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The gas-phase fragmentation of trineopentylstannyl cation: a rare example of β-methyl migration within a main group organometallic compound

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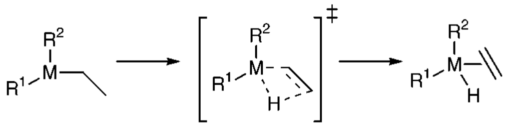
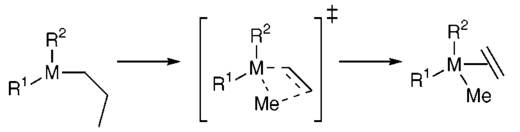
The lowest-energy fragmentation pathway of trineopentylstannyl cation is the first example of β-methyl migration to an organotin compound in the gas-phase; the origin of the migrating methyl groups is confirmed by an isotopic labelling experiment.

The migratory insertion of an unsaturated compound into a transition metal–hydrogen (or carbon) bond is a well established reaction.[1] The β-hydrogen [eqn. (1)] and β-methyl [eqn. (2)] elimination processes, being microscopic reversals of the insertion process, are of fundamental importance in the many catalytic processes involving transition metals,[2–4] including Ziegler–Natta polymerization.[2]


(1)


(2)

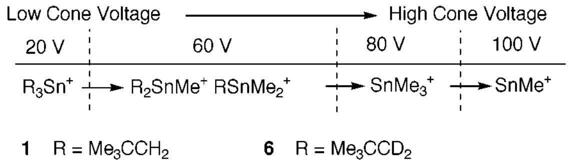
Although these processes are primarily associated with transition-metal organometallic compounds, they are also known to occur within organoaluminium compounds.[5] In particular, trineopentylaluminium dissociates reversibly into $AlMe_3$ and isobutene at 200 °C [eqn. (3)].[6] Whilst the observations in these early works are now attributed to the β-Me elimination process,[5] to the best of our knowledge, there are no other examples of β-Me elimination in main group organometallic chemistry.

$$(Me_3CCH_2)_3Al \xrightleftharpoons{200\ °C} Me_3Al + 3\ Me_2C{=}CH_2 \qquad (3)$$

As part of a comprehensive study into the gas-phase fragmentation of organostannyl cations, we investigated the fragmentation of trineopentylstannyl cation $[(Me_3CCH_2)_3Sn]^+$ (**1**), derived from trineopentylstannyl trifluoromethanesulfonate (**2**),† using ESMS. Initially designed as a very mild method of analyzing large biomolecules,[7] ESMS has since been widely used as an investigative tool in organometallic solution chemistry.[8]

While there is still significant debate over the exact nature of the electrospray ionization process,[9] it basically entails spraying the analyte solution into the mass spectrometer source followed by evaporation of the solvent molecules. In-source CID of the analyte ions can be made to occur by increasing the potential difference (cone voltage) across the skimmer cones.[10] This allows analyses to start under *extremely* mild conditions and the energy of the ions analyzed can be gradually increased. Organotin compounds, the halides in particular, have been investigated within several ESMS studies.[11]

Analysis of a solution of **2** in acetonitrile is first performed under mild conditions,‡ at a cone voltage of 20 V. The predominant species observed is the acetonitrile (solvent) adduct, [**1** + CH_3CN], along with a smaller peak corresponding to **1**.§ Increasing the cone voltage to 40 V causes dissociation of the acetonitrile adduct and **1** becomes the main species detected.

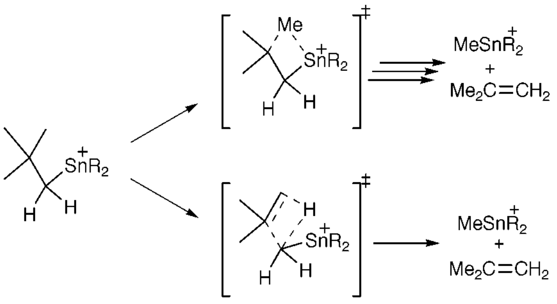


Scheme 1 Observed fragmentation patterns of **1** and **6**.

