Synthesis, structure and reactivity of ionogenic Sn(η-Cp^R)Cl derivatives

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Sn(η-Cp^s)Cl [Cp^s = $^-C_5Me_4(SiMe_2Bu^t)$] reacts with $SnCl_2$ in thf solution to yield the novel polyionic species [Sn_9(η-Cp^s)$_6Cl_{12}$] 1 which is characterised by solid- and solution-state multinuclear NMR spectroscopy and additionally by a single-crystal X-ray diffraction analysis.

In previous work the synthesis and characterisation of the covalent monomeric half-sandwich compounds [Sn(η-Cp^R)Cl] [Cp^R = $^-C_5Me_5$, $^-C_5Me_4(SiMe_2Bu^t)$] was performed.[1] In this report, we describe how the ionogenicity of the latter leads to an addition with $SnCl_2$. The ionogenicity of the $^-C_5Me_5$ half-sandwich derivative has been previously described, but always in terms of mono- or di-nuclear cations.[2] From the reaction of 2 equiv. of Sn{η-$C_5Me_4(SiMe_2Bu^t)$}Cl with 1 equiv. of $SnCl_2$ the polynuclear compound [Sn_9{η-$C_5Me_4(SiMe_2Bu^t)$}$_6Cl_{12}$] **1** was isolated.† The molecular structure of **1** was determined and is, remarkably, a cluster of nine Sn atoms arranged as two trigonal bipyramids each sharing a vertex (Fig. 1).‡ This common vertex is occupied by an $SnCl_6^{4-}$ anion, the Sn atom of which, Sn(1), sits on an inversion centre. The Cl^- ligand geometry about Sn(1) is almost perfectly octahedral,§ implying a stereochemically inactive lone pair, with all Sn–Cl distances equal at 2.822(4) Å. Each equatorial plane of the two trigonal bipyramids is comprised of three [Sn{η-$C_5Me_4(SiMe_2Bu^t)$}]$^+$ cations [Sn(2)]. The ligand geometry about Sn(2) is disorted square-based pyramidal with the basal plane occupied by four Cl^- ligands [Sn–Cl 2.963(3), 3.092(3), 3.486(4), 3.538(4) Å] and the apex occupied by a $C_5Me_4(SiMe_2Bu^t)$ group [the Sn atoms are 2.203(9) Å distant from the centroids of their respective $^-C_5Me_4(SiMe_2Bu^t)$ rings]. Finally, each plane is capped by an $SnCl_3^-$ anion [Sn(3)]. The geometry about each Sn(3) is trigonal pyramidal, implying a stereochemically active lone pair, with all Sn–Cl distances equal at 2.474 Å. These Sn–Cl distances are in good agreement with those previously measured for other divalent tin(II) chlorides (Table 1). An alternative description of the structure of **1**, based on the two short [2.963(3), 3.092(3)] and two long [3.486(4), 3.538(4) Å] Sn(2)–Cl interactions would be that of a dication {Sn_7(η-Cp^s)$_6Cl_6$}$^{2+}$ and two $SnCl_3^-$ anions. The solid-state ^{119}Sn CP

