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A New C_2-Symmetric Ligand for *ansa*-Metallocene Chemistry: Synthesis and X-ray Crystal Structure of the *ansa*-Stannocene Complex *rac*-[(CHBu^t)$_2$(C$_5$H$_2$Bu^t$_2$)$_2$]Sn

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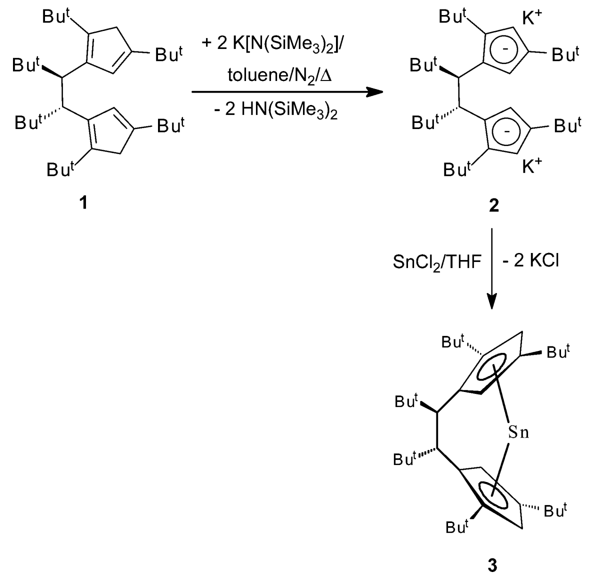
Summary: Reaction of the sterically demanding ligand precursor [(CHBu^t)$_2$(C$_5$H$_2$Bu^t$_2$)$_2$]K$_2$ with SnCl$_2$ in THF gave the air-stable ansa-stannocene complex rac-[(CHBu^t)$_2$(C$_5$H$_2$Bu^t$_2$)$_2$]Sn. A single-crystal X-ray structure of the ansa-stannocene revealed a C_2-symmetric and slipped bent structure, with the Sn^{2+} displaced toward an η^2 bonding mode between bridged, highly tilted, and staggered 2,4-di-tert-butylcyclopentadienyl rings.

Structurally diverse cyclopentadienyl ligands have important applications in main-group metallocene chemistry, and the investigation of ligand influences on structure and reactivity is a stimulating and expanding area of research.[1] Within the p block a diverse range of structural types have been observed and some electronic and structural aspects discussed in the literature.[1,2] Although bridged cyclopentadienyl (*ansa*) ligands play key roles in stabilizing and directing the reactivity of many metallocene complexes of the s, d, and f block elements,[3] there have been relatively few reports of p block *ansa*-metallocenes.[4] Our research is directed at the use of the sterically demanding C_2-symmetric, bridged dicyclopentadiene compound *rac*-[(CHBu^t)$_2$(C$_5$H$_3$Bu^t$_2$)$_2$] (**1**)[5] as a starting material for d, f, and main-group element chemistry. In this paper we report the single-crystal X-ray structure and NMR spectroscopic properties of the air-stable C_2-symmetric *ansa*-stannocene complex *rac*-[(CHBu^t)$_2$(C$_5$H$_2$Bu^t$_2$)$_2$]Sn (**3**), synthesized from the dicyclopentadienyl salt [(CHBu^t)$_2$(C$_5$H$_2$Bu^t$_2$)$_2$]K$_2$ (**2**) and SnCl$_2$ (Scheme 1). After an extensive literature search, we found that **3** is the first example of a p block *ansa*-metallocene characterized by single-crystal X-ray crystallography.

Scheme 1



The synthesis of **3** was carried out using a two-step procedure from **1** (Scheme 1).[6] Deprotonation of **1** with K[N(SiMe$_3$)$_2$] gave a quantitative yield of the air-sensitive ligand precursor **2**, which was purified by washing with toluene and pentane under N$_2$ to remove HN(SiMe$_3$)$_2$ and excess K[N(SiMe$_3$)$_2$]. The reaction of **2** with a slight excess of SnCl$_2$ in THF produced a greenish brown reaction mixture due to the formation of **3** and small amounts of unidentified byproducts (^{1}H NMR). Filtration of solids from a solution of the crude product in pentane gave a yellow filtrate from which pale yellow crystalline crops of **3** were obtained (30% combined yield) by repeated cooling of the mother liquor to −20 °C.

