

## Notes

New Approach to Silylmercury Compounds by Reaction of Mercury Halides with Decamethylsilicocene<sup>†</sup>

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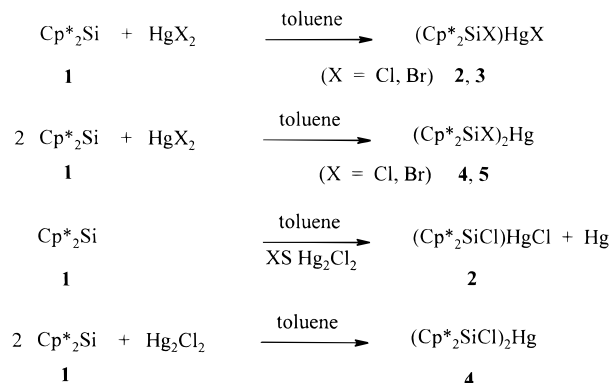
Received January 24, 2000

**Summary:** Formation of mercury–silicon bonds was effected in the reaction of the mercury halides  $\text{HgCl}_2$ ,  $\text{HgBr}_2$ , and  $\text{Hg}_2\text{Cl}_2$  with dekamethylsilicocene,  $\text{Cp}^*_2\text{Si}$  (**1**). Depending on the ratio of the reactants, the single- and double-insertion products  $(\text{Cp}^*_2\text{SiX})\text{HgX}$  (**2**,  $\text{X} = \text{Cl}$ ; **3**,  $\text{X} = \text{Br}$ ) and  $(\text{Cp}^*_2\text{SiX})_2\text{Hg}$  (**4**,  $\text{X} = \text{Cl}$ ; **5**,  $\text{X} = \text{Br}$ ), respectively, were obtained. The novel compounds were characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectroscopic data and, in the case of **2** and **5**, also by an X-ray crystal structure analysis.

## Introduction

Insertion reactions are typical for the chemistry of silylenes,<sup>1</sup> including that of dekamethylsilicocene (**1**),<sup>2</sup> but insertion into a mercury–halide bond has not been observed thus far. Here we report on the reaction of **1** with mercury halides, which results in the synthesis of monosilyl- and disilyl-substituted mercury compounds of the types  $(\text{Cp}^*_2\text{SiX})\text{HgX}$  (**2**,  $\text{X} = \text{Cl}$ ; **3**,  $\text{X} = \text{Br}$ ) and  $(\text{Cp}^*_2\text{SiX})_2\text{Hg}$  (**4**,  $\text{X} = \text{Cl}$ ; **5**,  $\text{X} = \text{Br}$ ). This strategy extends the synthetic methods for the formation of silylmercury compounds.<sup>3–6</sup>

## Scheme 1



## Results and Discussion

The reaction of  $\text{Cp}^*_2\text{Si}$  (**1**) with  $\text{HgCl}_2$  or  $\text{HgBr}_2$  in toluene at  $-70^\circ\text{C}$  in a 1:1 ratio led to the formation of the monosilyl mercury compounds  $(\text{Cp}^*_2\text{SiX})\text{HgX}$  (**2**,  $\text{X} = \text{Cl}$ ; **3**,  $\text{X} = \text{Br}$ ) (Scheme 1), which were obtained in about 80% yield as air- and moisture-sensitive yellow powders. Both are soluble in common organic solvents and can be stored in solution ( $-30^\circ\text{C}$ ) without decomposition for days. In the solid state they decompose even at low temperature within hours. Reaction of 2 equiv of **1** with  $\text{HgCl}_2$  or  $\text{HgBr}_2$  at room temperature in toluene led to the formation of the disilyl mercury compounds  $(\text{Cp}^*_2\text{SiX})_2\text{Hg}$  (**4**,  $\text{X} = \text{Cl}$ ; **5**,  $\text{X} = \text{Br}$ ), which were obtained in almost quantitative yield as air- and moisture-sensitive yellow solids (Scheme 1). They also dissolve in common organic solvents but decompose in solution within days at room temperature; in the solid state they can be stored at low temperature ( $-30^\circ\text{C}$ ) only for a few days without decomposition. Yellow crystals of **4** and **5** were obtained from toluene solution.

