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Bis(cyclopentadienyl)zirconium and -hafnium Macrocycles Containing Siloxane Bridges: Synthesis of $[(\eta^5\text{-}C_5H_5)_2M\{\mu\text{-}OSi(C_6H_5)_2O\}]_2$ (M = Zr, Hf) and Crystal Structure and EHMO Study for M = Zr

Edmond Samuel,[*,†] **John F. Harrod,**[‡] **Michael J. McGlinchey,**[§] **Claude Cabestaing,**[∥] **and Francis Robert**[⊥]

Laboratoire de chimie organométallique de l'ENSCP (URA 403, CNRS), 11 rue P. et M. Curie, 75231 Paris Cédex 05, France, Department of Chemistry, McGill University, Montreal, Canada, Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada, Unité de Recherche: Modélisation Appliquée à la Chimie et au Génie des Procédés (JE 47 ENSCP), 11 rue P. et M. Curie, 75231 Paris Cédex 05, France, and Laboratoire de Chimie des Métaux de Transition (URA 419, CNRS), Université P. et M. Curie, 4 Place Jussieu, 75005 Paris, France

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The reaction of Cp_2MMe_2 (M = Zr, Hf) with $Ph_2Si(OH)_2$ yields the eight-membered ring $[Cp_2M(\mu\text{-}OSiPh_2O)]_2$ (M = Zr (**1**), Hf (**2**)). **1** crystallizes in the space group $P\bar{1}$ with $a = 10.410(9)$ Å, $b = 12.140(6)$ Å, $c = 16.318(5)$ Å, $\alpha = 94.26(3)°$, $\beta = 103.42(5)°$, $\gamma = 93.16(6)°$, and $Z = 2$. The crystal structure reveals that the ring is not planar. The Cp_2Zr units are bent 20° out of the Si_2O_4 plane to give a "chaise longue" conformation; however, in solution the molecule is fluxional on the NMR time scale. The zirconium–oxygen distances of 1.974(2) and 1.983(2) Å are significantly longer than those reported in other Zr–O–Si compounds. EHMO calculations suggest that the Zr–O bond order may be rationalized in terms of an in-plane π-system.

Introduction

The group 4 metals Ti, Zr, and Hf are highly oxophilic and form readily organometallic derivatives possessing stable metal–oxygen bonds. These can be either terminal, as in alkoxides, or bridging, with M–O–M linkages. Another category of such compounds includes the cyclic tetramers, known mostly for titanium,[1] and also a small number of macrocycles containing Ti or Zr. Moreover, cyclic Ti and Zr systems containing siloxane bridges have been recently reported.[2]

Silanols formed on silica surfaces are widely postulated as intermediates in promoting the catalytic activity of these supports, so it can be reasonably assumed that incorporation of zirconium would have a cooperative effect in activating the substrate proximate to the surface by forming an intermediary metal–siloxy complex. In addition, because of the complexity of silicate surfaces, compounds resulting from the interaction of silanols with metal-containing entities are of interest as models which may be useful to elucidate the metal-to-surface interaction mode in heterogeneous silicon oxide-based catalysts.[3]

We here report the synthesis and X-ray crystallographic characterization of a novel eight-membered ring complex derived from the reaction of Cp_2ZrMe_2 with $Ph_2Si(OH)_2$. We also describe reactions of the congeneric Cp_2MMe_2 systems, where M = Ti or Hf. EHMO calculations are applied to explain some of the structural features of these and related molecules.

Experimental Section

All manipulations were carried out under an atmosphere of argon. NMR data were obtained on a Bruker AM 250 spectrometer operating at 250, 62.86, and 49.662 MHz for ^1H, ^{13}C, and ^{29}Si, respectively. Chemical shifts are reported relative to TMS. All abbreviations used are conventional.

