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Synthesis and Solid-State Structure of Zn(η^5-$C_5Me_4SiMe_3$)(η^1-$C_5Me_4SiMe_3$), a Zincocene with Nonparallel Cyclopentadienyl Rings

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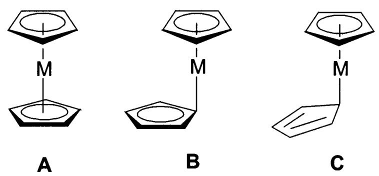
Summary: The reaction of $ZnCl_2$ with $KC_5Me_4SiMe_3$ provides $Zn(C_5Me_4SiMe_3)_2$, structurally characterized by X-ray crystallography as the first zincocene with nonparallel cyclopentadienyl rings.

At variance with transition-metal metallocenes, bis(cyclopentadienyl) derivatives of the nontransition elements encompass a variety of structures,[1] including the classical sandwich geometry **A**. Two others, **B** and **C**, contain one η^5 and one η^1 ring but differ in the coordination of the latter ring. In the so-called slipped-sandwich structure, or $\eta^5/\eta^1(\pi)$ (**B**), the η^1-Cp′ is parallel to the centrally bound ring and maintains some degree of aromaticity. This is the geometry characteristic of Be(C_5H_5)$_2$[2] and Be(C_5Me_4H)$_2$[3] and of the molecular zincocenes that have been characterized by X-ray methods.[4] In the alternative $\eta^5/\eta^1(\sigma)$ structure **C**, the two rings are nonparallel. To our knowledge, Cowley's X-ray investigation of the B(C_5Me_5)$^{2+}$ cation,[5] earlier characterized by Jutzi by NMR spectroscopy,[6] constitutes the only authenticated example of this structural variety.



This work was started with the objective of preparing a beryllocene or a zincocene with nonparallel rings, viz. with a structure of type **C**. Because of the much lower

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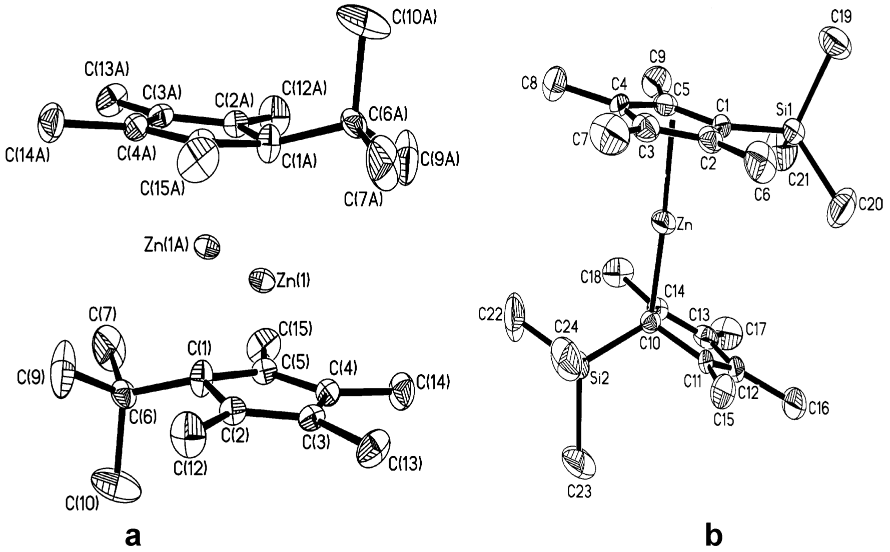

Figure 1. ORTEP structures of compounds **1** and **2**.

toxicity of Zn and its larger size,[7] which makes it compatible with bulky cyclopentadienyl ligands, our first efforts have concentrated on zincocenes. We have compared $Zn(C_5Me_4CMe_3)_2$ (**1**) and $Zn(C_5Me_4SiMe_3)_2$ (**2**), thinking that whereas their $Zn(\eta^5\text{-}Cp')$ moieties would be analogous to those of known zincocenes,[4] different geometries could hopefully define their $Zn(\eta^1\text{-}Cp')$ linkages. Specifically, **2** may be thought of as a cyclopentadiene with geminal C-5 substitution by $SiMe_3$ and $Zn(\eta^5\text{-}C_5Me_4SiMe_3)$ groups. Therefore, if the electronic effects of the silyl substituent could allow carbon-5 to remain almost tetrahedral, while at the same time keeping some ring aromatic character,[8] the two $C_5Me_4SiMe_3$ groups of **2** would adopt a nonparallel distribution. Encouragement to follow this approach comes from (i) the knowledge of the structural features of silyl-substituted cyclopentadienes[8−10] and of some of their complexes[11] (for instance, $C_5H_4(SiMe_3)_2$ exists mostly as the 5,5-isomer[9] and 5,5-disilylcyclopentadiene has been calculated to have almost tetrahedral C(5) and aromaticity close to that of furan[8]) and (ii) Haaland's findings on the gas-phase structures of $Zn(C_5Me_5)_2$ (slip-sandwich) and $Zn(C_5H_4SiMe_3)_2$ ($\eta^5/\eta^1(\sigma)$ geometry).[12] Compounds **1** and **2** are prepared in good yields by the room-temperature reaction of anhydrous $ZnCl_2$ and the corresponding KCp′ reagent (eq 1; see the Supporting Information for details and properties of the new compounds).