<sup>†</sup> Dedicated to Professor H. Vahrenkamp (Albert-Ludwigs-Universität Freiburg) on the occasion of his 60th birthday.

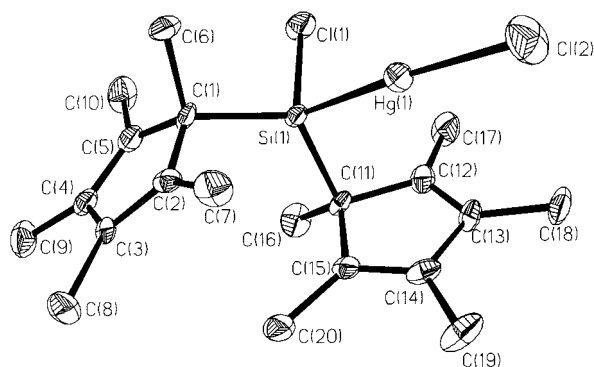
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(3) Na amalgam procedure:  $\text{R}_3\text{SiX} + \text{Na/Hg} \rightarrow (\text{R}_3\text{Si})_2\text{Hg} + 2\text{NaX}$ . (a) Wiberg, E.; Stecher, O.; Andrascheck, H.-J.; Kreuzbichler, L.; Staude, E. *Angew. Chem.* **1963**, *75*, 516–524. (b) Mitchell, T. N.; Marsmann, H. C. *J. Organomet. Chem.* **1978**, *150*, 171–177.

(4) Hydride method:  $\text{R}_3\text{SiH} + (\text{tBu})_2\text{Hg} \rightarrow (\text{R}_3\text{Si})_2\text{Hg} + 2\text{tBuH}$ . (a) Vyazankin, N. S. *Organomet. Chem. Rev. A* **1968**, *3*, 323. (b) Bettler, C. R.; Sendra, J. C.; Urry, G. *Inorg. Chem.* **1970**, *9*, 1060–1065. (c) Hovland, A. K.; Schaaf, T. F.; Oliver, J. P. *J. Organomet. Chem.* **1976**, *120*, 171–187. (d) Hengge, E.; Mitter, F. K. *Z. Anorg. Allg. Chem.* **1985**, *529*, 22–28.

(5) Metathesis reactions:  $\text{HgX}_2 + 2\text{R}_3\text{SiLi} \rightarrow (\text{R}_3\text{Si})_2\text{Hg} + 2\text{LiX}$ . Wiberg, N.; Amelunxen, K.; Lerner, H.-W.; Nöth, H.; Appel, A.; Knizek, J.; Polborn, K. Z. *Anorg. Allg. Chem.* **1997**, *623*, 1861–70.

(6) Ligand exchange:  $(\text{Me}_3\text{Si})_2\text{Hg} + \text{RHgX} \rightarrow (\text{Me}_3\text{Si})\text{HgR} + (\text{Me}_3\text{Si})\text{HgX}$ . (a) Vyazankin, N. S.; Glayshev, E. N.; Arkhangel'skaya, E. A.; Razuvaev, G. A. *J. Organomet. Chem.* **1969**, *17*, 340–344. (b) Mitchell, T. N. *J. Organomet. Chem.* **1974**, *71*, 27–38.



**Figure 1.** Molecular structure of  $(\text{Cp}^*_2\text{SiCl})\text{HgCl}$  (**2**). Thermal ellipsoids are given at 50% probability.

Reaction of **1** with  $\text{Hg}_2\text{Cl}_2$  in a 2:1 ratio yielded compound **4** together with elemental mercury in nearly quantitative yield. If the reaction was carried out in a 1:1 ratio, a mixture of compounds **2** and **4** (1:3) was obtained. Exclusive formation of **2** can only be observed when a large excess of  $\text{Hg}_2\text{Cl}_2$  is used (Scheme 1).

