

Molecular Structure and Bonding in Cyclopentadienylgermanium Chloride, $(C_5H_5)GeCl$, the Cyclopentadienylgermanium Cation, $[(C_5H_5)Ge]^+$, and Germanium Dichloride, $GeCl_2$, Investigated by *Ab Initio* Molecular Orbital Calculations

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Ab initio molecular orbital calculations with better than double zeta basis have been carried out on the species $(C_5H_5)GeCl$, $[(C_5H_5)Ge]^+$ and $GeCl_2$ and correlated with previously published calculations on $(C_5H_5)_2Ge$. The dominant stereochemical feature in all these species is the presence of an electron lone pair on Ge: Calculations on the $(C_5H_5)Ge$ cation in which the metal atom is surrounded by eight valence electrons, and the lone pair occupies an *sp* hybrid pointing away from the ring, yields an optimum Ge-to-ring distance of $h=1.99$ Å, about 0.10 Å shorter than the experimental distance in $(C_5Me_5)GeCl$ and about 0.20 Å shorter than the experimental distance in $(C_5Me_5)_2Ge$. Calculations on a C_{5v} model of the more electron rich molecule $(C_5H_5)GeCl$ show that the lone pair is destabilized through strong antibonding interactions with both ligands. The strain is partly reduced when the angle between the Ge-to-ring vector and the Ge–Cl bond is reduced from 180° to the optimal value $\angle h, Ge-Cl=115^\circ$ (exp: 110°). The bending transforms the lone pair orbital to an *sp* hybrid pointing away from both ligands, but still considerably destabilized by interaction with the ring π electrons. The strain is further reduced when the $GeCl$ fragment is displaced parallel to the ring plane by $\delta=0.6$ Å (exp: 0.4 Å) in such a way as to place the Ge lone pair in the electron void above the ring center. The calculated barrier to internal rotation of the (C_5H_5) ring about a ring normal through the center is of the order of a few $kJ\ mol^{-1}$. In the still more electron rich molecule $(C_5H_5)_2Ge$ the bulk of the two rings prevents a significant release of strain through bending; the

release is achieved through stretching of the Ge-ring bonds only.

Recently we have determined the molecular structures of dimethylgermanocene, $(\eta-C_5H_4Me)_2Ge$,¹ decamethylgermanocene, $(\eta-C_5Me_5)_2Ge$,² and pentamethylcyclopentadienylgermanium chloride, $(C_5Me_5)GeCl$,² by gas electron diffraction. $(C_5H_4Me)_2Ge$ and $(C_5Me_5)_2Ge$ may be described as slightly bent sandwich molecules. The angle between the ring planes could not be determined with accuracy; in $(C_5H_4Me)_2Ge$ it is probably between 20 and 40° , in $(C_5Me_5)_2Ge$ between 0 and 20° . The metal atom resides on, or near, the intersection of the (approximate) fivefold symmetry axes of the rings.

The molecular structure of $(C_5Me_5)GeCl$ is shown in Fig. 2, Ref. 2. In contrast to $(C_5H_5)BeCl$ which has C_{5v} symmetry,^{3,4} $(C_5Me_5)GeCl$ is “nonlinear”, the angle between the Ge–Cl bond and the Ge-to-ring normal being $\angle h, Ge-Cl=110(2)^\circ$. The Ge atom does not reside above the ring center, but is displaced laterally by $\delta=0.43(6)$ Å. As a result of this displacement the Cl atom is moved well beyond the periphery of the ring, while the electron lone pair is moved closer to a position above the ring center. It is also noteworthy that the perpendicular Ge-to-ring distance is about 0.10 Å shorter in

$(C_5Me_5)GeCl$ than in $(C_5Me_5)_2Ge$ or $(C_5H_4Me)_2Ge$.

