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Registry No. $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$, 37366-09-9; $Cy_2PCH_2CH_2PCy_2$, 23743-26-2; $[(\eta^6\text{-}C_6H_6)RuCl(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$, 139378-00-0; $(\eta^6\text{-}C_6H_6)Ru(Cy_2PCH_2CH_2PCy_2)$, 139378-01-1; $[(\eta^6\text{-}C_6H_6)RuH(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$, 139378-03-3; $[(\eta^5\text{-}C_6H_7)RuH(Cy_2PCH_2CH_2PCy_2)]$, 139378-04-4; silver trifluoromethanesulfonate, 2923-28-6.

Molecular Structures of Germacyclohexane and 1,1-Dimethylgermacyclohexane As Determined by Gas-Phase Electron Diffraction

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Summary: The molecular structures of germacyclohexane and 1,1-dimethylgermacyclohexane have been studied by gas-phase electron diffraction. Both molecules exist in the chair conformation with similar structures. The important geometrical parameter values (r_g and $\angle_\alpha$) obtained from least-squares analysis for germacyclohexane are r(C–H) = 1.108 (6) Å, r(Ge–H) = 1.530 (32) Å, $r(\text{C–C})_{\text{av}}$ = 1.535 (3) Å, r(Ge–C) = 1.956 (4) Å, $\angle C_2C_3C_4$ = 114.4 (29)°, $\angle GeC_2C_3$ = 110.9 (20)°, FlapG [Flap angle at the germanium end of the ring] = 140 (9)°, Flap = 122 (3)°. Error limits are given as 2σ.

The molecular structures of germacyclohexane and several methyl-substituted germacyclohexanes have been studied by NMR spectroscopy and molecular mechanics calculations.[1] The calculations showed that the six-membered ring has a chair conformation flattened around the germanium atom. In 1-methylgermacyclohexane the axial form is slightly favored over the equatorial form. The ^{13}C and ^{73}Ge chemical shifts were consistent with the calculations.

We have been interested in the structure of five- and six-membered rings[2] and have reported the structure of silacyclohexane[3] which is found to exist in the gas phase in a chair conformation. The six-membered ring is slightly flattened at the silicon atom. The CSiC valence angle is smaller than the tetrahedral value. The Si–C bond length is comparable to the ones found in strained cyclic silanes. We felt that the structures of germacyclohexane and 1,1-dimethylgermacyclohexane would provide an interesting comparison with the structures of cyclohexane and silacyclohexane. Experimental structural information for germacyclohexane (GCH) and 1,1-dimethylgermacyclohexane (DMGCH) will help to improve the force field used in molecular mechanics calculations. In this note we are reporting the gas-phase structures of GCH and DMGCH obtained from electron diffraction experiments.

Table I. Structural Parameters Obtained from Least-Squares Analysis for Germacyclohexane and 1,1-Dimethylgermacyclohexane[a]

molecule	germacyclohexane	1,1-dimethyl-germacyclohexane
r(C–H)	1.108 (6)	1.107 (4)
r(Ge–H)	1.530 (32)	
$R(\text{C–C})_{\text{av}}$	1.535 (3)	1.539 (3)
r(Ge–C)	1.956 (4)	1.957 (2)[b]
$\angle C_2C_3C_4$	114.4 (38)	114.4 (15)
$\angle GeC_2C_3$	110.9 (30)	111.1 (15)
$\angle C_mGeC_m$[c]		114.0 (53)
FlapG[d]	140.7 (96)	140.6 (42)
Flap[e]	121.8 (30)	123.8 (31)
	Dependent Parameters	
$\angle C_2GeC_6$	102.5 (35)	103.1 (18)
$\angle C_3C_4C_5$	114.1 (28)	116.9 (32)
tGe234[f]	55.6 (47)	53.5 (25)
t2345	67.4 (37)	64.5 (37)
t2Ge65	42.0 (98)	42.3 (48)

[a] Distances (r_g) in angstroms, angles ($\angle_\alpha$) in degrees. Values in parentheses are 2θ which include estimates of systemic errors. [b] Average value, Ge–C$_2$ = Ge–C$_7$ assumed. [c] C_m (methyl carbon atoms, C_7 and C_8). [d] Flap value at the gemanium end of the molecule; angle between planes formed by atoms Ge, C_2, and C_6 and C_2, C_6, C_3, and C_5 (with planar = 180°). [e] Flap angle at the carbon end of the molecule; angle between planes formed by atoms C_4, C_3, and C_5 and C_3, C_5, C_2, and C_6 (with planar = 180°). [f] Torsion angle Ge–C_2–C_3–C_4.

