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The Tridurylsilylium and Tridurylstannylium Cations: Free and Not So Free

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Allyltridurylsilane has been prepared and converted to the tridurylsilylium cation by treatment with electrophiles. Allyltridurylstannane has been prepared and converted to the tridurylstannylium cation under similar conditions. The ^{29}Si chemical shift of the silylium cation indicates that it is free and tricoordinate, whereas the ^{119}Sn chemical shift of the stannylium cation indicates that it maintains loose fourth coordination with the solvent or the anion.

The synthesis of the first tricoordinate silyl cation, trimesitylsilylium, was accomplished by the 4-fold strategy of using aromatic solvents, an anion with very low nucleophilicity, extremely bulky substituents, and formation via allyl as the leaving group.[1,2] Subsequently, X-ray structures have been reported for two cations with electron-deficient silicon, one analogous to the tropylium ion[3] and one analogous to the homocyclopropenylium ion.[4] The three cations have in common high-frequency ^{29}Si chemical shifts: δ 225.5 for the trimesitylsilylium ion,[1,2] δ 142.9 for the tropylium analogue,[3] and δ 77.3 and 315.7 for the homocyclopropenylium analogue,[4] indicating considerable positive charge on silicon. Indeed, the case that trimesitylsilylium is planar and tricoordinate rests primarily on this very high-frequency chemical shift and on the close fit of the observed chemical shift to the value calculated for the planar cation in the gas phase.[5] To date, no X-ray structure has been reported for a simple silylium cation (R_3Si^+), one with the diagnostic high frequency ^{29}Si chemical shift.

To confirm that trimesityl has reached the extreme represented by tricoordination, we have sought a more sterically hindered substituent. The work of Berndt and co-workers[6] suggests that duryl might succeed. Whereas mesityl has methyl groups at the 2, 4, and 6 positions (ortho and para), duryl has methyls at positions 2, 3, 5, and 6 (ortho and meta). The para methyl in mesityl plays little or no role in the steric environment of the silyl center. On the other hand, the meta methyls in duryl can give rise to a *buttressing effect*. The ortho methyls in mesityl can bend away from each other toward the adjacent meta hydrogens in order to reduce steric congestion. In duryl, however, such bending of the ortho methyls encounters the adjacent meta methyls. The presence of the meta methyls in fact should cause the ortho methyls to move closer to the central silicon. Thus, duryl should present a somewhat higher degree of steric congestion around the silyl center than does mesityl.

The evolution of stannylium ions has followed a similar path to that of silylium ions. When we attempted to apply our 4-fold strategy to tin,[2] however, the ^{119}Sn chemical shift of the resulting trimesitylstannylium ion indicated that we had not achieved planar tricoordination. We estimated that the observed species had about 70−80% stannylium character. The longer bonds associated with Sn than Si permit easier access of unspecified nucleophiles (anion or solvent). Consequently, we thought that the use of duryl might lead to closer approach to the tricoordinate stannylium model.

We report herein the preparation of the allyl precursors to the duryl-substituted silyl and stannyl cations, removal of the allyl leaving groups in both cases, and characterization of the resulting ionic products.

Results and Discussion

The synthesis of both allyltridurylsilane (**1**, eq 1) and allyltridurylstannane (**2**, eq 2) began with bromodurene.

$$\mathrm{DurBr} \xrightarrow[\mathrm{HSiCl_3}]{\mathrm{Na}} \mathrm{Dur_3SiH} \xrightarrow{\mathrm{PCl_5}} \mathrm{Dur_3SiCl} \xrightarrow{\mathrm{allylLi}} \mathbf{1} \qquad (1)$$

The choices of metal (Na vs Li for DurNa and DurLi, Li vs MgBr for allyl) and of halogen (Cl vs Br for Dur_3M-X) were determined by yield.

$$\mathrm{DurBr} \xrightarrow[\mathrm{SnBr_4}]{\mathrm{BuLi}} \mathrm{Dur_3SnBr} \xrightarrow{\mathrm{allylMgBr}} \mathbf{2} \qquad (2)$$

Reaction of allyltridurylsilane with the free β-silyl cation 1,1-diphenyl-2-(triethylsilyl)ethylium tetrakis(pentafluorophenyl)borate ($Et_3SiCH_2CPh_2^+$ TPFPB$^-$) as an electrophile (E^+) in C_6D_6 at room temperature in a glovebox resulted in formation of the tridurylsilylium cation according to eq 3.

