Unprecedented Oxidative Chlorosilylation Addition Reactions to a Diarylgermylene and -stannylene

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Treatment of MAr_2 [$Ar^- = \bar{C}_6H_3(NMe_2)_2$-2,6 and M = Ge (**1**) or Sn (**2**)] with silicon tetrachloride, or **2** with $SiCl_3Me$, under mild conditions in diethyl ether afforded in good yields the appropriate silylgermane or -stannane $M(Ar)_2Cl(SiCl_3)$ [M = Ge (**3**), Sn (**4**)] and $Sn(Ar)_2Cl(SiCl_2Me)$ (**5**). The X-ray structures of **3** and **5** show that while in **3** there is no very close Ge⋯N contact (the molecule having germanium in a distorted tetrahedral environment), **5** has a distorted pyramidal structure around the tin atom, with a Cl and a N atom in apical sites. Solutions of **3** and **4** in C_6D_6 showed the former to be stable, while the latter slowly decomposed, yielding β-tin and $Sn(Ar)_2Cl_2$ among the products; solutions of **5** showed the presence of the equilibrium $2 + SiCl_3Me \rightleftharpoons 5$, and in $CDCl_3$ the mixture afforded $Sn(Ar)_2Cl(CDCl_2)$.
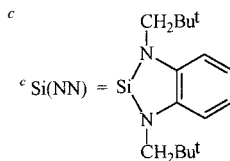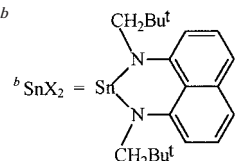
Introduction

The present work is a continuation of a study begun in 1997 dealing with metal complexes of the ligand $[C_6H_3(NMe_2)_2$-2,6$]^-$ (abbreviated as Ar^-),[1] readily prepared from $[Li(\mu$-Ar)]_3$.[2] A feature of such complexes is the facile on/off coordination of one of the pendant NMe_2 groups. The ligand Ar^- differs from the widely studied[3] bis(homo)analogue $[C_6H_3(CH_2NMe_2)_2$-2,6$]^-$ ($\equiv Ar'^-$) in that N→M association is largely strain-free for (M − Ar′)—but not (M − Ar)—complexes. Thus, we note that in three mononuclear, crystalline tin(II) complexes the angle subtended at the *ipso*-carbon atom of the five- or four-membered metallacyclic ring is close to the sp^2 value in $Sn(Ar')Cl$,[3] but has an average value of 104° in $SnAr_2$,[1] while in $Sn(Ar)Cl$ it is 112.1(4)°;[4] moreover, in toluene-d_8 solution there was rapid 2-NMe_2→Sn to 6-Me_2N→Sn exchange at ambient temperature for the latter two compounds,[1,4] but not for $Sn(Ar')Cl$.[3]

We have previously prepared 17 crystalline M−Ar complexes,[1,4−9] for 11 of which X-ray data are available, Table 1. In general, each Ar^- ligand has a close N⋯M contact, exceptions being $GeAr_2(BH_3)$ (in which only one

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Table 1. Previously Reported Crystalline 2,6-Bis(dimethylamino)phenylmetal Complexes

complex	coordination no. of M	ref
$[Li(\mu$-Ar)]_3$	2 + 2N	2
$GeAr_2$ (**1**)	2 + 1N	1, 9
$SnAr_2$ (**2**)	2 + 2N	1
$PbAr_2$	2 + 2N	1
$GeAr_2(BH_3)$ (**A**)	3 + 1N	5
$SnAr_2(BH_3)$ (**B**)	3 + 2N	5
$Sn(Ar)Cl$	2 + 1N	1, 4
$Sn(Ar)\{N(SiMe_3)_2\}$	a	1
$Sn(Ar)\{CH(SiMe_3)_2\}$	a	1
$GeAr_2(SnX_2)^b$ (**C**)	a	6
$SnAr_2(SnX_2)^b$ (**D**)	3 + 2N	6
$Sn(Ar)\{Si(NN)Ar\}^c$	2 + 2N	7
$Sn(Ar)\{Si(NN)N(SiMe_3)_2\}$	2 + 2N	7
$SnAr_2(NCO)_2$	a	9
$SnAr_2(NCS)_2$	4 + 2N	9
$BAr(Cl)Ph$	3 + 1N	8
$HgAr_2$	2	8

a Not determined. *b*

c

of the Ar^- ligands behaves in this fashion)[5] and the two-coordinate mercury(II) complex $HgAr_2$.[8]

Following the synthesis and structures of the crystalline complexes $GeAr_2$ (**1**) and $SnAr_2$ (**2**),[1] three classes of reactions of these MAr_2 compounds have been established. Their Lewis base character was shown by the demonstration that they displaced thf from BH_3(thf) to form the adducts **A**[5] and **B**,[5] and they formed the 1:1 adducts **C**[6] and **D**[6] with the Lewis acid 1,8-naphthale-nebis(neopentylamido)tin(II).[6] They were capable of

A

B

C   M = Ge
D   M = Sn
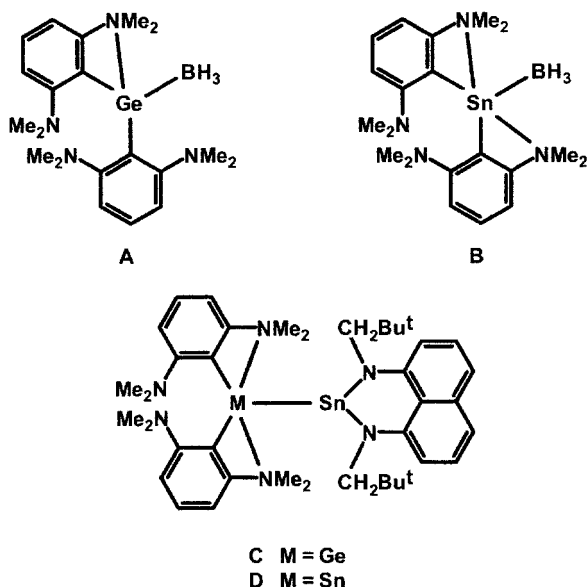
undergoing redox reactions; thus $SnAr_2$ (**2**) with silver iso- or isothiocyanate yielded $SnAr_2(NCX)_2$ (X = O or S) and silver.[9] Finally, $SnAr_2$ behaved as a substrate for oxidative addition by the halogenoalkane Bu^tBr or $(Me_3Si)_2CHBr$, yielding $SnAr_2(Br)R$ [R = Bu^t or CH-$(SiMe_3)_2$], respectively.[9]

