Similarly, bis(6-t-butyl-2,3,4-trimethylphenyl)germylene 28 shows a digermene structure in the solid state, while behaving as a germylene in solution.[21] This demonstrates that the two 6-t-butyl-2,3,4-trimethylphenyl groups are not enough to suppress the intermolecular interaction between the lone pair and the vacant p-orbital of the germylenes. However, the germylene 30 with two Mes* groups, which are bulkier than the 6-t-butyl-2,3,4-trimethylphenyl group, exists as the monomer even in the crystalline state, as confirmed by X-ray crystallographic analysis.[22] It follows that the crystal structure of germylenes should be very susceptible to subtle size differences of the substituents. So far, even a few examples of stable "monomeric" diarylgermylenes in the solid state have been reported. In the case of R$_{f2}$Ge: [31a, R$_f$ = 2,4,6-

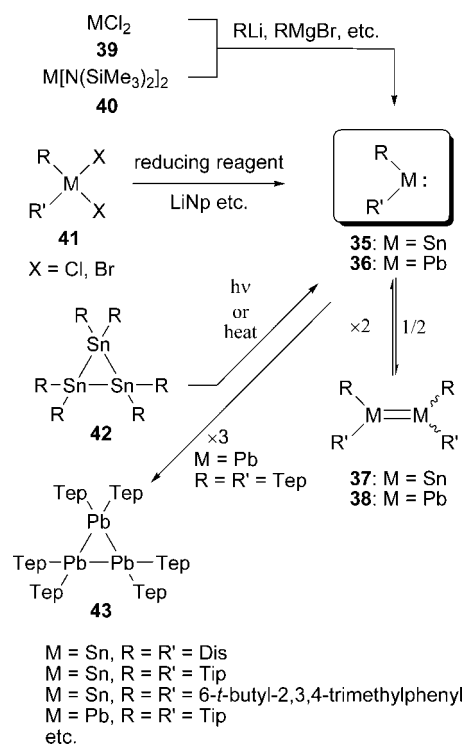**Scheme 6. Synthesis of Stable Germylenes**

Scheme 7. Synthetic Methods for Stable Stannylenes and Plumbylenes

M = Sn, R = R' = Dis
M = Sn, R = R' = Tip
M = Sn, R = R' = 6-*t*-butyl-2,3,4-trimethylphenyl
M = Pb, R = R' = Tip
etc.

Scheme 8. Bis(trimethylsilyl)methyl Substituted Stannylene and Plumbylene

44: M = Sn   46: M = Sn
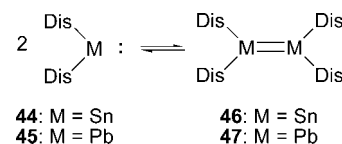45: M = Pb   47: M = Pb

tris(trifluoromethyl)phenyl)], however, on the basis of its structural parameters, weak intramolecular interactions between the fluorine atoms of the R_f substituents and the vacant p-orbital of the germylene center should exist.[23] As described above, Mes*$_2$Ge: (**30**) exists as a monomer even in the crystalline state;[22] however, it is only marginally stable in that it undergoes slow decomposition at room temperature to give Mes*H. The diarylgermylenes **31** and **32**, bearing extremely bulky aryl-substituents, are stable crystalline compounds under ambient conditions.[24,25] On the other hand, a germylene having Mes and Tbt groups (**33**) exists as an equilibrium mixture of germylenes and the corresponding digermene (**34**). The thermodynamic parameters are $\Delta H = 14.7 \pm 0.2$ kcal/mol and $\Delta S = 42.4 \pm 0.2$ kcal/mol.[26]

Stannylenes and plumbylenes are similar to each other but different to the silylenes and germylenes (Scheme 7). In the case of tin and lead (M = Sn, and Pb), the divalent species are easily obtained, since the M^{II} species are intrinsically stable. Therefore, stable divalent tin and lead compounds such as MCl_2 (M = Sn, Pb) or :M[N(SiMe$_3$)$_2$]$_2$ are available

as suitable precursors for making the stable stannylenes **35** and plumbylenes **36**. The reactions of MCl_2 (M = Sn, Pb) with RLi or RMg, the reduction of the dihalometallane R_2MX_2 (X = Cl, Br), and the thermolysis or photolysis of the cyclotristannane **42** all give the corresponding stannylenes and plumbylenes. This is similar to the synthesis of the germylenes.[10,11] Although a three-membered tin ring system, a cyclotristannane, is a stable compound,[27] the corresponding cyclotriplumbane is generally unstable and difficult to isolate, and to date only one example of a stable cyclotriplumbane has been reported.[28] Although the generation of a plumbylene by either the thermal or photochemical reaction of cyclotriplumbane **43** has not yet been reported, three-membered ring systems of tin are known to be good precursors for the generation of the corresponding metallylenes, as for silylenes and germylenes.[10,11] The judicial choice of bulky substituents should make it possible to control the structure of the metallylenes and dimetallenes as seen in the case of the Dis$_2$Ge: (**23**) and Dis(Tsi)Ge: (**27**). In the 1970s, Lappert et al. reported the synthesis of Dis$_2$Ge: as well as the tin and lead analogues, Dis$_2$Sn: (**44**) and Dis$_2$Pb: (**45**). They were found to be in equilibrium between the metallylenes and the corresponding dimers (distannene **46** and diplumbene **47**, respectively) in solution and dimers in the solid state (Scheme 8).[29] Dis$_2$Ge: (**23**) showed the same behavior.[21] However, the introduction of rigid bulkier ligands than a Dis group should make it possible for the stannylene and plumbylene compounds to exist as monomers even in the solid state. Hence, the stable dialkylstannylene **48**[30] and dialkylplum-

Scheme 9. Synthesis of Stable Stannylenes and Plumbylenes

48: M = Sn
49: M = Pb

54: M = Sn
55: M = Pb

56: M = Sn
57: M = Pb

Scheme 10. Stable Stannylenes and Plumbylenes, Which Exist As Monomers in the Solid State

60

a: Ar = Ar' = R$_f$
b: Ar = Tbt, Ar' = Tip
c: Ar = Tbt, Ar' = Ditp
d: Ar = Tbt, Ar' = Ar$_{cy}$
e: Ar = Bbt, Ar' = Titp
f: Ar = Ar' = Ar$_{mes}$
g: Ar = Ar' = Ar$_{dip}$

61

a: Ar = Ar' = R$_f$
b: Ar = Tbt, Ar' = Tip
c: Ar = Ar' = Tbt
d: Ar = Ar' = Ar$_{mes}$
e: Ar = Ar' = Ar$_{dip}$
f: Ar = Ar$_{tip}$, Ar' = t-Bu
g: Ar = Ar$_{tip}$, Ar' = Ph
h: Ar = Ar$_{tip}$, Ar' = Me
i: Ar = Ar$_{tip}$, Ar' = CH$_2$C$_6$H$_4$-4-(i-Pr)
j: Ar = Ar' = Ar$_{np}$
k: Ar = Ar' = Tpp

Scheme 11. Reactions of the Tetrathiametallolane Derivatives with Phosphine

62b: M = Sn, Ar = Tip
62d: M = Sn, Ar = Ar$_{cy}$
63b: M = Pb, Ar = Tip

60b
60d
61b

**64**   **65**

R = Me or Ph

66

bylene **49**[31] reported by Eaborn et al. can exist as monomeric metallylenes even in the solid state (Scheme 9). The attempted synthesis of Mes*$_2$M: (**54**,[32] M = Sn; **55**,[33] M = Pb), the aryl-substituted stannylene and plumbylene, which are heavier analogues of Mes*$_2$Ge: (**30**),[22] were reported by Weidenbruch et al. Mes*$_2$M: (**54** and **55**) were structurally characterized as monomers in the crystalline state, while the structure of Mes*$_2$Pb: is yet to be determined. Moreover, in both cases where M = Sn and Pb, they were found to undergo intramolecular cyclization to give the arylalkyl metallylenes **56** and **57** as stable metallylenes.[32,33] On the other hand, plumbylene **58** with two 6-t-butyl-2,3,4-tri-methylphenyl groups,[33] which is a slightly less-hindered ligand than the Mes* group, was found to exist as a monomer in the crystalline state, although stannylene **59** with the same ligands was found to exhibit weak intermolecular interaction between the Sn atoms and exists as a dimer in the crystalline state.[34] R$_{f2}$M: [**60a**,[35] M = Sn; **61b**,[36] M = Pb], were all synthesized as monomeric metallylenes. Plumbylenes bearing two Mes, 2,4,6-triethylphenyl, and Tip groups were reported as existing as dimers (diplumbenes) in the solid state,[7,37] even though these substituents should exhibit similar or even more steric hindrance effects than R$_f$. As is the case for R$_{f2}$Ge:,[23] the fluorine atoms of the substituent should weakly interact with the vacant p-orbital of the metallylene centers in **60a** and **61a**, respectively. A few examples of stable diarylstan-nylenes and diarylplumbylenes bearing extremely bulky aryl ligands have been reported so far. Some of them have been structurally characterized, showing they exist as monomeric structures even in the solid state (Scheme 10).[38,39] It should be noted that the bulky m-terphenyl ligand of 2,6-bis(2,4,6-triisopropylphenyl)phenyl (Ar$_{tip}$) has been found to afford great steric protection toward the central atom. Therefore, stannylenes and plumbylenes with one Ar$_{tip}$ group, together with a smaller organic substituent such as Me, Ph, t-Bu, were found to exist as monomers even in the solid state.[39] Interestingly, the plumbylene with a methyl group and a 2,6-bis(2,6-diisopropylphenyl)phenyl (Ar$_{dip}$) group, which is a
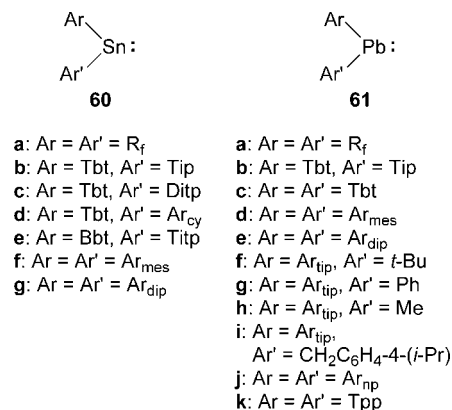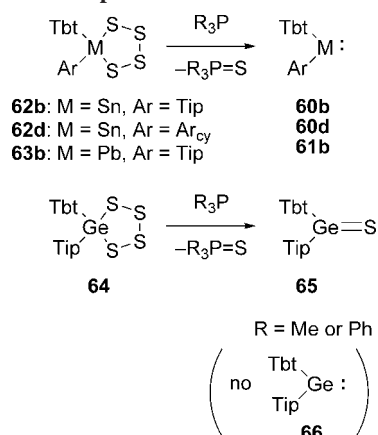
slightly smaller m-terphenyl ligand than the Ar$_{tip}$ group, was found to exhibit a dimeric structure in the crystalline state.[39b] Thus, even marginal differences in bulkiness can affect the crystalline structure of plumbylenes.

Another unique synthesis of overcrowded stannylenes and plumbylenes has been reported (Scheme 11). Tetrathiamet-allolanes **62b**, **62d**, and **63b** react with an excess of phosphines to give the corresponding metallylenes **60b**, **60d**, **61b**, respectively.[40] This is in contrast to the reaction of tetrathiagermolane **64** with an excess of phosphines, leading not to the formation of the corresponding germylene **66** but rather to the corresponding germanethione **65**.[41]

Recently, diazomethylstannylene **67** was synthesized as a stable carbon-substituted stannylene by Kira et al. (Scheme 12).[42] The stannylene **67** was found to be converted into another cyclic stannylene **70** by irradiation using a 500 W high-pressure mercury arc lamp. A stable compound is produced via the generation of an intermediate stannaacety-lene **69**, which is believed to be the carbene-substituted stannylene **68**.

The first isolable monomeric dialkylstannylene **78** was synthesized in 1991 by Kira et al. (Scheme 13).[43] The 1,1,4,4-tetrakis(trimethylsilyl)butane-1,4-diyl ligand **72** was found to be a good ligand for the isolation of monomeric metal-lylene species as evidenced by the fact that dialkylgermylene **77**[44] and dialkylsilylene **76**[45] have been successfully isolated as stable compounds in 1998 and 1999, respectively. Of particular note is the isolation of **76**, the first example of a stable dialkylsilylene. Although the stable dialkylstannylene **78** was synthesized by the reaction of SnCl$_2$ with the

Scheme 12. Generation and Intermediacy of a Stannyne to Afford a Cyclic Stannylene
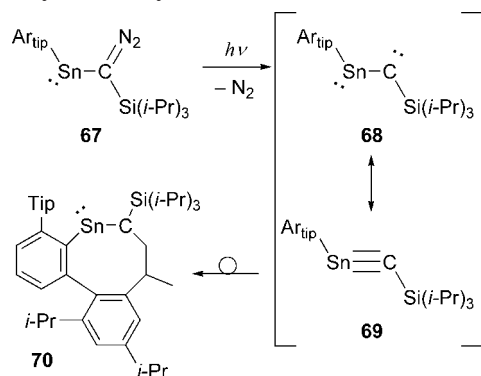
Scheme 13. Synthesis of Stable Dialkylmetallylenes 76−78

73: E = Si, X = Br   76: E = Si
74: E = Ge, X = Cl   77: E = Ge
75: E = Sn, X = Cl   78: E = Sn
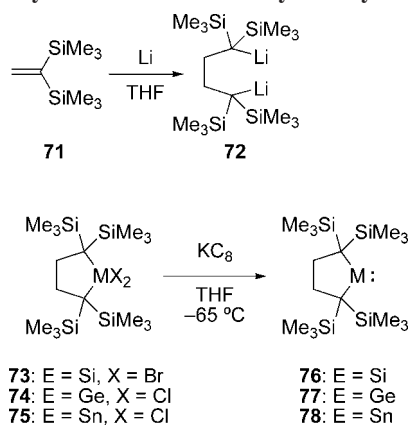
Scheme 14. Stable Stannylene with Intramolecular B−H···Sn Agostic Interactions
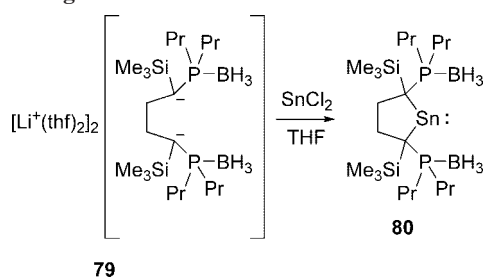
dilithiated compound **72**, prepared in turn by the reductive coupling reaction of $H_2C=C(SiMe_3)_2$ (**71**), the reaction of $GeCl_2 \cdot$dioxane, GeI_2, or $Ge[N(SiMe_3)_2]_2$ with **72** failed to give the corresponding germylene **77**. Finally, the stable dialkylmetallylenes **76−78** were successfully synthesized by the reduction of the corresponding dihalogenated compounds **73−75**, respectively, with KC_8 in THF at −65 °C.[1g−i,47]

Recently, a related stable stannylene **80** was isolated as a monomer, despite the presence of intramolecular coordination of the B−H unit to the central Sn atom via agostic interactions.[48] Interestingly, the intramolecular B−H···Sn agostic interactions were found to thermodynamically stabilize the electron-deficient stannylene unit by 30−40 kcal/mol (Scheme 14).

2.2. Properties

Some of the stable examples of carbon-substituted metallylenes introduced in the previous section have been structurally characterized using X-ray crystallographic analysis. Selected structural parameters of stable carbon-substituted

Table 1. Selected Structural Parameters of Stable Dialkylmetallylenes 76−78

	d(C−M)/Å	d(C−Si)/Å	∠C−M−C/°
M = Si	1.911(2)	1.911(2)	93.88(7)
(**76**)	1.904(2)	1.901(2)	
		1.915(2)	
		1.897(2)	
M = Ge	2.010(2)	1.905(2)	90.9(9)
(**77**)	2.020(2)	1.890(2)	
		1.899(2)	
		1.894(2)	
M = Sn	2.218(2)	1.887(2)	86.16(9)
(**78**)	2.226(3)	1.883(2)	
		1.885(2)	
		1.885(2)	

Table 2. Selected Structural Parameters of Stable Metallylenes

R_2M:	d(C−M)/Å	∠C−M−C/°	ref
TsiDisGe: (**27**)	2.067(4)	111.3(2)	20
	2.012(6)		
Ar$_{mes2}$Ge: (**31b**)	2.033(4)	114.4(2)	38c
Ar$_{dip2}$Ge:	2.033(2)	113.8(2)	38d
	2.048(2)		
Ar$_{np2}$Ge: (**31d**)	2.036(2)	102.72(9)	24
	2.030(2)		
Mes*$_2$Ge: (**30**)	2.053(4)	18.0(2)	22
	2.041(4)		
Bbt(Titp)Sn: (**60e**)	2.196(8)	106.4(2)	38b
	2.219(9)		
Ar$_{mes2}$Sn: (**60f**)	2.225(5)	114.7(2)	38c
Ar$_{dip2}$Sn: (**60g**)	2.255(2)	117.56(8)	38d
Ar$_{tip}$(Ph)Sn:	2.220(3)	96.87(10)	39a
	2.187(3)		
Mes*$_2$Sn: (**54**)	2.255(4)	103.6(1)	32
	2.267(4)		
48	2.286(3)	117.6(1)	30
	2.284(3)		
(Tpp)$_2$Pb: (**61k**)	2.322(13)	98.8(5)	38a
	2.327(13)		
Ar$_{np2}$Pb: (**61j**)	2.347(4)	100.40(13)	38a
	2.322(4)		
57	2.344(9)	94.8(4)	33
	2.476(14)		
58	2.357(4)	103.04(13)	33
	2.376(4)		
Ar$_{mes2}$Pb: (**61d**)	2.334(12)	114.5(6)	38c
Ar$_{dip2}$Pb: (**61e**)	2.390(8)	121.5(3)	38d
	2.379(9)		
49	2.397(6)	117.1(2)	31
	2.411(5)		
Tbt$_2$Pb: (**61c**)	2.327(13)	116.3(7)	38e
Ar$_{tip}$(t-Bu)Pb:	2.289(11)	100.5(11)	39d
	2.329(14)		
Ar$_{tip}$(Me)Pb:	2.272(9)	101.4(4)	39d
	2.274(15)		
Ar$_{tip}$(Ph)Pb:	2.321(3)	95.64(11)	39d
	2.264(3)		

metallylenes are partially summarized in Tables 1 and 2. Although the structural parameters of metallylenes are to some extent affected by the bulkiness of the substituents, the characteristic structural features of the carbon-substituted
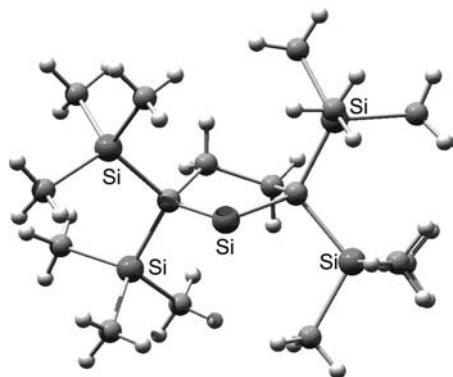
Figure 5. Molecular structure of dialkylsilylene **76**.

metallylenes R_2M: (M = Si, Ge, Sn, Pb) are as follows. (i) The C−M−C angles are smaller than 120°. This should be the ideal bond angle for the sp^2-hybridized carbon atom, i.e., close to ca. 90°, indicating that the intrinsic nature of the heavier metallylenes is the $(ns)^2(np)^2$ valence electron configuration. (ii) The C−M bond lengths are slightly greater than those of the corresponding C−M^{IV} compounds (typical C−M^{IV} bond lengths are 1.87 Å (M = Si), 1.95 Å (M = Ge), 2.17 Å (M = Sn), and 2.29 Å (M = Pb)).[49] This suggests a higher p-character for the C−M^{II} bond in metallylenes compared to the C−M^{IV} bond of tetravalent species of the heavier Group 14 elements.[5]

Such structural features seem to be enhanced in the order Si < Ge < Sn < Pb, reflecting the inherent $(ns)^2(np)^2$ valence electron configuration due to the size difference between the ns and np orbitals. While the fundamental structural features are as described above, the steric and electronic effects of the substituents must also be considered in order to fully understand the metallylene structures. In the first instance, one can interpret these substituent effects in electronic and steric terms as follows. For electronic effects, σ-electron-donating groups such as alkyl groups are expected to make the C−M−C angle larger, since electropositive substituents would make the metallylene ns orbital large enough to be mixed with the np orbital, resulting in partially hybridized orbitals. Conversely, σ-electron-withdrawing groups such as aryl groups would make the C−M−C angle smaller. With respect to steric effects, it can be predicted that bulky substituents would make the C−M−C angle larger. The larger C−M−C angle would then enhance the s-character of the C−M bonds and the p-character of the lone pair of the metallylene. Thus, the structural and electronic properties are interdependent.

