Synthesis and Characterization of Sn(η^5-C$_5$Me$_5$)Cl and Sn{η^5-C$_5$Me$_4$(SiMe$_2$Bu^t)}Cl

Steven P. Constantine, Geraldo M. De Lima, Peter B. Hitchcock,
Julian M. Keates, Gerard A. Lawless,* and Ivan Marziano

*The Chemistry Laboratory, School of Chemistry, Physics and Environmental Science,
University of Sussex, Brighton BN1 9QJ, U.K.*

Received September 23, 1996[⊗]

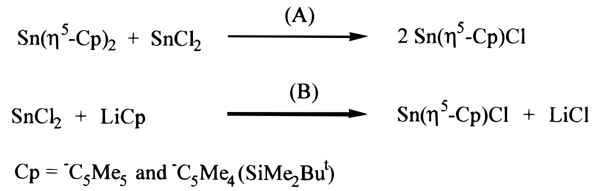
*Summary: The preparation and structural characterization of two monomeric covalent species, Sn(η^5-C$_5$Me$_5$)Cl (**1**) and Sn{η^5-C$_5$Me$_4$(SiMe$_2$Bu^t)}Cl (**2**), are reported, including solid- and solution-state multinuclear NMR spectroscopic data and, for **1**, a molecular structure determination.*

Introduction

Although the structural and chemical properties of the stannocenes have been extensively documented, the half-sandwich "Sn(η^5-Cp)X" analogues have been less well characterized.[1] To date, such half-sandwich complexes have been predominantly described as monomeric in solution, while in the solid state they have been shown to be either a covalent coordination polymer, as for Sn(η^5-C$_5$H$_5$)Cl, or discrete ions, as in the case of [Sn(η^5-Cp)]$^+$[X]$^-$ (Cp = $^-$C$_5$Me$_5$, X = $^-$BF$_4$, $^-$SO$_3$CF$_3$, $^-$C$_5$(COOMe)$_5$; Cp = $^-$C$_5$H$_4$Bu^t, X = $^-$BF$_4$).[2−5] More recently, despite "frustrating attempts to isolate them in pure form",[6] it has been suggested that it is the cation-stabilizing effect of such highly alkylated cyclopentadienyl systems as [Sn(η^n-C$_5$Me$_5$)]$^+$, in comparison to their unsubstituted analogue [Sn(η^5-C$_5$H$_5$)]$^+$, which renders these half-sandwich Sn(η^5-Cp)X derivatives unstable with respect to redistribution and addition reactions.[7] Hence, despite almost a quarter of a century of research**,** [Sn(η^5-C$_5$H$_5$)Cl] remains the sole example of this important class of compound to be structurally characterized[8] despite their synthetic utility.[9] In this note we report the synthesis and characterization of two further monomeric and covalent species, [Sn(η^5-C$_5$Me$_5$)Cl] (**1**) and Sn{η^5-C$_5$Me$_4$(SiMe$_2$Bu^t)}Cl (**2**).