In light of the formation of $MAr_2(BH_3)$ adducts **A** and **B**,[5] we have now examined reactions of $GeAr_2$ (**1**) or $SnAr_2$ (**2**) with the group 14 Lewis acids $SiCl_4$ and $SiCl_3$-Me. Among carbenes or heavier group 14 metal(II) analogues, only Arduengo-type carbene-silane adducts **E** have been established for $SiCl_4$, $SiCl_2Me_2$, and $SiCl_2$-Ph_2;[10] whereas the bis(amido)stannylene **F** (Z = Sn) reacted with $SiCl_4$ only under forcing conditions (190 °C, autoclave, 12 h) and then yielded the product **F** (Z = $SiCl_2$) of σ-bond metathesis.[11]

E   X = Cl and R = Me, Et, Pr^i;
or X = Me, Ph and R = Et, Pr^i

F   Z = Sn, SiCl$_2$
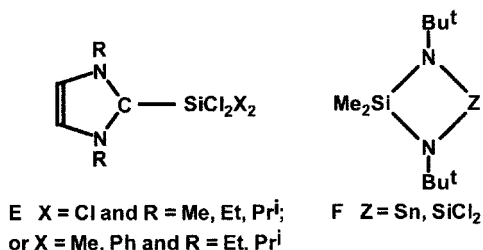
Results and Discussion

We now draw attention to unprecedented oxidative insertion reactions of a divalent monomeric diarylgermylene or -stannylene with a chlorosilane, which might occur through the intermediacy of a transient germylene/stannylene (as donor)−silane (as acceptor) complex and subsequent chloride migration from Si to Ge or Sn. Treatment of the recently described yellow diarylgermylene $GeAr_2$ (**1**) [Ar$^-$ = $\bar{C}_6H_3(NMe_2)_2$-2,6] or -stannylene $SnAr_2$ (**2**)[1] with tetrachlorosilane (for **1** and **2**), or also for **2** with an excess of methyltrichlorosilane in diethyl ether, and crystallization from Et_2O afforded colorless crystals of the silylgermane $Ge(Ar)_2Cl(SiCl_3)$

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(**3**) and the silylstannanes $Sn(Ar)_2Cl(SiCl_2R)$ [R = Cl (**4**) and R = Me (**5**)] in good yields, Scheme 1.

3

5
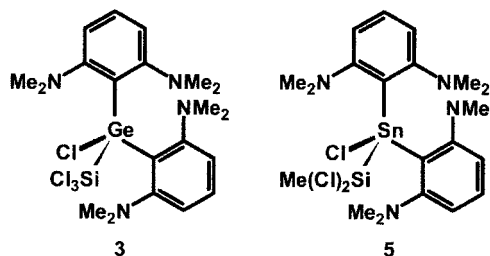
Each of the compounds **3**−**5** gave satisfactory microanalytical as well as NMR [^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$, and (for **4** and **5**) $^{119}Sn\{^1H\}$] and EI-MS spectra. Whereas compound **3** was thermally stable below 70 °C both in solution and in the solid state, the solution of the tin analogue **4** slowly deposited tin at ambient temperature, or if exposed to light for a prolonged period. In toluene at higher temperatures however (T > 100 °C), compound **4** decomposed within 3 to 4 h, Scheme 2. This thermal decomposition was also monitored in an NMR-tube scale reaction (in toluene + C_6D_6) by $^{119}Sn\{^1H\}$ NMR spectroscopy. Besides the formation of sponge-type aggregated metallic β-tin ("white tin"), confirmed by X-ray powder diffraction, the tin(IV) complex $Sn(Ar)_2Cl_2$ (**6**) was the only tin-containing complex detected and was also isolated as colorless crystals. This behavior parallels that observed in the $Sn[CH(SiMe_3)_2]_2$ + $SnCl_2$ system, which afforded $Sn-[CH(SiMe_3)_2]_2Cl_2$ + Sn.[9] Compound **6** was earlier shown to be generated together with metallic tin in a thermal decomposition−disproportionation reaction of the recently described heteroleptic chlorostannylene Sn(Ar)-Cl in toluene (T > 100 °C).[1,9] The $^{29}Si\{^1H\}$ NMR spectra of the reaction mixture revealed three signals at δ −18.9, −24.7, and −26.2. The signal at δ −18.9 is assigned to $SiCl_4$; the latter two are close to the chemical shift of the chlorosilane $Si(Ar)Cl_3$ (**7**) [$^{29}Si\{^1H\}$ δ −25.3], prepared from $[Li(\mu$-Ar$)]_3$[2] and $SiCl_4$.[9]

