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Reactivity of Silyl-Substituted Allyl Compounds with Group 4, 5, 9, and 10 Metals: Routes to η^3-Allyls, Alkylidenes, and *sec*-Alkyl Carbocations

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Whereas the reaction of alkali-metal salts of silyl−allyls $E^+[C_3H_3(SiMe_3)_2\text{-}1,3]^-$ (E = Li, K) with group 4 and group 5 metal halides gave intractable reduction products, $Co(acac)_3$ and $Ni(acac)_2$ reacted with $K[C_3H_3(SiMe_3)_2\text{-}1,3]$ to give $Co\{\eta^3\text{-}C_3H_3(SiMe_3)_2\text{-}1,3\}_2$ (**1**) and $Ni\{\eta^3\text{-}C_3H_3(SiMe_3)_2\text{-}1,3\}_2$ (**2**), respectively. The reaction of $K[C_3H_3(SiMe_3)_2\text{-}1,3]$ with Me_3SnCl afforded $Me_3SiCH{=}CHCH(SiMe_3)(SnMe_3)$ (**3**), which reacted cleanly with $TaCl_5$ to give $\{\eta^3\text{-}C_3H_3(SiMe_3)_2\text{-}1,3\}TaCl_4$ (**4**). Treatment of this complex with tetramethylethylenediamine led to HCl abstraction, and the allyl complex was transformed into the vinyl−alkylidene compound $Me_3SiCH{=}CHC(SiMe_3){=}TaCl_3(TMEDA)$ (**5**). Whereas in the case of $TaCl_5$ dehalostannylation was facile, the reaction of **3** with $ZrCl_4$ and $HfCl_4$ took a different course, leading instead to the addition of Me_3Sn^+ to **3** to give $[HC\{CH(SiMe_3)(SnMe_3)\}_2]^+[M_2Cl_9]^-$ (**6**, M = Zr; **7**, M = Hf), the first examples of isolable *sec*-alkyl carbocations. These salts are surprisingly thermally stable and melt >100 °C; this stability is largely due to delocalization of the positive charge over the two tin atoms. The crystal structures of **1**, **2**, and **5**−**7** are reported.

Introduction

Although metal allyl complexes have long been recognized as an important and versatile class of compounds, many homoleptic compounds of the parent C_3H_5 ligand either are thermally very unstable, such as $(C_3H_5)_nM$ (M = Co, V, Ni), or are not known (M = Fe, Mn).[1] In contrast, silyl-substituted allyl ligands provide a striking stability increase. A variety of alkali-metal[2] and alkaline-earth-metal[3] silylallyl complexes have been structurally characterized. In late-transition-metal chemistry various σ- and π-monosilylallyl complexes of Mn, Fe, Co, Ni, Mo, Pd, and W were reported, and the stabilizing effect of the silyl group was recognized.[4] This effect was clearly demonstrated by Hanusa's isolation of thermally stable $M\{\eta^3\text{-}C_3H_3(SiMe_3)_2\text{-}1,3\}_2$ complexes (M = Cr, Fe).[5] More recently, related anionic tris(allyl) complexes of manganese(II)[6] and of a series of lanthanide metals of the type $[LnI\{C_3H_3(SiMe_3)_2\}_3]^{-}$ [7] have been reported, as well as tetraallyl actinide[8] complexes. The reaction of potassium silylallyl compounds with group 4 metal halides may proceed with reduction of the metal center; thus, Eisen reported the synthesis of Zr(III) and Ti(III) 1,3-bis(*tert*-butyldimethylsilyl)allyl complexes and their use as propene polymerization catalysts.[9] On the other hand, the reaction of group 4 halides with the *ansa*-bis(allyl) ligand $[Me_2Si(C_3H_3SiMe_3)_2]^{2-}$ gave the Zr(IV) and Hf(IV) complexes $M\{(\eta^3\text{-}C_3H_3SiMe_3)_2SiMe_2\}_2$.[10] We have recently described the synthesis of a number of lanthanide complexes containing the allyl ligands $[1\text{-}C_3H_4SiMe_3]^-$, $[C_3H_3(SiMe_3)_2\text{-}1,3]^-$, and $[R_2Si(C_3H_3SiMe_3)_2]^{2-}$ (R = Me, Ph) and their application as catalysts for the polymerization of butadiene,[11] methyl methacrylate, and ϵ-caprolactone.[12] Here we report the synthesis and structures of complexes of tantalum, cobalt, and nickel, as well as the unexpected reaction of the bulky tin allyl derivative $Me_3SiCH{=}CHCH(SiMe_3)(SnMe_3)$ with group 4 chlorides.

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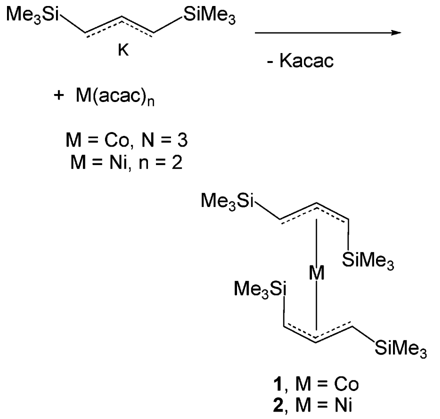
Results and Discussion

The most straightforward method for introducing a silylallyl ligand is the metathesis of metal halides with the potassium and lithium compounds E[$C_3H_3(SiMe_3)_2$-1,3] (E = Li, K). However, the reaction of K[$C_3H_3(SiMe_3)_2$-1,3] with Ti, Zr, Hf, Nb, and Ta chlorides leads to reduction. The products were collected as deeply colored oils which gave broad NMR signals and resisted all attempts at crystallization.