If we consider the series of stable dialkylmetallylenes, **76** (Figure 5),[45] **77**,[44] and **78**,[43] the following interesting features are summarized in Table 1. The C−$SiMe_3$ bond lengths in **76** (M = Si), **77** (M = Ge), and **78** (M = Sn) are ca. 1.91, 1.90, and 1.89 Å, respectively, which are somewhat longer C−Si bond lengths than typical C−Si bond lengths of ca. 1.87 Å.[11g,43−45] The increase in C−$SiMe_3$ bond length gets smaller in the order **76** (M = Si) > **77** (M = Ge) > **78** (M = Sn). This increase in adjacent C−$SiMe_3$ bonds could be due to effective σ−π hyperconjugation between the C−Si bond and the vacant π orbital of the metallylene center. Thus, it could be expected that the dialkylmetallylenes would be, to some extent, thermodynamically stabilized by this σ−π hyperconjugation. In addition, the C−M−C angles of **76**−**78** also get smaller in the order **76** (M = Si) > **77** (M = Ge) > **78** (M = Sn), confirming a higher tendency to keeping the

**Table 3. Spectral Data for the Stable Metallylenes**

R_2M:	λ_{max}/nm	^{29}Si, ^{119}Sn, ^{207}Pb chemical shift (δ)	ref
76	440	+567	45
77	450		44
$Ar_{dip2}Ge$:	608		38d
Tbt(Tip)Ge: (**32**)	580		53
Mes*$_2$Ge: (**30**)	430		50
Dis_2Ge: (**23**)	414		51
$R_{f2}Ge$: (**31a**)	374		23
$Ar_{mes2}Ge$: (**31b**)	578		38c
78	486	+2323	43
48	546	+2299	30
$Ar_{mes2}Sn$: (**60f**)	553	+1971	38c, 54
$Ar_{dip2}Sn$: (**60g**)	600	+2235	38d
Tbt(Tip)Sn: (**60b**)	561	+2208	55
BbtTiptSn: (**60e**)	547	+1657	38b
Dis_2Sn: (**44**)	495	+2328	51a, 56
Mes*$_2$Sn: (**54**)	476	+980	32
$R_{f2}Sn$: (**60a**)	345	+723	35a
49	610	+10050	31
Tbt_2Pb: (**61c**)	610	+9751	38e
$Ar_{dip2}Pb$: (**61e**)	586	+9430	38d
$Ar_{tip}(CH_2C_6H_4$-4-i-Pr)Pb: (**61i**)	556	+8858	39b
Tbt(Tip)Pb: (**61b**)	550	+8888	38e
Tbt(Dis)Pb:	531	+8884	38e
$Ar_{mes2}Pb$: (**61d**)	526	+8844	38c,39d
$Ar_{dip}(t$-Bu)Pb:	520	+8275	39b
$Ar_{dip}(C_6H_4$-4-t-Bu)Pb:	462	+7275	39b
$Ar_{tip}(t$-Bu)Pb:	470	+7853	39d
$Ar_{dip}(Me)Pb$:	470	+8738	39b
$Ar_{tip}(Me)Pb$:	466	+7420	39d
$Ar_{tip}(Ph)Pb$:	460	+6657	39d
Mes*$(CH_2CMe_2C_6H_2$-2,5-t-Bu_2)Pb: (**57**)	406	+5067	33

inherent $(ns)^2(np)^2$ valence electron configuration in the same order Sn > Ge > Si.[5]

Metallylenes are generally colored in hydrocarbon solutions. The stable metallylenes show weak absorption maxima in the visible light region in their UV/vis spectra due to their symmetry forbidden n−p electron transitions (Table 3). Although the absorption maxima (λ_{max}) vary with their substituents, it can be roughly concluded that the n−p electron transitions will be red-shifted as the central element goes from Si < Ge < Sn < Pb. This is in parallel with the singlet−triplet energy differences ΔE_{ST} for the metallylenes $[\Delta E_{ST} = E(triplet) − E(singlet)]$. In addition, aryl-substituted metallylenes have relatively longer λ_{max} values than those of the corresponding dialkylmetallylenes. For example, the λ_{max} value for Mes*$_2$Ge: is 430 nm,[50] whereas that of Dis_2Ge: is 414 nm.[51] The slightly longer λ_{max} values of the diaryl-metallylenes than the dialkylmetallylenes suggest an effective interaction between the vacant p orbital of the diarylmetal-lylene and the π* orbital of the aromatic substituent.

The ^{29}Si NMR spectrum of the stable silylene **76** showed a dramatically down-shifted signal at +567.4 ppm.[45] Although this is the only example of the ^{29}Si NMR spectrum of a carbon-substituted silylene, it was found that the dialkylsilylene showed extremely downfield chemical shifts compared to both the disilenes[5a] and the donor-stabilized silylenes (see below). Similarly, the ^{119}Sn and ^{207}Pb NMR spectra, respectively, of stable stannylenes and plumbylenes with carbon substituents showed characteristic downfield chemical shifts compared to both the corresponding tetravalent species and dimeric and/or donor-stabilized metallylenes. Such characteristic NMR features of these metallylenes could

Scheme 15. Reactions of Stable Dialkylsilylene 76

Scheme 16. Synthesis of Lewis Base Complex of Dimesitylgermylene
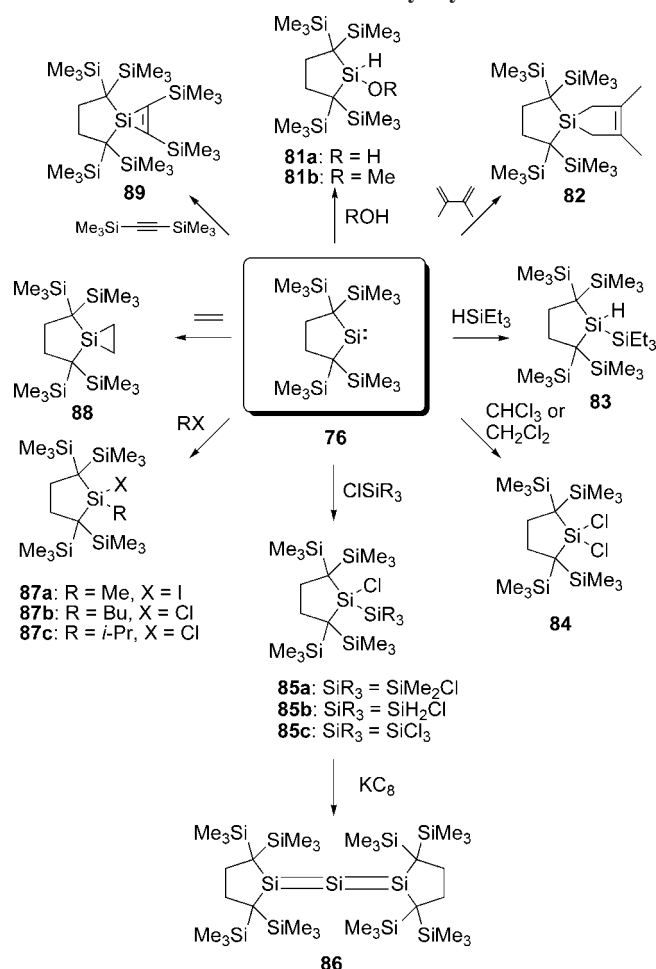
be due to the paramagnetic term in the chemical shifts correlated with the n−p electron transitions (λ_{max}).[52]
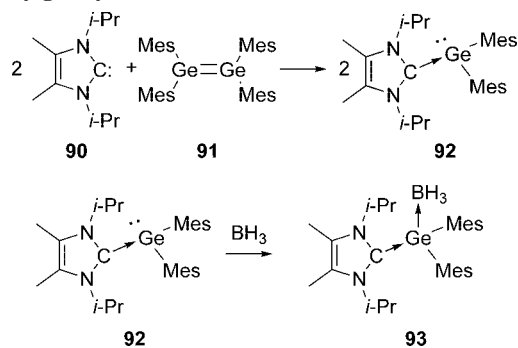
2.3. Reactivities

The reactions of stable carbon-substituted metallylenes have been reported and some reviews have also appeared.[10,11,57] Some representative examples of the reactions of stable dialkylsilylene **76** are shown in Scheme 15.

The diverse range of reported reactivities of stable metallylenes can be roughly categorized into five types: (i) insertion, (ii) cycloaddition, (iii) reduction, (iv) oxidation, and (v) coordination reactions. A valid explanation of this diverse range of reactions is the initial formation of a Lewis acid−base complex between the metallylene and the reagent with the metallylene acting as a Lewis acid with high electrophilicity. As described above, a metallylene has two reactive sites, namely, the vacant p orbital and the lone pair of electrons based on its singlet ground state. However, the lone pair is expected to be relatively "inert" as a nucleophile, since it exhibits high s character due to its $(ns)^2(np)^2$ valence electron configuration. On the other hand, due to the 6 valence electrons and the octet rules, the vacant p orbital should make the metallylene highly electrophilic. Thus, almost all the metallylene reactivity can be initiated by the nucleophilic reaction of the reagents toward the vacant p orbital.

For example, reactions of the stable metallylenes R_2M: with haloalkanes (R′X, X = halogen) such as MeI or MeOH (R′OH) are known to give the corresponding insertion
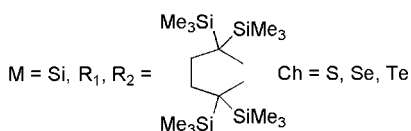
products $R_2MR'X$ (X = halogen or OH) [reactivity (i)]. Such insertion reactions can be initiated by the nucleophilic attack of the halogen or oxygen lone pair, leading to the formation of the Lewis acid−base complex, e.g., $R_2M^{\delta-}-X^{\delta+}-R'$.[9] Since the nucleophilicity of the central metallylene moiety (M) should be enhanced by this coordination, the next step in the nucleophilic reaction is expected to be that of the M toward the R′ moiety. Recently, Baines et al. demonstrated that dimesitylgermylene (Mes_2Ge:) was stabilized by the coordination of an N-heterocyclic carbene (NHC), giving the carbene−germylene complex **92**. Its lone pair exhibited high nucleophilicity toward BH_3 to afford the Lewis acid−base complex germylene **93** (Scheme 16).[58] Other unique metallylene insertion reactions toward systems such as Si−H, Si−Cl, B−H, and B−B bonds[57,59] can also be explained by an initial interaction between the vacant p orbital and the reactive bond with a high highest occupied molecular orbital (HOMO) level. For example, as shown in Scheme 15, the reaction of **76** with chlorosilanes afforded the insertion products **85**, which were good precursors for producing the novel low-coordinated organosilicon compound, trisilaallene **86**. In the case of cycloadditions with unsaturated organic compounds such as alkenes and alkynes, the corresponding [1 + 2]-cycloadducts, metalliranes and metallirenes, are obtained, while the [1 + 4]-cycloadducts are obtained when the butadiene derivatives are reacted with the metallylenes [reactivity (ii)]. In these reactions, the p-bonds of unsaturated compounds attack the vacant p orbitals of the metallylenes. The reaction with 1,3-butadiene, leading to the formation of the corresponding cycloadducts, can be explained by two possible mechanisms: a direct [1 + 4] pericyclic reaction between the HOMO of the 1,3-butadiene and the lowest unoccupied molecular orbital (LUMO), the vacant p orbital of the metallylene, or an initial [1 + 2] cycloaddition reaction followed by a rearrangement leading to the formation of the corresponding four-membered ring system, the formal [1 + 4]-cycloadduct.[60] Interestingly, some carbon-substituted metallylenes were reported as reacting with phosphaalkyne derivatives to give the corresponding heterocyclic compounds, which are quite unique. Such unusual reactions can also be explained by an initial coordination of the reagents toward the vacant p orbitals of the metallylenes.[61]

On the other hand, the vacant p orbital of a metallylene can also accept an electron. Some photoinduced insertion reactions of dialkylsilylene **76** have been reported (Scheme 17). This would seem to indicate a $^1B_1$ and $^3B_1$ electron configuration of the excited states.[62] In addition, the generation of a radical anion species of carbon-substituted metallylenes has also been reported.[63] Again this suggests elec-
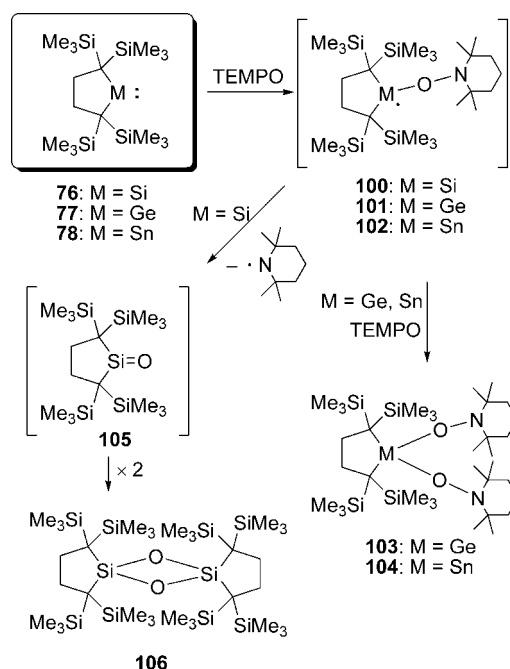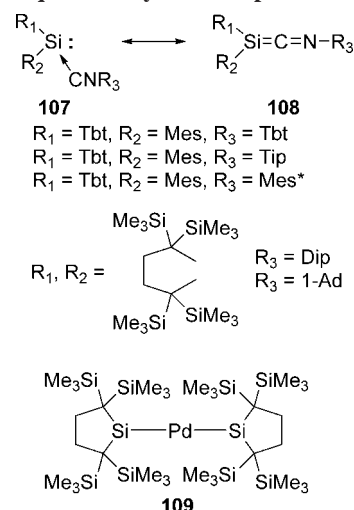
Scheme 17. Photochemical Reactions of Stable Dialkylsilylene 76 with Unsaturated Compounds
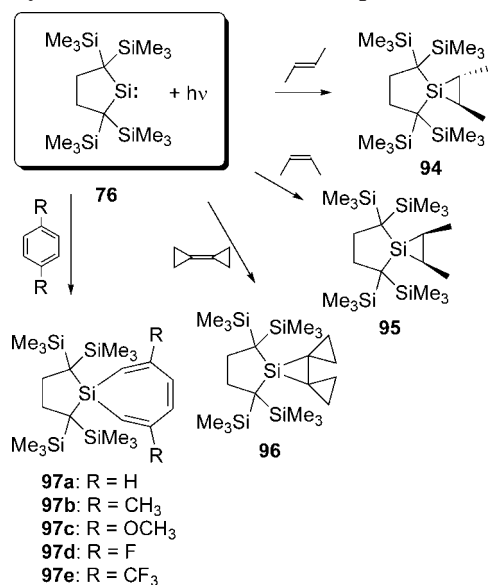
Scheme 18. Chalcogenation Reactions of Metallylenes Leading to the Formation of "Heavy Ketones"
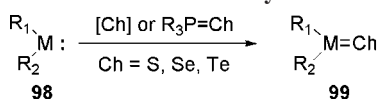
Scheme 19. Reactions of Stable Dialkylmetallylenes with TEMPO

Scheme 20. Unique Metallylene Complexes

tronic structures where one electron is in the vacant p orbital of the corresponding metallylene [(iii) reduction reactions].

