Syntheses and molecular structures of [Sn{η-$C_5Me_4(SiMe_2Bu^t)$}$_2$] and [Fe{η-$C_5Me_4(SiMe_2Bu^t)$}$_2$]

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Reaction of 2 equiv. of LiCp^s [Cp^s = $C_5Me_4(SiMe_2Bu^t)$] with MCl_2 (M = Sn or Fe) affords the metallocene compounds, [M(η-Cp^s)$_2$], in high yield; single-crystal X-ray analyses of these metallocenes reveal the planar cyclopentadienyl rings to be parallel for both Sn and Fe derivatives.

In accordance with their VSEPR-expected stereochemical distortions from high-symmetry geometries, metallocenes of Sn^{II} typically exhibit a bent structure, with the rings becoming parallel with increasing steric bulk of the ring substituents {*cf.* [Sn(η-C_5Me_5)$_2$], α = 144.1°; [Sn{η-$C_5(CH_2Ph)_5$}$_2$], α = 155.9°; [Sn{η-C_5H_2(1,2,4-$SiMe_3$)}$_2$], α = 162° and [Sn(η-C_5Ph_5)$_2$], α = 180°}.[1–4] In [Sn(η-C_5Ph_5)$_2$], the Sn sits on an inversion centre between exactly parallel, planar, staggered and equidistant cyclopentadienyl rings. For this ligand the Ge and Pb,[5] Ni,[6] Fe[7] and Mo[8] analogues have also been synthesised. The main limitation of bulky cyclopentadienyl derivatives such as $C_5Ph_5^-$ and indeed of the free cyclopentadiene ligand precursor, is their insolubility in almost all common organic solvents, *e.g.* crystals of [Sn(η-C_5Ph_5)$_2$] were grown only from hot 1-methylnaphthalene. Improved solubility may be obtained by modifying the phenyl groups of the pentaphenylcyclopentadiene but none of the resulting derivatives afford crystalline products,[9] even though pentaphenylcyclopentadiene and its bromide, C_5Ph_5Br, have been known for some seventy years.[10]

We now report a facile, high yield route to sterically saturated bis(cyclopentadienyl) derivatives of main-group and transition metals, the molecular structure of [Sn(η-Cp^s)$_2$] **1** and the molecular structure of [Fe(η-Cp^s)$_2$] **2**.

The Cp^s ligand and its lithium salt were synthesised in high yield from $C_5H_2Me_4$.† Subsequent reaction of 2 equiv. of the lithium salt with $SnCl_2$ in Et_2O affords **1** or similarly with $FeCl_2$ **2**, both in high yield (88.5, 71.3% respectively).‡ Recrystallisation of **1** was from hexane and hexane–toluene for **2**. Compounds **1** and **2** are sufficiently stable to be handled in air for a brief period of time without significant decomposition.

The molecular structure of **1** was determined by a single-crystal X-ray diffraction study and confirmed as monomeric.§ The $SiMe_2Bu^t$ substituents are rotated by 180° with respect to one another, with the Me groups directed towards, and the Bu^t group away from the Sn. Thus the Sn sits on an inversion centre between equidistant cyclopentadienyl rings which are planar, staggered and exactly parallel (Fig. 1) The Si–C(1) bond is bent 1.8° out of the plane of the cyclopentadienyl ring and away from, the Sn centre. The Sn–centroid distance, 2.379(2) Å, is shorter than any previously measured {[Sn(η-C_5Me_5)$_2$], av. 2.396(5), range 2.388–2.400 Å;[1] [Sn(η-C_5Ph_5)$_2$], 2.401(6) Å[4] and [Sn(η-C_5H_5)$_2$], av. 2.422(13), range 2.410–2.436 Å[13]}. The

