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Bis(cyclooctatetraenyl)zirconium: X-ray Crystal Structure and Solution and Solid-State NMR Spectra

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The structure of bis(cyclooctatetraenyl)zirconium, $Zr(C_8H_8)_2$, has been investigated by variable-temperature solution and solid-state NMR spectroscopy and by X-ray crystallography. The solution ^1H and ^{13}C NMR data show that all 16 protons and all 16 carbon atoms are equivalent on the NMR time scale even at -100 °C. No line broadening due to decoalescence of a fluxional process was noted, and the spectra are thus consistent with the original proposal that $Zr(C_8H_8)_2$ adopts a symmetric sandwich structure. However, the CPMAS ^{13}C NMR spectrum contains two resonances and the X-ray crystallographic results unambiguously reveal a structure with one η^8- and one η^4-C_8H_8 ring. The exchange barrier for the fluxional process that makes the two C_8H_8 rings equivalent has been estimated to be <7.5 kcal mol^{-1} in solution and >13.5 kcal mol^{-1} in the solid state. A second fluxional process which involves 1,2-shifts of the η^4-C_8H_8 ring has a much lower barrier that has been estimated to be <5.5 kcal mol^{-1} in the solid state. Neither electronic nor steric factors clearly favor the asymmetric structure over the symmetric sandwich alternative. Similar conclusions are drawn for the structure of the hafnium analogue $Hf(C_8H_8)_2$. Crystal data for $Zr(C_8H_8)_2$ at -75 °C: monoclinic; space group Pn; $a = 7.049$ (5), $b = 7.695$ (4), $c = 11.217$ (10)Å; $\beta = 95.08$ (7)°; $V = 606$ (1)Å^3; $Z = 2$; $R_F = 0.054$; $R_{wF} = 0.057$ for 153 variables and 1023 independent reflections with $I > 2.58\sigma(I)$.

Introduction

Since ferrocene was discovered and its significance recognized in the 1950's, chemists have been interested in molecules that contain two cycloalkene or cycloalkenyl rings bonded to a transition metal.[1-4] "Sandwich" molecules such as ferrocene,[5-12] bis(benzene)chromium,[13,14] and bis(tetraphenylcyclobutadienyl)nickel[15,16] are of great interest since they serve as ideal model systems in which to explore the nature of the metal–carbon bond and the electronic structure of organometallic molecules.

Bis(cyclooctatetraenyl)actinide compounds constitute a similarly significant class of organometallic species.[17-20] These compounds provide an opportunity to assess the extent to which f orbitals participate in metal–ligand bonding. Theoretical[17,21-29] and experimental[30-35] studies suggest that in uranocene there is overlap between empty f_{xyz} and $f_{(x^2-y^2)z}$ orbitals on uranium and filled orbitals of E_{2u} symmetry on the cyclooctatetraenyl rings. Even though the extent of overlap is probably small, it undoubtedly enhances the preference for a symmetric sandwich structure and may contribute to the considerable kinetic stability of uranocene toward hydrolysis.

Bis(cyclooctatetraenyl) complexes are also known for several transition metals, such as the group 4 metals titanium, zirconium, and hafnium.[36-39] Unlike the actinide

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complexes, bis(cyclooctatetraenyl)titanium, Ti(C_8H_8)$_2$, has been shown to adopt a nonsandwich structure with one η^8- and one η^4-C_8H_8 ring.[40,41] This arrangement is probably attributable to steric effects; i.e., titanium is not large enough to bond effectively to all 16 carbon atoms of two C_8H_8 rings. A similarly asymmetric structure is adopted by the tetrahydrofuran adduct of bis(cyclooctatetraenyl)zirconium, Zr(C_8H_8)$_2$(THF).[42] One of the two C_8H_8 rings is η^8 while the other is η^4; this gives an electron count of 18 for the zirconium center. The larger atomic radius of zirconium vs titanium makes it possible for the zirconium atom to interact with 12 carbon atoms *and* an additional Lewis base.

To date, the structures of unsolvated Zr(C_8H_8)$_2$ and Hf(C_8H_8)$_2$ have not been established. In particular, it is not known whether removal of the THF ligand from Zr(C_8H_8)$_2$(THF) would leave enough room in the coordination sphere to allow the zirconium center to interact with all 16 carbon atoms. Like uranocene and thorocene, Zr(C_8H_8)$_2$ is reported to be relatively insoluble in noncoordinating solvents such as toluene,[37] and this similarity might suggest that Zr(C_8H_8)$_2$ is isostructural with the two actinide compounds. No NMR studies of Zr(C_8H_8)$_2$ have been performed, and in fact Wilke and co-workers reported that no ^{1}H NMR signals could be detected due to the compound's low solubility.[37] In addition, the absence of bands characteristic of free C=C double bonds in the IR spectrum of Zr(C_8H_8)$_2$ and the resistance of Zr(C_8H_8)$_2$ toward hydrogenation led Wilke and co-workers to propose a symmetric sandwich structure for Zr(C_8H_8)$_2$ in which both rings are η^8.[37]