Reduction is also involved in the reaction of $Co(acac)_3$ (acac = acetylacetonate) with K[$C_3H_3(SiMe_3)_2$-1,3], to give the 15-electron Co(II) product Co{η^3-$C_3H_3(SiMe_3)_2$-1,3]}$_2$ (**1**) (eq 1). The compound was obtained in moderate yield as orange crystals after recrystallization from light petroleum and is thermally stable. In contrast, the parent allyl compound Co(η^3-C_3H_5)$_2$ cannot be isolated and disproportionates to give the Co(III) species Co(η^3-C_3H_5)$_3$; even though the latter is an 18-electron complex, it is thermally unstable and decomposes at >−50 °C.[13]



(1)

The analogous nickel complex Ni{η^3-$C_3H_3(SiMe_3)_2$-1,3}$_2$ (**2**) was similarly prepared from K[$C_3H_3(SiMe_3)_2$-1,3] and $Ni(acac)_2$ in THF. A dark red solution was initially obtained which gave a dark oil; this solidified slowly on standing to give **2** as orange crystals. The compound was very soluble in organic solvents, and satisfactory elemental analyses could not be obtained.

The structures of **1** and **2** were confirmed by X-ray diffraction (Figure 1). Selected bond lengths and angles are collected in Table 1. Compound **1** crystallizes in the monoclinic space group *P*2$_1$/*c* with one molecule per asymmetric unit. All hydrogen atoms of the allyl cores were located in the electron difference map and allowed to refine freely. In the C_2-symmetric molecule the allyl ligands are η^3 coordinated, with a variation in the Co−C bond lengths from 2.00 to 2.10 Å. The planes through the allylic C_3 cores are oriented in an almost parallel fashion, with a dihedral angle of 5.34(39)°. The metal occupies the center of a plane defined by the four lateral carbon atoms of the two allyl cores (C1−C3−C4−C6) and deviates from the idealized position by only 0.098(10) Å. The silyl substituents are found in a cis,trans arrangement in both ligands; this is in contrast with the bis(silyl)allyl compounds of calcium and lanthanide metals, where a trans,trans conformation is preferred.[3,7,8,11,12] The structural features of **1** are in good agreement with those of the Cr(II) complex Cr{$C_3H_3(SiMe_3)_2$-1,3}$_2$ reported by Hanusa et al.[5] The main differences between the two structures are the α-CH agostic interactions of the hydrogen atoms H3* and H6* with the cobalt center, at a distance of 2.39 Å. These two hydrogen atoms bend out of the allyl plane by 30°, in contrast to the other four, which form an angle of about 15° tipping in the opposite direction. The small Co(1)−C(3)−H(3*) and Co(1)−C(6)−H(6*) angles of 94.2(11) and 94.6(12)°, respectively, are also a result of these Co···HC interactions.

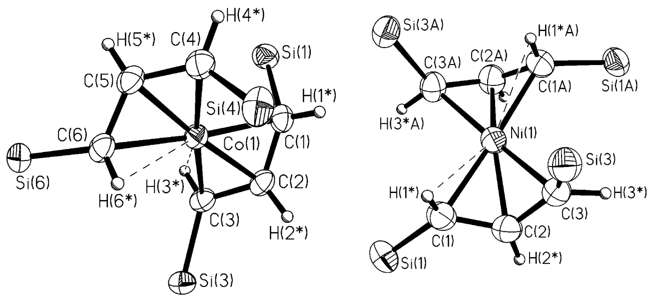


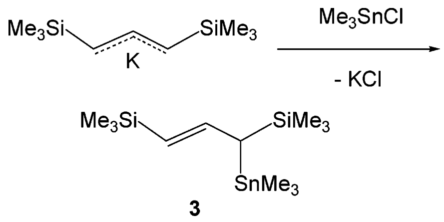
Figure 1. Molecular structures of Co{η^3-$C_3H_3(SiMe_3)_2$-1,3}$_2$ (**1**, left) and Ni{η^3-$C_3H_3(SiMe_3)_2$-1,3}$_2$ (**2**, right), showing the atomic numbering schemes. Thermal ellipsoids are shown at the 50% probability level. Methyl groups are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for M{η^3-$C_3H_3SiMe_3)_2$-1,3}$_2$

	M = Co (**1**)	M = Ni (**2**)
M−C(1)	2.049(2)	2.057(3)
M−C(2)	2.004(2)	1.972(3)
M−C(3)	2.099(2)	2.042(3)
C(1)−C(2)	1.417(3)	1.411(5)
C(2)−C(3)	1.412(3)	1.427(4)
Co−H(3*)	2.387	
Co−H(6*)	2.385	
Ni−H(1*)		2.323
C(1)−C(2)−C(3)	123.8(2)	122.7(3)
H(1*)−C(1)−M	117.8(12)	93(2)
H(3*)−C(3)−M	94.2(11)	118(2)
H(6*)−C(6)−Co	94.6(12)	

Compound **2** is isostructural with Fe{η^3-$C_3H_3(SiMe_3)_2$-1,3}$_2$.[5] Here, too, the silyl substituents adopt a cis,trans orientation. However, as in the cobalt analogue, we observed an α-CH agostic interaction, with a Ni−H(1*) bond length of 2.32 Å. H(1*) is bent out of the C(1)−C(2)−C(3) plane by 27.6°; the Ni(1)−C(1)−H(1*) angle is 93(2)°.