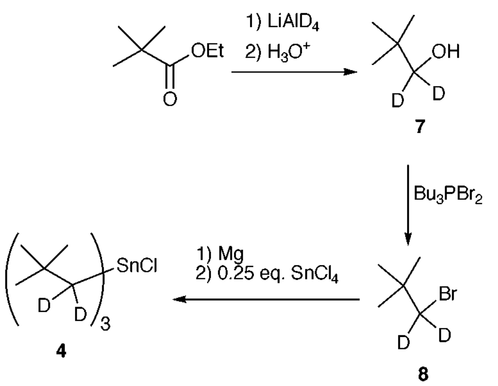
The cation **1** itself remains intact until the cone voltage is raised even further (~ 60 V), where the onset of fragmentation occurs. The fragmentation pattern observed is summarized in Scheme 1. For each neopentyl group lost, a methyl group remains on tin. No evidence for simple Sn–C bond cleavage was found. The presence of methyl residues on tin in the fragment ions can be rationalized through the two different pathways depicted in Scheme 2. The top pathway is analogous to the β-Me migration process known in transition metal complexes, whereas the bottom pathway resembles a well established[12] hydrocarbon pyrolysis process. Both reaction channels lead to the same products.

To resolve this issue, the deuterated trineopentylstannyl chloride (**4**) was synthesized *via* Scheme 3. The corresponding trifluoromethanesulfonate (**5**) was obtained *via* metathesis of **4** with silver trifluoromethanesulfonate. Subsequently the deuterated trineopentylstannyl cation (**6**) is derived from **5**.¶ In this case, the two different types of hydrogen atom in **6** are distinguished, allowing the discrimination between the two reaction channels.

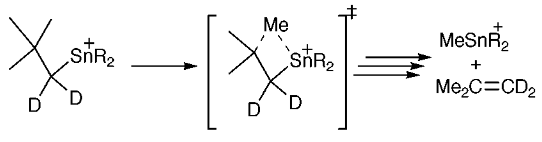
Analysis of an acetonitrile solution of **5** as before, afforded the fragment ions of **6**. The results obtained are depicted in Scheme 1, this time with R being the deuterated neopentyl group. The *m/z* values of the isotope distributions of the fragment ions clearly show that the methyl residues on tin are not deuterium labeled, thus unambiguously identifying the source of the methyl residue as being from the β-position (Scheme 4).



Scheme 2 Possible reaction channels for the fragmentation of **1**.



Scheme 3 Synthesis of deuterated trineopentylstannyl chloride analog **4**.



Scheme 4 Confirmed fragmentation pathway of **6**.

Repeating the ESMS in-source CID analyses on both **2** and **5** using deuterated acetonitrile as solvent and carrier afford the same daughter ions as when normal acetonitrile is used, thus eliminating the possibility that the acetonitrile solvent is the source of the CH_3 groups.

The observed β-Me elimination process is also reproducible under solvent-free (MS/MS) conditions.[‖] Selecting and trapping the relevant cations **1** and **6** followed by CID using helium as a collision gas again afforded fragmentation as depicted in Scheme 1.

In conclusion, we believe this is the first report of an unusual β-Me elimination process occurring within an organotin compound. Whilst the observation of complex processes in the gas-phase is not uncommon using conventional (*e.g.* EI or CI) mass spectrometric techniques, it is extremely important to note that the β-Me elimination we observe using ESMS is the first occurring dissociation process to be observed upon gradually raising the cone voltage. This demonstrates that the β-Me elimination observed is the lowest-energy dissociation pathway for this cation, as opposed to being an exotic high-energy process. We suggest that this process occurs *via* β-Me migration to afford a thermodynamically stabilised β-stannyl cation, which then loses isobutene to give the daughter ion. These results would be consistent with known work[13] concerning the importance of the Group 14 β-effect in the reactivities of Group 14 organometallic species.

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Notes and references

[†] **2** was obtained from trineopentylstannyl chloride (**3**) *via* metathesis with silver trifluoromethanesulfonate. **3** was synthesized using literature methods (H. Zimmer, I. Hechenbleikner, O. A. Homberg and M. Danzik, *J. Org. Chem.*, 1964, **29,** 2632.) **3**: $^{119}\mathrm{Sn}\{^{1}\mathrm{H}\}$ NMR (111.87 MHz, $CHCl_3$) δ = 126.2; δ_H (299.98 MHz, $CDCl_3$): 1.09 (s, 27H, Me_3C), 1.54 [s, 6H, CH_2Sn, $^{2}J(^{1}\mathrm{H},^{119}\mathrm{Sn})$ = 47 Hz]; $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (75.44 MHz, $CDCl_3$) δ 32.36 (quaternary), 33.27 [CH_3, $^{3}J(^{13}\mathrm{C},^{119}\mathrm{Sn})$ = 40 Hz], 40.49 [CH_2Sn, $^{1}J(^{13}\mathrm{C},^{119}\mathrm{Sn})$ = 328 Hz]. ν(KBr)/ cm^{-1}) 2954, 2900, 2860, 1464, 1384, 1364, 1239, 1143, 1113, 1011, 736, 604; mp 110–111 °C [lit. 112.5–113.5 °C].

