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Synthesis, Characterization, and Molecular Structure of Bis{(*tert*-butyldimethylsilyl)-tetramethylcyclopentadienyl}lead

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Summary: The reaction of 2 equiv of LiCp^s *[Cp*^{s} *=* $C_5Me_4(SiMe_2Bu^t)$*] with* $PbCl_2$ *affords the corresponding metallocene, [Pb(*η^5*-Cp*^{s}*)*$_2$*], in high yield. A single-crystal X-ray analysis reveals the planar cyclopentadienyl rings to be parallel.*

Recently we reported the synthesis of [Sn(η^5-Cp^s)$_2$] in which the sterically demanding cyclopentadienyl ligands, Cp^s, are parallel.[1] To date no such parallel configuration has been structurally characterized for any metallocenes of Pb^{II}, all of which exhibit nonparallel rings,[2–5] although the cyclopentadienyl rings become more parallel as the steric bulk of the ring substituents increases. It has been suggested that, by analogy with the Sn analogue,[6] Pb(η^5-C_5Ph_5)$_2$ also possesses parallel rings[7] (Table 1). We now report the synthesis and molecular structure of [Pb(η^5-Cp^s)$_2$], the first structurally characterized metallocene of Pb^{II} possessing a stereochemically inactive lone pair.

Table 1. Selected Structural Data for Plumbocenes

compd	M_1–Pb–M_2 angle/deg	Pb–M dist/Å
[Pb(η^5-C_5H_5)$_2$]^{a,b}	123	2.502, 2.820
[Pb(η^5-C_5Me_5)$_2$]^c	151	2.525, 2,497
[Pb{η^5-$C_5(CH_2Ph)_5$}$_2$]^d	153	2.507, 2.500
[Pb(η^5-Cp^s)$_2$]^e	180	2.460

[a] Reference 2. [b] Reference 3. [c] Reference 4. [d] Reference 5. [e] This work.

The reaction of 2 equiv of the lithium salt of Cp^s with $PbCl_2$ in Et_2O afforded [Pb(η^5-Cp^s)$_2$] in high yield (84%).[8] Recrystallization from hexane–toluene produced red needlelike crystals of which a single-crystal X-ray analysis revealed that the molecular structure of [Pb-

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(8) *Synthesis of [Pb(*η*-Cp*^{s}*)*$_2$*]:* To a Schlenk tube charged with a slurry of $PbCl_2$ (0.60 g, 2.15 mmol) in Et_2O (40 mL) at −78 °C was added over a 2 min period, with stirring, LiCp^s (1.04 g, 4.30 mmol) dissolved in Et_2O (40 mL). On warming of the solution to *ca.* −20 °C, a color change from white to yellow was observed. After stirring of the mixture at room temperature for 2 h, a white precipitate was formed and the color of the solution changed to deep orange. After a further 2 h of stirring, the solution was filtered and the Et_2O removed *in vacuo* to afford [Pb(η^5-Cp^s)$_2$] (1.20 g, 1.80 mmol) in 84% yield. Recrystallization from hexane–toluene afforded red needles. Mp: 178.5 °C. ^1H NMR (C_6D_6, 400.13 MHz): δ 2.27 (s, 6H), 2.11 (s, 6H), 0.97 (s, 9H), 0.32 (s, 6H). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.61 MHz): δ 127.05, 124.38, 111.09, 27.30, 19.86, 13.56, 10.66, −0.21. $^{29}Si\{^1H\}$ NMR (C_6D_6, 99.33 MHz): δ −3.11. $^{207}Pb\{^1H\}$ NMR (C_6D_6, 104.61 MHz): δ −4595. ^{13}C CP MAS NMR (400.13 MHz): δ 129, 128, 112, 30, 24, 16, 14, 4. ^{29}Si CP MAS NMR (79.48 MHz, 10.5 kHz): δ −1. ^{207}Pb CP MAS NMR (83.69 MHz): δ −4692. EI MS: M^+, *m/z* 678; M^+ − Cp^s, *m/z* 443; M^+ − Cp^s − Pb, *m/z* 235. Anal. Calcd (found) for $C_{30}H_{54}Si_2Pb$: C, 52.66 (53.14); H, 8.04 (8.03).