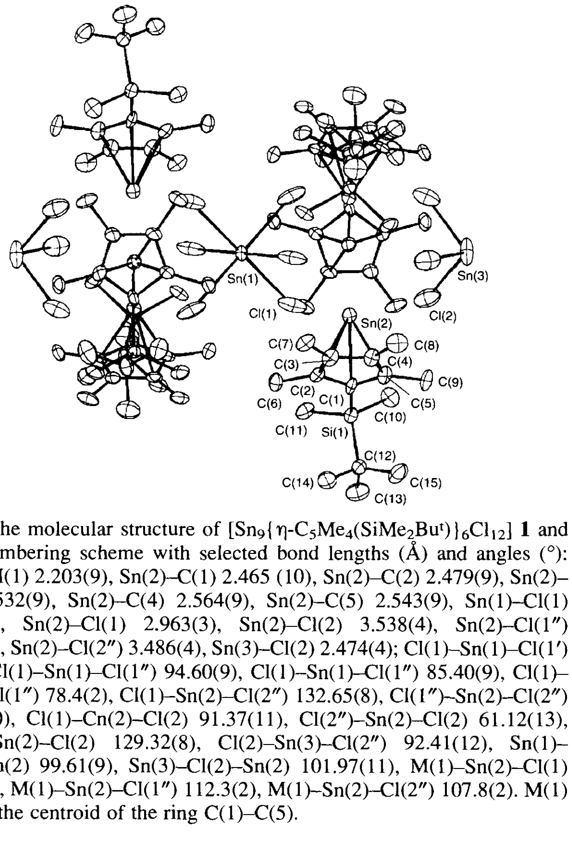
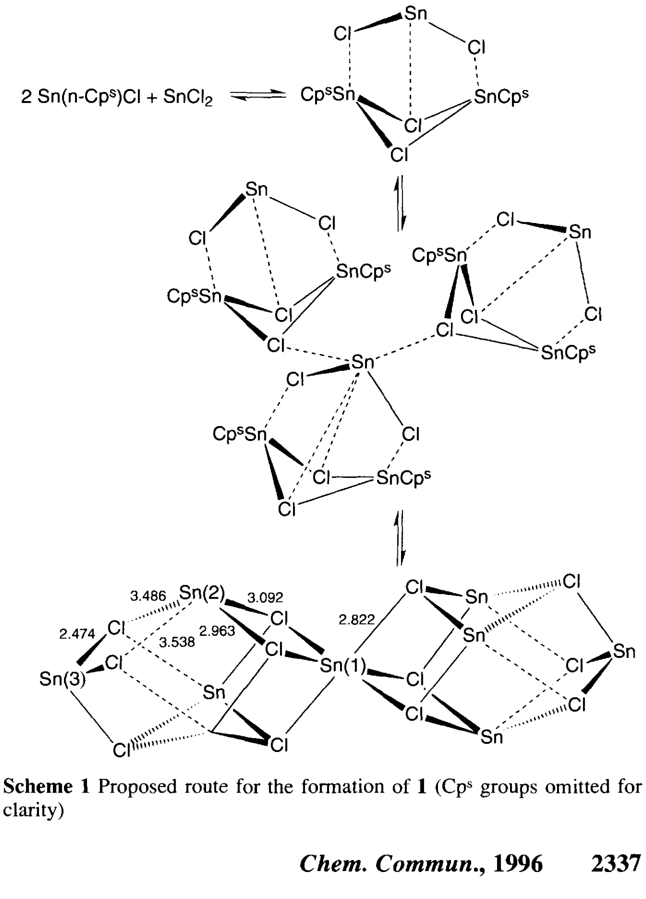


Fig. 1 The molecular structure of [Sn_9{η-$C_5Me_4(SiMe_2Bu^t)$}$_6Cl_{12}$] **1** and atom numbering scheme with selected bond lengths (Å) and angles (°): Sn(2)–M(1) 2.203(9), Sn(2)–C(1) 2.465 (10), Sn(2)–C(2) 2.479(9), Sn(2)–C(3) 2.532(9), Sn(2)–C(4) 2.564(9), Sn(2)–C(5) 2.543(9), Sn(1)–Cl(1) 2.822(4), Sn(2)–Cl(1) 2.963(3), Sn(2)–Cl(2) 3.538(4), Sn(2)–Cl(1″) 3.092(3), Sn(2)–Cl(2″) 3.486(4), Sn(3)–Cl(2) 2.474(4); Cl(1)–Sn(1)–Cl(1′) 180.0, Cl(1)–Sn(1)–Cl(1″) 94.60(9), Cl(1)–Sn(1)–Cl(1″) 85.40(9), Cl(1)–Sn(2)–Cl(1″) 78.4(2), Cl(1)–Sn(2)–Cl(2″) 132.65(8), Cl(1″)–Sn(2)–Cl(2″) 90.21(10), Cl(1)–Cn(2)–Cl(2) 91.37(11), Cl(2″)–Sn(2)–Cl(2) 61.12(13), Cl(1″)–Sn(2)–Cl(2) 129.32(8), Cl(2)–Sn(3)–Cl(2″) 92.41(12), Sn(1)–Cl(1)–Sn(2) 99.61(9), Sn(3)–Cl(2)–Sn(2) 101.97(11), M(1)–Sn(2)–Cl(1) 119.1(2), M(1)–Sn(2)–Cl(1″) 112.3(2), M(1)–Sn(2)–Cl(2″) 107.8(2). M(1) denotes the centroid of the ring C(1)–C(5).

Table 1 Selected structural data for Sn^{II}–Cl containing compounds

Compound	Sn–X/Å	Ref.
1		This work
Sn(1)–Cl	2.822(4)	
Sn(2)–Cl	2.963(3), 3.092(3), 3.486(4), 3.538(4)	
Sn(3)–Cl	2.474(4)	
$CsSnCl_3$	2.52	4
[Fe(η-C_5H_5)$(CO)_2SnCl_3$]	2.360	5
[Sn(η-C_5H_5)Cl]	2.679(5)	3
[Sn(η-C_5Me_5)Cl]	2.693(1), 2.657(1)	1



Scheme 1 Proposed route for the formation of **1** (Cp^s groups omitted for clarity)

