

# The Molecular Structures of Decamethylgermanocene, $(\eta\text{-C}_5\text{Me}_5)_2\text{Ge}$ , and Pentamethylcyclopentadienylgermanium Chloride, $(\eta\text{-C}_5\text{Me}_5)\text{GeCl}$ , by Gas Electron Diffraction

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The gas electron diffraction pattern of  $(\text{C}_5\text{Me}_5)_2\text{Ge}$  recorded with a nozzle temperature of about 135 °C, is consistent with an angular sandwich structure of  $C_s$  symmetry similar to those of crystalline  $(\text{C}_5\text{Me}_5)_2\text{Sn}$  and  $(\text{C}_5\text{Me}_5)_2\text{Pb}$ . The thermal-average value of the angle between the two  $C_5$  ring planes is  $\angle C_5, C_5 = 22(2)^\circ$ .

The perpendicular Ge-to-ring distance,  $h = 2.210(7)$  Å, corresponds to a mean Ge–C bond distance of 2.519(7) Å.

The electron diffraction pattern of  $(\text{C}_5\text{Me}_5)\text{GeCl}$  recorded with a nozzle temperature of about 130 °C, is consistent with an angular model of  $C_s$  symmetry in which the  $\text{C}_5\text{Me}_5$  ring is bonded to the Ge atom in an asymmetric, *polyhapto* fashion: The distance from the ring center to the ring normal through Ge is  $\delta = 0.43(6)$  Å. The perpendicular Ge-to-ring distance  $h = 2.11(2)$  Å is significantly shorter than in  $(\text{C}_5\text{Me}_5)_2\text{Ge}$ , the Ge–Cl bond distance Ge–Cl = 2.258(12) Å is significantly longer than in gaseous  $\text{GeCl}_2$ . The angle between the Ge–Cl bond and the ring normal through Ge ( $\angle h, \text{GeCl}$ ) is  $110(2)^\circ$ .

The synthesis of the first organic derivative of divalent germanium,  $(\text{C}_5\text{H}_5)_2\text{Ge}$  or germanocene, was reported by Scibelli and Curtis in 1973.<sup>1</sup> The compound is, however, rather unstable: after three hours at room temperature it is converted into a (polymeric) solid which is nonvolatile and insoluble in common organic solvents.<sup>1</sup> 1,1'-Dimethylgermanocene,  $(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Ge}$ , first prepared by Stobart and

co-workers,<sup>2</sup> is more stable and we have published the result of a gas electron diffraction (GED) study.<sup>3</sup> The molecule was found to have a "bent sandwich" structure similar to those previously found for  $(\eta\text{-C}_5\text{H}_5)_2\text{Sn}$  and  $(\eta\text{-C}_5\text{H}_5)_2\text{Pb}$  in the gas phase<sup>4</sup> and  $(\text{C}_5\text{H}_5)_2\text{Sn}^5$ ,  $(\text{C}_5\text{Me}_5)_2\text{Sn}^6$ , and  $(\text{C}_5\text{Me}_5)_2\text{Pb}^5$  in the solid phase. In  $(\text{C}_5\text{H}_4\text{Me})_2\text{Ge}$  the perpendicular metal-to-ring distance is 2.221(8) Å, corresponding to an *average* Ge–C bond distance of 2.531 (7) Å. The thermal-average value for the angle between the two ring planes was  $34(7)^\circ$ .

The synthesis of decamethylgermanocene from  $\text{GeCl}_2$  and  $(\text{C}_5\text{Me}_5)\text{Li}$  was published in 1980.<sup>6</sup> We had to retract the results of GED study of this compound<sup>7</sup> when we discovered that the sample used had in fact consisted of the then unknown compound  $(\text{C}_5\text{Me}_5)\text{GeCl}$ .<sup>8</sup> The complex chemistry involved in the synthesis of  $(\text{C}_5\text{Me}_5)_2\text{Ge}$  and  $(\text{C}_5\text{Me}_5)\text{GeCl}$  has now been elucidated.<sup>9</sup> In order to set the record straight we now publish the results of a new GED investigation of  $(\text{C}_5\text{Me}_5)_2\text{Ge}$  with an authentic sample, along with the results of an investigation of the novel compound  $(\text{C}_5\text{Me}_5)\text{GeCl}$ .