Syntheses of 1 and 2. In a typical experiment, Cp_2ZrMe_2 (0.2 g, 0.8 mmol) dissolved in diethyl ether (2 mL) at 0 °C was treated progressively with an ethereal solution of $Ph_2Si(OH)_2$ (Aldrich, 0.17 g, 0.8 mmol). The reaction proceeded with vigorous evolution of gas. When the reaction was complete, the solvent was evaporated, the residue was treated with toluene/hexane, and the resultant mixture was filtered. The filtrate was stored in the refrigerator for 2 days to yield colorless X-ray-quality crystals of **1** (0.31 g, 0.36 mmol; 90%). Anal. Calcd for $C_{44}H_{40}O_4Si_2Zr_2$: C, 50.52; H, 3.96. Found: C, 50.59; H, 3.96. ^1H-NMR ($CDCl_3$): δ 7.68 (d, J = 6.3 Hz, 2H), *ortho*; 7.47–7.42 (m, 3H), *meta* and *para*; 6.15 (s, 5H), C_5H_5. ^{13}C-NMR ($CDCl_3$): δ 140.0, 134.8, 129.9, 128.4 (*o*, *m*, *p*, ipso), phenyl C's; 113.5, C_5H_5. ^{29}Si-NMR: δ 4.41. Mass spectrum (CI, NH_3): m/z 869, $[M + H]^+$, for ^{90}Zr.

By the same method, **2** was prepared in 90% yield. ^1H-NMR (C_6D_6): δ 7.95–7.90 (d, J = 6.3 Hz, 2H), *ortho*; 7.4–7.2 (m, 3H), *meta* and *para*; 5.92 (s, 5H), C_5H_5. Mass spectrum (CI, NH_3): m/z 1045, $[M + H]^+$, for ^{178}Hf.

X-ray Crystallography. Suitable crystals of **1** were grown by slow crystallization from toluene/hexane. Accurate cell dimensions were obtained from least-squares refinements of 25 automatically centered reflections in the range 15° < θ < 16°. Data collection parameters are listed in Table 1.

Structure Solution and Refinement. The structure was solved using the direct methods routine in SHELXS[4] and refined with anisotropic thermal parameters. All hydrogen atoms, except two, were located by difference Fourier synthesis. Since there are two independent molecules, the structure was refined by least-squares techniques (in two blocks corresponding to molecules A and B) using CRYSTALS.[5] All heavy

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[†] URA 403, CNRS.

[‡] McGill University.

[§] McMaster University.

[∥] JE 47 ENSCP.

[⊥] URA 419, CNRS.

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Table 1. Crystallographic Data for **1**

formula	$Si_2Zr_2O_4C_{44}H_{40}$
fw	871.4
space group	$P\bar{1}$
a, Å	10.410(9)
b, Å	12.140(6)
c, Å	16.318(5)
V, Å	1995(29)
α, deg	94.26(3)
β, deg	103.42(5)
γ, deg	93.16(6)
Z	2
temp, °C	20
λ(Mo Kα), Å	0.710 69
μ(Mo Kα), cm^{-1}	6.13
d_{calc}, g cm^{-3}	1.453
R^a	0.0325
$R_w{}^a$	0.0336

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $R_w = [\Sigma w(|F_o| - |F_c|^2/\Sigma w(F_c)^2]^{1/2}$.

Table 2. Selected Bond Lengths and Angles for the Two Independent Molecules of **1**

Zr(1)–O(1)	1.981(3)	Zr(101)–O(101)	1.983(2)
Zr(1)–O(2)	1.973(2)	Zr(101)–O(102)	1.974(2)
Zr(1)–C(1)	2.573(4)	Zr(101)–C(101)	2.550(5)
Zr(1)–C(2)	2.566(4)	Zr(101)–C(102)	2.532(5)
Zr(1)–C(3)	2.550(4)	Zr(101)–C(103)	2.541(5)
Zr(1)–C(4)	2.552(4)	Zr(101)–C(104)	2.570(4)
Zr(1)–C(5)	2.577(4)	Zr(101)–C(105)	2.561(5)
Zr(1)–C(6)	2.523(5)	Zr(101)–C(106)	2.529(6)
Zr(1)–C(7)	2.540(5)	Zr(101)–C(107)	2.510(7)
Zr(1)–C(8)	2.524(5)	Zr(101)–C(108)	2.530(6)
Zr(1)–C(9)	2.526(5)	Zr(101)–C(109)	2.535(5)
Zr(1)–C(10)	2.533(5)	Zr(101)–C(110)	2.539(5)
Si(1)–O(1)	1.612(3)	Si(101)–O(101)	1.607(3)
Si(1)–O(2)	1.614(3)	Si(101)–O(102)	1.612(3)
Si(1)–C(11)	1.876(4)	Si(101)–C(111)	1.880(4)
Si(1)–C(17)	1.887(4)	Si(101)–C(117)	1.877(4)
O(2)–Zr(1)–O(1)	98.5(1)	O(102)–Zr(101)–O(101)	98.3(1)
O(2)–Si(1)–O(1)	111.1(1)	O(102)–Si(101)–O(101)	111.8(1)
C(11)–Si(1)–O(1)	107.8(2)	C(111)–Si(101)–O(101)	108.9(2)
C(11)–Si(1)–O(2)	109.7(2)	C(111)–Si(101)–O(102)	108.5(2)
C(17)–Si(1)–O(1)	112.2(2)	C(117)–Si(101)–O(101)	110.9(2)
C(17)–Si(1)–O(2)	106.6(2)	C(117)–Si(101)–O(102)	107.9(1)
C(17)–Si(1)–C(11)	109.4(2)	C(117)–Si(101)–C(111)	108.9(2)
Si(1)–O(1)–Zr(1)	154.3(2)	Si(101)–O(101)–Zr(101)	155.4(2)
Si(1)–O(2)–Zr(1)	164.0(2)	Si(101)–O(102)–Zr(101)	161.5(2)