Results and Discussion

Scheme 1. Synthetic Routes to Sn(η^5-Cp)Cl Derivatives



Two main routes to Sn(η^5-Cp)Cl derivatives have been reported (Scheme 1).[10] In our hands, **1** and **2** were best prepared by route A, since route B was complicated by the further reaction of both with SnCl$_2$.[7,12] Initially, **1** and **2** were characterized by solution- and solid-state multinuclear NMR spectroscopy; their ^{119}Sn NMR spectra each displayed a single resonance, shifted *ca.* 400 ppm to higher frequencies with respect to their metallocene precursors and the ionic species [Sn(η^5-C$_5$Me$_5$)][BF$_4$] (Table 1). It is noteworthy that neither solution- nor solid-state ^{119}Sn NMR spectra of **1** or **2** showed the presence of any redistribution products, while those of [Sn(η^5-C$_5$H$_5$)Cl] did. The molecular structure of **1** was determined (Table 2) and shows two crystallographically independent Sn centers (Sn(1) and Sn(2)) within the unit cell (Figure 1). Each Sn atom is bonded to a Cl atom (Sn(1)−Cl(1) = 2.693(1) Å and Sn(2)−Cl(2) = 2.657(1) Å) and is 2.271(3) or 2.282(3) Å distant from the centroids of their respective $^-$C$_5$Me$_5$ rings, which are oriented trans to one another (Table 3). These distances are typical of a covalently bonded cyclopentadienyl system and longer than those for ionic [Sn(η^5-C$_5$Me$_5$)]$^+$ species, in which the Sn−centroid distance typically measures 2.157 Å (Table 4). In common with other Sn−Cp derivatives the Sn atom of **1** "slips", with Sn−C bond lengths varying from 2.420(3) to 2.729(3) Å. Two other Sn centers (Sn(1′) and Sn(2′)), related to the first by an inversion center are also present.[13] Two weak Sn−Cl interactions, 3.086(1) and 3.444(3) Å, may be drawn for **1** as in [Sn(η^5−C$_5$H$_5$)Cl][8] (which has a Sn−Cl bond of 2.679(5) Å and two weak Sn−Cl interactions, 3.242(5) and 3.262(5) Å)[14] thereby combining to produce a pseudopolymeric ladder structure. That **1**, **2**, and [Sn(-C$_5$H$_5$)Cl] are best described as covalent monomers is further supported by a comparison of the solution- and solid-state, isotropic ^{119}Sn chemical shift data. For **1** the solid-state isotropic shift δ_{iso} is −1644, while in toluene or thf solution δ_{iso} is −1612 or −1637, respectively, indicating little increase in coordination geometry

---

* To whom correspondence should be addressed. E-mail: G.A.Lawless@sussex.ac.uk.

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

(1) Jutzi, P. *Adv. Organomet. Chem.* **1986**, *26*, 217.

(2) Jutzi, P.; Kohl, F. X. *J. Organomet. Chem.* **1979**, *164*, 141.

(3) Jutzi, P.; Kohl, F. X. *Chem. Ber.* **1981**, *114*, 488.

(4) Hofmann, P.; Krüger, C.; Tsay, Y.-H. *Chem. Ber.* **1980**, *113*, 757.

(5) Hani, R.; Geanangle, R. A. *J. Organomet. Chem.* **1985**, *293*, 197.

(6) Burkey, D. J.; Hanusa, T. P. *Organometallics* **1995**, *14*, 11.

(7) Constantine, S. P.; De Lima, G. M.; Hitchcock, P. B.; Keates, J. M.; Lawless, G. A. *J. Chem. Soc., Chem. Commun.* **1996**, 2337.

(8) Bos, K. D.; Bulten, E. J.; Noltes, J. G.; Spek, A. L. *J. Organomet. Chem.* **1975**, *99*, 71.

(9) Veith, M.; Mathur, M.; Huch, V. *Organometallics* **1996**, *15*, 2858.

(10) Another route, the solid-state reaction of Sn(η^1-C$_5$Me$_5$)$_2$Br$_2$ with Sn(η^5-C$_5$Me$_5$)$_2$, has been reported to yield Sn(η^5-C$_5$Me$_5$)Br, although its stability in solution seems uncertain.[11]

(11) Jutzi, P.; Hielscher, B. *Organometallics* **1986**, *5*, 1201.

(12) Kohl, F. X.; Dickbreder, R.; Jutzi, P.; Müller, G.; Huber, B. *Chem. Ber.* **1989**, *122*, 871.

(13) We thank one of the reviewers for pointing out that the opposite nature of the mutually *trans* cyclopentadienyl substituents of Sn(1′) and Sn(2′) compared to those of Sn(1) and Sn(2) permits better packing of the molecules.

(14) Due to difficulties in refining the molecular structure of {Sn(η^5-C$_5$H$_5$)Cl}$_n$, it is not clear as to whether these two distances, 3.26 and 3.24 Å, are significantly different.

