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Solid-State Structures and Solution Studies of Novel Cyclopentadienyl Mercury Compounds

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New mercury cyclopentadienyl complexes Hg(η^1-Cp′)Cl have been prepared by the reaction of $HgCl_2$ and the appropriate KCp′ salts or by the transmetalation of $HgCl_2$ with $ZnCp'_2$ (Cp′ = C_5Me_4H, **1**; $C_5Me_4Bu^t$, **2**; $C_5Me_4SiMe_3$, **3**; $C_5H_4SiMe_3$, **4**). By contrast, only the $SiMe_3$-substituted bis(cyclopentadienyl) derivatives, $Hg(C_5Me_4SiMe_3)_2$ (**5**) and $Hg(C_5H_4SiMe_3)_2$ (**6**), can be isolated by the above synthetic procedures and the appropriate ratio of reagents or from HgCp′Cl and KCp′. Solution NMR studies reveal nonfluxional behavior of the $SiMe_3$-substituted complexes **3**, **5**, and **6**. X-ray studies of the solid-state structures show that the six compounds contain η^1-Cp′ ligands, with linear or almost linear C–Hg–Cl or C–Hg–C coordination environments. The two $HgCp'_2$ compounds, **5** and **6**, have the expected insular structures, but the HgCp′Cl derivatives show supramolecular associations by means of weak secondary Hg···Cl interactions. Thus, the HgCp′Cl compounds **1**, **3**, and **4** form three different polymeric chain structures with typically two Hg···Cl interactions of 3.04–3.46 Å per mercury. By contrast, **2** forms a tetramer, $[Hg(C_5Me_4SiMe_3)Cl]_4$, with a cubelike arrangement of four Hg and four Cl atoms. Density functional theory has been used to investigate the electronic structure of the compounds.

Introduction

Despite the early report by Piper and Wilkinson on the preparation and properties of $Hg(C_5H_5)_2$ some 50 years ago,[1] studies on mercury derivatives of substituted Cp′ ligands (Cp′ denotes any cyclopentadienyl ligand) remain scarce, probably due to a combination of two factors, viz., the high toxicity of mercury and the weakness of the Hg−C bonds.[2] Other early investigations on compounds of this type include $Hg(C_9H_7)_2$ (C_9H_7 = 1-indenyl)[3] and $Hg(C_5H_4Me)_2$,[4] whereas more recent studies have dealt with $Hg(C_5H_2Bu^t{}_3)_2$[5] and $Hg(C_5Me_4SiMe_2Bu^t)_2$.[6] Mono(cyclopentadienyl) derivatives, HgCp′X, are also known for various cyclopentadienyl ligands and X groups (e.g., C_5H_5, C_5Me_5, or C_5Cl_5; X = Cl, Br, I, Me, Ph).[7−10] All of these compounds, whether of the $HgCp'_2$ or of the HgCp′X type, have been described as highly fluxional in solution[1,3−5,7,9,10] and in some cases also in the solid state.[8] Exceptions to this are the $C_5Me_4SiMe_2Bu^t$

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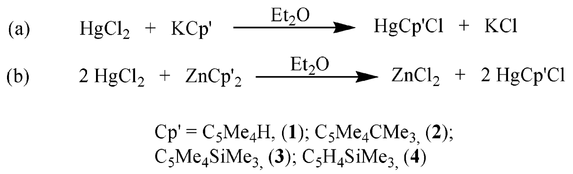
Scheme 1. Synthesis of Mono(cyclopentadienyl) Mercury Complexes **1**−**4**



derivatives HgCp′Cl and HgCp′$_2$, shown by Lawless and coworkers to possess rigid structures in solution and in the solid state.[6]

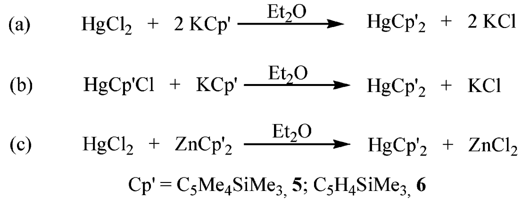
Some of these mercury cyclopentadienyls have been characterized by X-ray crystallography. Compounds HgCp′$_2$, for Cp′ = C_5H_5,[11] $C_5H_2Bu^t{}_3$,[5] and $C_5Me_4SiMe_2Bu^t$,[6] contain η^1-Cp′ rings and linear, or almost linear, C−Hg−C linkages, with Hg−C distances of 2.10−2.15 Å. Only two HgCp′Cl compounds have been investigated by X-ray techniques, namely, Hg(C_5Me_5)Cl[9b] and Hg($C_5Me_4SiMe_2Bu^t$)Cl.[6] The former has an interesting polymeric double-chain structure,[9b] whereas in the latter the replacement of one Me ring substituent by the bulky $SiMe_2Bu^t$ group leads to tetrameric [Cl−Hg−Cp′]$_4$ units.[6]

The scarcity of solid-state structural studies on Hg−Cp′compounds, particularly on those of composition Hg(η^1-Cp′)Cl, and the interesting structural effects that appear to be exerted by the ring substituents have prompted us to undertake the synthesis and solid-state characterization of some new members of the HgCp′Cl and HgCp′$_2$ families of compounds, this chemistry being a natural extension of earlier work from our group on beryllocenes[11] and zincocenes.[12] Even if Hg(η^1-Cp′)Cl complexes can be readily obtained for Cp′ = C_5Me_4H, **1**; $C_5Me_4Bu^t$, **2**, and $C_5Me_4SiMe_3$, **3**, only the latter ligand allows access to the corresponding HgCp′$_2$ derivative **5**. To emphasize further the effect that the $SiMe_3$ substituent appears to exercise on the strength of the Hg−C bond, the related pair of organomercury compounds Hg($C_5H_4SiMe_3$)Cl (**4**) and Hg($C_5H_4SiMe_3$)$_2$ (**6**) has also been investigated. The X-ray structures of compounds **1**−**6** are herein reported and are complemented with density functional theory (DFT) calculations performed with some of these complexes.

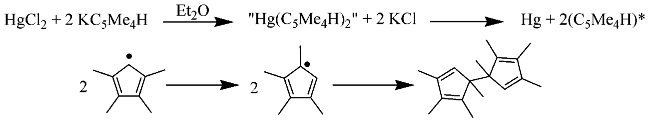
Results and Discussion

Synthesis and Solution Properties of HgCp′Cl (1−4) and HgCp′$_2$ (5 and 6) Complexes. The mono(cyclopentadienyl) derivatives HgCp′Cl (**1**−**4**) have been prepared from a 1:1 mixture of $HgCl_2$ and KCp′ (Scheme 1a), at room temperature, for a period of 1−5 h, employing diethyl ether as the reaction solvent. The resulting organomercury compounds remain in the ether solution and are isolated as yellow-orange crystalline solids following standard workup

Scheme 2. Synthesis of Complexes HgCp′$_2$, **5**, and **6**



Scheme 3. Proposed Formation of (C_5Me_4H)$_2$ from $HgCl_2$ and KC_5Me_4H



and crystallization procedures. Alternatively, complexes **1**−**4** may be generated by the transmetalation reaction of Scheme 1b, using the appropriate zincocene as the Cp′ transfer reagent. This is in line with the well-known ability of organozinc compounds ZnR_2 to act as as alkyl or aryl transfer reagents.[2b,13] Compounds **1**−**4** are soluble in common, nonpolar organic solvents. They are reactive toward oxygen and water, particularly in solution, and are also sensitive to the action of light. However, they can be stored in the dark, under an atmosphere of dinitrogen, for long periods of time without apparent decomposition.