The pentamethylcyclopentadienylgermanium cation, $[(C_5Me_5)Ge]^+$, has been synthesized as a $[BF_4]^-$ salt by Jutzi and co-workers.⁵ The structure is unknown, but an X-ray diffraction investigation of the analogous tin compound showed that the solid consists of discrete cat- and an-ions.⁵ The $[(C_5Me_5)Sn]^+$ ion has C_{5v} symmetry, and the perpendicular Sn-to-ring distance is about 0.14 Å shorter than in crystalline $(C_5H_5)SnCl$ ⁶ and about 0.22 Å shorter than in $(C_5Me_5)_2Sn$.⁵

We have previously published the results of extensive *ab initio* molecular orbital calculations on $(C_5H_5)_2Ge$.¹ In this article we publish the results of similar calculations on $(C_5H_5)GeCl$, $[(C_5H_5)Ge]^+$ and $GeCl_2$. When discussing the results, we shall seek answers to the following questions: Why is $(C_5Me_5)GeCl$ "nonlinear"? Why is the Ge atom displaced from the symmetric, *pentahapto* bonding position? How should the bonding between the metal and the ring best be described, *i.e.* what is the hapticity of the ring? How large is the barrier to internal rotation of the cyclopentadienyl ring? How large is the metal-to-ring distance in $[(C_5H_5)Ge]^+$? Why does the metal-to-ring distance increase in the series $[(C_5H_5)Ge]^+$, $(C_5Me_5)GeCl$ and $(C_5Me_5)_2Ge$?

CALCULATIONS

The *ab initio* molecular orbital calculations were carried out with the program DISCO⁷ employing Gaussian type basis functions. The basis sets for Ge, C and H were the same as those previously used for calculations on $(C_5H_5)_2Ge$ ¹: For Ge a (14,11,5) basis contracted to (8,7,3),⁸ for C a (7,3) basis contracted to (4,2),⁹ and for H a (4) basis contracted to (2).¹⁰ For Cl we used a (10,7,1) basis contracted to (6,5,1),⁹ and for Sn a (15,11,6) basis contracted to (10,8,4).¹¹

Ab initio molecular orbital calculations on $(C_5H_5)Fe$ with a double zeta basis yield an optimal metal to ring distance (1.88 Å) which is 0.23 Å longer than the experimental value.¹² Since calculations with much larger basis sets (triple to quadrupole zeta plus polarization functions on the ligand) fail to reduce the discrepancy, it has been suggested that it is due to a failure of the Hartree-Fock model for complexes of the

transition elements.¹² MO calculations on complexes of main group metals do not appear to suffer from such defects, thus calculations on $(C_5H_5)_2Mg$ with a double zeta basis yield an optimal metal to ring distance which is only 0.07 Å greater than the experimental value and calculations with a larger basis set reduce the discrepancy to 0.02 Å.¹³ Our calculations yield optimal metal to ring distance in $(C_5H_5)_2Ge$ and $(C_5H_5)_2Sn$ which are 0.12 and 0.10 Å greater than the experimental, *i.e.* discrepancies of about 5 and 4 %, respectively.

RESULTS AND DISCUSSION

$GeCl_2$. The geometry was fully optimized under C_{2v} symmetry by calculating the total energy for nine different combinations of assumed values for the Ge-Cl bond distance and the $\angle ClGeCl$ angle. Interpolation yields the optimal values Ge-Cl=2.21 Å and $\angle ClGeCl=100.5^\circ$, which are in good agreement

Table 1. Total energies and energies of the Ge lone pair orbital obtained for optimal models of $GeCl_2$,^a $(C_5H_5)GeCl$ ^b and $(C_5H_5)Ge^+$.^c

	E (a.u.)	$-\epsilon_{l.p.}$ (eV)
$GeCl_2$	-2993.3409	10.77
$(C_5H_5)GeCl$	-2725.9550	8.17
$(C_5H_5)Ge^+$	-2266.3664	16.69

^a $r(Ge-Cl)=2.21$ Å, $\angle ClGeCl=100.5^\circ$.

^b $h(Ge-ring)=2.21$ Å, $r(Ge-Cl)=2.36$ Å,
 $\alpha(\angle h, Ge-Cl)=115^\circ$, $\delta=0.58$ Å.

^c $h(Ge-ring)=1.99$ Å.

Table 2. Orbital energies and experimental ionization energies for $GeCl_2$.

	$-\epsilon$ (eV)	IE(eV) ^a
15 a_1 (Ge l.p.)	10.77	10.55
10 b_1 (Cl l.p.)	12.36	11.44
3 a_2 (Cl l.p.)	12.63	11.70
5 b_2 (Cl l.p.)	13.35	12.58
14 a_1 (Cl l.p.)	13.64	12.69
9 b_1 (Ge-Cl)	14.41	13.41
13 a_1 (Ge-Cl)	18.58	16.73

^a Ref. 15.