Experimental Section

Germacyclohexane (GCH) and 1,1-dimethylgermacyclohexane (DMGCH) were prepared and purified according to the procedures described in the literature.[1] The electron diffraction patterns were recorded using the Colgate apparatus with an r^3 sector at nozzle-tip temperatures of 23 °C (GCH) and 65 °C (DMGCH), an accelerating voltage of 40 keV, exposure times of 1 (long camera) to 3 min (short camera) and a background pressure of 1.2×10^{-5} Torr with the help of a liquid nitrogen trap. Benzene calibration plates taken under conditions identical with those of the experiment were used for the wavelength calibration standard.[4] For each molecule, four plates from the 100-mm and four plates from the 245-mm camera distances were used for the analysis.

The photographic plates were traced on the densitometer at intervals of 0.20 mm for the long and 0.15 mm for the short camera plates. These data were corrected for emulsion saturation, plate flatness, and sector imperfections and interpolated to integral $q[(40/\pi)\sin(\theta/2)]$ units. Least-squares analysis of the data was

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Table II. Geometrical Parameter Values Obtained for GCH, DMGCH, and Related Molecules[a]

	GADAM	GCH	DMGCH	SADAM	SCH	CH
r(C–C)	1.545 (2)	1.535 (3)	1.539 (3)	1.547 (2)	1.550 (3)	1.536 (2)
r(M–C)[b]	1.954 (3)	1.956 (4)	1.957 (2)	1.879 (3)	1.885 (3)	
∠CMC[b]	101.9 (5)	102.5 (35)	103.1 (18)	103.2 (5)	104.2 (14)	111.4 (2)
∠MCC[b]	106.3 (5)	110.9 (30)	111.1 (15)	107.7 (4)	110.6 (6)	
∠234[c]		114.4 (38)	114.4 (15)		113.7 (1)	
∠345		114.1 (28)	116.9 (32)			

[a] Distances (r_g) in angstroms and angles in degrees. GADAM = 1-methyl-1-germaadamantane, GCH = germacyclohexane, DMGCH = 1,1-dimethylgermacyclohexane, SADAM = 1-methyl-1-silaadamantane, SCH = silacyclohexane, and CH = cyclohexane. [b] M = Ge, Si, or C. [c] ∠234 = ∠$C_2C_3C_4$.

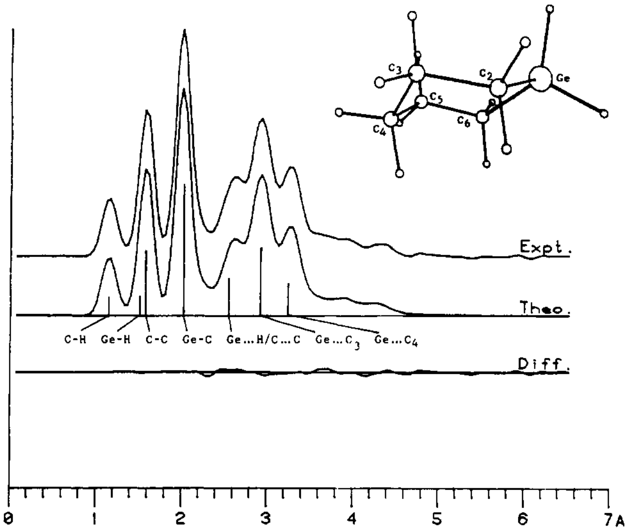

Figure 1. Radial distribution curve for germacyclohexane.