atoms were refined anisotropically, and in the final stage of refinement, H atoms were placed in idealized positions [d(C–H) = 0.96 Å] and allowed to ride on the relevant carbons. Selected bond distances and angles are collected in Table 2, and final atomic coordinates are listed in Table 3.

EHMO Calculations. Molecular orbital calculations were performed via the extended Hückel method using weighted H_{ij}'s.[6] Orbital parameters were taken from Tatsumi et al.[7]

Results and Discussion

Synthesis. Treatment of Cp_2MMe_2, where M = Zr or Hf, with an equimolar quantity of $Ph_2Si(OH)_2$ in diethyl ether resulted in vigorous evolution of methane and formation of the cyclic metallasiloxanes $[Cp_2M(\mu\text{-}OSiPh_2O)]_2$ (M = Zr (**1**), Hf (**2**)). Both compounds are white solids, stable in air, and soluble in common organic solvents.[8]

Table 3. Final Atomic Coordinates of **1** with Isotropic Thermal Parameters (Å^2)

atom	x/a	y/b	z/c	U(eqv)^a
Zr(1)	0.22403(3)	–0.03327(3)	0.09886(2)	0.0359
Si(1)	–0.1111(1)	–0.10547(8)	0.08575(7)	0.0372
O(1)	0.0479(2)	–0.1010(2)	0.1021(2)	0.0444
O(2)	0.1735(3)	0.0306(2)	–0.0108(2)	0.0402
C(1)	0.2694(5)	–0.2105(4)	0.0169(3)	0.0538
C(2)	0.2733(5)	–0.2380(4)	0.0989(3)	0.0564
C(3)	0.3811(5)	–0.1790(4)	0.1546(3)	0.0625
C(4)	0.4472(5)	–0.1142(4)	0.1062(4)	0.0663
C(5)	0.3778(5)	–0.1350(4)	0.0208(4)	0.0581
C(6)	0.1761(7)	0.1475(5)	0.1685(4)	0.0699
C(7)	0.1906(6)	0.0754(6)	0.2305(4)	0.0722
C(8)	0.3229(8)	0.0493(5)	0.2483(3)	0.0742
C(9)	0.3864(5)	0.1082(6)	0.1968(4)	0.0735
C(10)	0.2941(8)	0.1683(4)	0.1488(4)	0.0722
C(11)	–0.1765(4)	–0.2537(3)	0.0558(2)	0.0400
C(12)	–0.2988(4)	–0.2925(4)	0.0654(3)	0.0585
C(13)	–0.3506(5)	–0.3995(4)	0.0377(4)	0.0690
C(14)	–0.2816(5)	–0.4714(4)	–0.0010(3)	0.0611
C(15)	–0.1605(5)	–0.4358(4)	–0.0115(3)	0.0567
C(16)	–0.1077(4)	–0.3287(3)	0.0166(3)	0.0508
C(17)	–0.1667(4)	–0.0512(3)	0.1822(2)	0.0405
C(18)	–0.1902(4)	0.0606(4)	0.1925(3)	0.0524
C(19)	–0.2343(5)	0.1034(4)	0.2615(3)	0.0591
C(20)	–0.2569(5)	0.0359(4)	0.3209(3)	0.0619
C(21)	–0.2339(5)	–0.0741(4)	0.3127(3)	0.0611
C(22)	–0.1888(4)	–0.1173(4)	0.2441(3)	0.0504
Zr(101)	0.07288(4)	0.55368(3)	0.36648(2)	0.0376
Si(101)	0.19767(9)	0.40489(8)	0.54034(6)	0.0333
O(101)	0.1769(2)	0.4818(2)	0.4630(2)	0.0425
O(102)	–0.0714(2)	0.5999(2)	0.4182(2)	0.0407
C(101)	0.2354(6)	0.6655(5)	0.3039(5)	0.0750
C(102)	0.2906(5)	0.6689(5)	0.3894(5)	0.0699
C(103)	0.2135(6)	0.7299(4)	0.4323(4)	0.0676
C(104)	0.1078(5)	0.7656(4)	0.3716(4)	0.0591
C(105)	0.1212(5)	0.7248(4)	0.2926(4)	0.0657
C(106)	–0.1163(6)	0.4475(8)	0.2590(5)	0.0760
C(107)	–0.062(1)	0.3748(8)	0.3103(5)	0.0927
C(108)	0.053(1)	0.3575(6)	0.2982(4)	0.0819
C(109)	0.0838(6)	0.4214(7)	0.2410(4)	0.0754
C(110)	–0.027(1)	0.4831(5)	0.2132(3)	0.0827
C(111)	0.3470(3)	0.4631(3)	0.6241(2)	0.0399
C(112)	0.3876(4)	0.4089(4)	0.6969(3)	0.0510
C(113)	0.4877(5)	0.4573(4)	0.7649(3)	0.0597
C(114)	0.5475(5)	0.5591(5)	0.7602(3)	0.0635
C(115)	0.5118(6)	0.6124(4)	0.6889(4)	0.0727
C(116)	0.4115(5)	0.5640(4)	0.6206(3)	0.0597
C(117)	0.2245(4)	0.2594(3)	0.5042(2)	0.0361
C(118)	0.3502(4)	0.2277(3)	0.5059(3)	0.0536
C(119)	0.3729(5)	0.1193(4)	0.4813(3)	0.0641
C(120)	0.2684(6)	0.0418(4)	0.4549(3)	0.0587
C(121)	0.1428(5)	0.0708(3)	0.4513(3)	0.0535
C(122)	0.1199(4)	0.1787(3)	0.4758(3)	0.0470