S0276-7333(96)00805-9 CCC: $14.00

Table 1. Solid- and Solution-State ^{119}Sn NMR Chemical Shift Data for Selected Sn^{II} Derivatives

compd	δ/ppm	δ_{iso}/ppm
1[a]	−1612	−1644
2[a]	−1598	−1734
[Sn(η^5-C_5H_5)Cl][a]		−1483, −1578
Sn{η^5-$C_5Me_4(SiMe_2C_5HMe_4)$}Cl[b]	−1579	
Sn(η^5-C_5Me_5)Br[c]	−1630	
[Sn(η^5-C_5Me_5)$_2$][d]	−2129	
[Sn{η^5-$C_5Me_4(SiMe_2Bu^t)$}$_2$][e]	−2204	
[Sn(η^5-C_5Me_5)][BF$_4$][d]	−2247	

[a] This work. [b] Reference 12. [c] Reference 11. [d] Jutzi, P. *J. Organomet. Chem.* **1990**, *400*, 1. [e] Constantine, S. P.; Hitchcock, P. B.; Lawless, G. A.; De Lima, G. M. *J. Chem. Soc., Chem. Commun.* **1996**, 1101.

Table 2. Crystal Structure Determination and Refinement of [Sn(η^5-C_5Me_5)Cl]−Toluene Solvate (1)[a]

formula	$C_{30}H_{30}Cl_2Sn \cdot 0.5(C_7H_8)$
fw	624.8
cryst dimens, mm	0.40 × 0.35 × 0.35
color	colorless
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	10.029(3)
b, Å	11.577(5)
c, Å	11.838(4)
α, deg	77.34(3)
β, deg	75.98(3)
γ, deg	75.61(3)
V, Å^3	1273.1(8)
Z	2
d_{calcd}, g/cm^3	1.63
diffractometer	Enraf-Nonius CAD4
temp, K	173(2)
scan type	$\omega/2\theta$
scan range, deg	$2 < \theta < 28$
total no. of unique data	6142
criteria for observn	$I > 2\sigma(I)$
no. of unique obsd data	5321
$R(F)$ (for $I > 2\sigma(I)$)	0.029
$R^w(F^2)$ (for all rflns)	0.072

[a] Refinement was on F^2 for *all* reflections. Non-H atoms were refined as anisotropic. Methyl H's were refined in riding mode with the torsional angle defined. Toluene solvate molecules were disordered across an inversion center and modeled by five anisotropic C atoms without H atoms.

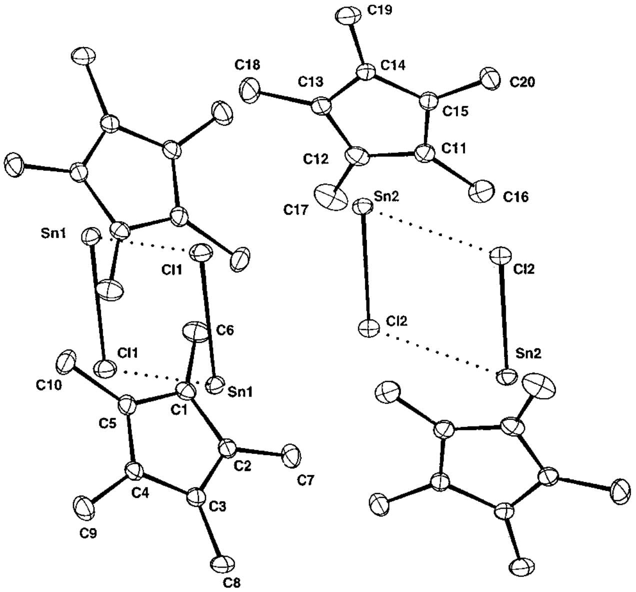


Figure 1. Molecular structure of {Sn(η^5-C_5Me_5)Cl} (**1**) and atom-numbering scheme. Selected bond lengths (Å) and angles (deg): Sn(1)−M(1), 2.271(2); Sn(1)−Cl(1), 2.693(1); Sn(1)−Cl(2), 3.444(2); Sn(2)−M(2), 2.282(3); Sn(2)−Cl(2), 2.657(1); Sn(2)−Cl(1), 3.413(2); M(1)−Sn(1)−Cl(1), 117.96(3); M(2)−Sn(2)−Cl(2), 118.08(3).

