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## Structural Characterization of

Carbonyl(diphenylacetylene)tris( $\eta^5$ -cyclopentadienylrhodium), $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)$ , and Its Bis(pentafluorophenyl)acetylene Homologue, $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5)$ . An Assessment of Their Molecular Dissimilarity<sup>1a</sup>TRINH-TOAN,<sup>1b</sup> ROBERT W. BROACH,<sup>1b</sup> SYLVIA A. GARDNER,<sup>1c</sup> MARVIN D. RAUSCH,<sup>1c</sup> and LAWRENCE F. DAHL<sup>\*1b</sup>

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Crystallographic studies of the diamagnetic  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)$  (**1**) and  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5)$  (**2**) homologues have revealed in accord with their spectral properties two different solid-state molecular architectures which from qualitative bonding considerations can be rationalized on the basis of electronic effects involving the nature of the acetylene substituents. The molecular configurations of **1** and **2** both consist of a triangular array of  $\text{Rh}(\eta^5\text{-C}_5\text{H}_5)$  fragments which are linked not only by electron-pair Rh–Rh bonds but also by the acetylene ligand which is analogously distorted to an olefinic-like geometry that may be considered to form one-electron-donating  $\sigma$  bonds with two rhodium atoms, Rh(2) and Rh(3), and a two-electron  $\mu$ -type bond with the third rhodium atom, Rh(1). The major structural variation between **1** and **2** is the nature of the bridging carbonyl ligand; in **1** it is situated on the opposite side of the trirhodium plane from the diphenylacetylene ligand and is coordinated to all three rhodium atoms whereas in **2** it is positioned on the same side of the trirhodium plane as the bis(pentafluorophenyl)acetylene ligand and bonded to Rh(2) and Rh(3). The common  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{CC}_2\text{C})$  fragment in both **1** and **2** closely conforms to  $C_s$ - $m$  symmetry with the entire  $\text{RC}_2\text{R}'$  ligand similarly disposed with respect to the isosceles trirhodium triangle in each complex. The bonding implications resulting from the observed stereochemistries of **1** and **2** are examined in connection with the known carbonyl frequencies of these and other  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{RC}_2\text{R}')$  complexes, and it is proposed from orbital energetic arguments that the composite  $\pi$ -donor and  $\pi^*$ -acceptor interaction of the  $\text{RC}_2\text{R}'$  ligand with Rh(1) in competition with the relative  $\pi$ -acceptor ability of the carbonyl as a triply bridging ligand in its interaction with Rh(1) is the prime driving force which gives rise either to the triply bridging carbonyl structure found for **1** or to the doubly bridging carbonyl structure found for **2**. Four molecules of **1** and two solvent benzene molecules crystallize in a monoclinic unit cell of symmetry  $P2_1/c$  and of dimensions  $a = 14.398$  (3) Å,  $b = 15.726$  (3) Å,  $c = 12.072$  (3) Å, and  $\beta = 95.735$  (8)°; least-squares refinement of the determined structure converged at  $R_1 = 4.4\%$  and  $R_2 = 5.5\%$  for 2940 independent diffractometry-collected data with  $I \geq 2\sigma(I)$ . The crystal structure of **2**, which also has four molecules contained in a monoclinic unit cell of symmetry  $P2_1/c$  and of dimensions  $a = 10.271$  (1) Å,  $b = 13.499$  (1) Å,  $c = 19.620$  (2) Å, and  $\beta = 92.957$  (2)°, was refined by least squares to  $R_1 = 5.8\%$  and  $R_2 = 6.4\%$  for 2668 independent diffractometry-collected data with  $I \geq 2\sigma(I)$ .

## Introduction

Several unusual di- and trinuclear organorhodium cluster complexes have been isolated by Gardner, Andrews, and Rausch<sup>2</sup> from the two condensation reactions of diphenylacetylene and bis(pentafluorophenyl)acetylene catalyzed by  $\eta^5$ -cyclopentadienyldicarbonylrhodium. Of particular stereochemical and bonding interest are the two cluster complexes which from analytical and mass spectral results appeared to be homologous, with compositions  $\text{Rh}_3(\text{C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{H}_5\text{-C}_2\text{C}_6\text{H}_5)$  (**1**) and  $\text{Rh}_3(\text{C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5)$  (**2**). However, infrared and <sup>1</sup>H NMR data<sup>2</sup> indicate that there must be pronounced variations in their molecular architectures in that **1** has an extremely low carbonyl stretching frequency at 1675  $\text{cm}^{-1}$  and exhibits only one cyclopentadienyl proton peak at  $\tau$  4.80, whereas **2** possesses a much higher carbonyl stretching frequency in the doubly bridging carbonyl region at 1810  $\text{cm}^{-1}$  and two different cyclopentadienyl proton resonances at  $\tau$  4.25 and 4.53 in a 1:2 ratio.<sup>3,4</sup>

This paper presents the results of x-ray diffraction investigations which have established unambiguously that the configurational differences between the two compounds in the solid state are in accord with their spectral properties.<sup>5,6</sup> A prime incentive for this study in our laboratories was a detailed assessment of the mode of interaction of the acetylene ligand with the tris(cyclopentadienylrhodium) fragment in each complex, especially in connection with the remarkable variety of linkages of acetylenes to triangular iron cores found<sup>7</sup> in several organoiron carbonyl complexes which were synthesized a number of years ago by Hubel and co-workers.<sup>8</sup> Our structural work, which was communicated earlier,<sup>1a</sup> is also related to recent structural studies<sup>9</sup> of electronically equivalent triruthenium-, tetraruthenium-, and triosmium-acetylene

carbonyl systems<sup>9a,10,11</sup> which have aroused considerable interest concerning the coordination and reactivity of unsaturated hydrocarbons at the "surface" of a metal cluster.

## Experimental Section

**X-Ray Measurements.** Dark purple, air-stable crystals of  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)^{1/2}\text{C}_6\text{H}_6$  were obtained by recrystallization from a benzene-hexane solution, and dark green, air-stable crystals of  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5)$  were obtained by slow evaporation from a dichloromethane-toluene solution.

Preliminary Weissenberg and precession photographs of both cluster complexes showed  $C_{2h}2/m$  Laue symmetry characteristic of the monoclinic system. Mo  $K\alpha$  ( $\lambda$  0.7107 Å) radiation was used in the crystal line-up and collection of intensity data for  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)^{1/2}\text{C}_6\text{H}_6$ , while Cu  $K\alpha$  ( $\lambda$  1.542 Å) was used for  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5)$  in that this latter complex appeared to be sensitive to the Mo  $K\alpha$  radiation. Crystals of approximate dimensions 0.17 × 0.29 × 0.59 mm and 0.10 × 0.14 × 0.21 mm, respectively, for  $\text{Rh}_3(\text{C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)^{1/2}\text{C}_6\text{H}_6$  and the bis(pentafluorophenyl)acetylene homologue were utilized. Data for both compounds were obtained on a Daxel-controlled General Electric diffractometer equipped with an E&A full-circle goniometer. The procedures of crystal line-up, collection, and treatment of diffraction data have been described elsewhere.<sup>12-14</sup>

For the diphenylacetylene compound, intensity data were gathered for one asymmetric unit at a takeoff angle of 2.0° via a (stationary background)–( $2\theta$  scan)–(stationary background) counting sequence for  $2\theta \leq 45^\circ$  (Mo  $K\alpha$  radiation). Symmetric ranges in  $2\theta$  of 2.5° for  $2\theta \leq 10^\circ$ , 2.0° for  $10^\circ < 2\theta \leq 20^\circ$ , and 1.5° for  $20^\circ < 2\theta \leq 45^\circ$  were scanned for each reflection at a scan rate of 2.0°  $\text{min}^{-1}$  with background counts of 25 s being recorded at both ends of the scan scope. Four standard reflections sampled regularly during the data collection at intervals of every 100 reflections showed no significant intensity changes. After corrections for Lorentz and polarization effects, the data were converted to structure factor amplitudes and then merged<sup>14a</sup> to obtain 3807 independent reflections, of which 2940

diffraction maxima with  $I \geq 2\sigma(I)$  were used in the structural determination and refinement. Absorption corrections<sup>14b</sup> were applied in that, based upon a linear absorption coefficient of  $17.6 \text{ cm}^{-1}$  for Mo K $\alpha$  radiation, the transmission coefficient ranged from 0.62 to 0.75.

The same procedure was applied for  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5)$ . Intensity data for two symmetric units were measured for  $2\theta \leq 124^\circ$  (Cu K $\alpha$  radiation). Symmetric ranges of  $2\theta$  of  $1.2^\circ$  for  $2\theta \leq 40^\circ$  and  $1.0^\circ$  for  $2\theta > 40^\circ$  were scanned for each reflection at a scan rate of  $2.0^\circ/\text{min}$  with background counts of 15 s. Absorption corrections were applied, since the linear absorption coefficient of  $158.6 \text{ cm}^{-1}$  for Cu K $\alpha$  radiation is large. Data were then merged to yield 3783 independent reflections, of which 2668 with  $I \geq 2\sigma(I)$  were utilized in the structural determination and refinement.

**Crystal Data.** (a)  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)^{1/2}\text{C}_6\text{H}_6$ . Least-squares refinement of the diffractometer settings of 20 independent reflections,<sup>14c</sup> which were carefully centered, yielded monoclinic dimensions of  $a = 14.398(3) \text{ \AA}$ ,  $b = 15.726(3) \text{ \AA}$ ,  $c = 12.072(3) \text{ \AA}$ , and  $\beta = 95.735(8)^\circ$ ;  $V = 2720 \text{ \AA}^3$ .

