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Persistent Dialkyl(silyl)stannylium Ions

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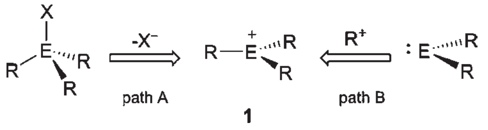
S Supporting Information

ABSTRACT: The synthesis of dialkyl(silyl)stannylium borates **2**[$B(C_6F_5)_4$] by reaction of a stable β-silyl-substituted stannylene **3** with silylarenium borates **4**[$B(C_6F_5)_4$] is reported. The stannylium borates **2**[$B(C_6F_5)_4$] are characterized by NMR spectroscopy and single-crystal X-ray diffraction, supported by the results of quantum mechanical calculations. The accumulated experimental and theoretical data indicate that the stannylium ions **2** are not stabilized by β-silyl hyperconjugation and that intramolecular C−H/Sn^+ interactions are not important.

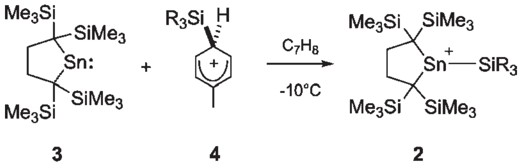
Carbocations are omnipresent intermediates in organic chemistry, and recently their higher homologues R_3E^+ (**1**), in particular silylium ions (E = Si), have gained increasing interest in synthetic organic main-group chemistry and catalysis.[1−5] To successfully exploit the extreme electrophilicity of the R_3E^+ species (E = Si, Ge, Sn, Pb), for example in bond activation processes,[3−5] novel approaches for their synthesis are required. In addition, for any attempt to control the high reactivity of these species, a solid understanding of the bonding situation is mandatory. The conventional approach to organometallic group 14 element cations **1** is E−X bond cleavage from neutral, tetracoordinated compounds (Scheme 1, path A) either by direct bond heterolysis or in some cases by homolytic scission of E−E bonds to give tricoordinated radicals, $R_3E^\bullet$, and their subsequent oxidation to give the corresponding cations, R_3E^+.[6] An alternative preparative approach, which circumvents the severe synthetic problems that arise from the high steric demands made on the substituents for stabilizing the resulting cations **1**, is the addition of a cationic species to heavy carbenes (Scheme 1, path B).[7] Recently, we were able to demonstrate that in the case of silaimidazolium ions, this procedure is superior to the conventional cation synthesis from tetravalent precursors via bond cleavage reactions.[7d] This approach should be particularly fruitful for the synthesis of stannylium ions, R_3Sn^+ (**1**, E = Sn), in which case stable stannylenes are available as starting materials. In addition, we exploited this reaction for the synthesis of a Sn^{2+}/arene complex.[8] Here we report on the synthesis and complete characterization of dialkyl(silyl)stannylium ions **2** by reaction between silylated arenium ion salts **4** and a stable stannylene **3**.

As starting material, dialkyl-substituted stannylene **3**, synthesized previously by Kira, Sakurai, and co-workers, was chosen.[9] Stannylene **3** exists as a monomer both in solution and in the solid state and is therefore perfectly suited for our study. Reaction of stannylene **3** with 1 equiv of the toluenium tetraarylborates **4**[$B(C_6F_5)_4$] in toluene gave brown-beige products, which were identified by NMR spectroscopy as the [$B(C_6F_5)_4$] salts of stannylium ions **2** (Scheme 2).

Scheme 1. Possible Synthetic Pathways to Organometallic Group 14 Cations (E = Si, Ge, Sn, Pb)



Scheme 2. Synthesis of Stannylium Ions 2 (a, R = Et; b, R = *i*Pr)