[a] U(eqv) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

$$Cp_2ZrMe_2 + (HO)_2SiPh_2 \rightarrow [Cp_2Zr(\mu\text{-}OSiPh_2O)]_2 + 2MeH$$

Initial identification was provided by the mass spectra which reveal not only molecular ion peaks but also an excellent fit of the experimental and calculated isotopic abundance patterns. This illustrates the merit of the chemical ionization technique for such oligomeric species, which would be expected to show under conventional electron impact conditions a fragmentation pattern with the monomer as the first principal ion peak.[9]

Although alkoxyzirconium compounds have been known for a number of years,[10] the corresponding siloxy analogues appear to have been less extensively investigated. Typically, the Cp_2-

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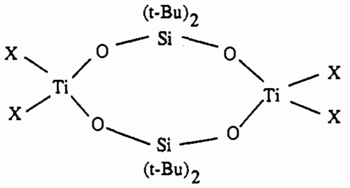
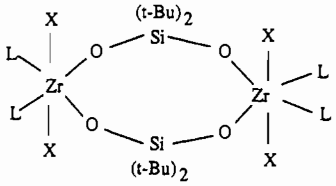
$Zr(OSiR_3)_2$ monomers, where R = Et or Ph, have been prepared by elimination of methane from Cp_2ZrMe_2 and the appropriate silanol.[11] Subsequently $(DME)ZrCl_2(OSiPh_3)_2$ (**3**) was claimed to have been the first structurally characterized siloxyzirconium complex.[12a] However, the crystal structure of a siloxyzirconate(IV) obtained in very low yield was described earlier.[12b] Recently, Roesky and co-workers reported that direct condensation of titanium or zirconium tetrahalides with $(t\text{-}Bu)_2Si(OH)_2$ yielded the cyclic systems **4**–**6** with alternating metal, oxygen, and silicon atoms in the ring.[2] In these molecules, the titanium is in a tetrahedral environment while the larger zirconium is octahedral as a result of the coordination of two solvent molecules. We are unaware of any previous reports of hafnium siloxanes.



4: X = Cl

5: X = Br



6: X = Cl; L = THF

The molecules **1** and **2** provide the first examples of cyclic siloxanes in which group 4 metallocene units have been incorporated into the ring. The ^1H NMR spectrum of **1** exhibits the expected singlets for the cyclopentadienyl rings. However, there is another facet of this spectrum which merits comment and which alerted us to the possibility of steric interference between the cyclopentadienyl and phenyl rings. The *ortho*-protons of the phenyl rings are anomalously deshielded relative to their *meta*- and *para*-proton partners with which they strongly overlap in the starting material $Ph_2Si(OH)_2$.

