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. Sandwich molecules such as ferrocene, bis(benzene)chromium, and bis(tetraphenylcyclobutadienyl)nickel 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)zirconium constitutes a similarly significant class of organometallic species.

These compounds provide an opportunity to assess the extent to which f orbitals participate in metal-ligand bonding. Theoretical and experimental studies suggest that in uranocene there is overlap between empty $f_{1g}$ and $f_{2g}$ orbitals on uranium and filled orbitals of $E_u$ 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)zirconium complexes are also known for several transition metals, such as the group 4 metals, titanium, zirconium, and hafnium. Unlike the actinide

(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(C8H8)2, has been investigated by variable-temperature solution and solid-state NMR spectroscopy and by X-ray crystallography. The solution 1H and 13C 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(C8H8)2 adopts a symmetric sandwich structure. However, the CP MAS 13C NMR spectrum contains two resonances and the X-ray crystallographic results unambiguously reveal a structure with one $v^2$- and one $v^2$-C8H8 ring. The exchange barrier for the fluxional process that makes the two C8H8 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 $v^4$-C8H8 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(C8H8)$_2$. Crystal data for Zr(C8H8)$_2$ at -76 °C: monoclinic; space group $Pn$; $a = 7.049$ (5); $b = 7.695$ (4); $c = 11.217$ (10)Å; $\beta = 95.08$ (7)$^\circ$; $V = 606$ (1)Å$^3$; $Z = 2$; $R_F = 0.054$; $R_wF = 0.057$ for 153 variables and 1023 independent reflections with $I > 2.5\sigma(I)$. 


complexes, bis(cyclooctatetraeny1)tinanium, Ti(C8H8)2, has been shown to adopt a nonsandwich structure with one \( \eta^8 \) and one \( \eta^4 \)-C8H8 ring.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 C8H8 rings. A similarly asymmetric structure is adopted by the tetrahydrofuran adduct of bis(cyclooctatetraenyl)zirconium, Zr(C8H8)2(THF).42 One of the two C8H8 rings is \( \eta^8 \) while the other is \( \eta^4 \); 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(C8H8)2 and Hf(C8H8)2 have not been established. In particular, it is not known whether removal of the THF ligand from Zr(C8H8)2(THF) would leave enough room in the coordination sphere to allow the zirconium center to interact with 12 carbon atoms and an additional Lewis base.

At first glance Zr(C8H8)2 would appear to be a 20-electron species, but in fact this is not the case. The same two ligand orbitals of \( \eta^8 \) symmetry that can overlap only with \( f_{d3g} \) and \( f_{d4g} \) wave functions have no energetically accessible acceptor orbitals on a d-block metal. Thus, Zr(\( \eta^8 \)-C8H8)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.

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(C8H8)2. We 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(C8H8)2.

## Results

### Variable-Temperature Solution NMR Spectra

Since Zr(C8H8)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(\( \eta^8 \)-C8H8)(\( \eta^4 \)-C8H8) could be obtained in chlorobenzene,43 and similarly, we have found that Zr(C8H8)2 is readily soluble in dichloromethane.44 The solutions are indefinitely stable at room temperature in the absence of air and water.

Proton and \( ^{13} \)C NMR spectra of Zr(C8H8)2 in CD3Cl2 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 decaesence process. The hafnium analogue Hf(C8H8)2 exhibits essentially identical behavior.

The solution NMR data are consistent with two alternatives. First, if Zr(C8H8)2 adopts an asymmetric structure, then the two inequivalent C8H8 rings must undergo rapid (presumably intramolecular) exchange even at -100 °C. The second possibility is that Zr(C8H8)2 adopts a symmetric sandwich structure with two equivalent \( \eta^4 \) rings as proposed by Wilke.