Although the obtained borates **2**[$B(C_6F_5)_4$] were stable for weeks in the solid state at −18 °C, at room temperature decomposition occurred rapidly, giving several unidentified tin-containing products, as indicated by ^{119}Sn NMR spectroscopy. The identity of stannylium ions **2** is confirmed by NMR spectroscopy. For each cation, only one ^{119}Sn signal is detected in toluene-d_8 solution. The respective resonances are located in a spectral region (δ ^{119}Sn = 1412 (**2a**), 1441 (**2b**))[10] that is approximately halfway between the ^{119}Sn NMR chemical shifts that were found for tris-arylstannylium ions (δ ^{119}Sn (Ar_3Sn^+) = 697−806)[11] and that detected for trisilyl-substituted stannylium ion ($(tBu_2MeSi)_3Sn^+$ **5** (δ ^{119}Sn for **5** = 2653).[12] The established ^{29}Si NMR chemical shifts of the α-silicon atom Si(1) (δ ^{29}Si = 40.0 (**2a**) and 70.3 (**2b**)) agree with data reported for the silyl-substituted stannylium ion **5** (δ ^{29}Si = 64.9).[12] The direct linkage between the silicon and tin atom is indicated by the ^1J(SnSi) coupling constants detected for cations **2** (^1J(SiSn) = 50 (**2a**) and 46 Hz (**2b**)), although these values are low for ^1J(SiSn) coupling constants (i.e., in $(Me_3Sn)_4Si$, ^1J(SnSi) = 220 Hz).[13] The increase in the coordination number during the reaction from stannylene **3** to give the stannylium ions **2** is accompanied by a considerable high-field shift $\Delta\delta^{119}$Sn of the ^{119}Sn resonance ($\Delta\delta$ ^{119}Sn = −911 (**2a**) and −882 (**2b**)). The ^{13}C and ^{1}H NMR data

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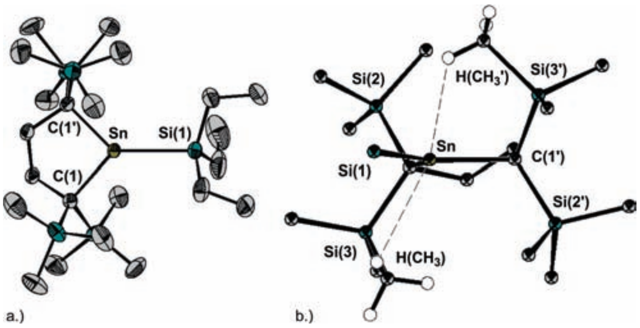
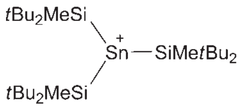


Figure 1. Ellipsoid presentation of the molecular structure of cation **2a** in the crystal (at 50% probability). View a) perpendicular to the C(1)SnC(1′) plane (hydrogen atoms are omitted) and b) along the Si(1)Sn vector indicating the close spatial proximity of the H(CH$_3$) and H(CH$_3$′) to the tin atom (Et groups at Si(1) and all hydrogen atoms but those attached to methyl groups close to the tin atom are omitted).

are also in agreement with the proposed structures.[14] Structural evidence for the formation of stannylium ions **2** comes from X-ray diffraction (XRD) analysis of the salts **2**[B(C$_6$F$_5$)$_4$]. Suitable crystals for single-crystal XRD analysis of these compounds were grown from toluene at −18 °C. The solid-state structures[14] of the salts revealed in both cases that stannylium ions **2** are clearly separated from the borate anion; in particular, no fluorine atom of the borate anion approaches the positively charged tin atom at a distance smaller than 500 pm. The borate **2b**[B(C$_6$F$_5$)$_4$] crystallizes with half a molecule of the solvent toluene in the asymmetric unit. However, no direct interaction between the positively charged tin atom and the toluene molecule is indicated by any structural parameter. The crystal structure of the borate **2a**[B(C$_6$F$_5$)$_4$] indicates some positional disorder of one of the ethyl groups at the silicon atom, which was resolved by using a split model with a 6:4 occupation. The tin atoms in stannylium ions **2** adopt trigonal planar coordination environments (see Figure 1 for the molecular structure of cation **2a**) and enforce for the stannacyclopentane rings half-chair conformations. Planarity around the tin atoms is indicated in both cases by the summation of the C−Sn−C and the two C−Sn−Si bond angles α to 360°. The Si(1)−Sn bond lengths in stannylium ions **2** are comparable to reported Si−Sn bonds in cation **5** (264.53 (**2a**) and 267.89 pm (**2b**) vs 268.63 pm (**5**)).[12] The Sn−C(1) and Sn−C(1′) bond lengths (214.43−216.53 pm) also do not differ significantly from those found for related stannyl cations (i.e., Sn−C(sp^3): 216 pm in *n*Bu$_3$Sn[CB$_{11}$Me$_{12}$]; 217.0 pm in stannyl cation **6**).[15,16] These SnC bonds are, however, significantly shorter (by 5.8−7.9 pm) than those in the starting stannylene **3**,[9] in agreement with a significantly increased contribution of the 5s orbital to the Sn−C bond in the tricoordinated cation. Experimentally determined and calculated bonds and angles are summarized in Table 1.