Bis(cyclopentadienyl) complexes HgCp′$_2$ (Cp′ = $C_5Me_4SiMe_3$, **5**; $C_5H_4SiMe_3$, **6**) can be obtained similarly, using a 1:2 ratio of $HgCl_2$/KCp′, also in Et_2O (Scheme 2). The two derivatives may also be obtained from the corresponding HgCp′Cl complex and KCp′ (Scheme 2b) or from $HgCl_2$ and ZnCp′$_2$ (Scheme 2c). It is worth mentioning in this regard that attempts to form Hg(C_5Me_4H)$_2$ or Hg($C_5Me_4Bu^t$)$_2$ by either of these procedures have proved unsuccessful. For instance, the reaction of $HgCl_2$ and KC_5Me_4H in a 1:2 ratio leads to a gray material and to octamethyl-1,1′-bis(cyclopenta-2,4-diene), (C_5Me_4H)$_2$ (compound **8** in the Experimental Section). Formation of the organic product (Scheme 3) was first ascertained by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and its structure was subsequently confirmed by X-ray diffraction methods (an *ORTEP* representation of the molecules of this compound can be found in the Supporting Information). A similar decomposition during the reaction between $HgCl_2$ and KC_5Me_5 (1:2 ratio) led to a product incorrectly formulated[14] as Hg(C_5Me_5)$_2$, subsequently shown to exhibit properties identical to those of (C_5Me_5)$_2$.[15]

As briefly noted, Hg(C_5H_5)Cl[7b,d] and Hg(C_5Me_5)Cl[9a] are fluxional molecules that exhibit solution dynamic behavior. For example, the $^{13}C\{^1H\}$ NMR spectrum of Hg(C_5H_5)Cl shows[7d] a sharp singlet at 116.3 ppm that converts into three signals (131.3, 128.1, and 60.0 ppm, with an approximate 2:2:1 intensity ratio) upon cooling at −122 °C. For the permethylated analogue, the ^{13}C signal due to the ring carbon atoms is not visible at room temperature, whereas

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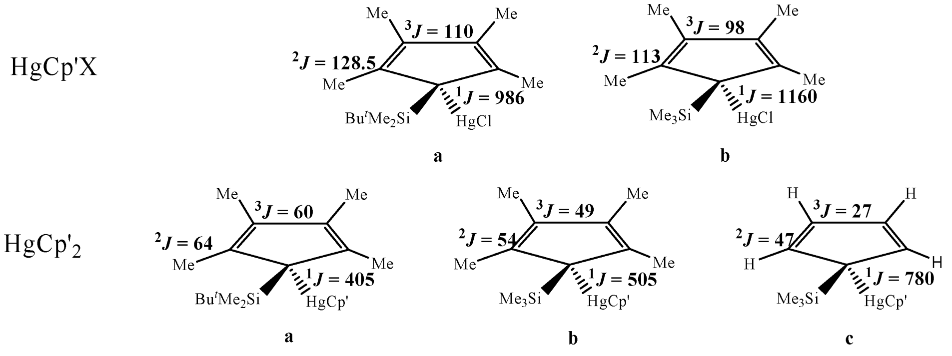

Figure 1. ^{13}C−^{199}Hg coupling constants (Hz) for HgCp′X and HgCp′$_2$ compounds: (a) $C_5Me_4SiMe_2Bu^t$ (ref 6); (b and c) $C_5Me_4SiMe_3$ and $C_5H_4SiMe_3$, respectively (this work).

at −80 °C three resonances are recorded at 133.9, 133.3, and 79.8 ppm, the latter exhibiting a ^{13}C−^{199}Hg coupling of 1266 Hz.[9a] In marked contrast, Hg($C_5Me_4SiMe_2Bu^t$)Cl has a static, well-defined η^1 structure at room temperature featuring resonances at 136.5, 131.9, and 82.4 ppm, with ^{13}C−^{199}Hg couplings of 109, 127, and 986 Hz, respectively.[6]

Of the four HgCp′Cl compounds we have investigated, only **3** has a solution behavior that could be confidently attributed to a rigid structure (Figure 1). Its ^{13}C{^{1}H} NMR spectrum recorded at 25 °C shows, in addition to the Me signals in the range −0.6 to +15.3 ppm (see the Experimental Section), resonances at 80.9 ($J_{\mathrm{CHg}} = 1157$ Hz), 131.0 ($J_{\mathrm{CHg}} = 98.5$ Hz), and 135.9 ($J_{\mathrm{CHg}} = 113$ Hz) that experience very little variation with temperature in the interval from −60 to +40 °C. At variance with these observations, the NMR spectra of the remaining HgCp′Cl compounds **1**, **2**, and **4** are suggestive of dynamic behavior, as reported for the related C_5H_5[7b,d] and C_5Me_5[9a] derivatives. With the consideration of this literature precedent and the relatively low solubility properties of some of these complexes, low-temperature solution NMR studies have not been undertaken.

In contrast with these observations, the bis(cyclopentadienyl) complexes **5** and **6** seem to have a defined, rigid structure in solution. For the two compounds, ^{1}H and ^{13}C{^{1}H} chemical shifts and the ^{13}C−^{199}Hg coupling constants change very little with temperature. Moreover, as shown in Figure 1, these couplings have magnitudes comparable to those found for Hg($C_5Me_4SiMe_2Bu^t$)$_2$.[6] For example, the ^{13}C{^{1}H} NMR spectrum of **5** exhibits cyclopentadienyl ring resonances with chemical shift and coupling-constant values of 89.1 (505 Hz), 130.4 (54 Hz), and 133.9 (47 Hz). Note that the ^{13}C−^{199}Hg couplings decrease to about half their values from the mono-$C_5Me_4SiMe_3$ compound **3** to the corresponding HgCp′$_2$ derivative **5**, possibly as a consequence of the smaller s character of the Hg−C bonds of **5** in comparison with that of the single Hg−C bond of **3**. Similar variations are found for the two $C_5Me_4SiMe_2Bu^t$ compounds, HgCp′$_2$ and HgCp′Cl,[6] as well as for other organomercury compounds, e.g., $HgMe_2$ (692 Hz) and HgMeCl (1431 Hz).[2b]

Solid-State Structures of the Mercury Cyclopentadienyl Complexes 1−6. As briefly noted, only two HgCp′Cl compounds have been studied previously by X-ray diffraction methods, Hg(η^1-C_5Me_5)Cl[9b] and Hg(η^1-$C_5Me_4SiMe_2Bu^t$)Cl.[6] Both feature η^1-Cp′ rings, with Hg−C and Hg−Cl bond distances of ca. 2.10 and 2.35 Å, respectively, and almost linear C−Hg−Cl groups (164−177°). Their solid-state structures differ, however, in the degree of association of the molecules of HgCp′Cl, as the C_5Me_5 derivative forms a ladderlike double-chain polymer,[9b] whereas Hg(η^1-$C_5Me_4SiMe_2Bu^t$)Cl contains tetrameric units that have been described as eight-membered rings characterized by alternate short and long Hg···Cl lengths (2.33 and ca. 3.11 Å, respectively), although two additional intra-annular Hg···Cl interactions measure only 3.26 Å.[6]

Table 1. Selected Bond Distances (Å) and Angles (deg) for Mono(cyclopentadienyl) Complexes **1**−**4**[a]

	C_5Me_4H (**1**)	$C_5Me_4CMe_3$ (**2**)	$C_5Me_4SiMe_3$ (**3**)	$C_5H_4SiMe_3$ (**4**)
Hg−Cl	2.327(6)	2.3741(9)	2.3751(11)	2.348(2)
Hg−C_i	2.13(3)	2.137(3)	2.133(3)	2.094(6)
C_i−C_α	1.46(3)	1.522(5)	1.505(4)	1.482(10)
C_α−C_β	1.36(3)	1.349(6)	1.359(5)	1.350(10)
C_β−$C_{\beta'}$	1.47(3)	1.462(6)	1.461(5)	1.445(11)
Hg−C_i−R	109	111.2(2)	114.6(2)	107.5(3)
Hg−C_i−C_α	109.4(17)	102.8(2)	106.4(2)	111.3(4)

[a] The data are mean values for the corresponding quantities in each compound.

