

# The Preparation of Bis(pentamethylcyclopentadienyl)zinc and Bis(trimethylsilylcyclopentadienyl)zinc, and their Molecular Structures Determined by Gas Electron Diffraction

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The syntheses of two derivatives of dicyclopentadienylzinc,  $(C_5Me_5)_2Zn$ (I) and  $(C_5H_4SiMe_3)_2Zn$ (II), Me = CH<sub>3</sub>, are described. The gas electron diffraction patterns were recorded with nozzle temperatures of about 130 °C (I) and 100 °C (II). Molecular models with two  $\eta^5$ -bonded or two  $\eta^1$ -bonded rings are not compatible with the GED data. The molecular structure of I is  $(\eta^5-C_5Me_5)Zn(\eta^1-C_5Me_5)$  with Zn–C( $\eta^5$ ) = 228(2) pm and Zn–C( $\eta^1$ ) = 204(6) pm. The former is similar to the Zn–C( $\eta^5$ ) bond distance in  $(\eta^5-C_5H_5)ZnCH_3$ . The latter appears to be longer than the Zn–C( $\sigma$ ) bond distances in  $(C_5H_5)ZnCH_3$  and  $Zn(CH_3)_2$ . The angle between the Zn–C( $\eta^1$ ) bond and the C<sub>5</sub> ring plane is 84(4)°. The best fit between calculated and experimental intensities is obtained with CC bond distances in the  $\eta^1$ -bonded ring corresponding to localized single and double bonds. The electron diffraction data of (II) are consistent with a similar model with the  $(\eta^5-C_5H_4SiMe_3)Zn$  and Me<sub>3</sub>Si groups attached to the same carbon atom, C(5), of the  $\eta^1$ -bonded ring. The presence of other isomers can, however, not be ruled out. NMR spectra of both compounds show that exchange of  $\eta^5$ - and  $\eta^1$ -bonded rings is rapid on the NMR time-scale at room temperature, but <sup>13</sup>C spectra of II show that this exchange is frozen out at –37 °C.

The synthesis and characterization of methyl(cyclopentadienyl)zinc was reported by Wade and coworkers in 1978.<sup>1</sup> We carried out a GED (gas electron diffraction) investigation of the monomer and found the structure to be that of an openfaced sandwich,  $(\eta^5-C_5H_5)ZnCH_3$ .<sup>2</sup> In the crystalline phase the compound is polymeric; each zinc atom is surrounded by two bridging cyclopentadienyl rings and a terminal methyl group.<sup>1</sup> The bridging Cp rings are disordered but

the zinc atoms are clearly attached to the periphery.<sup>1</sup>

The synthesis of dicyclopentadienylzinc, ZnCp<sub>2</sub>, had been reported by E. O. Fischer and coworkers as early as in 1959.<sup>3</sup> We made an attempt to determine the molecular structure by GED, but found the vapor pressure and thermal stability to be too low. We then decided to study two derivatives, bis(pentamethylcyclopentadienyl)zinc (I) and bis(trimethylsilylcyclopentadienyl)zinc (II). While this study was carried out in Oslo, an X-ray study of crystalline ZnCp<sub>2</sub> was carried out at the University of Utrecht: In the

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solid phase  $\text{ZnCp}_2$  is polymeric, each zinc atom is surrounded by two peripherally bonded bridging Cp rings and one more or less  $\eta^1$ -bonded terminal ring.<sup>4</sup>

## Experimental

**Syntheses.** The sample of bis(pentamethylcyclopentadienyl)zinc, compound **I**, used for gas electron diffraction had been prepared in small yield from  $(\text{C}_5\text{Me}_5)\text{Li}$  and  $\text{ZnCl}_2$  in toluene. Much higher yields are obtained by the reaction of  $(\text{C}_5\text{Me}_5)\text{Na}$  and  $\text{ZnCl}_2$  in THF:  $(\text{C}_5\text{Me}_5)\text{Na}$  is prepared by refluxing  $\text{Me}_5\text{C}_5\text{H}$  with a 20 % excess of NaH in THF for 24 hrs. The excess NaH is removed by centrifugation and the supernatant solution is evaporated to dryness. The solid residue is washed with pentane and crystallized from THF. Yield: 75 %.

