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Tin-Centered Radical and Cation: Stable and Free

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The chemistry of stable free radicals and free cations of heavier group 14 elements is one of the most fascinating topics in recent years.[1,2] The story of these Si- and Ge-centered species has undergone a spectacular evolution from transient intermediates to stable compounds that can be isolated and even structurally characterized.[3,4] However, a stable stannyl radical and a stable free tricoordinated stannylium ion were still lacking. The only crystal structure for a nonsolvated Sn cation was reported for the tri(*n*-butyl)stannylium ion,[5] but in this compound the cationic Sn-center is not free, being coordinated with the methyl groups of the carborane counterion.[6] In this paper, we report the first stable representative of the stannyl radical and its subsequent one-electron oxidation to a three-coordinated free stannylium ion.

The method we selected for the synthesis of a stable stannyl radical was based on the one-electron oxidation of the corresponding stannyl anion ($^tBu_2MeSi)_3Sn^-Na^+$ generated in situ by the reaction of $SnCl_2$–dioxane with $^tBu_2MeSiNa$ in diethyl ether (Scheme 1).[7]

Scheme 1

$$SnCl_2 \cdot dioxane \xrightarrow[Et_2O]{3\ ^tBu_2MeSiNa} (^tBu_2MeSi)_3Sn\bullet$$

1
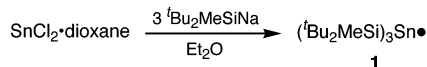
The stannyl radical **1** was isolated as extremely air- and moisture-sensitive orange prisms by recrystallization from hexane in 32% isolated yield.[8] Its crystal structure was unequivocally established by X-ray crystallography to show a planar structure (359.9° for the sum of the bond angles around the Sn center) with in-plane orientation of three methyl groups on the silyl-substituents, which allows the most effective steric protection of the radical center and minimizes steric hindrances (Figure 1).[8] The Sn atom is sp^2-hybridized, forcing the unpaired electron to occupy a vacant $5p_z$-orbital, which implies that **1** is truly a π-radical.[9]

The radical **1** showed a sharp signal in the electron paramagnetic resonance (EPR) spectrum measured in hexane at room temperature with a *g*-value of 2.0482,[8] which is slightly above the typical range for Sn-centered radicals.[10] Surprisingly, we did not observe two distinct pairs of satellites that one would expect from the coupling of the unpaired electron with two paramagnetic ^{117}Sn and ^{119}Sn nuclei. Instead, the central signal showed only one pair of satellite signals with the hyperfine coupling constant (hfcc) $a(^{119,117}Sn)$ of 32.9 mT. Most likely, this value is an average between the $a(^{117}Sn)$ and $a(^{119}Sn)$ coupling constants, because the difference between these last two values was estimated to be very small ($\sim$1.5 mT), which was difficult to detect under the measurement conditions (line width 1.1 mT). The hfcc value of 32.9 mT is 1 order of magnitude less than those of all previously known Sn-centered radicals.[11] This fact undoubtedly gives evidence that radical **1** preserves its π-character in solution, being trigonal planar in both the solid and the liquid states.

The successful preparation of stannyl radical **1** prompted us to generate the corresponding stannylium ion by one-electron oxidation of radical **1**. The reaction of stoichiometric amounts of **1** and
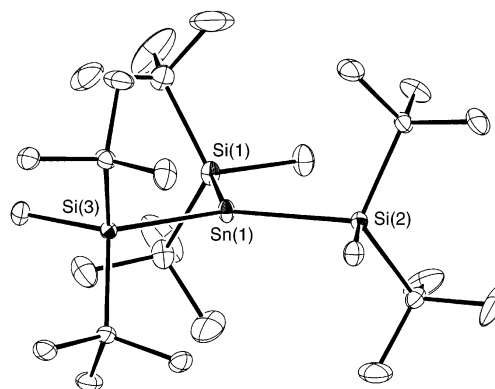

Figure 1. ORTEP drawing of **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Sn(1)–Si(1) = 2.6146(5), Sn(1)–Si(2) = 2.6193(5), Sn(1)–Si(3) = 2.6189(5). Selected bond angles (deg): Si(1)–Sn(1)–Si(3) = 119.684(16), Si(1)–Sn(1)–Si(2) = 120.229(16), Si(3)–Sn(1)–Si(2) = 119.988(16).
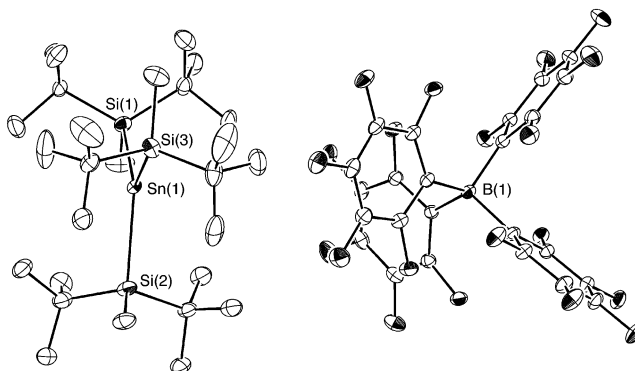
Figure 2. ORTEP drawing of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Sn(1)–Si(1) = 2.6930(7), Sn(1)–Si(2) = 2.6868(8), Sn(1)–Si(3) = 2.6792(8). Selected bond angles (deg): Si(3)–Sn(1)–Si(2) = 118.03(3), Si(3)–Sn(1)–Si(1) = 120.40(3), Si(2)–Sn(1)–Si(1) = 121.56(2).

