The Ni(II)–S coordinative covalent distance, 2.456 (2) Å, is comparable with the sum of the corresponding Pauling covalent radii,[32] 2.43 Å, indicating a strong interaction. The corresponding distance in [Ni(PMS)Cl]ClO_4 was found to be 2.472 (5) Å.[13]

The octahedral Ni(II) to Br^- distance, 2.544 (1) Å, is also approximately the sum of the corresponding Pauling covalent radii,[32] 2.50 Å, and is close to the reported values of 2.606 (3) Å in dibromodiaquo(*N*,*N*,*N*',*N*'-tetramethyl-*o*-phenylenediamine)nickel(II),[33] 2.635 (5) Å in dibromotetrakis(1,8-naphthyridine)dinickel(II) tetraphenylborate,[34] and 2.54 Å in *trans*-dibromobis(acetylacetone)nickel(II).[35]

The pattern of closest nonbonded contacts is similar to that already discussed for the isostructural [Ni(PMS)Cl]ClO_4.[13] The best defined oxygen, O(4), is 2.29 Å from an amino hydrogen atom, H(15); and O(7), next best defined according to the thermal foreshortening of its Cl–O bond length, is 2.39 Å from the other amino hydrogen atom, H(22). See Figure 1. The remaining perchlorate oxygen atoms do not participate in such close approaches.

Acknowledgment. This work was supported by the National Institutes of Health (Grant No. GM-18813-03). We are also indebted to the University of Hawaii Computing Center.

Registry No. [Ni(PMS)Br]ClO_4, 55267-64-6.

Supplementary Material Available. A listing of the structure factor amplitudes (×10) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC500305.

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Organometallic Compounds with Metal–Metal Bonds. XXI. Crystal and Molecular Structure of (η-Benzene)carbonylbis(trichlorogermyl)ruthenium, (η-C_6H_6)Ru(CO)($GeCl_3$)$_2$[1]

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Received January 23, 1975 AIC500599

The structure of (η-C_6H_6)Ru(CO)($GeCl_3$)$_2$ has been determined by single-crystal X-ray techniques. The compound crystallizes in the orthorhombic *Pnma* space group with four molecules in the unit cell of dimensions a = 14.3071 (6), b = 13.2024 (6), and c = 8.3497 (5) Å. Intensity data were collected by counter methods and the 720 observed independent reflections were refined using full-matrix least-squares procedures to a final R factor of 3.9%. The molecule has a "piano stool" geometry with a crystallographic mirror plane passing through the ruthenium atom, the carbonyl group, and two carbon atoms of the benzene ring and therefore has an eclipsed conformation when viewed perpendicular to the ring. The benzene ring is planar and all ruthenium–ring carbon distances are equal at 2.29 (1) Å. The ruthenium–germanium distance is 2.408 (2) Å.

Introduction

Recent synthetic work in this laboratory has made available complexes of the type (arene)Ru(CO)($GeCl_3$)$_2$ (arene = benzene, toluene, *o*-, *m*-, and *p*-xylene, mesitylene).[1] A structural investigation of a representative of these compounds was of interest from several points of view. The first was a comparison with the known structures of *cis*- and *trans*-Ru$(CO)_4$($GeCl_3$)$_2$.[2] The second was the relation to the extensively studied[3–7] arenechromium tricarbonyl compounds, with respect particularly to the symmetry maintained in the aromatic ring, and its conformation relative to the three ligands making up the opposite face of the idealized octahedron. Finally, the report[8] of slightly nonplanar arene rings in the complexes (arene)Ru[$PCH_3(C_6H_5)_2$]Cl_2 suggested that other

Table I. Positional and Thermal Parameters

(a) Positional Parameters

Atom	x	y	z
Ru	0.10218 (8)	0.25000	0.04145 (14)
Ge	0.08945 (7)	0.12090 (7)	0.24316 (13)
Cl1	0.19978 (26)	0.11192 (25)	0.41845 (38)
Cl2	−0.03458 (29)	0.11257 (32)	0.38829 (54)
Cl3	0.09605 (26)	−0.03270 (21)	0.01033 (38)
O	−0.1081 (7)	0.2500	0.0344 (17)
C5	−0.0283 (12)	0.2500	0.0337 (19)
C1	0.1154 (8)	0.2500	−0.2323 (15)
C2	0.1515 (6)	0.1577 (2)	−0.1750 (11)
C3	0.2237 (6)	0.1577 (2)	−0.0605 (11)
C4	0.2598 (8)	0.2500	−0.0032 (15)
H1	0.064	0.250	−0.313
H2	0.126	0.093	−0.216
H3	0.249	0.093	−0.021
H4	0.311	0.250	0.077