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$$E^+ + Dur_3SiCH_2CH{=}CH_2 \rightarrow Dur_3Si^+ + CH_2{=}CHCH_2E \quad (3)$$

As always for this reaction in aromatic solvents, two layers were formed. The lower layer, possibly a liquid clathrate, was viscous and highly colored and contained the ionic species.[7] The upper layer was less viscous and less highly colored and contained the allyl product of eq 3. The solvent for both layers was benzene. The anion was TPFPB throughout this study. We syringed off the upper layer and analyzed the lower layer by NMR spectroscopy. The ^{29}Si spectrum exhibited only one peak, aside from the broad absorption from the NMR tube, so that the lower layer contained a single Si-containing species. The peak occurred at δ 226.8, very close to the value observed for the trimesitylsilylium ion (δ 225.5)[1] and to the value calculated for the trimesitylsilylium ion in the gas phase (δ 230.1).[5]

This observation is consistent with an essentially free tridurylsilylium cation. The fact that mesityl and duryl produced almost the same ^{29}Si chemical shift, both very similar to the calculated gas phase value, requires that both species are close to the planar, tricoordinate extreme. The approximately 1 ppm shift to higher frequency (closer to the gas-phase value) of Dur_3Si^+ may indicate a freer cation than trimesitylsilylium by a very slight degree. More likely, however, the differences are not significant. All efforts to obtain crystals of the product failed. Reaction of the ionic solution with Bu_3SnH produced tridurylsilane as the major product.

The results are not so clear for the stannylium ion. Treatment of allyltridurylstannane with the solvated silylium ion (triethylsilylium TPFPB) or with the free β-silyl cation in C_6D_6 at room temperature in a glovebox produced an oil of the stannylium ion, whose ^{119}Sn spectrum contained a single broad peak at ca. δ 720. Again, no crystals were obtained. We calculated that a free triarylstannylium ion should have a ^{119}Sn chemical shift close to about δ 1100.[2] In our previous work, trimesitylstannylium TPFPB exhibited a chemical shift of δ 806 and phenylbis(2,4,6-triisopropylphenyl)stannylium TPFPB of δ 697.[2] The newly observed value for tridurylstannylium TPFPB of ca. δ 720 is within this range. Thus, we failed to achieve a higher frequency resonance and hence a less solvated (or anion-complexed) cation. It is likely that the longer C−Sn bonds nullify any differences provided by the buttressing effect.

Trimesitylstannylium and tridurylstannylium TPFPB are considerably more ionic (higher stannylium ion character) than tributylstannylium dodecamethylcarba-*closo*-dodecaborate ($Bu_3SnCB_{11}Me_{12}$), published recently.[8] Whereas the two aryl cations in the liquid phase are shifted 65−80% toward the expected ^{119}Sn value for a free triarylstannylium cation at δ ca. 1100, the value for the tributylstannylium case[8] at δ 454 is shifted only about 25% toward the expected value for a free trialkylstannylium cation at δ ca. 1700. The published X-ray structure[8] shows coordination between the cation and methyl groups in the anion, raising the coordination number above tricoordination. Similar interactions must be present in the liquid.

To produce a freer triarylstannylium cation, it will be necessary to operate directly on the ortho substituents, as we attempted to do with the TIPS groups.[2] The larger the ortho substituents, however, the more difficult it is to synthesize the allyltriaryl precursor. In our previous study,[2] we tried several ortho groups larger than methyl. Except for phenyldi(TIPS), we were unable to attach three aryl groups onto tin when any of them was larger than mesityl. The synthesis invariably produced diaryl or monoaryl products.