During the search for alternative synthetic routes to allyl complexes, the dehalostannylation reactions of transition-metal halides were investigated, using the trisubstituted propene (Me_3Si)CH=CHCH($SiMe_3$)($SnMe_3$) (**3**). Compound **3** was prepared in a clean reaction from K[$C_3H_3(SiMe_3)_2$-1,3] and Me_3SnCl in high yield (eq 2).



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(2)

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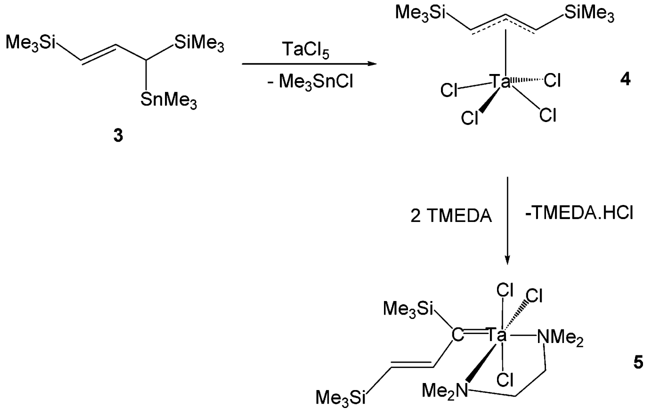
Scheme 1



The tin allyl **3** is an air-stable colorless oil which hydrolyzes slowly on exposure to moisture and can be vacuum-distilled without decomposition. Compound **3** exists exclusively as the isomer with Sn in the 3-position.

The reaction of $TaCl_5$ with **3** afforded the expected dehalostannylation product $\{\eta^3\text{-}C_3H_3(SiMe_3)_2\text{-}1,3\}TaCl_4$ (**4**), which was isolated from light petroleum at −20 °C as red microcrystals (Scheme 1). The reaction proceeded cleanly, and the byproduct Me_3SnCl could be easily removed in vacuo and recycled after distillation. While allyl niobium and tantalum entities carrying also other π-ligands are well-known,[13−15] monoallyl tantalum halides of the general formula $ATaCl_4$ have, to our knowledge, not been reported before. Compound **4** is highly soluble in common organic solvents, is stable at room temperature for days in the pure state, and melts at 72−73 °C. The ^1H NMR spectrum showed the expected coupling pattern for the C_3H_3 allyl core, a doublet at δ 5.30 and a triplet at δ 6.87, and the elemental analysis confirmed the presence of one allyl ligand per metal center.

As we were not able to obtain crystals suitable for X-ray diffraction, we reacted **4** with neutral electron donor molecules. Thus, the addition of tetramethylethylenediamine (TMEDA) afforded the tantalum alkylidene complex $Me_3SiCH{=}CHC(SiMe_3){=}TaCl_3(TMEDA)$ (**5**), evidently the product of dehydrochlorination by the base, accompanied by the formation of TMEDA·HCl. Tantalum alkylidene complexes are of course a well-known class of compounds; however, an allyl-to-alkylidene transformation has to our knowledge not been observed before.[16,17] In vinyl alkylidene complexes Schrock et al. observed an equilibrium with the corresponding metallacyclobutene with loss of a neutral donor ligand in solution.[17e] However, the ^{13}C NMR spectra of **5** were almost unchanged over a temperature range of from 25 to −80 °C; here only the noncyclic form is present. The ^{13}C NMR signal for the α-C atom at δ 265.8 (−80 °C) or δ 268.2 (25 °C) is in good agreement with those for other tantalum alkylidene complexes.

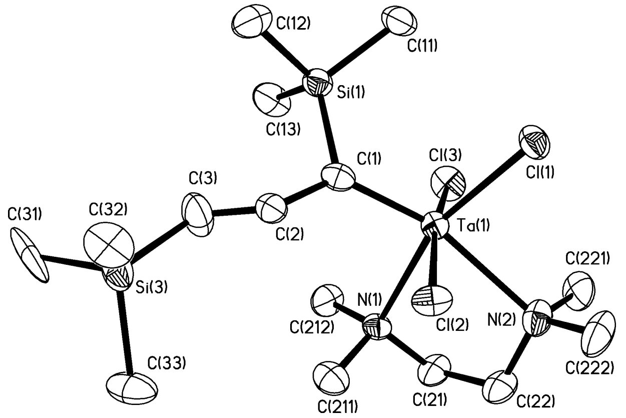


Figure 2. Molecular structure of $Me_3SiCH{=}CHC(SiMe_3){=}TaCl_3(TMEDA)$ (**5**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Me_3SiCH{=}CHC(SiMe_3){=}TaCl_3((TMEDA)$ (5)

Ta(1)−C(1)	1.953(7)	Ta(1)−N(1)	2.374(5)
Ta(1)−N(2)	2.507(6)	Ta(1)−Cl(1)	2.355(2)
Ta(1)−Cl(2)	2.382(2)	Ta(1)−Cl(3)	2.374(2)
C(1)−C(2)	1.488(9)	C(2)−C(3)	1.320(10)
C(1)−Ta(1)−N(2)	164.1(2)	C(1)−Ta(1)−Cl(1)	105.9(2)
C(1)−Ta(1)−Cl(2)	89.3(2)	C(1)−Ta(1)−Cl(3)	100.6(2)
N(1)−Ta(1)−Cl(1)	160.42(13)	Cl(2)−Ta(1)−Cl(3)	167.73(6)