### X-ray Crystal Structure of Zr(C8H8)2

Single crystals of Zr(C8H8)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(C8H8)2 adopts an asymmetric structure in which one of the two C8H8 rings is \( \eta^8 \) while the other is \( \eta^4 \). Thus, the structure of

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**Table I. Crystal Data for Zr(\( \eta^6 \)-C8H8)(\( \eta^4 \)-C8H8)**

<table>
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<th>Parameter</th>
<th>Value</th>
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<td>( T )</td>
<td>-75 °C</td>
</tr>
<tr>
<td>( V )</td>
<td>606 (1) Å³</td>
</tr>
<tr>
<td>space group</td>
<td>( Pn )</td>
</tr>
<tr>
<td>( Z )</td>
<td>2</td>
</tr>
<tr>
<td>( a )</td>
<td>7.049 (5) Å</td>
</tr>
<tr>
<td>( b )</td>
<td>7.696 (4) Å</td>
</tr>
<tr>
<td>( c )</td>
<td>11.217 (10) Å</td>
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<tr>
<td>( \beta )</td>
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<td>( \mu_{calcd} )</td>
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**Table II. Atomic Coordinates for Zr(\( \eta^6 \)-C8H8)(\( \eta^4 \)-C8H8)**

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<td>0.054 (4)</td>
<td>0.443 (3)</td>
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</table>

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(43) Similar symmetry restrictions create purely ligand-based nonbonding orbitals in compounds such as Zr(BH4)2, Cp2ZrX2, W(CO)6(CB11H11)2, and W(CO)6(CB11H11)X2; see: Chen, S. Y.; Hoffmann, R. J. Phys. Chem. 1982, 86, 1585-1587. For a recent example, see: Manion, A. B.; Erikson, T. K. G.; Spaltenstein, E.; Mayer, J. M. Organometallics 1989, 8, 1871-1873.
Figure 1. Solution NMR spectra for Zr(C8H8)2 in CD3Cl at -90 °C: (a) 1H NMR spectrum with peak due to residual protons in the solvent indicated by an asterisk and (b) 13C[1H] spectrum.

Figure 2. Molecular structure of Zr(C8H8)2. The ORTEP diagram shows the 35% probability density surfaces.

Zr(C8H8)2 closely resembles that of the titanium analogue Ti(η4-C8H8)(η4-C8H8).40 The Zr-C distances to the η4 ring are all very similar and average 2.41 (2) Å; this value is quite comparable to those of other η8-C8H8 zirconium complexes.42,43,44,45 By contrast, the Zr-C distances to the η6 ring differ significantly, as expected for a butadiene-type ligand. The Zr-C distances to the outer, wing-tip carbon atoms (Cl 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 η6 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 η4 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 ring in Zr(C8H8)(THF)42 and slightly smaller than the ca. 30° fold in (C6Me6)Zr(η6-C8H8)(C8H8).43

Table III. Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations for Zr(η4-C8H8)(η4-C8H8)

| Bond Distances | Zr-C1 | Zr-C2 | Zr-C3 | Zr-C4 | Zr-C9 | Zr-C10 | Zr-C11 | Zr-C12 | Zr-C13 | Zr-C14 | Zr-C15 | Zr-C16 | C1-C2 | C2-C3 | C3-C4 | C4-C5 | C142-C3 | C7-C8 | C6-C7 | C9-C10 | C12-C13 | C13-C14 | C14-C15 | C15-C16 | C16-C9 |
|----------------|-------|-------|-------|-------|-------|--------|--------|--------|--------|--------|--------|--------|-------|-------|-------|-------|-----------|-------|-------|--------|----------|----------|----------|----------|--------|--------|
|                | 2.65 (1) | 2.34 (1) | 2.29 (1) | 2.51 (1) | 2.44 (2) | 2.39 (2) | 2.39 (2) | 2.42 (2) | 2.44 (2) | 2.46 (2) | 2.37 (2) | 2.40 (2) | 1.40 (2) | 1.39 (2) | 1.33 (2) | 1.41 (3) | 136 (1) | 132 (1) | 133 (1) | 134 (1) | 132 (1) | 134 (1) | 132 (1) | 135 (2) | 132 (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 η6 and the η4 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(C8H8)2 and several related molecules: Ti(C8H8)2,40 Zr(C8H8)(THF),42 (C6Me6)Zr(C8H8)(C8H8),43 [Ce(C8H8)2]50 Th(C8H8)251 and U(C8H8)2.52 A comparison of chemically equivalent bonds in Zr(C8H8)2 and Zr(C8H8)(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 η4-C8H8 ring in the THF-free compound. The apparently stronger bonding to the C8H8 rings in Zr(C8H8)2 is consistent with both steric...

