

The Molecular Structure of Bis(pentamethylcyclopentadienyl)zinc determined by Gas Electron Diffraction

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Bis(pentamethylcyclopentadienyl)zinc, $(\text{Me}_5\text{C}_5)_2\text{Zn}$, in the gas phase contains one η^5 -bonded ring with $\text{Zn}-\text{C}(\eta^5)$ 230(2) pm and one approximately σ -bonded ring with $\text{Zn}-\text{C}(\sigma)$ 209(5) pm; the angle between the $\text{Zn}-\text{C}(\sigma)$ bond and the plane defined by the σ -bonded ring is 87(3)°.

Bis(pentamethylcyclopentadienyl)zinc, $(\text{Me}_5\text{C}_5)_2\text{Zn}$, was synthesized in low yield from $(\text{Me}_5\text{C}_5)\text{Li}$ and ZnCl_2 in toluene.¹ The solvent was removed, the residue heated to 160°C for 3 h, and the chlorine-free product isolated by vacuum sublimation at 110°C. The product was characterized as $(\text{C}_5\text{Me}_5)_2\text{Zn}$ by elemental analysis (C and H), ¹H n.m.r.

(one sharp singlet at δ 1.98 at room temperature) and i.r. spectroscopy. The gas electron diffraction (g.e.d.) pattern from $s = 25$ to 230 nm^{-1} was recorded on Balzers Eldigraph KDG-2 with nozzle and reservoir temperatures of ca. 130°C, corresponding to a vapour pressure of 1 Torr. The data were processed by standard procedures. Three molecular models

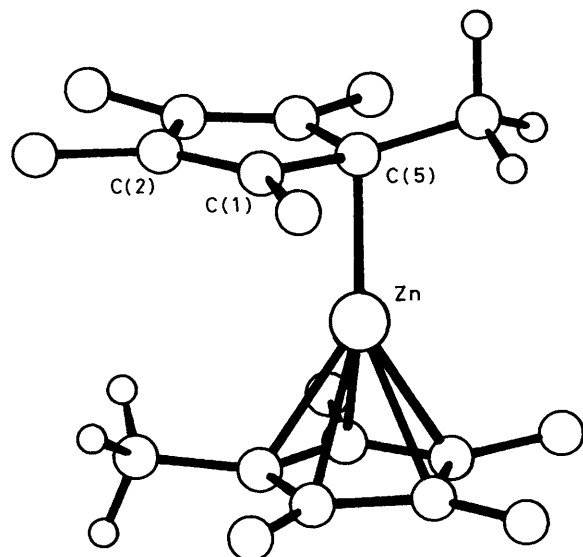


Figure 1. Molecular structure of $(C_5Me_5)_2Zn$ in the gas phase. Most hydrogen atoms have been omitted for clarity.

were considered: (i) a model with two η^5 -bonded rings; (ii) a model with two η^3 -bonded rings; (iii) a model with one η^5 - and one σ -bonded ring. The first two models were not in agreement with the g.e.d. data and were discarded.

The $(\eta^5-Me_5C_5)Zn(\sigma-Me_5C_5)$ model is shown in Figure 1. It was assumed that the $(\eta^5-Me_5C_5)Zn$ fragment has C_{5v} symmetry; the bond distances C-H, C-C (in ring), C-C(Me), and Zn-C(η^5) were refined along with the angle between the C-C(Me) bond and the ring plane. The Zn($\sigma-C_5Me_5$) fragment was assumed to have C_s symmetry. The C-H and C-C(Me) bond distances were assumed equal to those in the η^5 -bonded ring, and the C-C (in ring) bond distances and the endocyclic valence angles assumed equal to those in cyclopentadiene.² The Zn-C(σ) bond distance, the angle between the Zn-C bond and the C_5 ring plane, and two exocyclic angles, $\angle C=C-C(Me)$ determining the position of the methyl groups were refined. The valence angle $\angle Zn-C-C(Me)$ did not converge; after some trial and error it was fixed at 106° .