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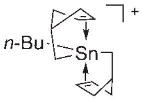

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Table 1. Comparison of Experimentally Obtained and Computed (Italic) Structural Parameters of Cations 2

compd	Sn−Si(1) [pm]	Sn−C(1)/ Sn−C(1′) [pm]	C(1)−Sn−C(1′) [deg]	C(1)−Si/ C(1′)−Si [pm]
2a[a]	264.53(5)	214.88(9)/ 214.43(13)	91.934(42)	189.62− 191.23
2a[b]	*268.25*	*215.91/* *216.36*	*91.70*	*190.93−* *191.81*
2b[c]	267.89(3)	215.68(13)/ 216.53(9)	91.813(42)	190.86− 193.02
2b[b]	*271.69*	*217.36/* *217.62*	*91.05*	*191.43−* *193.24*
3[d]		221.8(7)/ 222.3(7)	86.7(2)	186.9− 189.8
3[b]		*224.86*	*85.95*	*189.00/* *189.00*

[a] From single-crystal XRD of **2a**[B(C$_6$F$_5$)$_4$]. [b] Optimized molecular structure obtained using MPW1K/SDD(Sn)6-311+G(d,p)(C,H,Si). [c] From single-crystal XRD of **2b**[B(C$_6$F$_5$)$_4$]·0.5C$_7$H$_8$. [d] Taken from ref 9.

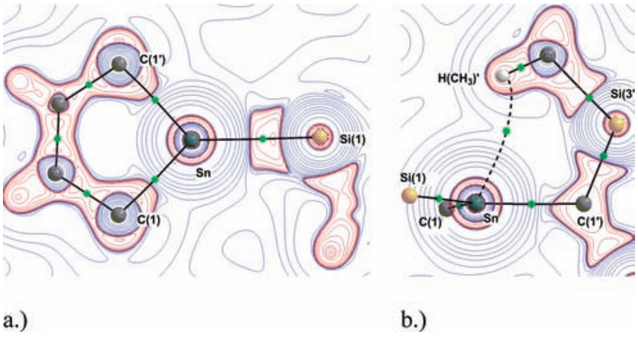

Figure 2. Contour plots of the calculated Laplacian of the electron density, $\nabla^2\rho(r)$, of stannylium ion **2a**, (a) in the C(1)−Sn−Si(1) plane and (b) in the Sn−bcp(SnH)−H(CH$_3$′) plane. The bond paths are shown by solid (ρ(bcp) > 0.025 e bohr^{-5}) or dashed (ρ(bcp) > 0.025 e bohr^{-5}) black lines, and the corresponding bcp's are shown as green circles. Red contours indicate regions of local charge accumulation ($\nabla^2\rho(r) < 0$), and blue contours indicate regions of local charge depletion ($\nabla^2\rho(r) > 0$).

These structural features clearly identify **2a** and **2b** as tricoordinated stannylium ions. There are, however, two peculiarities in the molecular structures of the cations which deserve particular attention. (i) The Sn−Si and Sn−C bond lengths (see Table 1) are all in the expected range;[17] however, the Si−C bonds in the β-position to the positively charged Sn atom are relatively long (189.62−193.02 pm in **2a**,**b** vs 186.0 pm for regular Si−C(sp^3)).[17] These Si−C bonds are even somewhat longer than those in stannylene **3** (by 2.0 (**2a**/**3**) or 3.5 pm (**2b**/**3**), see Table 1). These structural effects are small though, and in view of the high steric congestion in both cations, we conclude that they are too small to firmly indicate β-silyl stabilization of the stannylium ions **2a** and **2b**. (ii) Due to the half-chair conformation of the stannacyclopentane ring in cations **2**, one hydrogen atom of the methyl groups of each of the pseudo-axial-orientated trimethylsilyl groups is placed above and below the C(1)−Sn−C(1′) plane, in close proximity to the tin atom (**2a**, H(C(Me))−Sn 280.7 pm, H(C(Me′)−Sn 255.7 pm, see Figure 1b; **2b**, H(C(Me))−Sn 284.1 pm, H(C(Me′)−Sn 267.8 pm, see Supporting Information). These distances clearly exceed every