## EXPERIMENTAL

Samples of  $(\text{C}_5\text{Me}_5)_2\text{Ge}$  and  $(\text{C}_5\text{Me}_5)\text{GeCl}$  were synthesized and characterized (by elemental analysis, MS and other techniques) as described elsewhere.<sup>6,9</sup> Both compounds are thermally

stable below 150 °C. The electron scattering patterns were recorded on Balzers Eldigraph KDG-2 with nozzle to plate distances of about 50 and 25 cm. The data for  $(C_5Me_5)_2Ge$  were recorded with nozzle and reservoir temperatures of about 135 °C and a torus-shaped nozzle which permits electron diffraction data to be recorded with a gas pressure of about 1 Torr. The data were processed by standard procedures. Complex atomic scattering factors were calculated<sup>10</sup> from analytical representations of the scattering potentials.<sup>11</sup> The average modified molecular intensity data obtained from four 50 cm plates extended from  $s=1.50$  to  $15.00 \text{ \AA}^{-1}$  with an increment of  $0.125 \text{ \AA}^{-1}$ , the average intensity data obtained from five 25 cm plates extended from  $s=2.25$  to  $30.00 \text{ \AA}^{-1}$  with an increment of  $0.25 \text{ \AA}^{-1}$ .

The electron diffraction data of  $(C_5Me_5)GeCl$  had already been recorded in the belief that the sample consisted of  $(C_5Me_5)_2Ge$ . A new set of data was, however, recorded with the torus-shaped low pressure nozzle, a reservoir temperature of about 130 °C and a nozzle to plate distance of about 50 cm. The data thus obtained were indistinguishable from those previously obtained with a convergent beam scattering geometry,<sup>7</sup> but appeared to contain less noise. The structure reported here is based on four new 50 cm plates which yielded an average molecular intensity curve ranging from  $s=2.00$  to  $14.75 \text{ \AA}^{-1}$  with an increment of  $0.125 \text{ \AA}^{-1}$ , and the five 25 cm plates previously recorded which yielded molecular intensities ranging from  $s=4.50$  to  $22.00 \text{ \AA}^{-1}$  with an increment of  $0.25 \text{ \AA}^{-1}$ .

## STRUCTURE ANALYSIS

Least-squares refinement of the molecular structure of  $(C_5Me_5)_2Ge$  was based on the molecular model of  $C_5$  symmetry shown in Fig. 1. This model has staggered cyclopentadienyl rings, and is similar to the molecular structures of  $(C_5Me_5)_2Sn$  and  $(C_5Me_5)_2Pb$  determined by X-ray diffraction.<sup>5,6</sup> It was assumed that the two  $(C_5Me_5)Ge$  fragments have  $C_{5v}$  symmetry, and that the methyl group have  $C_{3v}$  symmetry with the threefold axes coinciding with the C–C bonds. As indicated in Fig. 1, one C–H bond was assumed to point away from the metal atom. The molecular structure is then determined by seven independent parameters; the Ge–C, C(1)–C(2), C(1)–C(11) and C–H bond distances, the valence angle  $\angle CCH$ , the angle between the C(1)–C(11) bond and the  $C_5$  ring plane, which

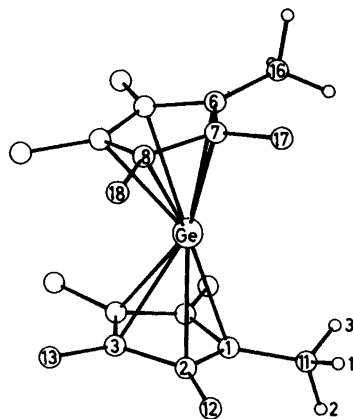


Fig. 1. Molecular model of  $(C_5Me_5)_2Ge$ . (Most H-atoms have been omitted.) The ligand rings are staggered and the molecular symmetry is  $C_5$ . The angle between the two ring planes is  $22^\circ$ , corresponding to the *thermal average* value.

we denote by  $\angle C_5, C-C$  and define as positive when the C–C bonds are bent *away* from the metal atom, and finally the angle between the planes of the two ligand rings which we denote by  $\angle C_5, C_5$ . Vibrational corrections ( $r_a - r_o$ ) for distances between atoms in the same ligand ring were taken from calculations on decamethylferrocene.<sup>12</sup> No corrections were applied for Ge-to-ring or ring-to-ring distances. The seven structure parameters and eight root-mean-square vibrational amplitudes were refined by least-squares calculations on the intensity data with a diagonal weight matrix. The best values are listed in Table 1 along with estimated standard deviations which have been multiplied by a factor of two to include the uncertainty due to data correlation and expanded to include an estimated scale uncertainty of 0.1 %.