Although reactions of metallylenes leading to the formation of the corresponding tetravalent species should also strictly be categorized as "oxidation reactions", since the oxidation number of the central metal atom is changed from M^{II} to M^{IV} during the reaction, "(iv) oxidation reactions" here actually means chalcogenation (O, S, Se, Te) reactions of the metallylenes (Scheme 18). In these cases, however, the nucleophilic oxidant acts as an oxidant toward the vacant p orbital of the metallylene. Thus, the lone pairs of the chalcogen atoms such as (S_8, Se, Te) and the phosphine chalcogenides can react with the vacant p orbital of the metallylenes. This gives the heavier ketone analogues, the so-called "heavy ketones" $R_2M=Ch$ (**99**), or the cyclic polychalcogenides containing the heavier group 14 elements. The latter have been shown to be precursors for producing the corresponding "heavy ketones".[5a,38b,64,65] However, attempted oxidation reactions leading to the formation of stable >M=O species have thus far been unsuccessful.[24,66] Reactions of the 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO) with the stable dialkylsilylene **76** afforded the 1,3,2,4-dioxadisiletane derivative **106**. Its formation was explained

in terms of an intermediate, the corresponding silanone derivative **105**. Dialkylgermylene **77** and dialkylstannylene **78** have been reported as giving the corresponding bis-adducts, **103** and **104**, respectively (Scheme 19).[67]

Metallylenes can, therefore, be characterized by their vacant p orbital. Accordingly, one can conclude that metallylenes can be stabilized by the coordination of a Lewis base, giving the corresponding donor-stabilized metallylenes, as described below (Scheme 20). For example, the reaction of isocyanides with silylenes gave the corresponding silylene—isocyanide complexes, which can be formulated as the silaketenimine resonance structure.[57,68] In addition, the unique palladium complex, **109**, coordinated by two molecules of dialkylsilylene **76**, was synthesized as a stable compound.[69] The isolation of this unique 14-electron palladium complex suggests that silylene **76** has a lone pair relatively reactive toward transition metals and can stabilize these low-coordinated transition metal species. In this case, the dπ-back-donation from the Pd atom toward the vacant p

Scheme 21. Generation of Silyl-Substituted Silylenes

Scheme 22. Anion Radical Species of Silyl- And Germyl-Substituted Metallylenes
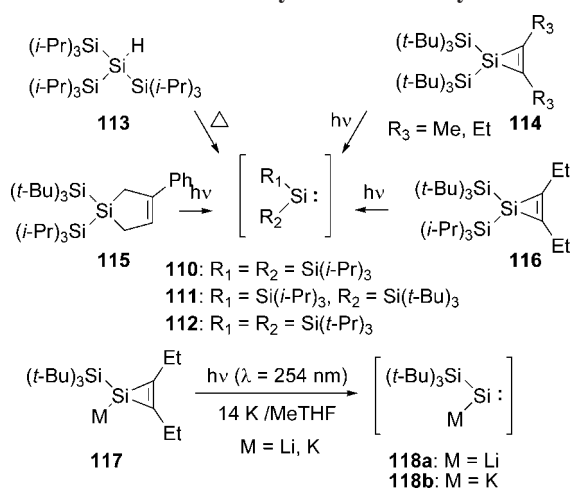
orbitals of the silylene unit effectively stabilizes the palladium complex **109**.

3. Stable Metallylenes Bearing Hydride, Silyl, Germyl, and Stannyl Substituents

As described in section 2, carbon-substituted metallylenes have singlet ground states due to the intrinsic nature of the $(ns)^2(np)^2$ valence electron configuration. Those compounds bearing electropositive substituents such as silyl groups would be expected to exhibit a smaller ΔE_{S-T} (singlet–triplet energy gap) than carbon-substituted metallylenes due to the fact that the p-character of the lone pair would be enhanced by the inductive effect of the electropositive substituents.[70] In addition, the bulkiness of the substituent would make the R–M–R angle greater than 90°. This would lead to a higher s-character of the R–M bonds as well as an increased p-character of the metallylene lone pair. It could be predicted, therefore, that electropositive and bulky substituents will increase, to some extent at least, the reactivity of the metallylene as a result of this triplet character. Indeed, theoretical calculations predicted that the triplet states of [(i-Pr)$_3$Si]$_2$Si: and [(t-Bu)$_3$Si]$_2$Si: should be more stable than their singlet states by 1.7 and 7.1 kcal/mol, respectively.[70b] However, because of their increased reactivity, it may prove difficult to synthesize such metallylenes as stable compounds. The introduction of extremely bulky substituents on the metallylene may make it possible to isolate stable metallylenes bearing electropositive substituents. Since these readily dimerize to give the corresponding dimetallenes (double-bond compounds), to date there has been no example of a stable silyl-substituted silylene reported.

There have, however, been some reports on the generation of silylenes bearing electropositive substituents (Scheme 21). It was found, on the basis of the trapping reactions, that [(i-Pr)$_3$Si]$_2$Si: (**110**),[71] [(i-Pr)$_3$Si][(t-Bu)$_3$Si]Si: (**111**),[72] and [(t-Bu)$_3$Si]$_2$Si: (**112**)[73] were generated by either the thermolysis or photolysis of the corresponding hydrosilanes or silirenes precursors. However, analysis of the products of these trapping reactions did not lead to any definitive conclusions as to whether these silylenes exhibit triplet ground states. Although Sekiguchi et al. have succeeded in observing the silyl- and metal-substituted silylenes, **118**, which were found to exhibit triplet ground states, they could not be isolated as stable compounds under ambient conditions (Scheme 22).[74]

On the other hand, Sekiguchi et al. successfully synthesized and isolated the radical anion species of a silylene
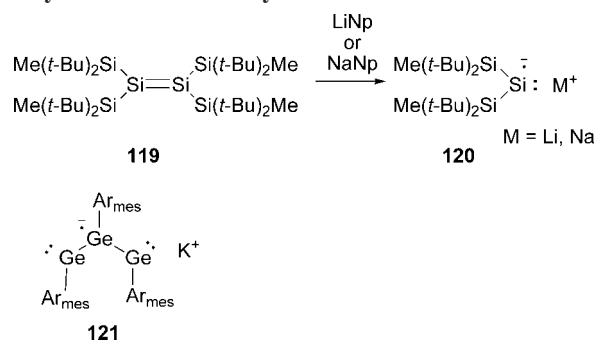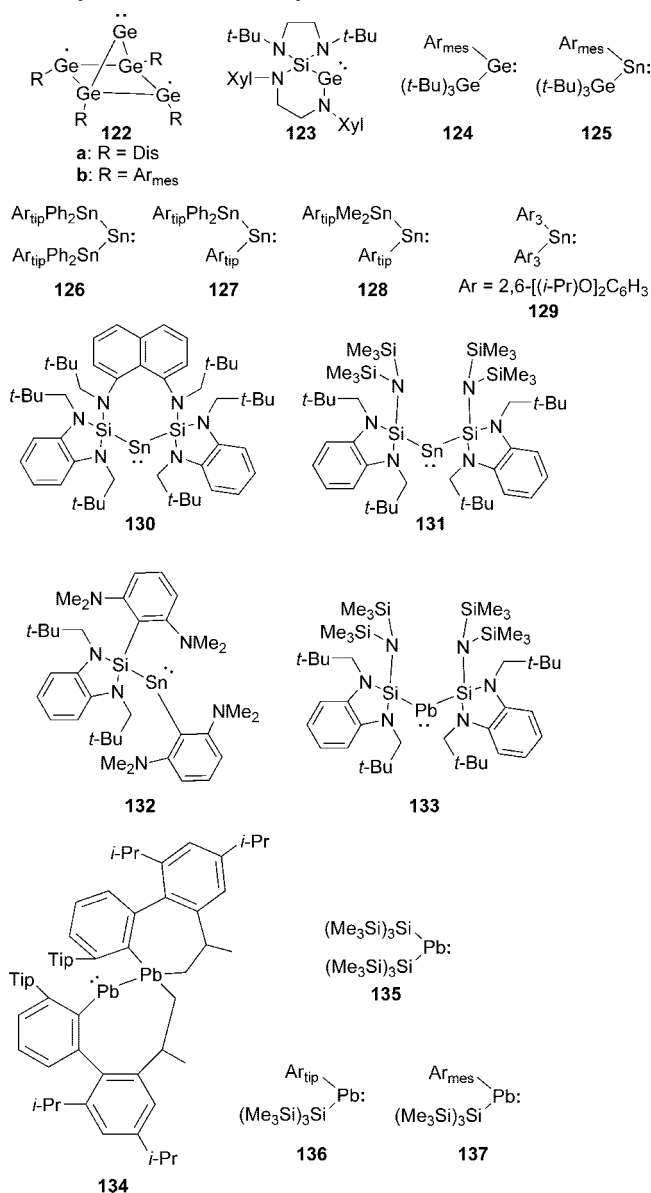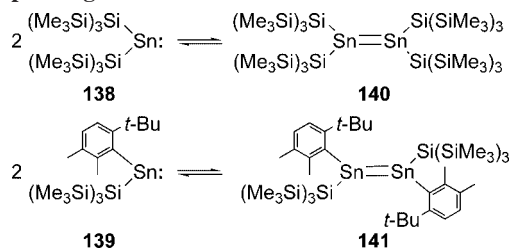
bearing silyl substituents. The anion radical **120** was obtained by the reduction of tetrasilyldisilene **119**.[75] In addition, the unique radical anion of the germyl-substituted germylene, **121**, was also synthesized as a stable compound.[76]
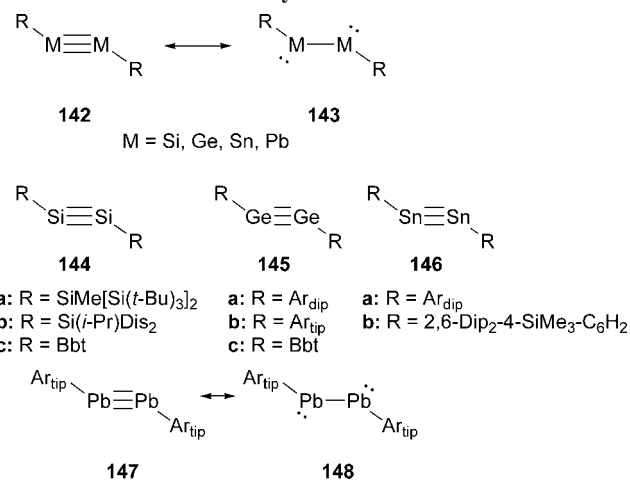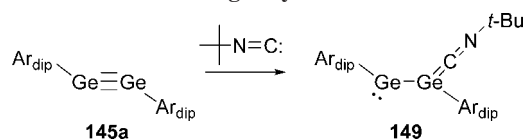
Monomeric germylenes, stannylenes, and plumbylenes all bearing electropositive substituents of the heavier Group 14 elements have all been synthesized (Scheme 23).[77–87] Although these metallylenes have electropositive substituents, they exhibit singlet ground states due to much larger ΔE_{S-T} values compared to silylene. The silyl-substituted stannylenes **138** and **139** are in equilibrium with their corresponding dimers (distannene) **140** and **141** in solution (Scheme 24), whereas they exist as dimers in the crystalline state.[86,88] In contrast to stannylene **138**, the bis-silylplumbylene **135** was found to exist as a monomer in the crystalline state.[86] The basis for these metallylene syntheses is of course their similarity to the synthesis of the carbon-substituted metallylenes as described in section 2. However, the photolysis of the bis-silyl derivatives [R$_2$M(SiMe$_3$)$_2$] or the cyclotrimetallane derivatives [(R$_2$M)$_3$] is not applicable to the synthesis of the corresponding metallylenes. This is because when R = Si, Ge, Sn, or Pb, the R–M bonds are also photosensitive. Some examples of isolated stable metallylenes are shown in Scheme 23.

Recently, heavier analogues of alkyne (dimetallyne), triply bonded compounds between the heavier Group 14 elements, have been synthesized and isolated as stable compounds. This was achieved by taking advantage of kinetic stabilization involving steric protection groups (Scheme 25).[89] The dimetallynes can be considered as resonance structures of the triply bonded compounds **142** and the bis-metallylene compounds **143** (Scheme 25). Although the Si–Si bonds of disilynes **144** exhibit triple-bond character in the solid state and even in solution,[90] the Pb–Pb bond of diplumbyne **147** is reported as featuring single-bond character in the crystalline state. Hence, it should not be depicted as diplymbyne **147** but rather as the bis-plumbylene **148**.[91] The bonding properties of the Ge–Ge and Sn–Sn bonds of the digermynes **145** and distannynes **146** can be considered as triple bonds,[92–94] in spite of the fact that they are sometimes depicted as having biradical M=M or bismetallylene :M–M: character depending on the electronic properties of the substituents. The reaction of digermyne **145a** with (t-Bu)NC: yielded the germyl–germylene **149** through the coordination of the isonitrile toward one of the low-coordinated germanium atoms of **145a** (Scheme 26).[94]

The hydrometallylenes, R(H)M: (M = Si, Ge, Sn, Pb), are of practical interest, not only because they are unique low-valent metal hydrides but also because they are noteworthy metallylenes with a hydrogen atom.[95] Power's group

Scheme 23. Stable Silyl-, Germyl-, Stannyl-, and Plumbyl-Substituted Metallylenes

122
a: R = Dis
b: R = Ar$_{mes}$

123

124

125

126

127

128

129
Ar = 2,6-[(i-Pr)O]$_2$C$_6$H$_3$

130

131

132

133

134

135

136

137

Scheme 24. Silylstannylenes in Equilibrium with Their Corresponding Distannenes

138

140

139

141

Scheme 25. Stable Dimetallynes

142   **143**

M = Si, Ge, Sn, Pb

144
a: R = SiMe[Si(t-Bu)$_3$]$_2$
b: R = Si(i-Pr)Dis$_2$
c: R = Bbt

145
a: R = Ar$_{dip}$
b: R = Ar$_{tip}$
c: R = Bbt

146
a: R = Ar$_{dip}$
b: R = 2,6-Dip$_2$-4-SiMe$_3$-C$_6$H$_2$

147   **148**

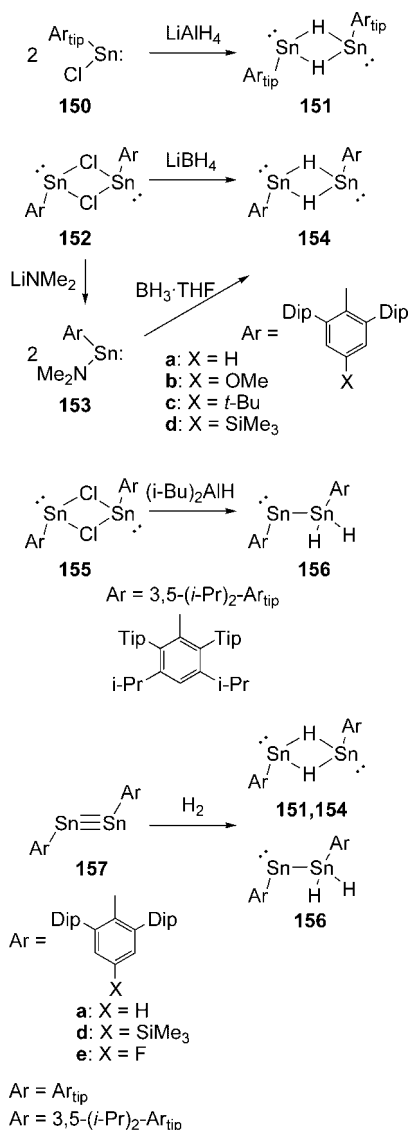**Scheme 26. Reaction of Digermyne 145a with t-Bu−NC**

145a   **149**

terphenyl ligands also have been synthesized. Their bridged-dimer structures have been characterized.[97] On the other hand, the stannylstannylene **156** is a result of a hydrogen migration in the bridged dimer of a hydrostannylene, which in turn was obtained when the chlorostannylene dimer **155**, with the ligand Ar = 3,5-(i-Pr)$_2$-2,6-Tip$_2$-C$_6$H,[98] was reduced with DIBAL [(i-Bu)$_2$AlH].[97] The different products are explained in terms of the steric effects of the m-terphenyl ligands. In addition, the addition reaction of the stannynes **157** with m-terphenyl ligands and hydrogen afforded either the corresponding hydrostannylene derivatives **151** and **154** or its isomer **156**.[99]

In the scheme above, there are compounds **151** and **154** with Ar and Ar$_{tip}$ groups, respectively. Further down, **151** and **154** are both under the Ar-substituted compound.
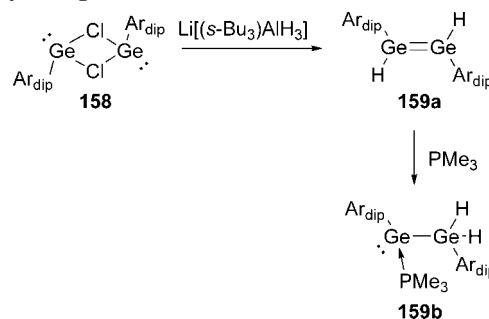
Treatment of chlorogermylene dimer **158**, [Ar$_{dip}$(Cl)Ge:]$_2$ (see section 4), with L-selectride (Li[(s-Bu)$_3$BH]) gave the 1,2-dihydrodigermene **159**, which is a dimer of the corresponding hydrogermylene (Scheme 28).[100] Thus, it appears that a hydrogermylene can exist as a stable isomeric dimer of 1,2-dihydrodigermene, which is in contrast to the case of hydrostannylene. In this latter case, the stable isomer is the bridged dimer. Such unique differences between hydrogermylenes and hydrostannylenes can best be interpreted in terms of the differences in ΔE_{S-T} values and the s-character of the metallylene lone pair.[98,101] Interestingly, the addition of PMe$_3$, a Lewis base, to 1,2-dihydrodigermene **159a** afforded the corresponding germylgermylene−PMe$_3$ complex, **159b**, via a 1,2-hydrogen shift.[101]

On the other hand, the attempted synthesis of the lead analogue, a hydroplumbylene, has been reported. Here Ar$_{tip}$(Br)Pb: (**160**) was reduced with LiAlH$_4$ to give the plumbylyne (bis-plumbylene) **147** (Scheme 29).[91] In this reaction, the formation of **147** can be interpreted in terms of an intermediate of hydroplumbylene **161**. This undergoes ready dimerization to give **147** along with the elimination of a hydrogen molecule (H$_2$). The synthesis of a hydrosilylene dimer, 1,2-dihydrodisilene Bbt(H)Si=Si(H)Bbt (**163**), was reported by Tokitoh et al.[90d,102] Dihydrodisilene **163** was
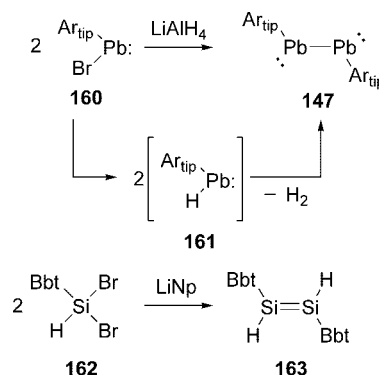
succeeded in the synthesis of hydrostannylene **151** as a stable compound by taking advantage of the bulky m-terphenyl ligand (Scheme 27).[96] The chlorostannylene, Ar$_{tip}$SnCl (**150**, see section 4), was reduced using LiAlH$_4$ to give hydrostannylene **151** as a deep orange solid. This was found to be a hydride-bridged dimer in the crystalline state. The Sn−H−Sn bonds should involve a 3-center-2-electron bond, which in turn should provide the intermolecular stabilization of the vacant p orbitals of the metallylene center. The synthesis of hydrostannylenes **154** bearing the slightly different m-

Scheme 27. Synthesis of Hydrostannylene Derivatives

Scheme 28. Synthesis and Isomerization of 1,2-Dihydrodigermene

Scheme 29. Attempted Synthesis of Hydroplumbylene and Hydrosilylene

found to exhibit disilene character with a well-defined Si=Si double bond in the solid state and even in solution.

