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The Molecular Structures of 1,1′-Dimethylgermanocene and 1,1′-Dimethylstannocene, $(C_5H_4Me)_2M$; M=Ge and Sn, Determined by Gas Electron Diffraction. Self-consistent Field Molecular Orbital Calculations on Germanocene, $(C_5H_5)_2Ge$

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The gas electron diffraction patterns of 1,1′-dimethylgermanocene and 1,1′-dimethylstannocene have been recorded with nozzle temperatures of about 100 °C. The diffraction patterns are consistent with "bent sandwich" structures of C_2 symmetry and perpendicular metal-to-ring distances of 2.221(8) Å (Ge) and 2.400(6) Å (Sn), respectively, corresponding to average bond distances Ge–C=2.531(7) Å and Sn–C =2.689(6) Å. The angle between the ring planes is 34(7)° in the Ge- and 50(6)° in the Sn-compound. *Ab initio* molecular orbital calculations on $(C_5H_5)_2Ge$ indicate that metal-to-ring bonding is due primarily to interaction between the e_1 π-orbitals of the rings and the $4p_x$ and $4p_y$ orbitals on Ge. The totally symmetric "lone pair" orbital is predominantly a Ge 4*s* orbital. The 3*d* electrons of Ge are of secondary importance for the bonding. The potential energy curves obtained by the MO calculations and the vibrational amplitudes obtained in the GED study of $(C_5H_4Me)_2Ge$ and $(C_5H_4Me)_2Sn$ indicate that the molecules undergo large amplitude ring-metal-ring bending and deformation vibrations.

The synthesis of the first stable organic derivatives of divalent tin and lead, dicyclopentadienyltin and -lead, stannocene and plumbocene, was reported by Fischer and Grubert in 1956.[1] Gas electron diffraction (GED) studies carried out ten years later[2] confirmed earlier suggestions[3,4] that both molecules possess "bent sandwich" structures: The two $(C_5H_5)M$ fragments have at least approximate C_{5v} symmetry, but the ligand rings are not parallel. In $(C_5H_5)_2Pb$ the angle between the planes defined by the two rings is 45(5)°. The angular structures have, like the angular structures of the gaseous dihalides, been rationalized as due to the presence of a stereochemically active lone pair on the metal.

An early X-ray diffraction investigation of one of the two crystalline modifications of $(C_5H_5)_2Pb$ revealed a polymeric structure where each lead atom is surrounded by one terminal *pentahapto* and two bridging cyclopentadienyl rings.[5] Though this study brought out the main features, a reinvestigation would be desirable in order to determine the position of the bridging ligand rings more accurately and to provide clues to the direction of the electron lone pair.

More recently, the structures of the monomeric compounds $(C_5H_5)_2Sn$,[6] bis(pentamethylcyclopentadienyl)tin,[7] $(C_5Me_5)_2Sn$ and $(C_5Me_5)_2Pb$[6] have been determined by X-ray crystallography. In general, these studies confirm the results of the early GED investigations, but due to the low molecular symmetry of these species, the X-ray studies provide more exact information. In particular the angle between the ring planes is determined to the nearest degree.

The X-ray studies also show that in all these molecules the metal atom is displaced by 0.2 or 0.3 Å from the intersection of the fivefold symmetry axes of the rings, approximately in the

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direction of the intersection of the two ring planes. We shall return to these points in our discussion.

The synthesis of germanocene, $(C_5H_5)_2Ge$, was reported by Scibelli and Curtis in 1973.[8] The compound is, however, rather unstable: After only three hours at room temperature it is completely polymerized to give a solid which is nonvolatile and insoluble in common organic solvents.[8] Since 1,1'-dimethylgermanocene, $(C_5H_4Me)_2Ge$, was reported to be more stable,[9] we decided to attempt a structure determination of this and the analogous tin compound by GED. Since the results of an earlier GED study of $(C_5Me_5)_2Ge$[10] have been withdrawn,[11] $(C_5H_4Me)_2Ge$ is the first germanocene to be structurally characterized.

At the same time, we report the results of a series of SCF MO calculations on $(C_5H_5)_2Ge$ which elucidate the nature of the metal to carbon bonds and the potential energy surface of the molecule.