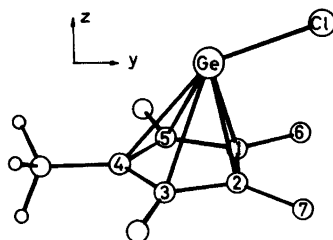


Fig. 2. Molecular model of  $(C_5Me_5)GeCl$ . (Most H-atoms have been omitted.) The molecular symmetry is  $C_5$ .

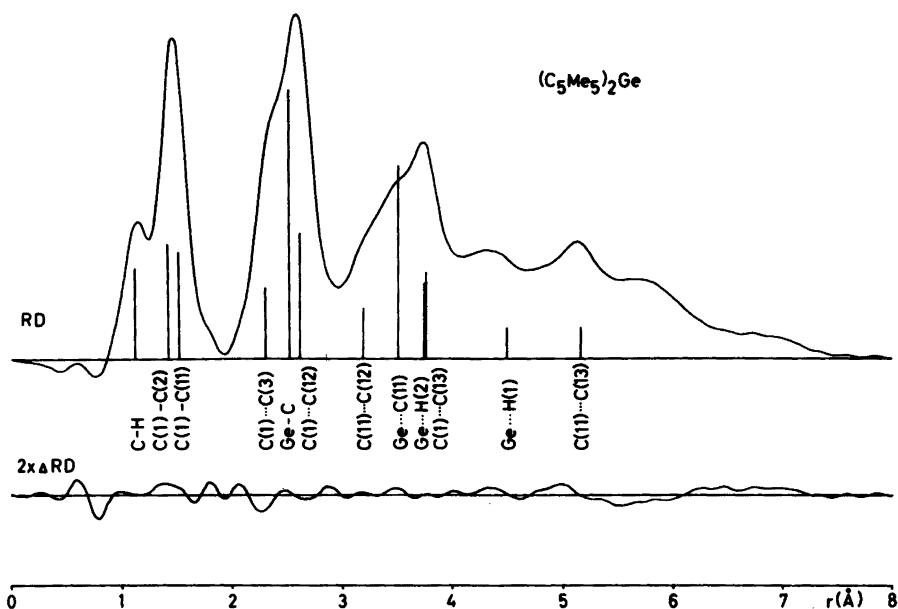
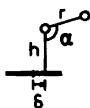


Fig. 3. Above: Experimental radial distribution curve for  $(\text{C}_5\text{Me}_5)_2\text{Ge}$ . Artificial damping constant  $k=0.002 \text{ \AA}^2$ . Major interatomic distances are indicated by bars of height approximately proportional to the area under the corresponding peak. Below: difference between the experimental curve and the theoretical RD curve calculated for the best model (double scale).

Refinement of the molecular structure of  $(\text{C}_5\text{Me}_5)\text{GeCl}$  was based on the  $C_s$  symmetry model shown in Fig. 2. Even though the Ge atom is no longer required to reside over the center of the ring, the  $\text{C}_5\text{Me}_5$  ligand was assumed to retain  $C_5$  symmetry. As in the case of  $(\text{C}_5\text{Me}_5)_2\text{Ge}$ , the structure of the ligand is determined by the C(1)–C(2), C(1)–C(6) and C–H bond distances, the valence angle  $\angle\text{CCH}$  which was fixed at  $112^\circ$ , and the angle  $\angle\text{C}_5\text{C}-\text{C}$ . Four additional parameters are required to fix the positions of the Ge and Cl atoms relative to the ring. We chose the Ge–Cl bond distance ( $r$ ), the perpendicular Ge-to-ring distance ( $h$ ), the angle between the Ge-to-ring normal and the Ge–Cl bond  $\alpha = (\angle h, \text{Ge}-\text{Cl})$ , and finally the distance from the ring center to the Ge-to-ring normal ( $\delta$ ):



All vibrational amplitudes of atom pairs in the same  $\text{C}_5\text{Me}_5$  ligand were fixed at the values calculated for  $(\text{C}_5\text{Me}_5)_2\text{Fe}$ .<sup>12</sup> Vibrational ampli-

tudes of Ge–C bond distances and nonbonded  $\text{Ge}\cdots\text{C}$  and  $\text{Cl}\cdots\text{C}$  distances were refined in groups as indicated in Table 2. The Ge–Cl amplitude was, rather haphazardly, fixed at  $0.08 \text{ \AA}$ . Vibrational corrections were ignored.