In contrast to the above-mentioned decomposition reaction, a solution of colorless $Sn(Ar)_2Cl(SiCl_2Me)$ (**5**) in aromatic solvents at ambient temperature was stable with respect to the formation of elemental tin, but turned yellow as soon as it was dissolved. There was clear evidence from ^1H and heteronuclear NMR spectra that besides the desired silylstannane **5**, both starting materials, the diarylstannylene **2** and $SiCl_3Me$ (ratio = 1:1), were present. It was also shown by NMR spectroscopic experiments that the 2:3 ratio between the diarylstannylene **2** and the silylstannane **5** did not change after 1 week at ambient temperature or 2 days at 70 °C in benzene or toluene. However, when an excess of $SiCl_3Me$ was added to **5** in toluene, the stannylene **2** was nearly quantitatively reconverted into the silylstannane **5**. These observations indicate that there was an equilibrium between the chlorosilane/stannylene and the silylstannane **5** in aromatic (or ethereal) solvents. As mentioned above, in the absence of an excess of methyltrichlorosilane, the dissolved crystalline complex **5** partially reverted to the starting stannylene and the silane in aromatic solvents. When deuterated chloroform was used in an NMR-tube scale experiment, the equilibrium between **2** and **5** was shown to be shifted in
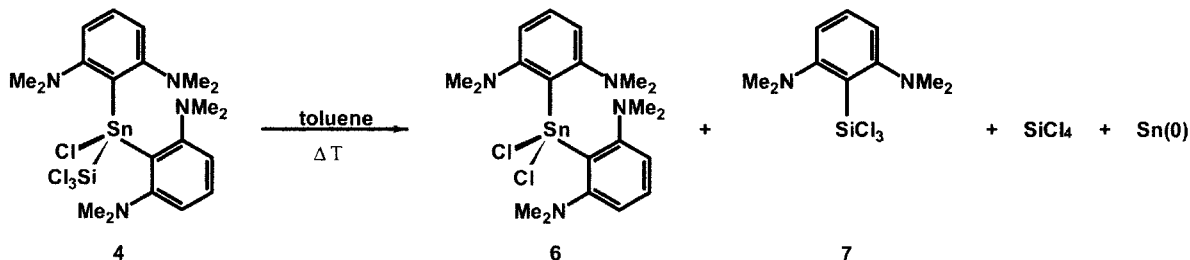
Scheme 1. **Synthesis of Ge(Ar)₂Cl(SiCl)₃ (3), Sn(Ar)₂Cl(SiCl)₃ (4), and Sn(Ar)₂Cl(SiCl₂Me) (5); Ar = C̄₆H₃(NMe₂)₂-2,6**
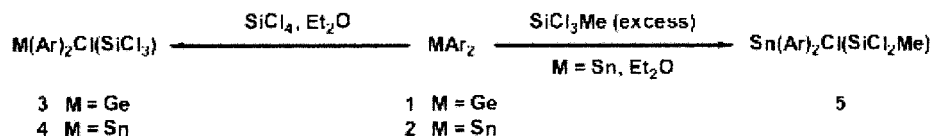
Scheme 2. **Thermal Decomposition of Sn(Ar)₂Cl(SiCl₃) (4)**

Scheme 3. **Formation and Dissociation of Sn(Ar)₂Cl(SiCl₂Me) (5)**
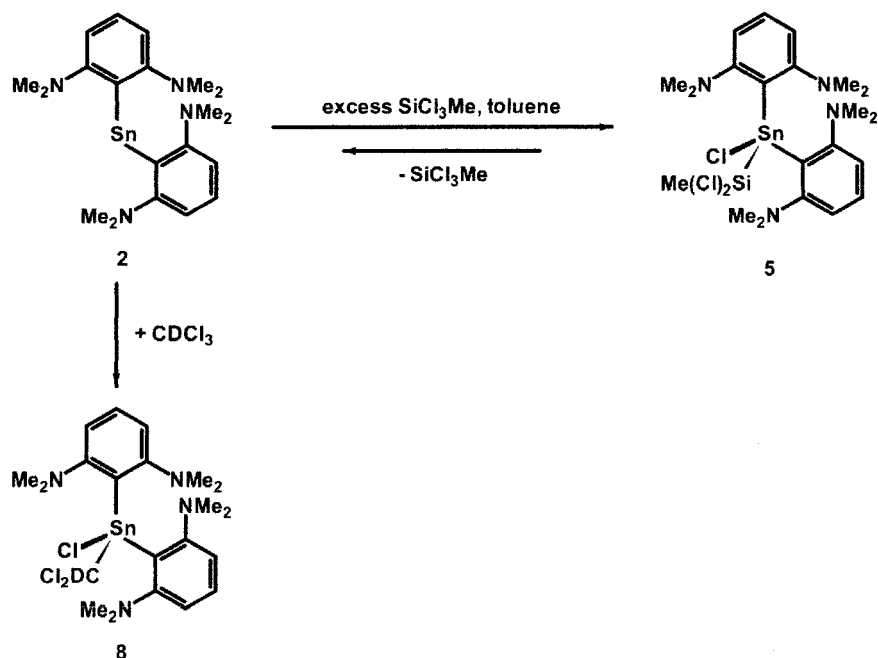
favor of **2**, which, as soon as formed, was consumed by the CDCl₃ to produce Sn(Ar)₂Cl(CDCl₂) (**8**), Scheme 3. Crystalline **5** turned yellow upon storage at ambient temperature and was best kept at −30 °C.