At first glance Zr(η^8-C_8H_8)$_2$ would appear to be a 20-electron species, but in fact this is not the case. The same two ligand orbitals of E_{2u} symmetry that can overlap only with f_{xyz} and $f_{(x^2-y^2)z}$ wave functions have no energetically accessible acceptor orbitals on a d-block metal. Thus, Zr(η^8-C_8H_8)$_2$ would actually be a 16-electron species with the other four electrons in metal–ligand nonbonding orbitals. Since no metal–ligand antibonding orbitals would be occupied, there is no obvious electronic reason for the symmetric sandwich structure to be intrinsically unstable.[43]

In order to determine whether bis(cyclooctatetraenyl) sandwich compounds exist for any transition metal, we have determined the single-crystal X-ray structure of the most likely candidate, Zr(C_8H_8)$_2$. We also describe its variable-temperature solution ^{1}H NMR spectra, its solution and solid-state ^{13}C NMR spectra, and similar studies of the hafnium analogue Hf(C_8H_8)$_2$.

Results

Variable-Temperature Solution NMR Spectra. Since Zr(C_8H_8)$_2$ is essentially insoluble in toluene and forms Lewis base adducts in coordinating solvents such as THF and DMSO, these media cannot be used for NMR studies of the unsolvated molecule. Significantly, however, Schwartz showed that ^{1}H NMR spectra of Ti(η^8-C_8H_8)(η^4-C_8H_8) could be obtained in chlorobenzene,[41] and similarly, we have found that Zr(C_8H_8)$_2$ is readily soluble in dichloromethane.[44] The solutions are indefinitely stable at room temperature in the absence of air and water.

Table I. Crystal Data for Zr(η^8-C_8H_8)(η^4-C_8H_8)

$T = -75$ °C	$V = 606$ (1) Å^3
space group: *Pn*	$Z = 2$
$a = 7.049$ (5) Å	mol wt: 299.52
$b = 7.695$ (4) Å	$d_{calcd} = 1.641$ g cm^{-3}
$c = 11.217$ (10) Å	$\mu_{cald} = 8.64$ cm^{-1}
$\beta = 95.08$ (7)°	size: 0.1 × 0.1 × 0.2 mm

diffractometer: Enraf-Nonius CAD-4
radiatn: Mo K$\bar{\alpha}$, $\bar{\lambda} = 0.71073$ Å
monochromator: graphite crystal, $2\theta = 12°$
scan range, type: $2.0 \leq 2\theta \leq 54.0°$, ω/θ
scan speed, width: 4–16° min^{-1}, $\Delta\omega = 1.50\ (1.20 + 0.35 \tan \theta)°$
reflcns: 1522, 1382 unique, 1023 with $I > 2.58\sigma(I)$
internal consistency: $R_i = 0.068$

$R_F = 0.054$	variables: 153
$R_{wF} = 0.057$	p factor = 0.020

Table II. Atomic Coordinates for Zr(η^8-C_8H_8)(η^4-C_8H_8)

atom	x/a	y/b	z/c
Zr	0.25	0.2077 (1)	0.25
Cl	0.118 (2)	0.037 (2)	0.431 (1)
C2	0.214 (2)	−0.057 (2)	0.349 (1)
C3	0.397 (2)	−0.045 (2)	0.313 (1)
C4	0.549 (2)	0.068 (2)	0.344 (1)
C5	0.597 (2)	0.177 (2)	0.444 (1)
C6	0.523 (2)	0.221 (2)	0.550 (1)
C7	0.340 (2)	0.197 (2)	0.589 (1)
C8	0.168 (2)	0.135 (2)	0.532 (1)
C9	−0.058 (2)	0.352 (2)	0.220 (2)
C10	−0.018 (3)	0.276 (2)	0.113 (2)
C11	0.136 (4)	0.277 (2)	0.048 (1)
C12	0.330 (3)	0.340 (2)	0.065 (2)
C13	0.431 (3)	0.428 (3)	0.152 (2)
C14	0.392 (3)	0.499 (2)	0.263 (2)
C15	0.235 (4)	0.493 (2)	0.330 (2)
C16	0.054 (4)	0.443 (3)	0.307 (2)

Proton and ^{13}C NMR spectra of Zr(C_8H_8)$_2$ in CD_2Cl_2 have been obtained at temperatures between -100 °C and 25 °C (Figure 1). The spectra indicate that all 16 protons and all 16 carbon atoms are chemically equivalent on the NMR timescale at all temperatures. At the lowest temperatures examined (-100 °C), the single ^{1}H NMR resonance is sharp while the ^{13}C NMR resonance is slightly broadened. Viscosity effects could account for the latter, and thus there is little evidence of the onset of any decoalescence process. The hafnium analogue Hf(C_8H_8)$_2$ exhibits essentially identical behavior.