Figure 2 contains *ORTEP* perspective views of individual molecules of **1**−**4**. Selected bond distances and angles for **1**−**4** are summarized in Table 1. Only the first independent monomeric molecule of HgCp′Cl out of the two of **2** and **4**, and of the four found for compound **4**, is shown. As expected, they all exhibit η^1-Cp′ coordination, with Hg−C distances of 2.09−2.14 Å and Hg−Cl distances of 2.33−2.37 Å and C−Hg−Cl groups that are almost linear (angles between 163° and 175°). At variance with the η^1-Cp′ coordination found in zincocenes,[12a,16] considered to be of the $\eta^1(\pi)$ type, that in the Hg compounds appears to be closer to $\eta^1(\sigma)$, as revealed by Hg−C−Cp$_{\mathrm{centr}}$ angles of 108−127°[17a] and by differences of about 0.10 Å between the C_β−C_β and C_α−C_β bonds of the coordinated Cp′ rings (α and β denote the position of the carbon atoms relative to the metal-bonded

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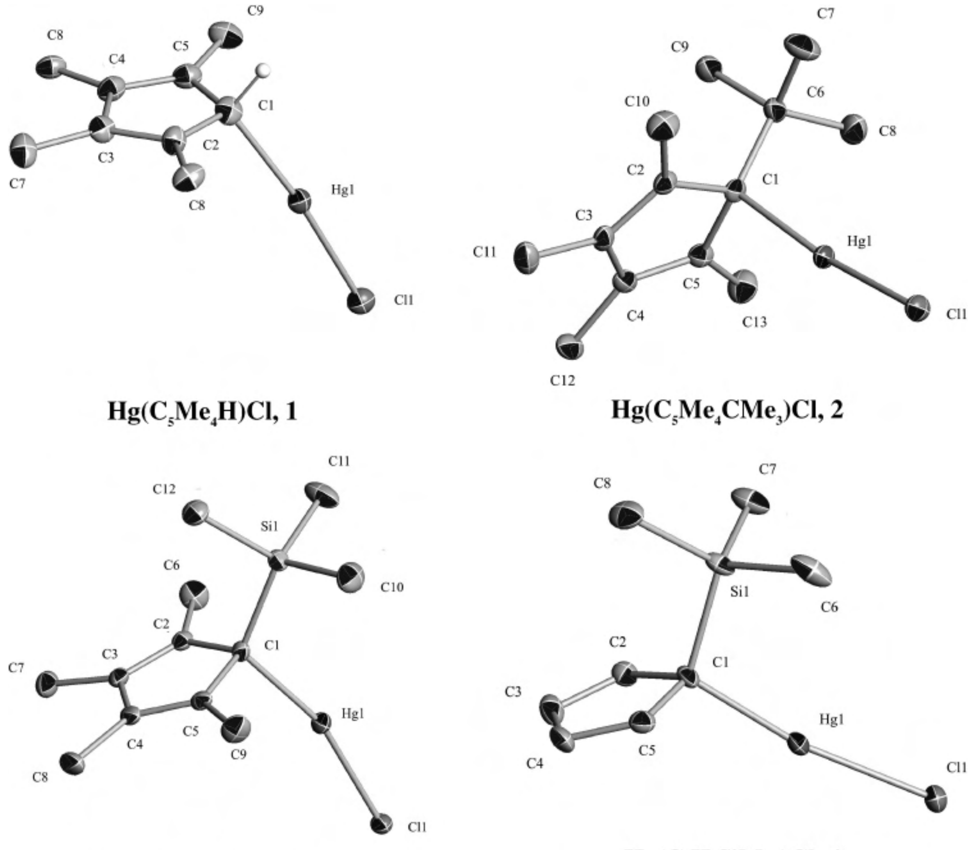

Hg(C_5Me_4H)Cl, 1

Hg($C_5Me_4CMe_3$)Cl, 2

Hg($C_5Me_4SiMe_3$)Cl, 3

Hg($C_5H_4SiMe_3$)Cl, 4

Figure 2. *ORTEP* representations of the solid-state structures of the mono(cyclopentadienyl)mercury compounds **1**−**4**. In each case, only one independent monomeric HgCp′Cl entity is shown (see text). Hydrogen atoms here and in subsequent figures are omitted for clarity.

Table 2. Mercury Coordination Including Secondary Hg···Cl Interactions[a] and Association Types of HgCp′Cl Units in Compounds **1**−**4** and **7**

compound, mercury atom	Hg−C (Å)	Hg−Cl (Å)	C−Hg−Cl (deg)	Hg···Cl′ (Å)	Hg···Cl″ (Å)	association type
1, Hg(1)	2.13(3)	2.327(6)	170.2(6)	3.375(6)	3.447(6)	ladderlike double chain
2, Hg(1)	2.139(3)	2.3697(8)	168.4(1)	3.173(1)	3.195(1)	tetramer with cubelike HgCl core
2, Hg(2)	2.135(4)	2.3785(10)	167.0(1)	3.095(1)	3.122(1)	
3, Hg(1)	2.114(3)	2.3653(11)	164.1(1)	3.063(1)	3.404(1)	
3, Hg(2)	2.114(3)	2.3655(11)	163.0(1)	3.035(1)	3.402(1)	
3, Hg(3)	2.114(3)	2.3542(11)	174.9(1)	3.195(1)	3.330(1)	ladderlike double chain
3, Hg(4)	2.101(3)	2.3432(11)	173.9(1)	3.404(1)	3.460(1)	
4, Hg(1)	2.090(7)	2.355(2)	169.0(2)	3.327(1)	3.352(1)	
4, Hg(2)	2.099(6)	2.341(2)	170.8(2)	3.334(1)	3.377(1) and 3.047(1)	quadruple chain
7, Hg(1)	2.106(3)	2.3285(8)	172.3(1)	3.227(1)		head-to-tail dimer

[a] Hg···Cl′ ≡ head-to-tail-type interactions; Hg···Cl″ ≡ other interactions; all Hg−Cl distances below 4 Å taken into account.

carbon). However, partial $\eta^1(\pi)$ character appears to exist,[17] since for one $C_5Me_4Bu^t$ complex in **2**, the Hg−C−Cp_{centr} angle is only 108°.