EXPERIMENTAL

$(C_5H_4Me)_2Ge$ and $(C_5H_4Me)_2Sn$ were synthesized from $(C_5H_4Me)K$ and GeI_2 and $SnCl_2$, respectively, as described by Stobart and coworkers.[9]

The scattering patterns of both compounds were recorded on Balzers Eldigraph KDG-2. In order to keep the temperature as low as possible, the data for the Ge compound were recorded with a convergent electron beam and a nozzle with a wide opening.[12] The nozzle temperature was about 100 °C. After the sample had evaporated, the ampoules were found to contain small amounts of yellow solid which we initially assumed to be a polymerization product. Subsequent analysis by neutron activation showed, however, that the sample as prepared contained significant amounts of iodine, possibly in the form of $(C_5H_4Me)GeI$. Consequently a new sample was prepared which by neutron activation analysis was free from iodine. When the electron diffraction experiment was repeated with the new sample, no residue was found and the scattering data were in agreement with those obtained with the impure sample.

The data for the tin compound were recorded with a narrow parallel electron beam and a new nozzle system: The inlet system ends in a torus (hollow doughnut) surrounding the electron beam. The gas emerges from a narrow horizontal slit extending over 360°. Trial runs with benzene show that this nozzle permits the recording of electron diffraction data with a gas pressure of about 1 torr and a conventional beam geometry. Structure refinements of benzene based on several plate sets, show no systematic errors due to broadening of the molecular beam. The diffraction data of $(C_5H_4Me)_2Sn$ were recorded with a temperature of about 100 °C.

Exposures were made with nozzle-to-plate distances of 50 and 25 cm. The number of plates used were five 50 cm and four 25 cm plates for M=Ge, and six 50 cm and six 25 cm plates for M=Sn.

The data were processed by standard methods. The complex atomic scattering factors, $f'(s)$, of Ge, C and bonded H were calculated from an analytical representation of the atomic potential[13] using a program written by Yates.[14] The scattering factor of Sn was obtained by interpolation of numerical tables.[15] The molecular intensities were modified through multiplication with $s/|f_C(s)|\ |f_M(s)|$. The average modified molecular intensities from the 50 cm plates ranged from s=2.00 to 15.00 Å^{-1} with s=0.125 Å^{-1}, and the molecular intensities from the 25 cm plates ranged from s=4.00 to 28.50 Å^{-1} with s=0.25 Å^{-1}.

STRUCTURE ANALYSIS

A molecular model for $(C_5H_4Me)_2M$, M=Ge or Sn is shown in Fig. 1. It was assumed that an

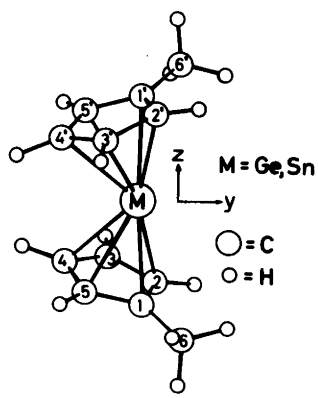

Fig. 1. Molecular model of $(C_5H_4Me)_2M$, M=Ge or Sn. The molecular symmetry is C_2 with the symmetry axis coinciding with the y-axis. In this model the position of the metal atom is such that all M–C bond distances are equal. Displacement of the metal atom from this position along the y-axis is denoted by δy and defined as positive when the metal atom is moved to the right.

adequate model for the C_5H_4Me ligand in either compound could be constructed from a C_5H_5 ring with D_{5h} symmetry by removing one H atom and replacing it by an Me group. The methyl groups were assumed to have C_{3v} symmetry with the symmetry axis along the C–C bonds and with one C–H bond in a plane perpendicular to the C_5 ring as indicated in Fig. 1. All C–H bonds were assumed equal. The structure of the ligand in each compound is then determined by the following independent parameters: The C–H, C(1)–C(2) and C(1)–C(6) bond distances, the methyl ∠CCH bond angle, and the angle between the C(1)–C(6) bond and the ring plane which we denote by $\angle C_5$,C–C and define as positive when the Me group is bent *away* from the metal atom.

The metal atom was assumed to lie on the fivefold symmetry axis of each ring at a perpendicular distance h from each. The ten M–C bond distances are then equal. (We shall return to the validity of this assumption below.)

Finally the molecular symmetry was assumed to be C_2 with the symmetry axis coinciding with the y-axis in Fig. 1. The molecular structure is then determined by eight independent parameters; the five parameters describing the ligands plus the M–C bond distance, the angle between the two ring planes which we denote by $\angle C_5,C_5$ and a dihedral angle, ϕ, determining the orientation of the ligand rings. We define ϕ as the angle between the yz plane and a plane through M and the C(1)–C(6) bond. When $\phi=0$, the C(1)–C(6) and C(1′)–C(6′) bonds are pointing along the positive y axis. It should here be pointed out that ϕ is determined primarily by the five distances C(1,2,3,4 or 5) to C(6′), rather than by the distance C(6) to C(6′). Subsequent least-squares refinement gave $\phi=55(25)°$ when M=Ge and $\phi=62(15)°$ when M=Sn. We do not feel that any significance can be attached to these values.