The structure of Ge(Ar)₂Cl(SiCl₃) (**3**), investigated by single-crystal X-ray diffraction, is illustrated in Figure 1, with selected bond lengths and angles in Table 2. The molecule **3** has the germanium atom in a distorted tetrahedral environment; the average of the six angles subtended at the germanium atom by the atoms C1, C11, Cl1, and Si is 109.3° and range from 96.26(6)° (Si−Ge−Cl1) to 115.15(13)° (Si−Ge−C1). The shortest of the contacts between the four nitrogen atoms is 2.88(1) Å (Ge···N3) and is surely nonbonding, as evident from the 2.479(11) and 2.508(11) Å Ge···N contacts in two independent molecules of GeAr′(Cl)(Me)Ph (Ar′ = C₆H₄-CH₂NMe₂)[12] and the 2.394(6) and 2.722(6) Å in GeAr₂[1,9] [cf.[1] the Sn···N distance in SnAr₂ of 2.607(5) and 2.669-(5) Å]. As a result of the relatively proximate Ge···N3

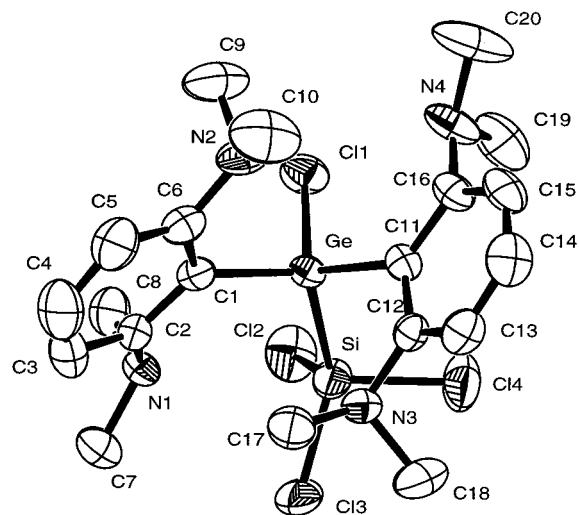(12) Brelière, C.; Carré, F.; Corriu, R. J. P.; de Saxce, A.; Poirier, M.; Royo, G. *J. Organomet. Chem.* **1981**, *205*, C1.

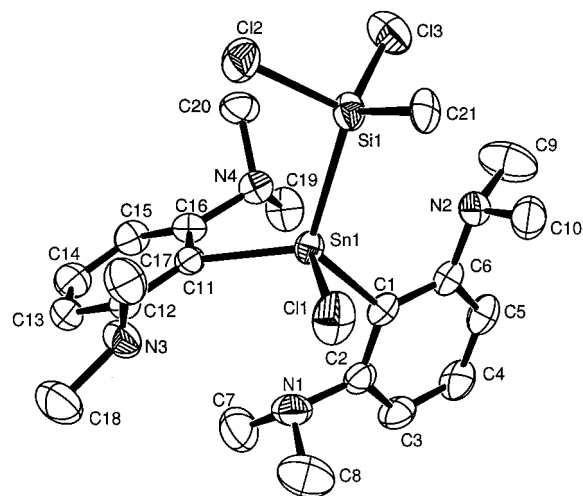**Figure 1.** Molecular structure of Ge(Ar)₂Cl(SiCl₃) (**3**) showing the atom-labeling scheme, with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure 2. Molecular structure of $Sn(Ar)_2Cl(SiCl_2Me)$ **(5)** showing the atom-labeling scheme, with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Ge(Ar)_2Cl(SiCl_3)$ (3)

Ge–C1	1.936(4)	Si–Cl2	2.046(2)
Ge–C11	1.962(4)	Si–Cl3	2.039(2)
Ge–Cl1	2.181(1)	Si–Cl4	2.061(2)
Ge–Si	2.379(2)	Ge⋯N3	2.88(1)
C1–Ge–C11	111.3(2)	Cl1–Ge–Si	96.26(6)
C1–Ge–Cl1	107.95(13)	Cl2–Si–Ge	114.14(8)
C11–Ge–Cl1	114.22(13)	Cl3–Si–Ge	123.37(9)
C1–Ge–Si	115.15(13)	Cl4–Si–Ge	104.45(7)
C11–Ge–Si	111.18(13)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Sn(Ar)_2Cl(SiCl_2Me)$ (5)

Sn1–C1	2.125(4)	Si1–Cl2	2.0806(16)
Sn1–C11	2.145(4)	Si1–Cl3	2.04(2)
Sn1–Cl1	2.4442(15)	Si1–C21	1.901(4)
Sn1–Si1	2.5939(14)	Sn1⋯N4	2.624(4)
C1–Sn1–C11	114.14(15)	Cl1–Sn1–Si1	90.41(5)
C1–Sn1–Cl1	99.54(12)	C21–Si1–Sn1	115.90(14)
C11–Sn1–Cl1	108.25(12)	Cl3–Si1–Sn1	117.96(7)
C1–Sn1–Si1	122.29(12)	Cl2–Si1–Sn1	105.01(6)
C11–Sn1–Si1	116.00(10)		

contact, the C(*ortho*)–C(*ipso*)–Ge angles in **3** [C16–C11–Ge, 127.6(3)°; C12–C11–Ge, 112.9(3)°] deviate significantly from the sp^2 value for one of the Ar$^-$ ligands, unlike the situation for the other [C2–C1–Ge, 121.5(3)°; C6–C1–Ge, 118.5(3)°]. The Ge–Si bond length of 2.379(2) Å is unexceptional [cf. 2.384(1) Å in $Ge(Ph)_3SiMe_3$[13] and 2.326(6)–2.445(1) Å in $Ge(C_6H_4-NMe_2-2)_3(SiX_2X')$ (X = H, X' = Me; or X = Me, X' = Bu^t) in which no close GeLN contact was noted[14]].