Conclusions

Treatment of allyltridurylsilane with electrophiles results in expulsion of the allyl group and production of the tridurylsilylium cation. The ^{29}Si chemical shift of δ 226.8 is consistent with a free cation with tricoordination around silicon. This species constitutes the second free acyclic silylium cation. The coincidence of chemical shift with that of the reported trimesitylsilylium cation[1,2] supports the conclusion that both species are free. Treatment of allyltridurylstannane with electrophiles also results in expulsion of the allyl group. The tridurylstannylium cation so produced, however, apparently is not entirely free. Its ^{119}Sn chemical shift of δ ca. 720 is well to lower frequency of the expected value close to δ 1100 for a free, tricoordinate stannylium cation, although still indicating high stannylium character (>70%). The sensitivity of the ^{119}Sn chemical shift to the nature of the substituent confirms the presence of partial coordination of Sn with a fourth group. These findings report the second free, acyclic silylium cation, but an entirely free, acyclic stannylium cation remains an unrealized goal.

Experimental Section

Tridurylsilane. A 200 mL, three-necked, round-bottomed flask, equipped with a rubber septum, a condenser, and a glass stopper, was charged with pieces of Na (2.4 g, 0.105 atom), bromodurene (6.38 g, 0.03 mol), dry benzene (75 mL), and a magnetic stirring bar and was placed under a N_2 atmosphere. Trichlorosilane (1 mL, 0.01 mol) was added via a syringe through the septum. The mixture was heated to reflux and stirred overnight. The resulting dark blue solution was cooled and filtered through a Celite pad. The now yellow solution was concentrated by rotary evaporation. The dark yellow residue was crystallized from hexane to give white crystals: 1.2 g (28%); mp 169−170 °C; ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 18H), 2.37 (s, 18H), 5.93 (s, 1H), 7.18 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 20.4, 21.3, 133.2, 134.0, 137.9, 140.8; ^{29}Si NMR ($CDCl_3$) δ −40.3.

Chlorotridurylsilane. A 100 mL, round-bottomed flask was charged with tridurylsilane (1.49 g, 3.5 mmol), PCl_5 (1.12 g, 5.4 mmol), CCl_4 (30 mL), and a magnetic stirring bar. The mixture was heated at reflux under N_2 for 36 h. The resulting yellow solution was concentrated by rotary evaporation, and the residue was dissolved in 50 mL of hexane. Methanol (15 mL) was added slowly to decompose the unreacted PCl_5. The organic layer was separated, dried ($MgSO_4$), and concentrated by rotary evaporation to give a yellow solid. Crystallization of the solid from hexane produced a white powder: 1.25 g (77%); mp 228−30 °C; ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 18H), 2.22 (s, 18H), 7.05 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 20.7, 22.4, 133.5, 133.7, 134.7, 139.3, 139.9, 141.1; ^{29}Si NMR ($CDCl_3$) δ −2.7. Anal. Calcd for $C_{30}H_{39}SiCl$: C, 77.80; 8.49. Found: C, 77.85; H, 8.45.

Allyltridurylsilane. A 100 mL, round-bottomed flask fitted with a rubber septum was charged with allyltriphenylstannane (4.27 g, 11.0 mmol) and a magnetic stirring bar. Anhydrous tetrahydrofuran (25 mL) and (quickly) phenyllithium (1.8 M, 6.1 mL, 11.0 mmol) in ether/cyclohexane were added via a syringe through the septum. After 30 min, the