The single-crystal X-ray diffraction analysis[7] of **3** (Figure 1) shows a unique C_2-symmetric structure with the Sn^{2+} displaced toward an η^2 bonding mode between bridged 2,4-di-*tert*-butylcyclopentadienyl rings. Although structural data for a group 14 *ansa*-metallocene[4] is not available for direct comparison to **3**, analysis of

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(1) (a) Jutzi, P.; Burford, N. *Chem. Rev.* **1999**, *99*, 969 and references therein.

(2) (a) Beswick, M. A.; Palmer, J. S.; Wright, D. S. *Chem. Soc. Rev.* **1998**, *27*, 225. (b) Baxter, S. G.; Cowley, A. H.; Lasch, J. G.; Lattman, M.; Sharum, W. P.; Stewart, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 4064. (c) Constantine, S. P.; Cox, H.; Hitchcock, P. B.; Lawless, G. A. *Organometallics* **2000**, *19*, 317. (d) Smith, J. D.; Hanusa, T. P. *Organometallics* **2001**, *20*, 3056.

(3) Shapiro, P. J. *Coord. Chem. Rev.* **2002**, *231*, 67 and references therein.

(4) Syntheses were reported, but crystal structure data were unavailable for [C$_2$Me$_4$(C$_5$H$_5$)$_2$]M (M = Sn, Pb),[4a] *o*-, *m*-, and *p*-[C$_6$H$_4$-(CH$_2$C$_5$H$_4$-η^5)$_2$]Sn,[4b] and [C$_2$H$_4$(Me$_2$Si(Me$_4$C$_5$H))$_2$]M (M = Sn, Ge).[4c] (a) Tacke, M. *Organometallics* **1994**, *13*, 4124. (b) Dory, T. S.; Zuckerman, J. J. *J. Organomet. Chem.* **1984**, *264*, 295. (c) Jutzi, P.; Dickbreder, R. *Chem. Ber.* **1986**, *119*, 1750.

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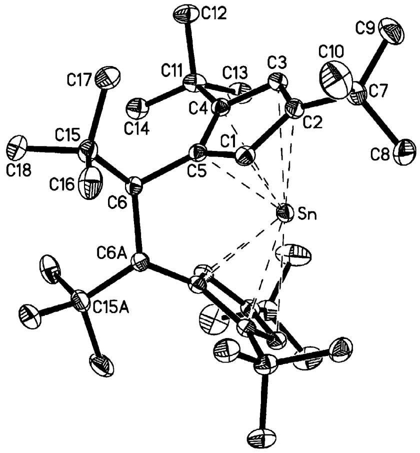

Figure 1. Structure of *rac*-$[(CHBu^t)_2(C_5H_2Bu^t{}_2)_2]Sn$ (**3**). Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Sn−C1 = 2.509(2), Sn−C2 = 2.822(2), Sn−C3 = 2.871(2), Sn−C4 = 2.680(2), Sn−C5 = 2.466(2), C1−C2 = 1.423(3), C2−C3 = 1.387(3), C3−C4 = 1.430(3), C4−C5 = 1.439(3), C1−C5 = 1.439(3), C6−C6A = 1.601(4), Sn−(ring normal) = 2.329(1), Sn−(ring centroid) = 2.385; (ring normal)−Sn−(ring normal) = 104.6, (ring centroid)−Sn−(ring centroid) = 129.4, Sn−(ring centroid)−(ring plane) = 77.6.