The structure of crystalline $Sn(Ar)_2Cl(SiCl_2Me)$ **(5)** is shown in Figure 2, with selected geometric parameters in Table 3. One of the two aryl ligands is bonded in a *C,N*-chelate fashion to the tin atom, which lies at the center of a distorted trigonal bipyramid with the Cl1 and N4 atoms occupying the apical sites [Cl1–Sn–N4, 167.4(2)°]. The Sn⋯N4 distance of 2.624(4) Å is appropriate for a dative interaction [cf. the similar Sn⋯N distances in SnAr$_2$ (vide supra)[1] and the 2.435(5) and

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2.718(6) Å for the Sn⋯NMe$_2$ distances in each of the two Ar$^-$ ligands of $Sn(Ar)_2(NCS)_2$[9]] and is much shorter than any of the Sn⋯N(1,2,3) contacts, which range from 3.111(5) Å for N1 to 3.662(5) Å for N3. As a consequence of the short Sn⋯N4 distance, the C11–Sn bond is strongly tilted toward N4, as evident from the C16–C11–Sn and C12–C11–Sn angles of 103.3(3)° and 135.7(3)°, respectively. The Sn–Si distance of 2.594(2) Å is unexceptional [cf. 2.597(3) and 2.604(3) Å in $SnCl_2$-$[Si(SiMe_3)_3]_2$,[15] 2.609(14) and 2.611(14) Å in [Sn-$(SiMe_3)_3]_2$,[16] and 2.630(4) and 2.642(4) Å in $SnCl[Si(Cl)-\{(NBu^t)_2C_2H_2-1,2\}]_3$.[17]

The ^{1}H and ^{13}C$\{^1$H$\}$ NMR spectra in C$_6$D$_6$ at 298 K for each of **4** and **5** showed one sharp singlet NMe$_2$ signal, indicating either that the Sn⋯N dative contacts are absent or there is rapid 2-Me$_2$N→Sn to 6-Me$_2$N→Sn exchange. By contrast, the silylgermane **3** displayed a broad NMe$_2$ signal in both the corresponding ^{1}H and ^{13}C$\{^1$H$\}$ NMR spectra, possibly due to some C–NMe$_2$ restricted rotation. The ^{119}Sn$\{^1$H$\}$ chemical shifts in **4** (δ −212) and **5** (δ −208) were closely similar and for the latter coupling was reasonably resolved, $^1J(^{119}$Sn-^{29}Si) = 1667 Hz. These $\delta[^{119}$Sn] data may be compared with those for SnAr$_2$ (δ = 442)[1] and SnAr$_2$(NCS)$_2$ (δ = −341).[9] The ^{29}Si$\{^1$H$\}$ signal for the germane **3** was at δ −1.8, whereas for the isoleptic stannane **4** it appeared at higher frequency, δ 16.6, and for the stannane **5** the signal at δ 37 showed well-resolved tin satellites, $^1J(^{29}$-Si$-^{117/119}$Sn) = 1409/1479 Hz.

There was no reaction between SnAr$_2$ and dimethyl-dichloro- or trimethylchlorosilane, even when used in excess. As far as oxidative chlorosilylation is concerned, not only the choice of chlorosilane but also the nature of the ligand X$^-$ in MX$_2$ was crucial. Thus, under conditions similar to those used for the synthesis of **3**–**5**, the bis(amido)stannylene Sn[N(SiMe$_3$)$_2$]$_2$ did not react with SiCl$_4$ and the bis(alkyl)stannylene Sn[CH(SiMe$_3$)$_2$]$_2$ yielded SnCl$_2$ and a waxy and as yet unidentified material. Treatment of the diarylplumbylene PbAr$_2$ with SiCl$_4$ gave lead powder in quantitative yield. It is clear that while the reactions of Scheme 1 demonstrate inter alia a new method of Ge–Si or Sn–Si bond formation, they are unlikely to supersede established routes to such compounds, namely, interactions of lithium germanates or stannates with halosilanes,[14] Wurtz-type cross-coupling of MClX$_3$ (M = Ge or Sn) and SiClX'$_3$,[18] or dehydrochlorination of MClX$_3$ with SiCl$_3$H in the presence of triethylamine.[19]

The decomposition of $Sn(Ar)_2Cl(SiCl_3)$ **(4)** yielding not only β-tin but also $Sn(Ar)_2Cl_2$ **(6)** may indicate that the first step in the reaction sequence was a 1,2-shift of chloride from silicon to tin, affording transiently dichlorosilylene. A parallel would be the generation of dichlorosilylene from Si$_2$Cl$_6$.[20]

It is proposed that the first step in the oxidative chlorosilylation of the bivalent group 14 diarylmetal

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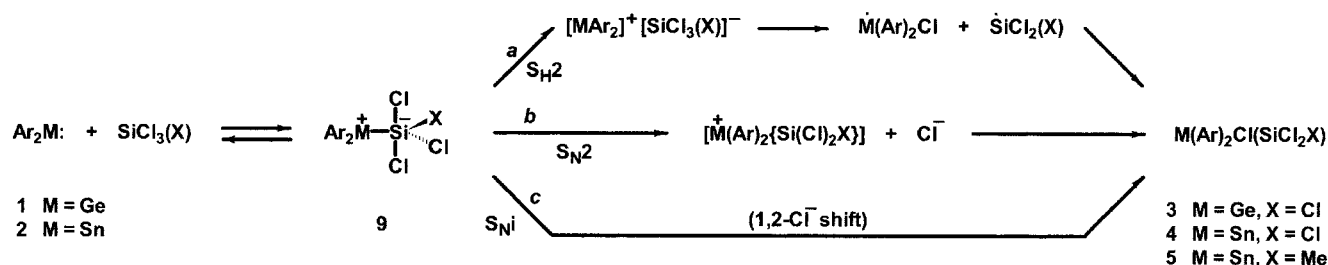(17) Denk, M. K.; Hatano, K.; Lough, A. J. *Eur. J. Inorg. Chem.* **1998**, 1067.
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Scheme 4. Alternative Reaction Pathways *a*, *b*, and *c* for Chlorosilylation of MAr₂ (X = Cl or Me)