Selected structural parameters are summarized in Table 4. The structural features cannot be systematically discussed, because the parameters depend on the substituents. The examples that are stable are shown in Scheme 23 and Table 4, and all have unique substituents. (See Figure 6 for structure of **135**).

4. Stable Monohalogenated Organometallylenes

As described in section 2, Sn(II) and Pb(II) dihalides such as SnCl$_2$ and PbCl$_2$ are well-known compounds and are stable enough to be handled under ambient conditions. Although it is difficult to isolate GeCl$_2$ itself, stabilization of dichlorogermylene is achieved through the intermolecular donation of a Lewis base such as dioxane and THF into the vacant p orbital of the dichlorogermylene (Figure 7).[3,103,104] Thus, as described above, the dihalides of Ge(II), Sn(II), and Pb(II) species are all known to be good precursors for metallylenes. Recently, a stable series of dihalogermylenes (**164**, **165**, **166**, **167**) stabilized by the presence of a N-heterocyclic carbene has been isolated by Baines et al.[105] The synthesis of a GeI$_2$ complex of the N-heterocyclic carbene (**162**) was reported by Arduengo et al. (Scheme 30).[106] By utilizing such

stabilized dihalogermylenes as precursors, the unique Ge(II) dication species **169**[105b] and **170**[107] were synthesized and isolated. To date, no stable example of a silicon dihalide complex has been synthesized, although trapping reactions of transient SiCl$_2$ species have been reported.[2] Reduction of the SiCl$_4$ complex **171**, coordinated by a N-heterocyclic carbene with 6 equiv of KC$_8$ in hexane, afforded the unique bischlorosilylsilylene **172**, which is also stabilized by the N-heterocyclic carbene (Scheme 31).[108] Interestingly, **171** was also reduced with 8 equiv of KC$_8$ in THF to give the unique Si$_2$ complex **173** bearing two molecules of the same N-heterocyclic carbene.[108]

The monohalometallylenes RMX (R = organic substituent, M = heavier Group 14 element, X = halogen) have attracted a great deal of attention. Such monohalometallylenes can be obtained by the reaction of dihalometallylene derivatives with an equimolar amount of an organometallic reagent such as RLi or RMgBr. Halogermylenes, halostannylenes, and haloplumbylenes, which are all thermodynamically stabilized by π-electron donation such as Cp*GeCl (Cp* = pentamethylcyclopentadienide), are described below. For the isolation of the monomeric halometallylenes, the introduction of an extremely bulky steric protection group is necessary. In this way, the two dimerization modes should be prevented by the introduced steric repulsion. That is, halogen-bridged dimerization through coordination of the halogen lone pair toward the metallylene center and M=M dimerization leading to the formation of the corresponding 1,2-dihalodimetallene will both be prevented (Figure 8).

In the case of silicon, only two stable compounds of the monohalogenated Si(II) species have been reported.[90d,109] However, they exist as the corresponding 1,2-dihalodisilene dimers, **175** and **177**. Both contain a well-defined Si=Si double bond in the crystalline state and even in solution. They were synthesized by the reduction of the corresponding

Table 4. Selected Structural Parameters of Stable Metallylenes with Electropositive Substituents

R_1R_2M:	$d(R_1-M)$/Å	$d(R_2-M)$/Å	$\angle C-M-C$/°	λ_{max}/nm	δ (^{119}Sn, ^{207}Pb) (central atom of metallylene)	ref
122a	Ge–Ge: 2.464(1)	Ge–Ge: 2.458(1)	82.11	orange		77
122b	Ge–Ge: 2.693(3)	Ge–Ge: 2.699(2)		black		77
123	Si–Ge: 2.461(2)	N–Ge: 1.832(4)	97.5(2)	460		78
124	Ge–Ge: 2.5439(7)	Ar$_{mes}$–Ge: 2.011(5)	114.87(13)	719 (ε 340)		79
149	Ge–Ge: 2.3432(9)	Ar$_{dip}$–Ge: 1.966(5)	102.77(15)	490 (ε 3000)		94
160	Ge–Ge:(P) 2.5304(7)	Ar$_{tip}$–Ge: 2.070(3)	101.59(7)	yellow		100
125	Ge–Sn: 2.7224(11)	Ar$_{mes}$–Sn: 2.202(8)	112.7(2)	673 (ε 400)	+2960	79
126	Sn–Sn: 2.9644(3)	Sn–Sn: 2.9630(3)	115.19(1)	311 (ε 7300)	+3752	80
127	Sn–Sn: 2.9688(5)	Ar$_{tip}$–Sn: 2.261(2)	108.48(6)	462 (ε 1660)	+2870	39a
128	Sn–Sn: 2.8909(2)	Ar$_{tip}$–Sn: 2.201(2)	119.30(6)	689 (ε 271)	+2856.9	39c
129	Sn–Sn: 2.865	Sn–Sn: 2.867	110.705			81
130	Si–Sn: 2.6691(10)	Si–Sn: 2.6854(11)	92.78(3)	Red-brown		82
131	Si–Sn: 2.712(1)	Si–Sn: 2.712(1)	106.77(5)	Dark-green		83
132	C–Sn: 2.210(8)	Si–Sn: 2.636(2)	107.0(2)	Yellow-orange	+412	84
151 (X-ray)	Ar$_{tip}$–Sn: 2.210(2)	H–Sn: 1.89(3) 1.95(3)	91.7(9) 93.6(9)	608 (ε 160), 395 (ε 360)	+698.7	96a
151 (neutron)	Ar$_{tip}$–Sn: 2.193(4)	H–Sn: 1.943(7) 1.941(7)	92.4(2) 91.6(2)			96b
154a	Ar–Sn: 2.221(6)	H–Sn:1.82(8) 1.99(8)	99(2)	595 (ε 70)	+657	97
154b	Ar–Sn: 2.216(4) 2.219(4)	H–Sn: 1.94(2) 1.94(2)	91(2) 91.9(15)	598 (ε 50)	+687	97
154c	Ar–Sn: 2.208(6)	H–Sn: 1.93(2)	100.0(19)	594 (ε 100)	+667	97
154d	Ar–Sn: 2.216(3) 2.200(3)	H–Sn: 1.95(3) 1.90(3)	95.1(11) 98.5(11)	582 (ε 175), 440 (sh)		97
156	Ar–Sn: 2.228(5) 2.247(6)	Sn–Sn: 2.9157(10)	106.37(17)	622 (ε 220), 480 (sh), 422 (ε 540)	+34	97
133	Si–Pb: 2.776(3)	Si–Pb: 2.776(3)	105.8(1)	Black-green		83
134	Pb–Pb: 2.9928(3)	C–Pb: 2.314(3)	97.99(6)	713 (ε 350), 402 (ε 3400)		85
135	Si–Pb: 2.700(3)	Si–Pb: 2.704(3)	113.56(10)	black		86
136	Si–Pb: 2.7230(11)	Ar$_{tip}$–Pb: 2.296(3)	110.82(9)	725 (ε 260), 415 (ε 270)	+10745	39b
137	Si–Pb: 2.7120(12)	Ar$_{mes}$–Pb: 2.290(4)	109.17(11)	720 (ε 230), 399 (sh, ε 243)	+10510	87
148	Pb–Pb: 3.1881(1)	Ar$_{tip}$–Pb: 2.303(2)	94.26(4)	719 (ε 5200), 397 (ε 29000)		91

trihalosilanes **174** and **176** since, in this case, the dihalosilylene derivatives cannot be used as suitable precursors as described above. In the case of the germanium compounds,
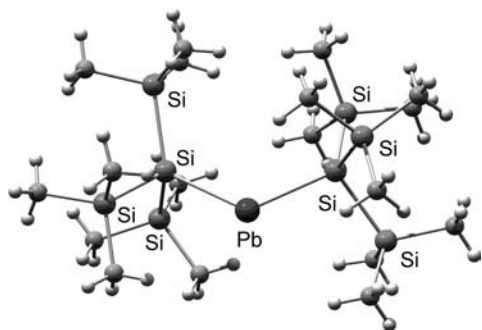
Figure 6. Molecular structure of [(Me$_3$Si)$_3$Si]$_2$Pb: (**135**).
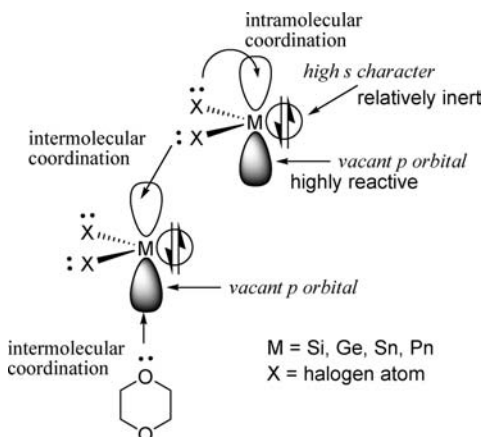
**Figure 7.** Thermodynamic stabilization of dihalometallylenes.

Mes*GeCl (**178**)[110] and TsiGeCl·LiCl·3(thf) [**179**, Tsi = C(SiMe$_3$)$_3$],[111] which were described as being monomers both in solution and in the solid state, they have not yet been structurally characterized (Scheme 32). Both Ar$_{mes}$GeCl (**180a**)[38c] and Ar$_{dip}$GeCl (**180b**)[112] were found to exist as dimers with weak Ge=Ge interactions. That is, as 1,2-dichlorodigermene **181a** and **181b**, respectively, in the crystalline state, although the Ge=Ge interactions should be weak since these dimers are cleaved into chlorogermylene monomers in solution (Scheme 33). Interestingly, the *m*-terphenyl group of the Ar$_{tip}$ group should be the limit of intermolecular Ge=Ge interactions in the crystalline state. Ar$_{tip}$GeCl **180c** afforded different types of crystals depending on the conditions. Both the monomers **180c**[113] and the dimer **181c**[114] with Ge=Ge interactions of the Ar$_{tip}$GeCl molecules have been reported. On the other hand, the bromogermylene, BbtGeBr (**182**), was synthesized as a stable compound in solution, whereas it exists as the dimer 1,2-dibromodigermene **177** in the crystalline state.[115] In this case, the equilibrium between the monomeric bromogermylene and the 1,2-dibromodigermene in solution was confirmed by spectroscopic methods. It should be noted that the Ge=Ge interactions between the halogermylenes leading to the formation of the corresponding 1,2-dihalodigermene is favored over the halogen-bridged dimeric state.

In the case of tin (Scheme 34), two crystalline monomeric halostannylenes of Ar$_{tip}$SnCl (**185c**)[116] and Ar$_{tip}$SnI (**184**)[113] have been reported (Figure 9). However, Ar$_{tip}$SnCl (**185c**) was found to exist as the Cl bridged dimer of Ar$_{tip}$SnCl, [Ar$_{tip}$Sn(μ-Cl)]$_2$ (**186c**), in the crystalline state on the basis of the X-ray crystallography data.[116] The crystal structure of Ar$_{tip}$SnCl may be too fragile for the crystallization conditions, as was found in the case of Ar$_{tip}$GeCl (**180c**).[113,114]

Scheme 30. Dihalogermylenes Stabilized by the Coordination of a N-Heterocyclic Carbene
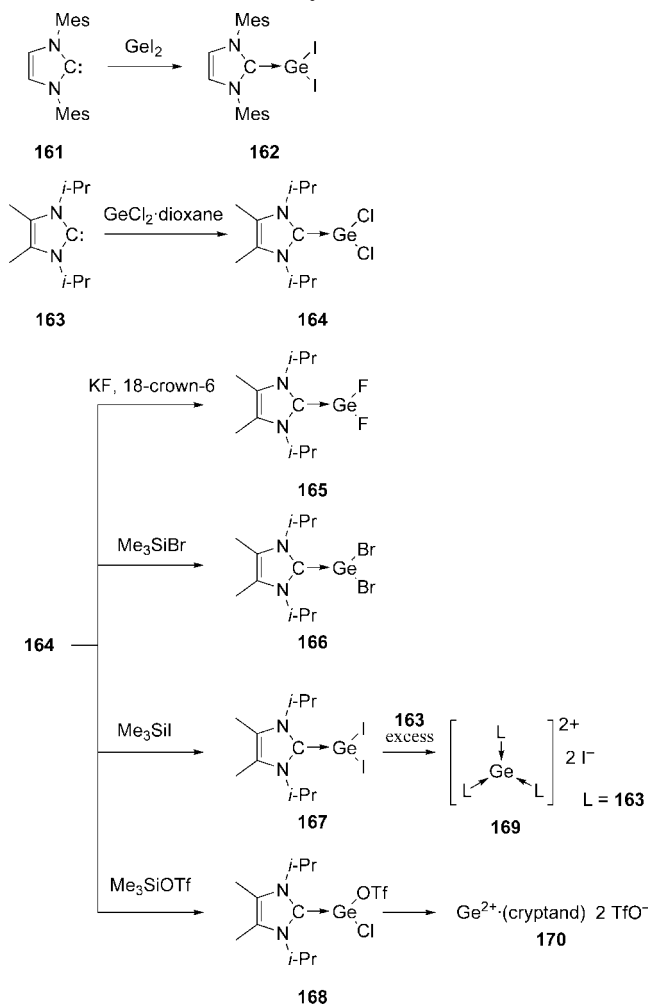
Scheme 31. Unique Low-Coordinated Organosilicon Compounds Stabilized through Coordination with a N-Heterocyclic Carbene
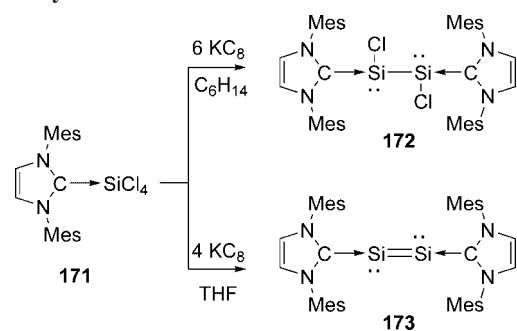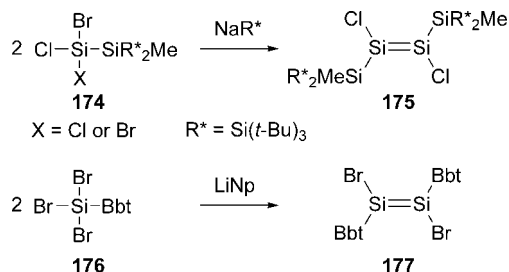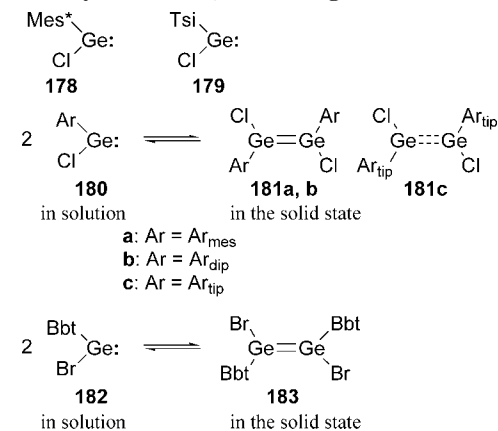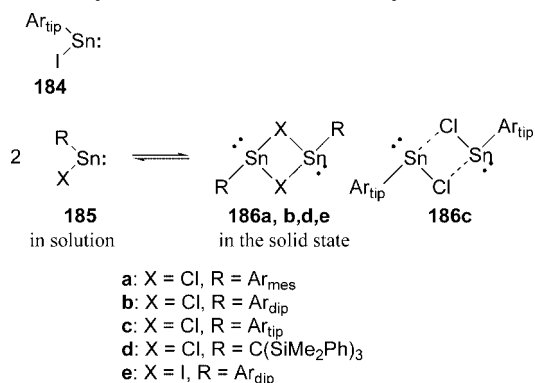

The stable halostannylenes $Ar_{mes}SnCl$ (**185a**),[38c] $Ar_{dip}SnCl$ (**185b**),[112] $[(Me_2PhSi)_3C]SnCl$ (**185d**),[117] and $Ar_{dip}SnI$ (**185e**)[116] have all been synthesized, and their crystal structures all indicated the presence of the halogen-bridged dimers in the solid state, **186a**, **186b**, **186d**, and **186e**, respectively. On the basis of spectroscopic analysis and their chemical reactivities, all these halostannylenes were reported as behaving as monomeric stannylenes in solution.

Stable haloplumbylenes are similar to the halostannylenes (Scheme 35). Bromoplumbylene **187c**, $Ar_{tip}PbBr$, was cocrystallized with pyridine to give a monomeric crystalline structure with weak coordination to pyridine (**189**).[39d] Other haloplumbylenes, **187**, are reported to exist as the halogen-
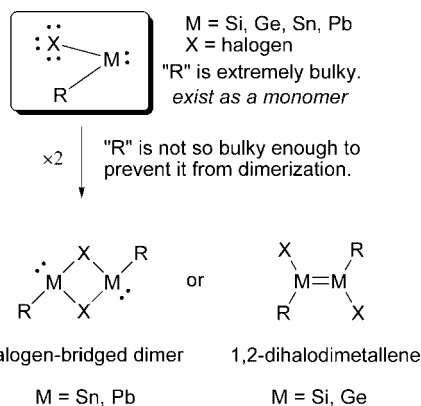
Figure 8. Dimerization modes for the halometallylenes.

bridged dimers **188** in the crystalline state.[39b,d,117−119] Interestingly, the chloroplumbylene of TsiPbCl (**190**) showed a trimeric structure (**191**) with a Pb−Cl−Pb−Cl−Pb−Cl six-membered ring skeleton.[117]

Thus, stable halostannylenes and haloplumbylenes are monomeric species in solution and undergo dimerization in

Scheme 32. Synthesis of 1,2-Dihalodisilenes

Scheme 33. Synthesis of 1,2-Dihalodigermenes

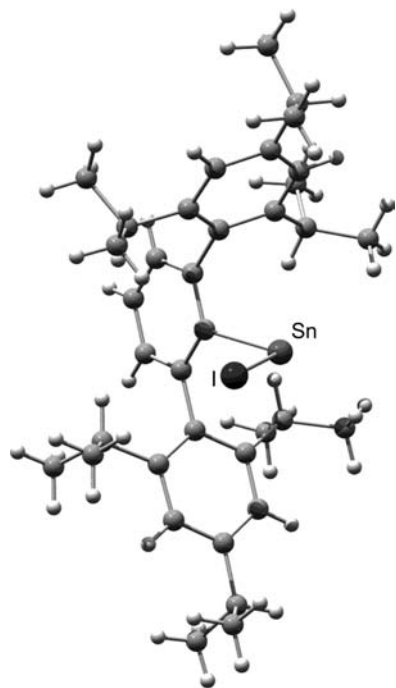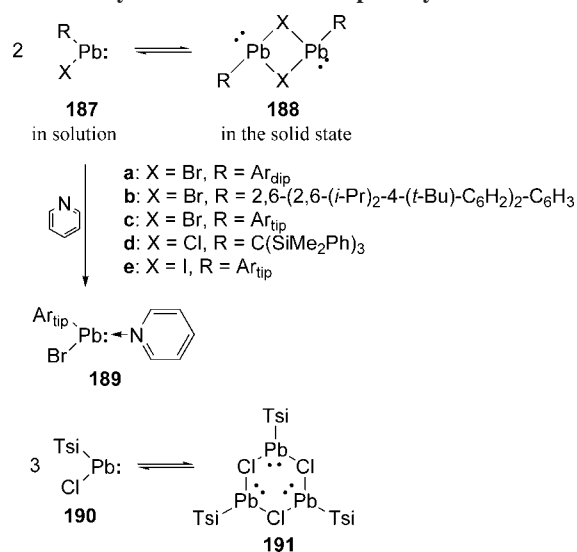**Scheme 34. Synthesis of Stable Halostannylenes**

Figure 9. Molecular structure of monomeric iodostannylene **184**.

the crystalline state to give, not the corresponding dimetallenes, but rather the halogen-bridged dimers (or trimer) with a few exceptions. These exist as monomers even in the crystalline state in contrast to the halosilylenes and

Scheme 35. Synthesis of Stable Haloplumbylenes

a: X = Br, R = Ar$_{dip}$
b: X = Br, R = 2,6-(2,6-(i-Pr)$_2$-4-(t-Bu)-C$_6$H$_2$)$_2$-C$_6$H$_3$
c: X = Br, R = Ar$_{tip}$
d: X = Cl, R = C(SiMe$_2$Ph)$_3$
e: X = I, R = Ar$_{tip}$

halogermylenes, which never form the halogen-bridged dimers.[120] The structural and spectroscopic features of the stable halometallylenes are summarized in Table 5.