The new compounds **2**–**5** were characterized by spectroscopic data. No satisfactory elemental analyses could be obtained; this is most probably due to the high reactivity of the compounds toward even trace amounts of air and moisture and their thermal instability in the solid state. Crystals of **2**, **4**, and **5** suitable for X-ray structure analysis were grown from toluene solution at  $-60^\circ\text{C}$ .<sup>7</sup>

The molecular structure of **2** is presented in Figure 1. Crystallographic data are given in Table 1, and selected bond lengths and angles are collected in Table 2.

Compound **2** crystallizes in the triclinic space group  $P\bar{1}$ . The silicon atom is coordinated in a distorted tetrahedral configuration by two  $\sigma$ -bonded  $\text{Cp}^*$  rings, a chlorine atom, and a Hg–Cl unit. The Hg–Si bond length of 2.4076(16) Å, which compares with 2.437(3) Å in  $^t\text{Bu}_3\text{SiHgCl}$  (**6**), is the shortest Hg–Si bond reported thus far.<sup>5</sup> The Si–Hg–Cl(2) unit is nearly linear ( $172.16(6)^\circ$ ). The intermolecular Hg–Cl distances are approximately 3.7 Å (sum of van der Waals radii 3.3 Å).<sup>8</sup> The only other structurally investigated compound with a Si–Hg–Hal unit is **6**, which crystallizes as a tetramer with Cl–Hg–Cl interactions in the range of 3.1 Å and with Si–Hg–Cl angles varying from  $157.6$  to  $160.9^\circ$ .<sup>5</sup> The conformation of the planar  $\text{Cp}^*$  rings in **2** differs from the parallel arrangement generally found in  $\text{Cp}^*_2\text{SiR}_2$  compounds.<sup>2c–e,9</sup> One  $\text{Cp}^*$  ring is orientated toward the Hg atom which is located above the  $\text{Cp}^*$  ring plane. The  $\text{Cp}^*_\text{centroid}$ –Hg distance (3.158(8) Å) is only slightly shorter than the van der Waals distance (sum of van der Waals radii 3.2 Å).<sup>8,10</sup> Since no anomaly in the C–C bond lengths of the Hg-oriented  $\text{Cp}^*$  ring could be observed (Table 2), we assume only weak interactions between the Hg atom and the  $\text{Cp}^*$  system.

(7) A discussion of bond lengths and angles of **4** is not admissible due to the poor quality of the obtained crystals. Nevertheless, the connectivity could be proven.

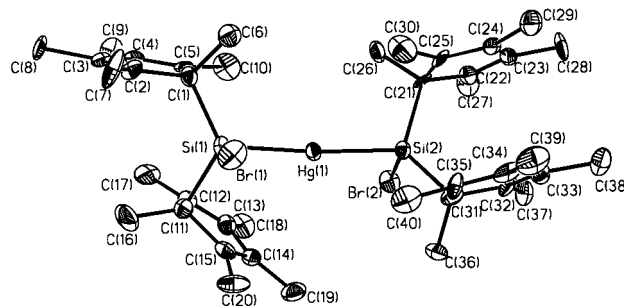
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**Table 1.** Crystallographic Data for  $(\text{Cp}^*_2\text{SiCl})\text{HgCl}$  (**2**) and  $(\text{Cp}^*_2\text{SiBr})_2\text{Hg}$  (**5**)