The independent structure parameters were refined by least-square calculations on the intensity data with diagonal weight matrices and under the constraints of geometrically consistent r_a structures.[16] For $(C_5H_4Me)_2Ge$ five r.m.s. vibrational amplitudes were included in the refinement, in the case of $(C_5H_4Me)_2Sn$ seven amplitudes could be refined. The refinements converged to give the structure parameters listed in Table 1. The estimated standard deviations have been multiplied by a factor of three to include uncertainty due to correlation in the experimental data and errors introduced by the assumptions made regarding the molecular model.

Experimental radial distribution curves calculated by Fourier inversion of experimental modified molecular intensity curves are shown in

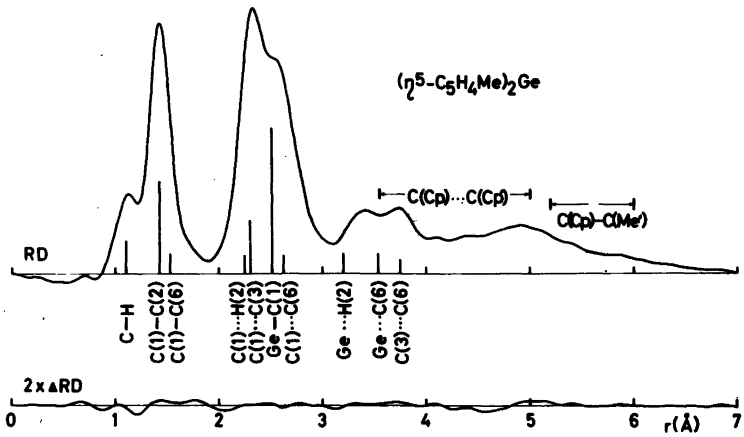

Fig. 2. Above: Experimental radial distribution (RD) curve for $(C_5H_4Me)_2Ge$. Artificial damping constant $k=0.002$ Å^2. Major interatomic distances are indicated by bars of height approximately proportional to the area under the corresponding peak. C(Cp)---C(Cp′) indicates the range of distances between carbon atoms in different C_5 rings. C(Cp)---C(Me′) indicates the range of distances from carbon atoms in one C_5 ring to the methyl C atom on the other. *Below:* Difference between the experimental curve and the theoretical curve calculated for the best model.

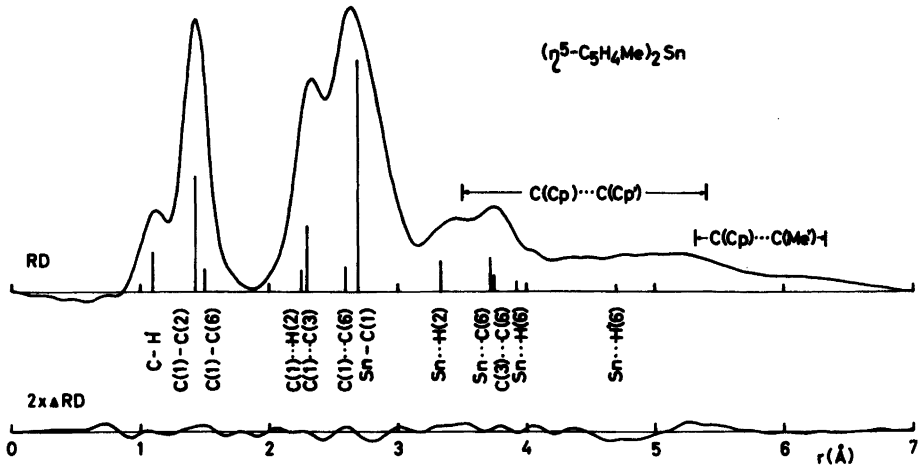

Fig. 3. Experimental RD curve and difference curve for $(C_5H_4Me)_2Sn$. For further comments consult text below Fig. 2.

Figs. 2 and 3 along with the difference between these curves and their theoretical counterparts calculated for the best model. We consider the agreement satisfactory.