(b) Anisotropic Thermal Parameters ($\times 10^4$)

Atom	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Ru	340 (2)	237 (7)	324 (7)	0	17 (8)	0
Ge	437 (6)	285 (6)	419 (7)	66 (6)	41 (7)	61 (6)
Cl1	1145 (30)	485 (20)	692 (23)	−9 (21)	−427 (22)	105 (18)
Cl2	998 (28)	1121 (33)	1542 (38)	604 (27)	874 (29)	904 (32)
Cl3	1072 (27)	312 (16)	729 (22)	−138 (21)	−49 (23)	−28 (15)
O	347 (70)	544 (80)	1220 (110)	0	−170 (90)	0
C5	687 (116)	135 (80)	373 (100)	0	−96 (100)	0

(c) Hindered-Rotor Parameters[c]

Hindered rotors	x_c[a]	y_c[a]	z_c[a]	B_{ring}, Å^2	Bd[b]	Radius, Å
Benzene C	0.1876 (5)	0.2500	−0.1178 (9)	3.4 (2)	0.94 (8)	1.408 (6)
Benzene H	0.1876	0.2500	−0.1178	3.4	0.94	2.4

[a] Fractional coordinates of center of gravity of the hindered rotor. [b] Bd is the relative barrier potential and is equal to $V_0/2kT$ where V_0 is the barrier potential to rotation, k is Boltzmann's constant, and T is absolute temperature. [c] The orientation of the planes of the two hindered rotors is given by $D = 0.0$, $E = 2.395$ (8), and $F = 0.0$ (in radians) as explained in ref 10.

examples of ruthenium(II) complexes with arenes should be studied.

Experimental Section

Yellow needlelike crystals of $(C_6H_6)Ru(CO)(GeCl_3)_2$ were kindly supplied by Dr. R. K. Pomeroy. Preliminary X-ray studies from Weissenberg photographs of the $hk0$, $hk1$, and $hk2$ planes and precession photographs of the $0kl$, $h0l$, and $1kl$ planes showed the systematic absences $hk0$ ($h = 2n$) and $0kl$ ($k + l = 2n + 1$) which are consistent with the orthorhombic space groups *Pnma* and $Pn2_1a$ (unconventional). The cell dimensions $a = 14.3071$ (6), $b = 13.2024$ (6), and $c = 8.3497$ (5) Å were obtained by a least-squares fit of 10 general high-angle reflections ($2\theta > 72°$) whose positions were accurately determined using Cu Kα_1 (λ 1.54051 Å) radiation at 23°. The density of the crystal was determined by flotation in a CCl_4–CBr_4 mixture to be 2.37 (1) g cm^{-3}, which is in good agreement with the calculated value of 2.38 g cm^{-3} based on four molecules per unit cell. The dimensions of the crystal used for diffraction intensity data collection were 0.232 × 0.086 × 0.095 mm, corresponding to separations between the faces (001) and (00$\bar{1}$), (2$\bar{1}$0) and ($\bar{2}$10), and (010) and (0$\bar{1}$0), respectively. With the crystal mounted along the c axis, intensity data were measured manually on a Picker four-circle diffractometer equipped with a graphite monochromator (002 reflection) using Mo Kα radiation (0.7107 Å). Reflections with $2\theta < 45°$ were included in the measurement using the θ–2θ scan method with a scan width of 2° at 2° min^{-1}. Background counts were taken for 30 sec at both ends of the scan limits. Three standard reflections were recorded at intervals of 4 hr or less, and their fluctuation throughout the data collection was ±1.0%. No absorption correction was applied to the data ($\mu_{\text{Mo K}\alpha} = 58.8$ cm^{-1}); the largest variation at $\chi = 90°$ for the 200 reflection being ±6.3%. The data were corrected for Lorentz and polarization effects and reduced to structure factor amplitudes with standard deviations estimated by the procedure of Doedens and Ibers[9] using a p factor of 0.03. Of the 1078 independent reflections measured, 720 were considered "observed" above background using a criterion $I/\sigma(I) > 3.0$ where $\sigma(I)$ was estimated from counting statistics.