$$ZnCl_2 + 2KC_5Me_4R \xrightarrow{20\ °C} \underset{\mathbf{1,\,2}}{Zn(C_5Me_4R)_2} + 2KCl \quad (1)$$

$$R = CMe_3\ (\mathbf{1}),\ SiMe_3\ (\mathbf{2})$$

Their ^1H and $^{13}C\{^1H\}$ NMR spectra are simple and present, down to −90 °C, signals due to only one kind of ring (for instance, **2** exhibits three ^1H resonances at δ 0.14 (Si*Me*$_3$) and 1.96 and 2.04 (α- and β-C*Me*); corresponding $^{13}C\{^1H\}$ resonances are found at 1.3, 10.8, and 14.0 ppm, respectively, accompanied by others at δ 78.7 (*C*SiMe$_3$) and 122.7 and 125.0 ppm (C_α and C_β). Clearly the molecular inversion process that exchanges the two rings[13] is very fast, even at the lowest temperatures investigated. This is a general phenomenon for all known zincocenes[4] and beryllocenes.[2,3,13]

As shown in Figure 1a, compound **1** has the expected slip-sandwich structure.[14] The zinc atom is disordered between two equivalent sites that exchange the coordination modes of the ring. The Zn(1)−C(1A) distance of 2.159(2) Å, albeit shorter than the corresponding distance in $Zn(C_5HPr^i{}_4)_2$ (2.223(4) Å),[4a] is well above the average of Zn−C covalent bonds[15] (ca. 2.005(3) Å). The two $C_5Me_4CMe_3$ rings are parallel, and the Zn(1)−C(1A) bond is practically perpendicular to the plane of the η^1 ring (angle of 94.4°).

Comparison of parts a and b of Figure 1, the latter displaying the structure of the molecules of **2**, evinces the differences between the two geometries.[16] Despite some variations in the Zn−C distances, the coordination of the $\eta^5\text{-}C_5Me_4SiMe_3$ ligand can be considered normal (Zn−C bond lengths range from 2.154(3) to 2.323(3) Å, i.e., about 8% difference). This irregularity is smaller than in $Zn(C_5Me_4Ph)_2$[4b] and $Zn(C_5HPr^i{}_4)_2$,[4a] and it is manifested by a ring slippage[4] of 0.18 Å (0.20 and 0.32

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[14] Crystal data for **1** at 296 K: $C_{26}H_{42}Zn$, fw 419.97, monoclinic, space group $P2_1/c$, $a = 8.7494(5)$ Å, $b = 16.8068(10)$Å, $c = 8.8744(6)$ Å, $\beta = 113.1450(10)°$, $V = 1183.62(12)$ Å^3, $Z = 2$. The final R1 factor was 0.0459 for 2365 independent reflections with $I > 2\sigma(I)$ (wR2 = 0.1235). GOF = 1.089.

[15] Data taken from a computer search at the CCDC.

[16] Crystal data for **2** at 173 K: $C_{24}H_{42}Si_2Zn$, fw 452.13, monoclinic, space group $P2_1/c$, $a = 9.0211(7)$ Å, $b = 34.925(3)$ Å, $c = 8.8173(7)$ Å, $\beta = 112.114(2)°$, $V = 2573.6(4)$ Å^3, $Z = 4$. The final R1 factor was 0.0418 for 5401 independent reflections with $I > 2\sigma(I)$ (wR2 = 0.0994). GOF = 0.571.

Å in the above zincocenes, respectively; 0.33 Å in compound **1**).