These stable halometallylenes with bulky substituents have proven good precursors for making other metallylene or dimetallyne derivatives using nucleophilic substitution reactions or reductions (Scheme 36). In many cases, the stable metallylenes described in this review were synthesized using these stable halometallylenes as precursors (see section 3).

Table 5. Selected Structural Parameters of Stable Monohalometallylenes or Their Dimers

RXM:	d(R−M)/Å	d(X−M)/Å	d(M−M)/Å	∠R−M−X/°	λ$_{max}$/nm	δ (^{29}Si, ^{119}Sn, ^{207}Pb) (central atom of metallylene)	ref
175	Si−Si: 2.401(3)	Cl−Si: 2.091(3)	2.163(4)	120.8(1)	orange−red		109
177	C−Si: 1.8851(19)	Br−Si: 2.2467(6)	2.2264(8)	106.77(6)	434 (ε 25000)	79.4	90d
180c	C−Ge: 1.989(5)	Cl−Ge: 2.2026(19)		101.31(15)	393 (ε 950)		113
181a	C−Ge: 2.000(6)	Cl−Ge: 2.120(2)	2.443(2)	109.1(2)	orange		38c
181b	C−Ge: 1.9758(17)	Cl−Ge: 2.2167(5)	2.4624(4)	102.51(5)	orange		112
181c	C−Ge:(P) 1.973(7)	Cl−Ge: 2.209(2)	2.363(2)	118.03(19)			114
183	C−Ge: 1.983(3)	Br−Ge: 2.3659(5)	2.5087(7)	100.04(10)	449		115
184	C−Sn: 2.213(13)	I−Sn: 2.766(2)		102.6(3)	428 (ε 3000)	+1140	113
185c	C−Sn: 2.180(2)	Cl−Sn: 2.4088(8)		99.67(6)	395 (ε 1040), 284 (sh, ε 330)	+793.4	116
186a	C−Sn: 2.222(5)	Cl−Sn: 2.600(2) 2.685(2)	3.997(1)	92.35(14) 102.11(14)	yellow	+562	38c
186b	C−Sn: 2.225(6)	Cl−Sn: 2.650(1) 2.967(1)		91.14(7)	orange	+817	112
186c	C−Sn: 2.214(2)	Cl−Sn: 2.5768(6) 2.5978(7)		92.61(6) 98.21(6)			116
186d	C−Sn: 2.296(10)	Cl−Sn: 2.596(3) 2.779(3)		99.1(3) 111.1(2)	orange	+777	117
186e	C−Sn: 2.2303(18)	I−Sn: 2.7700(5) 3.1227(5)		90.92(5)	420, 391	+1042	116
188a	C−Pb: 2.322(3)	Br−Pb: 2.8125(5) 3.0346(5)		91.23(8) 109.64(9)	416.0 (ε 740		39b
188b	C−Pb: 2.338(5) 2.346(4)	Br−Pb: 2.9202(7) 2.9191(7) 2.8713(7) 2.9419(7)		108.02(11) 97.17(11) 106.82(11) 98.41(10)	417.0 (ε 760)		39b
188c	C−Pb: 2.329(11) 2.306(13)	Br−Pb: 2.7892(16) 3.0157(17) 2.9902(17) 2.7841(16)		95.4(3) 98.0(3)	416.5 (ε 1580)		39d
188d	C−Pb: 2.435(10)	Cl−Pb: 2.729(3) 2.962(3)		98.5(2) 112.0(2)	yellow		97
188e	C−Pb: 2.326(6)	I−Pb: 2.9499(7) 3.2764(8)	4.603(1)	97.3(2) 115.1(2)			118
189	C−Pb: 2.322(4)	Br−Pb: 2.7063(6)		92.39(11)	417 (ε 1760)		39d

Scheme 36. Reactions of Stable Halometallylenes
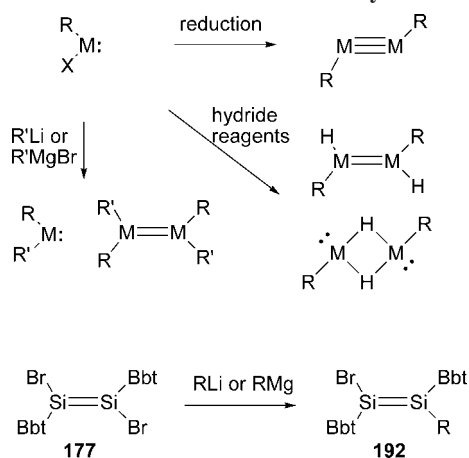
5. Metallylenes Stabilized by Group 15 and 16 Elements

The stabilization of metallylenes using Group 15 (N or P) and 16 (O or S) elements is highly effective especially in the case of silylenes, where the isolation of stable monomeric forms is very difficult as described previously. Therefore, this group have a longer history than any of the other types described above.[121−123] Their stabilization methods can be summarized into three categories as follows (Figure 10): (1) direct substitution, (2) coordination, and (3) introduction of delocalized, monoanionic bidentate ligands [this is, in fact, a hybrid of (1) and (2)]. In all of these compounds, their frontier orbitals are strongly perturbed by interactions with the lone pair electron orbitals of the heteroatoms. Accordingly, their structures and reactivities are quite unique and different from those of their singlet carbene analogues.

5.1. Direct Substitution (Two-Coordinated)

5.1.1. Acyclic

5.1.1.1. Homoleptic (Symmetrical) Substitution. Diamino-substituted metallylenes have been widely investigated since the 1970s. The acyclic germylene, stannylene, and plumbylene diamides, $M[N(SiMe_3)_2]_2$ (**20**: M = Ge; **53**: M = Sn; **193**: M = Pb), and $M[N(SiMe_3)(t\text{-}Bu)]_2$ (**194−196b**: M = Ge, Sn, Pb), were all prepared as stable compounds by Lappert's group in 1974.[124] As previously mentioned, these compounds have proven useful as precursors for making other divalent species. To date, various kinds of diamino-substituted derivatives for Ge(II), Sn(II), and Pb(II) have been reported (Scheme 37).[125,126] Almost all of these compounds have monomeric central atoms, as evidenced by their NMR spectra, and in some cases also by X-ray crystallography data. On the other hand, the silicon analogues were found to be relatively unstable. For example, the formation of $Si[N(i\text{-}Pr)_2]_2$ (**197**, 1998, Kira's group)[127] and $Si[N(SiMe_3)_2]_2$ (**198**, 2003, West's group)[128] were reported, although it was
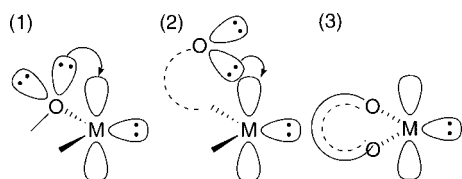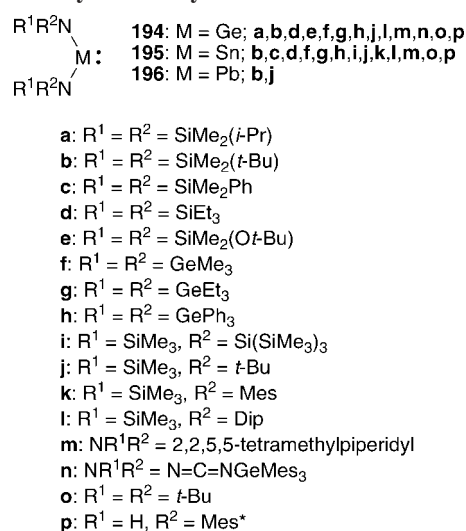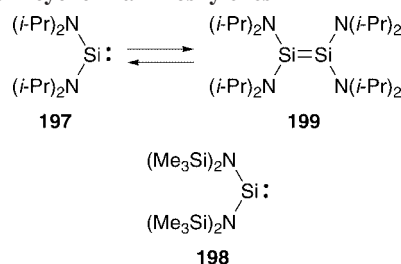

Figure 10. Stabilization of metallylenes by heteroatoms (e.g., by oxygen atom).

Scheme 37. Acyclic and Symmetrical Diaminometallylenes

194: M = Ge; **a,b,d,e,f,g,h,j,l,m,n,o,p**
195: M = Sn; **b,c,d,f,g,h,i,j,k,l,m,o,p**
196: M = Pb; **b,j**

a: $R^1 = R^2 = SiMe_2(i\text{-}Pr)$
b: $R^1 = R^2 = SiMe_2(t\text{-}Bu)$
c: $R^1 = R^2 = SiMe_2Ph$
d: $R^1 = R^2 = SiEt_3$
e: $R^1 = R^2 = SiMe_2(Ot\text{-}Bu)$
f: $R^1 = R^2 = GeMe_3$
g: $R^1 = R^2 = GeEt_3$
h: $R^1 = R^2 = GePh_3$
i: $R^1 = SiMe_3$, $R^2 = Si(SiMe_3)_3$
j: $R^1 = SiMe_3$, $R^2 = t\text{-}Bu$
k: $R^1 = SiMe_3$, $R^2 = Mes$
l: $R^1 = SiMe_3$, $R^2 = Dip$
m: $NR^1R^2 = 2,2,5,5\text{-tetramethylpiperidyl}$
n: $NR^1R^2 = N=C=NGeMes_3$
**o**: $R^1 = R^2 = t\text{-}Bu$
**p**: $R^1 = H$, $R^2 = Mes^*$

Scheme 38. Acyclic Diaminosilylenes

explained that the former is in equilibrium in solution with disilene (>Si=Si<, **199**). This dimeric structure was examined from both theoretical calculations and an experimental point of view.[129] The latter is unstable in solution above 0 °C and decomposes to give unidentified products (Scheme 38).

A few examples of diphosphino-substituted metallylenes are also known (Scheme 39). Despite the incorporation of bulky groups, such as $P(SiMe_3)_2$[130] and $P(t\text{-}Bu)_2$,[131] phosphorus-bridged dimers **200** or ate complexes **201** were formed. The synthesis of $Sn[P(SiPh_3)_2]_2$ (**202**) was reported in 1994 by Buhro's group, and its monomeric structure was characterized using NMR spectroscopy and cryoscopy.[132] In 1995, Driess's group succeeded in synthesizing the heavier metallylenes **203−206** by introducing very bulky silyl groups onto the phosphorus atoms. The monomeric structures of the Sn and Pb derivatives were determined by X-ray crystallography.[133] In addition, the synthesis and the structural determination of the diarsino-substituted stannylene **207** was achieved by using the same combination of the substituents.[133]
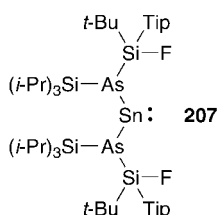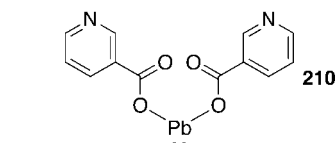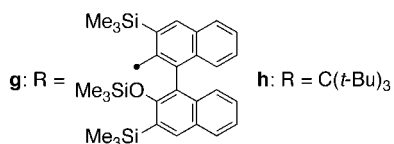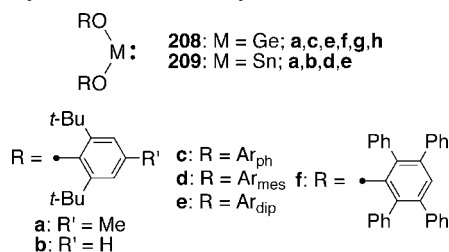
Many diaryloxy- or dialkoxy-substituted metallylenes have been isolated as stable compounds. They have a higher tendency to oligomerize than the diamino-substituted metallylenes, probably due to the decrease in the number of substituents. The structures of their monomers as determined by X-ray crystallography are shown in Scheme 40.[134−138] Lappert's group reported the preparation and structural characterization of the overcrowded, monomeric aryloxy compounds **208a** (Ge) and **209a** (Sn) in 1980.[134] Introduction of less bulky substituents (Mes or Dip) resulted in dimer formation for (Ge).[135] The alkoxy derivatives of (Ge and Sn) have also been described. They are usually found to be cyclodimeric (R = t-Bu) or oligomeric (R = Me, Et, i-Pr). Association is through intermolecular MO coordination and

Scheme 39. Diphosphino- and Diarsino-Substituted Metallylenes


200   **201**
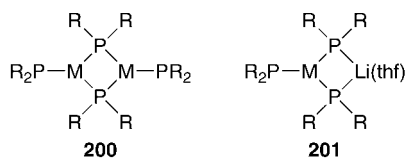
M = Ge, Sn, Pb
R = SiMe$_3$, t-Bu
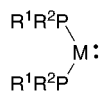
202: M = Sn, R^1 = R^2 = SiPh$_3$
203: M = Ge, R^1 = Si(F)Tip$_2$, R^2 = Si(i-Pr)$_3$
204: M = Sn, R^1 = Si(F)Tip$_2$, R^2 = Si(i-Pr)$_3$
205: M = Sn, R^1 = Si(F)(t-Bu)Tip, R^2 = Si(i-Pr)$_3$
206: M = Pb, R^1 = Si(F)(t-Bu)Tip, R^2 = Si(i-Pr)$_3$

207

Scheme 40. Established Structures of Monomeric Diaryloxy- Or Dialkoxy-Substituted Metallylenes

208: M = Ge; **a,c,e,f,g,h**
209: M = Sn; **a,b,d,e**

c: R = Ar$_{ph}$
d: R = Ar$_{mes}$
e: R = Ar$_{dip}$
a: R' = Me
b: R' = H
f: R =

**g**: R =   **h**: R = C(t-Bu)$_3$

210

is monomeric (R = t-Bu$_3$C, **208h**) depending on the size of the RO groups.[136]

Some thioalkoxy- and thioaryloxy-substituted derivatives have also been reported. In almost all cases, dimers or higher oligomers were formed. The 2,6-diisopropylphenyl-substituted tin and lead derivatives form trimers **211** bearing two three-coordinated metal atoms and one four-coordinated metal atom.[139] On the other hand, the introduction of more bulky substituents, such as 2,4,6-tri(t-butyl)phenyl, makes it possible to isolate all the Ge, Sn, and Pb derivatives **212** as monomers (Scheme 41).[139]

5.1.1.2. Heteroleptic (Unsymmetrical) Substitution. Various combinations of substituents, such as two different amino-, arylamino-, aryloxyamino-, halogenoamino-, halogenoaryloxy-, and arylthioaryloxy-, have all been reported.

Scheme 41. Dithioaryloxy-Substituted Metallylenes
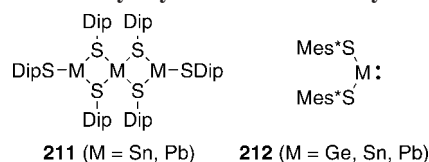
211 (M = Sn, Pb)   **212** (M = Ge, Sn, Pb)

**Scheme 42. Isomerization of Plumbanethione (Pb=S)**
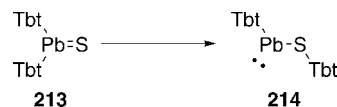
213   **214**

Scheme 43. Structures of Monomeric Metallylenes with Two Different Substituents

215   **216**

217   **218**

219   **220**
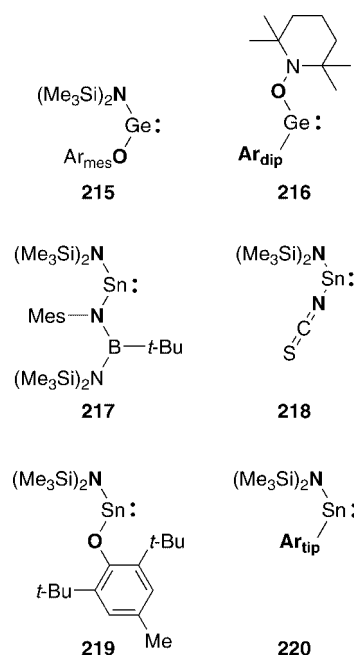
Synthesis of these unsymmetrical derivatives was generally achieved by one of the following: (1) the stepwise reaction of MX$_2$ (M = Ge, Sn, Pb; X = halogen) with nucleuophiles, (2) disproportionation reactions (e.g., diamino + diaryloxy, dihalo + diaryloxy), or (3) the deamination reaction of the diamino derivatives with alcohol. Uniquely, TbtS−Pb−Tbt (**214**) was obtained by the migration of plumbanethione **213** (lead−sulfur double-bond compound) (Scheme 42).[113,140] The structures of some monomeric metallylenes, as determined by X-ray crystallography, are shown in Scheme 43.[141]

In addition, some compounds with two metallylene centers have been successfully synthesized (Scheme 44). Bisgermylene **221** was generated by the fractional crystallization of diaminogermylene **194p**.[125g] Similarly the μ-NR type bisstannylene **222** was obtained by the reaction of distannyne (−Sn≡Sn−, **146a**) with trimethylsilylazide.[94] Interestingly, a similar reaction with digermyne (−Ge≡Ge−, **145a**) did not afford a bisgermylene but rather the biradical **223**. The reactions of dimetallynes with azobenzene gave novel bismetallylenes **224** in moderate yields. Bismetallylenes bridged by p-phenylene or cyclohexa-1,4-diyl **225**−**228** were reported by Lappert's group in 1994.[142]

5.1.1.3. Structures. Selected structural parameters of the acyclic and monomeric metallylenes described in sections 5.1.1.1 and 5.1.1.2 are summarized in Table 6.