Dark cubic crystals of **5** were obtained from petroleum ether at −20 °C. The structure is shown in Figure 2; selected bond lengths and angles are collected in Table 2. The tantalum center possesses a distorted-octahedral environment with an trans alkylidene−nitrogen arrangement: C(1)−Ta(1)−N(2) = 164.1(2)°. The Ta−C(1) bond length of 1.953(7) Å is in good agreement with literature values.[16,17] The TMEDA ligand is unsymmetrically bonded, with the Ta(1)−N(2) bond trans to the alkylidene ligand being significantly longer (2.507(6) Å) than the Ta(1)−N(1) bond which is trans to Cl (2.375(5) Å). The vinylalkylidene−metallacyclobutene equilibrium referred to above requires the creation of a vacant cis position; here this is inhibited because it would involve the breaking of the stronger tantalum−

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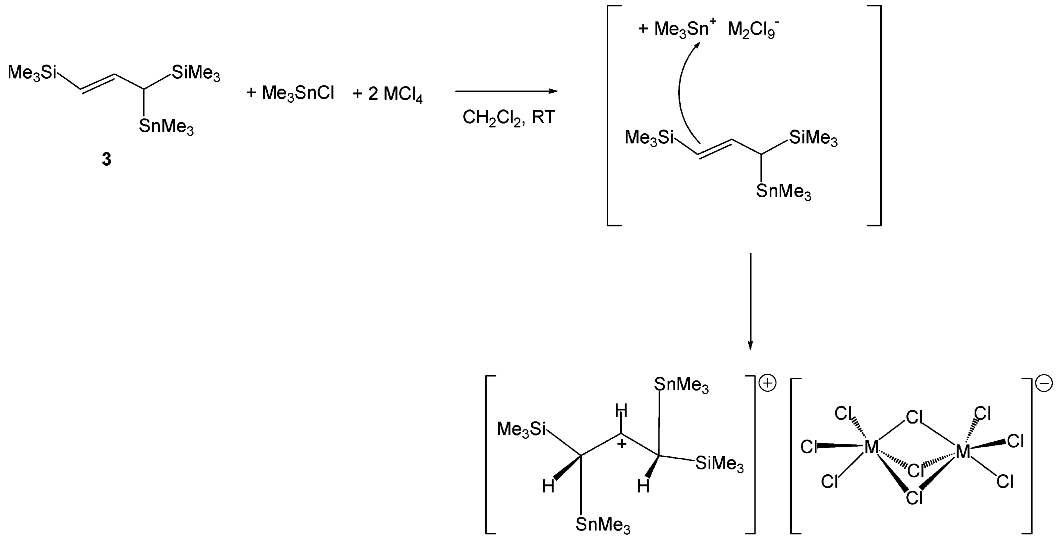
Scheme 2



6, M = Zr
7, M = Hf

nitrogen bond. The C(2)−C(3) bond length of 1.320(10) Å indicates the presence of a nondelocalized double bond and confirms the formation of a vinyl alkylidene structure.

The reaction of **3** with group 4 metal chlorides takes a rather different course. Treatment of **3** with $ZrCl_4$ or $HfCl_4$ in dichloromethane at room temperature over 4−16 h gave a straw-colored solution. When the solution was cooled, pale yellow cubes separated in moderate yield, which were soluble in dichloromethane but insoluble in hydrocarbons. These products were identified crystallographically as the salts of carbocations, $[HC\{CH(SiMe_3)(SnMe_3)\}_2]^+M_2Cl_9^-$ (M = Zr (**6**), Hf (**7**)). Evidently these compounds are formed by attack of Me_3Sn^+ on **3** to give a sterically highly hindered, tin-substituted carbocation, in preference to the expected dehalostannylation and the formation of zirconium and hafnium allyl species (Scheme 2). To our knowledge these are the first examples of isolable and thermally stable *sec*-alkyl carbocations. A preliminary account of this reaction has appeared.[18]

The addition of Me_3Sn^+ implies that some **3** must have undergone dehalostannylation with MCl_4 to generate Me_3SnCl, which in turn reacted with further MCl_4 accompanied by chloride abstraction. While it did not prove possible to identify any organometallic byproducts arising from that reaction, the participation of Me_3SnCl in the reaction sequence was supported by the observed increase in yield once 1 equiv Me_3SnCl had been added to the **3**/MCl_4 mixture.

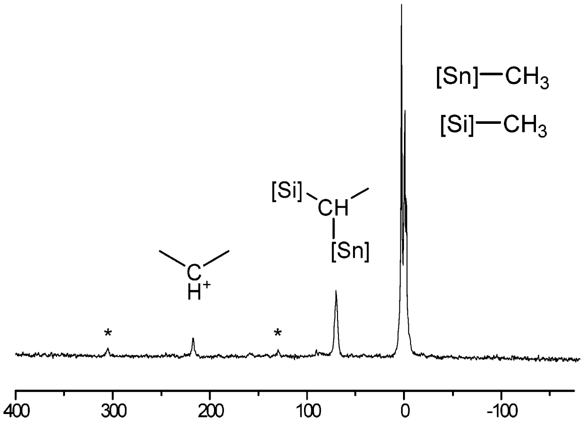


Figure 3. Solid-state ^{13}C MAS NMR spectrum of **6** (75.4 MHz). Spinning sidebands are indicated by an asterisk.