$Ph_3C^+\bullet B(C_6F_5)_4^-$ in benzene resulted in the immediate formation of a two-layer reaction mixture, in which the dark-red lower layer was found to contain the target stannylium ion **2** (Scheme 2).[8] The

Scheme 2

$$1 \xrightarrow[C_6H_6\ /\ r.t.]{Ph_3C^+\bullet B(C_6F_5)_4^-} (^tBu_2MeSi)_3Sn^+\bullet\ B(C_6F_5)_4^-$$

2
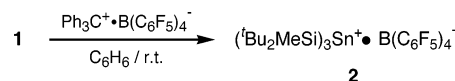
cation **2** was nearly quantitatively isolated by recrystallization from CH_2Cl_2 as dark-brown cubic-shaped crystals. X-ray analysis showed that the cationic part of **2** has a perfectly planar geometry around the central sp^2-hybridized Sn atom (360.0° for the sum of the bond angles around the Sn center) with the same in-plane arrangement of methyl groups on the silyl substituents (Figure 2).[8] The closest distance between the cationic Sn atom and the fluorine atom of

the counteranion is greater than 5 Å, which is outside of the range of van der Waals interactions. The average Si−Sn bond length in **2** was 2.6863(8) Å, which is quite normal for the Si−Sn bond length.[12] On the other hand, the average Si−Sn bond length in **1** of 2.6176(5) Å is shorter than that in **2**, which can be explained by the hyperconjugation between the $5p_z$-orbital on the Sn atom and the σ^*-orbitals of the Si−C(^{t}Bu) bonds in **1**.

The crucial point is the chemical shift of the free cationic Sn atom, which was anticipated to be greatly deshielded.[2e] According to an extrapolation based on the empirical correlation of ^{29}Si and ^{119}Sn NMR chemical shifts, one can expect the resonance of the free stannylium ion to be in the range of $+1500-2000$ ppm.[13] In fact, the real free stannylium ion is even more deshielded: careful measurement of the ^{119}Sn NMR spectrum of **2** in CD_2Cl_2 allowed us to detect the signal corresponding to the cationic Sn atom at $+2653$ ppm.[8] It is worth mentioning that this value is much more downfield shifted than any of the very few other examples reported for stannylium ions: counteranion-coordinated ^{n}Bu$_3$Sn$^+$ ($+454$ ppm),[5] Mes$_3$Sn$^+$ ($+806$ ppm),[14] and Tip$_3$Sn$^+$ ($+714$ ppm).[6] Moreover, the chemical shift of $+2653$ ppm greatly exceeds the calculated value for a free triorganostannylium ion of ca. $+1000$ ppm calculated at the HF/DZ+P and MP2/DZ+P levels using IGLO/DZ and IGLO/DZ+P methods.[15] The ^{119}Sn NMR chemical shift of $+2841$ ppm calculated for the model stannylium ion (H$_3$-Si)$_3$Sn$^+$ at the GIAO-B3LYP/[7s6p5d](Sn):6-311G(d)(Si,C,H)// B3LYP/[6s5p4d](Sn):6-31G(d)(Si,C,H) level using the Gaussian 98 program agrees reasonably with the experimental value of $+2653$ ppm.

Supporting Information Available: Experimental procedures, spectral data of **1** and **2**, tables of crystallographic data including atomic positional and thermal parameters for **1** and **2**, EPR chart of **1**, NMR charts of **2** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) In this reaction, SnCl$_2$−dioxane plays two roles: as a substrate for the generation of the stannyl anion, and as a one-electron oxidizing reagent. The right choice of the oxidizing reagent was crucial. Thus, when we used SnCl$_2$ itself, we were not able to isolate the stannyl radical because of unavoidable direct oxidation of ^{t}Bu$_2$MeSiNa by SnCl$_2$ ($E_{1/2}$(red) = -0.21 and -1.20 V) to form ^{t}Bu$_2$MeSiSiMe^{t}Bu$_2$ and metallic tin. However, when we applied SnCl$_2$−dioxane complex ($E_{1/2}$(red) = -0.78 V), in which the oxidizing ability of the stannylene unit is decreased by complexation with dioxane, we have achieved the exact matching of redox properties of SnCl$_2$−dioxane and ^{t}Bu$_2$MeSiNa to prevent the undesirable direct oxidation of silylsodium. For electrochemical studies of SnCl$_2$ and SnCl$_2$−dioxane, see: Lee, V. Ya.; Basova, A.; Matchkarovskaya, I. A.; Faustov, V. I.; Egorov, M. P.; Nefedov, O. M.; Rakhimov, R. D.; Butin, K. P. *J. Organomet. Chem.* **1995**, *499*, 27.

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(9) All other experimentally known to date stannyl radicals were found to be pyramidal σ-radicals: Iley, J. In *The Chemistry of Organic Germanium, Tin and Lead Compounds*; Patai, S., Ed.; John Wiley & Sons Ltd.: New York, 1995; Chapter 5.

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