The solution NMR data are consistent with two alternatives. First, if Zr(C_8H_8)$_2$ adopts an *asymmetric* structure, then the two inequivalent C_8H_8 rings must undergo rapid (presumably intramolecular) exchange even at -100 °C. The second possibility is that Zr(C_8H_8)$_2$ adopts a *symmetric* sandwich structure with two equivalent η^8 rings as proposed by Wilke.

X-ray Crystal Structure of Zr(C_8H_8)$_2$. Single crystals of Zr(C_8H_8)$_2$ were obtained by slow sublimation at 170 °C in an evacuated glass tube. The compound crystallizes in the monoclinic space group *Pn*. Crystal data are given in Table I, atomic coordinates are listed in Table II, while bond distances and angles are presented along with estimated standard deviations in Table III. No crystallographic symmetry is imposed on the molecule (Figure 2).

The X-ray study clearly shows that *Zr(C_8H_8)$_2$ adopts an asymmetric structure in which one of the two C_8H_8 rings is η^8 while the other is η^4.* Thus, the structure of

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[43] Similar symmetry restrictions create purely ligand-based nonbonding orbitals in compounds such as Zr(BH_4)$_4$, Cp_2ZrX, W(RC≡CR)$_3$(CO), [Mo(RCCR)$_3$X$^-$], and [W(RCCR)$_3$X$^-$]; see: Chu, S. Y.; Hoffmann, R. *J. Phys. Chem.* **1982**, *86*, 1289–1297. For a recent example, see: Manion, A. B.; Erikson, T. K. G.; Spaltenstein, E.; Mayer, J. M. *Organometallics* **1989**, *8*, 1871–1873.

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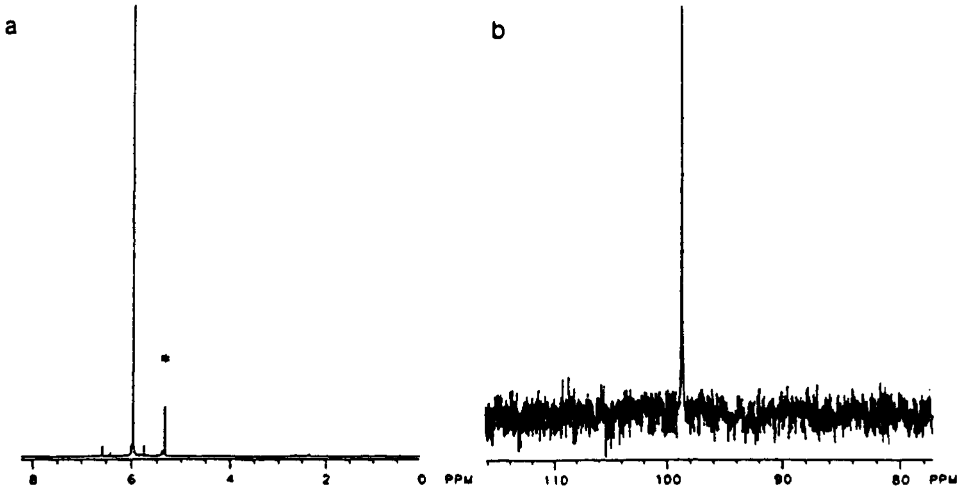

Figure 1. Solution NMR spectra for $Zr(C_8H_8)_2$ in CD_2Cl at -90 °C: (a) ^1H NMR spectrum with peak due to residual protons in the solvent indicated by an asterisk and (b) $^{13}C\{^1H\}$ spectrum.

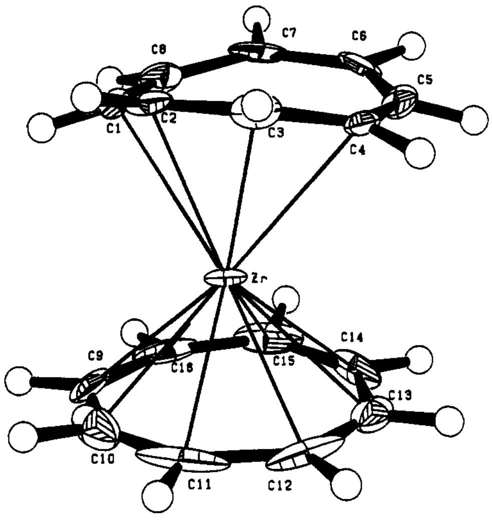

Figure 2. Molecular structure of $Zr(C_8H_8)_2$. The ORTEP diagram shows the 35% probability density surfaces.