The greatest differences between the solid-state structures of compounds **1**−**4** proceed from the spatial arrangement that their constituents adopt in the corresponding unit cells, with different ways of association of the individual HgCp′Cl molecules by means of long secondary Hg···Cl interactions ranging in distance from 3.0 to 3.5 Å. These secondary Hg···Cl interactions represent mainly dipole−dipole forces. According to simple bond-distance vs bond-valence models,[18] their strength is ca. 5−10% that of a Hg−Cl single bond. Figures 4−7 reveal the spatial distributions found for these compounds, which correspond to the formation of isolated

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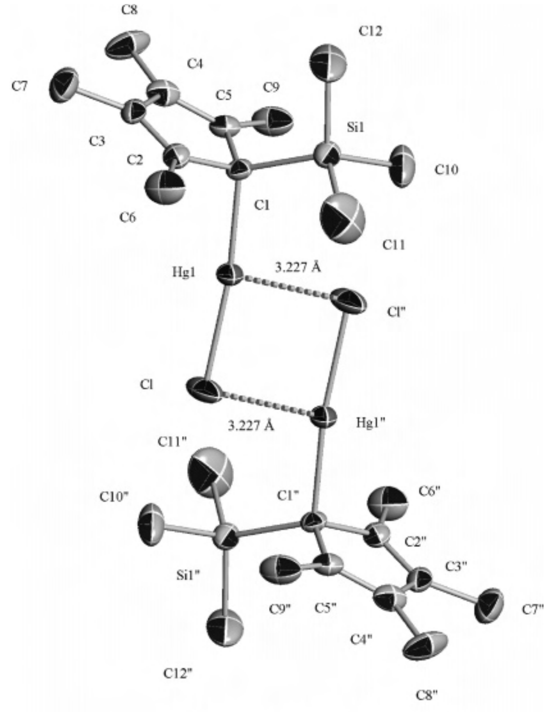
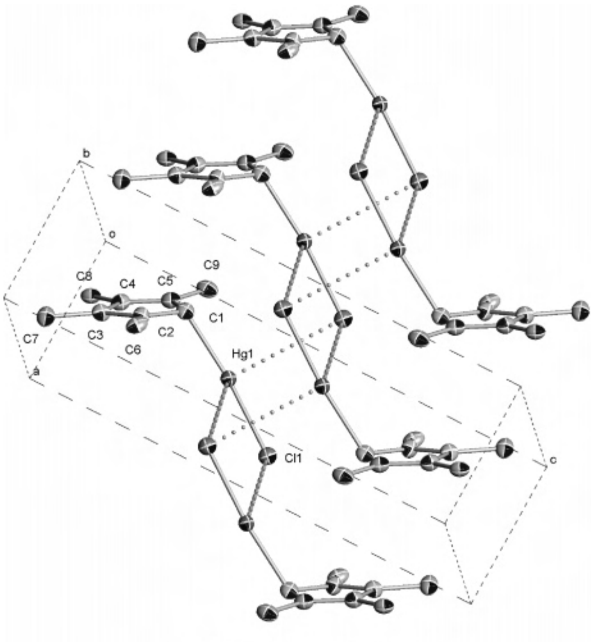


$Hg(C_5Me_4SiMe_3)Cl$ **7**

Figure 3. Head-to-tail dimer formation of $Hg(C_5Me_4SiMe_3)Cl$ in the solid-state structure of cocrystal compound **7**. No Hg···Cl interactions other than those shown are present.



$Hg(C_5Me_4H)Cl$, **1**

Figure 4. Solid-state structure of compound **1**, showing a double chain extending along the *a* axis and the $\pi-\pi$ stacking of the Cp′ moieties within this chain.

tetramers (compound **2**), infinite double chains (complex **1** and **3**), and infinite quadruple chains (complex **4**). Briefly, we consider the main features of these structures. Supporting geometric data are given in Table 2. This table includes also compound **7**, $Hg(C_5Me_4SiMe_3)Cl \cdot Hg(C_5Me_4SiMe_3)_2$, because it contains a key element of the association of linear R−Hg−Cl units (R = alkyl, aryl), namely, the head-to-tail association of a pair of units to form a dimer that is held together by two secondary Hg···Cl interactions (Figure 3). In crystal lattices, this motif frequently includes either a center of symmetry or a twofold axis. If the bulk of R is large, the association may end with the dimer formation, but if it is small, like in the case of Cp′, it proceeds via further Hg···Cl interactions to oligo- and polymerization.[19] In the case of **7**, the termination at the dimerization stage can be explained by the simultaneous presence of $HgCp'_2$ moieties as diluting species, which prevent HgCp′Cl from further self-associations.

Compound **1** has in the solid state a triclinic lattice with space group $P\bar{1}$ in which the molecules of $Hg(C_5Me_4H)Cl$ form infinite zigzag double chains or ladders along the *a* axis (Figure 4) with two secondary Hg···Cl bonds of about 3.4 Å per mercury (Table 2). The head-to-tail dimer motif as part of the chain structure can be readily recognized. Moreover, $\pi-\pi$ stacking and C−H···π interactions between adjacent Cp′ rings within these double chains (plane−plane separations between adjacent Cp′ are ca. 3.6 Å, as seen in Figure 4) appear to contribute to their coherence. Complex **2** crystallizes monoclinic with space group *C*2/*c* and contains two independent molecules of $Hg(C_5Me_4CMe_3)Cl$ in its asymmetric unit. In this case, four molecules (two of each sort) associate to give a distorted cube with corners of alternating Hg and Cl atoms. The four short edges of this distorted cube represent the ordinary Hg−Cl bonds (2.370 and 2.379 Å), whereas the eight long edges represent the secondary Hg···Cl interactions (Hg−Cl = 3.1 − 3.2 Å), as shown in Figure 5. Crystallographically, this clear-cut and well-defined tetramer has a C_2 symmetry but approaches on a molecular level a S_4 symmetry quite well. It differs in this respect notably from the tetrameric associate of $Hg(C_5Me_4SiMe_2Bu^t)Cl$, which as already mentioned was described as a distorted ringlike structure but has further intra-annular Hg−Cl interactions.[6] However, a tetramer with a cubelike arrangement of Hg and Cl has been found previously in chloromercurio vinylimidazoline of tetragonal space group symmetry $I4_1/a$.[19] Although this tetramer has point symmetry S_4, it differs topologically from **3** by the orientation of the RHgCl moieties relative to the S_4 axis (parallel in the latter and perpendicular in **3**).

As represented in Figure 6, the structure of **3** resembles that of $Hg(C_5Me_5)Cl$,[9b] since it is built up from four independent $Hg(C_5Me_4SiMe_3)Cl$ complexes present in the unit cell, space group $P\bar{1}$, that form head-to-tail dimers with their C−Hg−Cl moieties, which then link together by weaker Hg···Cl interactions. For this compound **3**, two types of alternating dimers are observed, one type (Hg···Cl contacts of 3.03 Å) formed between two units of symmetrically independent complexes and another type of dimer (Hg···Cl

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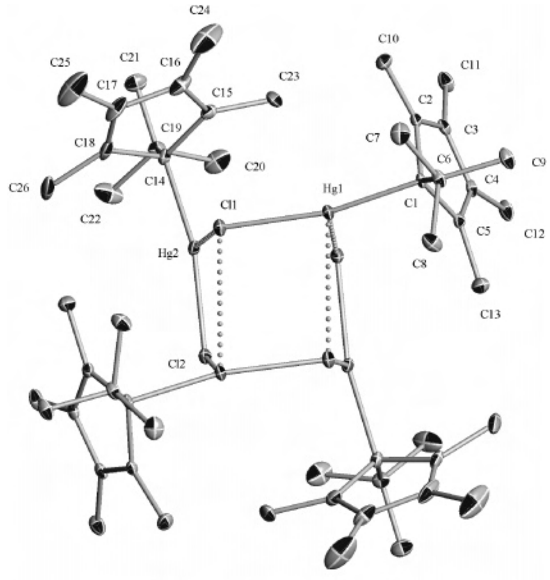
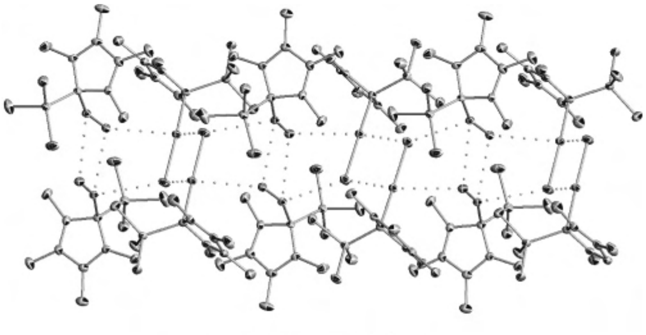
(19) To the best of our knowledge, a timely synopsis on supramolecular associations of chloromercury(II) organyls, RHgCl, is lacking. Therefore, only some useful literature entries are given here: (a) Cambridge Structural Database (CSD); Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380. (b) Beckwith, J. D.; Tschinkl, M.; Picot, A.; Tsunoda, M.; Bachman, R.; Gabbai, F. P. *Organometallics* **2001**, *20*, 3169 and references therein. (c) Kuz'mina, L. G.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1987**, *28*, 118.