The calculated density of  $1.86 \text{ g cm}^{-3}$  for four  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)$  molecules and two benzene molecules per unit cell is in accord with the experimental density of  $1.83 \text{ g cm}^{-3}$  obtained by the flotation method. Observed systematic absences of  $\{h0l\}$  for  $l = 2n + 1$  and  $\{0k0\}$  for  $k = 2n + 1$  uniquely indicate the centrosymmetric space group  $P2_1/c$  ( $C_{2h}^2$ ; No. 14). Hence the structural analysis required the location of 3 rhodium, 1 oxygen, 33 carbon, and ideally 28 hydrogen atoms, corresponding to one trirhodium molecule of site symmetry  $C_{1-1}$  and half of one benzene molecule of site symmetry  $C_{1-1}$ .

(b)  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5)$ . Lattice dimensions of  $a = 10.271(1) \text{ \AA}$ ,  $b = 13.499(1) \text{ \AA}$ ,  $c = 19.620(2) \text{ \AA}$ , and  $\beta = 92.957(2)^\circ$  were obtained from least-squares refinement of the diffractometer settings of 22 selected reflections<sup>14c</sup> for the monoclinic crystal of  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5)$ . The calculated density of  $2.18 \text{ g cm}^{-3}$  for four formula species per cell is in agreement with the experimental value of  $2.15 \text{ g cm}^{-3}$  obtained by the flotation method. Systematic absences showed that the crystal of this perfluorophenylacetylene homologue also conforms to the centrosymmetric space group  $P2_1/c$ .

**Determination and Refinement of the Structures.** (a)  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)^{1/2}\text{C}_6\text{H}_6$ . A vector analysis<sup>14d</sup> of a computed Patterson function<sup>14e</sup> provided the positions of the three rhodium atoms. Successive Fourier synthesis<sup>14e</sup> coupled with least-squares refinements<sup>14f</sup> revealed the coordinates of enough nonhydrogen atoms such that the remaining unresolved carbon atoms of the three cyclopentadienyl and two phenyl rings could be assigned idealized coordinates<sup>14e</sup> based upon the well-known ring geometries. Isotropic least-squares refinement with each ring constrained as a rigid body converged at  $R_1 = 5.2\%$  and  $R_2 = 6.7\%$ .<sup>15-17</sup> Further least-squares cycles were then carried out with anisotropic thermal parameters for all nonhydrogen atoms and with the rigid-body constraints on the rings removed; the ring hydrogen atoms were included as fixed atom contributors with assigned isotropic temperature factors and with their idealized coordinates being calculated after each cycle from the new coordinates of the ring carbon atoms. This latter refinement converged at  $R_1 = 4.4\%$  and  $R_2 = 5.5\%$ . The final Fourier difference map was virtually flat.

(b)  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5)$ . Initial coordinates for the three rhodium atoms were obtained from an analysis of the Patterson map, while the locations of all other nonhydrogen atoms were determined by Fourier syntheses coupled with least-squares refinements. After refinement with anisotropic thermal parameters for the rhodium atoms, a Fourier difference map revealed residual peaks between adjacent carbon atoms for two of the three independent cyclopentadienyl rings, analogous to those found<sup>18</sup> for other metal-cyclopentadienyl complexes. Hence, further least-squares cycles were performed in which carbon atoms for these two cyclopentadienyl rings along with the three rhodium atoms were refined anisotropically while isotropic temperature factors were used for all other nonhydrogen atoms. This refinement converged at  $R_1 = 5.8\%$  and  $R_2 = 6.4\%$ .<sup>15-17</sup> A final difference electron density map did not show any unusual features. No attempt was made to identify the hydrogen atoms of the cyclopentadienyl rings.

Atomic parameters from the output of the last least-squares cycle are given in Table I for  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)^{1/2}\text{C}_6\text{H}_6$  and in Table II for  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5)$ . Interatomic

distances and selected bond angles (with estimated standard deviations calculated<sup>14h</sup> from the full inverse matrix) are presented in Table III. Equations of mean planes<sup>14i</sup> together with perpendicular distances of atoms from these planes and angles between the normals to these planes are tabulated in Table IV. The observed and calculated structure factors for both compounds are given as supplementary material.

## Results and Discussion

### General Description of the Crystal and Molecular Structures.

(a)  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)^{1/2}\text{C}_6\text{H}_6$ . This compound crystallizes as discrete molecules together with benzene solvent molecules. Figure 1a and b<sup>14j</sup> shows that the geometry of the trirhodium-diphenylacetylene molecule (**1**) consists of a completely bonding triangle of rhodium atoms which is capped above by a diphenylacetylene ligand and below by a carbonyl ligand, with the cyclopentadienyl rings symmetrically attached to the rhodium atoms. The diphenylacetylene ligand may be viewed as an olefinic group which is bonded to two equivalent rhodium atoms, Rh(2) and Rh(3), via two  $\sigma$  bonds and symmetrically coordinated to the unique (nonequivalent) Rh(1) via a  $\mu$ -type bond.<sup>19-21</sup> Likewise, to a first approximation, the triply bridging carbonyl ligand is symmetrically linked to Rh(2) and Rh(3) but asymmetrically coordinated at a longer distance to Rh(1). With the neglect of the phenyl substituents and with the assumption of cylindrical symmetry for each cyclopentadienyl ring, the resulting  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{CC}_2\text{C})$  fragment of **1** approximately conforms to bilateral  $C_s$ - $m$  symmetry.

Figure 2<sup>14j</sup> shows the arrangement in the monoclinic unit cell of the four molecules of **1** along with the two benzene molecules which are each constrained by a center of symmetry. The crystal packing appears to be dominated by normal van der Waals interactions among the bulky **1** molecules in that the closest intermolecular contact of  $2.59 \text{ \AA}$  between the carbonyl oxygen and phenyl H(5-2) corresponds roughly to the sum of the van der Waals radii for hydrogen and oxygen. The benzene molecules of cocrystallization are situated in the cavities formed by the cluster molecules of **1**; the shortest H $\cdots$ H contact between a benzene molecule and a molecule of **1** is  $2.28 \text{ \AA}$ , which is close to the van der Waals separation of  $2.4 \text{ \AA}$ .

(b)  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5)$ . This compound also crystallizes as discrete molecules with a configuration depicted in Figure 1c and d. The two molecular views show a triangular  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3$  framework with a doubly bridging carbonyl ligand situated on the same side of the trirhodium plane as the bis(pentafluorophenyl)acetylene ligand. The latter is symmetrically disposed to the three rhodium atoms in an overall analogous fashion to that found in **1**. If the two bis(pentafluorophenyl) substituents are neglected and each cyclopentadienyl ring is again assumed to possess cylindrical symmetry, the same resulting  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{CC}_2\text{C})$  fragment also possesses a pseudo mirror plane containing Rh(1), the carbonyl ligand, and the midpoint of the Rh(2)-Rh(3) line.

Figure 3<sup>14j</sup> exhibits the orientations of the four molecules of **2** in the monoclinic unit cell. The packing of these molecules is presumably dictated by van der Waals interactions in that there are no unusually short intermolecular contacts.

**Stereochemical Comparison of  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)$  (**1**) and  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5)$  (**2**).**

(a) **The Tris( $\eta^5$ -cyclopentadienylrhodium) Fragment.** The molecular configurations of **1** and **2** both consist of a triangular array of three  $\text{Rh}(\eta^5\text{-C}_5\text{H}_5)$  fragments linked to one another by electron-pair Rh-Rh bonds. The assumption that the common  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{CC}_2\text{C})$  fragment conforms to a  $C_s$ - $m$  geometry (vide supra) results in an isosceles rhodium triangle with equivalent Rh(2) and Rh(3) atoms and a nonequivalent Rh(1) atom.