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suspension was transferred under N_2 through a wide bore cannula to an enclosed glass frit and filtered into a 100 mL flask containing 1.50 g (3.2 mmol) of chlorotridurylsilane. The resulting dark red solution was stirred at room temperature for 3 days. The yellow mixture was then quenched with H_2O and extracted twice with hexane. The combined organics were dried ($MgSO_4$) and concentrated by rotary evaporation. The residue was chromatographed over neutral alumna with hexane as eluent to give a white solid: 0.70 g (46%); mp 184−5 °C; ^{1}H NMR (C_6D_6) δ 2.08 (s, 18H), 2.24 (s, 18H), 2.47−2.52 (m, 2H), 4.85−5.00 (m, 2H), 5.76−5.90 (m, 1H), 6.94 (s, 3H); ^{13}C NMR (C_6D_6) δ 21.2, 23.1, 30.5, 115.6, 133.4, 134.6, 138.9, 141.0, 142.3; ^{29}Si NMR ($CDCl_3$) δ −17.4; MS (EI) *m/z* 468 (M^+, 1), 428 (38), 427 (100), 293 (16), 262 (21). Anal. Calcd for $C_{33}H_{44}Si$: C, 84.55; H, 9.46. Found: C, 84.81; H, 9.33.

Tridurylsilylium Tetrakis(pentafluorophenyl)borate (TPFPB). In a N_2-filled glovebox was dissolved trityl TPFPB (160 mg, 0.17 mmol) in dry C_6D_6 (0.7 mL) in a valved 5 mm NMR tube. Addition of triethylsilane (25 mg, 0.22 mmol) produced two layers. The colorless top phase containing triphenylmethane was removed with a syringe. 1,1-Diphenylethene (40 mg, 0.22 mmol) was added to the brown oil residue, which then became deep green. Addition of allyltridurylsilane (89.1 mg, 0.19 mmol) in 0.7 mL of C_6D_6 created two layers again, the lower, red one containing the ionic product. The light orange, top phase was removed, and the lower layer was analyzed by NMR spectroscopy: ^{1}H NMR (C_6D_6) 1.86 (s, 18H), 2.01 (s, 18H), 6.92 (s, 3H); ^{13}C NMR 19.3, 22.6, 136.1, 137.1 (d from the anion), 137.8, 138.2 (d from the anion), 139.7, 140.9, 149.0 (d from the anion); ^{29}Si NMR (C_6D_6) δ 226.8. The solvent was removed under high vacuum to produce a deep red oil, which was washed twice with dry toluene to remove nonpolar materials. The oil was dissolved in 2/1 toluene/hexane, and the resulting solution was allowed to stand in the glovebox, but no crystals formed.

Product Studies. The concentrated lower layer containing triduryl TPFPB was washed with 3 × 2 mL of toluene to remove nonpolar materials. Addition of Bu_3SnH (0.14 g, 0.48 mmol) changed the color of the oil from red to brown. Toluene (1.5 mL) was added, and the new top layer was removed via syringe and analyzed by GC/MS. The major product was tridurylsilane: MS (EI) *m/z* 428 (M^+, 1), 294 (21), 279 (7), 160 (100), 133 (8), 119 (7).

Bromotridurylstannane. Butyllithium (2.5 M, 23.6 mL, 58.9 mmol) in hexane was added at 0 °C under N_2 to a solution of bromodurene (10.4 g, 48.8 mmol) in diethyl ether (80 mL) in a 250 mL three-necked, round-bottomed flask. The mixture was warmed slowly to room temperature and then stirred for 3 h. The mixture thickened quickly as duryllithium precipitated out. A solution of tetrabromotin (5.94 g, 13.5 mmol) in 50 mL of toluene was transferred to the flask through a cannula. The mixture was stirred overnight at room temperature and then refluxed for 6 h. A white solid (LiBr) was removed by filtration, and the pale yellow solution was concentrated by rotary evaporation. The brown residue was washed with 30 mL of acetone to remove colored impurities. The resulting white powder consisted of about 80% bromotridurylstannane and 20% dibromodidurylstannane according to ^{1}H NMR analysis. Stirring the mixture with 100 mL of acetone dissolved all of the dibromodidurylstannane. The less soluble, desired bromotridurylstannane was isolated as a white powder by filtration: 3.3 g, 41%; mp 261−3 °C; ^{1}H NMR ($CDCl_3$) δ 2.19 (s, 18H), 2.31 (s, 18H), 6.99 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 20.9, 23.9, 133.3, 134.7, 139.7, 148.3; ^{119}Sn NMR ($CDCl_3$) δ −124.0. Anal. Calcd for $C_{30}H_{39}SnBr$: C, 60.23; H, 6.57. Found: 61.26; H, 6.46.