The choice of the correct metal halide is obviously important and is possibly dictated by the stability of the resulting halometalate anion. For example, the attempted reaction of **3** with either $TiCl_4$ or $AlCl_3$ took a different course and led to intractable materials.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **6** and **7** in CD_2Cl_2 indicate complex equilibria in solution, and even measuring solution NMR spectra at low temperature allowed no conclusive identification. However, the solid-state magic-angle spinning ^{13}C NMR spectrum supported the formation of the proposed species and showed a peak at δ 217 for the cationic R_2CH^+ carbon (Figure 3). This chemical shift indicates significant stabilization of the cationic carbon, very similar to that found in CPh_3^+ (δ 210.4).[24] By comparison, the corresponding resonance of the isopropyl cation Me_2CH^+ in SO_2ClF/SbF_5 at low temperature was observed at δ 317.[25] The charge delocalization to the tin substituents is apparent in the solid-state magic-angle spinning ^{119}Sn NMR chemical shift of δ 173.9, significantly deshielded com-

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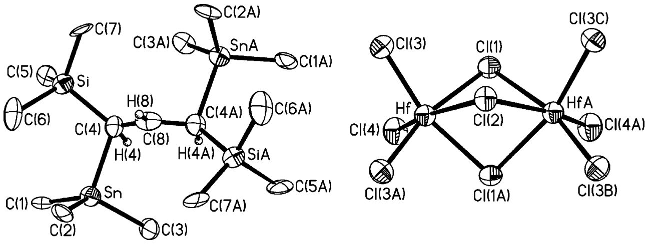


Figure 4. Structure of the ion pair $[HC\{CH(SiMe_3)(SnMe_3)\}_2]^+Hf_2Cl_9^-$ (**7**), showing the atomic numbering scheme. Ellipsoids are drawn at the 50% probability level.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[HC\{CH(SiMe_3)(SnMe_3)\}_2]^+M_2Cl_9^-$ (M = Zr (6), Hf (7))

	6	7
Sn−C(1)	1.96(3)	2.07(4)
Sn−C(2)	2.04(3)	2.14(3)
Sn−C(3)	2.130(9)	2.128(14)
Sn−C(4)	2.213(2)	2.216(3)
C(4)−Si	1.963(6)	1.982(9)
C(4)−C(8)	1.422(8)	1.419(12)
M−Cl(1)	2.5985(14)	2.576(2)
M−Cl(2)	2.632(2)	2.611(2)
M−Cl(3)	2.3545(14)	2.341(2)
M−Cl(4)	2.350(2)	2.335(3)
C(1)−Sn−C(2)	114.5(9)	110.3(13)
C(1)−Sn−C(3)	110.9(6)	110.8(9)
C(1)−Sn−C(4)	105.3(6)	107.2(8)
C(8)−C(4)−Sn	105.6(2)	106.0(3)
C(8)−C(4)−Si	116.3(4)	116.1(6)
Si−C(4)−Sn	112.3(3)	111.4(5)
C(4A)−C(8)−C(4)	128.8(9)	126.2(13)
Cl(1A)−M−Cl(1)	77.23(7)	77.19(11)
Cl(1)−M−Cl(2)	77.12(5)	77.05(6)
Cl(3)−M−Cl(1)	90.24(5)	90.47(8)
Cl(3A)−M−Cl(1)	164.27(5)	164.34(7)
Cl(4)−M−Cl(1)	90.11(6)	90.48(8)
M(A)−Cl(1)−M	88.35(6)	88.45(8)
M(A)−Cl(2)−M	86.94(7)	86.95(10)

pared to $SnMe_4$ (δ 0.00) and even low field from $Bu^n{}_3SnCl$ (δ 144.0). In contrast, the silyl substituents are not involved in this stabilizing interaction, as indicated by the ^{29}Si chemical shift of δ 1.0.

The crystal structure of **7** is shown in Figure 4. Selected bond distances and angles for **6** and **7** are collected in Table 3. Since the CHR^1R^2 moieties in the cation $[HC\{CHR^1R^2\}_2]^+$ are chiral, the ion could in principle exist as two diastereomers with a rac (*R*,*R*/*S*,*S*) or meso (*R*,*S*) configuration. In the solid state only the rac isomer is found, and models show that the meso isomer would have several sterically unfavorable close contacts between the two trimethylstannyl substituents. Unlike previous crystal structures of aliphatic carbocations, **6** and **7** contain no close contacts between cations and anions. There are several C−H⋯Cl contacts at normal van der Waals distances, while the minimum C⋯Cl distance is 3.60 Å.