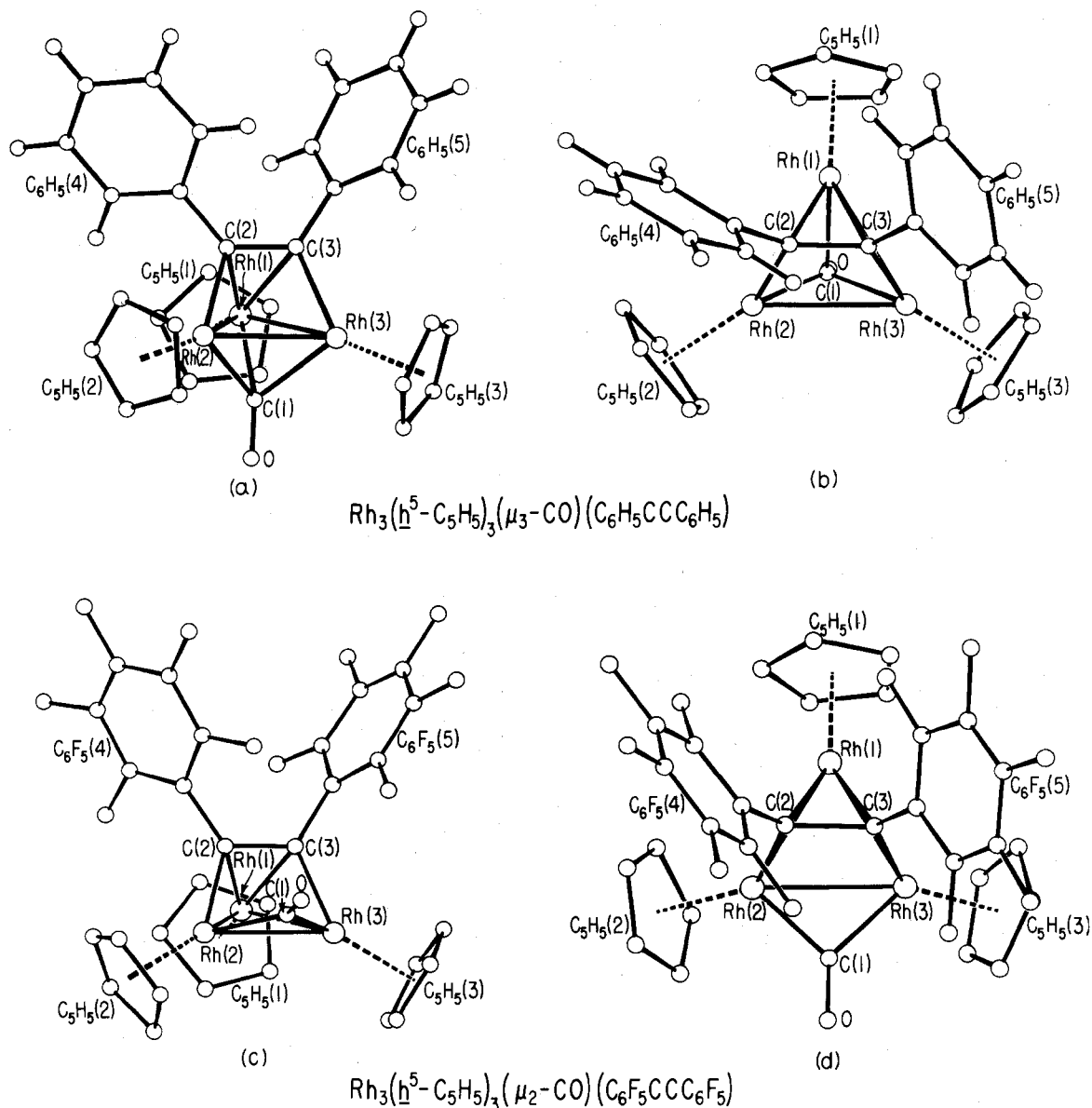


Figure 1. Molecular configurations of  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)$  (1) and  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5)$  (2).

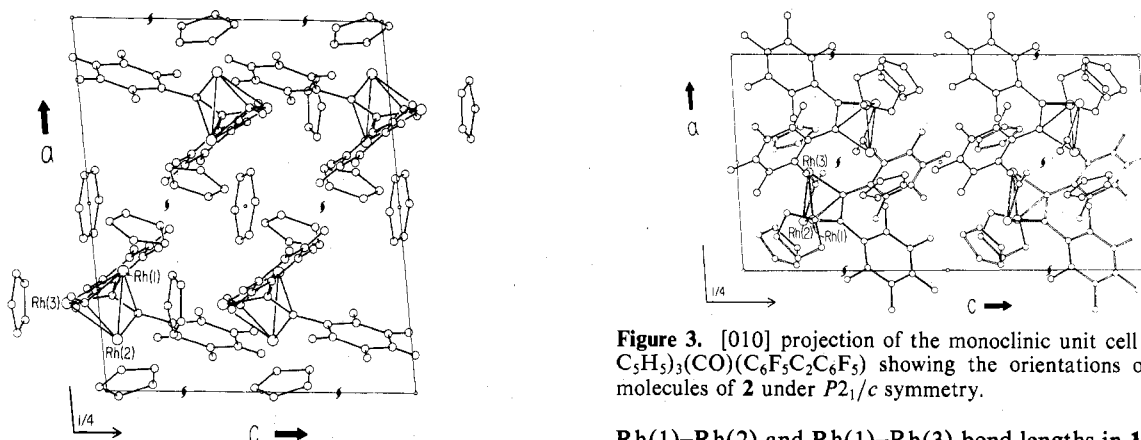


Figure 2. [010] projection of the monoclinic unit cell of  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)_1/2\text{C}_6\text{H}_6$  showing the arrangement of the four molecules of 1 and two benzene solvent molecules under  $P2_1/c$  symmetry.

The Rh–Rh bond lengths in 1 and 2 closely comply with this idealized mirror-plane geometry. The two equivalent

Figure 3. [010] projection of the monoclinic unit cell of  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5)$  showing the orientations of the four molecules of 2 under  $P2_1/c$  symmetry.

Rh(1)–Rh(2) and Rh(1)–Rh(3) bond lengths in 1 are 2.655 (1) and 2.639 (1) Å, respectively; their mean of 2.647 Å is only 0.027 Å shorter than the unique Rh(2)–Rh(3) bond length of 2.674 (1) Å. In 2 the Rh(2)–Rh(3) bond, which is parallel to the acetylene C(2)–C(3) bond, has a virtually unchanged length of 2.672 (1) Å, whereas the other two equivalent Rh(1)–Rh(2) and Rh(1)–Rh(3) bonds are significantly shorter with lengths of 2.599 (2) and 2.588 (1) Å,

Table I. Atomic Positional and Thermal Parameters for  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)^a$ 

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}^b$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Rh(1)	0.325 02 (4)	0.107 38 (4)	0.089 18 (5)	41	36	62	-3	6	0
Rh(2)	0.142 01 (4)	0.130 55 (4)	0.049 97 (5)	42	36	69	3	5	2
Rh(3)	0.237 23 (4)	0.052 08 (4)	-0.099 40 (5)	47	44	53	3	5	2
C(1)	0.237 2 (6)	0.175 1 (6)	-0.043 0 (7)	52	51	67	2	9	0
O(1)	0.253 4 (4)	0.241 4 (4)	-0.084 3 (5)	83	42	115	-1	28	30
C(2)	0.211 3 (5)	0.030 8 (5)	0.124 5 (6)	49	36	60	-3	11	3
C(3)	0.258 4 (5)	-0.012 7 (5)	0.047 4 (6)	43	39	54	0	-3	-1
C(1-1)	0.477 2 (6)	0.097 2 (6)	0.114 5 (9)	29	67	133	-6	-4	-24
C(1-2)	0.456 2 (7)	0.173 6 (7)	0.060 6 (8)	63	74	101	-31	14	-1
C(1-3)	0.406 4 (6)	0.223 8 (6)	0.132 1 (9)	59	37	156	-18	-7	-3
C(1-4)	0.398 7 (6)	0.177 8 (6)	0.231 3 (8)	59	55	100	-18	6	-21
C(1-5)	0.445 4 (6)	0.100 3 (6)	0.221 0 (8)	46	69	97	-17	-6	-8
C(2-1)	-0.013 1 (6)	0.119 2 (6)	0.038 0 (9)	41	46	167	3	1	6
C(2-2)	0.018 3 (7)	0.134 0 (7)	0.150 5 (9)	64	76	115	29	34	29
C(2-3)	0.062 7 (8)	0.213 4 (8)	0.162 1 (10)	78	75	146	18	20	-13
C(2-4)	0.058 0 (7)	0.251 4 (6)	0.056 0 (11)	54	43	207	16	15	0
C(2-5)	0.011 1 (6)	0.193 5 (6)	-0.021 4 (8)	41	66	135	21	2	26
C(3-1)	0.232 4 (8)	0.099 7 (7)	-0.277 0 (7)	96	93	49	6	2	24
C(3-2)	0.156 2 (7)	0.044 4 (7)	-0.267 3 (7)	69	91	59	2	-3	4
C(3-3)	0.190 4 (6)	-0.037 0 (6)	-0.238 2 (7)	63	75	52	-6	-1	-10
C(3-4)	0.288 2 (7)	-0.032 1 (7)	-0.229 3 (7)	83	66	76	31	26	-10
C(3-5)	0.314 0 (7)	0.050 6 (8)	-0.253 5 (7)	61	101	64	-9	9	2
C(4-1)	0.186 0 (5)	0.000 5 (5)	0.233 1 (6)	33	39	68	-4	3	1
C(4-2)	0.191 0 (6)	0.053 5 (5)	0.326 0 (7)	69	44	76	4	13	-4
C(4-3)	0.163 2 (7)	0.025 2 (7)	0.427 0 (7)	76	77	66	12	13	-6
C(4-4)	0.126 9 (7)	-0.054 4 (8)	0.437 4 (8)	84	96	76	-9	23	18
C(4-5)	0.122 0 (7)	-0.108 2 (7)	0.346 8 (9)	55	70	133	-10	6	30
C(4-6)	0.152 4 (6)	-0.081 4 (6)	0.245 8 (7)	65	59	65	-17	9	1
C(5-1)	0.299 6 (5)	-0.097 2 (5)	0.064 1 (6)	40	32	72	9	0	-4
C(5-2)	0.270 3 (6)	-0.164 7 (6)	-0.004 1 (8)	57	51	99	4	-9	-1
C(5-3)	0.299 8 (7)	-0.247 1 (6)	0.022 0 (9)	86	42	124	-10	1	-16
C(5-4)	0.360 1 (7)	-0.264 5 (6)	0.114 0 (8)	100	44	103	11	22	7
C(5-5)	0.392 0 (7)	-0.198 0 (6)	0.181 0 (7)	87	58	85	26	1	1
C(5-6)	0.362 3 (6)	-0.116 7 (5)	0.156 8 (7)	60	44	84	6	2	-9
C(6-1)	0.511 4 (7)	0.082 3 (6)	0.533 7 (7)	76	52	86	4	9	-6
C(6-2)	0.423 3 (7)	0.052 5 (6)	0.506 1 (8)	65	55	101	16	18	3
C(6-3)	0.409 9 (7)	-0.031 1 (6)	0.472 0 (8)	80	59	91	2	8	9