Structure Solution and Refinement. A Patterson synthesis map revealed Harker sections at $x = {}^1/_2$, $y = {}^1/_2$, and $z = {}^1/_2$. Solution of the structure in the centrosymmetric *Pnma* space group recovered the Ru and Ge atomic positions which were used to phase the structure factors for the computation of a Fourier electron density map (at $R = 33\%$). From this the positions of three chlorine atoms, the CO group, and a carbon atom of the benzene ring were found. Two cycles of full-matrix least-squares refinement brought R down to 18%. An electron density map then revealed the remaining carbon atoms. Since there were four molecules in the unit cell, the molecule possesses a crystallographic mirror plane which contains the Ru atom, the CO group, and two carbon atoms of the benzene ring. Several cycles of least-squares refinement on this model containing all the nonhydrogen atoms using isotropic temperature factors led to $R = 10.9\%$. A Fourier electron density different map showed significant anisotropic thermal motion about the Ru, Ge, and Cl atoms; inclusion of the appropriate parameters in two cycles of least-squares refinement gave $R = 4.6\%$. An electron density difference map showed as its largest feature the anisotropic thermal motion of the O atom, allowing for which reduced R to 4.5%. Another difference map showed substantial librational motion about the axis of the benzene ring. Since the four independent C–C intramolecular distances did not differ significantly from one another and since there was no significant deviation from planarity, the benzene ring was treated as a hindered rotor.[10] The result was a significant improvement in the R factor, $R = 4.1\%$, in spite of a substantial reduction in the number of parameters. The positions for all hydrogen atoms were found in the subsequent difference map, which also showed anisotropic thermal motion of the carbon atom of the carbonyl group. The hydrogen atoms were included in the structure factor calculations but not refined in the least-squares procedures, as a hindered rotor fixed at 1.0 Å away from the carbon atoms of the benzene ring. The carbonyl carbon atom was also allowed to have anisotropic thermal parameters. Refinement finally converged at $R = 3.8\%$ and R_w at 3.9%.

The scattering factors for nonhydrogen atoms were taken from Cromer's paper[11] with full allowance of anomalous scattering[12] for the Ge, Ru, and Cl atoms, while those for hydrogen atoms were taken from Stewart et al.[13] Introduction of anisotropic thermal parameters throughout the refinement have been justified in Hamilton's criterion.[14]

Table II. Interatomic Distances (Å) and Angles (deg)

(a) Interatomic Distances (<2.50 Å)

	Before riding correction	After riding correction
Ru-Ge	2.403 (2)	2.408 (2)
Ru-C5	1.87 (2)	
Ru-C1	2.29 (1)	
Ru-C2	2.29 (1)	
Ru-C3	2.29 (1)	
Ru-C4	2.29 (1)	
Ge-Cl1	2.156 (4)	2.182 (4)
Ge-Cl2	2.152 (4)	2.211 (4)
Ge-Cl3	2.164 (4)	2.186 (4)
C5-O	1.14 (2)	
C-C(benzene)	1.408 (6)	
C-H(benzene)	1.00	

(b) Bond Angles

Ge-Ru-Ge′	90.35 (7)	C5-Ru-C3	138.3 (4)
Ge-Ru-C5	87.0 (3)	C5-Ru-C4	168.6 (6)
Ge-Ru-C1	134.8 (3)	Cl1-Ge-Cl2	102.6 (2)
Ge-Ru-C2	101.5 (2)	Cl2-Ge-Cl3	100.6 (2)
Ge-Ru-C3	134.1 (2)	Cl1-Ge-Cl3	98.7 (2)
Ge-Ru-C4	100.9 (2)	Ru-Ge-Cl1	117.3 (1)
Ge-Ru-C3′	134.2 (2)	Ru-Ge-Cl2	119.6 (1)
Ge-Ru-C2′	162.5 (2)	Ru-Ge-Cl3	114.8 (1)
C5-Ru-C1	92.7 (5)	Ru-C5-O	178.0 (2)
C5-Ru-C2	106.3 (5)		

C(benzene)-Ru-C(benzene) (ortho)	35.8 (2)[a]
C(benzene)-Ru-C(benzene) (meta)	64.3 (3)[a]
C(benzene)-Ru-C(benzene) (para)	75.9 (3)[a]
H-C-H(benzene)	120.0 (5)[a]
H-C-Ru	127.9 (6)[a]