MOLECULAR ORBITAL CALCULATIONS

As a measure of economy, we chose to carry out MO calculations on the unsubstituted germanocene, $(C_5H_5)_2Ge$, rather than on the dimethyl derivative. Comparison of the results with those obtained for decamethylgermanocene shows that full methyl substitution has little effect on metal-to-ligand bonding.[11]

Ab initio MO calculations were carried out with better than double zeta basis. For Ge we used a (14,11,5) Gaussian type basis contracted to ⟨8,7,3⟩,[17] for C a (7,3) basis contracted to ⟨4,2⟩,[18] and for H a (4) basis contracted to ⟨2⟩.[19] The calculations were carried out with the program DISCO.[20]

In all calculations the (C_5H_5) rings were assumed to have D_{5h} symmetry with C–C and C–H bond distances equal to 1.411 Å and 1.120 Å, respectively.

In Table 3 we first list the SCF energies obtained with molecular models of D_{5d} symmetry (*i.e.* with parallel and staggered ligand rings) and different perpendicular metal-to-ring distances h. For three different values of h the calculations were repeated on models of D_{5h} symmetry (*i.e.* with eclipsed rings).

Calculations on "bent sandwich" models were first carried out with retention of the C_{5v} symmetry of each $(C_5H_5)Ge$ cone. The molecular symmetry was assumed to be C_{2v} (eclipsed rings) and the angle between the ring planes, $\angle C_5,C_5$, changed in steps of 20°.

Finally a model reasonably close to the GED structure of $(C_5H_4Me)_2Ge$ (h=2.216 Å and $\angle C_5,C_5$=20°) was selected for investigation of the variation of energy when the metal atom is displaced along the C_2 axis (the y axis in Fig. 1). When y=0, each $(C_5H_5)Ge$ cone has C_{5v} symmetry, further calculations were carried out with y= –0.2, –0.1 and +0.1 Å. The resulting energies are listed in Table 3.

RESULTS AND DISCUSSION

The molecular structures of $(C_5H_4Me)_2Ge$ and $(C_5H_4Me)_2Sn$ by GED. The best values for the structure parameters of dimethylgermanocene and dimethylstannocene are listed in Table 1. In Table 2 we compare the perpendicular metal-to-ring distances (h), the average M–C bond distances, and the angle between the planes of the ligand rings in Group IVB metallocenes studied by electron or X-ray diffraction. The values obtained for metal-to-ring distances or for aver-

Table 1. Interatomic distances, valence angles and vibrational amplitudes (l) of $(C_5H_4Me)_2Ge$ and $(C_5H_4Me)_2Sn$. Estimated standard deviations in parentheses in units of the last digit. The angles have not been corrected for shrinkage.

	r_a/Å	l/Å	r_a/Å	l/Å
$(C_5H_4Me)_2Ge$			$(C_5H_4Me)_2Sn$	
M–C	2.531(7)	2.689(6)	0.164(4)	
C(1)–C(2)	1.426(3)	0.051(5)[a]	1.427(3)	0.049(3)[a]
C(1)–C(6)	1.517(16)	0.058(5)[a]	1.499(12)	0.045(3)[a]
C–H	1.112(10)	0.080(10)	1.105(7)	0.076(7)
M···C(6)	3.57(5)	0.20(5)	3.73(3)	0.17(4)
C(1)···C(3)	2.307(4)	0.057(6)	2.308(4)	0.060(4)
C(2)···C(6)	2.622(14)	0.070(ass)	2.603(12)	0.070(ass)
C(3)···C(6)	3.778(15)	0.082(ass)	3.755(15)	0.082(ass)
C···C′	3.61 to 6.04	0.035(9)[b]	3.54 to 6.34	0.033(9)[b]
h[c]	2.221(8)		2.400(6)	
	(°)		(°)	
<(1)C(6)H	112(ass)		112(ass)	
<C_5,C–C[d]	3(3)		7(3)	
<C_5,C–H[e]	0(ass)		0(ass)	
<C_5,C_5[f]	34(7)		50(6)	

[a] l(C(1)–C(2)) and l(C(1)–C(6)) were refined with constant difference. [b] All inter-ligand C···C′ vibrational amplitudes were assumed equal. [c] Perpendicular distance from metal atom to the C_5-ring plane. [d] Angle between C(1)–C(6) bond and C_5 plane. [e] Angle between C(2,3,4 or 5)–H bond and ring plane. [f] Angle between the two C_5 ring planes.

