

Mercurycyclopentadienyl Derivatives Are Not Always Fluxional

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Over the past 30 years, the behavior of the cyclopentadienyl derivatives of Hg has been the subject of some dispute.¹ Initial reports of the nonfluxional behavior of $[\text{Hg}(\eta^1\text{-C}_5\text{Me}_5)_2]$ were quickly discounted and shown to be due to the dimer, $(\text{C}_5\text{Me}_5)_2$, derived from the facile thermal decomposition of $[\text{Hg}(\eta^1\text{-C}_5\text{Me}_5)_2]$.³ Subsequently all cyclopentadienyl derivatives of Hg reported to date have been presented as highly fluxional η^1 systems, both in solution,^{4–6} and often also in the solid state.⁷ We now report the synthesis and molecular structures of $[\text{Hg}(\eta^1\text{-Cp}^s)_4]$ **1** and $[\text{Hg}(\eta^1\text{-Cp}^s)_2]$ **2** $\{\text{Cp}^s = \text{C}_5\text{Me}_4(\text{SiMe}_2\text{Bu}')\}$ which are the first examples of Hg cyclopentadienyl derivatives not to exhibit “ring whizzing” behavior.

The reaction of either 1 or 2 equiv of the lithium salt of Cp^s with HgCl_2 in Et_2O at low temperature afforded **1** and **2**, respectively.⁸ The molecular structure of **1**⁹ showed two crystallographically independent Hg centers [Hg(1) and Hg(2)] within the unit cell (Figure 1). Each Hg atom is bound to a Cl atom [Hg(1)–Cl(1) 2.333(7) Å and Hg(2)–Cl(2) 2.336(6) Å] and, despite the bulk of the $\text{SiMe}_2\text{Bu}'$ substituent, also bound in an η^1 manner to the ring carbon atoms C(1) and C(16) [2.13(2) and 2.09(2) Å, respectively]. A second two Hg centers [Hg(1') and Hg(2')] related to the first by an inversion center are also present. In addition to the Hg(1)–Cl(1) and Hg(2)–Cl(2) bonds, weaker Hg–Cl interactions, Hg(1)–Cl(2') and Hg(2)–Cl(1) [3.105(6) and 3.117(7) Å, respectively], result in a novel tetrameric structure for **1**. $[\text{Hg}(\eta\text{-C}_5\text{Me}_5)\text{Cl}]$, the only other structurally characterized “Hg($\eta\text{-Cp}$)X” derivative, is polymeric.¹⁰ A single-crystal X-ray analysis of **2** revealed it to be monomeric.¹¹ The Hg atom, sitting on an inversion center, is once again bound, in an η^1 manner, to each of the ring carbon atoms C(1) and C(1') bearing the $\text{SiMe}_2\text{Bu}'$ substituents (Figure 2). The Hg–C(1) distance, 2.136(3) Å, compares well with other Hg η^1 bound cyclopentadienyl systems. The cyclopentadienyl rings are planar and unlike $[\text{Hg}(\eta\text{-C}_5\text{H}_5)_2]$ ¹² or $[\text{Hg}(\eta^1\text{-C}_5\text{Bu}'_3\text{H}_2)_2]$ ¹³ exactly parallel. The $\text{SiMe}_2\text{Bu}'$ substituents are rotated by 180° with respect to one another, with the Me groups directed toward and the Bu' group away from the Hg. The molecular structures of **1** and **2** represent the first structurally characterized pair of related mono- and bis-cyclopentadienyl Hg compounds.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1** and **2** each displayed eight resonances at 298 K (Figure 3a). The value of both the chemical

shifts and Hg coupling constants observed for the ring carbon atoms bearing the $\text{SiMe}_2\text{Bu}'$ substituents are very similar to those observed in the limiting low-temperature spectrum reported for the η^1 bound C atoms of $[\text{Hg}(\eta^1\text{-C}_5\text{Me}_5)\text{Cl}]$. Conclusive evidence for the nonfluxional behavior of **1** and **2**, however, comes from three principle observations: (i) The $^{13}\text{C}\{^1\text{H}\}$ CP MAS shifts, particularly for the η^1 bound C atoms are almost identical with those observed in solution (Table 1). (ii) None of the ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ solution state chemical shifts were significantly temperature dependent. (iii) The $^nJ(^{13}\text{C}\text{--}^{199}\text{Hg})$ couplings remained constant from +30 to –38 °C. Below the latter temper-