Allyltridurylstannane. In a 250 mL three-necked, round-bottomed flask, allylmagnesium bromide (1.0 M, 3.6 mL, 3.6 mmol) was added to bromotridurylstannane (2.0 g, 3.3 mmol) in 80 mL of toluene. The solution was refluxed for 24 h and cooled to room temperature. According to the ^{1}H NMR spectrum, some unreacted bromotridurylstannane remained. To complete the reaction, additional allylmagnesium bromide (1.0 M, 3.6 mL, 3.6 mmol) was added. The mixture was refluxed overnight and quenched with H_2O and 10% aqueous HBr. The organic portion was separated and washed with H_2O, $NaHCO_3$, and again with H_2O. The solution was dried ($MgSO_4$), and the solvent was removed by rotary evaporation to give a white powder: 1.8 g, 96%; mp 190−1 °C; ^{1}H NMR (toluene-d_8) δ 2.06 (s, 18H), 2.29 (s, 18H), 2.42 (d, 2H), 4.83 (m, 2H), 5.94 (m, 1H), 6.82 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 21.1, 23.6, 28.2, 113.3, 132.1, 133.8, 140.1, 148.9; ^{119}Sn NMR ($CDCl_3$) δ −161.7. Anal. Calcd for $C_{33}H_{44}Sn$: C, 70.85; H, 7.95. Found: C, 71.41; H, 7.87.

Tridurylstannylium Tetrakis(pentafluorophenyl)borate (TPFPB).

(a) From the Solvated Triethylsilyl Cation. In a N_2-filled glovebox, trityl TPFPB (160 mg, 0.17 mmol) was dissolved in dry C_6D_6 (0.7 mL) in a valved 5 mm NMR tube. Addition of triethylsilane (25 mg, 0.22 mmol) produced two layers, the lower of which was a light brown oil. The colorless top phase containing triphenylmethane was removed via a syringe. Allyltridurylstannane (106.3 mg, 0.19 mmol) in C_6D_6 was added, and two phases reformed. The yellow top layer was removed, and the remaining orange oil was examined by NMR spectroscopy: ^{1}H NMR (C_6D_6) δ 1.91 (s, 18H), 1.97 (s, 18H), 6.89 (s, 3H); ^{13}C NMR (C_6D_6) δ 19.8, 23.7, 137.1 (d from the anion), 137.4, 137.7, 138.4, 139.4 (d from the anion), 149.1 (d from the anion), 150.8; ^{119}Sn NMR (C_6D_6) δ 715 (br).

(b) From the Free *β*-Silyl Carbocation. In a N_2-filled glovebox was dissolved trityl TPFPB (160 mg, 0.17 mmol) in dry C_6D_6 (0.7 mL) in a valved 5 mm NMR tube. Addition of triethylsilane (25 mg, 0.22 mmol) produced two layers, the lower of which was a light brown oil. The colorless top phase containing triphenylmethane was removed via a syringe. 1,1-Diphenylethene (40 mg, 0.22 mmol) was added, and the oil became deep green. Allyltridurylstannane (106.3 mg, 0.19 mmol) in C_6D_6 was added. The yellow top phase was removed, and the remaining orange oil was examined by NMR spectroscopy: ^{1}H NMR (C_6D_6) δ 1.92 (s, 18H), 1.98 (s, 18H), 6.90 (s, 3H); ^{13}C NMR (C_6D_6) δ 19.8, 23.7, 137.1 (d from the anion), 137.4, 137.7, 138.4, 139.4 (d from the anion), 149.1 (d from the anion), 150.8; ^{119}Sn NMR (C_6D_6) δ 725 (br).

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