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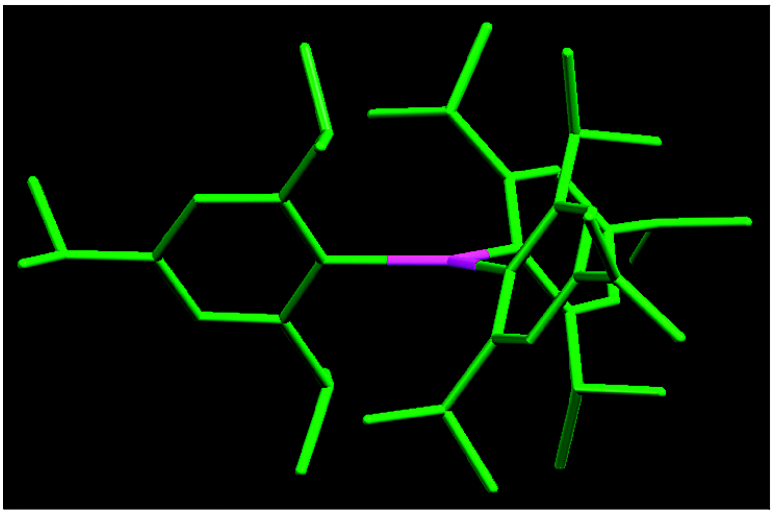

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A Free, Tricoordinate Stannylium Cation

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We report herein the preparation, NMR characterization, and crystal structure of a tricoordinate stannyl cation that is entirely free from coordination with solvent or anion. In 1997, we reported the preparation of the first free, tricoordinate silyl cation, trimesitylsilylium tetrakis(pentafluorophenyl)borate.[1] In collaboration with Reed, in 2002, we reported the crystal structure of the same cation, confirming its freedom from coordination.[2] The search for a free stannylium ion has proved to be slightly more difficult. The longer Sn−C bonds permit greater access of nucleophiles to the highly electrophilic Sn cationic center.

Modern efforts to prepare a free stannylium ion began in 1992 with the first use of aromatic solvents and low nucleophilic anions.[3] These discoveries ultimately led to the free silylium ion but apparently not to a free stannylium ion. For the case with three alkyl groups on tin, we[3] and others[4] obtained ^{119}Sn chemical shifts up to δ ca. 360. Comparison[5] with empirical correlations[6] suggested that such shifts represented only about 20% stannylium ion character. In 1999, we reported the stannyl cation analogous to the free silylium cation, trimesitylstannylium tetrakis(pentafluorophenyl)borate.[5] Because crystals were not obtained, questions of the geometry around tin and of possible coordination with solvent or anion remained open. The observed ^{119}Sn chemical shift of δ 806,[5] in the absence of an accurate theoretical measure, could not be interpreted in terms of geometry. We endeavored to place even more sterically demanding groups on tin, but in no case were we able to prepare a tetracoordinate precursor with three larger groups and the allyl group necessary to generate the cation.[5] Michl and co-workers[8] succeeded in obtaining the crystal structure of tributylstannylium $CB_{11}Me_{12}^-$. This cation was "weakly coordinated to methyl groups" of the anion, the geometry around tin was nonplanar (the C_α−Sn−C_α angles summed to 353.1° rather than 360° required for trigonal geometry), and the ^{119}Sn chemical shift was only δ 454.3, rather than δ ca. 1500 expected for the free cation. A very similar value was found for the same cation with a fluorinated anion.[9] The trigonal bipyramidal geometry around Sn is a common structural motif.[10] Michl's structure possesses such a geometry in the solid, with columns of alternating cations and anions in which there are three alkyl groups in a plane around Sn and methyl groups from the anions directly above and below Sn. Many other such structures have been reported, in which the apical atoms are O, N, S, or Cl.[10]