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>
H(1-1) <sup>c</sup>	0.5167	0.0434	0.0816	H(4-2)	0.2170	0.1133	0.3197
H(1-2)	0.4713	0.1917	-0.0236	H(4-3)	0.1666	0.0665	0.4927
H(1-3)	0.3782	0.2885	0.1137	H(4-4)	0.1064	-0.0744	0.5090
H(1-4)	0.3660	0.2001	0.3038	H(4-5)	0.0966	-0.1684	0.3522
H(1-5)	0.4516	0.0486	0.2840	H(4-6)	0.1470	-0.1216	0.1793
H(2-1)	-0.0493	0.0642	0.0021	H(5-2)	0.2250	-0.1534	-0.0728
H(2-2)	0.0105	0.0882	0.2194	H(5-3)	0.2755	-0.2958	-0.0308
H(2-3)	0.0937	0.2423	0.2399	H(5-4)	0.3813	-0.3238	0.1310
H(2-4)	0.0854	0.3135	0.0353	H(5-5)	0.4366	-0.2094	0.2507
H(2-5)	-0.0030	0.2035	-0.1116	H(5-6)	0.3860	-0.0669	0.2087
H(3-1)	0.2280	0.1671	-0.2991	H(6-1)	0.5220	0.1424	0.5585
H(3-2)	0.0810	0.0628	-0.2809	H(6-2)	0.3670	0.0905	0.5097
H(3-3)	0.1481	-0.0935	-0.2243	H(6-3)	0.3430	-0.0539	0.4508
H(3-4)	0.3366	-0.0858	-0.2075				

<sup>a</sup> In this and the following tables, the standard deviation of the last significant figure is given in parentheses following the number. <sup>b</sup> The form of the anisotropic thermal ellipsoids is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . The anisotropic thermal parameters have all been multiplied by  $10^4$ .

respectively. The invariance of the Rh(2)–Rh(3) bond length in **1** and **2** is presumed to be at least partly due to the geometrical requirements of the similarly positioned acetylene ligand which in its functioning as an olefinic coordinated group forms  $\sigma$  bonds with Rh(2) and Rh(3). The three Rh–Rh bond lengths in **1** and the Rh(2)–Rh(3) bond length in **2** are similar to the Rh–Rh single-bond lengths of range 2.62–2.85 Å found in other rhodium carbonyl, cyclopentadienyl, and acetylene cluster systems,<sup>22–24</sup> while the Rh(1)–Rh(2) and Rh(1)–Rh(3) bond lengths in **2** are slightly shorter.

The carbon atoms in each of the cyclopentadienyl rings in **1** and **2** are coplanar within 1.0 esd except for ring 1 in **1** where they are coplanar within 2.0 esd's. The determined Rh–C and C–C distances of 2.24 Å (average) and 1.41 Å (average), respectively, in **1** and 2.23 Å (average) and 1.42 Å (average), respectively, in **2** correspond to expected values found in other rhodium cyclopentadienyl clusters.<sup>23</sup>

Figure 1b shows that in **1** the three cyclopentadienyl rings are similarly displaced on the same side of the trirhodium plane; their almost perpendicular orientations relative to the trirhodium plane are indicated by the centroids of the chemically equivalent  $\text{C}_5\text{H}_5(2)$  and  $\text{C}_5\text{H}_5(3)$  rings attached to Rh(2) and Rh(3), respectively, being only 0.24 and 0.46 Å out of the trirhodium plane and by the dihedral angles of 82.8 and 77.0° formed by these two ring planes with the trirhodium plane. The greater tilt of the  $\text{C}_5\text{H}_5(1)$  ring from the trirhodium plane is evidenced by the larger perpendicular displacement of its centroid by 0.64 Å from the trirhodium plane and by the smaller dihedral angle of 69.5° which it forms with the trirhodium plane.

In contrast, Figure 1d shows that the three cyclopentadienyl rings in **2** are inclined much more out of the trirhodium plane at equivalent orientations as manifested by their ring centroids being located at 0.89, 0.87, and 0.88 Å out of the trirhodium

**Table II.** Atomic Positional and Thermal Parameters for  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)$ 

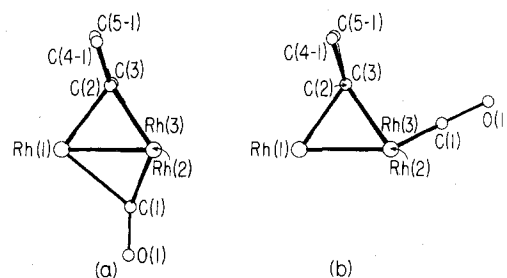
Atom	x	y	z	$B, \text{\AA}^2$
Rh(1)	0.235 62 (10)	0.115 65 (8)	0.177 05 (5)	a
Rh(2)	0.227 41 (10)	-0.073 64 (8)	0.153 04 (5)	a
Rh(3)	0.454 40 (9)	0.021 16 (8)	0.173 70 (5)	a
C(1)	0.400 3 (12)	-0.116 1 (11)	0.188 2 (6)	4.4 (3)
O(1)	0.449 8 (9)	-0.194 1 (8)	0.207 4 (5)	6.2 (2)
C(2)	0.226 0 (11)	-0.003 3 (9)	0.244 6 (6)	3.7 (3)
C(3)	0.346 3 (12)	0.045 7 (9)	0.255 0 (6)	3.8 (3)
C(1-1)	0.157 1 (15)	0.196 1 (12)	0.085 7 (7)	5.9 (3)
C(1-2)	0.057 6 (14)	0.190 8 (11)	0.135 4 (7)	5.5 (3)
C(1-3)	0.106 7 (14)	0.242 3 (12)	0.194 4 (7)	5.9 (3)
C(1-4)	0.234 8 (13)	0.280 4 (11)	0.183 4 (7)	5.3 (3)
C(1-5)	0.264 2 (14)	0.251 3 (12)	0.114 8 (7)	5.6 (3)
C(2-1)	0.028 6 (18)	-0.125 6 (18)	0.130 7 (10)	a
C(2-2)	0.103 7 (24)	-0.211 2 (17)	0.135 2 (11)	a
C(2-3)	0.195 7 (20)	-0.203 9 (18)	0.084 6 (14)	a
C(2-4)	0.166 2 (22)	-0.116 1 (21)	0.043 8 (8)	a
C(2-5)	0.057 1 (21)	-0.070 6 (16)	0.078 7 (11)	a
C(3-1)	0.558 7 (16)	0.103 3 (15)	0.091 7 (9)	a
C(3-2)	0.586 9 (17)	0.147 2 (14)	0.152 8 (11)	a
C(3-3)	0.652 5 (18)	0.081 7 (24)	0.198 1 (8)	a
C(3-4)	0.663 9 (16)	-0.010 3 (17)	0.159 7 (13)	a
C(3-5)	0.605 6 (18)	0.005 0 (16)	0.096 0 (10)	a
C(4-1)	0.136 3 (12)	-0.024 1 (9)	0.299 7 (6)	3.7 (2)
C(4-2)	0.013 5 (12)	0.013 7 (10)	0.304 3 (6)	4.1 (3)
C(4-3)	-0.061 4 (14)	-0.002 4 (10)	0.360 5 (7)	4.9 (3)
C(4-4)	-0.014 9 (13)	-0.058 4 (11)	0.411 4 (7)	4.6 (3)
C(4-5)	0.101 2 (13)	-0.097 9 (11)	0.411 5 (7)	4.7 (3)
C(4-6)	0.177 7 (12)	-0.082 1 (10)	0.356 0 (6)	4.1 (3)
C(5-1)	0.395 7 (12)	0.080 6 (10)	0.324 1 (6)	3.9 (3)
C(5-2)	0.342 4 (12)	0.160 5 (11)	0.359 3 (6)	4.5 (3)
C(5-3)	0.393 6 (13)	0.190 1 (11)	0.423 1 (7)	4.9 (3)
C(5-4)	0.488 2 (13)	0.143 8 (11)	0.453 8 (7)	4.9 (3)
C(5-5)	0.544 0 (13)	0.064 1 (11)	0.423 8 (7)	4.7 (3)
C(5-6)	0.496 7 (12)	0.032 7 (10)	0.360 0 (7)	4.3 (3)
F(4-2)	-0.040 6 (7)	0.068 6 (6)	0.252 4 (4)	5.7 (2)
F(4-3)	-0.182 5 (8)	0.038 3 (7)	0.358 0 (4)	6.7 (2)
F(4-4)	-0.091 2 (7)	-0.072 9 (6)	0.465 7 (4)	6.1 (2)
F(4-5)	0.149 0 (8)	-0.156 2 (7)	0.462 2 (4)	6.7 (2)
F(4-6)	0.296 5 (7)	-0.125 5 (6)	0.355 3 (4)	5.6 (2)
F(5-2)	0.241 2 (8)	0.211 8 (6)	0.331 1 (4)	6.1 (2)
F(5-3)	0.334 9 (8)	0.268 3 (7)	0.451 1 (5)	7.3 (2)
F(5-4)	0.536 0 (8)	0.170 2 (7)	0.516 4 (4)	6.6 (2)
F(5-5)	0.639 6 (8)	0.010 7 (6)	0.455 9 (4)	6.4 (2)
F(5-6)	0.550 7 (7)	-0.046 7 (6)	0.332 8 (4)	5.4 (2)

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Rh(1)	96 (1)	50 (1)	21 (1)	3 (1)	4 (1)	3 (1)
Rh(2)	100 (1)	56 (1)	21 (1)	-5 (1)	2 (1)	-3 (1)
Rh(3)	89 (1)	60 (1)	21 (1)	-2 (1)	8 (1)	-1 (1)
C(2-1)	165 (26)	111 (19)	49 (7)	-32 (18)	-7 (11)	-11 (10)
C(2-2)	231 (34)	98 (19)	60 (9)	-55 (21)	-10 (14)	-17 (11)
C(2-3)	167 (28)	134 (22)	65 (9)	25 (20)	-16 (14)	-53 (12)
C(2-4)	203 (30)	189 (26)	22 (5)	-89 (23)	4 (10)	-28 (9)
C(2-5)	215 (31)	107 (16)	46 (7)	-53 (19)	-50 (12)	10 (10)
C(3-1)	151 (22)	95 (16)	46 (7)	-10 (16)	19 (10)	15 (8)
C(3-2)	139 (22)	109 (17)	49 (7)	-51 (15)	18 (10)	-22 (9)
C(3-3)	123 (22)	263 (32)	28 (5)	-91 (22)	21 (9)	-7 (11)
C(3-4)	95 (19)	146 (21)	62 (9)	8 (16)	30 (11)	47 (11)
C(3-5)	156 (23)	114 (19)	48 (7)	-20 (16)	44 (11)	-10 (9)

<sup>a</sup> Anisotropic temperature factors of the form  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$  were used for the rhodium atoms and for the carbon atoms of cyclopentadienyl rings 2 and 3; the resulting thermal coefficients ( $\times 10^4$ ) are given in the lower part of this table.

plane and by their angles between their ring normals and the normal of the trirhodium plane being 61.5, 62.7, and 63.9°.