$Zr(C_8H_8)_2$ closely resembles that of the titanium analogue $Ti(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)$.[40] The Zr–C distances to the η^8 ring are all very similar and average 2.41 (2) Å; this value is quite comparable to those of other η^8-C_8H_8 zirconium complexes.[42,45–48] By contrast, the Zr–C distances to the η^4 ring differ significantly, as expected for a butadiene-type ligand. The Zr–C distances to the outer, wing-tip carbon atoms (C1 and C4) average 2.58 (7) Å, whereas the Zr–C distances to the inner carbon atoms (C2 and C3) average 2.32 (2) Å.

The η^8 ring is flat and the largest displacement of a carbon atom out of the least squares plane is only 0.06 Å. By contrast, the η^4 ring is folded about the C1⋯C4 vector, giving two sets of atoms that lie in two separate planes. Atoms C1–C4, which are directly bonded to the zirconium atom, and atoms C5–C8, which are not, describe two planes with a dihedral angle of 28.0 (9)°. This angle is slightly larger than the dihedral fold of 20.6° of the η^4 ring in $Zr(C_8H_8)_2(THF)$[42] and slightly smaller than the ca. 30° fold in $(C_5Me_5)Zr(\eta^4\text{-}C_8H_8)(C_3H_5)$.[49]

Table III. Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations for $Zr(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)$

	Bond Distances		
Zr–C1	2.65 (1)	C3–C4	1.40 (2)
Zr–C2	2.34 (1)	C4–C5	1.42 (2)
Zr–C3	2.29 (1)	C5–C6	1.37 (2)
Zr–C4	2.51 (1)	C6–C7	1.41 (2)
Zr–C9	2.44 (2)	C7–C8	1.40 (2)
Zr–C10	2.39 (2)	C8–C1	1.38 (2)
Zr–C11	2.39 (2)	C9–C10	1.39 (3)
Zr–C12	2.42 (2)	C10–C11	1.35 (3)
Zr–C13	2.44 (2)	C11–C12	1.45 (3)
Zr–C14	2.46 (2)	C12–C13	1.33 (3)
Zr–C15	2.37 (2)	C13–C14	1.41 (3)
Zr–C16	2.40 (2)	C14–C15	1.39 (3)
C1–C2	1.40 (2)	C15–C16	1.33 (4)
C2–C3	1.39 (2)	C16–C9	1.40 (3)
	Bond Angles		
C8–C1–C2	136 (1)	C16–C9–C10	132 (2)
C1–C2–C3	132 (1)	C9–C10–C11	134 (2)
C2–C3–C4	133 (1)	C10–C11–C12	136 (2)
C3–C4–C5	133 (1)	C11–C12–C13	134 (2)
C4–C5–C6	138 (1)	C12–C13–C14	135 (2)
C5–C6–C7	131 (1)	C13–C14–C15	133 (2)
C6–C7–C8	133 (1)	C14–C15–C16	135 (2)
C7–C8–C1	135 (1)	C15–C16–C9	139 (2)

The high thermal motion prevents a discussion of differences among the C–C bond distances since the esd's are large. All the C–C distances are considered to be statistically equivalent and the average C–C bond length is 1.39 (3) Å in both the η^8 and the η^4 ring. This value is comparable to the C–C bond lengths of 1.37–1.41 Å in other metal-bound cyclooctatetraenyl ligands.

Table IV gives a summary of crystallographic results for $Zr(C_8H_8)_2$ and several related molecules: $Ti(C_8H_8)_2$,[40] $Zr(C_8H_8)_2(THF)$,[42] $(C_5Me_5)Zr(C_8H_8)(C_3H_5)$,[49] $[Ce(C_8H_8)_2^-]$,[50] $Th(C_8H_8)_2$,[51] and $U(C_8H_8)_2$.[51] A comparison of chemically equivalent bonds in $Zr(C_8H_8)_2$ and $Zr(C_8H_8)_2(THF)$ reveals that all of the Zr–C distances are slightly shorter in the THF-free compound by about 0.05–0.07 Å, although these differences are of marginal statistical significance. More significant are the ca. 0.10–0.20 Å shorter Zr–C distances to the outer (wing-tip) carbons of the η^4-C_8H_8 ring in the THF-free compound. The apparently stronger bonding to the C_8H_8 rings in $Zr(C_8H_8)_2$ is consistent with both steric

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Table IV. Structural Parameters for $M(C_8H_8)_2$ and Related Complexes[a]

	η^8-C_8H_8 ring		η^4-C_8H_8 ring			
compd	M–C(mean), Å	M–Cn, Å	M–C_o, Å	M–C_i, Å	θ_{dihed}, deg	ref
$Ti(C_8H_8)_2$	2.32	1.45	2.5	2.2		33
$Zr(C_8H_8)_2$	2.41 (2)	1.60 (1)	2.51 (1)	2.29 (1)	28.0 (9)	this work
			2.65 (1)	2.34 (1)		
$Zr(C_8H_8)_2(THF)$	2.47 (2)	1.68 (2)	2.58 (1)	2.32 (2)	20.6	35
			2.85 (1)	2.40 (2)		
$Cp^*Zr(C_8H_8)(C_5H_5)$			2.521 (4)	2.386 (5)	30	42
			2.540 (6)	2.382 (6)		
$[Ce(C_8H_8)_2^-]$	2.742 (8)	2.056 (5)				43
$Th(C_8H_8)_2$	2.701 (4)	2.003 (2)				44
$U(C_8H_8)_2$	2.647 (4)	1.923 (5)				44

[a] Cn = centroid; C_o = outer wing-tip carbon atoms of η^4-C_8H_8 ring bonded to metal; C_i = inner carbon atoms of η^4-C_8H_8 ring bonded to metal.