compounds MAr$_2$ leading to the tetravalent M(Ar)$_2$Cl-(SiCl$_2$X) is the formation of the five-coordinate 1:1 adducts **9**, probably of trigonal bipyramidal structure, with the most electronegative chloride ligands occupying the apical sites, Scheme 4. Thus MAr$_2$ is taken to function as a base, of relative base strengths GeAr$_2$ > SnAr$_2$, consistent with the premise that the Ge−Si bond is stronger than the Sn−Si; it is also noted that whereas GeAr$_2$(BH$_3$) is stable both in solution and the solid, the Sn analogue in solution slowly decomposed, yielding a precipitate of tin.[5] As for the chlorosilanes, their Lewis acidity is at a premium the greater the number of Si−Cl bonds; that is, Lewis acidity decreases in the sequence SiCl$_4$ > SiCl$_3$Me > SiCl$_2$Me$_2$ > SiClMe$_3$. These considerations are consistent with the experimental observations that (i) the diaryl(chloro)trichlorosilylgermanium compound **3** is more robust than the isoleptic tin compound **4**, (ii) **4** is more readily formed than its methyldi(chloro)silyl analogue **5**, and (iii) SnAr$_2$ but not Sn[E(SiMe$_3$)$_2$]$_2$ (E = CH or N) is susceptible to oxidative chlorosilylation. As for (iii), we note that whereas each MAr$_2$ (**1** or **2**) formed a 1:1 adduct with BH$_3$ (Table 1), Sn[CH(SiMe$_3$)$_2$]$_2$ did not react with BH$_3$(thf) and hence is presumed to be a weaker base than SnAr$_2$ (**2**), while Sn[N(SiMe$_3$)$_2$]$_2$ was reduced by the borane, yielding metallic tin.[5]

As for the conversion of **9** to the final product **3**−**5**, three possible pathways *a*, *b*, and *c* are worthy of consideration. Route *a*, the homolytic (S$_H$2) path is similar to that established for the oxidative addition of a halogenoalkane RHal to the stannylene Sn[CH-(SiMe$_3$)$_2$]$_2$ yielding Sn[CH(SiMe$_3$)$_2$]$_2$(Hal)R;[21] this is also often the pathway for oxidative addition of RHal to certain Pt(0) substrates yielding alkylplatinum(II) halides.[22,23a] Route *b*, of S$_N$2 type, is observed in many other transition metal(*n*) → transition metal(*n* + 2) oxidative additions of RHal.[23b] However, in these cited comparative systems, RHal is unlikely to be an adequately strong Lewis base to yield an intermediate 1:1 adduct. For this reason, we suggest that the preferred route from **9** to the appropriate oxidative adduct **3**−**5** is likely to be *c* (S$_N$*i*), since five-coordination for silicon is well established and the compounds MAr$_2$ are known to be effective Lewis bases [(cf. MAr$_2$(SnX$_2$)[6] and MAr$_2$-(BH$_3$),[5] Table 1], and an intramolecular 1,2-shift of an apical chloride ligand from silicon to germanium or tin

from the appropriate adduct **9** yielding **3**−**5** appears to be energetically facile.

Conclusions

The unprecedented oxidative chlorosilylations of the divalent germanium (**1**) and tin (**2**) compounds MAr$_2$ using SiCl$_4$ or SiCl$_3$Me to yield the appropriate diaryl-(silyl)metal(IV) chlorides **3**−**5** provide a new route to compounds containing Ge−Si or Sn−Si bonds. It remains to be established whether (i) the procedure is general for bulky diarylmetal(II) substrates or whether the *o,o'*-NMe$_2$ groups have a significant stabilizing role, and (ii) these reactions can be extended to Lewis acids other than chlorosilanes, including halides or triflates of group 13 and 14 elements.

The molecular structures of the crystalline compounds Ge(Ar)$_2$Cl(SiCl$_3$) (**3**) and Sn(Ar)$_2$Cl(SiCl$_2$Me) (**5**) show that the group 14 metal is in a distorted tetrahedral (**3**) and trigonal bipyramidal (**5**) environment (only the latter having a very short M···N contact). Whereas the germane **3** was thermally stable below 70 °C, the isoleptic stannane **4** was less so and products of decomposition included β-tin and Sn(Ar)$_2$Cl$_2$ (**6**). The ^{119}Sn-{^{1}H} NMR spectral chemical shifts in C$_6$D$_6$ of compounds **4** and **5** were closely similar ($\delta = -210 \pm 2$ ppm), indicating that they are structurally similar, although it is likely that both showed a rapid 2-Me$_2$N→Sn to 6-Me$_2$N→Sn exchange for one of the two aryl ligands. Compound **5** in C$_6$D$_6$ solution was in equilibrium with its precursors SnAr$_2$ (**2**) and SiCl$_3$Me, as evident from the formation of the chloroalkylation adduct Sn(Ar)$_2$Cl-(CDCl$_2$) (**8**) in CDCl$_3$.

Experimental Section

General Considerations. All reactions were carried out under argon (99.994% purity) with usual Schlenk equipment and techniques. Solvents were predried over sodium wire and purified by distillation over sodium−potassium alloy (toluene) and sodium−benzophenone (diethyl ether) and stored over molecular sieves (4 Å). Deuterated solvents were stored over a potassium mirror and degassed prior to use. The starting materials GeAr$_2$ (**1**) and SnAr$_2$ (**2**) [Ar$^-$ = C̄$_6$H$_3$(NMe$_2$)$_2$-2,6] were obtained according to the published procedure[1] and purified by recrystallization from *n*-hexane. Tetrachlorosilane and methyltrichlorosilane were commercially available and used after redistillation. The NMR solution spectra were recorded on Bruker AC250 (for ^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn for compounds **3**−**7**), AMX 500 (^{29}Si for **2**), or Avance 400 (for **8**) instruments and referenced internally (^{1}H, ^{13}C) or externally (SiMe$_4$ for ^{29}Si or SnMe$_4$ for ^{119}Sn). Unless otherwise stated, all NMR spectra were examined at 293 K in C$_6$D$_6$ and, except for ^{1}H, were proton-decoupled. Electron impact mass spectra were taken on a Kratos MS 80 RF instrument. Elemental

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analyses (calculated data are for empirical formulas) were carried out by Medac Ltd, U.K. Melting points are uncorrected.