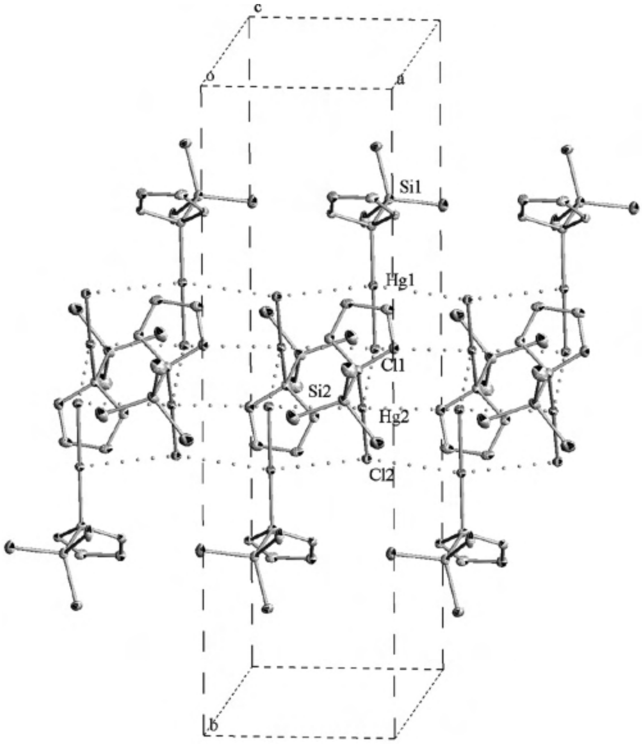
$Hg(C_5Me_4CMe_3)Cl$, **2**

Figure 5. Solid-state structure of compound **2** showing the formation of a tetramer viewed along the crystallographic C_2 axis.



$Hg(C_5Me_4SiMe_3)Cl$, **3**

Figure 6. Solid-state structure of compound **3**, showing a section of the infinite double chain extending along the *c* axis.



$Hg(C_5H_4SiMe_3)Cl$, **4**

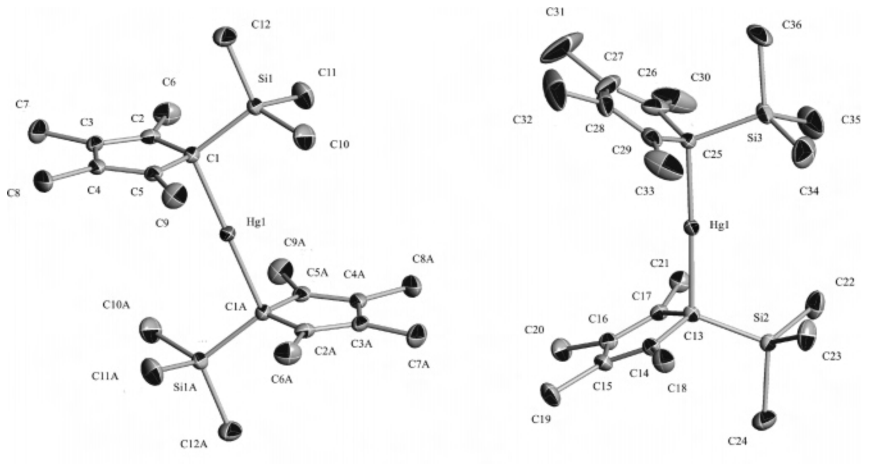
Figure 7. Solid-state structure of compound **4**, showing one quadruple chain extending along the *a* axis.

contacts of 3.33 and 3.46 Å) formed among the other two remaining independent complexes, each one with another one related by a crystallographic inversion center. Thus, the molecules of $Hg(C_5Me_4SiMe_3)Cl$ arrange in such a fashion that they form a Hg−Cl double chain (or ladder) with a sawtoothlike course parallel to the crystallographic *c* axis. In solid $Hg(C_5Me_5)Cl$, a crystallographically simpler form of the same motif is present within a triclinic structure, space group $P\bar{1}$, with the *c* axis halved in comparison to that of **3**.[9b] Finally, compound **4**, that contains the least substituted $C_5H_4SiMe_3$ group, features a pronounced polymeric structure (Figure 7) that can be best described as an infinite quadruple-chain structure extending along the 6.616 Å *a* axis of a monoclinic unit cell with space group $P2_1/c$. The two independent Hg−Cl bonds (Hg1−Cl1 and Hg2−Cl2) and one relatively short Hg···Cl interaction (Hg(2)−Cl(1) = 3.05 Å) are perpendicular to the chain direction, whereas all other secondary Hg···Cl interactions are in the direction of the *a* axis and hence close to $a/2$ = 3.3 Å in length. Although in all previously described compounds **1**−**3** the mercury atoms show one short Hg−Cl bond and two long Hg···Cl interactions, Hg(2) of the two independent mercury atoms in **4** deviates from this rule in having three long Hg···Cl interactions instead of two. Interestingly, the other mercury atom in **4**, Hg(1), shows instead an interaction with the π electrons of a Cp′ ring of its own chain, with Hg(1)···C(12) = 2.96 Å as the shortest Cp′ side-on contact.

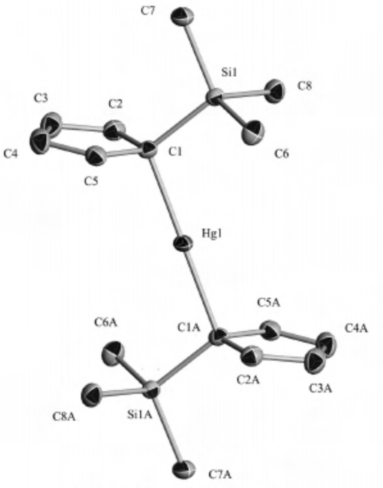
The molecular structures of the bis(cyclopentadienyl) complexes **5** and **6**, represented in Figure 8, are similar and are characterized by Hg−C distances of 2.13 Å, identical within experimental error to corresponding distances in $Hg(C_5Me_4SiMe_2Bu^t)_2$.[6] C−Hg−C angles for **5** and **6** are close to the ideal 180° value normally found in linear, two-coordinated Hg(II) compounds.

As Figure 8 displays, the asymmetric unit of the crystals of **5**, triclinic lattice, space group $P\bar{1}$, contains one complete and one half-molecule, the latter being completed to a full molecule by a crystallographic inversion center occupied by Hg(1). As a result, the two independent $HgCp'_2$ complexes in **5** differ in the mutual orientation of the Cp′ rings: For Hg(1), the $Si-C_i-C_i-Si$ dihedral angle is 180°, whereas for Hg(2), the dihedral angle is close to 0° (actual value 3.5(2)°, but one of the two independent Cp′ rings in this moiety shows indications for significant librations about the $Hg-C_i$ axis or a corresponding static disorder). Compound **6** crystallizes in a monoclinic lattice, space group $P2_1/c$, and contains like **5** a centrosymmetric molecule of $Hg(C_5H_4SiMe_3)_2$ with Hg on the inversion center. Hence, this complex shows a straight C−Hg−C group and an $Si-C_i-C-Si$ dihedral angle of 180° (Figure 8).