Least-squares refinement of eight structure parameters and three independent vibrational amplitudes converged to the values listed in Table 2. The estimated standard deviations have been multiplied by a factor of three to include uncertainty due to data correlation and possible errors introduced by the various assumptions made regarding the model. As the parameter  $\delta$  proved to be particularly sensitive to assumptions made regarding the relative magnitudes of the Ge–C bond distance amplitudes, the e.s.d. of this parameter has been multiplied by a factor of five.

Experimental radial distribution curves calculated by Fourier inversion of experimental modified molecular intensity curves, are shown in Figs. 3 and 4 along with the difference between these curves and the theoretical counterparts calculated for the best models. We consider the agreement satisfactory.

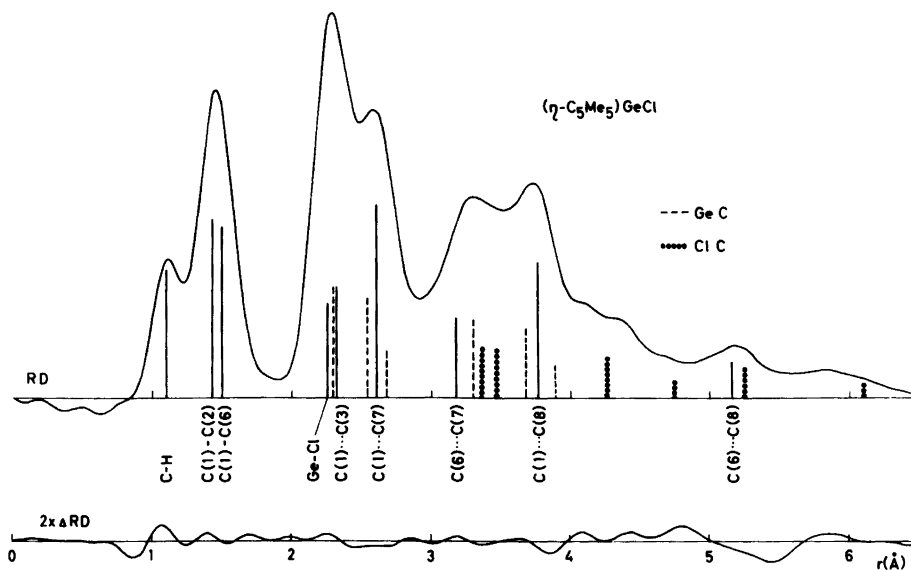


Fig. 4. Above: Experimental radial distribution curve for  $(\eta\text{-C}_5\text{Me}_5)\text{GeCl}$ . Artificial damping constant  $k=0.003 \text{ \AA}^2$ . Major interatomic distances are indicated by bars of height approximately proportional to the area under the corresponding peak. Ge–C distances are indicated by ---, Cl–C distances by ···. Below: difference between the experimental curve and the theoretical RD curve calculated for the best model (double scale).

## RESULTS AND DISCUSSION

$(\text{C}_5\text{Me}_5)_2\text{Ge}$ . The electron diffraction data of  $(\text{C}_5\text{Me}_5)_2\text{Ge}$  are consistent with the “bent sandwich” structure shown in Fig. 1. The in-ring C–C bond distance and the average Ge–C bond distance are indistinguishable from those of 1,1'-dimethylgermanocene,  $(\text{C}_5\text{H}_4\text{Me})_2\text{Ge}$ .<sup>3</sup> The value obtained for the angle between the two ring planes,  $\angle\text{C}_5, \text{C}_5=22(2)^\circ$ , is a *thermal average* value which has not been corrected for ring-metal-ring bending vibrations. Full methyl substitution is expected to force the ligand rings into a more parallel conformation and the value obtained for the angle between the ring planes in  $(\text{C}_5\text{Me}_5)_2\text{Ge}$  is smaller than in  $(\text{C}_5\text{H}_4\text{Me})_2\text{Ge}$ ,  $34(7)^\circ$ . The error limits of the latter are, however, too wide to allow us to conclude that the difference is real. Correction for ring-metal-ring bending vibrations would tend to reduce the value of  $\angle\text{C}_5, \text{C}_5$ , but it seems unlikely that the *equilibrium* conformation is one in which the rings are parallel, *i.e.* where  $\angle\text{C}_5, \text{C}_5=0$ .