This immediately suggested that these protons are situated close to the cyclopentadienyl ring planes, which, analogously to benzene and other Hückel-type rings, exhibit marked diamagnetic anisotropy. This in turn prompted us to obtain X-ray crystallographic data on **1** to examine the effect of annulation on the bond angles and distances within the ring.

X-ray Structure. $[Cp_2Zr(\mu\text{-}OSiPh_2O)]_2$ (**1**) crystallizes in the triclinic space group $P\bar{1}$, and the unit cell contains two independent molecules whose conformations differ only very slightly. The structure of one of these molecules is depicted in Figure 1. The molecules are centrosymmetric, and the Cp(centroid)–Zr–Cp(centroid) angles (average 129°) are in the normal range for monomeric bis(cyclopentadienyl)zirconium or -hafnium complexes. The phenyl rings on silicon are twisted relative to each other (presumably for steric reasons), and their planes form a dihedral angle of 73°. The zirconium–oxygen distances in **1**, 1.974(2) and 1.983(2) Å, are significantly longer than those reported in **3** (1.91(1) Å)[12] and **6** (1.925(5) Å).[2]

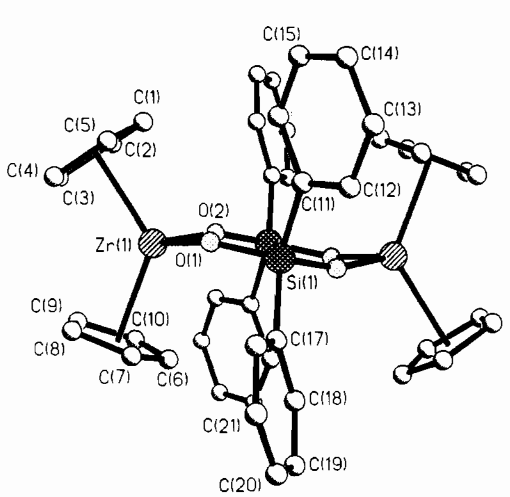


Figure 1. View of $[Cp_2Zr(\mu\text{-}OSiPh_2O)_2]_2$, showing the atom numbering.

The Si–O distances in **6** (1.635(3) Å) may be compared to the silicon–oxygen distances in **1** (1.607(3), 1.612(3), 1.612(3), 1.614(3) Å). That is, the replacement of the $(THF)_2ZrCl_2$ units in **6** by $ZrCp_2$ fragments in **1** leads to an overall shortening of the silicon–oxygen distances at the cost of lengthening the Zr–O bonds. One might interpret these observations in terms of greater Zr–O multiple bond character in **6** than in **1**. However, such a view would not take account of the differing steric requirements of the $(THF)_2ZrCl_2$ and $ZrCp_2$ moieties.

The main feature which differentiates this structure from those previously reported by Roesky (**4**–**6**) is the distinctly nonplanar character of the eight-membered ring. In **1** the Cp_2Zr units are folded one up and the other down, relative to the plane defined by the two silicon and the four oxygen atoms, by an average of 20°. It is also noteworthy that in **4** there are two distinctly different pairs of –Ti–O–Si– angles, 156 and 169°. This feature is also evident in the closely related Zr system **6**, for which the –Zr–O–Si– values are 161 and 169°. It is somewhat less apparent in **1** where the –Zr–O–Si– angles are 155.4 and 161.5°.

Molecular Orbital Calculations. One can consider the eight-membered ring in **1** to arise from the interactions of two $(Cp_2Zr)^{2+}$ moieties with two $[O\text{–}SiR_2\text{–}O]^{2-}$ groups. The frontier orbitals of the bent $(Cp_2Zr)^{2+}$ fragments are well-known from the work of Lauher and Hoffmann.[9] The four highest occupied orbitals of two well-separated zirconocene units give rise to in-phase and out-of-phase pairs; these combinations can be classified as possessing σ,π(in-plane), π(out-of-plane), and δ symmetry. In contrast, the in-phase and out-of-phase combinations of the three lowest vacant acceptor orbitals all lie in the *yz* plane, that is, the zirconium–siloxane ring plane.