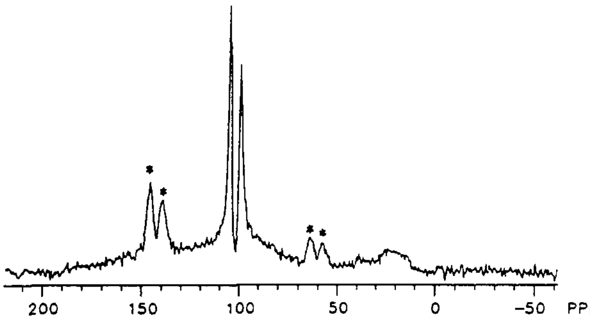

Figure 3. ^{13}C CPMAS NMR spectrum of $Zr(C_8H_8)_2$ at -100 °C. Spinning sidebands are indicated by asterisks.

and electronic effects: the lower coordination number and lower electron count in $Zr(C_8H_8)_2$ would both favor stronger metal–ligand bonding. The bonding between the η^4-C_8H_8 ring and the zirconium center in $Zr(C_8H_8)_2$ is similar to that in $(C_5Me_5)Zr(C_8H_8)(C_3H_5)$.[49]

Variable-Temperature CPMAS NMR Spectra. Since the solid-state structure of $Zr(C_8H_8)_2$ is asymmetric, the solution NMR data show that this molecule must be fluxional. In order to probe the details of the fluxionality, the ^{13}C NMR spectrum of solid $Zr(C_8H_8)_2$ has been studied at temperatures between -150 and 25 °C. At all temperatures, the cross-polarized magic angle spinning (CPMAS) ^{13}C NMR spectra (Figure 3) consist of two relatively narrow singlets 350 Hz apart at δ 104.0 and δ 99.2. The line widths of these peaks (fwhm = 150 Hz) are essentially temperature-independent. Since all of the $Zr(C_8H_8)_2$ molecules are related by symmetry in the unit cell, the resonances may be assigned to the η^8- and η^4-C_8H_8 rings. It is not possible, however, to determine from our observations which resonance arises from which ring.

The spectra are consistent with the solid-state structure of $Zr(C_8H_8)_2$ and show that this molecule undergoes two fluxional processes. The higher energy process involves interconversion of the η^8 and η^4 rings. In solution, the coalescence temperature T_c for this process is below -100 °C. Taking a chemical shift difference between the exchanging sites $\Delta\nu$ of 350 Hz in the ^{13}C NMR spectrum gives an upper limit of 7.5 kcal mol^{-1} for the activation free energy ΔG^* of the exchange process which makes the two C_8H_8 rings chemically equivalent in solution. For comparison, the barrier for interconverting the η^8 and η^4 rings in the asymmetric bis(cyclooctatetraenyl)titanium compound $Ti(\eta^8$-$C_8H_8)(\eta^4$-$C_8H_8)$ is 16.7 kcal mol^{1};[41] similar barriers were found for the $\eta^8 \leftrightarrow \eta^4$ interconversion process in several niobium and tantalum complexes.[52] A somewhat smaller barrier of 10.9 kcal mol^{-1} was observed for interconverting the η^6 and η^4 rings in $Fe(\eta^6$-$C_8H_8)(\eta^4$-$C_8H_8)$.[53] All of these values are considerably higher than the 7.5 kcal mol^{-1} upper limit for such a process in $Zr(C_8H_8)_2$. Since the two rings in $Zr(C_8H_8)_2$ are inequivalent in the ^{13}C CPMAS spectrum, taking $T_c > 25$ °C and $\Delta\nu = 350$ Hz gives a lower limit of $\Delta G^* > 13.5$ kcal mol^{-1} for the interconversion barrier for this same $\eta^8 \leftrightarrow \eta^4$ exchange process in the solid state.[54] Barriers for stereochemically nonrigid molecules are well known to increase in the solid state due to intermolecular forces that restrict molecular motions. Nevertheless, we can conclude that the $\eta^8 \leftrightarrow \eta^4$ ring interconversion barrier in $Zr(C_8H_8)_2$ is unusually low.