To conclude this section, it is worth mentioning that when equivalent mixtures of **3** and **5** are allowed to crystallize,



$Hg(C_5Me_4SiMe_3)_2$, **5**



$Hg(C_5H_4SiMe_3)_2$, **6**

Figure 8. *ORTEP* drawings of the $HgCp'_2$ molecules in the solid-state structures of compounds **5** (two different molecules present in the asymmetric unit; see text) and **6**. Selected bond lengths and angles (Å, deg): (**5**) Hg(1)−C(1) = Hg(1)−C(1A) 2.138(2), Hg(2)−C(13) 2.137(2), Hg(2)−C(25) 2.133(2), C(1)−Hg(1)−C(1A) 180.0, C(13)−Hg(2)−C(25) 177.7(1); (**6**) Hg(1)−C(1) = Hg(1)−C(1A) 2.124(2), C(1)−Hg(1)−C(1A) 180.0.

crystals of analytical composition $Hg_2(C_5Me_4SiMe_3)_3Cl$ are obtained (numbered **7** in the Experimental Section). X-ray studies show that the asymmetric unit contains one HgCp′Cl and one $HgCp'_2$ molecule, of which HgCp′Cl shows the dimerization depicted in Figure 3 and discussed above. The molecules of the $HgCp'_2$ partner are structurally similar to those of Hg(2) in **5**, but the dihedral $Si-C_i-C_i-C_i-Si$ angle is 17.3(2)°, both Cp′ rings are well ordered, and the molecule approaches a noncrystallographic C_2 symmetry. An *ORTEP* diagram of this complex is shown in the Supporting Information.

Theoretical Analysis of HgCp′Cl and $HgCp'_2$ Complexes. DFT calculations on several mono- and biscyclopentadienyl mercury complexes have been performed. The structures of the model complexes were optimized at the B3LYP level of theory using a mixed-valence (TZ and DZ quality) basis set (see Computational Details). Although we have optimized a total of nine different mono(cyclopentadienyl) mercury complexes, only the geometries, electronic structures, and properties of those corresponding to complexes **1**−**4** are discussed here. Information about all the model complexes studied can be found in the Supporting Information.

The optimized structures for model complexes **I**−**IV** are given in Figure 9, whereas selected bond distances and angles are reproduced in Table 3. The main structural parameters, bond distances, and angles are reproduced correctly in the calculations. Thus, the calculated Hg−Cl (2.37−2.39 Å) and Hg−C (2.15−2.18 Å) distances are in good agreement with the experimental values (2.33−2.37 and 2.09−2.14 Å, respectively). The calculated angles around the carbon atom connected to mercury are in all cases close to 109.5°, the theoretical angle for a tetrahedric carbon.

Nucleus-independent chemical shift (NICS) values were determined at the B3LYP level using the 6-311+G* basis set in the center of the cyclopentadienyl ring to determine the aromaticity of the η^1-Cp′ ligand. Calculated values of NICS for model complexes **I**−**IV** are given in Table 3, whereas those calculated for other model complexes not discussed in the text are given as Supporting Information. For comparative purposes, the calculated NICS values at the same level of theory of $[C_5H_5]^-$ and C_5H_6 are −12.5 and

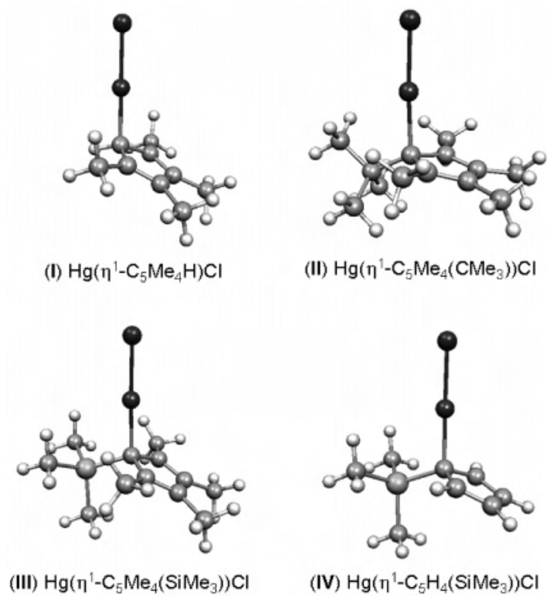


Figure 9. Optimized structures for calculated HgCp′Cl complexes **I**−**IV**.

Table 3. Bond Distances (Å), Angles (deg), and NICS Values for Calculated HgCp′Cl Complexes I−**IV**

	I	II	III	IV
Hg−Cl	2.377	2.387	2.378	2.366
Hg−C	2.152	2.184	2.155	2.148
$C-C_\alpha$	1.498	1.521	1.506	1.490
$C_\alpha-C_\beta$	1.358	1.359	1.363	1.361
$C_\beta-C_{\beta'}$	1.481	1.467	1.464	1.447
Hg−C−R	103.1	111.2	109.4	110.0
$Hg-C-C_\alpha$	109.0	101.8	106.8	106.0
Hg−C−D	121.9	109.5	119.0	117.0
NICS	−0.3	−2.1	−3.4	−5.6

−2.9, respectively. The calculated values are in all cases negative but small, therefore approaching that corresponding to C_5H_6, in accordance with the localized diene structure of the Cp′ rings suggested by the X-ray data. It is important to notice that models containing a silyl substituent in the ring present more negative values or NICS than analogous models with an alkyl substituent. It has been reported that the presence of two silyl substituents in a cyclopentadiene ring can make it as aromatic as furan.[17b] Also, the inclusion of methyl groups as substituents in the ring decreases NICS values. For example, the NICS value of model **IV**, −5.6, decreased to −3.4 in model **III**, where the Cp′ ring is permethylated.

We have also performed DFT calculations on other isomeric structures containing the Hg atom bound to the α and *β* positions of the ring, isomers B and C, respectively. The calculated energies for the different isomers of complexes **I**−**IV** are given in Table 4 as well as the energies of the transition states connecting the transformation of isomers A and B. The energy differences between isomers are similar to those calculated for CpZn($C_5Me_4SiMe_3$).[12a]

In all cases, isomers B and C are calculated to be higher in energy than isomer A, but the small differences found could suggest a dynamic behavior for all complexes, which is actually in disagreement with our experimental observation of a rigid structure for the $C_5Me_4SiMe_3$ derivative **3**. It seems that calculations at this level of theory fail to reproduce the solution properties of this $C_5Me_4SiMe_3$ complex **3**. However, the calculated energy for the transition state connecting isomers A and B is much higher and suggests that, at least at low temperatures, the dynamic behavior of complexes **1**−**4** should be static.

Table 4. Relative Energy (kcal mol^{-1}) between Isomeric Structures of Model Complexes **I**−**IV**[a]

	I	II	III	IV
isomer A	0.0	0.0	0.0	0.0
isomer B	+2.5	+1.6	+2.8	+1.0
isomer C	+3.7	+2.0	+5.5	+2.2
TS (A → B)	+11.2	+10.6	+11.7	+8.8
imag freq, cm^{-1}	180*i*	163*i*	151*i*	175*i*

[a] The energy of the transition state connecting isomers A and B and the value of the imaginary frequency are also given.

The optimized structures for model complexes **X** and **XI**, corresponding to complexes **5** and **6**, respectively, are given in the Supporting Information (Figure S3), together with selected bond distances and angles (Table S2). As in the case of HgCp′Cl derivatives, the main structural parameters for HgCp′$_2$ complexes are reproduced correctly in the calculations. Thus, the calculated Hg−C (2.19−2.20 Å) distances are in good agreement with the experimental values (2.12−2.14 Å). As observed for the HgCp′Cl derivatives, the calculated angles around the carbon atom connected to mercury are in all cases close to 109.5°, the theoretical angle for a tetrahedric carbon.