This large difference between the orientations of the three cyclopentadienyl rings in **1** and those in **2** can be readily rationalized from steric considerations as seen from an examination of the relative positions of the acetylene and carbonyl ligands in each trirhodium cluster. In **1** the diphenylacetylene and triply bridging carbonyl ligands are situated on opposite sides of the rhodium triangle such that



**Figure 4.** Projection down the Rh(2)–Rh(3) axis showing the orientation of the bridging carbonyl and acetylene ligands with respect to the trirhodium triangle in (a) the triply bridging carbonyl structure of  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)$  (**1**) and (b) the doubly bridging carbonyl structure of  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5)$  (**2**). The olefinic-like acetylene ligand, which is envisioned as forming  $\sigma$  bonds with Rh(2) and Rh(3) and a  $\mu$ -type bond with Rh(1), is geometrically disposed in a similar fashion in each complex.

the cyclopentadienyl ligands are nearly perpendicular to the trirhodium plane. The particular asymmetrical character of the triply bridging carbonyl ligand in **1** (vide infra) apparently allows the  $\text{C}_5\text{H}_5(1)$  ring to be tipped at a greater angle from the trirhodium plane toward the carbonyl group. In **2** the bis(pentafluorophenyl)acetylene and doubly bridging carbonyl group are located on the same side of the rhodium triangle thereby sterically forcing the three cyclopentadienyl rings to their equilibrium positions on the other side.

**(b) The Bridging Carbonyl Ligand.** The most notable structural difference between **1** and **2** is the nature of the linkage of the bridging carbonyl ligand. As can be clearly seen in Figure 4, the carbonyl ligand C(1)–O(1) in **1** is situated on the opposite side of the trirhodium plane from the diphenylacetylene ligand and is coordinated to all three rhodium atoms while in **2** it is positioned on the same side of the trirhodium plane as the bis(pentafluorophenyl)acetylene ligand and bonded to only two rhodium atoms, Rh(2) and Rh(3).

The triply bridging carbonyl ligand in **1** is asymmetrical in being 0.2 Å nearer to the Rh(2) and Rh(3) atoms with Rh–C(1) bond lengths of 1.985 (8) and 2.052 (9) Å, respectively, compared to the Rh(1)–C(1) bond length of 2.208 (8) Å. The mean value of 2.08 Å for these three Rh–C(1) distances is significantly shorter than that of 2.17 Å in  $\text{Rh}_6(\text{CO})_{16}$  where four carbonyl ligands are each coordinated symmetrically to three chemically equivalent rhodium atoms.<sup>22b</sup> This asymmetrical bridging character found for the carbonyl ligand in **1** is not at all surprising in view of the stereochemically different environment of the unique Rh(1) from that of Rh(2) and Rh(3). Furthermore, in several rhodium carbonyl anions<sup>22c–e</sup> the triply bridging carbonyl groups coordinated to nonequivalent rhodium atoms are found to exhibit similar varying degrees of asymmetry for the three Rh–CO bond lengths. Although to a first approximation the triply bridging carbonyl ligand in **1** may be considered to be symmetrically coordinated to two chemically equivalent Rh(2) and Rh(3) atoms, nevertheless a reasonably large variation of 0.07 Å is observed between the above mentioned Rh(2)–C(1) and Rh(3)–C(1) bond lengths. Due to its asymmetrical disposition the C(1)–O(1) bond in **1** deviates by 2.5° from being parallel with the normal to the trirhodium plane.

In **2** the doubly bridging carbonyl ligand is symmetrically coordinated at identical Rh–C bond lengths of 1.96 (1) Å to Rh(2) and Rh(3). The orientation of this carbonyl ligand on the same side of the trirhodium plane as the bis(pentafluorophenyl)acetylene ligand results in the Rh(2)–C(1)–Rh(3) plane forming a dihedral angle of 153° with the trirhodium plane. The C(1)–O(1) bond is not exactly coplanar with the Rh(2)–C(1)–Rh(3) plane but is bent slightly away from the

**Table III.** Interatomic Distances (Å) and Bond Angles (deg) for  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)$  (1) and  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5)$  (2)

A. Distances and Bond Angles for The Common $\text{Rh}_3(\text{CO})(\text{CC}_2\text{C})$ Fragment <sup>a</sup>					
	1	2		1	2
Rh(1)-Rh(2)	2.655 (1)	2.599 (2)	C(3)-C(2)-C(4-1)	128.3 (7)	123.8 (12)
Rh(1)-Rh(3)	2.638 (1)	2.588 (1)	C(2)-C(3)-C(5-1)	125.1 (7)	122.3 (12)
	2.647 (av)	2.594 (av)		126.7 (av)	123.1 (av)
Rh(2)-Rh(3)	2.674 (1)	2.672 (1)	C(2)-Rh(2)-Rh(3)	71.2 (2)	71.8 (4)
Rh(1)-C(2)	2.110 (7)	2.09 (1)	C(3)-Rh(3)-Rh(2)	71.7 (2)	71.8 (3)
Rh(1)-C(3)	2.154 (8)	2.09 (1)		71.5 (av)	71.8 (av)
	2.132 (av)	2.09 (av)	Rh(1)-C(2)-Rh(2)	79.8 (3)	78.2 (4)
Rh(2)-C(2)	2.022 (8)	2.03 (1)	Rh(1)-C(3)-Rh(3)	78.0 (3)	78.2 (4)
Rh(3)-C(3)	2.040 (7)	2.02 (1)		78.9 (av)	78.2 (av)
	2.031 (av)	2.03 (av)	C(2)-Rh(1)-Rh(2)	48.6 (2)	49.9 (3)
C(2)-C(3)	1.385 (10)	1.41 (2)	C(3)-Rh(1)-Rh(3)	49.1 (2)	49.8 (3)
C(2)-C(4-1)	1.47 (1)	1.48 (2)		48.9 (av)	49.9 (av)
C(3)-C(5-1)	1.46 (1)	1.50 (2)	C(2)-Rh(1)-C(3)	37.9 (3)	39.4 (4)
	1.47 (av)	1.49 (av)	Rh(1)-C(2)-C(3)	72.8 (4)	70.2 (7)
Rh(1)-C(1)	2.208 (8)		Rh(1)-C(3)-C(2)	69.3 (4)	70.4 (7)
Rh(2)-C(1)	1.985 (8)	1.96 (1)		71.1 (av)	70.3 (av)
Rh(3)-C(1)	2.052 (9)	1.96 (1)	Rh(1)-C(2)-C(4-1)	129.0 (5)	131.3 (9)
	2.019 (av)	1.96 (av)	Rh(1)-C(3)-C(5-1)	126.9 (5)	131.9 (9)
C(1)-O(1)	1.188 (9)	1.22 (1)		128.0 (av)	131.6 (av)
Rh(2)-C(2)-C(3)	109.7 (5)	107.6 (8)	Rh(2)-C(1)-Rh(3)	82.9 (3)	86.0 (6)
Rh(3)-C(3)-C(2)	107.3 (5)	108.8 (8)	Rh(1)-C(1)-Rh(2)	78.4 (3)	
	108.5 (av)	108.2 (av)	Rh(1)-C(1)-Rh(3)	76.5 (3)	
Rh(2)-C(2)-C(4-1)	119.4 (5)	126.1 (9)		77.5 (av)	
Rh(3)-C(3)-C(5-1)	126.7 (5)	126.3 (9)	Rh(2)-C(1)-O(1)	136.3 (7)	135.8 (11)
	123.1 (av)	126.2 (av)	Rh(3)-C(1)-O(1)	132.9 (6)	138.0 (11)
				134.6 (av)	136.9 (av)
			Rh(1)-C(1)-O(1)	127.2 (7)	
B. Distances and Bond Angles for the Cyclopentadienyl Rings					
	1	2		1	2
Rh(1)-C(1-1)	2.188 (8)	2.21 (2)	C(3-1)-C(3-2)	1.41 (1)	1.36 (2)
Rh(1)-C(1-2)	2.214 (8)	2.21 (1)	C(3-2)-C(3-3)	1.40 (1)	1.40 (3)
Rh(1)-C(1-3)	2.208 (8)	2.20 (2)	C(3-3)-C(3-4)	1.40 (1)	1.46 (3)
Rh(1)-C(1-4)	2.221 (8)	2.23 (2)	C(3-4)-C(3-5)	1.39 (1)	1.37 (3)
Rh(1)-C(1-5)	2.236 (9)	2.23 (2)	C(3-5)-C(3-1)	1.41 (1)	1.41 (2)
	2.213 (av)	2.22 (av)		1.40 (av)	1.40 (av)
Rh(2)-C(2-1)	2.231 (9)	2.18 (2)	C(1-1)-C(1-2)-C(1-3)	107.3 (8)	106.9 (13)
Rh(2)-C(2-2)	2.254 (9)	2.27 (2)	C(1-2)-C(1-3)-C(1-4)	108.6 (8)	110.0 (13)
Rh(2)-C(2-3)	2.267 (10)	2.23 (2)	C(1-3)-C(1-4)-C(1-5)	106.9 (8)	106.2 (13)
Rh(2)-C(2-4)	2.258 (9)	2.28 (1)	C(1-4)-C(1-5)-C(1-1)	108.3 (9)	108.8 (13)
Rh(2)-C(2-5)	2.224 (8)	2.22 (2)	C(1-5)-C(1-1)-C(1-2)	108.8 (9)	108.2 (13)
	2.247 (av)	2.24 (av)		108.0 (av)	108.0 (av)
Rh(3)-C(3-1)	2.266 (8)	2.27 (2)	C(2-1)-C(2-2)-C(2-3)	110.0 (9)	106.8 (21)
Rh(3)-C(3-2)	2.238 (9)	2.23 (2)	C(2-2)-C(2-3)-C(2-4)	107.9 (10)	108.5 (19)
Rh(3)-C(3-3)	2.236 (8)	2.22 (2)	C(2-3)-C(2-4)-C(2-5)	107.5 (9)	103.0 (16)
Rh(3)-C(3-4)	2.232 (8)	2.22 (2)	C(2-4)-C(2-5)-C(2-1)	108.4 (9)	109.3 (20)
Rh(3)-C(3-5)	2.257 (9)	2.24 (2)	C(2-5)-C(2-1)-C(2-2)	106.1 (9)	112.1 (22)
	2.246 (av)	2.24 (av)		108.0 (av)	107.9 (av)
C(1-1)-C(1-2)	1.39 (1)	1.45 (2)	C(3-1)-C(3-2)-C(3-3)	109.0 (9)	111.0 (19)
C(1-2)-C(1-3)	1.42 (1)	1.42 (2)	C(3-2)-C(3-3)-C(3-4)	107.1 (9)	105.0 (15)
C(1-3)-C(1-4)	1.41 (1)	1.44 (2)	C(3-3)-C(3-4)-C(3-5)	108.7 (9)	107.4 (18)
C(1-4)-C(1-5)	1.40 (1)	1.45 (2)	C(3-4)-C(3-5)-C(3-1)	108.6 (9)	109.1 (18)
C(1-5)-C(1-1)	1.41 (1)	1.42 (2)	C(3-5)-C(3-1)-C(3-2)	106.5 (10)	107.6 (17)
	1.41 (av)	1.44 (av)		108.0 (av)	108.0 (av)
C(2-1)-C(2-2)	1.41 (1)	1.39 (3)			
C(2-3)-C(2-3)	1.40 (1)	1.41 (3)			
C(2-3)-C(2-4)	1.41 (1)	1.45 (3)			
C(2-4)-C(2-5)	1.43 (1)	1.48 (3)			
C(2-5)-C(2-1)	1.43 (1)	1.31 (2)			
	1.42 (av)	1.41 (av)			
C. Distances and Bond Angles for the Acetylene Substituents					
	1	2		2	
C(4-1)-C(4-2)	1.39 (1)	1.37 (2)	C(4-2)-F(4-2)	1.36 (1)	
C(4-2)-C(4-3)	1.39 (1)	1.39 (2)	C(4-3)-F(4-3)	1.36 (2)	
C(4-3)-C(4-4)	1.37 (1)	1.32 (3)	C(4-4)-F(4-4)	1.37 (1)	
C(4-4)-C(4-5)	1.38 (1)	1.31 (2)	C(4-5)-F(4-5)	1.34 (1)	
C(4-5)-C(4-6)	1.40 (1)	1.39 (2)	C(4-6)-F(4-6)	1.35 (1)	