$(\text{C}_5\text{Me}_5)_2\text{Zn}$  is prepared by stirring a mixture of  $(\text{C}_5\text{Me}_5)\text{Na}$  and  $\text{ZnCl}_2$  in 2:1 molar ratio in THF for 1 h at room temperature. The NaCl which has formed is removed by centrifugation and washed twice with pentane. The combined supernatant solution and pentane washings are evaporated to dryness yielding very light-yellow  $(\text{C}_5\text{Me}_5)_2\text{Zn}$  in 96 % yield. The product has a clean  $^1\text{H}$  NMR spectrum and is sufficiently pure for preparative purposes.

The product was characterized as  $(\text{C}_5\text{Me}_5)_2\text{Zn}$  by elemental analysis (C; found 68.71, theoretical 71.53 %, H; found 8.92, theoretical 9.00 %),  $^1\text{H}$  NMR in d-Benzene (one sharp singlet at  $\delta = 1.98$  ppm at ambient temperature), and IR-spectroscopy.

Compound **II**,  $(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Zn}$ , is prepared similarly by reacting  $\text{NaC}_5\text{H}_4\text{SiMe}_3$  with  $\text{ZnCl}_2$  in diethylether:  $\text{NaC}_5\text{H}_4\text{SiMe}_3$  is obtained by stirring  $\text{C}_5\text{H}_5\text{SiMe}_3$  with a 50 % excess of NaH in diethylether at room temperature for 16 h. The excess of NaH is removed by centrifugation and the supernatant solution evaporated to leave a solid residue which is washed twice with pentane. The product is suited for the next step without further purification.

$(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Zn}$  is prepared by stirring a mixture of  $\text{NaC}_5\text{H}_4\text{SiMe}_3$  and  $\text{ZnCl}_2$  in 2:1 ratio in diethylether for 4 h at room temperature. After removal of the NaCl by centrifugation, the supernatant solution is evaporated to dryness and the residue recrystallized from pentane at  $-30^\circ$ . Yield: 87 % overall. Characterization: Mass spec-

troscopy and  $^1\text{H}$  and  $^{13}\text{C}$ NMR; Mass spectrum: molecular ion 338 with characteristic isotope pattern.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra show expected absorptions but are temperature-dependent in a very complicated way.

**NMR.** Variable temperature  $^1\text{H}$  and  $^{13}\text{C}$ NMR spectra were recorded on a BRUKER CXP-200 instrument at 200 MHz ( $^1\text{H}$ ) and 50 MHz ( $^{13}\text{C}$ ). Chemical shifts are given in the  $\delta$ -scale with TMS as reference. The  $^1\text{H}$ -shifts were measured with respect to benzene ( $\delta = 7.27$  ppm) and toluene (*meta* proton at  $\delta = 7.15$  ppm), the  $^{13}\text{C}$ -shifts with respect to toluene ( $\text{C}_1$  at  $\delta = 138$  ppm).

**Gas electron diffraction.** The electron scattering patterns of **I** and **II** were recorded on Balzers Eldigraph KDG-2. In order to keep the temperature at a minimum and thus avoid thermal decomposition we used a torus-shaped nozzle which permits the scattering pattern to be recorded with a reservoir pressure of 1 torr.<sup>6</sup>

The data for **I** were recorded with a nozzle temperature of about  $130^\circ\text{C}$ , the data for **II** with a nozzle temperature of about  $100^\circ\text{C}$ . The nozzle-to-plate distances were 50 and 25 cm. For **I** the data were based on 6 plates at 50 cm, and 3 plates at 25 cm. For **II** they were based on 6 plates at 50 cm, and 4 plates at 25 cm. The plates were photometered, and the data reduced by standard procedures. The complex atomic scattering factors,  $f'(s)$ , were calculated from an analytical representation of the potential,<sup>7</sup> using a program written by Yates.<sup>8</sup>