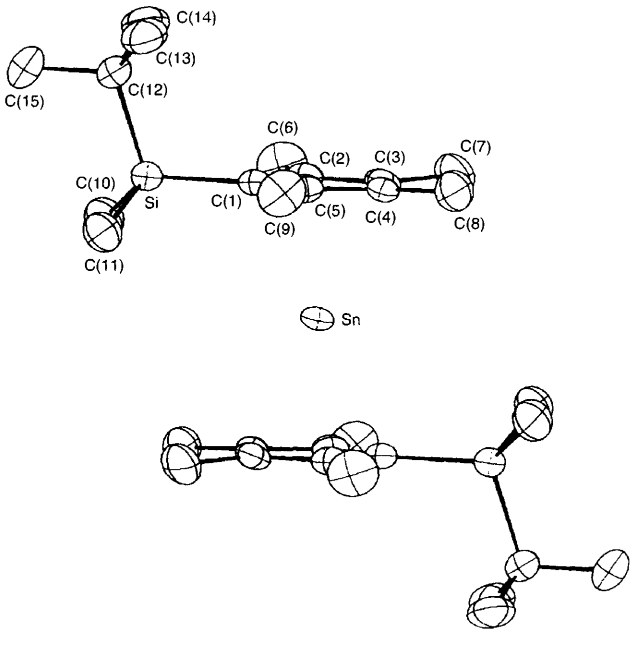

Fig. 1 The molecular structure of [Sn(η-Cp^s)$_2$] **1** and atom numbering scheme with selected bond lengths (Å) and angles (°): Sn–M(1) 2.379(2), Sn–C(1) 2.637(4), Sn–C(2) 2.652(4), Sn–C(3) 2.685(5), Sn–C(4) 2.691(5), Sn–C(5) 2.661(4), Si–C(1) 1.872(4), Si–C(10) 1.873(6), Si–C(11) 1.872(5), Si–C(12) 1.894(5); M(1)–S–M(1′) 180.0. M(1) denotes the centroid of the ring C(1) to C(5).

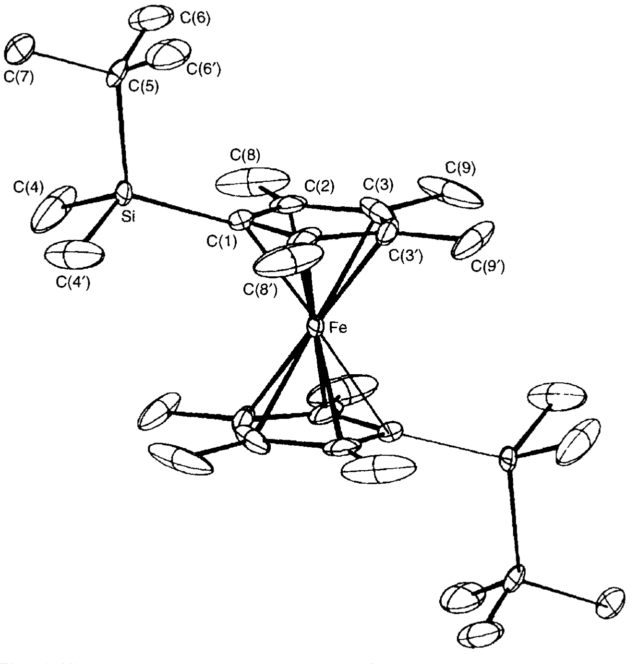

Fig. 2 The molecular structure of [Fe(η-Cp^s)$_2$] **2** and atom numbering scheme with selected bond lengths (Å) and angles (°): Fe–M(1) 1.673(9), Fe–C(1) 2.078(9), Fe–C(2) 2.043(7), Fe–C(3) 2.052(9), Si–C(1) 1.871(10), Si–C(4) 1.854(12), Si–C(5), 1.904(11); M(1)–Fe–M(1′) 180.0. M(1) denotes the centroid of the ring C(1) to C(2′).

average cyclopentadienyl ring C–C bond lengths and angles are unexceptional [1.413(14) Å, 108.0(9)°].

The molecular structure of **2** was also determined by a single-crystal X-ray diffraction study which confirmed that like **1** it too is monomeric and that the Fe sits on an inversion centre between equidistant cyclopentadienyl rings which are planar, staggered and exactly parallel (Fig. 2).¶ In addition, **2** possesses a mirror plane defined by C(5), Si and C(1). Owing to the smaller covalent radius of Fe the cyclopentadienyl rings are closer to one another by 1.4 Å than in **1**. Consequently the Si–C(1) bond is bent further out of the cyclopentadienyl plane (16.6°) than in the Sn analogue. The Fe–centroid distance is 1.673(9) Å. The average Fe–ring carbon distance, 2.054(10) Å, is similar to those measured for [Fe(η-C_5H_5)$_2$] [2.040(2)][14] and [Fe(η-C_5Me_5)$_2$] [2.050(2) Å].[15] The average cyclopentadienyl ring C–C bonds and angles are also unexceptional [1.400(23) Å, 107.98(19)°] and are similar to those measured for [Fe(η-C_5H_5)$_2$] [1.400(2)] and [Fe(η-C_5Me_5)$_2$] [1.419(2) Å]. The thermal ellipsoids suggest some librational disorder of the ligands within the cyclopentadienyl planes. Thus, the geometric parameters for **2** are not particularly accurate (final residuals, R = 0.108 and R' = 0.258). A similarly large R factor (0.159) was also obtained for [Fe(η-C_5Ph_5)$_2$].[16]