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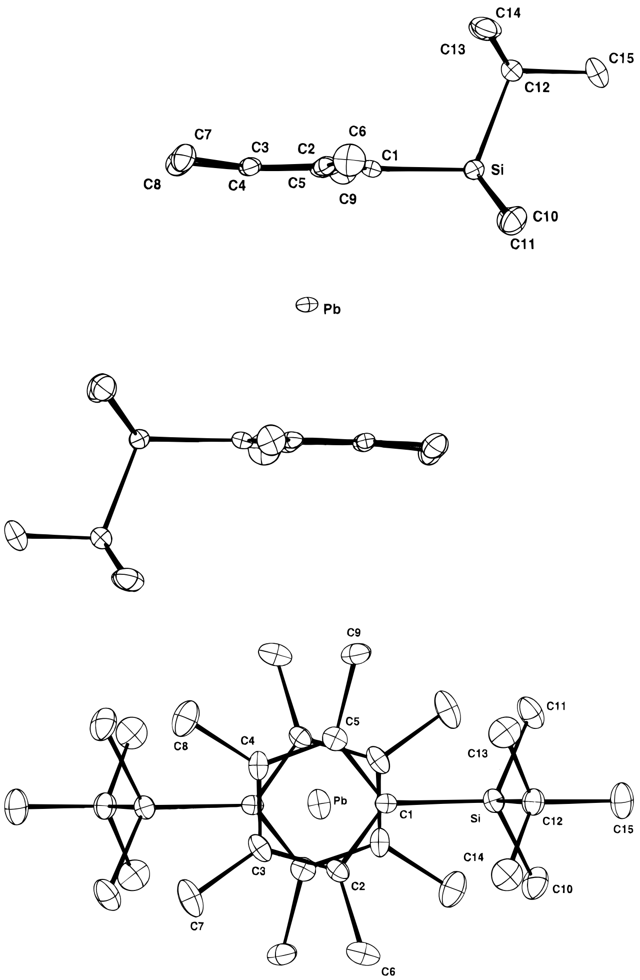

Figure 1. Molecular structure of $[Pb(\eta^5\text{-}Cp^s)_2]$ and atom-numbering scheme with selected bond lengths (Å) and angles (deg): Pb−M(1) 2.460(5), Pb−C(1) 2.707(5), Pb−C(2) 2.731(5), Pb−C(3) 2.770(5), Pb−C(4) 2.773(5), Pb−C(5) 2.736(5), Si−C(1) 1.869(5), Si−C(10) 1.874(6), Si−C(11) 1.866(6), Si−C(12) 1.899(6), M(1)−Pb−M(1′) 180.0. M(1) denotes the centroid of the ring C(1)−C(5).

$(\eta^5\text{-}Cp^s)_2]$ was isomorphous with its Sn analogue.[9] The Pb atom sits on an inversion centre between equidistant cyclopentadienyl rings which are planar, staggered, and exactly parallel (Figure 1). The $SiMe_2Bu^t$ substituents are rotated by 180° with respect to one another, with the Me groups directed toward, and the Bu^t group away from, the Pb. Despite the bulk of the cyclopentadienyl ligands the Pb−centroid distance, 2.460(5) Å, is shorter than those previously measured for any metallocene of Pb^{II} (Table 1). The average cyclopentadienyl ring C−C bond lengths and angles are unexceptional [1.427(16) Å, 108(10)°].