The molecular intensities of both **I** and **II** were modified by multiplication with  $s/|f'_{\text{Zn}}||f'_{\text{C}}|$ . Structure refinements of **I** were based on data extending from  $s = 25$  to  $150\text{ nm}^{-1}$  with  $\Delta s = 1.25\text{ nm}^{-1}$  (50 cm) and from  $s = 35$  to  $232.5\text{ nm}^{-1}$  with  $\Delta s = 2.5\text{ nm}^{-1}$  (25 cm). Structure refinements of **II** were based on data extending from  $s = 20$  to  $140\text{ nm}^{-1}$  with  $\Delta s = 1.25\text{ nm}^{-1}$  and from  $s = 40$  to  $210\text{ nm}^{-1}$  with  $\Delta s = 2.5\text{ nm}^{-1}$ .

## Model considerations and structure refinements

For both molecules we first considered models with a) two  $\eta^5$ -bonded rings (regular sandwich structure), and b) two  $\eta^3$ -bonded rings. Neither model could be brought into agreement with the electron diffraction data, and comparison of cal-

Table 1. Structure parameters (bond distances and valence angles) and root-mean-square vibrational amplitudes (I) of  $(C_5Me_5)_2Zn$  and  $(C_5H_4SiMe_3)_2Zn$ . Estimated standard deviations in parentheses in units of the last digit.

	$(C_5Me_5)_2Zn$ ; I		$(C_5H_4SiMe_3)_2Zn$ ; II	
	$r_a/\gamma$	$l/pm$	$r_a/\gamma$	$l/pm$
$\eta^5$ -bonded fragment:				
Bond distances/pm				
Zn–C( $\eta^5$ )	228(2)	17(2)	226(3)	19(4)
C–C(in ring)	142.2 <sup>a</sup>	4.7 <sup>a</sup>	142.2 <sup>a</sup>	4.7 <sup>a</sup>
C–C(Me)	151(2)	5.3 <sup>a</sup>	–	–
C–Si	–	–	188.0 <sup>a</sup>	5.7(9)
C–H	111.2(6)	7.7(9)	111.3(9)	7.6(10)
Angles/deg				
<C <sub>5</sub> , C–C	6(4)	–	–	–
<C <sub>5</sub> , C–Si	–	–	15(4)	–
$\eta^1$ -bonded fragment:				
Bond distances/pm				
Zn–C(5)	204(6)	16(4)	207(10)	11(4)
Average C–C(in ring)	146(1)	–	149(3)	–
C(5)–C(1)	154(2)	4.7 <sup>a</sup>	151(3)	4.7 <sup>a</sup>
C(1)–C(2)	137(2)	4.7 <sup>a</sup>	141(3)	4.7 <sup>a</sup>
C(2)–C(3)	150(2)	4.7 <sup>a</sup>	149(3)	4.7 <sup>a</sup>
LOC <sup>b</sup>	100% <sup>a</sup>	–	70(30)%	–
Angles/deg				
<C <sub>5</sub> , C–Zn	84(4)	–	53(7)	–
<ZnC(5)C(10)	130(10)	–	–	–
<ZnC(5)Si	–	–	113(5)	–
<C(2)C(1)C(6)	132(6)	–	–	–
<C(1)C(2)C(7)	134(3)	–	–	–

<sup>a</sup>Fixed values. <sup>b</sup>See section on structure refinement for definition.

culated and experimental radial distribution curves showed serious disagreement in the region from 190 to 250 pm, *i.e.* in the range covering Zn–C bond distances. Refinements were then based on models with one  $\eta^5$ - and one  $\eta^1$ -bonded ring.

I. Least-squares refinements were based on the molecular model of  $C_5$  symmetry shown in Fig. 1. The  $(\eta^5-C_5Me_5)Zn$  fragment was assumed to have  $C_5v$  symmetry and the C–C (in ring) bond distance fixed at the value found in  $(\eta^5-C_5H_5)ZnCH_3$ .<sup>2</sup> The methyl groups were fixed in the orientation indicated in Fig. 1, and the <CCH valence angles fixed at 109.4°. The C–H, C–C(Me) and Zn–C( $\eta^5$ ) bond distances were refined as independent parameters along with the angle between the C–C(Me) bonds and the  $C_5$  ring plane; <C<sub>5</sub>, C–C.