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Footnotes

† *Synthesis of* LiCp^s. A Schlenk tube was charged with C_5HMe_4-($SiMe_2Cl$)[11,12] (1.76 g, 8.22 mmol), thf (100 ml), a stirrer-bar and then cooled to −78 °C in a dry-ice–acetone slush-bath. Over a 10 min period 2 equiv. of LiBu^t (16.44 mmol, 1.7 mol dm^{-3} in pentane) was added, with stirring. Stirring was continued for a further 1 h, after which the mixture was allowed to warm to room temp. Stirring was continued for another 2 h and the thf removed *in vacuo*. The residue was washed with cold hexane (3 × 50 ml) and the product extracted with Et_2O (3 × 60 ml). Removal of the Et_2O *in vacuo* afforded LiCp^s as a fine white, air-sensitive powder. Yield 90% (1.79 g, 7.40 mmol). $^{13}C\{^1H\}$ NMR [C_6D_6–thf (5:95), 100.61 MHz], δ 117.28, 111.96, 97.5, 27.22, 14.52, 10.96, 0.85 (the resonance corresponding to the quaternary carbon of the Bu^t group was obscured by solvent); $^{29}Si\{^1H\}$ NMR [C_6D_6–thf (5:95), 79.48 MHz], δ −4.9.

‡ *Syntheses*: [Sn(η-Cp^s)$_2$]; to a Schlenk tube charged with a slurry of $SnCl_2$ (0.38 g, 2 mmol) in Et_2O (30 ml) was added, over a 2 min period with stirring, LiCp^s (1.11 g, 4.6 mmol) dissolved in Et_2O (60 ml). An immediate colour change from white to yellow was accompanied by the formation of a white precipitate. After 12 h stirring the Et_2O was removed *in vacuo* and the product extracted with hexane (50 ml). Removal of the hexane *in vacuo* afforded [Sn(η-Cp^s)$_2$] (1.04 g, 88.5%) as an intensely yellow powder. Mp 177.8 °C. ^1H NMR (C_6D_6, 400.13 MHz), δ 2.07 (s, 6H), 1.95 (s, 6H), 0.97 (s, 9H), 0.32 (s, 6H); $^{13}C\{^1H\}$ NMR (C_6D_6, 100.61 MHz), δ 126.08, 123.64, 111.18, 27.35, 19.48, 13.92, 11.02, −0.28; $^{29}Si\{^1H\}$ NMR (C_6D_6, 79.49 MHz), δ 2.13; $^{119}Sn\{^1H\}$ NMR (C_6D_6, 148.91 MHz), δ −2204. Elemental analysis for $C_{30}H_{54}Si_2Sn$: C 62.02 (61.11), H 9.40 (9.23%).

[Fe(η-Cp^s)$_2$]. A slurry of $FeCl_2$ (0.63 g, 4.92 mmol) in Et_2O (50 ml) was added over a 2 min period, whilst stirring, to LiCp^s (2.38 g, 9.84 mmol) dissolved in Et_2O (80 ml). After 12 h stirring, the Et_2O was removed *in vacuo* and the product extracted with hexane (2 × 50 ml). Removal of the hexane *in vacuo* afforded [Fe(η-Cp^s)$_2$] (1.85 g, 71.3%) as orange crystals. Mp 250.4 °C. ^1H NMR (C_6D_6, 400.13 MHz), δ 1.85 (s, 6H), 1.68 (s, 6H), 0.85 (s, 9H), 0.42 (s, 6H); $^{13}C\{^1H\}$ NMR (C_6D_6, 100.61 MHz), δ 84.92, 84.19, 67.02, 27.27, 20.11, 14.09, 10.89, −1.35; $^{29}Si\{^1H\}$ NMR (C_7D_8, 79.49 MHz), δ 4.22. Elemental analysis for $C_{30}H_{54}Si_2Fe$: C 68.29 (68.40), H 10.40 (10.33%).

§ *Crystal data* for **1** and **2**: for both compounds, crystallographic measurements were made on an Enraf-Nonius CAD4 diffractometer using Mo-Kα radiation, λ = 0.71073 Å. The structures were solved by direct methods and refined on F^2 by a full-matrix least-squares procedure. For **1**: $C_{30}H_{54}Si_2Sn$, T = 293(2) K. Specimen 0.3 × 0.3 × 0.2 mm, M = 589.6, monoclinic, space group $P2_1/n$, a = 13.126(2), b = 9.135(7), c = 13.769(2) Å, β = 92.41(10)°, U = 1649.5(13) Å^3, D_c = 1.19 g cm^{-3}, Z = 2. For reflections with $\theta < 25°$, $R(F)$ = 0.043 for 1956 observed reflections [$I > 2\sigma(I)$] and $wR(F^2)$ = 0.107 for all 2892 reflections.

¶ *Crystal data* for **2**: $C_{30}H_{54}FeSi_2$, T = 173(2) K. Specimen 0.3 × 0.3 × 0.1 mm, M = 526.8, orthorhombic, space group $Pnnm$ (no. 58), a = 7.969(9), b = 13.957(9), c = 13.448(4) Å, U = 1496(2) Å^3, D_c = 1.17 g cm^{-3}, Z = 2. For reflections with $\theta < 25°$, $R(F)$ = 0.108 for 826 observed reflections [$I > 2\sigma(I)$] and $wR(F^2)$ = 0.311 for all 1383 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 182/47.

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