	<b>2</b>	<b>5</b>
empirical formula	$\text{C}_{20}\text{H}_{30}\text{Cl}_2\text{HgSi}$	$\text{C}_{40}\text{H}_{60}\text{Br}_2\text{HgSi}_2$
fw	570.02	975.47
cryst color, habit	colorless, irregular	yellow, irregular
cryst size, $\text{mm}^3$	$0.50 \times 0.25 \times 0.20$	$0.40 \times 0.20 \times 0.15$
temp, K	173(2)	
wavelength	Mo K $\alpha$ 0.71073 Å (graphite monochromator)	
space group	$P\bar{1}$	$P2_1/n$
unit cell dimens		
<i>a</i> , Å	8.2620(10)	17.855(5)
<i>b</i> , Å	11.356(2)	13.537(3)
<i>c</i> , Å	12.004(4)	18.404(5)
$\alpha$ , deg	77.40(2)	90
$\beta$ , deg	86.11(2)	112.78(2)
$\gamma$ , deg	80.94(2)	90
<i>V</i> , Å <sup>3</sup>	1084.8(4)	4101.3(18)
<i>Z</i>	2	4
density (calcd), $\text{Mg/m}^3$	1745	1551
$\theta$ range for data collec., deg	1.74–27.06	1.92–25.00
no. of rflns collected	5118	7458
no. of indep rflns	4779 ( $R_{\text{int}} = 0.0318$ )	7211 ( $R_{\text{int}} = 0.0680$ )
abs cor		empirical from $\psi$ -scans
final $R(F)$	0.0828 (4134)	0.0996 (4521)
( $I > 2\sigma(I)$ )		
$R_w(F^2)$ (all data)	0.0873	0.1170
no. of params	227	421
largest diff peak and hole, $\text{e} \text{ \AA}^{-3}$	0.923 and $-1.105$	0.885 and $-0.774$
diffractometer used	Siemens P2(1) diffractometer	
programs used	Siemens SHELXTL plus/SHELXL-97	
structure refinement	full-matrix least squares on $F^2$	



**Figure 2.** Molecular structure of  $(\text{Cp}^*_2\text{SiBr})_2\text{Hg}$  (**5**). Thermal ellipsoids are given at 50% probability.

The molecular structure of **5** is presented in Figure 2. Crystal structure parameters are given in Table 1, and selected bond lengths and angles are summarized in Table 3.

Compound **5** crystallizes in the monoclinic space group  $P2_1/n$ . Both silicon atoms are coordinated in a distorted-tetrahedral arrangement by two  $\sigma$ -bonded  $\text{Cp}^*$  rings, a bromine atom, and a Hg–silyl unit. The Hg–Si distances are 2.466(3) and 2.479(3) Å. These values correspond to those found for other Hg–Si compounds.<sup>5,11</sup> The two silyl units are nearly linearly coordinated to the mercury atom ( $\text{Si}(1)$ –Hg– $\text{Si}(2) = 174.87(10)^\circ$ ). Interestingly, the two silyl subunits show different arrangements of the  $\text{Cp}^*$  substituents. The conformation of the two  $\text{Cp}^*$  rings at Si(1) is comparable to that found in **2**; the  $\text{Cp}^*_\text{centroid}$ –Hg distance (3.279(14) Å) is longer than the sum of van der Waals

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**Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2**

Hg(1)–Si(1)	2.4076(16)	Si(1)–C(1)	1.904(6)
Si(1)–Cl(1)	2.094(2)	Si(1)–C(11)	1.929(5)
C(1)–C(2)	1.510(7)	C(11)–C(12)	1.519(8)
C(1)–C(5)	1.513(8)	C(11)–C(15)	1.502(8)
C(2)–C(3)	1.354(8)	C(12)–C(13)	1.351(9)
C(3)–C(4)	1.460(8)	C(13)–C(14)	1.446(8)
C(4)–C(5)	1.356(8)	C(14)–C(15)	1.349(9)
		Hg(1)–Cp* <sub>Centroid</sub>	3.158(8)
Cl(2)–Hg(1)–Si(1)	172.16(6)	C(1)–Si(1)–Hg(1)	113.20(19)
C(1)–Si(1)–C(11)	121.4(2)	C(11)–Si(1)–Hg(1)	105.04(17)
C(1)–Si(1)–Cl(1)	104.63(18)	Cl(1)–Si(1)–Hg(1)	104.09(7)
C(11)–Si(1)–Cl(1)	107.06(18)		
C(2)–C(1)–C(5)	103.2(4)	C(12)–C(11)–C(15)	102.7(5)
C(2)–C(1)–C(6)	109.0(5)	C(12)–C(11)–C(16)	117.2(5)
C(5)–C(1)–C(6)	110.6(5)	C(15)–C(11)–C(16)	116.6(5)
C(2)–C(1)–Si(1)	112.3(4)	C(12)–C(11)–Si(1)	102.3(4)
C(5)–C(1)–Si(1)	114.3(4)	C(15)–C(11)–Si(1)	103.6(4)
C(6)–C(1)–Si(1)	107.4(4)	C(16)–C(11)–Si(1)	112.5(4)