(8) To a Schlenk tube charged with a slurry of HgCl_2 (1.68 g, 6.19 mmol) in Et_2O (20 mL), cooled to –78 °C using a dry ice/acetone slush bath, was added over a 2 min period with stirring a slurry of $\text{LiC}_5\text{Me}_4(\text{SiMe}_2\text{Bu}')$ (1.50 g, 6.19 mmol) in Et_2O (50 mL) at –78 °C. Stirring was continued for 0.5 h, after which the mixture was allowed to warm to 0 °C using an ice bath. After an additional 2 h of stirring, $[\text{Hg}\{\eta\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{Bu}')\}_2]$ was obtained as a pale orange, O_2 and H_2O stable powder by filtration of the solution and removal of the Et_2O in vacuo. Yield 85% (2.48 g, 5.26 mmol). Recrystallization from toluene at ca. –28 °C afforded pale orange prisms, mp > 70 °C (dec). ^1H NMR (CD_2Cl_2 , 400.13 MHz, 298 K): δ 2.05 [s, 6H], 1.85 [s, 6H], $^4J(\text{H}\text{--}^{199}\text{Hg})$ 76.9 Hz, 0.67 [s, 9H], 0.39 [s, 6H], $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100.61 MHz, 298 K): δ 136.50 [$C_{\text{meta}}\text{-}^2J(\text{C}\text{--}^{199}\text{Hg})$] 109.7 Hz, 131.85 [$C_{\text{ortho}}\text{-}^3J(\text{C}\text{--}^{199}\text{Hg})$] 128.4 Hz, 82.35 [$C_{\text{ipso}}\text{-}^1J(\text{C}\text{--}^{199}\text{Hg})$] 986.2 Hz, 27.39 [$\text{C}\text{--}(\text{CH}_3)_3$], 21.34 [$\text{C}\text{--}(\text{CH}_3)_3$], $^3J(\text{C}\text{--}^{199}\text{Hg})$ 109.5 Hz, 16.39 [$C_{\text{ortho}}\text{--CH}_3$], 11.58 [$C_{\text{meta}}\text{--CH}_3$], 0.03 [$\text{Si}\text{--CH}_3$]. $^{29}\text{Si}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 79.49 MHz, 298 K): δ 3.25 [$^2J(\text{Si}\text{--}^{199}\text{Hg})$] 221.6 Hz, $^1J(\text{Si}\text{--C})$ 52.5 Hz. $^{199}\text{Hg}\{^1\text{H}\}$ NMR (71.66 MHz, 298 K): δ –1270.72 [CD_2Cl_2], –1219.40 [C_7D_8], $^4J(^{199}\text{Hg}\text{--H})$ 70.9 Hz, $\Delta\delta$ (ppm/K) 0.0]. T_1 (Inversion recovery, 9 data points): 4.9 ms [235 K], 11.3 ms [255 K], 19.8 ms [275 K]. ^{13}C CP MAS (100.61 MHz): δ 138–133 [C_{meta} and C_{ortho}], 83 and 82 [$C_{\text{ipso}}\text{-}^1J(\text{C}\text{--}^{199}\text{Hg})$] 1130 and 1093 Hz], 30 [$\text{C}\text{--}(\text{CH}_3)_3$], 24 [$\text{C}\text{--}(\text{CH}_3)_3$], 20–12 [C_{ortho} and C_{meta}], 5–2 [$\text{Si}\text{--CH}_3$]. ^{29}Si CP MAS (79.49 MHz): δ 5 & 4 [$^2J(\text{Si}\text{--}^{199}\text{Hg})$] 248 Hz]. ^{199}Hg CP MAS (71.66 MHz): δ –808, –814, –824, –830. EI MS: $M^+ m/z$ 472 (28%), [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Bu}')\}]^+ m/z$ 235 (52%), [$\text{SiMe}_3\text{--}^+ m/z$ 73 (100%)]. Anal. Calcd (found) for $\text{C}_{15}\text{H}_{27}\text{--SiHgCl}$: C, 38.44 (38.21); H, 5.87 (5.77%). To a Schlenk tube charged with $[\text{Hg}\{\eta\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{Bu}')\}_2]$ (0.50 g, 1.06 mmol) in Et_2O (20 mL), cooled to –78 °C using a dry ice/acetone slush bath, was added over a 2 min period with stirring a slurry of $\text{LiC}_5\text{Me}_4(\text{SiMe}_2\text{Bu}')$ (0.26 g, 1.06 mmol) in Et_2O (20 mL) at –78 °C. Stirring was continued for 0.5 h, after which the mixture was allowed to warm to 0 °C using an ice bath. After an additional 1 h of stirring at 0 °C, $[\text{Hg}\{\eta\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{Bu}')\}_2]$ was obtained as a yellow, O_2 and H_2O stable powder by filtration of the solution and removal of the Et_2O in vacuo. Yield 95% (0.68 g, 1.01 mmol). Recrystallization from toluene at ca. –28 °C afforded yellow cubes, mp > ca. 60 °C (dec). ^1H NMR (CDCl_3 , 400.13 MHz): δ 1.97 [s, 6H], 1.88 [s, 6H], $^4J(\text{H}\text{--}^{199}\text{Hg})$ 37.6 Hz], 0.59 [s, 9H], 0.26 [s, 6H], $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.61 MHz): δ 133.56 [$C_{\text{meta}}\text{-}^3J(\text{C}\text{--}^{199}\text{Hg})$] 131.05 [$C_{\text{ortho}}\text{-}^2J(\text{C}\text{--}^{199}\text{Hg})$] 63.6 Hz, 87.21 [$C_{\text{ipso}}\text{-}^1J(\text{C}\text{--}^{199}\text{Hg})$] 405.5 Hz], 27.57 [$\text{C}\text{--}(\text{CH}_3)_3$], 22.09 [$\text{C}\text{--}(\text{CH}_3)_3$], $^3J(\text{C}\text{--}^{199}\text{Hg})$ 55.2 Hz], 16.28 [$C_{\text{ortho}}\text{--CH}_3$], 11.74 [$C_{\text{meta}}\text{--CH}_3$], –0.13 [$\text{Si}\text{--CH}_3$]. $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 79.49 MHz): δ 0.42 [$^2J(\text{Si}\text{--}^{199}\text{Hg})$] 126.4 Hz, $^1J(\text{Si}\text{--}^{13}\text{C})$ 49.4 Hz]. $^{199}\text{Hg}\text{--}\{^1\text{H}\}$ NMR (CDCl_3 , 71.66 MHz): δ –1112.35 [$\Delta\delta$ (ppm/K) 1.0]. ^{13}C CP MAS (100.61 MHz): δ 138, 137, 132, 131 [C_{meta} and C_{ortho}], 85 [$C_{\text{ipso}}\text{-}^1J(\text{C}\text{--}^{199}\text{Hg})$] 330 Hz], 30 [$\text{C}\text{--}(\text{CH}_3)_3$], 24 [$\text{C}\text{--}(\text{CH}_3)_3$], 18, 14, 13 [C_{ortho} and C_{meta}], 3 [$\text{Si}\text{--CH}_3$]. ^{29}Si CP MAS (79.49 MHz): δ 3 [$^2J(\text{Si}\text{--}^{199}\text{Hg})$] 134 Hz]. ^{199}Hg CP MAS (71.66 MHz): δ –884. EI MS: $M^+ m/z$ 672 (53%), [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Bu}')\}]^+ m/z$ 235 (35%), [$\text{C}_5\text{Me}_4(\text{SiMe}_2\text{Bu}')\text{--}^+ \text{Bu}' m/z$ 177 (100%). Anal. Calcd (found) for $\text{C}_{30}\text{H}_{54}\text{Si}_2\text{Hg}$: C, 53.74 (53.66); H, 8.35 (8.11).