Scheme 44. Compounds with Two Metallylene Centers
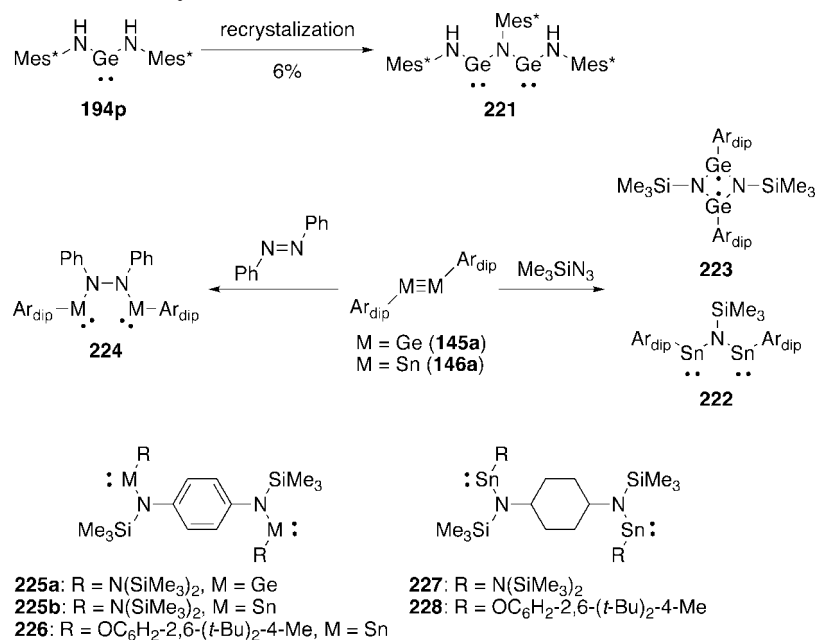
Table 6. Selected Structural Parameters of Acyclic and Monomeric Metallylenes (R^1-M-R^2) Substituted by Group 15 and 16 Elements

M	no.	R^1	R^2	$d(M-R^1)$/Å	$d(M-R^2)$/Å	$\angle R^1-M-R^2$/deg	ref
Ge	**20**	N[SiMe$_3$]$_2$	R^1	1.873(5)	1.878(5)	107.1(2)	125a
	194a	N[SiMe$_2$(i-Pr)]$_2$	R^1	1.897(2)	1.908(2)	105.26(8)	125b
	194e	N[SiMe$_2$(Ot-Bu)]$_2$	R^1	1.921(6)	1.939(6)	100.5(2)	125c
	194 l	N(SiMe$_3$)Dip	R^1	1.89	1.89	111.5	125d
	194m	TMP^d	R^1	1.87(1)	1.90(1)	111.4(5)	125e
	225a	N[SiMe$_3$]$_2$	N(SiMe$_3$)C$_6$H$_4-$	1.885(5)	1.855(2)	104.7(2)	142
	215	N[SiMe$_3$]$_2$	OAr$_{mes}$	1.851(2)	1.8414(16)	97.59(8)	137d
	224	$-$N(Ph)$-$N(Ph)$-$	Ar$_{dip}$	1.882(4)	2.025(5)	106.14(18)	94
				1.875(4)	2.039(5)	105.06(18)	
	208a	OAr^{1a}	R^1	1.802(8)	1.812(7)	92.0(4)	134
	208b	OAr^{2b}	R^1	1.82	1.80	92.1	137a
	208c	OAr$_{ph}$	R^1	1.817(1)	1.822(1)	92.10(5)	135
	208e	OAr$_{dip}$	R^1	1.8245(13)	1.8296(14)	92.54(6)	137b
	208f	O(C$_6$H$_1$-2,3,5,6-Ph)	R^1	1.826(1)	1.827(1)	91.09(7)	135
	208g	O(binaphtyl^c)	R^1	av. 1.814(2)		89.4(7)	137c
	208h	Ot-Bu	R^1	1.832(11)	1.896(6)	85.9(4)	136
	216	OTMP^d	Ar$_{dip}$	1.804(2)	2.033(2)	100.15(6)	141a
Sn	**53**	N[SiMe$_3$]$_2$	R^1	2.088(6)	2.096(1)	104.7(2)	126a
	195c	N[SiMe$_2$Ph]$_2$	R^1	2.124(2)	2.133(2)	101.51(7)	126b
	195i	N(SiMe$_3$)[Si(SiMe$_3$)$_3$]	R^1	2.093(3)	2.103(3)	111.3(1)	126c
	195j^e	N(SiMe$_3$)Mes	R^1	2.058(3)	2.060(3)	105.8(1)	126d
			R^1	2.057(3)	2.057(3)	105.6(1)	
	195 l	N(SiMe$_3$)Dip	R^1	2.093(3)	2.095(3)	111.04(11)	126b
	195m	TMP^d	R^1	2.093(6)	2.111(6)	109.7(2)	125a
	195p	N(H)Mes*	R^1	1.99(2)	2.06(2)	89.6(6)	125g
	227	N[SiMe$_3$]$_2$	N(SiMe$_3$)C$_6$H$_{10}-$	2.117(2)	2.062(2)	99.78(8)	142
	225b	N[SiMe$_3$]$_2$	N(SiMe$_3$)C$_6$H$_4-$	2.082(7)	2.066(6)	101.8(3)	142
	217	N[SiMe$_3$]$_2$	NMes{B(t-Bu)[N(SiMe$_3$)$_2$]}	2.12	2.16	106.0	141b
	218	N[SiMe$_3$]$_2$	N=C=S	2.25	2.08	94.1(2)	141c
	219	N[SiMe$_3$]$_2$	OAr^{1a}	2.079(3)	2.055(2)	96.4(1)	141d
	220	N[SiMe$_3$]$_2$	Ar$_{tip}$	2.094(5)	2.225(5)	108.4(2)	113
	222	μ-N(SiMe$_3$)	Ar$_{dip}$	2.111(6)	2.267(7)	107.0(2)	94
				2.055(6)	2.250(7)	108.1(2)	
	209a	OAr^{1a}	R^1	1.995(4)	2.022(4)	88.8(2)	134
	209b	OAr^{2b}	R^1	2.003(3)	2.044(3)	88.8(1)	137e
	209d	OAr$_{mes}$	R^1	2.039(3)	2.043(3)	87.32(11)	137d
	209e	OAr$_{dip}$	R^1	2.0450(16)	2.0493(16)	92.18(6)	137b
	212	SMes*	R^1	2.435(1)		85.4(1)	139
Pb	**193**	N[SiMe$_3$]$_2$	R^1	2.222(19)	2.260(18)	103.557	126a
	210	OC(O)(2-pyridyl)	R^1	2.39		82.6	138

^{a} Ar^1 = C$_6$H$_2$-2,6-(t-Bu)$_2$-4-Me. ^{b} Ar^2 = C$_6$H$_3$-2,6-(t-Bu)$_2$. ^{c} See Scheme 40. ^{d} TMP = 2,2,6,6-tetramethylpiperidyl. ^{e} Two independent molecules.

Scheme 45. Veith's Metallylenes

229a: M = Si
229b: M = Ge
229c: M = Sn
229d: M = Pb
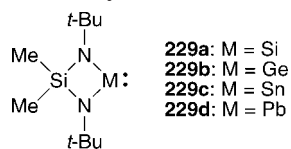
5.1.2. Cyclic

5.1.2.1. N-Heterocyclic. The chemistry of the heavier congeners of the N-heterocyclic carbenes (NHC) has been an active area of research in recent decades. In these systems, cyclization gives rise to chelating effects, which leads to increased stability of these compounds in addition to the perturbation caused by the nitrogen atoms (similar to the NHC systems). Therefore, these compounds are less reactive toward the substitution reactions of the nitrogen moiety than acyclic diaminometallylenes, which are used as the metallylene sources for other divalent species.

Veith's metallylenes **229b−d** (Ge−Pb) with a four-membered ring structure are known to be stable metallylenes (Scheme 45). Their chemistry has been widely investigated and reviewed many times.[143] Although the corresponding silylene **229a** has also been detected, it is known to be stable only in a glass matrix up to 77 K.[144]

Arduengo's carbene **230** was reported in 1991.[145] It was followed by the important class of heavier silicon and germanium congeners: the first silicon example by West in 1994[146] was followed by germanium in 1992 (Herrmann's group).[147] Although the tin analogue has also been described,[148] there is no report of the corresponding plumbylene synthesis. On the other hand, the analogues with saturated backbones **232** (Si−Pb)[149−151] and a number of benzene-,[152−155] pyridine-,[156,157] naphthalene-[158] and acenaphthene-[159] annulated derivatives **233−237** (Scheme 46) have all been reported. In addition, some bismetallylene species **238−241** (Scheme 47) were also synthesized.[160−162] All of these have been reviewed several times.[122,123b,163]

In metallylenes bearing unsaturated backbones and ring-fused annelated systems, aromatic resonance forms **A** (Scheme 48) play an important role in the stability of their electronic structures. Both theoretical and experimental results demonstrated that cyclic delocalization of the electrons promoted the thermodynamic stabilization. On the other hand, the contribution of the chelating form **B**, which bears a formally zerovalent atom, increases on going from silicon to lead. The result is a decrease in their stability.

The reactivity of these compounds has been widely investigated,[164] especially as ligands for transition metal complexes.[161b,165] Uniquely, silylene **232a** undergoes a tetramerization reaction to afford the disilene **242a**.[149,166] Similarly, the reaction of silylene **232a** with germylene **232g,i** gave the digermenes **242b** and **c**. Their regiochemistry was found to depend on the size of the substituent. When a more bulky substituent such as 2,6-dimethylphenyl was introduced, the expected intermediate **243** could be isolated (Scheme 49).[150] In addition, in 2008 Hahn's group succeeded in trapping the tin- and lead-homologues of carbon monoxide by using bisstannylene **240d** (Scheme 50) (For structure of silicon analogue of Arduengo's carbene **231a**, see Figure 11).[161a]

Driess's group reported the synthesis of the heterofulvene-like silylene **244a**[167] as well as the germylene **244b**.[168] The results of their X-ray analyses suggest a larger contribution

Scheme 46. Heavier Analogues of Arduengo's Carbene

230
Arduengo's carbenes

a: M = Si, R¹ = t-Bu, R² = H
b: M = Ge, R¹ = i-Pr, R² = H
c: M = Ge, R¹ = CH₂(t-Bu), R² = H
d: M = Ge, R¹ = Mes, R² = Me
e: M = Sn, R¹ = t-Bu, R² = H
f: M = Sn, R¹ = Mes, R² = H
g: M = Sn, R¹ = Mes, R² = Me
h: M = Sn, R¹ = Dip, R² = H
i: M = Sn, R¹ = Dip, R² = Me

231

a: M = Si, R¹ = t-Bu, R² = R³ = R⁴ = H
b: M = Si, R¹ = t-Bu, R² = R⁴ = Me, R³ = H
c: M = Si, R¹ = t-Bu, R² = R³ = Me, R⁴ = H
d: M = Si, R¹ = t-Bu, R² = Me, R³ = R⁴ = H
e: M = Si, R¹ = t-Bu, R² = t-Bu, R³ = R⁴ = H
f: M = Ge, R¹ = Me, R² = R³ = R⁴ = H
g: M = Ge, R¹ = i-Pr, R² = R³ = R⁴ = H
h: M = Ge, R¹ = t-Bu, R² = R³ = R⁴ = H
i: M = Ge, R¹ = Ph, R² = R³ = R⁴ = H
j: M = Ge, R¹ = C₆H₃-2,6-Me, R² = R³ = R⁴ = H
k: M = Pb, R¹ = Mes, R² = R³ = R⁴ = H
l: M = Pb, R¹ = Dip, R² = R³ = R⁴ = H

232

a: M = Si, R = CH₂(t-Bu)
b: M = Ge, R = CH₂(t-Bu)
c: M = Ge, R = SiMe₃
d: M = Sn, R = Me
e: M = Sn, R = Et
f: M = Sn, R = CH₂(t-Bu)
g: M = Sn, R = (CH₂)₂OMe
h: M = Sn, R = (CH₂)₃OMe
i: M = Sn, R = (CH₂)₂NMe₂
j: M = Sn, R = (CH₂)₃NMe2
k: M = Pb, R = Me
l: M = Pb, R = Et
m: M = Pb, R = CH₂(i-Pr)
n: M = Pb, R = CH₂(t-Bu)

233

233o

234

a: M = Sn, R¹ = Et, R² = (CH₂)₂OMe
b: M = Sn, R¹ = Et, R² = (CH₂)₂NMe₂
c: M = Sn, R¹ = Et, R² = (CH₂)₃NMe₂
d: M = Sn, R¹ = (CH₂)₂NMe₂, R² = (CH₂)₃NMe₂

235

a: M = Si, R = CH₂(t-Bu)
b: M = Ge, R = CH₂(t-Bu)

236

237

a: R = Dip b: R = [structure] c: R = [structure]

of the resonance form B (Scheme 51). Their syntheses and applications are described in section 5.3.2.

Other related compounds are shown in Scheme 52.[125g,151,169]

5.1.2.2. P- and O-Heterocyclic Compounds. P-Heterocyclic metallylenes are quite rare (Scheme 53). The first stable diphosphinyl germylene **253** was prepared by the reaction of GeCl₂·dioxane with a silaphospholane.[170] In 2008, the synthesis and structural characterization of the benzene-fused P-heterocyclic stannylene dianion **254** were reported.[171]
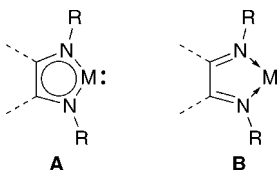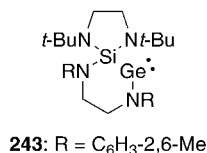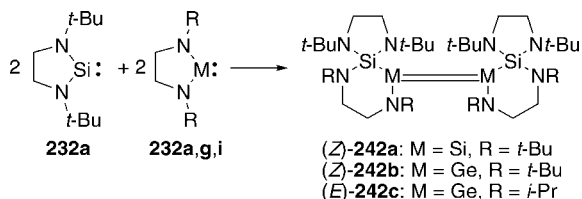
Concerning O-heterocyclic compounds, Hascall's group reported the divalent germanium and tin species involving calix[4]arene systems **256−260** (Scheme 54).[172] These compounds show either *exo* (two σ + two coordination bonds) or *endo* (only two σ bonds) forms, depending on the oxygen atom substituents. Their *exo*-isomers should be categorized as higher-coordinated metallylenes as described in section 5.2. Interestingly, the germanium analogue **256a**

**Scheme 47. Connected or Linked Systems of Some Heavier Congeners of Arduengo's Carbene**

238

239

240
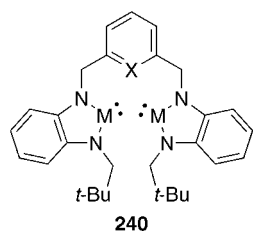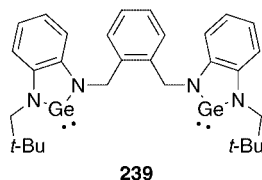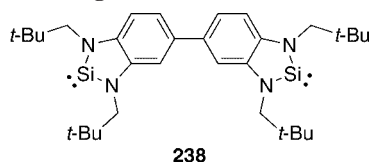
a: M = Ge, X = CH
b: M = Ge, X = N
c: M = Sn, X = CH
d: M = Sn, X = N

241
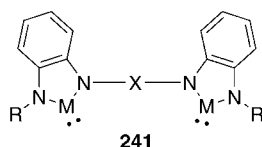
a: M = Ge, R = Et, X = (CH$_2$)$_4$
b: M = Ge, R = CH$_2$(t-Bu), X = (CH$_2$)$_4$
c: M = Ge, R = CH$_2$(t-Bu), X = (CH$_2$)$_5$
d: M = Sn, R = CH$_2$(t-Bu), X = CH$_2$(CMe$_2$)CH$_2$

Scheme 48. Resonance Forms of the Heavier Congeners of Arduengo's Carbene Bearing Unsaturated Backbones

A   B

Scheme 49. Reactivity Giving Disilenes or Digermenes

232a   **232a,g,i**   (Z)-**242a**: M = Si, R = t-Bu
(Z)-**242b**: M = Ge, R = t-Bu
(E)-**242c**: M = Ge, R = i-Pr

243: R = C$_6$H$_3$-2,6-Me

with SiMe$_3$ groups exhibits *exo/endo* isomerism. Cowley's group reported synthesizing the monomeric stannylene **261** using the same system.[173]

Scheme 50. Trapping of Tin- And Lead-Homologues of Carbon Monoxide

240d → M[N(SiMe$_3$)$_2$], H$_2$O

M = Sn, Pb
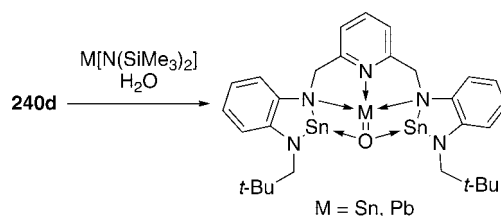
Scheme 51. Heterofulvene-like Silylene and Germylene

form A   form B

244a: M = Si
244b: M = Ge
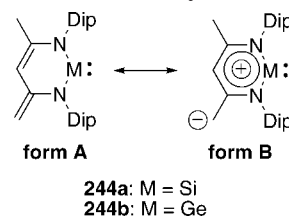
5.2. Coordination (Three-, Four-, or More-Coordinated) Systems

There are a large number of systems stabilized through coordination with Group 15 or 16 elements. One of these systems involves an intermolecular stabilization (Scheme 55)[174] as represented by the GeCl$_2$·dioxane complex.[174a] In addition, as mentioned previously, oligomeric forms of heteroatom-substituted metallylenes, e.g., compound **200**, can be classified as this type. Although there have been numerous examples reported, detailed discussion is beyond the scope of this review.