Table III (Continued)

## C. Distances and Bond Angles for the Acetylene Substituents (Continued)

	1	2		2
C(4-6)-C(4-1)	1.39 (1)	1.40 (2)		1.36 (av)
	1.39 (av)	1.36 (av)	C(5-2)-F(5-2)	1.34 (1)
C(5-1)-C(5-2)	1.38 (1)	1.41 (2)	C(5-3)-F(5-3)	1.35 (1)
C(5-2)-C(5-3)	1.39 (1)	1.39 (2)	C(5-4)-F(5-4)	1.35 (1)
C(5-3)-C(5-4)	1.37 (1)	1.28 (2)	C(5-5)-F(5-5)	1.35 (1)
C(5-4)-C(5-5)	1.37 (1)	1.37 (2)	C(5-6)-F(5-6)	1.33 (1)
C(5-5)-C(5-6)	1.37 (1)	1.39 (2)		1.34 (av)
C(5-6)-C(5-1)	1.40 (1)	1.38 (2)	F(4-2)-C(4-2)-C(4-1)	119.9 (11)
	1.38 (av)	1.37 (av)	F(4-2)-C(4-2)-C(4-3)	117.2 (11)
C(2)-C(4-1)-C(4-2)	121.7 (7)	126.0 (12)	F(4-3)-C(4-3)-C(4-2)	116.8 (12)
C(2)-C(4-1)-C(4-6)	121.1 (7)	120.4 (11)	F(4-3)-C(4-3)-C(4-4)	123.6 (13)
C(3)-C(5-1)-C(5-2)	121.3 (7)	124.2 (11)	F(4-4)-C(4-4)-C(4-3)	118.1 (12)
C(3)-C(5-1)-C(5-6)	121.9 (7)	121.5 (12)	F(4-4)-C(4-4)-C(4-5)	120.0 (12)
	121.5 (av)	123.0 (av)	F(4-5)-C(4-5)-C(4-4)	122.6 (13)
C(4-1)-C(4-2)-C(4-3)	121.8 (8)	122.9 (13)	F(4-5)-C(4-5)-C(4-6)	118.0 (12)
C(4-2)-C(4-3)-C(4-4)	121.2 (9)	119.6 (13)	F(4-6)-C(4-6)-C(4-5)	119.3 (12)
C(4-3)-C(4-4)-C(4-5)	118.6 (9)	121.9 (14)	F(4-6)-C(4-6)-C(4-1)	117.9 (11)
C(4-4)-C(4-5)-C(4-6)	120.7 (9)	119.3 (13)		119.3 (av)
C(4-5)-C(4-6)-C(4-1)	121.1 (8)	122.8 (12)	F(5-2)-C(5-2)-C(5-1)	120.4 (11)
C(4-6)-C(4-1)-C(4-2)	117.2 (7)	113.5 (13)	F(5-2)-C(5-2)-C(5-3)	118.1 (13)
	120.0 (av)	120.0 (av)	F(5-3)-C(5-3)-C(5-2)	115.8 (13)
C(5-1)-C(5-2)-C(5-3)	120.8 (8)	121.5 (13)	F(5-3)-C(5-3)-C(5-4)	122.4 (13)
C(5-2)-C(5-3)-C(5-4)	121.7 (8)	121.8 (15)	F(5-4)-C(5-4)-C(5-3)	122.2 (14)
C(5-3)-C(5-4)-C(5-5)	118.4 (8)	120.5 (14)	F(5-4)-C(5-4)-C(5-5)	117.4 (13)
C(5-4)-C(5-5)-C(5-6)	120.4 (8)	119.6 (13)	F(5-5)-C(5-5)-C(5-4)	122.1 (12)
C(5-5)-C(5-6)-C(5-1)	122.4 (8)	122.4 (13)	F(5-5)-C(5-5)-C(5-6)	118.2 (13)
C(5-6)-C(5-1)-C(5-2)	116.3 (7)	114.2 (12)	F(5-6)-C(5-6)-C(5-5)	118.3 (12)
	120.0 (av)	120.0 (av)	F(5-6)-C(5-6)-C(5-1)	119.3 (11)
				119.4 (av)

## D. Distances and Bond Angles for the Centrosymmetric Benzene Molecule of Cocrystallization with 1

C(6-1)-C(6-2)	1.36 (1)	C(6-3) <sup>b</sup> -C(6-1)-C(6-2)	122.0 (9)
C(6-2)-C(6-3)	1.39 (1)	C(6-1)-C(6-2)-C(6-3)	119.9 (9)
C(6-3)-C(6-1) <sup>b</sup>	1.40 (1)	C(6-2)-C(6-3)-C(6-1) <sup>b</sup>	118.1 (9)
	1.38 (av)		120.0 (av)

<sup>a</sup> Averaged in accord with assumed  $C_6$ - $m$  symmetry. <sup>b</sup>  $C(n-m)$  is related to  $C(n-m)$  by the center of symmetry at  $1/2, 0, 1/2$ .

bis(pentafluorophenyl)acetylene ligand with the O(1) atom being perpendicularly displaced by 0.034 Å out of the Rh(2)-C(1)-Rh(3) plane.

The triply bridging C(1)-O(1) distance of 1.19 (1) Å in 1 is comparable to the average values for the triply bridging carbonyls in a number of other metal clusters including  $\text{Rh}_6(\text{CO})_{16}$  (1.20 Å),<sup>22b</sup> the  $[\text{Rh}_6(\text{CO})_{15}\text{I}]^-$  monoanion (1.19 Å),<sup>22c</sup> the  $[\text{Rh}_7(\text{CO})_{16}]^{3-}$  trianion (1.19 Å),<sup>22d</sup> and the  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  dianion (1.19 Å).<sup>22e</sup> A qualitative bonding description of a carbonyl group linked to three metal atoms is given elsewhere.<sup>18a,25</sup>

The length of 1.22 (1) Å for the doubly bridging C(1)-O(1) bond in 2 is (from a statistical viewpoint) not significantly different from the above-mentioned length of 1.19 (1) Å for the triply bridging C(1)-O(1) bond in 1. In fact, the observed difference of 135  $\text{cm}^{-1}$  between their carbonyl stretching frequencies (vide supra) is in accord with the length for the doubly bridging carbonyl bond in 2 being actually *less* and *not greater* (as found) by ca. 0.02-0.03 Å than that for the triply bridging carbonyl bond in 1. The disparity may be attributed from crystallographic studies of related bridging carbonyl complexes to the determined C(1)-O(1) bond length of 1.22 (1) Å in 2 being too long by 0.05-0.06 Å; this error is not surprising for such bonds, especially since in 2 the carbonyl atoms were only refined with isotropic temperature factors.