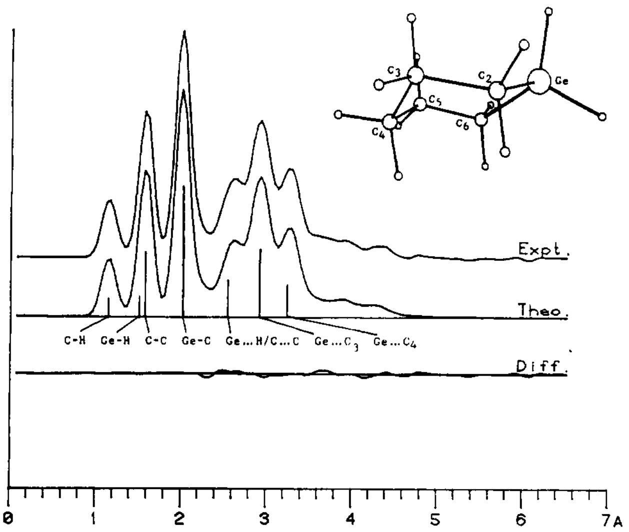

Figure 2. Radial distribution curve for 1,1-dimethylgermacyclohexane.

carried out simultaneously on the averaged long and averaged short camera intensity data by following the procedure outlined by Gundersen and Hedberg.[5] The elastic scattering and phase shift factors used in all the calculations were tabulated by Schafer et al.[6]

Data Analysis

Germacyclohexane. The molecule is assumed to be in the chair conformation with C_s symmetry. The following assumptions were made: (1) all C–C bonds are identical [reported MM2 calculations[1] showed a difference of 0.005 Å between the two different C–C bonds], (2) all ∠HCH angles are identical, and (3) all C–H bond lengthens are identical. The geometrical parameters chosen are r(C–H), r(Ge–H), r(C–C), r(Ge–C), ∠$C_2C_3C_4$, ∠GeC_2C_3, FlapG (angle between planes formed by atoms Ge, C_2, and C_6 and C_2, C_6, C_3, and C_5), and Flap (angle between planes formed by atoms C_3, C_4, and C_5 and C_3, C_5, C_2 and C_6). Amplitudes of vibration were calculated using a force field similar to the one used for silacyclohexane.[3]

Preliminary radial distribution curves revealed clearly that a chair conformation reproduced the experimental diffraction data very well. In the final refinement eight geometrical parameters and four amplitude parameters involving the germanium atom were refined simultaneously. The final results and the corresponding radial distribution curves are shown in Table I and Figure 1, respectively.

Dimethylgermacyclohexane. A chair conformation with C_s symmetry was assumed throughout the analysis. In addition to those constraints imposed on GCH, the methyl groups are assumed to have C_{3v} symmetry with C–H bond lengths equal to those in the germacyclohexane ring. The Ge–C_2 and Ge–C_m (methyl carbon atom) bond lengths are identical. The geometrical parameters chosen to define the structure are summarized in Table I.

Radial distribution curves calculated using the parameters obtained for germacyclohexane fit the data extremely well. It is obvious that the structures of these two germacyclohexanes are very similar, as expected. The final results and the corresponding radial distribution curve are shown in Table I and Figure 2, respectively.

Discussion

Table II summarized some of the geometrical parameters obtained for GCH, DMGCH, and related molecules. It is interesting to note that the Ge–C bond lengths in both GCH and DMGCH (1.956 (4) and 1.957 (2) Å) are very close to the value obtained for 1-methyl-1-germaadamantane (1.954 (3) Å).[7] In the silane analogue, the Si–C bond length in silacyclohexane[3] (1.885 (3) Å) is slightly longer than the ones in dimethylsilane[8] (1.874 (2) Å) but within error limit of the ones found in 1-methyl-1-silaadamantane[9] (1.879 (3) Å). The average C–C bond in silacyclohexane (1.550 (3) Å) is very slightly longer than the C–C bond length in cyclohexane[10] (1.536 (2) Å) and the average C–C bond length in GCH (1.535 (3) Å). The average C–C bond in silacyclopentane[2] is also found to be long (1.550 Å). However, the C–C bond in cyclopentane (1.546 (1) Å)[11] is

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known to be longer than the ones in cyclohexane.