**Table 3. Selected Bond Lengths (Å) and Angles (deg) for 5**

Hg(1)–Si(1)	2.466(3)	Hg(1)–Si(2)	2.479(3)
Br(1)–Si(1)	2.295(3)	Br(2)–Si(2)	2.293(3)
Si(1)–C(1)	1.940(11)	Si(2)–C(21)	1.920(11)
Si(1)–C(11)	1.947(12)	Si(2)–C(31)	1.919(10)
C(1)–C(2)	1.489(14)	C(21)–C(22)	1.504(15)
C(1)–C(5)	1.519(14)	C(21)–C(25)	1.542(14)
C(2)–C(3)	1.354(14)	C(22)–C(23)	1.364(15)
C(3)–C(4)	1.474(15)	C(23)–C(24)	1.441(15)
C(4)–C(5)	1.312(14)	C(24)–C(25)	1.339(14)
C(11)–C(12)	1.492(15)	C(31)–C(32)	1.495(15)
C(11)–C(15)	1.513(15)	C(31)–C(35)	1.540(14)
C(12)–C(13)	1.344(15)	C(32)–C(33)	1.359(14)
C(13)–C(14)	1.498(15)	C(33)–C(34)	1.466(16)
C(14)–C(15)	1.343(15)	C(34)–C(35)	1.341(15)
Hg(1)–Cp* <sub>Centroid</sub>	3.279(15)		
Si(1)–Hg(1)–Si(2)	174.87(10)	C(21)–Si(2)–C(31)	118.3(5)
C(1)–Si(1)–C(11)	120.5(5)	C(31)–Si(2)–Br(2)	105.5(3)
C(1)–Si(1)–Br(1)	102.4(3)	C(21)–Si(2)–Br(2)	106.5(4)
C(11)–Si(1)–Br(1)	106.6(4)	C(31)–Si(2)–Hg(1)	115.4(4)
C(1)–Si(1)–Hg(1)	114.4(3)	C(21)–Si(2)–Hg(1)	108.2(3)
C(11)–Si(1)–Hg(1)	108.9(4)	Br(2)–Si(2)–Hg(1)	101.12(11)
Br(1)–Si(1)–Hg(1)	101.61(11)	C(22)–C(21)–Si(2)	114.1(7)
C(2)–C(1)–Si(1)	115.3(7)	C(25)–C(21)–Si(2)	104.8(7)
C(5)–C(1)–Si(1)	109.6(7)	C(26)–C(21)–Si(2)	110.2(7)
C(6)–C(1)–Si(1)	105.7(7)	C(32)–C(31)–Si(2)	114.5(8)
C(12)–C(11)–Si(1)	101.7(7)	C(35)–C(31)–Si(2)	108.5(7)
C(15)–C(11)–Si(1)	100.5(7)	C(36)–C(31)–Si(2)	110.1(7)
C(16)–C(11)–Si(1)	114.0(9)		

radii.<sup>8,10</sup> The two Cp\* rings at Si(2) are located in a nearly parallel arrangement.

In solution, compounds **2–5** exhibit the expected sigmatropic rearrangements of the Cp\* units,<sup>12</sup> as indicated by one broad resonance for all methyl groups of the Cp\* systems in the <sup>1</sup>H and <sup>13</sup>C NMR spectra. NMR data are given in Table 4. The <sup>29</sup>Si NMR resonances are found in the expected range<sup>3b,5</sup> at 53.4 (**2**), 51.4 (**3**), 94.48 (**4**), and 98.84 (**5**) ppm, respectively.

By the approach described in this paper it is possible to prepare both monosilyl- and disilyl-substituted mercury compounds in very good yields without any side reactions. Investigation of insertion reactions of **1** into other metal–halide bonds is currently in progress.