The filled σ and σ^* and the in-plane π and π^* combinations of the $[Cp_2Zr\cdots ZrCp_2]^{4+}$ unit do not interact with the two highest energy frontier orbitals of the $[O\text{–}SiR_2\text{–}O]^{2-}$ fragments, which are made up of p_x orbitals on the oxygens.[14] These oxygen p_x orbitals do satisfy both the energy and symmetry criteria to yield a zirconium–oxygen out-of-plane π manifold via overlap with the in-phase d_{xz} orbitals and with the in-phase d_{xy} orbitals of the zirconocene fragments. However, since these are 4-electron interactions between pairs of filled orbitals, they are destabilizing, and indeed they give rise to the highest occupied orbitals of the system: the HOMO is depicted in Figure 2.

The strong zirconium–oxygen bonds which hold the fragments together are all in the plane of the eight-membered ring. Following the precepts outlined for Cp_2ZrR_2 systems by Lauher and Hoffmann,[13] Figure 3 shows the interactions between the in-plane orbitals of the two $[O\text{–}SiR_2\text{–}O]^{2-}$ fragments with the vacant frontier orbitals of the $[Cp_2Zr\cdots ZrCp_2]^{4+}$ unit.

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(14) There are, of course, four out-of-plane π-type molecular orbitals arising from oxygen p_x combinations. They have b_{3u}, b_{1g}, a_u, and b_{2g} symmetry; to avoid overly complicating the diagram, we show only the HOMO, which is b_{3u}. Note that the coordinate system chosen, in which zirconium atoms lie along the *z* axis and the oxygens are in the *yz* plane, follows that used in ref 13.

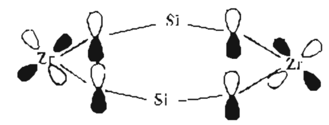

Figure 2. HOMO of **1** showing the antibonding character of the pπ–dπ overlaps between zirconium and oxygen.

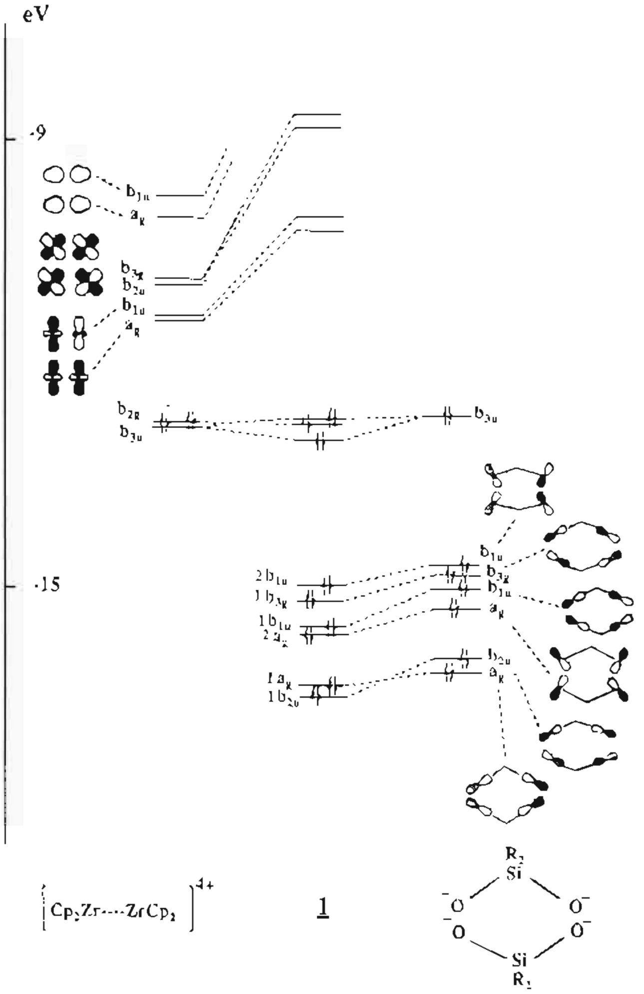

Figure 3. EHMO scheme showing the interactions between two zirconocene units and two bridging siloxy fragments to form **1**.