The current breakthrough was the result of success in preparing allyltris(2,4,6-triisopropylphenyl)stannane (allylTip_3Sn). The synthesis began with the reaction of TipBr with *t*BuLi at −78 °C after Suzuki et al.[11] to give TipLi. Reaction of the lithium reagent with $SnBr_4$ produced Tip_3SnBr. Excess allylmagnesium bromide reacted with Tip_3SnBr to afford allylTip_3Sn. Conversion to the tin cation followed our silicon method,[1,5] by treatment of the allyl compound with strong electrophiles at room temperature in a glovebox. As before, tetrakis(pentafluorophenyl)borate (TPFPB) was the anion. Nonionic byproducts were concentrated in the upper benzene layer and were syringed off. The resulting NMR spectra confirmed the clean conversion to a stannylium ion, Tip_3Sn^+, with a ^{119}Sn chemical shift of δ 714.

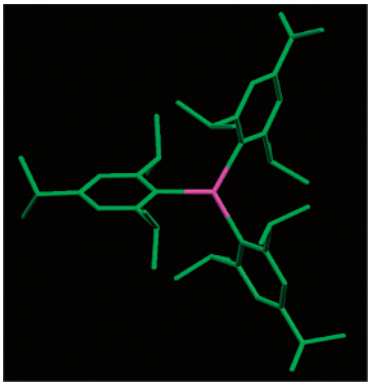

Figure 1. Face-on perspective of tris(2,4,6-triisopropylphenyl)stannylium, Tip_3Sn^+, from the crystal structure.

Crystals were obtained from a mixture of benzene and hexane, and the crystal structure was solved.[12] Figure 1 shows the cation face on. Solvent is absent, and no atom from the anion approaches to within 4 Å of Sn. Thus, the cation is entirely free from interactions with either solvent or anion. The sum of the C−Sn−C angles is 359.9(2)°, experimentally planar. The aryl rings are twisted in the usual propeller fashion from the plane of the tin atom and its three attached carbons. The aryl rings subtend an average angle of 61.1°, somewhat larger than the average of 49.2° found for the trimesitylsilylium cation,[2] as expected for the larger ortho substituents (isopropyl vs methyl).

The most important remaining question to answer is whether any of the hydrogen atoms on the isopropyl groups are coordinated with tin. The isopropyl methyl groups of Tip_3Sn^+ could conceivably approach more closely than those in Mes_3Si^+. Steric congestion around tin, however, forces the methyl groups to rotate to the outer surface, away from tin, leaving only the isopropyl methinyl protons in the vicinity of tin. The cogwheel geometry is very tight, so that the ortho isopropyl carbons and hydrogens are diastereotopic at room temperature. The ^{1}H resonances broaden and coalescence above 70 °C.

Examination of the region above and below the Sn atom revealed that there are no atoms along the axis passing through Sn and perpendicular to the plane of Sn and its three attached carbons, in contrast to the case of the tributylstannyl cation[8] and to all other reported trigonal bipyramidal tin geometries.[10] The entire region in which axial groups would exist in a trigonal bipyramid is vacant of atoms, including hydrogens.

The isopropyl methine carbons average 3.259 Å from Sn, much longer than the covalent Sn−C bond (2.14 Å), less than the sum of the van der Waals radii for Sn and C (4.17 Å), and longer than

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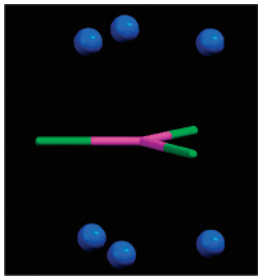

Figure 2. The immediate structure around Sn in Tip_3Sn^+, showing Sn (pink), ipso aryl carbon (green), and the six isopropyl methinyl hydrogens (blue).