**Table 4. Selected NMR Data (ppm) for 2–5<sup>a</sup>**

	2	3	4	5
<sup>1</sup> H NMR	1.67 (br) <sup>b</sup>	1.61 (br) <sup>c</sup>	1.81 (br) <sup>b</sup>	1.80 (br) <sup>c</sup>
<sup>13</sup> C NMR				
C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub>	12.0 (br) <sup>b</sup>	12.0 (br) <sup>c</sup>	13.3 (br) <sup>c</sup>	13.8 (br) <sup>b</sup>
C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub>	139.4 (br) <sup>b</sup>	139.4 (br) <sup>c</sup>	137.8 (br) <sup>c</sup>	137.0 (br) <sup>b</sup>
<sup>29</sup> Si NMR	53.40 <sup>b</sup>	51.40 <sup>c</sup>	94.48 <sup>c</sup>	98.84 <sup>c</sup>

<sup>a</sup> Measured at room temperature. <sup>b</sup> Measured in C<sub>6</sub>D<sub>6</sub>. <sup>c</sup> Measured in C<sub>7</sub>D<sub>8</sub>.

## Experimental Section

**General Comments.** All manipulations were carried out under a purified argon atmosphere using standard vacuum techniques. The solvents were commercially available, were purified by conventional means, and were distilled immediately prior to use. Cp\*<sub>2</sub>Si was prepared according to the literature.<sup>13</sup> The melting point determinations were performed using a Büchi 510 melting point apparatus. The NMR spectra were obtained on a Bruker Avance DRX 500 spectrometer (<sup>1</sup>H, 500.1 MHz; <sup>13</sup>C{<sup>1</sup>H}, 125.8 MHz; <sup>29</sup>Si{<sup>1</sup>H}, 99.4 MHz); <sup>1</sup>H and <sup>13</sup>C NMR data were referenced to residual solvent peaks and are reported relative to TMS. <sup>29</sup>Si NMR data were referenced to external TMS. Chemical shifts are reported in ppm. Mass spectrometry was performed using a VG Autospec spectrometer (70 eV, 200 μA emission). Only characteristic fragments and isotopes of highest abundance are listed.

**Preparation of (Cp\*<sub>2</sub>SiCl)HgCl (**2**) and (Cp\*<sub>2</sub>SiBr)HgBr (**3**) by Reaction of **1** with HgX<sub>2</sub> (X = Cl, Br).** A solution of 1 mmol (0.30 g) of **1** in toluene (10 mL) was added dropwise to a suspension of 1 mmol of the corresponding HgX<sub>2</sub> compound (X = Cl, 0.27 g; X = Br, 0.36 g) (1 mmol) in toluene (20 mL) at –70 °C. While the reaction mixture was warmed to room temperature, the color of the suspension changed from yellow to gray. All volatile components were removed in vacuo. The yellow-gray residue was treated with *n*-hexane and the resulting solution filtered. Again all volatile components were removed in vacuo to give (Cp\*<sub>2</sub>SiCl)HgCl (**2**) and (Cp\*<sub>2</sub>SiBr)HgBr (**3**), respectively, as yellow residues in 78% (X = Cl) and 89% (X = Br) yields, respectively. Compound **2** was crystallized at –60 °C from toluene.

**2:** <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 1.67 (broad signal, 30H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 70 °C) δ 1.60 (s, 30H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, –40 °C) δ 0.97 (s, 6H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 1.72 (broad signal, 18H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 1.83 (s, 6H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ 12.0 (broad signal, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 139.4 (broad signal, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>) δ 53.40; MS/CI (*m/z* (relative intensity, %)) 435 (2) [M – Cp\*]<sup>+</sup>, 368 (57) [M – Hg]<sup>+</sup>, 333 (100) [M – HgCl]<sup>+</sup>, 233 (75) [M – HgCp\*]<sup>+</sup>, 199 (5) [Hg]<sup>+</sup>, 163 (62) [Cp\*Si]<sup>+</sup>, 135 (73) [Cp\*]<sup>+</sup>.

**3:** <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>) δ 1.61 (broad signal, 30H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 100 °C) δ 1.61 (s, 30H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, –55 °C) δ 1.07 (s, 6H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 1.75 (3 s, 18H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 1.93 (s, 6H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); <sup>13</sup>C NMR (toluene-*d*<sub>8</sub>) δ 12.0 (broad signal, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 139.4 (broad signal, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); <sup>29</sup>Si NMR (toluene-*d*<sub>8</sub>) δ 51.40; MS/CI (*m/z* (relative intensity, %)) 658 (<1) [M]<sup>+</sup> (with the correct isotopic pattern), 458 (11) [M – Hg]<sup>+</sup>, 375 (32) [M – HgBr]<sup>+</sup>, 163 (100) [Cp\*Si]<sup>+</sup>, 135 (57) [Cp\*]<sup>+</sup>.