Table 2. Structure parameters of germanocenes, stannocenes and plumbocenes obtained by gas electron diffraction (GED) and X-ray crystallography (x).

		h/Å	R(M–C)[a]/Å		δ_1, δ_2 [b]/Å	$\angle C_5,C_5$/(°)	Ref.
$(C_5H_4Me)_2Ge$	GED	2.22	2.53		0 (ass)	34(7)	
$(C_5H_5)_2Sn$	GED	2.42	2.71		0 (ass)	~55	2
$(C_5H_5)_2Sn$	X[c]	2.40	2.67	(2.58 to 2.75)	0.21, 0.21[e]	48.4[e]	6
$(C_5H_5)_2Sn$	X[d]	2.42	2.68	(2.56 to 2.85)	0.36, 0.31[e]	45.9[e]	6
$(C_5H_4Me)_2Sn$	GED	2.40	2.69		0 (ass)	50(6)	
$(C_5Me_5)_2Sn$	X[c]	2.39	2.68	(2.57 to 2.78)	0.21, 0.26[e]	36.4	7
$(C_5Me_5)_2Sn$	X[d]	2.38	2.68	(2.59 to 2.77)	0.20, 0.24[e]	35.4	7
$(C_5H_5)_2Pb$	GED	2.50	2.78		0 (ass)	45(5)	2
$(C_5Me_5)_2Pb$	X	2.48	2.79	(2.60 to 2.90)	0.33, 0.24[e]	6	

[a] Mean value and range. [b] Distance from center of mass of each C_5 ring to projection of M onto the ring plane. [c] Molecule 1. [d] Molecule 2. [e] Calculated by us from the atomic coordinates.

age M–C bond distances in the different studies are in good agreement, and there is no indication that these parameters are changed when H-atoms are substituted by Me groups. The decrease of average M–C bond distances on going from Pb to Sn, about 0.10 Å, and from Sn to Ge, about 0.17 Å, is similar to the decrease of the M–Cl bond distances found in the dichlorides, MCl_2, Pb–Cl=2.443(1) Å,[21] Sn–Cl=2.347(7) Å,[22] and Ge–Cl=2.186(4) Å.[23] We assume, therefore, that these variations reflect the different bonding radii of Pb(II), Sn(II) and Ge(II).

The angle between the planes determined by the two ligand rings, $\angle C_5,C_5$, cannot be deter-

mined with accuracy by electron diffraction. Partly, this may be because this parameter is poorly defined by nature, *i.e.* because the molecules undergo large amplitude ring-metal-ring bending vibrations. On the other hand the GED and X-ray results leave no doubt that the equilibrium structures are bent, at least when M=Sn and Pb.

Comparison of the values for $\angle C_5,C_5$ in the complexes in Table 2, shows that full methyl substitution forces the two rings into a more parallel conformation, as indeed one would expect from steric effects. (The authors of Ref. 6 reached the opposite conclusion after confusing the angle between the ring normals with the ring-centroid metal ring-centroid angle.) One might also expect the angle between the ring planes to increase with the size of the metal atom, but no such effect is apparent from the data in Table 2.

Crystalline $(C_5H_5)_2Sn$ contains two crystallographically independent molecules, one of which is eclipsed (by space group symmetry), the other staggered, suggesting that the barrier to ring rotation is low. In the solid decamethyl compounds, $(C_5Me_5)_2Sn$ and $(C_5Me_5)_2Pb$, the ligand rings are approximately staggered.

As the maximum symmetry of a bent metallocene is C_{2v}, the ten M–C bond distances are no longer equal by symmetry: The metal atom needs no longer reside at the intersection of the C_5 symmetry axes of the rings, or more precisely the projection of the metal atom onto each ring needs not coincide with the center of mass of the ring. Indeed, the X-ray studies quoted in Table 2 show unequivocally that the individual M–C distances in one molecule may differ by as much as 0.30 Å. In each case the metal atom has moved away from the (approximate) fivefold symmetry axes of the rings towards the corner formed by the intersection of the two ring planes, *i.e.* roughly along the negative y axis in Fig. 1. In Table 2 we list the distance, δ, between the projection of the metal atom and the center of mass for each of the two rings. The different values obtained for δ in the two crystallographically independent molecules of $(C_5H_5)_2Sn$ and for the two rings in the same molecule of $(C_5Me_5)_2Pb$, show that the energy of the molecule varies slowly with δ. In other words the ring-metal-ring deformation (metal atom displacement) mode must be very soft.

Starting with a molecular model of D_{5h} symmetry, an idealized (C_{2v}) model of a bent metallocene may be obtained in two steps: A ring-metal-ring bending motion with retention of C_{5v} symmetry of the $(C_5H_5)M$ fragments, followed by displacement of the metal atom along the twofold symmetry axis y. In our structure refinements of $(C_5H_4Me)_2M$, we have explicitly assumed that the C_5M cones retain C_{5v} symmetry, *i.e.* that $\delta=0$. The large values obtained for the root-mean-square M–C vibrational amplitudes show that either this assumption is invalid for the equilibrium structure or that the metal displacement mode is very soft (or both). Indeed the M–C vibrational amplitudes obtained in the present study l(Ge–C)=0.201(7) Å and l(Sn–C)=0.164(4) Å, indicate that the equilibrium displacement is larger – or more softer – in the Ge than in the Sn compound.