Synthesis of Ge(Ar)₂Cl(SiCl₃) (3). $SiCl_4$ (0.51 g, 0.34 mL, 2.98 mmol) was added slowly to a solution of **1** (1.19 g, 2.98 mmol) in Et_2O (20 mL). The colorless solution was set aside. After 12 h at ambient temperature, colorless crystals of **3** were formed, and to complete crystallization, the solution was subsequently kept at −30 °C for a further 12 h to afford colorless crystals of **3** (1.33 g, 78%); mp ca. 89 °C (dec). Anal. Calcd for $C_{20}H_{30}Cl_4GeN_4Si$: C, 42.2; H, 5.31; N, 9.85. Found: C, 42.3; H, 5.53; N, 9.89. NMR (C_6D_6, 293 K): ^1H, δ 2.40 (s, br, 24H, NMe_2), 6.66 (d, 4H, H-3/5, $^3J(^1H-^1H)$ = 7.9 Hz), 7.03 (t, 2H, H-4, $^3J(^1H-^1H)$ = 7.9 Hz]; $^{13}C\{^1H\}$, δ 47.1 (br, NC_2), 117.2, 132.6, 135.8, and 161.2 (C_{aryl}); $^{29}Si\{^1H\}$, δ −1.85. MS: m/z (%, assignment): 532 (3, $[M - H - Cl]^+$), 435 (20, $[M - SiCl_3]^+$), 400 (35, $M - SiCl_3 - Cl]^+$), 237 (85, $[M - SiCl_3 - Cl - Ar]^+$).

Synthesis of Sn(Ar)₂Cl(SiCl₃) (4). A slight excess of $SiCl_4$ (0.42 g, 0.28 mL, 2.47 mmol) was added slowly to a solution of **2** (1.04 g, 2.34 mmol) in Et_2O (35 mL) at ca. 25 °C. The colorless solution was stirred overnight, whereupon a colorless microcrystalline precipitate of **4** was formed. To complete the crystallization, the mixture was kept at −30 °C for 12 h to yield compound **4** (1.32 g, 92%); mp ca. 75 °C (dec). Anal. Calcd for $C_{20}H_{30}Cl_4N_4SiSn$: C, 39.1; H, 4.92; N, 9.10. Found: C, 39.5; H, 5.52; N, 9.11. NMR (C_6D_6, 293 K): ^1H, δ 2.44 (s, 24H, NMe_2), 6.61 (d, 4H, H-3/5, $^3J(^1H-^1H)$ = 7.8 Hz), 7.04 [t, 2H, H-4, $^3J(^1H-^1H)$ = 7.8 Hz]; $^{13}C\{^1H\}$, δ 47.8 (NC_2), 116.5, 133.6, 138.3, and 160.8 (C_{aryl}); $^{29}Si\{^1H\}$, δ 16.6 [$SiCl_3$, $^1J(^{29}Si-^{117/119}Sn)$ = 1511/1584 Hz]; $^{119}Sn\{^1H\}$, δ −212 [$^1J(^{119}Sn-^{13}C)$ = 758 Hz]. MS m/z (%, assignment): 480 (5, $[M - SiCl_3]^+$), 446 (8, $[M - SiCl_3 - Cl]^+$), 318 (15, $[M - SiCl_3 - Ar]^+$), 283 (33, $[M - SiCl_3 - Cl - Ar]^+$).

Synthesis of Sn(Ar)₂Cl(SiCl₂Me) (5). An excess of Me-$SiCl_3$ (0.63 g, 0.5 mL, 4.25 mmol) was added to a solution of **2** (1.10 g, 2.47 mmol) in Et_2O (40 mL) at ambient temperature without stirring. The resulting pale yellow solution was set aside for 15 h at room temperature and subsequently placed in a freezer at −30 °C for 24 h, whereupon colorless crystals of **5** (1.09 g, 74%) were formed; mp > 70 °C (dec). Anal. Calcd for $C_{21}H_{33}Cl_3N_4SiSn$: C, 42.4; H, 5.59; N, 9.42. Found: C, 42.6; H, 5.70; N, 9.49. NMR (C_6D_6, 293 K): ^1H, δ 2.48 (s, 24H, NMe_2), 6.64 (d, 4H, H-3/5, $^3J(^1H-^1H)$ = 8.0 Hz), 7.07 [t, 2H, H-4, $^3J(^1H-^1H)$ = 8.0 Hz]; $^{13}C\{^1H\}$, δ 12.2 (CH₃, $[^2J(^{13}C-^{117/119}Sn)$ = 109 Hz], 47.7 (NC_2), 116.2, 128.6, 141.0, and 161,0 (C_{aryl}); $^{29}Si\{^1H\}$, δ 37.0 [$SiCl_3$, $^1J(^{29}Si-^{117/119}Sn)$ = 1409/1479 Hz]; $^{119}Sn\{^1H\}$, δ −208 [$^1J(^{119}Sn-^{29}Si)$ = 1467 Hz, $^1J(^{119}Sn-^{13}C)$ = 710 Hz]. MS m/z (%, assignment): 516 (0.5, $[M - SiCl_2]^+$), 480 (4, $[M - SiCl_3]^+$), 446 (17, $[M - SiCl_3 - Cl]^+$), 318 (28, $[M - SiCl_3 - Ar]^+$), 283 (76, $[M - SiCl_3 - Cl - Ar]^+$).