The Zn( $\eta^1-C_5Me_5$ ) fragment was assumed to have  $C_5$  symmetry. The  $C_5$  ring was assumed to be congruent with the  $C_5$  ring in cyclopentadiene,<sup>9</sup> only the scale was refined. C–H and C–C(Me) bond distance were assumed equal to those of the  $\eta^5$ -bonded ring, except C(5)–C(Me) which was fixed at 153.3 pm. The Zn–C(5) bond distance, the angle between this bond and the ring plane (<C<sub>5</sub>, C–Zn) and the valence angle <ZnC(5)C(Me) were refined as independent parameters. The four remaining methyl carbon atoms were assumed to lie in the ring plane, but the two exocyclic valence angles <C=C–C(Me) were refined.

After all these assumptions were made, the molecular structure is determined by nine independent parameters. These were refined by least-squares calculations on the intensity data with a

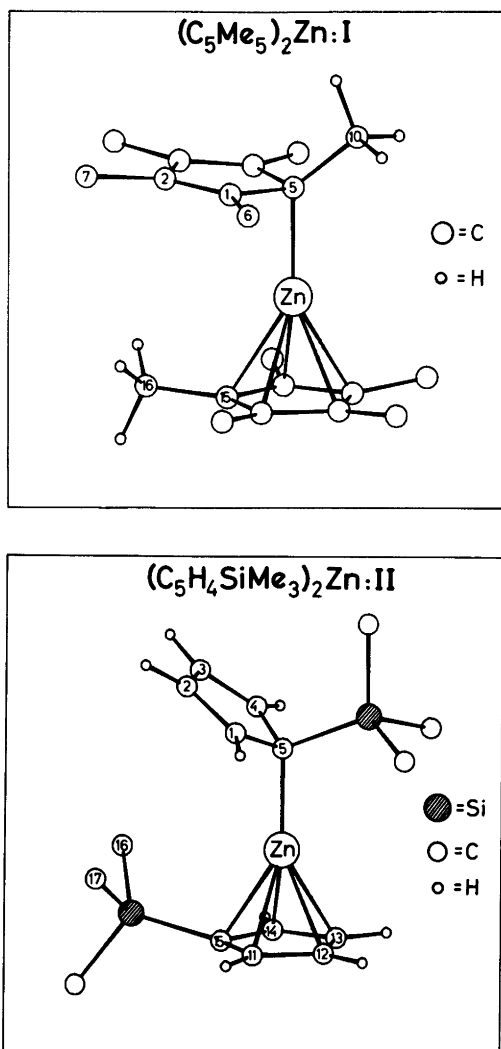


Fig. 1. Molecular models of bis(pentamethylcyclopentadienyl)zinc, I, of the bis(trimethylsilylcyclopentadienyl)zinc, II. Most hydrogen atoms have been omitted for clarity.

diagonal weight matrix together with four r.m.s. amplitudes of vibration,  $l$ .<sup>10</sup> Shrinkage corrections were neglected. Non-refined  $l$ -values were mostly taken from Ref. 11.

The best values for the refined parameters are listed in Table 1. The estimated standard deviations have been multiplied by a factor of three in order to compensate for data correlation and

uncertainty introduced by nonrefined parameters.

Even though the geometry of the best model (Fig. 1 and Table 1) indicates that bonding between the Zn atom and the upper ring is confined to C(5), refinements were also carried out on a model in which this ring had  $C_{5v}$  symmetry. The  $R$ -factor obtained with this model, was 6.8% as compared to 6.3% for the best model. A few refinements were also carried out on models in which the angle between the fivefold symmetry axis of the  $(\eta^5-C_5Me_5)Zn$  fragment and the Zn-C(5) bond was assumed to deviate from  $180^\circ$ . The introduction of this new independent parameter did not lead to a significant improvement of the fit.

II. The asymmetric substitution of the cyclopentadienyl rings in  $(C^5H_4SiMe_3)_2Zn$  introduces two conformational degrees of freedom into the  $\eta^5/\eta^1$  model.