The lower energy fluxional process involves 1,2-shifts ("ring-whizzing") of the η^4-C_8H_8 ring. Since this process is still fast in the CPMAS spectrum even at -150 °C and we cannot determine the frequency difference between the exchanging sites, it is difficult to estimate the 1,2-shift activation energy. However, taking $T_c < -150$ °C and arbitrarily choosing $\Delta\nu = 350$ Hz gives an upper limit of $\Delta G^* < 5.5$ kcal mol^{-1} for the process that makes all of the η^4-C_8H_8 carbon atoms equivalent in the solid state. Presumably, this barrier would be even lower in solution. This value for ΔG^* may be compared with the activation energies of 1,2-shifts in η^4-C_8H_8 complexes of the later transition metals. In molecules such as $(\eta^4$-$C_8H_8)Fe(CO)_3$, $(\eta^4$-$C_8H_8)Ru(CO)_3$, and $(\eta^4$-$C_8H_8)Os(CO)_3$, solution ^1H NMR spectra of the static structures are observable (or nearly so), and Arrhenius plots give activation energies of 7.0–12 kcal mol^{-1}.[55,56] A wide-line NMR study of $(C_8H_8)Fe(CO)_3$ gave an activation energy of 8.3 kcal mol^{-1} for 1,2-shifts in the solid state.[57] For $Fe(C_8H_8)_2$, an upper limit of 5.4 kcal mol^{-1} was estimated for the 1,2-shift barrier in solution.[53] Like the $\eta^8 \leftrightarrow \eta^4$ ring interconversion process, the activation barrier in $Zr(C_8H_8)_2$ for 1,2-shifts is apparently low. Cotton has previously proposed that low barriers for 1,2-shifts are correlated with small dihedral angles for the η^4-C_8H_8 ring.[58] The dihedral angle of 28° in $Zr(C_8H_8)_2$ is smaller than the values of 33–45° in η^4-C_8H_8 complexes of the later transition metals[56] and is consistent with this hypothesis.

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Further evidence that the 1,2-shift is a low-energy process in the solid state comes from the structural results. Specifically, the crystallographic data at -75 °C show that even at this temperature, the thermal ellipsoids for the carbon atoms of the η^4 ring are oriented with their long axes more or less tangent to the ring circumference. Similar orientations are seen for the thermal ellipsoids of the η^8 ring. These elongations of the thermal ellipsoids in the direction of the ring tangents are often seen in cyclooctatetraenyl complexes, and are consistent with low-energy barriers to 1,2-shifts. Since the eight carbon atoms in each C_8H_8 ring of $Zr(C_8H_8)_2$ are crystallographically inequivalent in the solid state, both rings must undergo rapid 1,2-shifts at low temperature to account for the two ^{13}C CPMAS NMR singlets observed at -150 °C.

Infrared Spectra. Wilke originally reported that $Zr(C_8H_8)_2$ lacks IR bands near 1630 cm^{-1} that would indicate the presence of free C=C double bonds; this result supported the proposed symmetric sandwich structure for $Zr(C_8H_8)_2$.[37] However, the IR absorptions for free C=C double bonds of η^4-C_8H_8 rings attached to early transition metals actually appear elsewhere in the IR spectrum. For example, $Ti(C_8H_8)_2$,[59] $V(C_8H_8)_2$,[59] $Zr(C_8H_8)_2(THF)$,[42] and $(C_5Me_5)Zr(C_8H_8)(C_3H_5)$,[49] all of which contain an η^4-C_8H_8 ring, exhibit C=C double bond stretches at 1433, 1425, 1509, and 1509 cm^{-1}, respectively. Similarly, we have determined that base-free $Zr(C_8H_8)_2$ exhibits an IR absorption at 1515 cm^{-1} that we assign to the free C=C stretch of the η^4 ring.

Discussion

The most interesting aspect of the molecular structure of $Zr(C_8H_8)_2$ is that it does not adopt a "sandwich" arrangement of two planar η^8 rings. Despite initial expectations, removal of the THF ligand from $Zr(C_8H_8)_2(THF)$ does not allow an additional one or two double bonds to interact with the zirconium center. As noted in the introduction, a symmetric sandwich structure would not necessarily be unfavorable electronically, since symmetry considerations lead to a 16-electron count for a hypothetical $Zr(\eta^8$-$C_8H_8)_2$ molecule. We have therefore explored whether the unsymmetrical structure of bis(cyclooctatetraenyl)zirconium can be rationalized on steric grounds.