the average Sn/CH_2 distance in the tributylstannyl cation (2.81 Å).[8] The only candidates for agostic interactions with Sn are the isopropyl methinyl hydrogens, which were refined and located during the solution of the crystal structure. Figure 2 shows the location of these hydrogens, in a prismatic geometry identical to that of the closest ortho hydrogens in the trimesitylsilylium cation.[2] The Sn/H distances average 2.64 Å, well beyond the covalent Sn−H bond length of 1.70 Å but less than the sum of the van der Waals radii (3.37 Å). The van der Waals radius of cationic Sn, however, is unknown and is almost certainly less than that of neutral Sn, so these comparisons are somewhat misleading. There is no angular distortion within the isopropyl groups of Tip_3Sn^+. The $C_{ipso}-C_{ortho}-CH$ angles average to a very normal sp^2 121.5° (122.2° in trimesitylsilylium[2]), and the $C_{ortho}-C-H$ angles average to a normal sp^3 106.5°.

It is worthwhile to compare the X-ray structure with the results of calculation, which refer to the gas phase.[13] The DFT/B3LYP geometry optimization showed that the crystal and gas phase structures are essentially identical. An atoms in molecule (AIM) calculation[14] showed that there are no bond critical points between Sn and the six methinyl hydrogens and that there are bonds only between Sn and the three aryl carbons. The ^{119}Sn chemical shift was calculated to be δ 763 with Gaussian 98 using the GIAO method and the MPW1PW91 density functional.[18] Calculations at this level are systematically higher frequencies than are observation values.[19] The plots of a more extensive study in the Supporting Information demonstrate that the calculated value of δ 763 is entirely consistent with the observed value of δ 714.

In summary, the crystal structure of tris(2,4,6-triisopropylphenyl)-stannylium tetrakis(pentafluorophenyl)borate reveals a geometry around Sn that is planar and tricoordinate. There is no solvent present, and the distance between the cation and anion is quite long. The isopropyl methyl groups are positioned away from Sn, and the methinyl hydrogens are well beyond the sum of the covalent radii. There are no angle distortions within the isopropyl groups. There are no atoms along the central axis perpendicular to the plane through Sn and its attached carbon atoms, indicating no trigonal bipyramidality. The calculated structure is very similar to the crystal structure, and the calculated ^{119}Sn chemical shift is in good agreement with that observed in solution. AIM calculations indicate no bonding between the methinyl hydrogens and tin. The common structure in solid, liquid, and gas phases fulfills all criteria for a free, tricoordinate stannylium cation and provides a new coordination number for diamagnetic Sn.

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Supporting Information Available: Atom coordinates from the X-ray structure, NMR characterization and CIF file of the cation, and details of the DFT, AIM, and tin chemical shift calculations. This information is available free of charge via the Internet at http://pubs.acs.org.

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(12) Crystal data for Tip_3Sn^+ $TPFPB^-$: $C_{69}H_{69}BF_{20}Sn$, M = 1407.74, space group $C2/c$, a = 29.336(7), b = 13.324(3), and c = 34.701(10) Å, α = 90°, β = 95.07(2)°, γ = 90°, V = 13510(6) Å^3, Z = 8, D_c = 1.384 g cm^{-3}, μ(Mo Kα) = 0.473 mm^{-1}, 859 variables refined with 16,615 unique reflections to R1 = 0.0499. Mass spectrum: M^+ (nominal) 727; M^+ (obs) 727−730. Anal. Calcd: C, 58.87; H, 4.94. Found: C, 58.71; H, 4.66.
(13) Geometry optimization from the X-ray structure was carried out at the DFT/B3LYP level with the effective core potential basis set of LACVP** for Sn and 6-31G for all other atoms, as implemented in the program Jaguar 4.2 (Schrödinger, Inc., Portland, OR). There are only minor differences from the X-ray structure. Bonding was studied by the AIM method.[14] Huzinaga's full valence basis set[15] as implemented by GamessUS[16] was used to calculate the electron density of the geometry-optimized complex for input into Morphy.[17] The only bond (3, −1) critical points involving Sn were between Sn and the ipso aryl carbons.
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