In Fig. 1 we show a model in which the  $Me_3Si$  group is bonded to C(5) in the  $\eta^1$ -bonded ring, but models in which the  $Me_3Si$  group is bonded to C(1) or C(2) must also be considered, though a model with the  $Me_3Si$  group bonded to C(1) is unlikely for steric reasons.

An NMR investigation of  $(Me_3Si)_2C_5H_4$  concluded that the 5,5-isomer is the most stable, at  $100^\circ C$  the conformational composition is 80% 5,5- and 20% 2,5 isomers.<sup>12</sup> We carried out refinements on the conformational composition of II and found them to converge to 100% 5,5. The predominance of this conformer is consistent with the  $^1H$  NMR-spectra (see below). Final refinements were therefore carried out with the 5,5-model in Fig. 1 as the only conformer.

The GED data does not appear to contain any information about the relative orientation of the two ligands: The  $\eta^5-C_5H_4SiMe_3$  ring probably undergoes virtually non-hindered internal rotation about the Zn to ring-center axis. Such rotation would smear all interligand distances out over several hundreds of pm. Rather arbitrarily we chose to fix the two  $Me_3Si$  groups in an *anti* conformation as indicated in Fig. 1, yielding a model of overall  $C_s$  symmetry.

All Si-C bonds were assumed equal and fixed at 188.0 pm. All  $\langle C(\text{in ring})Si-C(\text{Me})$  angles were assumed equal and fixed at  $112^\circ$ , equal to the  $\langle C^iSiC(\text{Me})$  angle of  $H_2C^i(SiMe_3)_2$ .<sup>13</sup> All C-H bonds were assumed equal and  $\langle SiCH$  fixed at  $115^\circ$ .<sup>13</sup> The orientation of the  $Me_3Si$

groups with respect to rotation about the Si–C (in ring) bonds are indicated in Fig. 1.

The  $(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Zn}$  fragment was generated from a  $(\text{C}_5\text{H}_5)\text{Zn}$  fragment of  $C_{5v}$  symmetry and a planar  $\text{C}_5\text{H}_5$  ring by removing one H-atom and replacing it by the  $\text{Me}_3\text{Si}$  group. The C–C in ring bond distance was again assumed equal to that of  $(\eta^5\text{-C}_5\text{H}_5)\text{ZnCH}_3$ .<sup>2</sup> The C–H and Zn–C( $\eta^5$ ) bond distances and the angle between the C(in ring)–Si bond and  $\text{C}_5$  ring plane were refined as independent parameters.

Initial refinements were made on models in which the  $\text{C}_5\text{H}_4$  fragment of the  $\eta^1$ -bonded ring was assumed to be congruent with that of cyclopentadiene;<sup>9</sup> only a scale was refined. The model was later modified by the introduction of a factor LOC which allowed all interatomic distances to vary linearly between the value in scaled cyclopentadiene and a ring model of  $D_{5h}$  symmetry (the  $\text{Me}_3\text{Si}$  group excluded). LOC=1 corresponded to a localized bonding mode à la cyclopentadiene, LOC=0 to a delocalized bonding mode. The average C–C(in ring) bond distance, LOC, the Zn–C(5) bond distance, the valence angle  $\angle\text{ZnC(5)Si}$  and the angle between the Zn–C(5) bond and the ring plane,  $\angle\text{C}_5\text{C–Zn}$ , were refined as independent parameters.

Refinement of eight structure parameters and four vibrational amplitudes converged to the values listed in Table 1. Non-refined amplitudes were mostly taken from Reference 13. The fit between experimental and calculated intensities is not as good as that obtained for **I**. It is not clear whether this is due to lower quality data or the large number of assumptions built into our model. The estimated standard deviations listed in Table 1 have been multiplied by a factor of three, but may still be to small.

## Results and discussion

Molecular models of  $(\text{C}_5\text{Me}_3)_2\text{Zn}$  (**I**) and  $(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Zn}$  (**II**) are shown in Fig. 1. Structure parameters obtained by least-squares calculations are listed in Table 1. Fig. 2 shows experimental radial distribution curves and difference curves.