(9) Crystal data for $[\text{Hg}(\eta^1\text{-Cp}^s)(\mu\text{-Cl})_2]$ ($\text{C}_{60}\text{H}_{108}\text{Cl}_4\text{Hg}_4\text{Si}_4$): The structure was solved by direct methods and refined on F^2 by the full-matrix least-squares procedure. For $T = 173(2)$ K, specimen $0.3 \times 0.2 \times 0.1$ mm (cut from a large crystal), $M = 1886$, triclinic, spacegroup $P1$ (No. 2), $a = 8.940(10)$, $b = 14.02(2)$, and $c = 14.04(2)$ Å, $\alpha = 92.01(12)^\circ$, $\beta = 95.91(11)^\circ$, $\gamma = 98.50(11)^\circ$, $V = 1730(4)$ Å³, $D_{\text{calcd}} = 1.81$ g cm^{–3}, $Z = 4$. For reflections with $2 \leq \theta \leq 25$, $R(F) = 0.081$ for 3978 observed reflections [$I > 2\sigma(I)$] and $wR(F^2) = 0.231$ for all 6077 reflections.

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(11) Crystal structure data for $[\text{Hg}\{\eta^1\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{Bu}')\}_2]$: The structure was solved by direct methods and refined on F^2 by the full-matrix least-squares procedure. For $\text{C}_{30}\text{H}_{54}\text{HgSi}_2$: $T = 173(2)$ K, specimen $0.3 \times 0.2 \times 0.08$ mm, $M = 671.5$, triclinic, spacegroup $P1$ (No. 2), $a = 8.744(4)$, $b = 8.769(6)$, and $c = 11.136(4)$ Å, $\alpha = 80.72(4)^\circ$, $\beta = 76.59(3)^\circ$, $\gamma = 76.23(5)^\circ$, $V = 801.6(7)$ Å³, $D_{\text{calcd}} = 1.39$ g cm^{–3}, $Z = 1$. For reflections with $2 \leq \theta \leq 25$, $R(F) = 0.0218$ for 2827 observed reflections [$I > 2\sigma(I)$] and $wR(F^2) = 0.0554$ for all 2827 reflections.

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Table 1. Selected NMR Chemical Shift Data for **1**, **2**, and [Hg(η^1 -C₅Me₅)Cl]

compound	$^{13}\text{C}\{^1\text{H}\}$ δ /ppm ($^nJ\{^{199}\text{Hg}-^{13}\text{C}\}$)/Hz	$^{199}\text{Hg}\{^1\text{H}\}$ δ /ppm
1 (CD ₂ Cl ₂ 298 K) CPMAS	136.51 (109), 131.88 (127), 82.38 (986), 27.44, 21.37 (107), 16.44, 11.63, 0.07 138–133, 83 (1130), 82 (1093), 30, 24, 20–12, 5–2	–1219 –808, –814, –824, –830
2 (C ₇ D ₈ 298 K) CPMAS	133.92(47), 130.50 (72), 86.95 (405), 27.48, 22.01 (55), 16.16, 11.50, 0.23	–1127 –884
[Hg(η^1 -C ₅ Me ₅)Cl] (CD ₂ Cl ₂ 300 K) (CD ₂ Cl ₂ 193 K)	13.4 133.9, 133.3, 79.8 (1266), 17.7, 12.1, 11.1.	

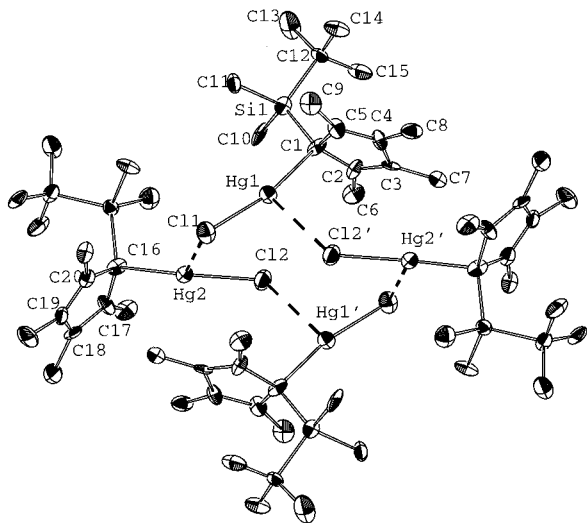


Figure 1. The molecular structure of **1** and atom numbering scheme with selected bond lengths (Å) and angles (deg): Hg(1)–C(1) 2.13(2), Hg(1)–Cl(1) 2.333(7), Hg(1)–Cl(2') 3.105(6), Hg(2)–C(16) 2.09(2), Hg(2)–Cl(2) 2.336(6), Hg(2)–Cl(1) 3.117(7), C(1)–Hg(1)–Cl(1) 167.5(5), Cl(1)–Hg(1)–Cl(2') 98.7(5), Hg(1)–Cl(1)–Hg(2) 91.4(2), C(16)–Hg(2)–Cl(2) 163.6(6), Cl(1)–Hg(2)–Cl(2) 82.4(2), Hg(2)–Cl(2)–Hg(1') 128.0(2).