Table 3. Selected Bond Lengths (Å) and Angles (deg) of [Sn(η^5-C_5Me_5)Cl] (1)[a]

Sn(1)−Cl(1)	2.693(1)	Sn(1′)−Cl(1)	3.080(1)
Sn(2)−Cl(2)	2.657(1)	Sn(2′)−Cl(2)	3.130(1)
Sn(1)−Cl(2)	3.444(2)	Sn(2)−Cl(1)	3.413(2)
Sn(1)−C(1)	2.453(3)	Sn(1)−C(2)	2.654(3)
Sn(1)−C(3)	2.729(3)	Sn(1)−C(4)	2.598(3)
Sn(1)−C(5)	2.420(3)	Sn(1)−M(1)	2.271(3)
Sn(2)−C(11)	2.426(3)	Sn(2)−C(12)	2.437(3)
Sn(2)−C(13)	2.643(3)	Sn(2)−C(14)	2.764(3)
Sn(2)−C(15)	2.628(3)	Sn(2)−M(2)	2.282(3)
M(1)−Sn(1)−Cl(1)	117.96(3)	M(2)−Sn(2)−Cl(2)	118.08(3)

[a] M(1) denotes the centroid of the ring C(1) to C(5); M(2) denotes the centroid of the ring C(11) to C(15).

Table 4. Selected Structural Data for Sn(η^5-Cp)-Containing Compounds

compd	Sn−X dist/Å	Sn−M dist/Å
1[a]	2.693(1), 2.657(1)	2.271(3), 2.282(3)
[Sn(η^5-C_5H_5)Cl][e]	2.679(5)	2.34
[Sn{η^5-$C_5Me_4(SiMe_2Bu^t)$}$_2$][d]		2.379(2)
[Sn(η^5-C_5Me_5)$_2$][c]		2.396 (av)
[Sn{η^5-$C_5Me_4(SiMe_2C_5HMe_4)$}][BF$_4$][b]		2.22
[Sn(η^5-C_5Me_5)][BF$_4$][c]		2.157
[Sn{η^5-$C_5H_4Bu^t$][BF$_4$][f]		2.182
[Sn(μ-Cl){N(SiMe$_3$)$_2$}]$_2$[g]	2.598(1), 2.741(1)	
[Sn(μ-Cl){N[CMe$_2$(CH$_2$)$_3$CMe$_2$]}]$_2$[g]	2.704(1), 2.786(2)	

[a] This work. [b] Reference 12. [c] Jutzi, P. *J. Organomet. Chem.* **1990**, *400*, 1. [d] Constantine, S. P.; Hitchcock, P. B.; Lawless, G. A.; De Lima, G. M. *J. Chem. Soc., Chem. Commun.* **1996**, 1101. [e] Reference 8. [f] Reference 5. [g] Reference 15.