Intramolecular stabilization of the aryl or alkyl substituents using Group 15 or 16 elements has been widely investigated (Scheme 56, Figure 12).[123a,175] In addition, there are many examples of O- or N-containing substituents with Group 15 or 16 elements in their side chains: regarded as a combination of direct substitution (section 5.1) and coordination systems (Scheme 57).[123a,176]
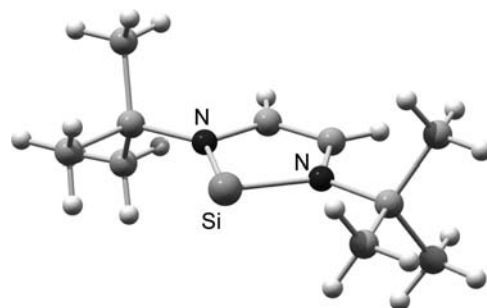

Figure 11. Molecular structure of silicon analogue of Arduengo's carbene **231a**.
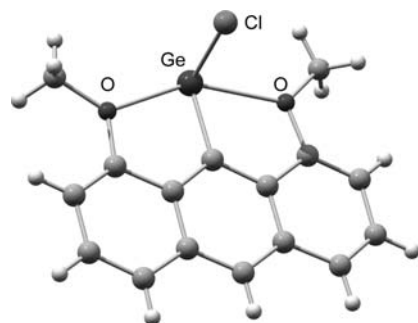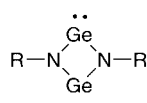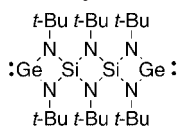

Figure 12. Molecular structure of chlorogermylene with a 1,8-dimethoxyanthracene ligand.[175b]
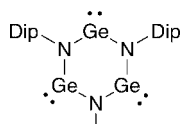
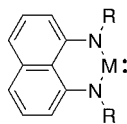**Scheme 52. Other Examples of N-Heterocyclic Metallylenes**
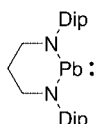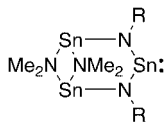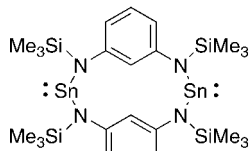

245a: R = Mes*
245b: R = R$_f$

246

247

248
a: M = Ge, R = i-Pr
b: M = Sn, R = i-Pr
c: M = Sn, R = SiMe$_3$
d: M = Sn, R = Si(i-Pr)$_3$
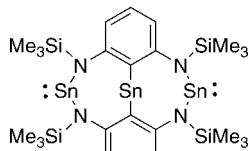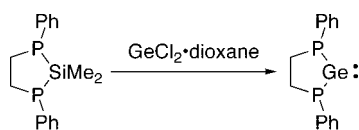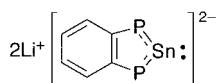
249

250a: R = Mes
250b: R = Dip

251

252

**Scheme 53. P-Heterocyclic Metallylene and a Related Compound**

253

254

The principal coordination numbers found for the Group 14 metallylenes with such ligands are shown in Figure 13. They can be summarized as follows: (A) the coordination number (CN) is three, involving one ligand and one substituent, (B) the CN is four with two ligands, and finally (C) the CN is three. Case C is derived from case B and is found in those cases where steric hindrance prevents the ligand from attaching at the second site.

5.3. Delocalized and Anionic Bidentate Ligands

A typical example of a delocalized and monoanionic bidentate ligand is the acetylacetonate anion (acac) that forms complexes with many transition metal ions. Recently, using a range of typical elements, this type of ligand was used to synthesize and isolate various kinds of unusual metallylene species. Pioneering work in this field are Karsch's metal-lylenes (Scheme 58),[177a−c] which have two diphosphi-nomethanide ligands. Their two phosphorus atoms in the one ligand are distinguishable in the X-ray crystallographic data analysis. That is, they are situated at the axial and equatorial
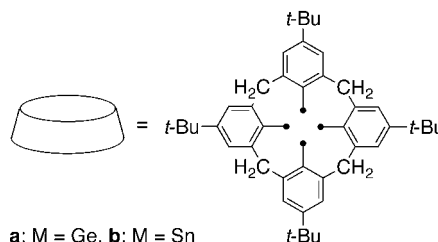
Scheme 54. Divalent Germanium and Tin Species with Calix[4]arene Systems
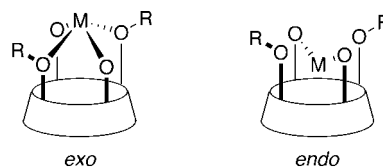
	R	exo	endo
256	SiMe$_3$	Ge, Sn	Ge
257	Si(i-Pr)$_3$		Ge, Sn
258	Me	Ge, Sn	
259	CH$_2$Ph	Sn	Ge
260	CH$_2$C$_6$H$_4$(t-Bu)	Sn	
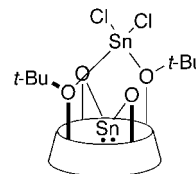
261

a: M = Ge, b: M = Sn

Scheme 55. Examples of Intermolecular Coordination with Group 15 or 16 Elements
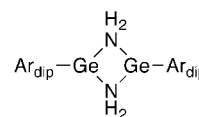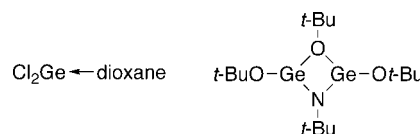
positions of trigonal bipyramidal structures, respectively. In their ^{31}P NMR spectra, on the other hand, only a singlet was observed, indicating the equilibration of the phosphorus moieties.
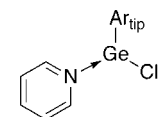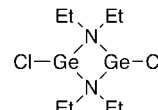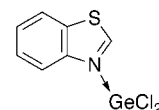
The ligands used are shown in Scheme 59. In particular, the systems with nitrogen atoms have attracted much attention because of the ease in fine-tuning the steric or electronic character by varying the substituents on the N atoms.

There are a number of reviews covering the many examples reported so far,[121,123b,c,177−180] so we limit ourselves here to some recent examples whose structures have been elucidated and where the characteristic features are reported.

Scheme 56. Examples of Intramolecular Coordination of Group 15 or 16 Elements with Aryl or Alkyl Substituents
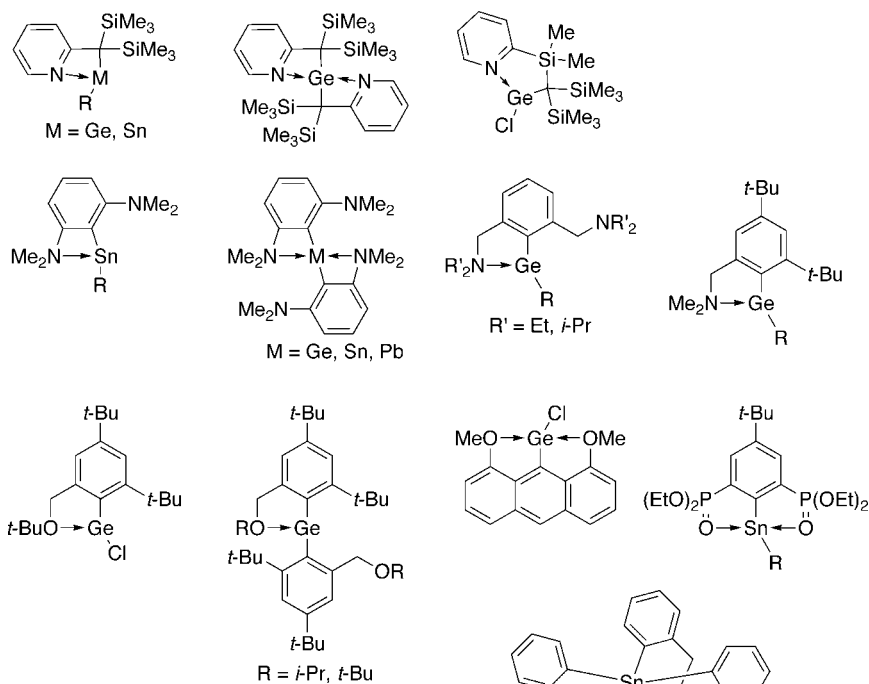
Scheme 57. Examples of Intramolecular Coordination by O- or N-Substituents with Group 15 or 16 Elements in the Side Chains
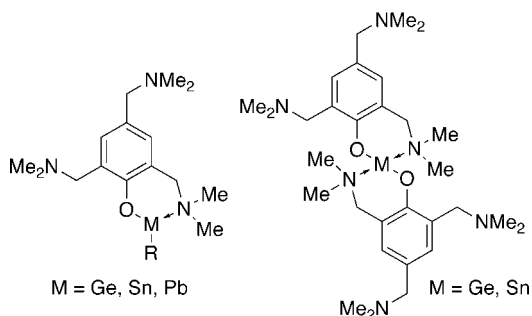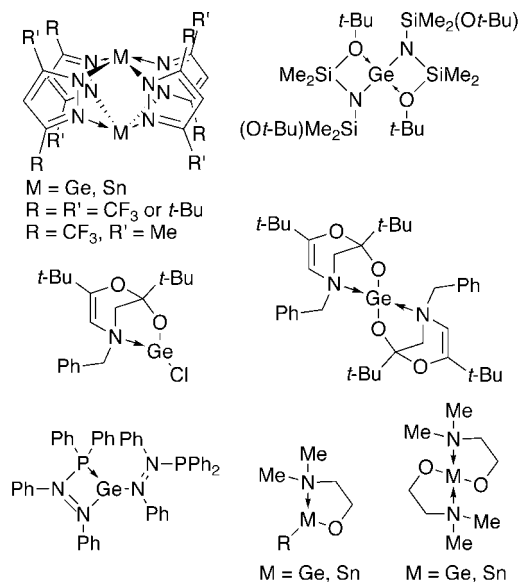
Scheme 58. Karsch's Metallylenes
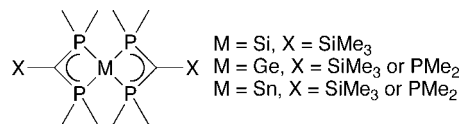
5.3.1. 4π Electron Systems

The amidinate (and the related guanidinate) ligands are both important examples of this class, and some stable examples are shown in Scheme 60.[181−184] The chemistry of the silicon and germanium analogues are reviewed by Kühl et al.[123b] and Roesky et al.[121]

Roesky's group synthesized the first silicon analogue **262** in 2006. It is noteworthy that the Cl-substituted compound is the first stable monomeric chlorosilylene. The compounds **264**[182] can be regarded as formal Ge(I) dimers, equivalent to digermyne (−Ge≡Ge−). Their Ge−Ge bond lengths are 2.6380(8) and 2.569(5) Å, respectively. These values are close to the typical single bond length (2.61 Å) and longer than those of the digermenes (>Ge=Ge<) (2.21−2.51 Å). This indicates a lack of multiple-bond character in the Ge−Ge bonds in **264**.

5.3.2. 6π Electron Systems

Some examples of β-diketonate ligands containing acetylacetonate—which are common bidantate ligands, are used to stabilize metallylenes, have structures that have been determined—are shown in Scheme 61.[185]

Figure 13. Coordination modes of substituents with heteroatoms in the side chains.

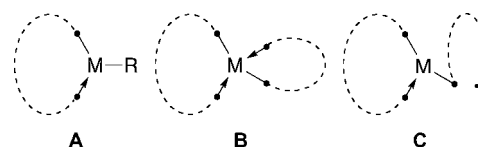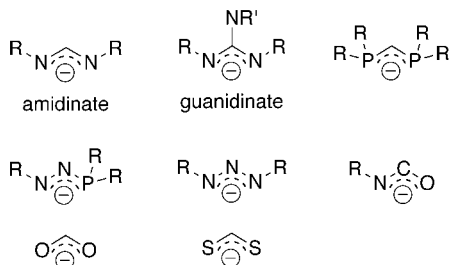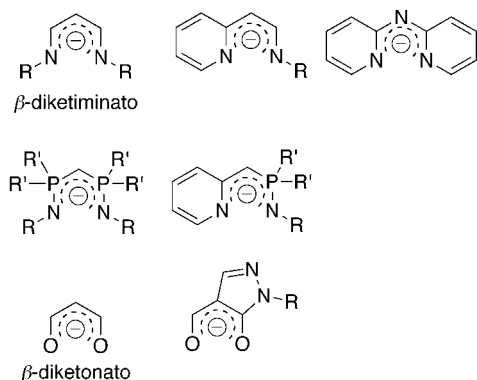**Scheme 59. Examples of Monoanionic Bidentate Ligands**

Scheme 60. Metallylenes Bearing Amidinate Ligands

Scheme 61. Examples of Metallylenes Bearing β-Diketonate Ligands

Scheme 62. Synthesis of Heterofulvene-Like Silylene 244a and β-Diketiminato Complex 271
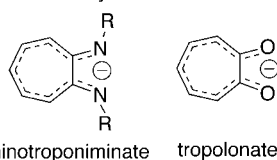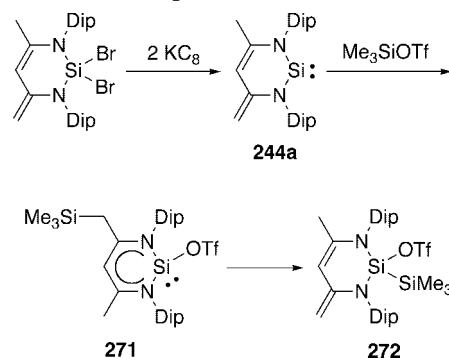
The β-diketiminate ligand, which is isoelectronic with β-diketonate, is a particularly versatile ligand used for the stabilization of single-site metal centers in unusually low valence states. Its coordination features resemble those of the related N-heterocyclic ligands, which are used for the synthesis of unusually low-coordinate metal complexes. The low-valent (or low-coordinate) metal centers in such complexes benefit from intramolecular N→M donor−acceptor bonds and the presence of sterically demanding substituents at the nitrogen atoms. The first application using the Group 14 elements was reported for germanium and tin systems in 2001.[186] The syntheses of silicon (2006) and lead (2007) analogues have already been achieved in addition to the germanium and tin analogues, which have been widely investigated and reviewed in detail.[121,123b,c,187]

The first β-diketiminato complex of the divalent silicon **271** was reported by Driess's group in 2006.[167] Because of the lack of suitable sources for divalent silicon, a modified synthetic route was used to make **271** (LiL + RMX, L = β-diketiminato, M = metal, X = leaving group). It was obtained by the reaction of heterofulvene-like stable silylene **244a** with Me₃SiOTf (Scheme 62). At ambient temperatures, **271** slowly isomerized to the thermodynamically more stable product **272**.

As shown in Scheme 63,[188] the reaction of silylene **244a** with water gave the second example of a β-diketiminato complex of divalent silicon, namely, the mixed-valent

Scheme 63. Reactivity of Heterofulvene-Like Silylene 244a and Related Compounds
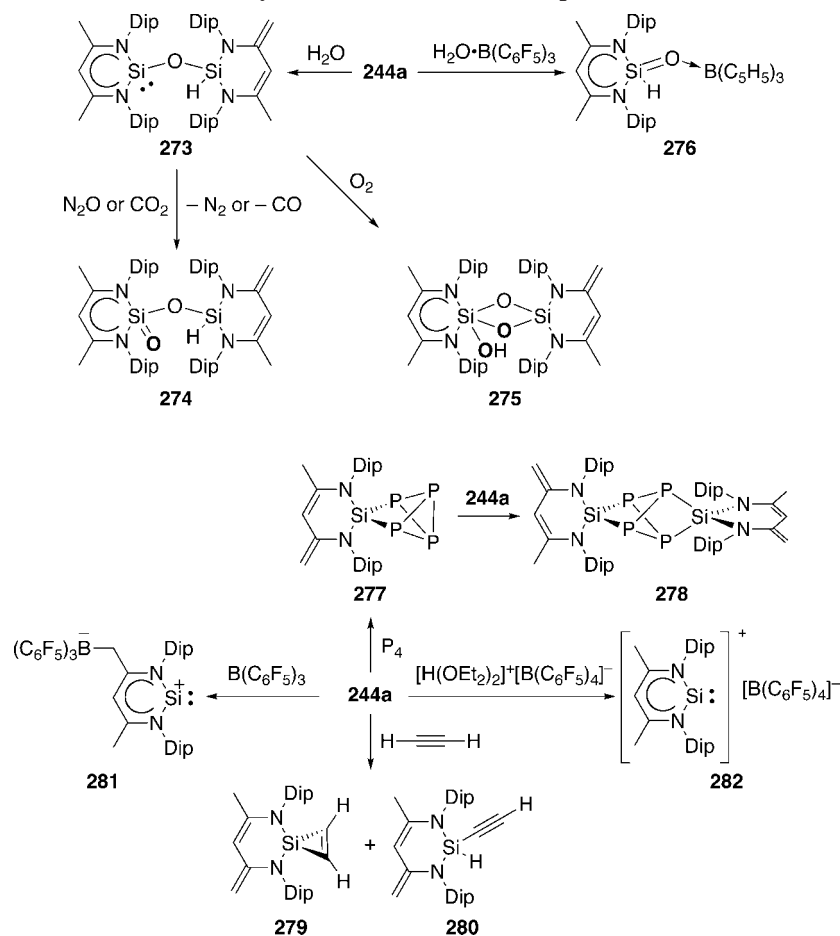
disiloxane **273**. It contains both Si(II) and Si(IV) centers.[188e] The oxygenation of disiloxane **273** by N₂O or CO₂ afforded the first silanoic ester **274** with a silanone (Si=O) moiety.[188f] Transient silanone species postulated in the synthesis of **273** were stabilized by B(C₆F₅)₃ to afford the complex **276**.[188e] In addition, silylene **244a** shows a range of reactivities such as a stepwise P₄ activation giving **277** and **278**,[188d] the C−H activation of acetylene giving **280** with the [1 + 2]-cycloadduct **279**,[188b] and the generation of the cationic species **281** and **282**.[188g]

Various germanium and tin analogues of this type have already been synthesized. Chlorometallylenes **283** (see Figure 14), synthesized by the reaction of lithium β-diketiminato with MCl₂ (M = Ge, Sn), are key starting compounds in their synthesis, and a summary of their reactions is shown in Scheme 64. In the case of germanium, a broader reactivity

Scheme 64. Synthesis and Common Reactions of the β-Diketiminato Complexes of Divalent Germanium and Tin

has been reported[189] and was summarized in detail by Roesky et al.[121] These derivatives are available for the synthesis of the unique low-valency germanium species: germane−imine **284**, thione **285**, selone **286** and **287**, thioacid **288**, selenoacid **289**, thioacid halide **290**, and selenoacid halide **291**. Recently, facile syntheses for several germylenes **292−295** bearing a phosphorus substituent have been reported (Scheme 65).[189c]

Figure 14. Molecular structure of chlorogermylene **283a**.