Gaseous **I** and **II** both have open-faced sandwich structures with one  $\eta^5$ -bonded and one  $\eta^1$ -bonded ring, rather than regular sandwich structures with two  $\eta^5$ -bonded rings.

We admit to being surprised by this result: Mg, which has the same number of valence electrons as Zn (except for the filled  $3d$  subshell of the latter), and a similar atomic (and ionic) radius, forms a regular sandwich compound  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mg}$  with Mg–C=234 pm in both the gaseous<sup>14</sup> and solid<sup>15</sup> phases: High spin  $(\text{C}_5\text{H}_5)_2\text{Mn}$ , where the metal atom differs from Zn in having a half filled rather than a filled  $3d$  subshell, adopts a sandwich structure in the gas phase<sup>16</sup> with Mn–C=238 pm;  $(\text{C}_5\text{H}_5)_2\text{Ge}$  in the solid phase<sup>17</sup> and  $(\text{C}_5\text{Me}_3)_2\text{Ge}$  in the gas phase,<sup>6,18</sup> where the metal atom has the electron configuration of Zn plus two electrons, adopt angular sandwich structures with mean Ge–C=252 pm.

It might be argued that the Zn atom is smaller than the others and thus unable to accommodate two  $\eta^5$ -bonded cyclopentadienyl rings. The difference is, however, small: The Zn–C( $\eta^5$ ) bond distances in  $(\eta^5\text{-C}_5\text{H}_5)\text{ZnCH}_3$ , **I** and **II** are 228.0(9), 228(2) and 226(3) pm, while the Mg–C( $\eta^5$ ) bond distances in  $(\eta^5\text{-C}_5\text{H}_5)\text{MgCH}_2\text{CMe}_3$ <sup>19</sup> and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mg}$  are 232.8(7) and 233.9(4) pm, respectively.

Comparison of the structures of  $(\text{C}_5\text{H}_5)\text{ZnCH}_3$  and  $(\text{C}_5\text{H}_5)\text{MgCH}_2\text{CMe}_3$  indicates that metal-to-ring bonding is considerably weaker in the former: In  $(\text{C}_5\text{H}_5)\text{ZnCH}_3$  the Zn–C( $\eta^5$ ) bond distance is about 38 pm longer than the Zn–C  $\sigma$  bond distance: In the Mg-compound the difference is about 20 pm: The metal–C ( $\eta^5$ ) vibrational amplitude in  $(\text{C}_5\text{H}_5)\text{ZnCH}_3$  is 15(1) pm, in the Mg-compound it is 8.3(7) pm.

We choose therefore to see the structures of **I** and **II** as another manifestation of the relative reluctance of the Group II B metals to form strong complexes with electron donors or otherwise increase their coordination numbers<sup>20</sup>: Dimethylmagnesium polymerizes through formation of methyl bridges, dimethylzinc is monomeric. Monomeric dialkylmagnesium compounds interact strongly with electron donors, while dialkylzinc compounds can be separated from ethers through distillation. In this connection it may also be pertinent to recall that the cyclopentadienyl rings in  $(\text{C}_5\text{H}_5)\text{HgCH}_3$ <sup>21</sup> and  $(\text{C}_5\text{H}_5)_2\text{Hg}$ <sup>22</sup> appear to be  $\sigma$ -bonded to the metal.

Unsubstituted dicyclopentadienylzinc is polymeric in the solid state.<sup>23</sup> Each of the two crystallographically independent Zn atoms is surrounded by two bridging Cp rings and one terminal. The geometry of the terminal Zn( $\text{C}_5\text{H}_5$ )