and electronic effects: the lower coordination number and lower electron count in Zr(C8H8)2 would both favor stronger metal–ligand bonding. The bonding between the lower electron count in Zr(C8H8)2 would both favor the sp3 bonding of Zr(C8H8) and show that this molecule must be at temperatures between -150 and 25 °C. At all temperatures, the line widths of these peaks (hwm = 350 Hz apart at 104.0 and δ 99.2) are essentially temperature-independent. Since all of the Zr(C8H8)2 molecules are related by symmetry in the unit cell, the resonances may be assigned to the sp3 and sp4-C8H8 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(C8H8)2 and show that this molecule undergoes two fluxional processes. The higher energy process involves interconversion of the sp3 and sp4 rings. In solution, the coalescence temperature Tc for this process is below -100 °C. Taking a chemical shift difference between the exchanging sites Δω = 350 Hz gives an upper limit of ΔG* < 5.5 kcal mol⁻¹ for the process that makes all of the sp3-C8H8 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 sp3-C8H8 complexes of the later transition metals. In molecules such as (sp3-C8H8)Fe(CO)₅, (sp3-C8H8)Ru(CO)₅, and (sp3-C8H8)Os(CO)₅, 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⁻¹.⁵⁶ A wide-line NMR study of (C₅H₅)Fe(CO)₅ gives an activation energy of 8.5 kcal mol⁻¹ for 1,2-shifts in the solid state.⁵⁷ For Fe(C8H8)2, an upper limit of 14.4 kcal mol⁻¹ was estimated for the 1,2-shift barrier in solution.⁵⁸ Like the sp3 ↔ sp4 ring interconversion process, the activation barrier in Zr(C8H8)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 sp3-C8H8 ring.⁵⁹ The dihedral angle of 28° in Zr(C8H8)2 is smaller than the values of 33–45° in sp3-C8H8 complexes of the later transition metals⁶⁰ and is consistent with this hypothesis.

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![Figure 3. ²⁹C CPMAS NMR spectrum of Zr(C8H8)2 at -100 °C. Spinning sidebands are indicated by asterisks.](image-url)
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 \( \eta^4 \)-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 \( \eta^5 \)-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 \( \text{Th(C}_8\text{H}_8) \) and \( \text{U(C}_8\text{H}_8) \) of Zr(\( \text{C}_8\text{H}_8 \)) and U(\( \text{C}_8\text{H}_8 \)) are crystallographically inequivalent, this result supports the proposed symmetric sandwich structure for Zr(\( \text{C}_8\text{H}_8 \)).

Infrared Spectra. Wilke originally reported that Zr-(\( \text{C}_8\text{H}_8 \)) lacks IR bands near 1600 cm\(^{-1} \) that would indicate the presence of free C=C double bonds; this result supported the proposed symmetric sandwich structure for Zr(\( \text{C}_8\text{H}_8 \)). However, the IR absorptions for free C=C double bonds of \( \eta^5 \text{C}_8\text{H}_8 \) rings attached to early transition metals actually appear elsewhere in the IR spectrum. For example, Ti(\( \text{C}_8\text{H}_8 \)), V(\( \text{C}_8\text{H}_8 \)), Zr(\( \text{C}_8\text{H}_8 \))(THF), Cr(\( \text{C}_8\text{H}_8 \))(THF), and (\( \text{C}_8\text{H}_8 \))Cr(\( \text{C}_8\text{H}_8 \))(THF), all of which contain an \( \eta^5 \text{C}_8\text{H}_8 \) ring, exhibit C=C double bond stretches at 1433, 1425, 1509, and 1509 cm\(^{-1} \), respectively. Similarly, we have determined that base-free Zr(\( \text{C}_8\text{H}_8 \)) exhibits an IR absorption at 1515 cm\(^{-1} \) that we assign to the free C=C double bond stretches at 1433, 1425, 1509, and 1509 cm\(^{-1} \), respectively. Since the eight carbon atoms in each \( \text{Th(C}_8\text{H}_8) \) and \( \text{U(C}_8\text{H}_8) \) ring, exhibit C=C double bond stretches at 1433, 1425, 1509, and 1509 cm\(^{-1} \), respectively. Similarly, we have determined that base-free Zr(\( \text{C}_8\text{H}_8 \)) exhibits an IR absorption at 1515 cm\(^{-1} \) that we assign to the free C=C double bond stretches at 1433, 1425, 1509, and 1509 cm\(^{-1} \), respectively.