Table 2. Properties of the Electron Density at the Bond Critical Points of Sn−X Bonds (X = C, Si, H) in Cations 2 and Model Tin Compounds According to QTAIM Analysis

bond type	compd	$\rho(r)$ [e bohr^{-3}]	$\nabla^2\rho(r)$ [e bohr^{-5}]	atomic distance [pm]
Sn−C	Me_4Sn	0.0996	+0.1450	216.5
	2a	0.0995/0.0988	+0.1401/ +0.1369	214.9/214.4
	2b	0.0962/0.0976	+0.1268/ +0.1331	215.7/216.5
Sn−Si	$(Me_3Si)_4Sn$	0.0693	−0.0358	261.1
	2a	0.0646	−0.0587	264.5
	2b	0.0615	−0.0521	267.9
Sn−H	Me_3SnH	0.1071	+0.1463	172.1
	$[H_3Sn-\mathit{H}-CH_3]^+$	0.0330	+0.0676	212.7
	2a	0.0154	+0.0433	255.7

reported Sn−H bond length,[17] but they are significantly smaller than the sum of the van der Waals radii (327 pm)[18] and suggest a higher coordination of the tin atom and possibly involvement of the central tin atom and the distant hydrogen atoms of the methyl groups in multiple-center bonding. This question was addressed by applying density functional theory at the MPW1K level.[14,19] In addition, the results of the DFT calculations were used to confirm the structure of cations **2** in solution and to investigate the bonding in stannylium ions **2**. The results of the computations predict molecular structures for both cations **2** having all important structural features very close to those determined experimentally (see Table 1). The stannylium ions **2** also persist in arene solution, as indicated by the close accordance between computed ^{29}Si NMR chemical shifts for Si(1) and the experimental determined values (**2a**, $\delta\ ^{29}Si^{exp}(Si(1)) = 40.0$, $\delta\ ^{29}Si^{calc}(Si(1)) = 41$; **2b**, $\delta\ ^{29}Si^{exp}(Si(1)) = 70.3$, $\delta\ ^{29}Si^{calc}(Si(1)) = 73$). In view of the principal problems associated with the computation of tin NMR properties of tin compounds,[6c,11a,20] the calculated ^{119}Sn NMR chemical shifts for cations **2a**,**b** are also in full agreement with the experimental data (**2a**, $\delta\ ^{119}Sn^{calc} = 1605$; **2b**, $\delta\ ^{119}Sn^{calc} = 1590$).[14] The newly formed Sn−Si linkages in **2a**,**b** are relatively strong, despite the high steric strain imposed by the large substituents. That is, the Gibbs free energy for redissociation into stannylene and silylium ion is substantial ($G^{298} = 137$ (**2a**) or 99 kJ mol^{-1} (**2b**)). According to an analysis based on the quantum theory of atoms in molecules (QTAIM),[21] the Sn^+−Si bond in cations **2** is predominately covalent, as indicated by substantial electron density, $\rho(r)$, computed at the bond critical point (bcp) and the negative Laplacian of the electron density, $\nabla^2\rho(r)$, at this point, which indicates charge accumulation (see Figure 2a and Table 2). In contrast, the Sn^+−C bond has large ionic contributions (i.e., $\rho(r)$ is large at both bcp's and $\nabla^2\rho(r) > 0$). The characteristics of electron density at the bcp's of the Sn−C and Sn^+−Si bonds in cations **2** are very similar to those computed for standard compounds such as $(Me_3Si)_4Sn$ and Me_4Sn (see Table 2). Interestingly, QTAIM analysis predicts no bond paths between the hydrogen atoms ($H(CH_3)$ and $H(CH_3')$) of the pseudo-axial-oriented trimethylsilyl groups and the central tin atom, despite their relative spatial proximity. The only exception is the Sn/$H(CH_3)$ pair in **2a**, with the smallest separation (255.7 pm), for which a weak bcp is found (see Figure 2b). Comparison of the computed properties of the charge density at this bcp in **2a** with those of SnH bonds of standard compounds such as Me_3SnH (two-electron, two-center (2e-2c) bond) and the $[H_3Sn-H-CH_3]^+$ cation (2e-3c bond, see Table 2) suggests only a very small interaction between the central tin atom and the distant methyl protons. Therefore, QTAIM analysis provides no resilient indication for significant multiple-center bonding between these hydrogen atoms and the central tin atom.[22]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, NMR spectra, and crystal structure data for $2[B(C_6F_5)_4]$, and computational details, including NMR chemical shift calculations and Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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