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Isolation and Structure of $[HC\{CH(SiMe_3)(SnMe_3)\}_2]^+$: A Remarkably Stable *sec*-Alkyl Cation

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Carbocations are well-known as reactive intermediates in many organic reactions.[1] The first recognized example of cationic carbon leading to compounds of salt-like character was CPh_3^+ which is stabilized by charge delocalization over the aromatic rings.[2] Other important classes are carbocations bound to heteroatoms carrying lone electron pairs, for example Me_2CER^+ (e.g., ER = OR, NR_2, halide), where C−E π-bonding is significant.[3] In superacidic media at low temperatures carbocations are sufficiently long-lived for spectroscopic detection,[1,4] including the isopropyl cation, $Me_2CH^+SbF_6^-$.[5] The stability of simple alkyl-substituted carbocations declines dramatically in the order tertiary > secondary > primary, as evidenced by the increase in the hydride affinities for Me_3C^+ (230) < Me_2CH^+ (247) < $MeCH_2^+$ (274 kcal mol^{-1}),[6] while the hydride affinities for phenyl-substituted carbocations are much lower.[7] While the solid-state structures of many carbocation salts with phenyl or heteroatom substituents have been determined,[3] the only reports of structurally characterized *aliphatic* cations are of *tert*-carbocations, notably $Me_3C^+Sb_2F_{11}^-$[8] and the adamantyl cation.[9,10] These species are thermally unstable and require synthesis and recrystallization at low temperatures, typically at −20 to −60 °C. In the crystal the cations are stabilized by $C^+\cdots F$ bonding to the counteranions and by CH⋯F hydrogen bonds.

We report here the synthesis and crystal structure of $[HCR_2]^+[M_2Cl_9]^-$ (R = $CH(SiMe_3)(SnMe_3)$, M = Zr or Hf). Not only are these compounds, to the best of our knowledge, the first examples of isolated and structurally characterized *sec*-alkyl carbocations, they are also thermally stable at room temperature and do not require strongly acidic media for their formation or stabilization.

Stirring a mixture of $ZrCl_4$, Me_3SnCl and $Me_3SiCH{=}CHCH(SiMe_3)(SnMe_3)$ (**1**) in a 2:1:1 molar ratio in dichloromethane at room temperature, followed by crystallization at −16 °C, afforded colorless crystals of $[HC\{CH(SiMe_3)(SnMe_3)\}_2]^+Zr_2Cl_9^-$ **2a** in ca. 50% yield (Scheme 1). An analogous compound **2b** was obtained with $HfCl_4$.[11] The product is formed by formal electrophilic attack by a $SnMe_3^+$ cation on the substituted propene **1**.

The crystalline solids are stable at room temperature under nitrogen for days and melt at 109 °C (**2a**) and 120 °C (**2b**). The magic-angle spinning solid ^{13}C NMR of **2a** shows the signal for the R_2CH^+ carbon atom at δ 217.[11] This value is similar to CPh_3^+ (δ 210.4)[12] and indicates significant stabilization of the cationic carbon.

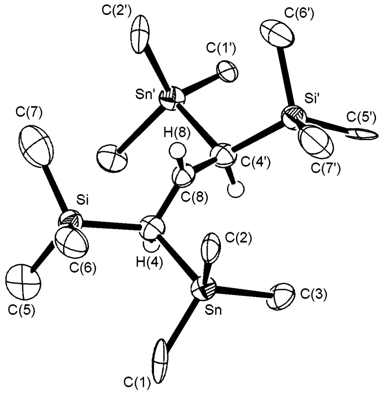
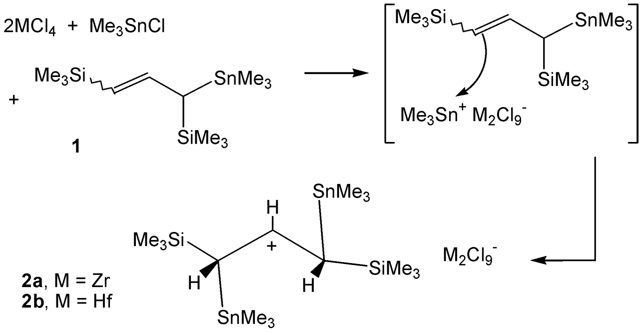


Figure 1. Crystal structure of the $[HC\{CH(SiMe_3)(SnMe_3)\}_2]^+$ cation in **2a**. Selected distances (Å) and angles (deg): Sn−C(4) 2.213(2), Si−C(4) 1.963(6), C(4)−C(8) 1.422(8), Sn−C(1) 1.96(3), Si−C(5) 2.00(3), C(8)−C(4)-Sn 105.6(2), C(8)−C(4)-Si 116.3(4), C(4′)−C(8)−C(4) 128.8(9), Si−C(4)−Sn112.3(3).