**Discussion**

The most interesting aspect of the molecular structure of Zr(\( \text{C}_8\text{H}_8 \)) is that it does not adopt a “sandwich” arrangement of two planar \( \eta^5 \) rings. Despite initial expectations, removal of the THF ligand from Zr(\( \text{C}_8\text{H}_8 \))(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 necessarily be unfavorable electronically, since symmetry considerations lead to a 16-electron count for a hypothetical Zr(\( \eta^5 \text{C}_8\text{H}_8 \)) molecule. The IR absorption at 1433 cm\(^{-1} \), however, indicates that Zr(\( \eta^5 \text{C}_8\text{H}_8 \)) does not adopt a “sandwich” arrangement of two planar \( \eta^5 \) rings.

**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 13C NMR spectra were obtained on a General Electric QE-300 instrument at 300 MHz and 75.48 MHz, respectively. Solid-state CP/MAS 13C NMR spectra were recorded on a General Electric G-300/WS instrument at 75.48 MHz. Chemical shifts are reported in \( \delta \) units (positive shifts to higher frequency).

**Bis(cyclooctatetraenyl)zirconium.** Bis(cyclooctatetraenyl)zirconium is prepared from tetra(allyl)zirconium and cyclooctatetraene at 55 °C as previously described. Single crystals of Zr(\( \text{C}_8\text{H}_8 \)) 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 wall of the tube during a period of six weeks. IR (cm\(^{-1} \)) 3040, 1515, 1435 w, 1325 w, 1132 w, 1150 w, 905 w, 865, 800, 775, 752 s, 680 s, 450 w, 400, 400 w, 340 m, 300 w, 295 w, 290 w, 280 m, 270 m, 260 m, 250 m, 240 m, 230 m, 220 m, 210 m, 200 m, 190 m, 180 m, 170 m, 160 m, 150 m, 140 m, 130 m, 120 m, 110 m, 100 m, 90 m, 80 m, 70 m, 60 m, 50 m, 40 m, 30 m, 20 m, 10 m, 0 m. 1H NMR (CDCl\(_3\) -90 °C): \( \delta \) 5.95 (s). 13C NMR (CDCl\(_3\) -90 °C): \( \delta \) 86.4 dm, \( \delta \) 160 Hz, \( \delta \) 120 Hz. 13C CP/MAS NMR (-150 °C): \( \delta \) 104.0 (s), 99.2 (s). Anal. Calcd.

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for C\textsubscript{16}H\textsubscript{16}Zr: C, 64.1; H, 5.39. Found: C, 62.6; H, 5.28.  

For details of the data collection and refinement procedure, see: 

**Formation of Organodilithium Compounds via Lithium–Tin Exchange**

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The reaction of methylolithium in THF with 2,5-bis(trimethylstannyl)-1,5-hexadiene (6) affords 2,5-dilithio-1,5-hexadiene (2) via the intermediary of lithium stannates. The similar reaction of (2Z,4Z)-2,5-bis(trimethylstannyl)-2,4-hexadiene (11) affords (2E,4E)-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. Several derivatives of lithiation factors being 0.951 and 0.892. Systematically absent reflections were deleted, and only those data with I > 2.58σ(I) were used in the least-squares refinement.

The structure was solved in the centric space group P2\textsubscript{1}/n by using Patterson (SHELX-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 P2\textsubscript{1} gave more satisfactory results. The quantity minimized by the least-squares program was Σw(|Fo| - |Fc|)\textsuperscript{2} where w = 0.99(σ(Fc))\textsuperscript{2} + (ρF\textsubscript{c})\textsuperscript{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 = 0.98 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\textsubscript{1}/n converged to give similar structural features for the Zr(C\textsubscript{8}H\textsubscript{8})\textsubscript{2} molecule, but was rejected in favor of the ordered model in space group P2\textsubscript{1}/n.

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**Supplementary Material Available:** A table of calculated hydrogen atom coordinates, a full list of anisotropic thermal parameters for Zr(C\textsubscript{8}H\textsubscript{8})\textsubscript{2}, and a complete table of bond distances and angles (4 pages); a listing of final observed and calculated structure factors for Zr(C\textsubscript{8}H\textsubscript{8})\textsubscript{2} (7 pages). Ordering information is given on any current masthead page.