about the Sn^{II} center. Additionally, the M(1)−Sn(1)−Cl(1) and M(2)−Sn(2)−Cl(2) angles for **1** (117.96(3) and 118.08(3)°, respectively) are consistent with the presence of a stereochemically active lone pair. Furthermore, the Sn−Cl distances differ by some 22% if such a coordination polymer is proposed; this is much greater than that typically found in dimeric species such as {Sn(μ-Cl)-[N(SiMe$_3$)$_2$]}$_2$ and {Sn(μ-Cl){N[CMe$_2$(CH$_2$)$_3$CMe$_2$]}$_2$,[15] which are 5.2 and 2.9%, respectively. Finally, a comparison of the solution-state ^{119}Sn NMR chemical shift data for **1** and **2** with those reported for Sn{η^5-$C_5Me_4(SiMe_2C_5Me_5H)$}Cl and Sn(η^5-C_5Me_5)Br, which by cryoscopic measurements are monomeric in solution, supports a monomeric formula for **1** and **2** in solution (Table 1). We therefore conclude that both **1** and **2** are covalent monomeric species, both in nonpolar solvents and in the solid state, and that they, though highly alkylated, are stable with respect to redistribution. Moreover, their iogenicity may be controlled and is determined more by the ionizing nature of the solvent and SnCl$_2$ rather than the nature of the cyclopentadienyl ring substituents. Finally, it is noteworthy how ^{119}Sn NMR spectroscopy may be used to distinguish the covalent and ionic forms of such compounds.

Experimental Section

All compounds were handled with the rigorous exclusion of air and water using standard Schlenk techniques. All solvents were freshly distilled and dried by reflux over sodium or

---

(15) Chorley, R. W.; Hitchcock, P. B.; Jolly, B. S.; Lappert, M. F.; Lawless, G. A. *J. Chem. Soc., Chem. Commun.* **1991**, 1302.

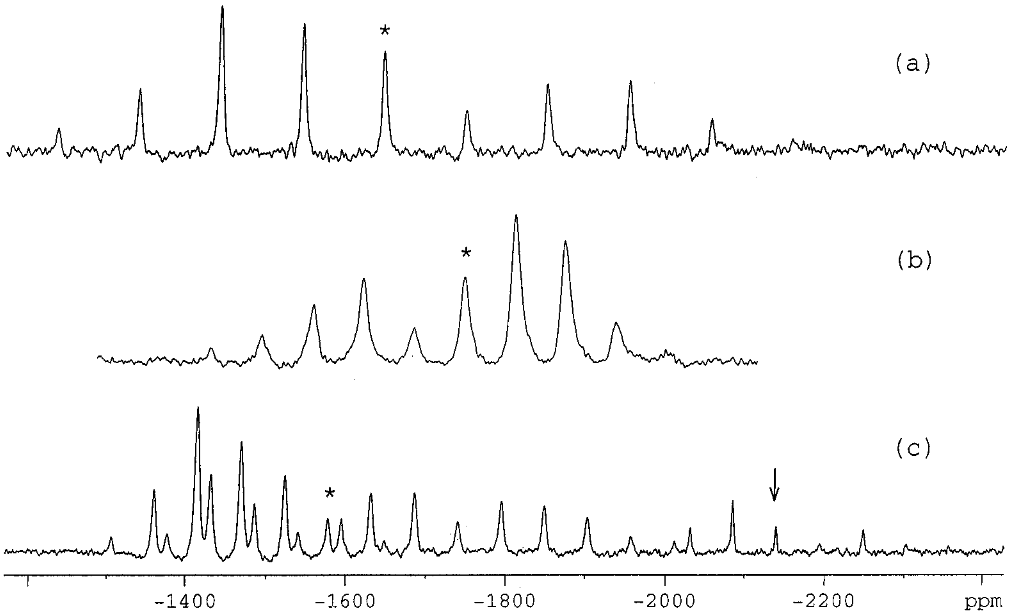


Figure 2. ^{119}Sn{^{1}H} CP MAS NMR spectra of (a) **1** (ν_R = 15 kHz, 531 transients), (b) **2** (ν_R = 9.5 kHz, 352 transients), and (c) [Sn(η^5-C_5H_5)Cl] (ν_R = 8 kHz, 2048 transients, ↓ denotes [Sn(η^5-C_5H_5)$_2$] impurity). The isotropic chemical shifts are denoted by asterisks.

sodium–potassium alloy under a dinitrogen atmosphere. NMR spectra were recorded at 100.62 MHz (^{13}C) and 148.97 MHz (^{119}Sn) using a Bruker DMX-400 spectrometer equipped with an 89 mm wide-bore magnet. Samples (100–150 mg) were ground in a glovebox operating at <1 ppm H_2O and <1 ppm O_2 and packed into Zirconia rotors with a Kel-F end cap. Samples were spun at the magic angle with N_2. No sample decomposition was observed. Spin rates between 2.5 and 15 kHz were utilized. High-power ^{1}H decoupling was applied during acquisition. ^{13}C shifts are reported relative to $SiMe_4$ and ^{119}Sn shifts relative to $SnMe_4$.