The large Ge–C r.m.s. vibrational amplitude obtained in our study of  $(\text{C}_5\text{H}_4\text{Me})_2\text{Ge}$ ,

Table 1. Interatomic distances, valence angles and root-mean-square vibrational amplitudes ( $l$ ) of  $(\text{C}_5\text{Me}_5)_2\text{Ge}$ . Estimated standard deviations in parentheses in units of the last digit.

	$r_a/\text{\AA}$	$l/\text{\AA}$
C(1)–C(2)	1.424(3)	(0.048)
C(1)–C(11)	1.517(4)	(0.053)
C–H	1.121(5)	0.071(6)
$\angle\text{CCH}^\circ$	117(3)	
$\angle\text{C}_5, \text{C}^\circ$	1(1)	
Ge–C(1)	2.519(7)	0.140(7)
$h$	2.210(7)	
$\angle\text{C}_5, \text{C}_5^\circ$	22(2)	
Ge···C(11)	3.52	0.197(11)
Ge···H(1)	3.75	(0.35)
Ge···H(2)	4.50	(0.30)
C(1)···C(3)	2.30	0.065(8)
C(1)···C(12)	2.61	0.074(6)
C(1)···C(13)	3.77	0.081(7)
C(11)···C(12)	3.20	0.13(2)
C(11)···C(13)	5.17	0.09(2)
C···C'	3.8 to 6.9	0.15 to 0.25

Table 2. Interatomic distances, valence angles and root-mean-square vibrational amplitudes (*l*) of (C<sub>5</sub>Me<sub>5</sub>)GeCl. Estimated standard deviations in parentheses in units of the last digit.

	<i>r</i> <sub>a</sub> /Å	<i>l</i> /Å
C(1)–C(2)	1.434(10)	(0.048)
C(1)–C(6)	1.503(10)	(0.053)
C–H	1.109(10)	(0.077)
∠CCH (°)	(112)	
∠C <sub>5</sub> ,CC (°)	7(2)	
Ge–Cl	2.258(12)	(0.080)
<i>h</i>	2.11(2)	
∠ <i>h</i> ,Ge–Cl (°)	110(2)	
$\delta$	0.43(6)	
Ge–C(1)	2.30	0.09(2) <sup>a</sup>
Ge–C(3)	2.54	0.11(2) <sup>a</sup>
Ge–C(4)	2.68	0.13(2) <sup>a</sup>
Ge...C(6)	3.30	0.14(3) <sup>b</sup>
Ge...C(8)	3.67	0.16(3) <sup>b</sup>
Ge...C(9)	3.89	0.18(3) <sup>b</sup>
Cl...C(1)	3.36	0.15(3) <sup>c</sup>
Cl...C(3)	4.27	0.20(3) <sup>c</sup>
Cl...C(4)	4.75	0.18(3) <sup>c</sup>
Cl...C(6)	3.47	0.21(3) <sup>d</sup>
Cl...C(8)	5.25	0.26(3) <sup>d</sup>
Cl...C(9)	6.09	0.26(3) <sup>d</sup>

<sup>a,b,c,d</sup> These four groups of amplitudes were refined with constant differences.

*l*=0.201(7) Å, indicates that the Ge atom is displaced from the fivefold symmetry axes of the rings and/or that the ring-metal-ring deformation mode is very soft. The Ge–C vibrational amplitude in (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ge appears to be significantly smaller. The reason is not clear, but if the rings in (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ge are closer to being parallel, the metal atom would be expected to be closer to the symmetry axes and the deformation mode to be less soft.

(C<sub>5</sub>Me<sub>5</sub>)GeCl. The electron diffraction data are consistent with the molecular model shown in Fig. 2. The best values for the structure parameters are listed in Table 2. (C<sub>5</sub>Me<sub>5</sub>)GeCl is a relatively large molecule with low symmetry, and this is reflected in the rather large error limits.