Table 3. Orbital populations, gross atomic populations and overlap populations for the optimal models of $(C_5H_5)_2Ge$, $GeCl_2$, $[(C_5H_5)Ge]^+$ and three models of $(C_5H_5)GeCl$.

	$(C_5H_5)_2Ge^a$	$GeCl_2^b$	$[(C_5H_5)Ge]^+^c$	$(C_5H_5)GeCl^d$		
				$\alpha=180^\circ$ $\delta=0.0 \text{ \AA}$	$\alpha=115^\circ$ $\delta=0.0 \text{ \AA}$	$\alpha=115^\circ$ $\delta=0.58 \text{ \AA}$
Orbital populations						
Ge <i>s</i>	8.21	8.11	8.18	8.24	8.16	8.14
<i>p_x</i>	4.48	4.17	4.38	4.39	4.39	4.36
<i>p_y</i>	4.48	4.68	4.38	4.39	4.50	4.54
<i>p_z</i>	4.11	4.37	4.32	4.31	4.23	4.30
<i>d</i>	9.79	9.79	9.74	9.80	9.77	9.78
Gross atomic populations						
Ge	31.07	31.11	30.98	31.12	31.04	31.10
C	6.34	—	6.36	6.33	6.35 ^e	6.34 ^f
H	0.76	—	0.65	0.73	0.73 ^e	0.72 ^e
(C_5H_5)	35.47	—	35.02	35.30	35.38	35.33
Cl	—	17.44	—	17.59	17.58	17.56
Overlap populations						
Ge—C	−0.01	—	0.04	−0.05	0.01 ^g	0.01 ^h
Ge— (C_5H_5)	−0.05	—	0.17	−0.30	0.03	0.05
Ge—Cl	—	0.17	—	0.02	0.06	0.10

^a D_{5h} symmetry, $h=2.34 \text{ \AA}$, z axis equal to C_5 symmetry axis. See Ref. 1. ^b C_{2v} symmetry, y axis equal to C_2 symmetry axis, x axis perpendicular to $GeCl_2$ plane. ^c C_{5v} symmetry, z axis equal to C_5 symmetry axis. ^d For definition of axes see Fig. 2 in Ref. 2. $h=2.21 \text{ \AA}$, $r=2.36 \text{ \AA}$. Optimal model in last column. ^e Average values. ^f Average value; C(1), C(2)=6.47, C(3), C(5)=6.26, C(4)=6.26. ^g Average value, Ge—C(1), C(2)=0.05, Ge=C(3), C(5)=0.02, Ge—C(4)=−0.09. ^h Average value, Ge—C(1), C(2)=0.06, Ge—C(3), C(5)=0.01, Ge—C(4)=−0.04.

with the experimental values $Ge-Cl=2.183(4) \text{ \AA}$ and $\angle ClGeCl=100.3(4)^\circ$.¹⁴

Calculations on the optimal geometry yield the orbital energies listed in Table 2 along with the experimental ionization energies obtained by photoelectron spectroscopy.¹⁵ We consider the agreement satisfactory. The highest occupied molecular orbital (HOMO) is $15a_1$ which may be described as a Ge $4s$ lone pair orbital.

Some of the parameters obtained by Mulliken population analysis are listed in Table 3. The gross atomic population on Ge corresponds to a net charge of +0.89. Taking Ge^{2+} (with the electron configuration of Zn) as our point of departure, bond formation is accompanied by transfer of 1.05 electron into the two $4p_\sigma$ orbitals and 0.17 electron into the $4p_\pi$ ($4p_x$) orbital. Comparison with the population parameters of $(C_5H_5)_2Ge$ show that of the two ligands Cl^- is the

better σ -donor and $(C_5H_5)^-$ the better π -donor.

$[(C_5H_5)Ge]^+$. The symmetry was assumed to be C_{5v} in accordance with the structure of $[(C_5Me_5)Sn]^+$ as determined by X-ray crystallography.⁵ As in our calculations on $(C_5H_5)_2Ge$ we assumed the cyclopentadienyl to be planar with bond distance $C-C=1.41 \text{ \AA}$ and $C-H=1.12 \text{ \AA}$. Variation of the perpendicular Ge-to-ring distance yielded an optimum value of $h=1.99 \text{ \AA}$, corresponding to a Ge—C bond distance of 2.32 \AA . Calculations on $(C_5H_5)_2Ge$ with the same basis set yielded an optimum Ge-to-ring distance of $h=2.34 \text{ \AA}$,¹ about 0.12 \AA greater than the experimental value for $(C_5H_4Me)_2Ge$ or $(C_5Me_5)_2Ge$. It might therefore be suspected that the calculated distance in $[(C_5H_5)Ge]^+$ is considerably larger than the true value. For this reason we carried out similar *ab initio* molecular orbital calculations on $(C_5H_5)_2Sn$