[Sn(η^5-C_5Me_5)Cl] (1). In a Schlenk tube charged with a solution of $SnCl_2$ (1.90 g, 10 mmol) in thf (50 mL) at −78 °C was added, over a 10 min period with stirring, [Sn(η^5-C_5Me_5)$_2$] (3.90 g, 10 mmol) also dissolved in thf (40 mL). Within 15 min a color change from orange to pale yellow was observed. The mixture was warmed to ambient temperature and stirring continued for a further 3 h. The thf was removed *in vacuo*, and after recrystallization from toluene, **1** was afforded in 92% yield (5.20 g, 17.90 mmol). Mp: 127 °C. ^{1}H NMR (C_6D_6): δ 2.27. ^{13}C{^{1}H} NMR (C_6D_6): δ 117.5, 10.2. ^{119}Sn{^{1}H} NMR (C_7D_8): δ −1612. ^{13}C CP MAS: δ 119, 12.7. ^{119}Sn CP MAS: δ −1644. MS: M$^+$ *m/z* 290, M$^+$ − Cl *m/z* 255, M$^+$ − Sn *m/z* 135. Anal. Calcd for $C_{10}H_{15}ClSn$: C, 41.51; H, 5.22; Found: C, 40.86; H, 5.18.

Sn{η^5-C_5Me_4($SiMe_2Bu^t$)}Cl (2). In a Schlenk tube charged with [Sn{η^5-C_5Me_4($SiMe_2Bu^t$)}$_2$] (1.50 g, 2.54 mmol) in thf (50 mL) at −78 °C was added with stirring a solution of $SnCl_2$ (0.48 g, 2.54 mmol). After 30 min of stirring, the mixture was warmed to ambient temperature, stirred for 2 h, and filtered. The thf was removed *in vacuo* and the pale yellow solid extracted with hot hexane. Removal of the hexane *in vacuo* afforded Sn{η-C_5Me_4($SiMe_2Bu^t$)}Cl in 83% yield (1.62 g, 4.20 mmol). Mp: 138 °C. ^{1}H NMR (C_6D_6): δ 2.11 (s, 6H), 1.96 (s, 6H) 0.96 (s, 9H), 0.46 (s, 6H). ^{13}C{^{1}H} NMR (C_6D_6): δ 127.5, 124.8, 111.8, 27.1, 19.4, 13.9, 10.7, −0.12. ^{29}Si{^{1}H} NMR (C_6D_6): δ −0.59. ^{119}Sn{^{1}H} NMR (C_6D_6): δ −1598. ^{119}Sn CP MAS: δ −1734. MS: M$^+$ *m/z* 390, M$^+$ − Cl *m/z* 355, M$^+$ − Bu^t *m/z* 333, M$^+$ − Cl − Bu^t *m/z* 298. Anal. Calcd for $C_{15}H_{27}ClSiSn$: C, 46.24; H, 6.98. Found: C, 45.18; H, 6.96.

Acknowledgment. We thank Dr. J. McVie (Dow Corning) for a CASE award (S.P.C.), the CNPq (G.M.D.L.), the EPSRC (J.M.K.), and the School of Chemistry, Physics and Environmental Science, University of Sussex (I.M.), for financial support.

Supporting Information Available: Figures giving additional views and listings of anisotropic thermal parameters, atomic coordinates for hydrogen atoms, and bond distances and angles for compound **1** (8 pages). Ordering information is given on any current masthead page.

OM9608059