The Zr–C distances to the η^8 ring in $Zr(C_8H_8)_2$ are some 0.20–0.25 Å shorter than the Th–C and U–C distances in $Th(C_8H_8)_2$ and $U(C_8H_8)_2$, as expected from the relative radii of Zr^{IV}, Th^{IV}, and U^{IV} ions.[60] It is possible that the C···C contacts between carbon atoms of the two η^8-C_8H_8 rings in hypothetical $Zr(\eta^8$-$C_8H_8)_2$ would be unacceptably short. The zirconium center in $Zr(\eta^8$-$C_8H_8)(\eta^4$-$C_8H_8)$ lies 1.60 (1) Å out of the plane of the η^8 ring; thus, the ring-plane to ring-plane distance in a hypothetical $Zr(\eta^8$-$C_8H_8)_2$ molecule would be approximately 3.20 Å. This value is somewhat less than the 3.40 Å van der Waals contact distance between two aromatic π-systems.[61] While the distances between the two ring planes are 4.007 Å in $Th(C_8H_8)_2$ and 3.845 Å in $U(C_8H_8)_2$, in other sandwich compounds the ring–ring distances are much shorter: 3.534 Å in Cp_2Fe[62-64] and 3.212 Å in $Cr(\eta^6$-$C_6H_6)_2$.[65-67] Therefore, $Zr(\eta^8$-$C_8H_8)_2$ would possess C···C contacts between the two C_8H_8 rings that are comparable to those in bis(benzene)chromium; accordingly, nonbonded repulsions between carbon atoms are probably not responsible for the asymmetric structure.

It is also possible that the H···H contacts between the ring-bound hydrogen atoms in $Zr(\eta^8$-$C_8H_8)$ would be unacceptably short. The bonding between metals and η^8-cyclooctatetraenyl rings is improved if the carbon p orbitals that constitute the aromatic π-system are canted toward the metal atom. This effect has been observed in several complexes that contain ring-substituted C_8H_8 groups, and the ring substituents are displaced about 4° out of the ring plane toward the metal.[68] By contrast, in transition-metal arene complexes the hydrogen atoms lie almost exactly in the ring plane. Thus, while the H···H separations in $Cr(\eta^6$-$C_6H_6)_2$ are 3.21 Å, in hypothetical $Zr(\eta^8$-$C_8H_8)_2$ they would be approximately 3.08 Å. This separation is greater than the sum of the van der Waals radii for two hydrogen atoms of 2.40 Å. Evidently, steric repulsions between the ring hydrogen atoms also cannot account for the preference of $Zr(C_8H_8)_2$ to adopt an asymmetric structure.

Interestingly, we can find no obvious steric factor that clearly disfavors a symmetric sandwich structure for $Zr(C_8H_8)_2$. Despite the lack of obvious electronic factors that would rule out the sandwich structure as noted in the Introduction, the asymmetric nature of $Zr(C_8H_8)_2$ must have an electronic origin. It is possible, however, that the sandwich structure is a thermally accessible excited state.[69] Certainly the low $\eta^8 \leftrightarrow \eta^4$ interconversion barrier in $Zr(C_8H_8)_2$ indicates that the potential energy surface is relatively flat. The $\eta^8 \leftrightarrow \eta^4$ interconversion may very well occur via a symmetric $Zr(\eta^8$-$C_8H_8)_2$ structure, although other intermediates with different connectivities, such as $Zr(\eta^6$-$C_8H_8)_2$, are also conceivable.

Experimental Section

All operations were conducted under an atmosphere of dry argon or under vacuum. The IR spectra were recorded on a Perkin-Elmer 599B instrument as Nujol mulls, and solution ^1H and ^{13}C NMR spectra were obtained on a General Electric QE-300 instrument at 300 MHz and 75.48 MHz, respectively. Solid-state CPMAS ^{13}C NMR spectra were recorded on a General Electric GN-300WB instrument at 75.468 MHz. Chemical shifts are reported in δ units (positive shifts to higher frequency).

Bis(cyclooctatetraenyl)zirconium. Bis(cyclooctatetraenyl)zirconium was prepared from tetra(allyl)zirconium[70] and cyclooctatetraene at 55 °C as previously described.[37] Single crystals of $Zr(C_8H_8)_2$ were obtained by sublimation in a sealed glass tube under vacuum. The bottom half of the tube, which contained the crude solid, was heated to ca. 170 °C in an oven and the crystals grew on the cold (25 °C) upper walls of the tube over a period of six weeks. IR (cm^{-1}): 3040 m, 1515 m, 1435 w, 1325 w, 1312 w, 1150 w, 900 m, 865 m, 800 m, 775 s, 752 s, 722 s, 680 s, 450 w, 400 m. ^1H NMR (CD_2Cl_2, -90 °C): δ 5.95 (s). ^{13}C NMR (CD_2Cl_2, -90 °C): δ 98.6 (dm, $^1J_{CH}$ = 160 Hz, $^2J_{CH} \approx$ 3 Hz). ^{13}C CPMAS NMR (-150 °C): δ 104.0 (s), 99.2 (s). Anal. Calcd