There is, of course, no difficulty in principle in modifying our model to include a metal atom displacement coordinate along the y axis. The difficulty is that when $\delta = 0$, not only are the M–C bond distances unequal, but so are their vibrational amplitudes. Our experience in a GED study of $(C_5Me_5)GeCl$ shows that the value obtained for δ depends critically on the values of these amplitudes.[24] We have therefore preferred to study the lateral displacement of the metal atom in connection with self-consistent field molecular orbital calculations on $(C_5H_5)_2Ge$.

Molecular orbital calculations on $(C_5H_5)_2Ge$. No *ab initio* MO studies on germanocene or the other Group IVB metallocenes have been published. Stannocene has, however, been studied by Extended Hückel calculations: Jutzi, Hofmann and their coworkers[7] carried out calculations on models with different values for the angle $\angle C_5,C_5$, and suggested that the driving force responsible for the bending is the two "lone pair" electrons occupying the highest molecular orbital: The energy of this orbital was found to fall rapidly when the molecule is bent. This suggestion is in agreement with earlier rationalizations in terms of a stereochemically active lone pair.

The SCF energies obtained by *ab initio* calculations on various geometrical models of $(C_5H_5)_2Ge$ are listed in Table 3. The lowest energy was obtained with a model of D_{5h} symmetry and a metal-to-ring distance of h=2.34 Å, about 0.12 Å greater than the experimental

value for $(C_5H_4Me)_2Ge$. We do not regard this discrepancy as serious, though it does indicate that our calculations fail to account for the full strength of the metal-to-ligand bond. The failure of the Hartree-Fock approximation to give metal-to-ring distances in agreement with experiments for sandwich compounds of the transition elements has recently been the subject of extensive discussions.[25,26]

The barrier to internal rotation of the cyclopentadienyl rings is very small. At the experimental metal-to-ring distance the calculated energy difference between eclipsed (D_{5h}) and staggered (D_{5d}) models corresponds to a barrier of only 0.2 kJ mol^{-1}. At the optimal metal-to-ring distance the calculated barrier is even smaller.

Gross atomic populations and overlap populations obtained for three different geometries of $Ge(C_5H_5)_2$ are listed in Table 4. The gross population on Ge corresponds to a formal charge of +1.0. If two neutral (C_5H_5) rings and a Ge atom with electron configuration Ar $(3d)^{10}$ $(4s)^2$ $(4p_x)^1$ $(4p_y)^1$ are taken as point of departure, the orbital populations suggest that the major change introduced by bond formation is the transfer of

Table 3. Total energies (in atomic units) obtained by SCF MO calculations on different models of $(C_5H_5)_2Ge$.

Model	$-E-2458.0$ (a.u.)
D_{5d}	
h=1.987 Å	0.47500
h=2.087 Å	0.51742
h=2.216 Å[a]	0.54567
h=2.287 Å	0.55136
h=2.337 Å[b]	0.55196
h=2.387 Å	0.55101
h=2.487 Å	0.54083
C_{2v}, h=1.987 Å	
$\angle C_5,C_5$=0° (D_{5h})	0.47493
$\angle C_5,C_5$=20°	0.47646
$\angle C_5,C_5$=50°	0.47161
C_{2v}, h=2.216 Å[a]	
$\angle C_5,C_5$=0° (D_{5h})	0.54567
$\angle C_5,C_5$=20°	0.54543
$\angle C_5,C_5$=40°	0.54101
C_{2v}, h=2.337 Å[a]	
$\angle C_5,C_5$=0° (D_{5h})	0.55196
$\angle C_5,C_5$=20°	0.55159
$\angle C_5,C_5$=40°	0.54730
C_{2v}, h=2.216 Å,[a]	
$\angle C_5,C_5$=20°	
δy= 0[c]	0.54543
δy=+0.10 Å	0.54415
δy=−0.10 Å	0.54518
δy=−0.20 Å	0.54330

[a] Experimental value (for $(C_5H_4Me)_2Ge$). [b] Optimal value. [c] Displacement of metal atom along the y-axis in Fig. 1. See text for details.