and $[(C_5H_5)Sn]^+$. The optimum Sn-to-ring distance in the former turned out to be 0.10 Å greater than the experimental value for $(C_5Me_5)_2Sn$, but the optimum Sn-to-ring distance in $[(C_5H_5)Sn]^+$ reproduced the experimental value for $[(C_5Me_5)Sn]^+$ to the nearest 0.01 Å. We believe, therefore, that the calculated Ge-to-Ring distance in $[(C_5H_5)Ge]^+$ is within a few hundredths of an Å unit from the true value.

The HOMOs of $[(C_5H_5)Ge]^+$ are the degenerate e_1 π -orbitals of the ligand ring stabilized through interaction with the appropriate $4p$ orbitals on Ge, $\epsilon = -15.38$ eV. The Ge lone pair orbital is found at slightly lower energy and may be described as an s , p_z hybrid pointing away from the ring, but nevertheless slightly stabilized through interaction with the ring a_1 π -orbital.

$(C_5H_5)GeCl$. Full structure optimization of a molecule of this size and complexity was beyond our computational resources. Partial optimization was carried out in three steps:

(i) The Ge atom was assumed to occupy a position above the center of the ring corresponding to a symmetric, *pentahapto* bonding mode. The angle between the Ge-to-ring normal and the Ge-Cl bond $\alpha = \angle h, Ge-Cl$ was optimized for several combinations of assumed values for the perpendicular Ge-to-ring distance (h) and the Ge-Cl bond distance (r). The optimal values ranged from 112 to 118°. In subsequent calculations α was fixed at 115°.

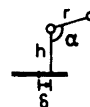
(ii) The total energy was calculated for nine different combinations of assumed values for h

and r . Interpolation yielded the optimal values $h = 2.21$ Å and $r = 2.36$ Å.

(iii) The assumption that the Ge atom resides on the symmetry axis was abandoned. The parameters α , h and r were fixed at their previously determined optimal values, while the GeCl fragment was allowed to move parallel to the y -axis (and to the ring plane; for definition of y -axis, see Fig. 2, Ref. 2). In Fig. 1A we plot the total energy as a function of the displacement from the symmetric position, δ . It is seen that while displacement of the GeCl fragment in the *negative* y -direction *increases* the energy, displacement by 0.58 Å in the *positive* y -direction leads to an energy gain of nearly 40 kJ mol⁻¹.

The optimum values for α , h , r and δ obtained by this procedure are in reasonable agreement with the experimental values for $(C_5Me_5)GeCl$:

	opt	exp
α (°)	115	110(2)
h (Å)	2.21	2.11(2)
r (Å)	2.36	2.24(1)
δ (Å)	0.58	0.43(6)



In Table 4 we compare the orbital energies calculated for the optimal model of $(C_5H_5)GeCl$ to the experimental ionization energies of $(C_5Me_5)GeCl$ obtained by Fragalà and co-workers.¹⁶ In this connection it should be recalled that permethylsubstitution of cyclopentadienyl metal complexes has been found to reduce ionization energies by 0.7 to 1.3 eV.¹⁷

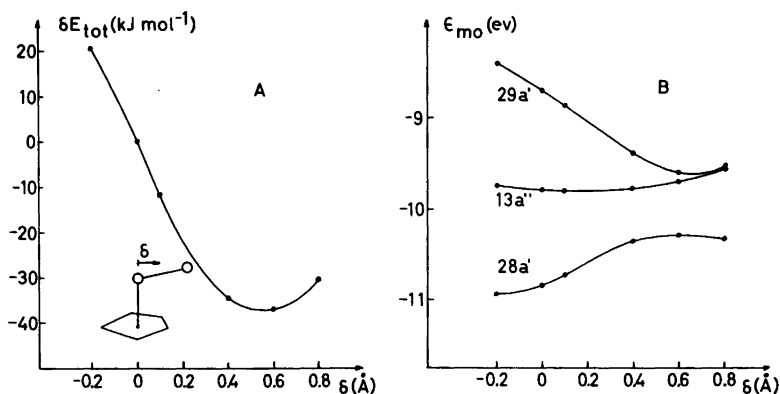


Fig. 1. A. The variation of the total energy of $(C_5H_5)GeCl$ when the Ge-Cl is displaced along the y -axis. B. The energies of the three highest occupied molecular orbitals as a function of the displacement.