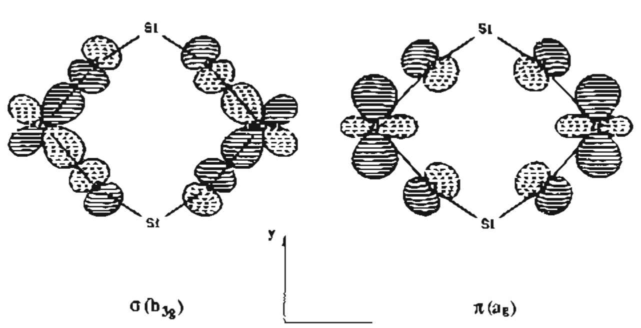

Figure 4. Views of selected molecular orbitals in **1**, assuming D_{2h} symmetry. These are the $\sigma(b_{3g})$ and in-plane $\pi(a_g)$ combinations.

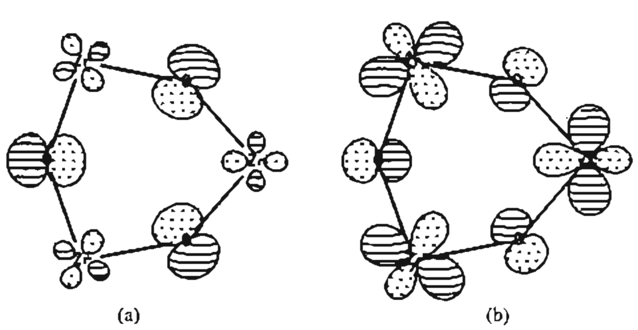
(a) (b)

Figure 5. (a) Totally symmetric in-plane π orbital of $(Cp_2ZrO)_3$. (b) Corresponding in-plane π* orbital, which is the LUMO in $(Cp_2ZrO)_3$.

Zirconium–oxygen dπ–pπ bonding has previously been invoked to account for the short bonds between these elements, and we note in particular the in-plane π-type overlaps ($2a_g$ and $1b_{1u}$ orbitals). Figure 4 depicts selected examples of σ and in-plane π-type molecular orbitals. The delocalized π-type interactions which augment the bonding between such a zirconium atom and its attached oxygens lie *in the ring plane* and not orthogonal to it as is the case with conventional aromatic rings or phosphazenes. We note also that such an interaction between the so-called $d_y{}^2$ ($1a_1$) orbital of a bent Cp_2M unit and an in-plane p orbital has been invoked to rationalize the orientation of the methylene carbene ligand in $Cp_2Ta(CH_3){=}CH_2$.[15]

In **1**, the two delocalized O--Zr--O moieties are insulated from each other by the intervening SiR_2 groups; for complete cyclic delocalization it is necessary to have suitable in-plane orbitals on all ring atoms. Such a situation arises for $[Cp_2ZrO]_3$, which has a planar hexagonal structure with Zr–O distances of 1.959(3) Å.[16] In this molecule, the bonding in-plane π-system is occupied, and additional electrons, such as would be the case for $(Cp_2MoO)_3$, would populate the in-plane π* orbitals (see Figure 5), reducing the metal–oxygen bond order and probably leading to a nonplanar structure.

The relevance of Si–O π-bonding has been widely discussed,[17] and such evidence as large Si–O–Si angles in silyl ethers and the planarity and lack of basicity of trisilylamine[18] is frequently invoked. In the present case, inclusion of silicon d orbitals in the basis set has essentially no effect on the bonding orbitals and it is apparent that π interactions between zirconium and oxygen are the more favored.

Molecular orbital calculations at the extended Hückel level were initially carried out on the assumption that the eight-membered ring is planar since there is a literature precedent, *viz.* **6**. Moreover, the closely analogous titanium systems, **4** and **5**, also exist as planar octagonal molecules in the solid state.[2] It was therefore surprising that the X-ray crystal structure of **1** revealed that the two zirconocene units were folded back ≈20° into a "chaise longue" conformation. This nonplanar structure must be dictated by steric factors since an EHMO calculation on the nonhindered $[Cp_2Zr(\mu\text{-}O\text{–}SiMe_2\text{–}O)]_2$ system revealed that bending the two Cp_2Zr moieties out of the plane costs approximately 7.5 kcal mol^{-1}. The crystal structure also shows the twisting of the phenyl substituents bonded to the silicons. It is apparent that the observed conformation is a compromise in which one must pay a small electronic penalty to minimize the steric hindrance between the phenyl substituents on silicon and the cyclopentadienyl rings on zirconium.

Gratifyingly, our initial assumption that the *ortho*-protons lie in the deshielding portion of the cone of anisotropy of the cyclopentadienyl rings was borne out by the X-ray crystallographic data. A space-filling model which clearly illustrates this point appears as Figure 6.