ansa-metallocene geometric parameters reveals the characteristic "slipped-bent" structure for **3**. The relatively small value for the (ring normal)−Sn−(ring normal) angle ($\beta = 104.6°$) as well as the angle between the Sn−(ring centroid) vectors and the least-squares planes of the 2,4-di-*tert*-butylcyclopentadienyl rings (δ 77.6°) compare well with those reported for the bis(2,5-di-*tert*-butylazacyclopentadienyl)tin complex, $[C_4(Bu^t)_2H_2N]_2Sn$ ($\beta = 114.4°$, $\delta = 75.95°$),[8] and are substantially smaller than the same angles in $[C_5(Pr^i)_4H]_2Sn$ ($\beta = 152.2°$, $\delta = 83.60°$)[9] and $[C_5(PhCH_2)_5]_2Sn$ ($\beta = 147.2°$, $\delta = 85.65°$).[10] The 24.8° difference between the (ring centroid)−Sn−(ring centroid) γ (129.4°) and β (104.6°) angles for **3** is also reflected in the large differences between Sn−ring C distances (largest difference 0.41 Å: Sn−C5, 2.466(2) Å; Sn−C3, 2.871(2) Å, Figure 1) and the distance that the projections of the Sn−(ring normal) and the Sn−(ring centroid) vectors onto the ring plane are displaced relative to each other (slippage from ideal η^5 coordination 0.51 Å). A notable feature in the structure of **3** is the considerable twist observed about the C6−C6A bond axis compared to **1** (Figure 2). The result is a larger ring torsion angle (C5(C6C6A)C5A, $\theta_{ring} = 34.4(3)°$) and a correspondingly smaller bridge torsion angle (C15(C6C6A)C15A, $\theta_{bridge} = 74.0(3)°$) for **3** compared to **1**[5] ($\theta_{ring} = 15.6(2)°$, $\theta_{bridge} = 119.0(1)°$) and 2,4-di-*tert*-butylcyclopentadienyl rings which approach a staggered conformation (Figure 2). In the crystal structure molecules of **3** lie on special positions imposed by the *C*2/*c* space group with no obvious crystal-packing effects that account for the observed geometric parameters.

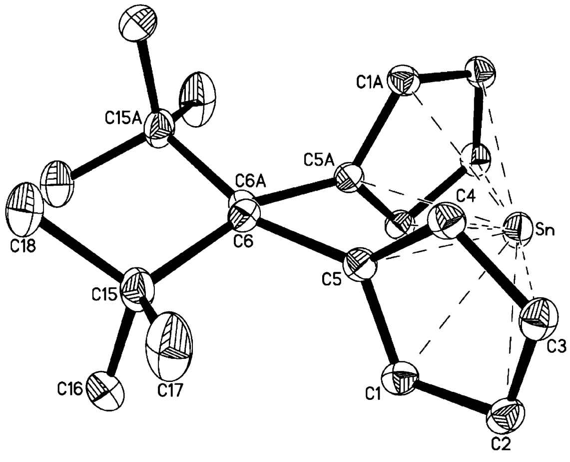

Figure 2. View of **3** along the C6−C6A bond axis showing the staggered conformation of the 2,4-di-*tert*-butylcyclopentadienyl rings. Thermal ellipsoids are shown at the 50% probability level. The ring torsion angle is 34.4(3)°, and the bridge torsion angle is 74.0(3)°.

The C_2-symmetric and slipped metallocene structure was also apparent from analysis of the solution NMR spectrum of **3**. Pairs of symmetry-related Bu^t and bridge-C*H*Bu^t protons gave rise to well-resolved singlet peaks in the ^1H NMR spectrum of **3**. Comparison of the ^1H NMR spectra of **2** and **3** (Figure 3) shows the ring $^4J_{H-H}$ coupling as well as $Sn^{117(119)}$ satellites observed for only one ring-C*H* resonance, with the $^4J_{H-H}$ (2.6 Hz) and $^2J_{Sn-H}$ (27.3 Hz) coupling constants similar to those reported for the unbridged stannocene complex $[Bu^t{}_2C_5H_3]_2Sn$ ($^4J_{H-H} = 2.3$ Hz, $^2J_{Sn-H} = 26$ Hz).[11] In the temperature range of −20 to +90° C, line width changes for two of the Bu^t resonances of **3** were observed, but the Sn−H coupling pattern remained