Table 4. Orbital energies for $(C_5H_5)GeCl$ and experimental ionization energies for $(C_5Me_5)GeCl$.

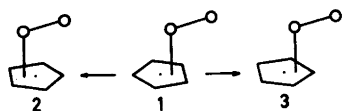
	$-\varepsilon(eV)$	IE(eV) ^a
29 a' (Ge l.p.)	9.49	8.13
13 a'' (Ge $4p_x + e_1\pi$)	9.56	8.32
28 a' (Ge $4p_y + e_1\pi$)	10.09	9.07
12 a'' (Cl l.p.)	11.69	10.47

^a Ref. 16.

The HOMO of $(C_5H_5)GeCl$ is the lone pair orbital on Ge, and the energy of this orbital appears to determine the shape of the molecule. When calculations are carried out on a "linear" C_{5v} model, the lone pair orbital may be described as the Ge $4s$ orbital destabilized by antibonding interactions with both ligands, the $a_1 \pi$ -orbital of the ring and the s and p_z orbitals of Cl. When α is reduced from 180° , *i.e.* when the molecule is bent, the HOMO is gradually transformed to an sp hybrid pointing away from the ligands, the antibonding interactions are reduced (but not eliminated) and the energy of the HOMO falls.

In Fig. 1B we plot the energies of the three highest occupied molecular orbitals as a function of the displacement δ . It is seen that the energy of the lone pair (29 a_1) orbital decreases when the GeCl fragment is moved into the equilibrium position while the energies of the other two orbitals are constant or increase. Population analysis (See Table 3) shows that the displacement is accompanied by reduction of the negative overlap population between Ge and C(4) and an increase of the positive overlap between Ge and C(1)/C(2). We conclude that the driving force is provided by the antibonding interaction between the Ge lone pair and the ring π -electrons above C(4).

We now turn our attention to internal rotation of the cyclopentadienyl ring:



Model 2 is obtained from the equilibrium model 1 by rotating the ring 180° about the Ge-to-ring normal, model 3 is obtained from 1 by rotating the ring 36, 108 or 180° about the (approximate)

fivefold symmetry axis. Calculations on model 2 where the Ge lone pair has been brought into close contact with the ring π -electron, yield an energy more than 80 kJ mol^{-1} higher than that of 1. Calculations on model 3 yield an energy only 2 kJ mol^{-1} above that of 1. We conclude that the barrier to internal rotation is of the order of a few kJ mol^{-1} if carried out in such a manner as to leave the Ge lone pair in the electron void over the ring center.

It would seem a matter of taste whether the cyclopentadienyl ring in model 1 is described as *dihapto*- or *tetrahapto*-bonded to the metal. The *trihapto* model 3 is moreover of very similar energy. We therefore prefer to describe the bonding between metal atom and ring as asymmetric, *polyhapto*. It should also be noted that CC overlap populations indicate that the π electrons of the ring remain largely delocalized.

Ge-to-ring bond distances. In $[(C_5H_5)Ge]^+$ the metal atom is surrounded by eight valence electrons. The electron lone pair on Ge resides in a hybrid orbital pointing away from the ligand. The addition of Cl^- to form $(C_5H_5)GeCl$ introduces an additional electron pair which must be accommodated in the immediate surroundings of the metal atom. Calculations on a model of C_{5v} symmetry show that the lone pair now occupies an orbital which is strongly antibonding to both ligands. The strain is released both through deformation to C_s symmetry and through stretching of metal to ligand bonds. (The calculations show that the energy of the lone pair orbital decreases rapidly with increasing bond distances).

When $(C_5H_5)^-$ is added to $[(C_5H_5)Ge]^+$ to form $(C_5H_5)_2Ge$, a total of fourteen electrons must be accommodated in the vicinity of the metal atom. Calculations on a model of D_{5h} symmetry show that the lone pair again occupies an orbital which is strongly antibonding to both ligands.¹ In this case, however, the bulk of the ligands prevents a significant release of strain through bending, and in consequence the Ge-to-ring distance becomes even larger than in $(C_5H_5)GeCl$.

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