Synthesis of Sn(Ar)₂Cl₂ (6). A solution of $Sn(Ar)_2Cl(SiCl_3)$ **(4)** (1.2 g, 1.96 mmol) in toluene (20 mL) was heated above 100 °C for 4 h. After filtration of the reaction mixture, the obtained solution was evaporated to dryness. The colorless residue was finally recrystallized from Et_2O/hexane (3:1) to afford compound **6** (0.37 g, 37%); mp 155 °C. Anal. Calcd for $C_{20}H_{30}Cl_2N_4Sn$: C, 46.6; H, 5.86; N, 10.85. Found: C, 46.6; H, 5.95; N, 10.83. NMR (C_6D_6, 293 K): ^1H, δ 2.49 (s, 24H, NMe_2), 6.64 [d, 4H, H-3/5, $^3J(^1H-^1H)$ = 7.9 Hz], 7.04 [t, 2H, H-4, $^3J(^1H-^1H)$ = 7.9 Hz]; $^{119}Sn\{^1H\}$, δ −245. MS m/z (%, assignment): 515 (0.5, $[M]^+$), 480 (26, $[M - Cl]^+$), 444 (4, $[M - Cl - Cl]^+$), 325 (43, $[Ar_2]^+$), 281 (5, $[M - Cl - Cl - Ar]^+$).

Synthesis of SiArCl₃ (7). Addition of $SiCl_4$ (2.36 g, 14.1 mmol) to a solution of $[Li(\mu-Ar)]_3^2$ (2.3 g, 13.53 mmol) in diethyl ether (60 mL) at room temperature and subsequent refluxing for 1 h afforded **8** as a colorless crystalline material (3.55 g, 88%), after filtration through a glass filter to remove LiCl, removal of the solvent in vacuo, and recrystallization from hexane; mp 165−169 °C. Anal. Calcd for $C_{10}H_{15}Cl_3N_2Si$: C, 40.4; H, 5.08; N, 9.41. Found: C, 40.4; H, 5.16; N, 9.44. NMR (C_6D_6, 293 K): ^1H, δ 2.49 (s, 24H, NMe_2), 6.64 [d, 4H, H-3/5,

Table 4. Molecular Parameters for Compounds 3 and 5

	$C_{20}H_{30}Cl_4GeN_4Si$ **(3)**	$C_{21}H_{33}Cl_3N_4SiSn$ **(5)**
M_r	568.96	594.653
T(K)	293(2)	217(2)
cryst size (mm)	0.25 × 0.25 × 0.20	0.70 × 0.40 × 0.40
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	Cc
a (Å)	9.440(4)	1.4350(3)
b (Å)	10.821(4)	1.3078(3)
c (Å)	14.241(4)	1.4838(3)
α (deg)	72.84(3)	90
β (deg)	84.85(3)	103.12(3)
γ (deg)	68.43(3)	90
V (Å³)	1292.3(8)	2711.9(9)
Z	2	4
D_{calc} (g cm⁻³)	1.46	1.456
abs. coeff (mm⁻¹)	1.66	1.297
θ_{max} for data colln (deg)	24.97	28.57
no. of ind reflns	4528	4057 (R_{int} = 0.0475)
no. of reflns with $I > 2\sigma I$	3224	3990
no. of data/ restraints/ params	4528/0/271	4057/2/280
R1 ($I > 2\sigma I$)	0.045	0.0327
wR2 (all data)	0.095	0.0854
goodness-of-fit	1.023	1.064
largest diff peak and hole (e Å⁻³)	0.33 and −0.31	0.923 and −0.954

$^3J(^1H-^1H)$ = 7.9 Hz], 7.04 [t, 2H, H-4, $^3J(^1H-^1H)$ = 7.9 Hz]; $^{13}C\{^1H\}$, δ 46.2 (NC_2), 113.7, 120.2, 135.1, and 161.8 (C_{aryl}); $^{29}Si\{^1H\}$, δ −25.0. MS m/z (%, assignment): 298 (43, $[M]^+$), 261 (30, $[M - Cl]^+$), 245 (12, $[M - Cl - Cl]^+$).

SnAr₂(Cl)CDCl₂ (8). A slight excess of $CDCl_3$ (0.1 g, 0.85 mmol) was added to a yellow solution of **2** (0.31 g, 0.67 mmol) in Et_2O (20 mL) at ca. 25 °C. The resulting colorless solution was stirred for a further 2 h and the solvent removed in vacuo. The residual crystalline colorless precipitate was treated with a small quantitiy of hexane and kept at −30 °C for 12 h to yield compound **8** (0.36 g, 96%); mp > ca. 105 °C (dec), C_{21}-DH₃₀Cl₃N₄Sn. NMR (C_6D_6, 300 K): ^1H, δ 2.44 (s, 24H, NMe_2), 6.63 [d, 4H, H-3/5, $^3J(^1H-^1H)$ = 8.0 Hz], 7.01 [t, 2H, H-4, $^3J(^1H-^1H)$ = 8.0 Hz]; $^{13}C\{^1H\}$, δ 47.3 (NC_2), 116.8, 132.3, 141.6 [$^1J(^{13}C-^{117/119}Sn)$ = 769/804 Hz] and 160.5 (C_{aryl}); $^{119}Sn\{^1H\}$, δ −185. MS m/z (%, assignment): 563 (20, $[M]^+$) 481 (53, $[M - CDCl_2]^+$), 444 (8, $[M - CDCl_2 - Cl]^+$), 325 (25, $[M - 2Ar]^+$), 163 (70, $[Ar]^+$).

X-ray Structure Determinations of Compounds 3 and 5. Unique data sets were collected with an Enraf-Nonius CAD4 **(3)** diffractometer or a Bruker AXS CCD area detector **(5)** using a crystal in a sealed capillary at 293(2) K **(3)** or a crystal coated with a perfluorinated ether at 217(2) K **(5)**. Refinement was on F^2 for all reflections using SHELXL-93 for **3**[24] or SHELXL-97[25] for **5**. All non-H atoms were anisotropic, and the hydrogen atoms were included in the riding mode. Parameters are listed in Table 4.

Supporting Information Available: Tables giving X-ray crystallographic data for compounds **3** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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