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Bis(cyclooctatetraenyl)hafnium. To $HfCl_4(THF)_2$ (1.89 g, 4.07 mmol) and magnesium turnings (0.5 g, 21 mmol) suspended in tetrahydrofuran (60 mL) was added cyclooctatetraene (1.1 mL, 9.7 mmol). After being heated to 55 °C for 1 h, the solution developed a dark red color. The solution was stirred for 20 h at 55 °C, and then for 3 h at 70 °C. The cooled solution was filtered, and the remaining red-orange powder was extracted with THF (5 × 20 mL). The combined filtrates were taken to dryness, and the red-orange residue was dried for 6 h at 60 °C under vacuum. The dark brick-red powder was extracted with dichloromethane (3 × 50 mL), and the filtered extracts were combined, concentrated to ca. 50 mL, and cooled to -78 °C to yield small dark-red plates. The crystals were dried for 4 h at 100 °C to remove dichloromethane solvate molecules. Additional crops of crystals were obtained by further concentration and cooling of the supernatant. Yield: 0.72 g (50%). IR (cm^{-1}): 3040 w, 1430 w, 1308 w, 900 s, 860 m, 790 m, 722 s, 540 br, 450 br. ^1H NMR (CD_2Cl_2, -90 °C): δ 5.98 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, -90 °C): δ 97.6 (s).

Crystallographic Studies.[71] Single crystals of $Zr(C_8H_8)_2$ were mounted on a thin glass fiber using oil (Paratone-N, Exxon), transferred to the diffractometer, and immediately cooled to −75 °C in a cold nitrogen gas stream. A suitable crystal was chosen, and preliminary photographs revealed a weak overall diffraction pattern and a broad mosaic spread, probably due to the high thermal motion. Standard peak search and automatic indexing procedures, followed by least-squares refinement using 25 reflections yielded the cell dimensions given in Table I.

Data were collected in one quadrant of reciprocal space ($\pm h$, $+k$, $-l$) by using measurement parameters listed in Table I. Axial photographs clearly indicated the $2/m$ Laue group, and systematic absences for $h0l$, $h + l \neq 2n$ were consistent with space groups $P2/n$ and Pn. The average values of the normalized structure factors suggested the centric choice $P2/n$, but the acentric choice Pn was confirmed by successful refinement of the proposed model. The measured intensities were reduced to structure factor amplitudes and their estimated standard deviations by correction for background, scan speed, and Lorentz and polarization effects. While corrections for crystal decay were unnecessary, absorption corrections were applied, the maximum and minimum transmission factors being 0.951 and 0.892. Systematically absent reflections were deleted, and only those data with $I > 2.58\ \sigma(I)$ were used in the least-squares refinement.

The structure was solved in the centric space group $P2/n$ by using Patterson (SHELXS-86) and weighted difference Fourier methods. The position of the zirconium atom was deduced from a sharpened Patterson map, and subsequent Fourier calculations revealed the positions of the remaining non-hydrogen atoms, which appeared disordered about the 2-fold axis. However, refinement of an ordered model in the acentric space group Pn gave more satisfactory results. The quantity minimized by the least-squares program was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 0.99/(\sigma(F_o)^2 + (pF_o)^2)$. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both real and imaginary components of anomalous dispersion. In the final cycle of least squares, all non-hydrogen atoms were independently refined with anisotropic thermal coefficients, and a group isotropic thermal parameter was varied for the hydrogen atoms, which were fixed in "idealized" positions with C–H = 0.95 Å. Successful convergence was indicated by the maximum shift/error of 0.048 in the last cycle. Final refinement parameters are given in Table I. The final difference Fourier map had no significant features. Refinement of a disordered model in space group $P2/n$ converged to give similar structural features for the $Zr(C_8H_8)_2$ molecule, but was rejected in favor of the ordered model in space group Pn.

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Supplementary Material Available: A table of calculated hydrogen atom coordinates, a full list of anisotropic thermal parameters for $Zr(C_8H_8)_2$, and a complete table of bond distances and angles (4 pages); a listing of final observed and calculated structure factors for $Zr(C_8H_8)_2$ (7 pages). Ordering information is given on any current masthead page.

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Formation of Organodilithium Compounds via Lithium–Tin Exchange

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The reaction of methyllithium in THF with 2,5-bis(trimethylstannyl)-1,5-hexadiene (**6**) affords 2,5-dilithio-1,5-hexadiene (**2**) via the intermediacy of lithium stannates. The similar reaction of (2*Z*,4*Z*)-2,5-bis(trimethylstannyl)-2,4-hexadiene (**11**) affords (2*E*,4*E*)-2,5-dilithio-2,4-hexadiene (**3**). The more favorable formation of **3** suggests a greater relative stability over **2**. Ab initio calculations indicate that the symmetrical dilithium-bridged structure found for **3** is more favorable than the unsymmetrical dilithium-bridged structure found for **2**.

Introduction

Lithium bridging is a common structural feature of organopolylithium compounds.[1] Several derivatives of (1*Z*,3*Z*)-1,4-dilithio-1,3-butadiene (**1**) adopt a symmetrical bridged structure **1′** in the solid state.[2-4] Calculations by

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