[‡] The following general analysis procedure was used: approximately 100 mg of trineopentylstannyl chloride was combined with one equivalent of silver trifluoromethanesulfonate and stirred in 10 mL of dry CH_2Cl_2 for 15 to 30 min with protection from light. The resultant trineopentylstannyl trifluoromethanesulfonate solution was decanted from the AgCl precipitate and diluted with dry acetonitrile to a concentration of approximately 1 mM for ESMS analysis. ES mass spectra were obtained with a Micromass Platform II single quadrupole mass spectrometer using an acetonitrile mobile phase. Spectra were collected at cone voltages of 20, 40, 60, 80, and 100 V each. All peak assignments were unambiguously confirmed *via* comparison with calculated isotope distributions.

[§] In all spectra low intensity peaks corresponding to the $[(R_3Sn)_2Tf]^+$ and (if the solvents used were not absolutely dry) $[(R_3Sn)_2OH]^+$ clusters were observed. MS/MS experiments confirm that the presence of these clusters do not have any bearing on the β-Me migration results observed.

[¶] The deuterated trineopentylstannyl cation (**6**) was derived from tris(1,1-dideutero-2,2-dimethylpropyl)stannyl trifluoromethanesulfonate (**5**), which was obtained from tris(1,1-dideutero-2,2-dimethylpropyl)stannyl chloride (**4**) *via* metathesis with silver trifluoromethanesulfonate. The synthesis of **7** was achieved by modifying literature methods (I. Dostrovsky and F. S. Klein, *J. Chem. Soc.*, 1955, 4401; S. Sarel and M. S. Newman, *J. Am. Chem. Soc.*, 1956, **78**, 5416): ethyl trimethylacetate was reacted with $LiAlD_4$ to afford **7** in 61% yield; δ_H (299.98 MHz, $CDCl_3$) 0.87 (s, 9H, Me_3C), 2.03 (s, 1H, OH); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (75.44 MHz, $CDCl_3$) δ = 25.91 (CH_3), 32.35 (quaternary), 72.50 (1:2:3:2:1 quintet, CD_2OH, $^{1}J(^{13}\mathrm{C},^{2}\mathrm{H})$ = 42 Hz). Using the literature (G. A. Wiley, R. L. Hershkowitz, B. M. Rein and B. C. Chung, *J. Am. Chem. Soc.*, 1964, **86,** 964) method of converting neopentyl alcohol into neopentyl bromide, **7** was converted to **8** in 50% yield; δ_H (299.98 MHz, $CDCl_3$) 1.04 (s, 9H, Me_3C); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (75.44 MHz, $CDCl_3$) δ 27.69 (CH_3), 32.00 (quaternary), 47.57 (1:32.00 (quaternary), 47.57 (2:3:2:1 quintet, CD_2Br, $^{1}J(^{13}\mathrm{C},^{2}\mathrm{H})$ = 46 Hz); MS (70 eV): *m*/*z* (%): 57 (100) $[(CH_3)_3C^+]$, 137 (11) $[^{79}BrCD_2(CH_3)_2C^+]$, 139 (11) $[^{81}BrCD_2(CH_3)_2C^+]$, 152 (1) [M^+ containing ^{79}Br], 154 (1) [M^+ containing ^{81}Br]. The Grignard reagent of **8** was formed by reaction of **8** with magnesium turnings in THF. Using this Grignard reagent, the literature procedure (H. Zimmer, I. Hechenbleikner, O. A. Homberg and M. Danzik, *J. Org. Chem.*, 1964, **29,** 2632) for the synthesis of **3** afforded **4** in 18% yield; $^{119}\mathrm{Sn}\{^{1}\mathrm{H}\}$ NMR (111.87 MHz, $CHCl_3$) δ 126.8; δ_H (299.98 MHz, $CDCl_3$) 1.09 (s, 27H, Me_3C); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (75.44 MHz, $CDCl_3$) δ 31.95 (quaternary), 32.92 [CH_3, $^{3}J(^{13}\mathrm{C},^{119}\mathrm{Sn})$ = 40 Hz], 39.55 [1:2:3:2:1 quintet, CD_2Sn, $^{1}J(^{13}\mathrm{C},^{2}\mathrm{H})$ = 39Hz]. IR (KBr)/cm^{-1} ν 2954, 2900, 2860, 2194 (CD_2), 2133 (CD_2) 1461, 1391, 1364, 1238, 1049, 622; mp 113–114 °C

[‖] MS/MS experiments were performed using standard isolation and excitation procedures on mass selected ions generated *via* electrospray ionization using a Finnigan model LCQ (San Jose, CA, USA) quadrupole ion trap mass spectrometer.

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