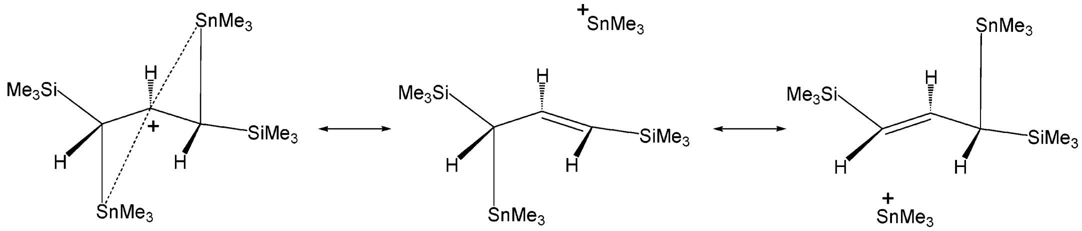
As might be expected in a carbocation, the C−C bonds of the C_3 core are significantly shorter than a normal C−C single bond, 1.422(8) Å. The C−Si bonds are normal. However, the C(4)−Sn bonds of 2.213(2) Å are long compared to the average $Sn-CH_3$ distance of 2.04 Å. These bond length variations are accompanied by characteristic changes in bond angles. There are significant differences between Si and Sn. Whereas the C−C−Si angle of 116.3(4)° is unremarkable, the C−C−Sn angle is much smaller, 105.6(2)°. It is evident, therefore, that the elongation of the C(4)−Sn bond is accompanied by an inclination of the $SnMe_3$ substituents toward the positively charged carbon C(8). Although this inclination is not sufficient to bring C(8) and Sn into a bonding contact (Sn⋯C(8) = 2.935 Å), the structure shows an almost linear $Sn\cdots C^+\cdots Sn$ arrangement (Scheme 3). This allows the empty p orbital on C(8) and the two C−Sn bonds to be aligned parallel to one another. The structural features in these carbocations are a nice illustration of the effect of charge delocalization by hyperconjugation (Scheme 3), in agreement with the observed ^{13}C and ^{119}Sn chemical shifts.

Compounds **6** and **7** are surprisingly thermally stable and melt at 109 and 120 °C, respectively, without decomposition. For comparison, carbocations can also be stabilized by delocalization over aromatic rings,[19] by a heteroatom carrying lone electron pairs (Me_2C^+-E, where E = OR, NR_2, halide)[20] or in superacidic SbF_5-based media by $C^+\cdots F$ interactions.[21] While the delocalization over an aromatic ring or by a heteroatom leads to thermally stable products, there are only a handful of examples of structurally characterized aliphatic carbocations; all are tertiary and are thermally unstable.[22,23]

Conclusion

Trimethylsilyl substituents on allyl ligands significantly increase the thermal stability of the resulting complexes. The successful introduction of this ligand is, however, strongly dependent on the synthetic route, with alkali-metal allyls being prone to reduction. Although the dehalostannylation method was successful for the synthesis of the first example of a tantalum monoallyl complex of the type $LTaCl_4$ from $Me_3SiCH{=}CHCH(SiMe_3)(SnMe_3)$ and $TaCl_5$, the analogous reaction with zirconium and hafnium tetrachloride unexpectedly gave $M_2Cl_9^-$ salts of tin-substituted carbocations, $[HCR_2]^+$ (R = $CH(SiMe_3)(SnMe_3)$). These salts are surprisingly thermally stable due to charge delocalization to Sn; unlike previous examples of structurally characterized alkyl carbocations, there are no close contacts with the counteranion. The effect of stannyl substitution as the stabilizing principle in carbocation chemistry is currently under investigation.

Scheme 3



Experimental Section

All manipulations were performed under nitrogen, using standard Schlenk techniques. Solvents were predried over sodium wire (toluene, light petroleum, THF, diethyl ether) or calcium hydride (dichloromethane) and distilled under nitrogen from sodium (toluene), sodium−potassium alloy (light petroleum, bp 40−60 °C), sodium−benzophenone (THF, diethyl ether), or calcium hydride (dichloromethane). Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze−thaw cycles. NMR spectra were recorded using a Bruker Avance DPX-300 spectrometer. ^{1}H NMR spectra (300.1 MHz) were referenced to the residual solvent proton of the deuterated solvent used. ^{13}C NMR spectra (75.5 MHz) were referenced internally to the D-coupled ^{13}C resonances of the NMR solvent. $Co(acac)_3$, $Ni(acac)_2$, Me_3SnCl, and $TaCl_5$ were used as supplied; $ZrCl_4$ and $HfCl_4$ were sublimed prior to use. Tetramethylethylenediamine (TMEDA) was dried over KOH. $K[C_3H_3(SiMe_3)_2\text{-}1,3]$ was prepared by following a literature procedure.[11]

Preparation of $Co\{\eta^3\text{-}C_3H_3(SiMe_3)_2\text{-}1,3]\}_2$ (1). A solution of $K[C_3H_3(SiMe_3)_2\text{-}1,3]$ (7.02 g, 31.3 mmol) in diethyl ether (50 mL) was added dropwise to suspension of $Co(acac)_3$ (3.36 g, 9.43 mmol) also in diethyl ether (100 mL) at −78 °C. The reaction mixture was warmed slowly to room temperature, during which time the color changed from green to orange, until all the $Co(acac)_3$ had dissolved. The volatiles were removed in vacuo, and the resulting orange powder was extracted with light petroleum (100 mL). The extract was concentrated to ca. 5 mL and stored at −30 °C to give **1** as orange crystals: yield 1.33 g (32.8%). A satisfactory elemental analysis could not be obtained. The identity of the product was confirmed by single-crystal X-ray diffraction.

Preparation of $Ni\{\eta^3\text{-}C_3H_3(SiMe_3)_2\text{-}1,3]\}_2$ (2). A solution of $K[C_3H_3(SiMe_3)_2\text{-}1,3]$ (5.00 g, 22.3 mmol) in THF (40 mL) was added dropwise to a solution of $Ni(acac)_2$ (2.60 g, 10.1 mmol) in THF (60 mL) at −78 °C. The mixture was warmed to room temperature, at which time the solution had become dark red. After a further 16 h, the solvent was evaporated, the residue extracted with light petroleum (100 mL), and the extract filtered. Concentrating the filtrate left an oil which slowly crystallized on standing. The product was obtained as orange crystals, yield 1.78 g (41.2%). Satisfactory analysis could not be obtained. The identity of the product was confirmed by single-crystal X-ray diffraction.