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(6) Synthesis of **2**: compound **1** (1.60 g, 3.24 mmol) was combined with $KN(SiMe_3)_2$ (2.10 g, 10.53 mmol) in toluene (100 mL), and the reaction mixture was vigorously stirred under reflux conditions under N_2 for 16 h. Crude **2** was filtered (medium-porosity frit layered with Celite) from the reaction mixture and the filter cake washed with toluene (50 mL) and pentane (50 mL) under N_2. Vacuum drying gave **2** as an off white, air-sensitive solid in quantitative yield (1.83 g, 99%). ^1H NMR (THF-d_8, 30 °C): δ 0.96, 1.11, 1.39 (s, 54 H, C*Me*$_3$); 3.67 (s, 2H, bridge-C*H*Bu^t); 5.03, 5.25 (d, 4 H, ring-C*H*, $^4J = 2.9$ Hz). ^{13}C NMR (THF-d_8, 30° C): δ 32.8, 34.2, 36.0 (C*Me*$_3$); 32.5, 35.8, 37.7 (*C*Me_3); 49.8 (bridge-*C*HBu^t); 94.7, 101.0 (ring-*C*H); 122.0, 125.9, 126.5 (ring-*C*). Synthesis of **3**: slow dropwise addition of a solution of $SnCl_2$ (0.54 g, 2.85 mmol) in THF (20 mL) to a vigorously stirred solution of **2** (1.56 g, 2.73 mmol) in THF (15 mL) was carried out over a period of 25 min at ambient temperature under N_2. The resulting greenish brown reaction mixture was stirred for 30 min, and THF was removed under vacuum. Extraction of the dark residue into pentane and filtration (medium-porosity glass frit, Celite layer) of solids under N_2 gave a yellow filtrate. Removal of pentane gave 1.67 g of a yellow crude product containing 80% of **3** (^1H NMR). Crystalline crops of **3** were obtained (0.50 g, 30% combined yield) by repeated cooling of pentane solutions of **3** to −20° C. Anal. Calcd for $C_{36}H_{60}Sn$: C, 70.70; H, 9.89. Found: C, 71.07; H, 9.92. ^1H NMR (THF-d_8, 30° C): δ 1.05, 1.17, 1.49 (s, 54 H, C*Me*$_3$); 3.47 (s, 2 H, bridge-C*H*Bu^t); 5.43 (d, 2 H, Bu^tCHC-C*H*CBu^t, $^4J_{H-H} = 2.6$ Hz; dd, $Sn^{117(119)}$ satellites, $^2J_{Sn-H} = 27.3$ Hz); 5.88 (d, Bu^tCC*H*CBu^t). ^{13}C NMR (THF-d_8, 30 °C): δ 32.0, 33.2, 35.7 (C*Me*$_3$); 32.1, 35.0, 37.3 (*C*Me_3); 47.2 (bridge-*C*HBu^t); 101.0, 108.8 (ring-*CH*; d, $Sn^{117(119)}$ satellites, $J_{Sn-C} = 51.2$, 50.4 Hz); 125.5, 135.9, 142.2 (ring-*C*; d, $Sn^{117(119)}$ satellites, $J_{Sn-C} = 66.2$, 26.5, 19.3 Hz). Crystals of high enough quality for single-crystal X-ray diffraction were obtained by washing suitable crystalline crops of **3** with cold (−20 °C) pentane followed by vacuum drying.

(7) Crystal data for **3** (100 K): $C_{36}H_{60}Sn$, $M_w = 611.53$; monoclinic, *C*2/*c* ($a = 20.5919(10)$ Å, $b = 9.9813(5)$ Å, $c = 16.8732(8)$ Å, $\alpha = \gamma = 90°$, $\beta = 108.8930(10)°$, $V = 3281.2(3)$ Å^3, $Z = 4$); $D_c = 1.238$; 9894 reflections collected ($2\theta_{max} = 55°$), 3653 unique ($R_{int} = 0.0397$); Bruker Smart Apex CCD; Mo Kα, $\lambda = 0.710\,73$ Å; final GOF = 1.066, R1 = 0.0296, wR2 = 0.0809 ($I > 2\sigma(I)$); structure solved using Patterson method; refinement, full-matrix least squares on F^2.