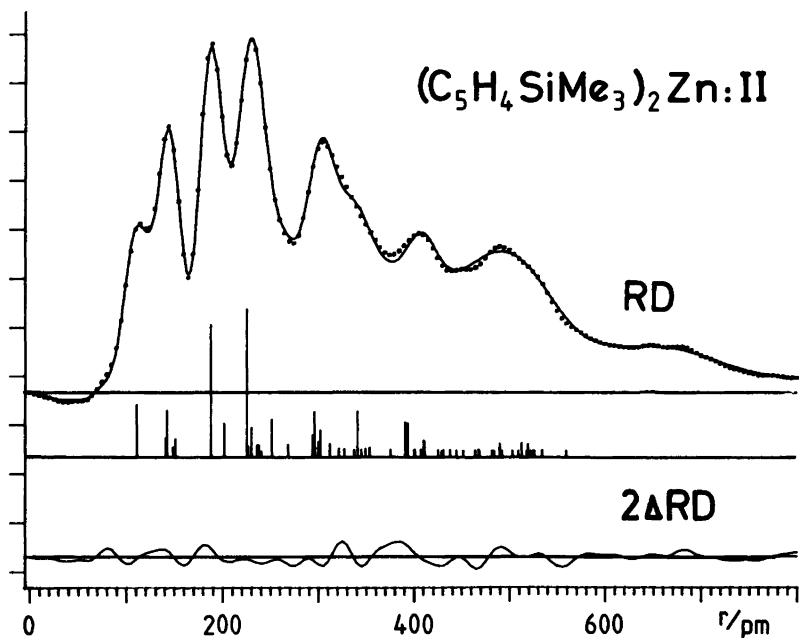
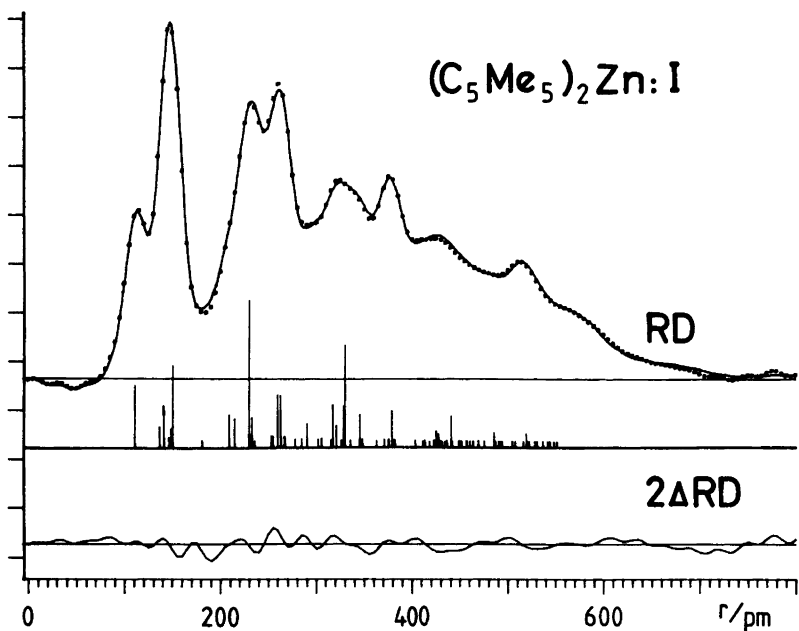


Fig. 2. Experimental (dotted) and theoretical (full line) radial distribution curves for bis(pentamethylcyclopentadienyl)zinc, I, and bis(trimethylsilylcyclopentadienyl)zinc, II. The bars indicate the distribution and weight of the different interatomic

distances in the molecules. The lower curve in each plot is the difference between experimental and theoretical curve for the best model multiplied with a factor of two. The artificial damping constant,  $k$ , is  $20 \text{ pm}^2$  for I and  $30 \text{ pm}^2$  for II.

fragment is roughly similar to the geometry of the Ge( $\sigma$ -C<sub>5</sub>H<sub>5</sub>) fragment in H<sub>3</sub>Ge(C<sub>5</sub>H<sub>5</sub>)<sup>24</sup>, but there are chemically significant differences: The Ge–C(5) bond distance in H<sub>3</sub>Ge(C<sub>5</sub>H<sub>5</sub>), 196.5(9) pm by X-ray and 196.9(5) pm by GED, is only slightly longer than in Ge(CH<sub>3</sub>)<sub>4</sub>, 194.5(3) pm.<sup>25</sup> The angle between the Ge–C(5) bond and the C<sub>5</sub> ring plane is about 64°, if C(5) was perfectly sp<sup>3</sup> hybridized the angle would be 55°. Hence the structure of H<sub>3</sub>Ge(C<sub>5</sub>H<sub>5</sub>) suggests the presence of a localized single bond between Ge and C(5).