Conclusions

In summary, the structural characterization by X-ray methods of six new mercury cyclopentadienyl complexes broadens our understanding of the solid-state structures of this family of compounds, which somewhat surprisingly, was an underdeveloped aspect of mercury metallocenes. In addition, the rigid structure found in solution for the $-SiMe_3$-substituted complexes **3**, **5**, and **6** corroborates previous results based on the use of the $C_5Me_4SiMe_2Bu^t$ ligand[6] and suggests the existence of a silyl effect that significantly strengthens the Hg−C($SiMe_3$) bond. Our failure to generate Hg(η^1-Cp′)$_2$ compounds other than **5** and **6**, that respectively contain the $C_5Me_4SiMe_3$ and $C_5H_4SiMe_3$ groups, points to the same direction. Although the picture appears to be complete from an experimental point of view, additional theoretical work should shed further light on this issue.

Experimental Section

General Methods. All preparations and manipulations were carried out under oxygen-free argon using conventional Schlenk techniques.[20] Solvents were rigorously dried and degassed before use.[20] Microanalyses were obtained at the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla). Infrared spectra were recorded on a Bruker Vector 22 spectrometer. NMR spectra were recorded on Bruker AMX-300, DRX-400, and DRX-500 spectrometers. The ^{1}H and ^{13}C NMR resonances of the solvent

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(20) (a) Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley Interscience: New York, 1986. (b) Perrin, D .D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 2nd. ed.; Pergamon Press: Oxford, 1980.

Table 5. Summary of Crystallographic Data and Structure Refinement Results for **1**−**8**

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
formula	$C_9H_{13}ClHg$	$C_{13}H_{21}ClHg$	$C_{12}H_{21}ClHgSi$	$C_{16}H_{26}Cl_2Hg_2Si_2$	$C_{24}H_{42}HgSi_2$	$C_{16}H_{26}HgSi_2$	$C_{36}H_{63}ClHg_2Si_3$	$C_{18}H_{26}$
fw	357.23	413.34	429.42	746.63	587.35	475.14	1016.76	244.40
cryst syst	triclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a, Å	4.1704(6)	25.2360(1)	13.352(3)	6.6159(5)	8.7264(1)	7.9219(3)	13.603(2)	6.9998(4)
b, Å	8.7597(1)	9.0785(4)	14.702(4)	22.6512(2)	11.3098(2)	9.2815(3)	13.808(2)	7.5808(4)
c, Å	13.318(2)	26.7146(1)	18.093(3)	15.1872(1)	22.744(3)	12.4204(5)	14.618(2)	8.3361(4)
α, deg	92.219(6)	90	68.94(2)	90	93.496(2)	90	91.692(4)	64.618(1)
β, deg	91.385(5)	114.163(1)	81.23(2)	91.469(2)	99.672(2)	91.824(1)	116.356(4)	68.721(0)
β, deg	97.150(5)	90	63.21(2)	90	111.419(2)	90	118.452(4)	69.637(1)
V, Å^3	482.17(1)	5584.2(5)	2958.5(1)	2275.2(3)	2041.6(5)	912.77(6)	2059.4(6)	362.55(3)
Z	2	16	8	4	3	2	2	1
D_{calc}, Mg m^{-3}	2.461	1.967	1.928	2.180	1.433	1.729	1.640	1.119
μ, mm^{-1}	16.173	11.186	10.638	13.815	5.749	3.550	7.620	0.062
θ_{max}, deg	30.6	30.6	30.0	30.5	30.0	30.6	30.0	30.6
temp, K	100	100	173	100	173	100	173	100
no. reflns collected	8712	24 944	53 741	30 864	37 050	22 077	42 768	11 140
no. reflns used	2784	8370	16672	6579	11630	2798	11675	2193
no. of params	100	271	558	205	380	91	392	90
$R_1(F)$ [$F^2 > 2\sigma(F^2)$][a]	0.066	0.032	0.026	0.046	0.024	0.016	0.022	0.039
$R_2(F^2)$[b] (all data)	0.162	0.0859	0.054	0.101	0.049	0.044	0.051	0.111
S[c] (all data)	1.077	1.006	1.002	1.061	1.027	1.047	1.029	1.077

[a] $R_1(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$ for the observed reflections [$F^2 > 2\sigma(F^2)$]. [b] $R_2(F^2) = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum w(F_o{}^2)^2\}^{1/2}$. [c] $S = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/(n - p)\}^{1/2}$ (n = number of reflections, p = number of parameters).

were used as the internal standard, and the chemical shifts are reported relative to TMS. The cyclopentadienyl reagents KCp′ were prepared from Cp′H and K as described elsewhere.[21,22]

General Procedure for 1−4. A solution of 1 equiv of $HgCl_2$ in diethyl ether was added to a suspension of 1 equiv of KC_5R_4R' in the same solvent. After the mixture was stirred at room temperature for 1−4 h, the solvent was removed under vacuum. Extraction and crystallization from the appropriate solvent yielded the expected compound. Alternatively, compounds **1**−**4** can be obtained by reacting $HgCl_2$ and the corresponding $ZnCp'_2$ in a 2:1 ratio, also in Et_2O as the solvent. After stirring at room temperature for ca. 4 h, the reactions were worked up as above.

Hg(C$_5$Me$_4$H)Cl, 1: 543 mg (2 mmol) of $HgCl_2$ in diethyl ether (20 mL) and 320 mg (2 mmol) of KC_5Me_4H in the same solvent (30 mL). The pale-yellow solid was extracted with diethyl ether (30 mL) and crystallized from this solvent. Yield: 520 mg (75%). Anal. Calcd: C, 30.26; H, 3.67. Found: C, 30.2; H, 3.7. ^{1}H NMR (300 MHz, C_6D_6, 25 °C, ppm): 1.54 (s, Me$_\beta$, 6H), 1.68 (s, Me$_\alpha$, 6H), 3.06 (s, C*H*, 1H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C, ppm): 11.2 (s, C−*Me*$_\beta$), 13.6 (s, C−*Me*$_\alpha$), 69.1 (s, CH), 129.1 (s, ring C$_\alpha$), 135.6 (s, ring C$_\beta$).

Hg(C$_5$Me$_4$Bu^t)Cl, 2: 271 mg (1 mmol) of $HgCl_2$ in diethyl ether (10 mL) and 216 mg (1 mmol) of $KC_5Me_4CMe_3$[22] also in ether (20 mL). The pale-yellow solid was extracted with hexane (30 mL) and crystallized from this solvent. Yield: 132 mg (32%). Anal. Calcd: C, 37.73; H, 5.09. Found: C, 37.7; H, 5.2. ^{1}H NMR (500 MHz, C_6D_6, 25 °C, ppm): 0.92 (s, C*Me*$_3$, 9H), 1.60 (s, Me$_\beta$, 6H, $^3J_{\mathrm{Hg-H}} = 66$ Hz), 1.74 (s, Me$_\alpha$, 6H). ^{13}C{^{1}H} NMR (125 MHz, C_7D_8, −70 °C, ppm): 11.9 (s, C−*Me*$_\beta$), 17.5 (s, C−*Me*$_\alpha$), 32.4 (s, C*Me*$_3$), 37.9 (s, *C*Me$_3$), 98.5 (s, *C*−CMe$_3$), 131.4 (s, ring C$_\beta$), 137.3 (s, ring C$_\alpha$).