284: Z = NSiMe₃, X = F
285: Z = S, X = Me
286: Z = Se, X = Me
287: Z = Se, X = n-Bu
288: Z = S, X = OH
289: Z = Se, X = OH
290: Z = S, X = Cl
291: Z = Se, X = Cl

R = Ph, C₆H₃-2,6-Me, Dip
X = Cl, F

Scheme 65. Synthesis of Phosphino–Germylene Derivatives
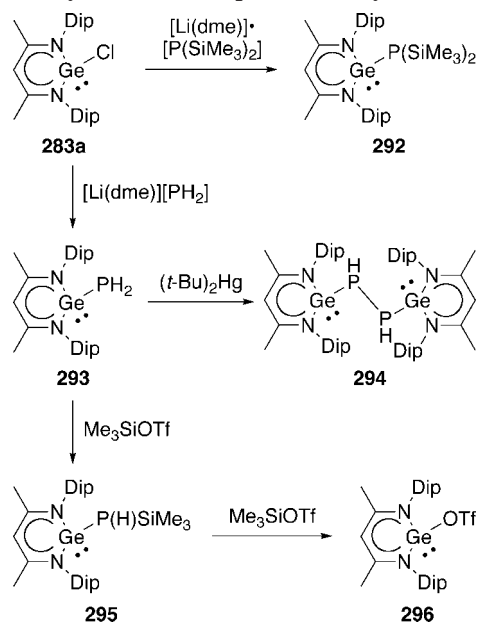
Scheme 66. Reaction of Germylene 283a with Potassium
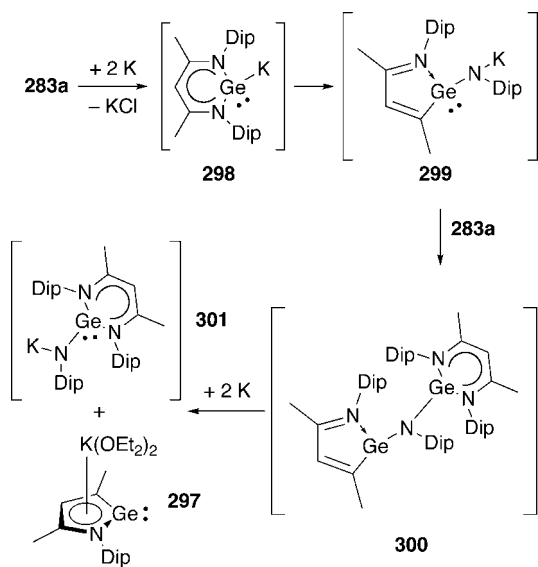
The reduction of **283a** by potassium afforded the cyclopentadienide analogue containing a germanium atom **297** (Scheme 66).[189b] Its structure was determined by X-ray crystallographic analysis and showed a typical η^5-coordination mode. The generation of compounds **297** and **301** was reasonably interpreted in terms of the intermediates **298–300**, and **301** was fully characterized.

As in the case of silicon, the heterofulvene-like germylene **244b** has also been reported.[168] Germylene **244b** was generated by the direct reaction of the chloro-substituted complex **283a** with LiN(SiMe₃)₂. Alternatively, the stepwise reaction via the cation **302** can be used. These differ from the synthetic methods for **244a** (Scheme 67). Although the reaction of compound **244b** with Me₃SiOTf gave germylene **303**, the germanium analogue of **271**, the stability of **244b** is much greater than that of **271**. Interestingly, the reactions of **244b** with acetylenes afforded compound **305**, which is a unique structure and is quite different from that of the silicon compound.[189a]

In contrast to germanium and tin, the reaction of PbCl₂ with LLi(OEt₂) (L = β-diketiminato) in an ethereal solvent

Scheme 67. Synthesis and Reactivity of Heterofulvene-Type Germylene 244b
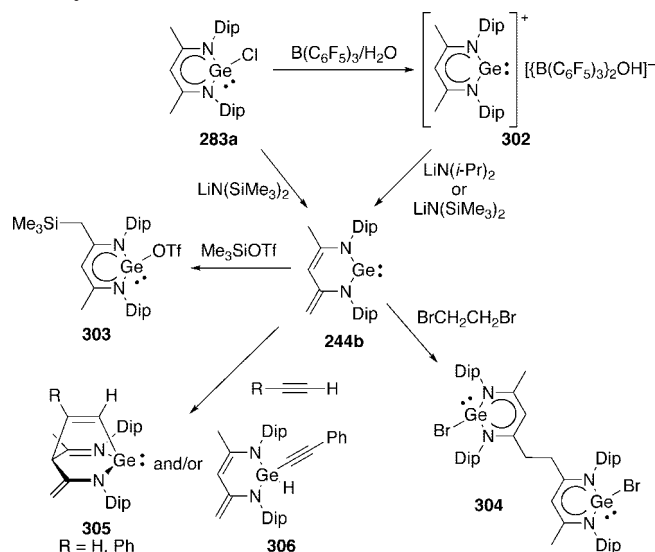
Scheme 68. Synthesis and Reactivity of β-Diketiminato Complexes of Divalent Lead
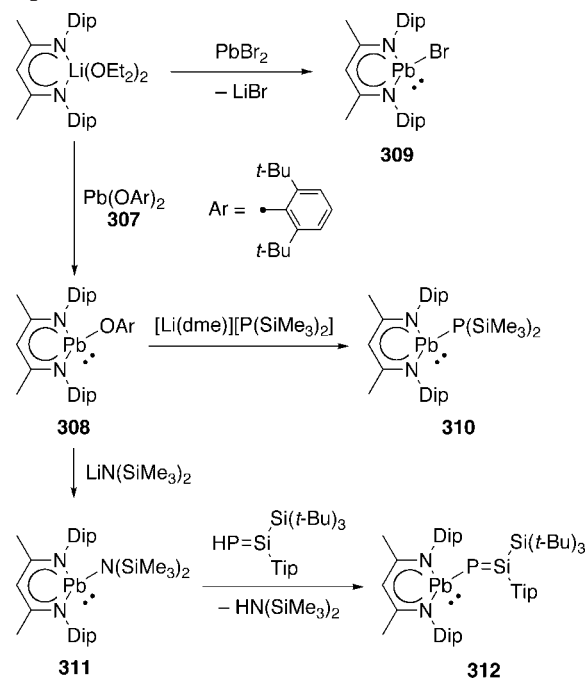
gave elemental lead. Therefore, Pb(II) diphenolate **307** was used as an alternative precursor (Scheme 68).[190] Using the initially generated plumbylene **308**, it was possible to synthesize other plumbylenes **310–312**.[190] On the other hand, PbBr₂ proved useful for the synthesis of the β-diketiminato lead complex **309**.[191]

6. Group 14 Metallocene Chemistry

The Group 14 metallocenes **313** (silicocene, germocene, stannocene, and plumbocene) are sandwich-type compounds bearing two cyclopentadienyl groups (Scheme 69). Subsequent to the syntheses of the parent metallocenes [M(C₅H₅)₂]: stannocene (Fisher, 1956),[192] plumbocene (Fisher, 1956),[193] and germocene (Curtis, 1973), many other ring-substituted derivatives have been reported. However, the silicon example, Si(C₅Me₅)₂ (**315**), which was reported by Jutzi's group in 1989,[194] is still the only silicon example. In 2006, however,

Scheme 69. Group 14 Metallocenes and Related Compounds

313
M = Si–Pb

314

321

315: R^1–R^{10} = Me
316: R^1–R^5 = Me, R^6–R^{10} = H
317: R^1–R^5 = Me, R^6–R^{10} = i-Pr
318: R^1–R^5 = Me, R^6 = R^8 = SiMe$_3$,
   R^7 = R^9 = R^{10} = H
319: R^1–R^5 = Me, R^6 = R^7 = R^9 = Me,
   R^8 = R^{10} = H
320: R^1 = R^2 = R^4 = R^6 = R^7 = R^9 = Me,
   R^3 = R^5 = R^8 = R^{10} = H
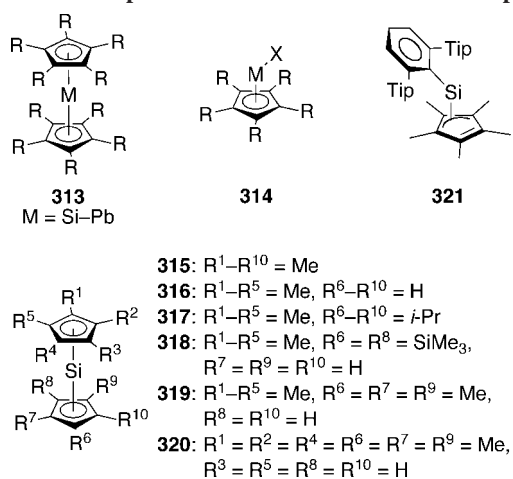
Scheme 70. General Syntheses of Group 14 Metallocene Derivatives

lithium naphthalenide → **315**

CpM + SnCl$_2$ Cp$_2$SnX$_2$

Cp$_2$Sn

SnX$_2$

CpSnX
322

Cp'M   RM

CpSnCp'   CpSnR
323   **324**

M = alkali metals, etc.
X = leaving group (halogen etc.)
Cp' = substituted cyclopentadienyl
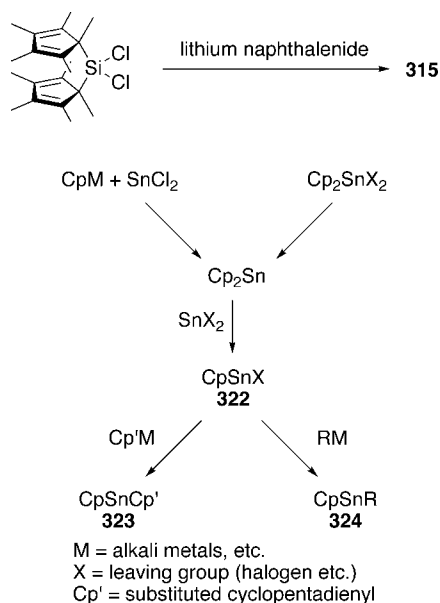
a series of new silicocene derivatives, **316**−**320**, were successfully synthesized.[195] With the exception of silicon, a number of neutral half-sandwich type compounds **314** have been reported for the other elements. Quite recently, the aryl-substituted silicon analogue **321** was reported as the first example of a stable monomeric arylsilicon(II).[196] Although these compounds contain the formal M(II) center with the CN higher than two, they are regarded as "resting states" for dicoordinated compounds.

The chemistry of these compounds has been widely investigated and described in numerous articles.[197] Their syntheses, structures, and properties have all been reviewed and summarized by Jutzi et al.[198,199] Therefore, we shall limit our discussion in this section to an overview and the most recent results.

6.1. Synthesis

As summarized in Scheme 70, there are two approaches to the syntheses of the Group 14 metallocenes: (i) the reduction of dicyclopentadienyl(dihalo)metallane (Si−Sn)[200] and (ii) the direct substitution of two metal cyclopentadien-ides with a divalent metal halide (Ge−Pb). Half-sandwich halides **322** are obtained either by the stoichiometric reaction
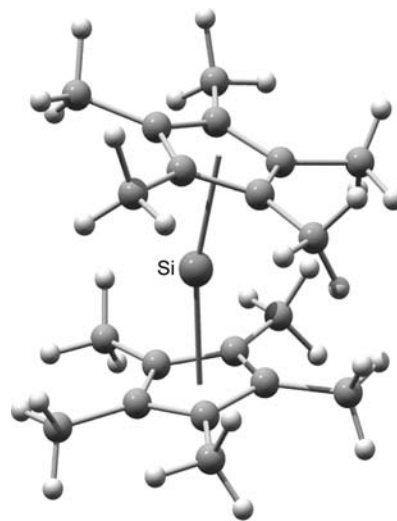
Figure 15. Molecular structure of decamethylsilicocene **315**.

of metal cyclopentadienides with a divalent metal halide or by the disproportionation reaction of metallocene with a divalent metal halide. These half-sandwich compounds can be good precursors for the syntheses of asymmetrical metallocenes **323** or other half-sandwich derivatives **324**.

6.2. Structures

The most interesting feature of these compounds is their molecular structures, which change from tilted to axial as the steric bulk of the peripheral substituents increases. Numerous theoretical calculations confirm that the bent structures are energetically favored.[201]

Linear structures were observed in Si(C$_5$Me$_5$)$_2$[194] (crystal-lized in both linear and bent forms), Si(C$_5$Me$_5$)[C$_5$(i-Pr)$_5$],[195] Ge[C$_5$Me$_4$(SiMe$_2$$t$-Bu)]$_2$,[201d]Sn(C$_5Ph_5$)$_2$,[202]Sn[C$_5Me_4$(SiMe$_2$$t$-Bu)]$_2$,[201d,203] Sn[C$_5$($i$-Pr)$_5$]$_2$,[204] Pb[C$_5Me_4$(SiMe$_2$$t$-Bu)]$_2$,[201d,205] and Pb[C$_5H_2$($i$-Pr)$_3$]$_2$.[206] In 2006, the structure of Ge(C$_5$Me$_5$)$_2$ was deter-mined by Schnepf's group,[207] thus making it possible for us to compare the Group 14 metallocenes bearing the same ligands.

6.3. Reactivities

The reactions of the Group 14 metallocenes **315** (see Figure 15) and **325**−**327** with HBF$_4$ or related reagents[208] result in the protonation and release of a ligand, giving rise to the cations **328**, which can be regarded as a derivative of metallyliumylidene cation, HM$^+$ (M = Si, Ge, Sn, Pb). In the case of germanium[209] and tin,[210] these cations exist as monomers (Scheme 71). In the case of silicon, the proton-ation of **315** with HBF$_4$ presumably affords the corresponding cation **328**, which decomposes to give the polymer **329**. On the other hand, the reaction of **315** with the proton-transfer reagent [Me$_5$C$_5$H$_2$][B(C$_6$F$_5$)$_4$] yielded the free cation **331**.[211] In the case of lead, the protonation of **327** with HBF$_4$ gives the dimer **330**.[212] When Pb(C$_5$H$_5$)$_2$ was used as the precursor, the product was polymeric. The introduction of bulky substituents into the cyclopentadienyl ring or the use of a bulky counteranion prevents oligomerization. The syntheses of the free cations **332**−**334** have all been reported.[213]

These species can be good precursors for the syntheses of related compounds. The silicon analogue **331** leads to the metallocenes **316**−**320**. The decamethyl derivatives **334** (Sn, Pb) react directly with Cp*$_2$M (M = Sn, Pb) to give the tripledecker cations Cp*MCp*MCp* (**335**) (Scheme 72).[214]

Scheme 71. Synthesis of Half-Sandwich Type Cations
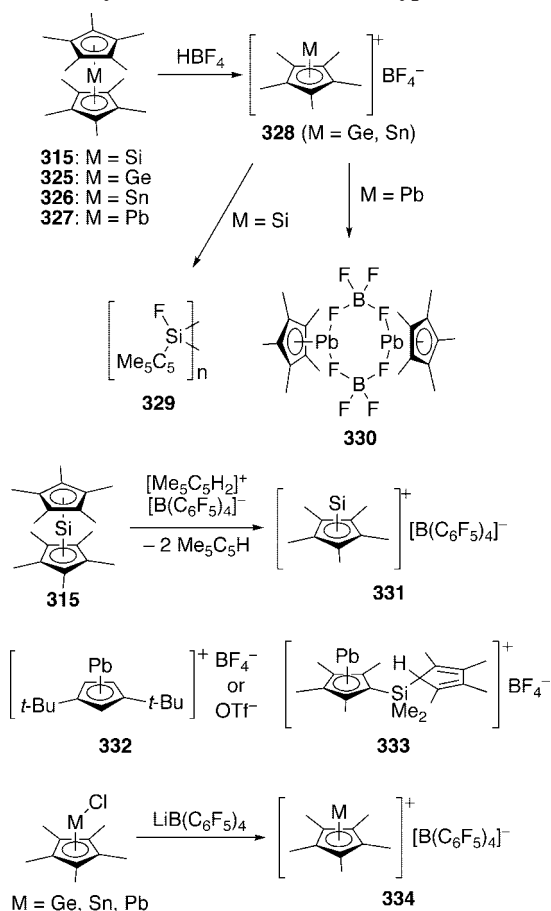
Scheme 72. Synthesis of Triple-Decker Cations

Scheme 73. *ansa*-Type Group 14 Metallocenes
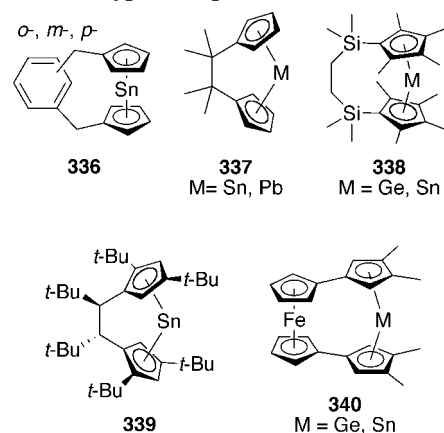
Scheme 74. Bismetallocenes

6.4. Recent Applications

Bridged cyclopentadienyl (*ansa*) ligands have been successfully used in stabilizing and controlling the reactivity of the s, d, and f block element metallocenes. On the other hand, application to the p block elements is yet to be fully explored. Although some *ansa*-Group 14 metallocenes **336**−**339** have been reported (Scheme 73),[215] the first successful X-ray structural determination was for **339** by Balaich's group in 2005.[216] Related ferrocenyl-bridged examples **340** were reported by Castel and Riviére's group in 2004, who also made the Ge and Sn bis(ferrocenyl)metallocenes.[217]

Riviére also prepared bisgermocenes and stannocenes linked through phenylene, biphenylene, or thiophene spacers **341** in 2000 (Scheme 74).[213a,b,218]

7. Conclusion

It is hoped that this review has demonstrated that a broad range of the heavier analogues of carbenes are neither imaginary species nor reactive intermediates but, when appropriately stabilized by kinetic and/or thermodynamic methods are stable, are isolable compounds. The study of a metallylene series revealed their characteristic electronic structures involving the inert lone pair and a vacant p orbital. Although all these stable metallylenes have not yet been structurally characterized, it has been established that their molecular structures can be successfully correlated with their reactivities. The fact that stable metallylenes can exist under ambient conditions means we can investigate the physical and chemical properties of metallylenes and low-coordinated species of the heavier Group 14 elements in detail using a suit of analytical methods such as spectroscopic and crystallographic techniques. Almost all of the metallylenes isolated exhibit "singlet" ground states due to the intrinsic nature of the heavier Group 14 elements, which favors the $(ns)^2(np)^2$ valence electronic configuration. Theoretical studies guided us toward ideal syntheses of "triplet metallylenes", where "bulky substituent" and "electropositive substituents" make the ΔE_{S-T} energy gaps smaller. Although a few examples of "triplet ground state silylenes" have been reported, the experimental results for triplet metallylenes are not enough for us to fully understand the properties of these metallylenes. The combined understanding and experimental data on the stable metallylenes described here should contribute greatly to helping us to achieve the goal of synthesizing "stable triplet metallylenes".

In addition, we have demonstrated that the stable metallylenes introduced in this review are good precursors and building blocks for the creation of unique and novel species of the heavier Group 14 elements. As a result of this, and because of the detailed knowledge of the metallylenes accumulated over the last three decades, there should be a

considerable ripple effect on interdisciplinary research and increased effort and challenges in this exciting field.

8. Acknowledgments

9. References

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