The C_2GeC_6 valence angle in GCH (102.5 (35)°) is smaller than tetrahedral, as the CSiC angle in silacyclohexane (104.2 (14)°), while the CCC angle in cyclohexane is 111.4 (19)°. This variation is expected in order for the long Ge–C and Si–C bonds to close the ring. Both GCH and DMGCH exist in a flattened chair conformation. The chair at the germanium end is less puckered than the carbon end of the molecule. Similar puckering angles were observed in silacyclohexane.

Molecular mechanics (MM2) calculations using a force field reported by Ouelette have been carried out by Takeuchi and co-workers.[1] The calculated Ge–C bond length is shorter than the experimental value. The Ge–C_m bond length is found to be 0.002 Å longer than the Ge–C_2 bond in the ring. The two different types of C–C bonds have a calculated difference of 0.005 Å and an average value of 1.540 Å, which are in fairly good agreement with the experimental results. The calculated valence angles and torsional angles in general agreed very well with the observed values. Calculations using the MM3[12] force field showed that the Ge–C_m bonds in DMGCH are 0.02 Å shorter than the Ge–C_2 bonds. The experimental average Ge–C bond lengths for GCH (1.956 (4) Å) and DMGCH (1.957 (2) Å) suggest that the Ge–C bonds in DMGCH should be very similar in length. MM3 calculations showed that for dimethylsilacyclohexane, the two types of Si–C bonds are virtually identical.

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Registry No. GCH, 289-62-3; DMGCH, 60958-60-3.

Supplementary Material Available: Figures of leveled experimental and theoretical intensity curves, tables of experimental intensity data, and correlation and error matrices for germacyclohexane and 1,1-dimethylgermacyclohexane (6 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of the Trimolybdenum Cluster $[(CpMoCl)_3(\mu\text{-}Cl)_4(\mu_3\text{-}O)]$

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Summary: The title compound is obtained from $CpMoCl_3$ in warm THF. The source of the oxygen atom is the solvent, the byproduct being 1,4-dichlorobutane. The structure shows a triangular array of molybdenum atoms without direct metal–metal bonds. Each atom bears one cyclopentadienyl group and a terminal Cl ligand, and four additional Cl atoms edge-bridge the triangular unit, two on one edge and the others one each on the two remaining edges. The oxygen atom is bonded to all three Mo atoms to complete a pseudooctahedral geometry for two metals and a four-legged piano stool geometry for the other metal. Crystal data: monoclinic, $P2_1/m$, a = 7.950 (2) Å, b = 13.442 (4) Å, c = 10.049 (4) Å, β = 97.87 (3)°, V = 1063.7 (6) $Å^3$, Z = 2, and R = 2.98%. The solid-state structure is consistent with the magnetic susceptibility and with the ^{1}H-NMR spectrum of the compound. These indicate that two unpaired electrons are localized on the electronically unsaturated unique metal.

Recent investigations in our laboratory have focused on the chemistry of cyclopentadienylmolybdenum(III) complexes.[2] The most convenient starting material for these complexes is $CpMoCl_2$ (Cp = η^5-C_5H_5), which can be prepared by reduction of $CpMoCl_4$.[3] We have previously reported the kinetics and mechanism of the halide exchange on the $CpMoX_2(PMe_3)_2$ (X = Cl, I) class of compounds.[4] During these studies it was discovered that these substitutions are catalyzed by oxidation leading to the production of complexes with the metal in the +IV oxidation state.[5] This observation led to our interest in synthesizing cyclopentadienylmolybdenum(IV) complexes in order to probe their role as catalytic entities in the above substitution reactions. An attractive entry into this chemistry is $CpMoCl_3$, a material that was not reported before we began our investigations.[6] We have recently[7] described the preparation and the physical properties of this compound, but because of its practically complete insolubility in organic solvents, its molecular structure could not be determined. To date only a relatively few examples of (ring)MX_3 compounds have been characterized structurally.[6] However, we noted that the material dissolves in warm THF. The compound obtained by this treatment, which results from oxygen abstraction from the

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