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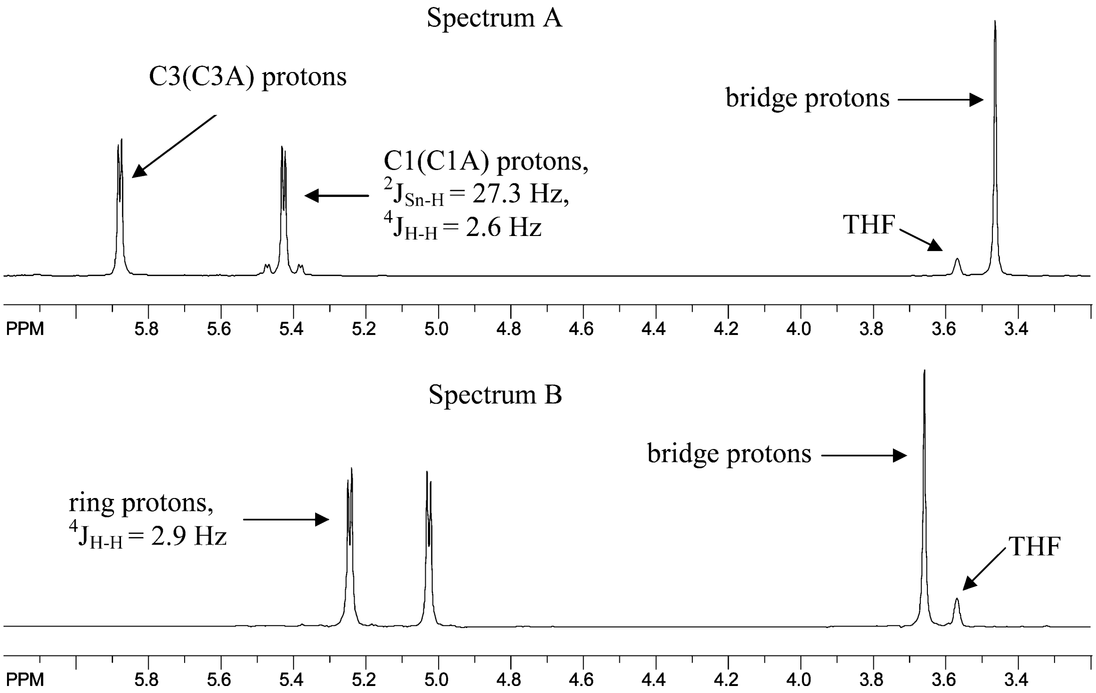

Figure 3. Proton NMR spectra (300 MHz, 30 °C, THF-d_8) in the CHBu^t and ring-CH chemical shift region of **3** (spectrum A) compared to **2** (spectrum B).

temperature invariant. In the ^{13}C NMR spectrum of **3**, Sn$^{117(119)}$ satellites with different $J_{\mathrm{Sn-C}}$ coupling constants were observed for all ring-C resonances, reflecting the unequal Sn−C interactions in the structure of **3**. The NMR data indicate that **3** is conformationally rigid in solution and support the idea that distortions in the bonding observed in the solid state are not an artifact of crystal packing. It is unlikely that the metal-centered lone pair of electrons has any dominant effect[2] on the structure of **3,** and this would be difficult to access, given the rigid *ansa*-ligand backbone. The molecular structure is more likely a result of the conformational limits enforced by the bulky and highly substituted *ansa* ligand of **3**.

Structural data presented for **3** have relevance to the expanding area of p block metallocene chemistry. The future synthesis of chiral metallocenes using **2** will be an ongoing investigation in our group, studying the reactivity of **2** with metal-containing compounds. We are currently investigating the reactivity of **3** as well as the incorporation of d, f, and other main-group elements into the framework of the ligand precursor **2**.

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Supporting Information Available: Text describing experimental details, tables of crystallographic data, figures giving ^{1}H and ^{13}C NMR spectra, and elemental analysis data. This material is available free of charge via the Internet at http://pubs.acs.org.

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