(c) Intramolecular Nonbonding Distances x ($2.41 < x < 4.50$ Å)

Ru···O	3.009	Cl3···H3	3.101
Ru···Cl1	3.896	C5···C1	3.026
Ru···Cl2	3.938	C5···H1	3.187
Ru···Cl3	3.849	C5···C2	3.338
Ru···H	3.009[a]	C···C(meta)	2.439[a]
Ge···C5	2.967	C···C(para)	2.816[a]
Ge···C3	3.218	C···H(ortho)	2.095[a]
Ge···H3	3.194	C···H(meta)	3.342[a]
Cl1···Cl2	3.362	H···H(ortho)	2.408
Cl1···Cl3	3.278	Ge···Ge′	3.409
Cl2···Cl3	3.319	Cl1···Cl1′	3.671
Cl1···O	3.322	Cl2···Cl2′	3.629
Cl2···C5	3.473	Cl3···Cl3′	3.856

(d) Intermolecular Contacts (<3.7 Å)

Atoms	Dist	Symmetry[b]	Atoms	Dist	Symmetry[b]
Cl1···Cl3	3.671	1	Cl2···H1	3.388	3
Cl1···O	3.322	2	Cl2···H2	3.329	6
Cl1···C1	3.645	3	Cl2···H3	3.292	5
Cl1···C2	3.516	3	Cl2···H4	2.871	5
Cl1···H1	3.478	3	Cl3···O	3.274	6
Cl1···H2	3.243	3	Cl3···C5	3.408	6
Cl1···H3	2.837	1	Cl3···H2	3.311	6
Cl2···Cl2	3.646	4	Cl3···H3	3.598	1
Cl2···C4	3.587	5	O1···H4	3.436	5

[a] Average values. [b] The symmetry transformations are as follows: (1) $\frac{1}{2} - x, -y, \frac{1}{2} + z$; (2) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (3) $x, y, 1 + z$; (4) $\frac{1}{2} - x, -y, 1\frac{1}{2} + z$; (5) $x - \frac{1}{2}, y, \frac{1}{2} - z$; (6) $-x, -y, -z$.

The final electron density difference map revealed peaks no greater than 0.6 e/Å^3. The weighting scheme used throughout the refinement was $w = 1/\sigma^2(|F_o|)$ and the distribution of $(w\Delta^2)_{av}$ showed no trend with respect to F_o and $(\sin\theta)/\lambda$. The major computer programs used were as described in ref 2, with local modification of SFLS 5 (by C. T. Prewitt) to include hindered-rotor and rigid-body treatments.[10]

Positional and thermal parameters for all atoms are listed in Table I, and interatomic distances and angles, in Table II. Calculated and observed structure factors obtained from the last cycle of least-squares refinement are presented elsewhere.[15] Figures 1 and 2 show the

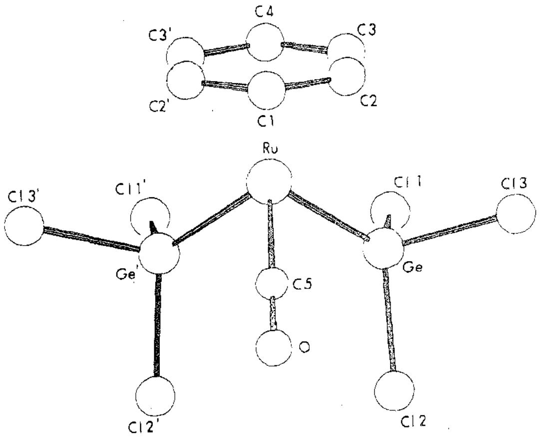

Figure 1. Molecular structure of $(\eta\text{-}C_6H_6)Ru(CO)(GeCl_3)_2$ with hydrogen atoms omitted.

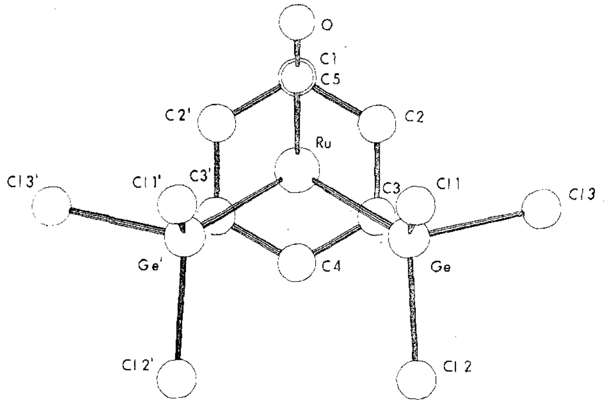

Figure 2. Projection of the $(\eta\text{-}C_6H_6)Ru(CO)(GeCl_3)_2$ molecule normal to the plane of the benzene ring, showing eclipsed conformation. Hydrogen atoms are not shown.