The Ge atom is bonded to the Cl atom and to a *polyhapto* C<sub>5</sub>Me<sub>5</sub> ring. The Ge–Cl bond distance is 2.258(12) Å, considerably longer than in gaseous GeCl<sub>2</sub>, Ge–Cl=2.183(4) Å.<sup>13</sup> On the other hand, the perpendicular Ge-to-ring distance *h*=2.11(2) Å is significantly shorter than in

decamethylgermanocene, *h*=2.210(7) Å. The increase in the valence angle at Ge on going from GeCl<sub>2</sub> where ∠ClGeCl=100.3(4)°, to (C<sub>5</sub>Me<sub>5</sub>)GeCl where ∠*h*,GeCl=110(2)°, to (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ge where the angle between the two ring normals is close to 180°, probably reflects the bulk of the C<sub>5</sub>Me<sub>5</sub> ligand.

The metal atom is displaced  $\delta$ =0.43(6) Å from the (approximate) fivefold symmetry axis of the C<sub>5</sub>Me<sub>5</sub> ring towards the midpoint of the C(1)–C(2) bond. *Ab initio* MO calculations described in the following article indicate that the displacement reduces antibonding interactions between the lone pair electrons on Ge and C(4).<sup>14</sup> As a result of this displacement the Cl atom appears to nest relatively comfortably at a distance of 3.4 Å from the four C atoms C(1), C(2), C(6) and C(7).

The structure of (C<sub>5</sub>Me<sub>5</sub>)GeCl thus appears to be closely related to that found for (C<sub>5</sub>H<sub>5</sub>)SnCl by X-ray crystallography.<sup>15</sup> In the crystal, however, (C<sub>5</sub>H<sub>5</sub>)SnCl exhibits two short intermolecular Sn–Cl contacts at 3.25 Å, and the intramolecular Sn–Cl bond distance at 2.68 Å is 0.33 Å longer than in gaseous SnCl<sub>2</sub> where Sn–Cl=2.347(7) Å.<sup>16</sup>

Since the metal atom does not lie over the center of the ligand ring, the ligand may show small deviations from fivefold symmetry. Such deviations may be responsible for some of the disagreement between the experimental and calculated RD curves in Fig. 4.

Finally, we wish to consider the following question: how was it possible to refine the molecular structure of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ge into satisfactory agreement with intensity data collected with a sample consisting of (C<sub>5</sub>Me<sub>5</sub>)GeCl? In this connection it is instructive to compare the RD curve of (C<sub>5</sub>Me<sub>5</sub>)GeCl (Fig. 4) with that expected for (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ge with a similar Ge–C bond distance and a relative scale factor of 0.5: all peaks representing distances between atoms in the same (C<sub>5</sub>Me<sub>5</sub>) ligand would occur in both curves with the same weight.

The RD curves would in fact differ only in two respects: (i) the unresolved complex of peaks between 2.0 and 2.9 Å in the RD curve of (C<sub>5</sub>Me<sub>5</sub>)GeCl contains peaks representing *five* Ge–C bond distances, *five* C(1)···C(3) distances, *ten* C(1)···C(7) distances, *fifteen* C···H distances and *one* Ge–Cl distance. The RD curve of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ge with a relative scale factor of 0.5 would contain the same peaks with the same

weight except that the Ge-Cl peak would be missing. The resulting area discrepancy is not very large and would be reduced by refinement of scale factors and vibrational amplitudes. (ii): the RD curve of  $(C_5Me_5)GeCl$  contains peaks representing ten nonbonded Cl...C distances with large vibrational amplitudes between 3.4 and 6.1 Å. None of these peaks is clearly resolved. The RD curve of  $(C_5Me_5)_2Ge$  would contain broad peaks representing hundred C...C interligand distances (with scale equal to 0.5) in the same range. Comparison of the RD curve in Fig. 4 with the RD curve in Ref. 5. Show that the difference between the RD curves in this range is primarily one of the position of the zero-line. Hence we found that the structure of  $(C_5Me_5)_2Ge$  could be refined to the  $(C_5Me_5)GeCl$  data if the background was modified below  $s=5 \text{ \AA}^{-1}$ . The required background modification was monotonic and without inflection points.

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