Table 4. Orbital populations, gross atomic populations and overlap populations in $(C_5H_5)_2Ge$.

h / $\angle C_5,C_5$	2.337 Å[a] 0°	2.216 Å[b] 0°	2.216 Å[b] 20°
Orbital populations			
Ge s	8.21	8.24	8.22
p_x	4.48	4.47	4.45
p_y	4.48	4.47	4.46
p_z	4.11	4.06	4.12
d	9.79	9.76	9.76
Gross atomic populations			
Ge	31.07	30.99	31.01
C	6.34	6.35	6.36[c]
H	0.76	0.75	0.75[c]
(C_5H_5)	35.47	35.51	35.50
Overlap populations			
Ge–C	−0.01	−0.03	−0.03[c]
Ge–(C_5H_5)	−0.05	−0.19	−0.17

[a] Optimal value. [b] Experimental value. [c] Average values.

Table 5. Ionization potentials (in ev) calculated from Koopmans' theorem (IE= $-\varepsilon$) and from SCF energies of cation and neutral molecule [IE=ΔE_{SCF} = E_{SCF}(ion$^+$) − E_{SCF} (molecule)].

h (Å)	2.287	2.487
$-\varepsilon(9a_{1g})$	9.61	10.89
$E_{SCF}(^2A_{1g})-E_{SCF}(^1A_{1g})$	8.78	10.14
$-\varepsilon(5e_{1g})$	8.04	7.85
$E_{SCF}(^2E_{1g})-E_{SCF}(^1A_{1g})$	7.60	7.43
$-\varepsilon(6e_{1u})$	9.51	9.12
$E_{SCF}(^2E_{1u})-E_{SCF}(^1A_{1g})$	9.08	8.72

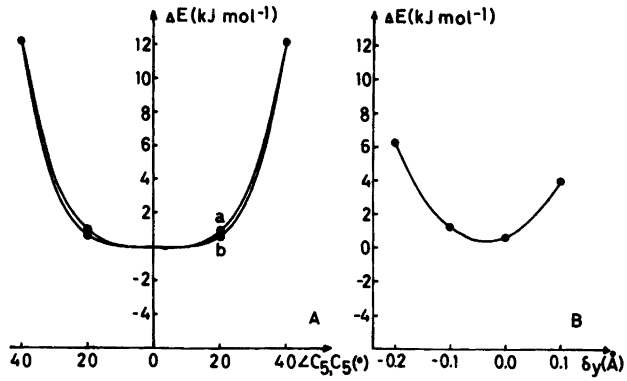

Fig. 4. A. Variation of SCF energy of $(C_5H_5)_2Ge$ with ring-metal-ring bending. $\angle C_5,C_5$ is the angle between the planes defined by the C_5 ligand rings. *a*: h=2.337 Å (optimal metal-to-ring distance) and *b*: h=2.216 Å (experimental distance). B. Variation of SCF energy with displacement of the metal atom along the C_2 symmetry axis of the molecule, *i.e.* the *y*-axis in Fig. 1. h=2.216 Å and $\angle C_5,C_5$=20°.

about 0.5 electron from each of the two *4p* orbitals into e_{1u} π-orbitals on the rings. The orbital population of the $4p_z$ orbital is insignificant, indicating that this orbital does not interact significantly with ligand orbitals. The orbital occupation of the Ge *d*-orbitals is 9.8 electrons, indicating a metal-to-ring donation of only 0.2 electrons, the involvement of *3d* electrons in bonding is thus clearly of secondary importance.

The energies of the three highest occupied molecular orbitals are listed in Table 5, the variation of orbital energies with the metal-to-ring distance is shown in Fig. 4. The $9a_{1g}$ orbital is predominantly a *4s* "lone pair" orbital on Ge, but it also contains a significant antibonding contribution from the ring a_{1g} π-orbitals. The total metal-ring overlap population in the a_{1g} representation is consequently negative (about –0.3), and the $9a_{1g}$ orbital energy falls rapidly with increasing metal-to-ring distance. The $5e_{1g}$ orbital is formed by combination of e_1 π-orbitals of the rings, as a good first approximation it may be regarded as nonbonding between metal and rings. The third high-lying orbital is $6e_{1u}$ which is a bonding combination of e_1 ring π-orbitals and $4p_x$ and $4p_y$ on Ge. The total metal-ring overlap population in the e_{1u} representation is about +0.2, and the energy of the $6e_{1u}$ orbital increases markedly with h. Because of the large negative overlap population in the a_{1g} representation, the total metal-ring overlap population becomes negative.