The most notable feature of the structure of **2** is, doubtless, the coordination of the η^1-Cp′ ring, bound to zinc through the silyl-bearing carbon atom, C(10).[11] The geometry around C(10) is comparable to that of the related atom in $B(C_5Me_5)_2^+$, the only $\eta^5/\eta^1(\sigma)$ metallocene authenticated by X-ray methods.[5] Thus, the Zn−C(10)−Si(2) and Zn−C(10)−ring angles of ca. 112 and 110°, respectively, are very similar to the corresponding angles in the boron cation (ca. 112 and 114°, respectively). Even if the hybridization of C(10) is not pure sp^3 (such an electronic distribution would be characterized by Zn−C(10)−C(11) and Zn−C(10)−C(14) angles close to the ideal 109.5° value; instead, in compound **2** they are ca. 102°), it approaches that hybridization significantly. Further indications are the nonparallel distribution of the rings (angles of ca. 18°) and the comparatively short, and therefore strong, Zn−C(10) bond, which, with a length of 1.953(3) Å, becomes almost equal to the Zn−Me bonds in $ZnMe_2$ (1.930(2) Å).[17]

One additional structural feature worthy of note is the partial aromatic character of the η^1 ring. The difference between the $C_\beta C_\beta$ and $C_\alpha C_\beta$ bonds in **2** is 0.07 Å (α and β refer to the positions with respect to C(10), i.e., the four-coordinated carbon of the η^1 ring). The calculated difference for $C_5H_4(SiMe_3)_2$ is 0.07 Å as well,[8] while in $B(C_5Me_5)_2^+$ it has double that value, i.e., 0.14 Å, in accord with a localized structure.[5] It thus appears that silyl ring substitution stabilizes the $\eta^1(\sigma)$ coordination by making the Zn−C bond to the η^1 ring stronger, whereas at the same time electron delocalization in the ring π system is maintained.[18] In agreement with the X-ray results, the $^{13}C\{^1H\}$ CP MAS NMR spectrum of **2** shows distinct resonances for the two rings. Thus, the ring carbon nuclei give two resonances at δ 59.3 and 94.5 (C−$SiMe_3$ of the η^1 and η^5 rings, respectively) and four more in the interval from 114.7 to 129 ppm (α- and β-carbon nuclei).

To gain knowledge of the electronic factors that determine the differences in the geometry of the η^1 rings of **1** and **2**, DFT calculations on the models $Zn(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5Me_4R)$, for R = CMe_3, $SiMe_3$, SiH_3, have been performed (B3LYP/LANL2DZ*, see the Supporting Information for details). In accord with experimental results, only those zincocenes that contain a Zn−C(SiR'_3) bond (R′ = H, Me) lead to calculated nonslip structures. For instance, $Zn(C_5H_5)(C_5Me_4CMe_3)$ is predicted to have a slipped geometry, characterized by a Zn−C(CMe_3)−ring angle of 97.4° (experimental value for **1** 94.4°). In contrast, the most stable isomer of $Zn(C_5H_5)(C_5Me_4SiMe_3)$, namely, that with a Zn−C($SiMe_3$) bond, has a Zn−C($SiMe_3$)−ring angle of 106° (experimental value for **2** 110°). Opposite to this, the other two isomeric structures corresponding to the latter formulation (that is, those with a Zn bond to the α- and the β-CMe) are ca. 3.5−5 kcal mol^{-1} higher in energy and have corresponding angles close to 90°, as shown in Figure 2.

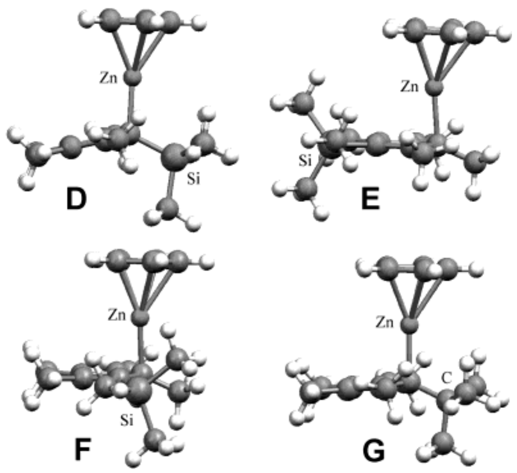

Figure 2. Optimized structures for isomers of the model complex $Zn(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5Me_4SiMe_3)$ (**D**−**F**; **D** is the most stable isomer) and of $Zn(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5Me_4CMe_3)$ (**G**).

It appears evident at this stage that a silyl substituent on a cyclopentadienyl ring favors the adoption by zincocenes of a nonslip sandwich structure.[12] Since both experiments and calculations point to considerable tetrahedral character for the Zn-coordinated carbon atom (which can therefore form a stronger C−Zn bond than the trigonal, sp^2-hybridized carbon of the slip-sandwich structure), with simultaneous electron delocalization within the ring, a reasonable explanation could be silyl hyperconjugative donation.[8] This notwithstanding, as at the present level our calculations do not provide clear-cut evidence in this direction, it is prudent to defer a definite explanation of this intriguing structural peculiarity until additional knowledge is gained.

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Supporting Information Available: Text giving experimental procedures and characterization data for compounds **1** and **2** and text and tables giving X-ray crystallographic data and computational data. This material is available free of charge via the Internet at http://pubs.acs.org.

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