**Preparation of (Cp\*<sub>2</sub>SiCl)<sub>2</sub>Hg (**4**) and (Cp\*<sub>2</sub>SiBr)<sub>2</sub>Hg (**5**) by Reaction of **1** with HgX<sub>2</sub> (X = Cl, Br).** A solution of 2 mmol (0.60 g) of **1** in toluene (10 mL) was added dropwise to a suspension of 1 mmol of the corresponding HgX<sub>2</sub> species (X = Cl, 0.27 g; X = Br, 0.36 g) (1 mmol) in toluene (20 mL) at room temperature. While the reaction mixture was stirred for 3 days, the suspension changed into a yellow solution. All volatile components were removed in vacuo. The yellow residue

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was crystallized at  $-60\text{ }^{\circ}\text{C}$  from toluene to give  $(\text{Cp}^*\text{SiCl})_2\text{Hg}$  (**4**) in 99% yield and  $(\text{Cp}^*\text{SiBr})_2\text{Hg}$  (**5**) in 100% yield, respectively.

**4:**  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.81 (broad signal, 60H,  $\text{C}_5(\text{CH}_3)_5$ );  $^1\text{H}$  NMR (toluene- $d_8$ ,  $60\text{ }^{\circ}\text{C}$ )  $\delta$  1.75 (s, 60H,  $\text{C}_5(\text{CH}_3)_5$ );  $^1\text{H}$  NMR (toluene- $d_8$ ,  $-40\text{ }^{\circ}\text{C}$ )  $\delta$  1.29 (s, 12H,  $\text{C}_5(\text{CH}_3)_5$ ), 1.90 (broad signal, 36H,  $\text{C}_5(\text{CH}_3)_5$ ), 2.07 (s, 12H,  $\text{C}_5(\text{CH}_3)_5$ );  $^{13}\text{C}$  NMR (toluene- $d_8$ )  $\delta$  13.3 (broad signal,  $\text{C}_5(\text{CH}_3)_5$ ), 137.8 (broad signal,  $\text{C}_5(\text{CH}_3)_5$ );  $^{13}\text{C}$  NMR (toluene- $d_8$ ,  $60\text{ }^{\circ}\text{C}$ )  $\delta$  13.5 (s,  $\text{C}_5(\text{CH}_3)_5$ ) (the signal of the  $\text{Cp}^*$  ring atoms was not observed);  $^{13}\text{C}$  NMR (toluene- $d_8$ ,  $-40\text{ }^{\circ}\text{C}$ )  $\delta$  11.6, 11.9, 13.4, 14.2, 16.1 ( $\text{C}_5(\text{CH}_3)_5$ ), 62.6 (broad signal, *vinyl-C* of  $\text{C}_5(\text{CH}_3)_5$ ), 139.8 (broad signal), 140.4 (s) (*allyl-C* of  $\text{C}_5(\text{CH}_3)_5$ );  $^{13}\text{C}$  NMR (toluene- $d_8$ ,  $-80\text{ }^{\circ}\text{C}$ )  $\delta$  11.3, 11.6, 14.2 ( $\text{C}_5(\text{CH}_3)_5$ ), 60.6–64.4 (broad signals, *vinyl-C* of  $\text{C}_5(\text{CH}_3)_5$ ), 137.1 (broad signal, *allyl-C* of  $\text{C}_5(\text{CH}_3)_5$ );  $^{29}\text{Si}$  NMR (toluene- $d_8$ )  $\delta$  94.48.