In Fig. 4A we show the change in SCF energies with ring-metal-ring bending. The potential energy curves obtained with optimal and experimental metal-to-ring distances are very similar with a minimum at – or close to – $\angle C_5,C_5$=0°, corresponding to a D_{5d} equilibrium structure. Both potential wells are very wide, $\angle C_5,C_5$ may reach nearly 30° before the potential energy becomes equal to the average thermal energy available at the temperature of the GED experiment, RT=3 kJ mol^{-1}. At small (~20°) values of $\angle C_5,C_5$ the energy curve obtained with the experimental value of h, falls below that obtained with the optimum value, and if the metal-to-ring distance is further decreased, the potential energy curve develops a maximum at $\angle C_5,C_5$=0°.

It may at first glance seem surprising that a bent form is calculated to be relatively more stable at short metal-to-ring distances when steric ring-ring repulsion would increasingly favor a parallel conformation. However, as suggested by Jutzi *et al.*, the driving force appears to be the two electrons in the $9a_{1g}$ lone pair orbital[7] and the energy of this orbital falls off more rapidly at short metal-to-ring distances when the orbital energy is higher.

Extended Hückel calculations[27] on $(C_5H_5)_2Ge$ with h fixed at the experimental value gave results similar to those obtained for $(C_5H_5)_2Sn$: The equilibrium structure was found to be bent with $\angle C_5,C_5$=50°. The energy of this conformation was 110 kJ mol^{-1} below that of a parallel

conformation. The reason for the large angle and high barrier appears to be that the EH calculations yield a $9a_{1g}$ orbital energy which is considerably higher than the $6e_{1u}$ orbital energy.

The value obtained for the angle between the two ligand rings in $(C_5H_4Me)_2Ge$ by means of GED, $<C_5,C_6=34(7)°$, is a *thermal average* and is expected to be greater than the *equilibrium value*. As already pointed out, the large estimated standard deviation of $\angle C_5,C_5$ may be regarded as an indication that the gas at a given instant contains molecules with very different bending angles, *i.e.* that the molecules undergo large amplitude bending motions.

The results obtained by GED and by SCF-MO calculations are therefore in reasonable – though not perfect – agreement. Taken together they indicate that *molecules in the gas phase are significantly bent with an average value at* $\angle C_5,C_5$ *between 20 and 40°, and that the molecules undergo large amplitude bending vibrations.* The *equilibrium* value of $\angle C_5,C_5$ remains uncertain, we estimate that it is between 10 and 30°.

Finally we carried out a series of calculations with h fixed at the experimental value $\angle C_5,C_5=20°$ and the metal atom displaced along the C_2 symmetry axis of the molecule, (the y-axis in Fig. 1). The displacement δy was defined as zero when all Ge–C bond distances are equal. The resulting potential energy curve is shown in Fig. 4B. The minimum appears to occur when the metal atom displaced two or three hundredths of an Å unit to the left in Fig. 1. Again the potential energy curve is very soft and the metal atom may move about 0.15 Å to either side of the minimum before the potential energy exceeds RT. This is in agreement with the large vibrational amplitude of the Ge–C bonds in $(C_5H_4Me)_2Ge$ obtained by least-squares refinement on a symmetrical ($\delta y=0$) model, $l=0.201(7)$ Å.

It is well known that the sequence of ionization potentials for transition metal complexes like ferrocene may differ from that obtained from the orbital energies using Koopmans' theorem.[28] In order to investigate whether similar discrepancies are to be expected for derivatives of germanocene, we have performed separate SCF calculations on some of the lower electronic states of $(C_5H_5)_2Ge^+$ and calculated the ionization energies from $IE=E_{SCF}(ion)-E_{SCF}(molecule)$. Inspection of Table 5 and Fig. 5 shows that the IE's obtained in this manner are somewhat smaller due to electronic relaxation. But the sequence of ionization potentials remains as predicted by Koopmans' theorem except near those values of h where orbital energy curves cross.

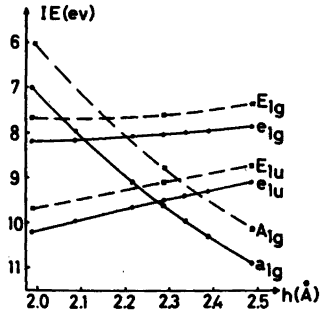

Fig. 5. Ionization energies of electrons in the three highest occupied molecular orbitals of $(C_5H_5)_2Ge$. ● and full line: calculated by Koopmans' theorem ($IE=-\varepsilon$). ■ and stippled line: calculated from SCF energies of cation and neutral molecule [$IE=\Delta E_{SCF}=E_{SCF}(ion)-E_{SCF}(molecule)$].

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