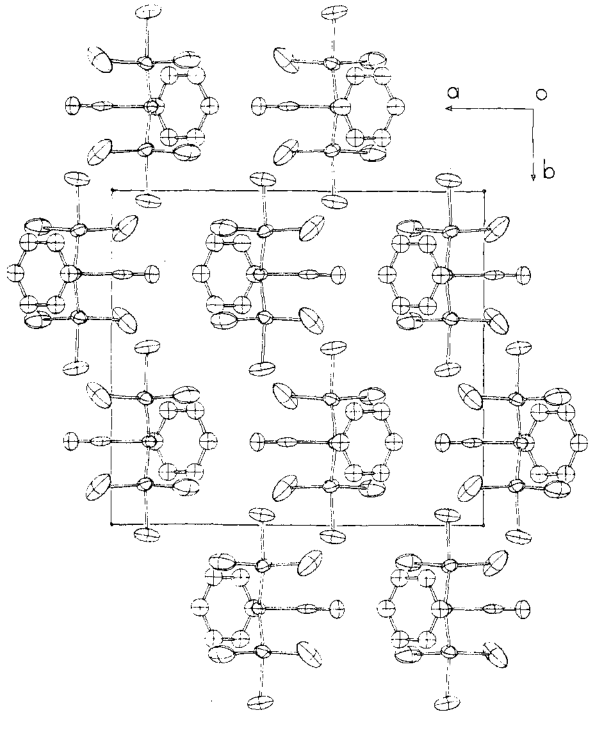

Figure 3. Crystal packing diagram for $(\eta\text{-}C_6H_6)Ru(CO)(GeCl_3)_2$ projected along the c axis. The thermal ellipsoids (spheres in the case of benzene carbon atoms which were given isotropic temperature factors) are scaled to contain 50% of the electron density.

molecular geometry while Figure 3 shows the unit cell packing.

Results and Discussion

The structure of $(C_6H_6)Ru(CO)(GeCl_3)_2$ as determined in this work (Figure 1) confirms the "piano stool" geometry which had been assumed in analogy to the related (arene)$Cr(CO)_3$ complexes.[1] As anticipated, the details of the structure afford interesting comparisons with those of related molecules.

A main feature is the *eclipsed* arrangement of ring carbon atoms with respect to the other three ligands; this is emphasized by the projection in Figure 2, which also shows the crystallographic mirror plane. A staggered conformation is characteristic of (arene)$Cr(CO)_3$ complexes where the arene lacks functional groups, as in benzene,[3] hexamethylbenzene,[4] or phenanthrene.[16] Although the eclipsed conformation has been found in (anisole)$Cr(CO)_3$,[5] (*o*-toluidine)$Cr(CO)_3$,[6] and (methyl benzoate)$Cr(CO)_3$,[7] the explanation advanced for this arrangement (involving a preferred orientation of localized octahedral σ orbitals of chromium toward carbon atoms of higher electron density) does not apply in the present case since the benzene ring is unsubstituted.

A factor leading to the eclipsed arrangement in $(C_6H_6)Ru(CO)(GeCl_3)_2$ may be the larger size of the ruthenium atom relative to chromium. Nonbonded intramolecular contacts provide some evidence for this view. The average carbonyl carbon–ring carbon distances were 2.91 and 2.88 Å in $(C_6H_6)Cr(CO)_3$ and $[(CH_3)_6C_6]Cr(CO)_3$, respectively, and would be shorter in a hypothetical eclipsed arrangement. In $(C_6H_6)Ru(CO)(GeCl_3)_2$, on the other hand, Cl···C5 is 3.03 Å and C3···Ge is 3.218 Å (in slight excess of the average C···Ge contact[2] of 3.188 Å in *trans*-$Ru(CO)_4(GeCl_3)_2$). The interaction between nonbonded atoms at these greater distances could well be sufficiently attractive to account for the eclipsed structure. It may be noted that refinement of the benzene ring as a hindered rotor showed a rather large thermal vibration tangential to the circumference of the ring;[17] one would accordingly expect a small potential barrier between the two conformations. The recent report of a staggered arrangement in the complex $(C_6H_6)Ru[P(CH_3)(C_6H_5)_2]Cl_2$[8] and preliminary results indicating an eclipsed structure in $(C_6H_6)Ru[P(n\text{-}C_4H_9)_3]Cl_{0.5}Br_{1.5}$[8] would suggest that fairly subtle factors are involved. Comparisons with the last two complexes are complicated by the asymmetric arene–metal bonding (see below), and, moreover, complete details of the structure determinations have not yet appeared.