MAS NMR spectrum of **1** displayed three isotropic resonances at δ_{iso} −16, −735, −2075, which we assign to $SnCl_3^-$, $SnCl_6^{4-}$ and $[Sn\{\eta\text{-}C_5Me_4(SiMe_2Bu^t)\}]^+$ respectively. These assignments were based both on a comparison of data and on the associated CSA determinations. The resonance for the $[Sn\{\eta\text{-}C_5Me_4(SiMe_2Bu^t)\}]^+$ at δ_{iso} −2075 clearly indicates a cationic rather than covalent formalism.[1] A clue to the mechanism of the formation of **1** was obtained when this reaction was monitored by ^{119}Sn NMR spectroscopy in C_6H_6 solution: addition of $SnCl_2$ to $Sn\{\eta\text{-}C_5Me_4(SiMe_2Bu^t)\}Cl$ caused the ^{119}Sn NMR resonance of the latter, at δ −1598, to disappear and be replaced by two new resonances at δ −123 and −1856 (in *ca.* 1 : 2 ratio). We assign these resonances to the $SnCl_2$ and $Sn\{\eta\text{-}C_5Me_4(SiMe_2Bu^t)\}Cl$ moieties respectively of the proposed trinuclear species **2**. The low frequency shift of the latter may be due to either the coordination of additional Cl lone pairs or an increase in the ionic character of this Sn centre. The formation of the addition product **2** has precedent in the reaction of $[Ge\{\eta\text{-}C_5Me_{54}[SiMe_2(C_5HMe_4)]\}Cl]$ with $GeCl_2$ which results in tetrameric $[\{Ge(\eta\text{-}C_5Me_4SiMe_2C_5HMe_4)\}_2(GeCl_3)_2]$.[6] We propose that **1** is derived from the trimerisation of **2** (with an $SnCl_2$ centre of one unit nucleating the cluster formation). This Sn centre ultimately becomes the $SnCl_6^{4-}$ core and each of the resulting $Sn\{\eta\text{-}C_5Me_4(SiMe_2Bu^t)\}^+$ bound to this Sn atom migrates to one of the other two incoming trimers, which then forms the equatorial planes of the two trigonal bipyramids (Scheme 1).¶

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Footnotes

† *Synthesis of* **1**: to a Schlenk tube charged with $Sn(\eta\text{-}C_5Me_4SiMe_2Bu^t)Cl$ (0.75 g, 1.92 mmol) in thf (50 ml) at room temperature, was added with stirring a solution of $SnCl_2$ (0.18 g, 0.96 mmol). After 3 h stirring, the solution was filtered and the thf removed *in vacuo*. The colourless solid was dissolved in Et_2O–C_6H_6 (9 : 1) and kept at −30 °C. Within 12 h, colourless cubic crystals of **1** were obtained in 68% yield (0.63 g, 0.22 mmol). Mp 153.5 °C. ^1H NMR (C_6D_6, 400.13 MHz), δ 2.10 (s, 6 H), 1.98 (s, 6 H) 0.93 (s, 9 H), 0.46 (s, 6 H); $^{13}C\{^1H\}$ NMR (C_6D_6, 100.61 MHz), δ 127.05, 125.92, 111.59, 27.21, 19.58, 13.65, 10.71, −0.76; $^{29}Si\{^1H\}$ NMR (C_6D_6, 79.49 MHz), δ −0.25; $^{119}Sn\{^1H\}$ NMR (C_6D_6, 149.21 MHz), δ −123, −1856; ^{119}Sn CP MAS (149.21 MHz), δ −16, −735, −2075. Analysis for $C_{90}H_{162}Si_6Sn_9Cl_{12}$, found (calc.): C, 36.32 (37.19); H, 5.50 (5.62%).

‡ *Crystal data* for **1**: $C_{90}H_{162}Cl_{12}Si_6Sn_9$. Crystallographic measurements were made on an Enraf-Nonius CAD4 diffractometer using Mo-Kα radiation, λ = 0.710 73 Å. The structure was solved by direct methods and refined on F^2 by a full-matrix least-squares procedure. T = 173(2) K. Specimen 0.40 × 0.30 × 0.30 mm, M = 2906.4, rhombohedral (on hexagonal axes), space group $R\bar{3}$ (no. 148), $a = b$ = 22.831(10), c = 19.924(6) Å, U = 8994(6) Å^3, D_c = 1.61 g cm^{-3}, Z = 3. For reflections with $2 < \theta < 25°$, $R(F)$ = 0.059 for 2120 observed reflections $[I > 2\sigma(I)]$ and $wR(F^2)$ = 0.138 for all 3778 reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/234.

§ There is a slight compression of the Cl(1)–Sn(1)–Cl(1′) angles with respect to the corresponding Cl(1)–Sn(1)–Cl(1′) (85 and 95°).

¶ In an analogous fashion 2 equiv. of $[Sn(\eta\text{-}C_5Me_5)Cl]$ were treated with 1 equiv. of $SnCl_2$. Again two new resonances were observed in solution (δ −123 and −1650) although, to date no solid material has been isolated from this reaction.

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