Scheme 1. Possible Mechanism for the Formation of **2** from Trisubstituted Propene **1** and Trimethyltin Chloride in the Presence of a Lewis Acidic Transition-Metal Chloride (M = Zr or Hf)



The cation $[HC\{CHR^1R^2\}_2]^+$, with two chiral C atoms, can exist as two diastereomers with (*R*,*R*)/(*S*,*S*) (*rac*-**2**) or (*R*,*S*) configuration (*meso*-**2**). The single-crystal structure determination of **2a** (Figure 1) shows that only the *rac*-isomer is present in the solid-state (as a 1:1 mixture of enantiomers in the centrosymmetric crystals).[13] The hafnium analogue **2b** is isostructural. Assuming similar bonding parameters, a model of *meso*-**2** shows increased steric hindrance due to close approach of the methyl groups of the two $SnMe_3$ substituents, which may disfavor this isomer. Unlike previous crystal structures of aliphatic carbocations, in **2** there are no close contacts between cations and anions (interactions are at normal van der Waals distances with several C−H⋯Cl contacts and a minimum C⋯Cl distance of 3.60 Å).

The C−C bonds of the propyl core (1.422(8) Å) are significantly shorter than a normal C−C single bond. While the C−Si bonds are normal, the C(4)−Sn bonds are longer than expected, 2.213(2) Å, compared to an average $Sn-CH_3$ distance of 2.04 Å. A consideration of the angles between the C_3 core and the heteroatom

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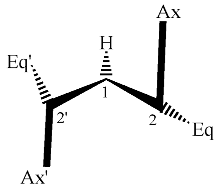
Table 1. Olefin Polymerizations Initiated with $[HC\{CH(SiMe_3)(SnMe_3)\}_2]^+M_2Cl_9^-$ [a]

initiator [10^{-6} mol]	M	monomer [mL]	temp [°C]	time [min]	polymer [yield/g]	M_w [10^3 g mol^{-1}]	M_w/M_n
12	Hf	isobutene (100)	−50	1	2.4	301 000	2.1
30	Hf	isobutene (100);isoprene (5)	−78	15	4.4	182 000[b]	2.1
30	Zr	α-methylstyrene (5)	−40	15	3.0	73 000	3.5

[a] Reactions with isobutene were conducted in 100 mL monomer, other monomers are 50 vol % solutions in dichloromethane. [b] Isoprene incorporation 4.0 mol %, 1,4-cis structure.



***rac*-2**: Ax = Ax' = $SnMe_3$; Eq = Eq' = $SiMe_3$
***meso*-2**: Ax = Eq' = $SnMe_3$; Eq = Ax' = $SiMe_3$
3: Ax, Ax', Eq, Eq' = $SiMe_3$

Figure 2. Geometry of silicon- and tin-substituted carbocations used for DFT calculations. *rac*-**2** and *meso*-**2** represent the two stereoisomers of **2**. Ax and Eq refer to "axially" and "equatorially" placed substituents. In compound **3** all substituents are $SiMe_3$.

substituents show instructive differences between Si and Sn. Whereas the C−C−Si angle is normal, 116.3(4)°, the C−C−Sn angle is much smaller, 105.6(2)°, that is, the two $SnMe_3$ substituents are inclined toward the positively charged carbon. Although this distance is too long to be regarded as bonding (C(8)···Sn 2.935 Å), the geometry shows a polarization with a near-linear Sn····C(8)····Sn arrangement. The observed bonding parameters are in agreement with stabilization by hyperconjugation, $Me_3Sn(R)CH-CH^{(+)}R' \leftrightarrow Me_3Sn^+\ RCH{=}CHR'$.