In crystalline (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Zn<sup>23</sup> the shortest Zn–C distances in the two crystallographically independent (terminal) Zn(C<sub>5</sub>H<sub>5</sub>) fragments are 208(3) and 204(6) pm, significantly longer than the Zn–C bond distance in Zn(CH<sub>3</sub>)<sub>2</sub>, 193.0(2) pm.<sup>26</sup> The angle between the Zn–C bonds and the C<sub>5</sub> ring planes, 74 and 80° respectively, places the metal atom just outside the periphery of the rings.

The interaction between the Zn and the upper ring in gaseous (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zn appears to be similar, Zn–C(5)=204(6) pm and <C<sub>5</sub>,C–Zn=84(4)°, and the bonding may similarly be described as “peripheral” or “more or less  $\eta^1$ ”. The structure of **II** is less accurately determined. The angle <C<sub>5</sub>,C–Zn is, however, significantly smaller than in **I** and corresponds to that expected for a tetrahedral C(5) atom. It appears that the Me<sub>3</sub>Si group stabilizes a strictly  $\eta^1$  bonding mode.

Molecules **I** and **II** are too large to allow us to determine individual C–C bond distances in the peripherally bonded ring. We stress, however, that for each molecule a model with localized single and double bonds as in cyclopentadiene<sup>9</sup> itself, is in better agreement with the data than models in which the peripherally bonded ring has fivefold symmetry.

Preliminary X-ray results indicate that the structure of crystalline (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zn closely resembles the  $\eta^1$ ,  $\eta^5$ -bonded structure found in the gas phase.<sup>27</sup> The infrared spectrum of solid (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zn contains two medium to strong absorption bands at 340 and 453 cm<sup>-1</sup> which we assign as metal-ring stretching modes. The lower frequency band overlaps with ring deformation modes. A doubling of a majority of the ring and C–CH<sub>3</sub> modes between 600 and 1450 cm<sup>-1</sup> is consistent with the presence of two differently bonded ligand rings. The highest C<sub>5</sub> ring mode is found at 1652 cm<sup>-1</sup>, virtually unchanged from

HC<sub>5</sub>Me<sub>5</sub>, and is assigned to an  $\eta^1$ -bonded ring with localized single and double bonds.

The <sup>1</sup>H NMR spectrum of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zn in deuterated benzene at room temperature consists of one sharp singlet at  $\delta = 1.98$  ppm. Clearly the exchange at  $\eta^1$ - and  $\eta^5$ -bonded rings is rapid on the NMR time scale. Such an exchange might proceed via a symmetric  $\eta^5$ ,  $\eta^5$  transition state.

Similarly the <sup>1</sup>H NMR spectrum of **II** in deuterated toluene at 25 °C consists of a sharp singlet at  $\delta$  0.2 (Si(CH<sub>3</sub>)<sub>3</sub>) and two “triplets” at  $\delta$  6.4 and 6.6 (cyclopentadienyl protons) as expected for an AA'BB' system. The proton decoupled <sup>13</sup>C spectrum at –3 °C contains singlets at  $\delta$  0.8 (Si(CH<sub>3</sub>)<sub>3</sub>Y),  $\delta$  87.2 (C(5), C(15)) and two peaks at  $\delta$  118.7 and 119.1 (C(1), C(4), C(11), C(14)) and (C(2), C(3), C(12), C(13)), respectively. Both spectra are consistent with the model in Fig. 1 with rapid exchange of  $\eta^1$ - and  $\eta^5$ -bonded rings. On cooling to –37 °C, the peak at  $\delta = 0.8$  in the <sup>13</sup>C spectrum splits into two peaks, indicating that ring exchange has been frozen out. The temperature variations of the NMR spectra are otherwise very complicated.

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