(c) **The Olefinic-Like Acetylene Ligand.** The interaction of the acetylene ligand with the three metal atoms in 1 and 2 occurs through a deformation of the acetylene fragment to an olefinic-like coordinating group which as a four-electron-donor forms  $\sigma$  bonds with two metal atoms and a  $\mu$ -type

bond with the other metal atom. This type of trimetal-acetylene linkage was first uncovered by Dodge and Schomaker<sup>7b</sup> from their structural analysis of the violet isomer of the Hübner-Braye  $\text{Fe}_3(\text{CO})_8(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)_2$  molecule and was subsequently found from x-ray diffraction analyses of  $\text{Os}_3(\text{CO})_7(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5)_4$ <sup>9c</sup> and  $\text{Os}_3(\text{CO})_{10}(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)_2$ <sup>9e</sup>. In contrast to an approximate symmetrical olefinic-like coordination of each of the diphenylacetylene ligands to the two chemically equivalent iron atoms in the triiron cluster system,<sup>7b</sup> in each of the two above triosmium molecules the diphenylacetylene ligand is coordinated unsymmetrically to the osmium triangle. This highly unsymmetrical triosmium-acetylene linkage may be rationalized mainly on the basis of the nonequivalent nature of the three osmium atoms in each complex due to the other ligands. In addition, the relatively large esd's associated with the distances and bond angles involving the light atoms in these two osmium complexes preclude any meaningful comparison of their molecular parameters with those determined for 1 and 2.

As can be seen from Figures 1 and 4, both the orientations of the acetylene ligands with respect to the rhodium triangles and the conformations of the corresponding ring substituents are nearly identical in 1 and 2 in spite of their different crystal packing arrangements (i.e., Figures 2 and 3). This close geometrical similarity is also evident from a comparison of the corresponding distances and angles given in Table III and of the corresponding mean planes and their dihedral angles with other common planes presented in Table IV. The two olefinic-like carbon atoms, C(2) and C(3), and their attached carbon substituents, C(4-1) and C(5-1), are within 0.022 Å of coplanarity in 1 and within 0.003 Å of coplanarity in 2. All

Table IV. Equations of Least-Squares Planes<sup>a,b</sup>

(a) Equations of Mean Planes for Rh<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>(CO)(C<sub>6</sub>H<sub>5</sub>C<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) and Distances (Å) of Atoms from the Planes

	Plane A	Plane B	Plane C	Plane D	Plane E
Rh(1)	0	C(1-1) 0.018	C(2-1) 0.005	C(3-1) -0.002	C(4-1) 0.011
Rh(2)	0	C(1-2) -0.009	C(2-2) -0.008	C(3-2) 0.000	C(4-2) 0.004
Rh(3)	0	C(1-3) -0.003	C(2-3) 0.008	C(3-3) 0.003	C(4-3) -0.016
		C(1-4) 0.014	C(2-4) -0.005	C(3-4) -0.004	C(4-4) 0.011
		C(1-5) -0.020	C(2-5) 0.000	C(3-5) 0.004	C(4-5) 0.005
					C(4-6) -0.016
A <sup>h</sup>	0.202	-0.830	0.896	0.083	-0.898
B	0.880	-0.399	-0.420	-0.237	0.334
C	-0.430	-0.390	-0.145	-0.968	-0.285
D	-1.949	6.747	1.066	-3.156	2.960

	Plane F	Plane G	Plane H	Plane I	Benzene
C(5-1)	-0.010	Rh(2) 0.010	Rh(2)* 0.474	Rh(2) 0.001	C(6-1) -0.002
C(5-2)	0.010	Rh(3) -0.010	Rh(3)* 0.476	Rh(3) -0.001	C(6-2) 0.002
C(5-3)	-0.003	C(2) -0.019	C(2) -0.022	C(2)* -0.208	C(6-3) -0.002
C(5-4)	-0.004	C(3) 0.019	C(3) 0.021	C(3)* -0.161	C(6-1') <sup>c</sup> 0.002
C(5-5)	0.004	C(4-1)* 0.299	C(4-1) 0.010	C(4-1) -0.001	C(6-2') -0.002
C(5-6)	0.003	C(5-1)* 0.283	C(5-1) -0.009	C(5-1) 0.001	C(6-3') 0.002
A	0.832	-0.774	-0.811	-0.792	0.145
B	0.130	-0.577	-0.397	-0.514	0.281
C	-0.540	-0.261	-0.429	-0.330	-0.949
D	-2.925	2.887	3.157	2.826	4.740

(b) Angles (deg) between Planes and with Selected Vectors for Rh<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>(CO)(C<sub>6</sub>H<sub>5</sub>C<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sup>d,e</sup>

A/B	69.45	B/C	59.70	C/E	82.96	A/G	56.52	G/H	14.31
A/C	82.78	B/D	66.21	C/F	55.91	A/H	70.82	J/K	89.04
A/D	77.02	B/E	43.66	D/E	25.34	A/I	61.97	J/L	2.15
A/E	76.40	B/F	57.89	D/F	39.73	A/K	2.47	J/M	2.12
A/F	59.03	C/D	71.69	E/F	56.64	I/AB	24.73	L/M	2.27

(c) Equations of Mean Planes for Rh<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>(CO)(C<sub>6</sub>F<sub>5</sub>C<sub>2</sub>C<sub>6</sub>F<sub>5</sub>) and Distances (Å) of Atoms from the Planes

	Plane N	Plane O	Plane P	Plane Q	Plane R
Rh(1)	0	C(1-1) -0.004	C(2-1) -0.024	C(3-1) 0.004	C(4-1) -0.004
Rh(2)	0	C(1-2) 0.002	C(2-2) 0.034	C(3-2) -0.002	C(4-2) 0.007
Rh(3)	0	C(1-3) 0.001	C(2-3) -0.031	C(3-3) -0.001	C(4-3) -0.007
C(1)*	0.651	C(1-4) -0.003	C(2-4) 0.016	C(3-4) 0.003	C(4-4) 0.004
O(1)*	1.173	C(1-5) 0.004	C(2-5) 0.004	C(3-5) -0.004	C(4-5) -0.002
					C(4-6) 0.002
					C(2)* -0.108
					F(4-2)* 0.045
					F(4-3)* 0.025
					F(4-4)* -0.005
					F(4-5)* 0.030
					F(4-6)* 0.035
A	0.073	-0.390	-0.616	0.894	-0.369
B	0.179	0.847	-0.505	0.307	-0.814
C	-0.981	-0.361	-0.605	-0.327	-0.449
D	2.961	-1.047	0.769	-4.884	2.772

	Plane S	Plane T	Plane U	Plane V	Plane W
C(5-1)	0.014	C(3)* 0.010	Rh(1)* -1.010	Rh(2) -0.002	Rh(2)* -0.587
C(5-2)	-0.014	F(5-2)* -0.034	Rh(2) 0	Rh(3) 0.002	Rh(3)* -0.550
C(5-3)	0.006	F(5-3)* -0.006	Rh(3) 0	C(2) 0.004	C(2) -0.003
C(5-4)	0.001	F(5-4)* -0.018	C(1) 0	C(3) -0.004	C(3) 0.003
C(5-5)	0.000	F(5-5)* -0.070	O(1)* 0.036	C(4-1)* -0.348	C(4-1) 0.002
C(5-6)	-0.008	F(5-6)* -0.044		C(5-1)* -0.391	C(5-1) -0.002
					C(2)* -0.012
					Rh(3) 0.012
					C(2)* 0.226
					C(3)* 0.227
					C(4-1) 0.010
					C(5-1) -0.010
A	0.670	0.291	-0.370	-0.443	-0.401
B	0.609	-0.231	0.813	0.881	0.850
C	-0.425	-0.928	-0.449	-0.167	-0.342
D	-0.449	1.920	-2.961	1.755	2.732

(d) Angles (deg) between Planes and with Selected Vectors for Rh<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>(CO)(C<sub>6</sub>F<sub>5</sub>C<sub>2</sub>C<sub>6</sub>F<sub>5</sub>)<sup>e-g</sup>

N/O	61.50	O/P	88.25	P/R	24.57	N/U	55.98	T/V	79.79
N/P	62.71	O/Q	88.31	P/S	62.47	N/V	73.17	U/V	17.20
N/Q	63.87	O/R	67.41	Q/R	64.36	N/W	62.74	X/Y	91.14
N/R	74.45	O/S	65.91	Q/S	22.41	N/Y	88.29	X/Z	0.68
N/S	54.90	P/Q	79.48	R/S	56.32	T/U	83.02	X/BA	0.89
				N/T	27.04	W/BB	41.08	Z/BA	0.74

<sup>a</sup> The equation of each plane is in the form  $AX + BY + CZ + D = 0$ . An asterisk indicates an atom not included in the least-squares calculation. Unit weights were used for all atoms in the application of the Smith least-squares planes program.<sup>14i</sup> <sup>b</sup> The equations of the planes are given in an orthogonal angstrom coordinate system ( $X, Y, Z$ ) which is related to the monoclinic fractional unit cell coordinate system ( $x, y, z$ ) by the transformation  $X = ax + cz \cos \beta$ ,  $y = by$ , and  $Z = cz \sin \beta$ . <sup>c</sup> C(6- $n'$ ) is related to C(6- $n$ ) by the center of symmetry located at  $1/2, 0, 1/2$ . <sup>d</sup> Vectors J, K, L, M, and AB are between Rh(2) and Rh(3), between C(1) and O(1), between C(2) and C(3), between C(4-1) and C(5-1), and from Rh(1) to the midpoint of C(2) and C(3), respectively. <sup>e</sup> Where given, angles are between vectors and the normal to the indicated plane. <sup>f</sup> Vectors X, Y, Z, BA, and BB are between Rh(2) and Rh(3), between C(1) and O(1), between C(2) and C(3), between C(4-1) and C(5-1), and from Rh(1) to the midpoint of C(2) and C(3), respectively. <sup>g</sup> Dihedral angles between each mean plane containing phenyl ring carbon atoms and the corresponding one containing both carbon and fluorine atoms are less than 0.5°. <sup>h</sup> A, B, C, and D are coefficients in the plane equation. See footnote a.