Hg(C$_5$Me$_4$SiMe$_3$)Cl, 3: $HgCl_2$ (543 mg, 2 mmol) in diethyl ether (20 mL) and $KC_5Me_4SiMe_3$[21] (464 mg, 2 mmol) in the same solvent (30 mL). The pale-yellow solid was extracted with 1:1 hexane/diethyl ether (30 mL) and crystallized from this mixture of solvents. Yield: 540 mg (63%). Anal. Calcd: C, 33.57; H, 4.89. Found: C, 33.4; H, 4.8. ^{1}H NMR (500 MHz, C_6D_6, 25 °C, ppm): −0.16 (s, SiMe$_3$, 9 H), 1.65 (s, Me$_\beta$, 6H), 1.73 (s, Me$_\alpha$, 6H, $^4J_{\mathrm{Hg-H}} = 65$ Hz). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C, ppm): −0.6 (s, Si*Me*$_3$, $^3J_{\mathrm{Hg-C}} = 52$ Hz), 11.1 (s, C−*Me*$_\beta$), 15.3 (s, C−*Me*$_\alpha$), 80.9 (s, *C*$_q$−Si, $^1J_{\mathrm{Hg-C}} = 1157$ Hz), 131.0 (s, ring C$_\beta$, $^3J_{\mathrm{Hg-C}} = 98$ Hz), 135.9 (s, ring C$_\alpha$, $^2J_{\mathrm{Hg-C}} = 113$ Hz).

Hg(C$_5$H$_4$SiMe$_3$)Cl, 4: 271 mg (1 mmol) of $HgCl_2$ in diethyl ether (10 mL) and 144 mg (1 mmol) of $LiC_5H_4SiMe_3$ in the same solvent (20 mL). The pale-yellow solid was extracted with diethyl ether (30 mL) and crystallized from the same solvent. Yield: 298 mg (80%). Anal. Calcd: C, 25.81; H, 3.25. Found: C, 25.2; H, 3.5. ^{1}H NMR (500 MHz, CD_2Cl_2, −80 °C, ppm): −0.09 (s, Si*Me*$_3$, 9H), 6.49 (s, 2H), 6.65 (s, 2 H). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, −80 °C, ppm): −0.8 (s, Si*Me*$_3$), 72.9 (C$_q$−Si), 130.2, 133.3 (s, ring C$_\beta$ and C$_\alpha$).

General Procedure for 5 and 6. A solution of 1 equiv of $HgCl_2$ in diethyl ether was added to a suspension of 2 equiv of $KC_5R_4SiMe_3$ in the same solvent. After the mixture was stirred at room temperature for 5 h, the solvent was removed under vacuum. Extraction and crystallization from hexane yielded the corresponding compound. The $HgCp'_2$ compounds **5** and **6** can also be prepared from the appropriate mono(cyclopentadienyl) derivative (**3** or **4**, respectively) by treatment with 1 equiv of KCp′ or by the direct reaction of equimolecular mixtures of $HgCl_2$ and $ZnCp'_2$.

Hg(C$_5$Me$_4$SiMe$_3$)$_2$, 5: 814 mg (3 mmol) of $HgCl_2$ in diethyl ether (20 mL) and 1.39 g (6 mmol) of $KC_5Me_4SiMe_3$[21] also in ether (30 mL). Yield: 1.37 g (78%). Anal. Calcd: C, 49.10; H, 7.15. Found: C, 48.7; H, 7.4. ^{1}H NMR (300 MHz, C_6D_6, 25 °C, ppm): 0.11 (s, SiMe$_3$, 9 H), 1.90 (s, Me$_\beta$, 6H), 2.02 (s, Me$_\alpha$, 6H, $^4J_{\mathrm{Hg-H}} = 28$ Hz). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C, ppm): 0.8 (s, Si*Me*$_3$, $^3J_{\mathrm{Hg-C}} = 52$ Hz), 11.7 (s, C−*Me*$_\alpha$), 16.1 (s, C−*Me*$_\beta$), 89.1 (s, *C*$_q$−Si, $^1J_{\mathrm{Hg-C}} = 505$ Hz), 130.4 (s, ring C$_\beta$, $^3J_{\mathrm{Hg-C}} = 54$ Hz), 134.3 (s, ring C$_\alpha$, $^2J_{\mathrm{Hg-C}} = 49$ Hz).

Hg(C$_5$H$_4$SiMe$_3$)$_2$, 6: 271 mg (1 mmol) of $HgCl_2$ in diethyl ether (20 mL) and 288 mg (2 mmol) of $KC_5H_4SiMe_3$ in the same solvent (30 mL). Yield: 0.40 g (84%). Anal. Calcd: C, 40.45; H, 5.52.

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Found: C, 39.85; H, 5.88. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C, ppm): 0.01 (s, $SiMe_3$, 9H), 6.42 (s, H_β, 2H), 2.02 (s, H_α, 2H, $^{3}J_{Hg-H}$ = 34 Hz). $^{13}C\{^{1}H\}$ NMR (75 MHz, CD_2Cl_2, 25 °C, ppm): −0.4 (Si*Me*$_3$, $^{3}J_{Hg-C} = 30$ Hz), 91.9 (s, C_q−Si, $^{1}J_{Hg-C} = 780$ Hz), 126.9 (s, ring C_β, $^{3}J_{Hg-C} = 27$ Hz), 127.8 (s, ring C_α, $^{2}J_{Hg-C} = 47$ Hz).

$(C_5Me_4H_2)_2$, 8: 271 mg (1 mmol) of $HgCl_2$ in 10 mL of diethyl ether and 320 mg (2 mmol) of KC_5Me_4H in 20 mL of the same solvent were stirred for 2 h at room temperature. A gray solid appeared, and the yellow solution was filtered off. Evaporation and cooling to −20 °C gave compound **8** as white crystals. Yield: 380 mg (80%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C, ppm): 1.11 (s, 3H), 1.67 (s, 3H), 1.77 (s, 3H), 1.80 (s, 3H), 6.07 (s, 1H). $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6, 25 °C, ppm): 10.6, 12.6, 13.8, 17.9, 58.2, 134.0, 139.2, 143.4, 135.9.

Computational Details. The electronic structures and geometries of the model complexes were computed within the DFT at the B3LYP level.[23] The Hg atom was described with the Stuttgart relativistic small core ECP basis set;[24] Si atoms, Cl atoms, and C atoms corresponding to the cyclopentadienyl ring and quaternary C atom of ^{t}Bu groups were described using the 6-311G* basis set, while 6-31G* was used for H atoms and C atoms of methyl groups. The wave functions of the model compounds HgCp′Cl, for Cp′ = C_5H_5, C_5H_4Me, and $C_5H_4SiH_3$, were tested for stability (see the Supporting Information). Vibrational frequency calculations were done by diagonalization of the analytically computed Hessian to ensure that the optimized structures were real minima (NImag = 0).NICS[25] values were calculated using the 6-311+G* basis set for all atoms at the center of the cyclopentadienyl ring. All calculations were performed using the *Gaussian03* package.[26] Figures were drawn using *Molekel*.[27] *XYZ* coordinates of all optimized complexes are available upon request.

X-ray Structure Analysis for 1−8. A summary of crystallographic data and structure refinement results for **1**−**8** is given in Table 5. Crystals coated with dry perfluoropolyether were mounted on glass fibers and fixed in a cold nitrogen stream (T = 100 or 173 K). Intensity data were collected on a Bruker-Nonius X8Apex-II CCD diffractometer (**1**, **2**, **4**, **6**, and **8**) or a Bruker SMART CCD diffractometer (**3**, **5**, and **7**), both operating with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data were reduced (*SAINT*)[28] and corrected for absorption effects by the multiscan method (*SADABS*).[28] The structures were solved by direct methods (*SIR-2002* and *SHELXS*)[29,30] and refined against all F^2 data by full-matrix least-squares techniques (*SHELXTL-6.12*)[28] minimizing $w[F_o^2 - F_c^2]$.[2]

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Supporting Information Available: X-ray crystallographic data in CIF format; table with selected bond distances for optimized complexes and figures with selected MOs; *ORTEP* drawings of complexes **7** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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