ature, the lack of observable couplings results from an increase in the T_1 relaxation rate of the Hg.¹⁴

Finally as previously reported, the solution-state $^{199}\text{Hg}\{^1\text{H}\}$ NMR chemical shifts of **1** and **2** showed little temperature dependence. The solid-state $^{199}\text{Hg}\{^1\text{H}\}$ MAS NMR chemical shifts of these cyclopentadienyl derivatives,¹⁵ which to our knowledge is the first report of such data, were significantly at a higher frequency compared with the solution state data thereby indicating an increased coordination number at the Hg center. While for **1** this shift may arise from the additional Cl ligation in the solid-state tetrameric structure, the origin of this shift for **2** is not as obvious.

In conclusion, these results demonstrate that for Hg cyclopentadienyl derivatives a single Si substituent presents a sufficiently

(15) Samples of **1** and **2** were ground in a glovebox operating at <1 ppm H₂O and <1 ppm O₂ and packed into zirconia rotors with Kel-F end caps and spun with N₂. NMR experiments were performed on a Bruker DMX-400 spectrometer (89 mm wide bore, 9.35 T magnet) with a 4 mm variable-temperature double-bearing probe. At spin rates in excess of 6 kHz, a variable amplitude (triangular ramp $\pm 25\%$) cross-polarization contact pulse was employed. Although only two of the four Hg atoms of the tetramer **1** were crystallographically independent, four isotropic resonances were observed in the ^{199}Hg NMR spectrum indicating that none of the four were magnetically equivalent.

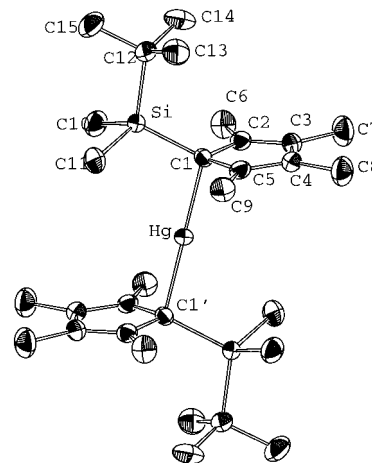


Figure 2. The molecular structure of **2** and atom numbering scheme with selected bond lengths (Å) and angles (deg): Hg–C(1) 2.136(3), C(1)–Hg–C(1') 180.0, Si–C(1)–Hg 105.5(2).

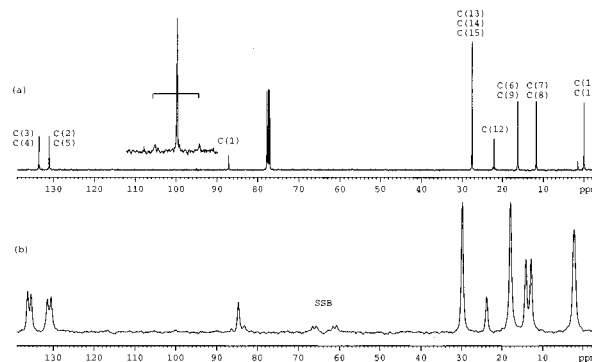


Figure 3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **2** (a) C₇D₈ at 298 K, (b) ^{13}C CP MAS ($\nu_r = 7.4$ kHz, 256 transients).

electronically unique site within the cyclopentadienyl ligand to prevent the “ring whizzing” behavior normally observed for C analogues in both solution and in the solid state.

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Supporting Information Available: Tables of X-ray crystallographic data and ^{199}Hg CP MAS spectrum (14 pages). An X-ray crystallographic file, in CIF format, is available through the Internet only. See any current masthead page for ordering and Internet access instructions.

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