This assessment of the bonding in **2** was borne out by density functional theory calculations on the isomers *rac*-**2** and *meso*-**2** and on the related all-Si compound **3** (Figure 2). *rac*-**2** is 10 kJ mol^{-1} more stable than *meso*-**2**. Energy is minimized when the C(4)−Sn bonds are aligned with the C(8) pπ orbital. The calculations confirm short C−C distances (1.40−1.41 Å), normal C−Si and long C−Sn (2.28 Å) distances, that is, the shortening of the C−C−C bonds is accompanied by a lengthening (weakening) of the bonds to substituents in axial sites. The Voronoi charges of the atoms show that all the Si and Sn atoms carry partial positive charge, although axial substituents are more positive than equatorial ones. The charge on the central atom C(8) increases in the series *rac*-**2** < *meso*-**2** < **3**, from 0.05 to 0.09, that is, Sn is significantly better in stabilizing the carbocationic center than Si.[11] In agreement with this model, the ^{119}Sn chemical shift in **2** is δ+173.9, significantly deshielded compared to $SnMe_4$ (0.00) and $Bu^n{}_3SnCl$ (δ+144.0), whereas the ^{29}Si value shows no such effect (δ+1.0).

It has long been known that Si or Sn substituents in β-position lead to dramatic rate enhancements in solvolysis reactions. This was explained by hyperconjugative stabilization of the transient carbocation.[14,15] This effect has been used for the formation of C=C double bonds by the facile extrusion of Me_3SiX in the reactions of the type $Me_3SiCH_2CH_2X \rightarrow CH_2{=}CH_2 + Me_3SiX$ (X = nucleofuge)[15] and for the generation of room-temperature persistent vinyl[16] and diphenylmethyl cations in solution.[17]

Compounds **2a** and **2b** polymerize a number of cationically polymerizable monomers. Thus, isobutene homo- and copolymerizations give high-molecular weight products (Table 1).

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Supporting Information Available: Preparative details for **2a** and **2b**, computational details (PDF). Crystallographic data for **2a** and **2b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Crystal data of **2a:** $C_{15}H_{39}Si_2Sn_2{\cdot}Zr_2Cl_9$, fw 1014.5; orthorhombic; *Cmcm* (no. 63), $a = 14.899(1)$ Å, $b = 12.310(1)$ Å, $c = 19.894(1)$ Å $U = 3648.7(4)$ Å^3; $Z = 4$; $D_{calc} = 1.847$ Mg/m^3; $\mu = 2.640$ mm^{-1}; $T = 140(1)$ K; $F(000) = 1960$; $2.1 \le \theta \le 25.4°$; $-16 \le h \le 16$, $-14 \le k \le 14$, $-23 \le l \le 23$; 8285 reflections collected, of which 1595 were unique [$R_{int} = 0.0222$] and 1548 observed [$I > 2\sigma I$)]. Data/restraints/parameters 1594/0/113; goodness of fit = 1.257. Final R indices [$I > 2\ \sigma I$)]: $R_1 = 0.043$, $wR_2 = 0.109$; R indices (all data): $R_1 = 0.045$, $wR_2 = 0.110$. Crystal data of **2b**: $C_{15}H_{39}Si_2Sn_2{\cdot}Hf_2Cl_9$, fw 1189.1; orthorhombic; *Cmcm* (no. 63), $a = 14.860(1)$ Å, $b = 12.280(1)$ Å, $c = 19.901(1)$ Å; $U = 3631.6(5)$ Å^3; $Z = 4$; $D_{calc} = 2.175$ Mg/m^3; $\mu = 7.792$ mm^{-1}; $T = 140(1)$ K; $F(000) = 2216$; $2.1 \le \theta \le 25.4°$; $-17 \le h \le 17$, $-14 \le k \le 14$, $-24 \le l \le 24$; 9920 reflections collected, of which 1760 were unique [$R_{int} = 0.0249$] and 1667 observed [$I > 2\ \sigma I$)]. Data/restraints/parameters 1757/0/113; goodness of fit = 1.218. Final R indices [$I > 2\ \sigma I$)]: $R_1 = 0.058$, $wR_2 = 0.142$; R indices (all data): $R_1 = 0.065$, $wR_2 = 0.145$. Data were collected on a Rigaku R-Axis II image plate diffractometer with a rotating anode X-ray source (λ(Mo Kα) 0.71069 Å) and graphite monochromator. Data were processed using the DENZO/SCALEPACK programs. The cation was modeled as a mixture of two enantiomers with equal occupancy lying disordered about a mirror-plane of symmetry through the C_3 group. Details of the crystal structure determination can be obtained from the Cambridge Crystallographic Data Centre, Cambridge, access no. CCDC 177524-5.

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