Preparation of $(Me_3Sn)(Me_3Si)CHCH{=}CHSiMe_3$ (3). A suspension of $K[C_3H_3(SiMe_3)_2\text{-}1,3]$ (5.0 g, 22 mmol) in diethyl ether (100 mL) at 0 °C was treated with a solution of Me_3SnCl (4.4 g, 22 mmol) in diethyl ether (30 mL). There was immediate formation of a voluminous KCl precipitate. The reaction mixture was warmed to room temperature and filtered, and the residue was extracted with ether (30 mL). The title compound was obtained as a pale yellow oil; yield 7.5 g (98%). The compound was used without further purification; however, an analytically pure sample was obtained after condensation to a cold trap. Anal. Calcd for $C_{12}H_{30}Si_2Sn$: C, 41.27; H, 8.66. Found: C, 41.67; H, 8.61. ^{1}H NMR ($CDCl_3$, 300 MHz): δ −0.01 (s, 9 H, $SnMe_3$), 0.00 (s, 9 H, $SiMe_3$), 0.07 (s, 9 H, $SiMe_3$), 1.52 (d, $^{3}J_{H-H}$ = 11.5 Hz, H, CH=CHC*H*), 5.23 (d, $^{3}J_{H-H}$ = 18.0 Hz, H, C*H*=CHCH), 5.97 (dd, H, CH=C*H*CH). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ −8.5 (satellites, $SnMe_3$), −0.2 ($SiMe_3$), 28.1 (CH=CH*C*H), 125.5 (*C*H=CHCH), 147.3 (CH=*C*HCH). MS (EI): *m/z* 350 (M^+), 335 ($M^+ - Me$), 165 ($SnMe_3^+$). IR (neat, KBr plates, cm^{-1}): 2955 (vs), 1583 (s), 1259 (s), 1248 (vs), 1051 (s), 1011 (s), 875 (vs), 837 (vs), 766 (s), 724 (s), 689 (s), 526 (s).

Synthesis of $[CH(CHSiMe_3)_2]TaCl_4$ (4). Neat **3** (1.0 g, 2.9 mmol) was added dropwise via syringe to a suspension of $TaCl_5$ (1.3 g, 3.6 mmol) in CH_2Cl_2 (30 mL) at 0 °C. The reaction mixture turned red. After the mixture was warmed to room temperature, all volatile components, including the byproduct Me_3SnCl, were removed in vacuo over 4 h. The residue consisted of a deep red oil. Addition of light petroleum (5 mL) and cooling to −30 °C afforded **4** as an analytically pure microcrystalline red solid: yield 0.71 g (49%), mp 72−73 °C. Another slightly impure batch was collected as a sticky solid after reducing the amount of solvent to 2−3 mL (0.36 g, total yield 74%) and subsequent cooling. Anal. Calcd for $C_9H_{21}Cl_4Si_2Ta$: C, 21.27; H, 4.16. Found: C, 20.78; H, 4.01. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.34 (s, 18 H, $SiMe_3$), 5.30 (d, $^{3}J_{H-H}$ = 15.0 Hz, 2 H, C*H*CHC*H*), 6.89 (t, $^{3}J_{H-H}$ = 15.0 Hz, H, CHC*H*CH). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 0.1 ($SiMe_3$), 134.6 (*C*HCH*C*H), 137.2 (CH*C*HCH). IR (Nujol, KBr plates, cm^{-1}): 1462 (s), 1250 (s), 935 (s), 840 (vs), 786 (s), 765 (s), 748 (s), 732 (s), 654 (s).

Synthesis of $Me_3SiCH{=}CH(SiMe_3)C{=}TaCl_3{\cdot}TMEDA$ (5). The procedure above for the synthesis of compound **4** was followed, and the reaction product was used without workup. The red oil was dissolved in light petroleum (30 mL), and tetramethylethylenediamine (TMEDA, 0.8 g, 6.9 mmol) was added at 0 °C. The solution turned black. Crystallization at −30 °C afforded **5** as dark block-shaped crystals, yield 0.48 g (28%), mp 89 °C. Anal. Calcd for $C_{15}H_{36}Cl_3N_2Si_2Ta$: C, 30.64; H, 6.17; Cl, 18.09. Found: C, 30.47; H, 6.32; Cl, 17.14. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.37, 0.79 (s, 9 H, $SiMe_3$), 1.81−1.83, 2.05−2.07 (m, 2 H, C*H*$_2$ (TMEDA)), 2.38, 2.74 (s, 3 H, C*H*$_3$ (TMEDA)), 4.47 (d, $^{3}J_{H-H}$ = 19.0 Hz, H, CH=C*H*($SiMe_3$)), 10.95 (d, $^{3}J_{H-H}$ = 19.0 Hz, H, C*H*=CH($SiMe_3$)). ^{13}C NMR (CD_2Cl_2, 75.5 MHz, −80 °C): δ 0.4, 4.3 ($SiMe_3$), 45.0, 50.9, 57.0, 61.3 (TMEDA), 121.0 (C_{ipso}), 153.7 (C_β), 265.8 (C_α).