The solution-state ^{207}Pb NMR spectrum of $[Pb(\eta^5\text{-}Cp^s)_2]$ consists of a single resonance at δ −4595 which compares well with other mononuclear Pb^{II} metallocenes for which ^{207}Pb NMR data have been reported (Table 2). The solid-state ^{207}Pb NMR isotropic shift, δ_{iso}, is −4692.[10,11] Interestingly, though no solution-state ^{207}Pb NMR data have been reported for $Pb(\eta^5\text{-}C_5Ph_5)_2$, due to its insolubility in common organic solvents, the solid-state ^{207}Pb δ_{iso} is reported as −6150.[12] The large difference between these two values may be due to either (i) a substantial difference in the structures of $Pb(\eta^5\text{-}C_5Ph_5)_2$ and $[Pb(\eta^5\text{-}Cp^s)_2]$ {corresponding solid-state ^{119}Sn NMR data for $[Sn(\eta^5\text{-}Cp^s)_2]$[11] and $[Sn(\eta^5\text{-}C_5Ph_5)_2]$[12] ($\delta_{iso} = -2236$ and -2215, respectively) differ little, and on the basis of these data, the predicted ^{207}Pb chemical shifts for $Pb(\eta^5\text{-}C_5Ph_5)_2$ and $[Pb(\eta^5\text{-}Cp^s)_2]$ would be $\delta_{iso} = -4929$ and -5043, respectively}[13] or (ii) a difficulty, due to the large csa associated with solid-state ^{207}Pb NMR spectroscopy, in the original assignment of δ_{iso} for $Pb(\eta^5\text{-}C_5Ph_5)_2$.

Table 2. Solution-State ^{207}Pb NMR Chemical Shift Data for Metallocenes of Pb^{II}

compd	$\delta(^{207}Pb)$
$[Pb(\eta^5\text{-}C_5Me_5)_2]^{a,b}$	−4390 or −4384
$Pb[\eta^5\text{-}C_5Me_4\{SiMe_2(C_5HMe_4)\}]_2^{c}$	−4538
$[Pb(\eta^5\text{-}Cp^s)_2]^{d}$	−4595
$Pb(\eta^5\text{-}C_5H_3Bu^t{}_2)_2^{e}$	−4756
$[Pb(\eta^5\text{-}C_5H_5)_2]^{a}$	−5030

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Supporting Information Available: Tables of X-ray data, positional and thermal parameters, bond distances and angles, and least-squares planes (7 pages). Ordering information is given on any current masthead page.

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(9) *Crystal data for $[Pb(\eta^5\text{-}Cp^s)_2]$ ($C_{30}H_{54}PbSi_2$):* Crystallographic measurements were made on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation, $\lambda = 0.710\,73$ Å. The structure was solved by direct methods and refined on F^2 by a full-matrix least-squares procedure. $T = 173(2)$ K. Data: specimen $0.3 \times 0.3 \times 0.2$ mm; $M = 678.1$; monoclinic, space group $P2_1/n$ (nonstandard No. 14); $a = 12.945(3)$, $b = 9.219(4)$, $c = 13.661(4)$ Å; $\beta = 93.96(2)°$; $V = 1626.4(9)$ Å^3; $D_c = 1.39$ g cm^{-3}; $Z = 2$. For reflections with $2 < \theta < 28°$, $R(F) = 0.044$ for 2734 observed reflections [$I > 2\sigma(I)$] and $wR(F^2) = 0.104$ for all 3903 reflections.

(10) A sample of $[Pb(\eta^5\text{-}Cp^s)_2]$ was ground in a glovebox operating at <1 ppm H_2O and <1 ppm O_2 and packed into zirconia rotors with Kel-F end caps and spun with N_2. NMR experiments were performed on a Bruker DMX-400 spectrometer (89 mm wide-bore magnet) with a 4 mm variable temperature double-bearing probe. The irradiation and detection frequencies were 400.13 and 83.69 MHz for ^1H and ^{207}Pb, respectively. At spin rates in excess of 8 kHz a variable-amplitude (triangular ramp ± 30%) cross-polarization contact pulse was employed. The principal components of the chemical shift tensors have been determined from spinning sideband analysis.

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