The relation between $(C_6H_6)Cr(CO)_3$ and $Cr(CO)_6$ is the same as that of $(C_6H_6)Ru(CO)(GeCl_3)_2$ to *cis*-$Ru(CO)_4(GeCl_3)_2$; in both pairs, three carbonyl groups have been replaced by the benzene ring, their formal equivalent in terms of the effective atomic number rule. In $(C_6H_6)Cr(CO)_3$, the mean Cr–CO distance is 1.842 (9) Å, while in $Cr(CO)_6$ it is 1.909 (3) Å,[18] a difference ascribed previously to the superior π-acceptor capability of the carbonyl group relative to benzene.[6] An entirely similar effect is observed in $(C_6H_6)Ru(CO)(GeCl_3)_2$, where Ru–CO is 1.87 (2) Å, and the average value in *cis*-$Ru(CO)_4(GeCl_3)_2$ is 1.96 Å.[2] An increased π-acceptor role for carbon monoxide in the benzene complex is also indicated by the carbonyl infrared stretching frequencies: the benzene complex absorbs at 2040 cm^{-1},[1] while the bands are observed for *cis*-$Ru(CO)_4(GeCl_3)_2$ at 2160, 2116, and 2103 cm^{-1}.[19]

The Ru–Ge bond length is also shorter in $(C_6H_6)Ru(CO)(GeCl_3)_2$ (2.408 (2) Å) than in *cis*-$Ru(CO)_4(GeCl_3)_2$ (average 2.481 (5) Å), which may be rationalized in a similar way if one regards groups such as Cl_3Ge as potential π-acceptor ligands.[20]

The C–C distance in the benzene ring is 1.408 (6) Å, the same within error as the hindered-rotor value of 1.415 (3) Å for $C_6H_6Cr(CO)_3$.[10] We stress that before the hindered-rotor model was adopted in the refinement at $R = 4.5\%$, the three independent C–C distances were 1.413, 1.412, and 1.411 Å, which did not differ significantly. At this stage also, the benzene ring did not differ significantly from planarity. Additionally, the ring is symmetrically bonded to ruthenium, with all ruthenium–ring carbon distances equal to 2.29 (1) Å.

This is in marked contrast to the nonplanar and unsymmetrically attached aromatic rings in the complexes $(C_6H_6)Ru[P(CH_3)(C_6H_5)_2]Cl_2$ and $[p\text{-}CH_3C_6H_4CH(CH_3)_2]Ru[P(CH_3)(C_6H_5)_2]Cl_2$.[8] These rings are bent, with dihedral angles of 5 and 2°, respectively. In both complexes there are two long (ca. 2.26 Å) and four short (ca. 2.20 Å) ruthenium–ring carbon distances; the longer bonds in each case are trans to the phosphine ligand, considering the complex as octahedral.[21] This was attributed to the greater trans bond-weakening property of the phosphine.[8]

The fact that such asymmetric bonding can occur but does not in $(C_6H_6)Ru(CO)(GeCl_3)_2$ is a further indication of the *similarity* of carbon monoxide and the trichlorogermyl group as far as their trans influence is concerned. This was first indicated by the carbonyl stretching force constants in *cis*-$Ru(CO)_4(GeCl_3)_2$[1] and subsequently by the structural parameters of the same molecule.[2]

Acknowledgment. We thank Professor M. J. Bennett for many helpful discussions and Dr. R. K. Pomeroy for supplying the sample. We are grateful to the National Research Council of Canada for financial support and for a postdoctoratal fellowship to L.Y.Y.C.

Registry No. (η-C_6H_6)Ru(CO)$(GeCl_3)_2$, 54932-36-4.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number AIC500599.

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