The X-ray crystal structure can be idealized as C_{2h}, while the most symmetric planar conformation is D_{2h}. In the former, the two cyclopentadienyl rings on each zirconium are nonequivalent as are the inner and outer edges of each phenyl ring. The room-temperature NMR spectrum exhibits a single cyclopentadienyl

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resonance in both the ^1H and ^{13}C regimes; furthermore, the phenyl rings show only single *ortho* and *meta* environments. In an attempt to measure the barrier to ring flipping, the NMR spectra were recorded at 163 K, but even at this low temperature, no line broadening was evident. Apparently, the barrier is too low to be detectable by variable-temperature NMR spectroscopy in solution.

Molecular modeling studies indicate that, in order to avoid unfavorable steric interactions, ring flipping must be accompanied by phenyl rotation. We have previously noted that the rotation of phenyl rings about an *ipso*-carbon--silicon axis is rather facile even when the phenyl rings bear bulky organometallic substituents as in $(C_6H_5)_3SiOH[Cr(CO)_3]_3$.[19] Such processes can be slowed on the NMR time scale either by incorporating bulky *ortho* substituents on the phenyl rings[20] or by pulling the π-complexed phenyl rings closer together as in $(C_6H_5)_3COH[Cr(CO)_3]$.[19]

Interestingly, although the reaction of Cp_2ZrMe_2 or Cp_2HfMe_2 with $Ph_2Si(OH)_2$ proceeds readily with elimination of methane, the corresponding reaction with Cp_2TiMe_2 does not. It may be the case that steric problems would arise between the $SiPh_2$ groups and the titanium-bonded cyclopentadienyl rings. However, given the demonstrated flexibility exhibited by the zirconium complex **1**, this hypothesis is probably not correct. One may instead offer a different rationale based on the relative ease of attack by the nucleophile $Ph_2Si(OH)_2$ at the coordinatively unsaturated Ti and Zr centers.

The LUMO in Cp_2MR_2 systems, where M = Ti, Zr, and Hf, is depicted in Figure 7; in the axis system shown, this vacant orbital has d_{y^2} character. Since attack along the z axis is blocked by the methyls or by the canted cyclopentadienyl ligands, the only realistic trajectory of approach for an incoming nucleophile involves attack along the y direction in the plane bisecting the two Cp rings. Clearly, such an approach is easier for the Zr or Hf cases than for the Ti, and this factor may well account for the difference in reactivity. The increased size of zirconium relative to titanium is also illustrated by the molecules **4**–**6**, in which the Ti atoms are tetrahedral but the zirconium atoms are 6-coordinate by virtue of two additional tetrahydrofuran ligands.

Conclusion

This work provides further confirmation that silanols are rather reactive toward complexes containing Zr–C or Hf–C σ bonds. Indeed, the normally weakly basic siloxy moiety behaves as a good donor to the extremely oxophilic Zr of Hf centers. These observations complement those of Silver et al., who have noted that a pendant siloxy unit can fold around and chelate to zirconium center.[21] Evidently, such metal–siloxy complexes will continue to attract attention because of their relevance as models of heterogeneous silicon-based catalytic surfaces.

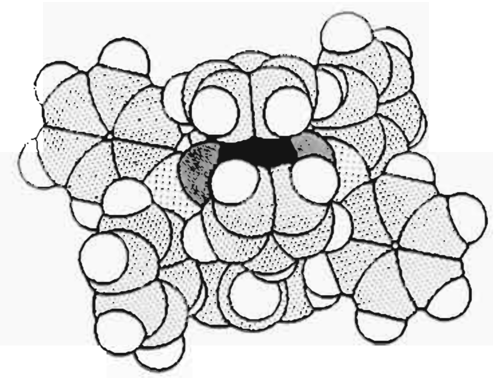

Figure 6. Space-filling model of **1** illustrating the proximity of the *ortho*-protons in the phenyls to the cyclopentadienyl rings.

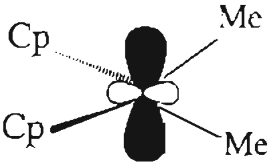

Figure 7. LUMO of Cp_2ZrMe_2. This is the site of attack for an incoming nucleophile.

EHMO calculations, which account for the main structural features of **1**, also indicate the possibility of transmission of electronic effects between transition metallocene moieties in delocalized systems.

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Supplementary Material Available: Tables S1–S3, listing hydrogen positional parameters, anisotropic thermal parameters, and bond lengths and angles (5 pages). Ordering information is given on any current masthead page.

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