Synthesis of $[CH\{CH(SiMe_3)(SnMe_3)\}_2]^+Zr_2Cl_9^-$ (6). A mixture of Me_3SnCl (0.6 g, 3.0 mmol) and **3** (1.0 g, 2.9 mmol) in CH_2Cl_2 (30 mL) was added to solid $ZrCl_4$ (1.4 g, 6.0 mmol). When the mixture was stirred for 4 h at room temperature, the solid dissolved and the solution turned yellow. After filtration the amount of solvent was reduced to 10 mL. Crystallization at −30 °C afforded the title compound as colorless crystals in 50% yield (1.5 g, 1.5 mmol), mp 109 °C. Solid-state magic angle spinning NMR: ^{13}C, δ −1.0, 3 ($SiMe_3$, $SnMe_3$), 70 (CH), 217 (CH^+); ^{29}Si, δ 1. ^{119}Sn NMR (standard $SnMe_4$): δ 173.9. Anal. Calcd for $C_{15}H_{39}Cl_9Si_2Sn_2Zr_2$: C, 17.76; H, 3.87; Cl, 31.45. Found: C, 17.82; H, 3.74; Cl, 32.15.

Synthesis of $[CH\{CH(SiMe_3)(SnMe_3)\}_2]^+Hf_2Cl_9^-$ (7). By the procedure for **6**, compound **7** was prepared from Me_3SnCl (0.6 g, 3.0 mmol), **3** (1.0 g, 2.9 mmol), and $HfCl_4$ (1.9 g, 6.0 mmol) as colorless crystals in 50% yield (1.7 g, 1.5 mmol), mp 120 °C. The ^{13}C, ^{29}Si, and ^{119}Sn solid-state NMR spectroscopic data were essentially identical with those for **6**. Anal. Calcd for $C_{15}H_{39}Cl_9Hf_2Si_2Sn_2$: C, 15.15; H, 3.31; Cl, 26.83. Found: C, 14.87; H, 3.19; Cl, 27.67.

X-ray Crystallography. Crystals coated in dried perfluoropolyether oil were mounted on glass fibers and fixed in a cold nitrogen stream. Diffraction intensities were measured on a Rigaku R-Axis IIc image-plate diffractometer equipped with a rotating-anode X-ray source, Mo Kα radiation, and graphite monochromators. Crystal and refinement data are collected in Table 4. Data were processed using the DENZO/SCALEPACK programs.[26] The structure was determined by the direct-methods routines in the XS[27] and SHELXS[28] programs and refined by full-matrix least-squares methods, on F^2's, in XL or SHELXL. Non-hydrogen atoms were refined with anisotropic displacement parameters. Scattering factors for neutral atoms were taken from the literature.[29] Computer programs were run on a Silicon Graphics Indy computer at

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Table 4. Crystal Data and Refinement Details

	1	**2**	**5**	**6**	**7**
formula	$C_{18}H_{42}CoSi_4$	$C_{18}H_{42}NiSi_4$	$C_{15}H_{36}Cl_3Si_4Ta$	$C_{15}H_{39}Si_2Sn_2{\cdot}Zr_2Cl_9$	$C_{15}H_{39}Si_2Sn_2{\cdot}Hf_2Cl_9$
fw	429.81	429.59	587.94	1014.5	1189.1
temp, K	140(1)	140(1)	140(1)	140(1)	140(1)
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/c$	$C2/c$	$P2_1/c$	*Cmcm*	*Cmcm*
a, Å	12.323(3)	16.578(3)	18.928(4)	14.899(1)	14.860(1)
b, Å	10.322(3)	12.430(3)	9.059(2)	12.310(1)	12.280(1)
c, Å	21.059(4)	12.698(3)	14.410(3)	19.894(1)	19.901(1)
β, deg	99.59(3)	90.84(3)	100.39(3)	90	90
V, Å^3	2641.2(9)	2616.3(9)	2430.4(8)	3648.7(4)	3631.6(5)
D_{calcd}, g cm^{-3}	1.081	1.091	1.607	1.847	2.175
Z	4	4	4	4	4
μ, mm^{-1}	0.830	0.924	4.952	2.640	7.792
no. of indep/obsd ($I > 2\sigma_I$) rflns	4832/4071	2365/2125	4397/4301	1595/1548	1760/1667
no. of data/restraints/params	4832/0/232	2365/0/117	4397/0/235	1594/0/113	1757/0/113
F(000)	932	936	1168	1960	2216
R_{int}[a]	0.0399	0.0499	0.0353	0.043	0.065
R_1 ($I > 2\sigma(I)$)[b]	0.0332	0.0463	0.0346	0.045	0.058
wR_2 (all data)[c]	0.0961	0.1306	0.1015	0.110	0.145
GOF on F^2	1.059	1.156	1.255	1.257	1.218

[a] $\sum|F_o^2 - F_o^2(\mathrm{mean})|/\sum F_o^2$. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = [2F_c^2 + \max(F_o^2, 0)]/3$.

the University of East Anglia or on a DEC-Alpha Station 200 4/100 computer in the Biological Chemistry Department, John Innes Centre. Crystal data are deposited with the Cambridge Crystallographic Data Centre, under the following CCDC numbers: 253620 (compound **1**), 253621 (**2**), 253623 (**5**), 177524 (**6**) and 177525 (**7**). These can be obtained without charge from www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Crystallographic data for compounds **1**, **2**, and **5**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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