Least-squares refinement of nine structure parameters and four root mean square amplitudes of vibration, l , yielded a best model in good agreement with the electron diffraction data, see Table 1. It is difficult to assess the error limits in a study like this, where only a fraction of the structure parameters can be refined. The estimated standard deviations listed in Table 1 have been multiplied by a factor of three to compensate for uncertainty introduced by non-refined parameters, but may still be too small.

The Zn-C(η^5) bond distance and vibrational amplitude, l , are indistinguishable from those in gaseous $(\eta^5-C_5H_5)ZnMe$,³ Zn-C 228(1) and l 15(1) pm, respectively. However, the values obtained for the Zn-C(σ) bond distance and amplitude indicate that this bond is longer and looser than the single Zn-C(Me) bond in $(\eta^5-C_5H_5)Zn-Me$; Zn-C 190.3(12) pm and l 7.3(13) pm. Moreover, the angle between the Zn-C(σ) bond and the C_5 ring plane of $87(3)^\circ$ indicates that the metal-ring interaction is not entirely limited to one C atom. This conclusion could in turn indicate that the π system of the σ -bonded ring is delocalized. It was, however, found that a model in which all in-ring C-C bond distances are equal gave poorer agreement with the g.e.d. data.

$(C_5H_5)_2Zn$ is polymeric in the crystalline phase.⁴ One terminal C_5H_5 ring is bonded to the metal in much the same

Table 1. Refined structure parameters for $Zn(C_5Me_5)_2$.

	r_a	l
$(\eta^5-C_5Me_5)Zn$ fragment:		
Zn-C(η^5)	230(2) pm	16(1) pm
C-C (in ring)	144(2) pm	4.7(8) pm ^a
C-C(Me)	151(1) pm	5.2(8) pm ^a
C-H	111(1) pm	7.3(8) pm
$\angle C_5, C-C(Me)$	2(3) ^o	
$(\sigma-C_5Me_5)Zn$ fragment:		
Zn-C(5)	209(5) pm	10(2) pm
$\angle C_5, C-Zn$	87(3) ^o	
$\angle C(1)C(2)C(Me)$	135(3) ^o	
$\angle C(2)C(1)C(Me)$	133(3) ^o	

^a These amplitudes were refined with a constant difference of 0.5 pm.

'nearly σ ' fashion as in $(\eta^5-C_5Me_5)Zn(\sigma-C_5Me_5)$; Zn-C(σ) 206(3) pm and a Zn-C bond- C_5 ring plane angle of 75° . The other ring bridges two zinc atoms in the same *transoid* 1,3 fashion as in solid $(C_5H_5)_2ZnMe$.⁵

By considering the σ - and η^5 -rings as one and five electron donors respectively, the Zn atom obtains a Kr electron configuration, while a structure with two η^5 -rings would place four more electrons in the valence shell of the metal. We are nevertheless surprised that the molecule should adopt a σ, η^5 structure; $(C_5Me_5)_2Ge$ with two electrons more than $(C_5Me_5)_2Zn$ adopts a slightly bent sandwich structure with two η^5 -bonded rings,⁶ Ge-C(η^5) 251.9(7) pm; $(C_5H_5)_2Mg$ where the metal atom is of similar size and possesses the same number of valence orbitals and valence electrons as Zn (except for the filled 3d subshell of the latter) adopts an η^5, η^5 structure in both the gaseous⁷ and solid state,⁸ Mg-C(η^5) 233.9(4) pm.

The 1H n.m.r. spectrum of $(C_5Me_5)_2Zn$ in deuterated benzene at room temperature consists of one sharp line. Clearly the exchange of σ - and η^5 -rings is rapid on the n.m.r. time scale at room temperature. Such an exchange might proceed *via* a symmetric η^5, η^5 transition state.

We are grateful to Deutscher Akademischer Austauschdienst for a fellowship (R. B.), and to the Norwegian Research Council for Science and Humanities for financial support.

Received, 8th October 1984; Com. 1418

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