**5:**  $^1\text{H}$  NMR (toluene- $d_8$ )  $\delta$  1.80 (broad signal, 60H,  $\text{C}_5(\text{CH}_3)_5$ );  $^1\text{H}$  NMR (toluene- $d_8$ ,  $60\text{ }^{\circ}\text{C}$ )  $\delta$  1.77 (s, 60H,  $\text{C}_5(\text{CH}_3)_5$ );  $^1\text{H}$  NMR (toluene- $d_8$ ,  $-60\text{ }^{\circ}\text{C}$ )  $\delta$  1.39 (s, 12H,  $\text{C}_5(\text{CH}_3)_5$ ), 1.91 (broad signal, 36H,  $\text{C}_5(\text{CH}_3)_5$ ), 2.09 (s, 12H,  $\text{C}_5(\text{CH}_3)_5$ );  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  13.8 (br,  $\text{C}_5(\text{CH}_3)_5$ ); 137.0 (broad signal,  $\text{C}_5(\text{CH}_3)_5$ );  $^{13}\text{C}$  NMR (toluene- $d_8$ ,  $60\text{ }^{\circ}\text{C}$ )  $\delta$  13.8 (s,  $\text{C}_5(\text{CH}_3)_5$ ) (the signal of the  $\text{Cp}^*$  ring atoms was not observed);  $^{13}\text{C}$  NMR (toluene- $d_8$ ,  $-40\text{ }^{\circ}\text{C}$ )  $\delta$  12.1 (broad signal,  $\text{C}_5(\text{CH}_3)_5$ ), 61.3 (broad signal, *vinyl-C* of  $\text{C}_5(\text{CH}_3)_5$ ), 139.2, 140.4 (broad signals, *allyl-C* of  $\text{C}_5(\text{CH}_3)_5$ );  $^{13}\text{C}$  NMR (toluene- $d_8$ ,  $-80\text{ }^{\circ}\text{C}$ )  $\delta$  12.1 (broad signal,  $\text{C}_5(\text{CH}_3)_5$ ), 61.2 (broad, *vinyl-C* of  $\text{C}_5(\text{CH}_3)_5$ ) (the signal of the *allyl-C* of the  $\text{Cp}^*$  ring atoms was not observed);  $^{13}\text{C}$  NMR (toluene- $d_8$ ,  $-100\text{ }^{\circ}\text{C}$ )  $\delta$  12.2 (broad signal,  $\text{C}_5(\text{CH}_3)_5$ ), 59.5–63.6 (broad signals, *vinyl-C* of  $\text{C}_5(\text{CH}_3)_5$ ) (the signal of the *allyl-C* of the  $\text{Cp}^*$  ring atoms was not observed);  $^{29}\text{Si}$  NMR (toluene- $d_8$ )  $\delta$  98.84.

**Preparation of 2 by Reaction of 1 with  $\text{Hg}_2\text{Cl}_2$ .** A solution of 1 mmol (0.30 g) of **1** in toluene (20 mL) was added dropwise to a suspension of 20 mmol (9.4 g) of  $\text{Hg}_2\text{Cl}_2$  in toluene (1.5 L) at room temperature. After 2 h the color of the suspension changed from yellow to gray. All volatile components were removed in vacuo. The yellow-gray residue was treated with *n*-hexane (50 mL) and filtered. Again all volatile components were removed in vacuo to give  $(\text{Cp}^*\text{SiCl})\text{HgCl}$  (**2**) in 62% yield. The analytical data correspond to those described above.

**Preparation of 4 by Reaction of 1 with  $\text{Hg}_2\text{Cl}_2$ .** A solution of 2 mmol (0.60 g) of **1** in toluene (20 mL) was added dropwise to a suspension of 1 mmol (0.47 g) of  $\text{Hg}_2\text{Cl}_2$  in toluene (20 mL) at room temperature. The suspension changed from yellow to gray. The suspension was filtered, and all volatile components were removed in vacuo to give  $(\text{Cp}^*\text{SiCl})_2\text{Hg}$  (**4**) in 100% yield. The analytical data correspond to those described above.

**Acknowledgment.** The support of this work by the Deutsche Forschungsgemeinschaft, the Universität Bielefeld, and the Fonds der Chemischen Industrie is gratefully acknowledged.

**Supporting Information Available:** Tables of crystal data, positional and thermal parameters, and bond lengths and angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM000060D