of the carbon atoms in each phenyl or pentafluorophenyl ring are coplanar within 0.020 Å except for  $\text{C}_5\text{H}_5(2)$  in **2** where they are within 0.034 Å; the perpendicular displacements of the fluorine atoms out of the mean carbon plane in each pentafluorophenyl ring in **2** were found to be considerably larger—viz., up to 0.045 Å in  $\text{C}_6\text{F}_5(4)$  and 0.070 Å in  $\text{C}_6\text{F}_5(5)$ . The very similar mode of attachment of the acetylene ligand to the rhodium triangle in **1** and **2** is revealed from the dihedral angles between the trirhodium plane and the mean {C(4-1), C(2), C(3), C(5-1)} and mean {C(2), Rh(2), Rh(3), C(3)} planes being 70.8° and 56.5°, respectively, in **1** compared to 73.2° and 56.0°, respectively, in **2**. The dihedral angle between these latter two planes is 14.3° in **1** and 17.2° in **2**. Analogous orientations of the corresponding  $\text{C}_6\text{H}_5$  and  $\text{C}_6\text{F}_5$  rings with respect to the rhodium triangle in **1** and **2** are shown from the similar dihedral angles of 76.4° vs. 74.5° for one pair and 59.9° vs. 45.9° for the other pair. Furthermore, the dihedral angles between the two rings in each complex are almost identical, being 56.6° in **1** and 56.3° in **2**.

The only possibly distinguishing structural feature between the common  $\text{Rh}_3(\text{CC}_2\text{C})$  fragment of approximate  $\text{C}_s$ - $m$  symmetry<sup>26</sup> in **1** and **2** is that the Rh(1)–C(2) and Rh(1)–C(3) distances of 2.110 (7) and 2.154 (8) Å, respectively, in **1** are longer (on the edge of statistical significance) than the corresponding ones of identical value 2.09 (1) Å in **2**. Both molecules have an identical mean of 2.03 Å for the Rh(2)–C(2) and Rh(3)–C(3) bond lengths, and the C(2)–C(3) bond length of 1.39 (1) Å in **1** is not significantly shorter than that of 1.41 (1) Å in **2**. These latter distances, which are significantly longer than a normal double-bond length of 1.33 Å for an uncoordinated olefin, are not unlike the corresponding iron-coordinated olefinic distances of 1.38 (3) and 1.40 (3) Å determined<sup>7b</sup> for the two structurally analogous diphenylacetylene ligands in the violet form of the  $\text{Fe}_3(\text{CO})_8(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)_2$  molecule. The olefinic-like complexation of the acetylene ligand to Rh(1) in both **1** and **2** also results in the four atoms (viz., Rh(2), Rh(3), C(4-1), and C(5-1)) attached to the olefinic C(2) and C(3) atoms being significantly bent away from Rh(1). This is indicated from the perpendicular displacement of C(2) and C(3) by 0.21 and 0.16 Å in **1** and by 0.23 and 0.23 Å in **2** from the mean plane formed by Rh(2), Rh(3), C(4-1), and C(5-1). This deformation of the presumed planar  $\sigma$  framework of the olefinic system may be attributed to the interaction between the olefinic bond and Rh(1) which causes an unsymmetrical charge distribution, thereby destroying the geometrical constraints which the olefinic double bond places upon attached substituents.

If the direction of the  $\pi$ -like orbitals of the olefin is presumed to be represented by the normal of the best plane comprised of Rh(2), Rh(3), C(4-1), and C(5-1), the angle of 25° formed by this normal and the line from Rh(1) to the center of the olefinic bond, C(2)–C(3), indicates that the  $\pi$ - and  $\pi^*$ -like olefin orbitals of the diphenylacetylene ligand in **1** do not point directly at Rh(1); in **2** the much larger corresponding angle of 41° indicates that the  $\pi$ - and  $\pi^*$ -like olefin orbitals of the bis(pentafluorophenyl)acetylene ligand in **2** would form highly bent bonds with the appropriate d orbitals of Rh(1). It must be emphasized that this localized representation of the trimetal–acetylene interaction as an olefin-to-trimetal ( $2\sigma + \mu$ )-type linkage is intended only for conceptual convenience and that the four electrons contributed by the acetylene ligand are presumably delocalized over all three metal atoms.

**Stereochemistry and Bonding Implications for  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{RC}_2\text{R}')$  Complexes.** The mode of carbonyl bridging in  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{RC}_2\text{R}')$  complexes falls into two different categories; the carbonyl ligand is either coordinated to Rh(1) as a face-bridging group in **1** or not coordinated

to Rh(1) as a doubly bridging group in **2**. This change in the mode of carbonyl bridging in **1** and **2** may be rationalized from the different electronic effects imposed by the  $\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5$  ligand in **1** vs. the  $\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5$  ligand in **2** in their competition with the carbonyl ligand for charge-density donation from Rh(1) via back-bonding. From an energetic viewpoint, it is expected for a triply bridging carbonyl group C(1)–O(1) that an increase in  $d[\text{Rh}(1)] \rightarrow \pi^*[\text{CO}]$  back-bonding will produce a larger Rh(1)–C(1) bonding interaction and hence a shorter Rh(1)–C(1) distance, which in turn will lead to a smaller C–O bonding interaction in harmony with a longer C–O bond length and lower carbonyl frequency (or force constant).<sup>27,28</sup> This latter trend is attributed to an overall increase in  $\pi^*[\text{CO}]$  population at a smaller Rh(1)–C(1) distance as a consequence of more overall back-bonding from the three rhodium atoms. At the same time, such an increase in the Rh(1)–C(1) interaction upon formation of a more symmetrical triply bridging carbonyl group should also decrease the overall  $5\sigma[\text{CO}]$  population (due to a greater net bonding interaction with three rhodium atoms) which per se would give rise to the opposite trend of a larger C–O bond order and hence a higher carbonyl frequency.<sup>27,28</sup> The available experimental data clearly support the premise that the electronic  $\pi^*[\text{CO}]$  effect dominates over the  $5\sigma[\text{CO}]$  effect upon a change from a doubly bridging toward a symmetrical triply bridging carbonyl group.

On the basis that the particular geometry adopted by a  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{RC}_2\text{R}')$  complex is dictated primarily from electronic effects, it is expected from orbital energetics alone that a replacement of the olefinic-like  $\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5$  ligand with a  $\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5$  ligand should result in an energy lowering of both the  $\pi[\text{olefin}]$  and  $\pi^*[\text{olefin}]$  levels relative to the  $4d[\text{Rh}]$  levels such that the higher energy  $\pi^*[\text{olefin}]$  level is drawn closer to the  $4d[\text{Rh}]$  levels while the lower energy  $\pi[\text{olefin}]$  level is drawn away. The net effect would be that the  $\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5$  ligand would be a weaker donor of its electrons to Rh(1) but a much stronger  $\pi$  acceptor from Rh(1) than the  $\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5$  ligand. It follows that the relatively better  $\pi$ -donor and poorer  $\pi^*$ -back-bonding interaction of the  $\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5$  ligand with Rh(1) in comparison with that of the  $\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5$  ligand apparently allows the carbonyl ligand to compete effectively in back-bonding from the Rh(1), whereas in the case of the  $\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5$  ligand the charge is sufficiently delocalized from the Rh(1) to the lower energy  $\pi^*[\text{olefin}]$  orbital to render unstable the Rh(1)–CO bond in favor of the observed geometry in **2**.

As the energy of the  $\pi^*[\text{olefin}]$  orbital of the  $\text{RC}_2\text{R}'$  ligand approaches more closely that of the  $4d[\text{Rh}(1)]$  orbitals, shorter Rh(1)–C(2) and Rh(1)–C(3) distances due to their larger bonding character and a longer C(2)–C(3) bond length due to its larger antibonding character are anticipated. These expectations are in harmony with the Rh(1)–C bond-length trend observed for the  $\text{C}_6\text{F}_5\text{C}_2\text{C}_6\text{F}_5$  ligand in **2** compared to that for the  $\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5$  ligand in **1** (vide supra) in that the Rh(1)–C(2) and Rh(1)–C(3) bond lengths of 2.09 Å (average) in **2** are 0.04 Å shorter than those of 2.13 Å (average) in **1**. The 0.025-Å difference between the C(2)–C(3) bond lengths in **1** and **2** is also in the right direction, although not statistically significant.

This qualitative rationale that the extent or lack of interaction of the carbonyl ligand with Rh(1) in  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{RC}_2\text{R}')$  complexes is determined mainly by the competitive extent of  $d[\text{Rh}(1)] \rightarrow \pi^*[\text{olefin}]$  vs.  $d[\text{Rh}(1)] \rightarrow \pi^*[\text{CO}]$  back-bonding is compatible with the carbonyl frequencies reported for the subsequently prepared bis(pentafluorophenyl)acetylene,<sup>29</sup> bis(trifluoromethyl)acetylene,<sup>30</sup> and pentachlorophenylphenylacetylene<sup>29</sup> homologues. The first molecule with the relatively strong electron-withdrawing

substituents ( $R = R' = C_6Cl_5$ ) has a carbonyl band at  $1810\text{ cm}^{-1}$  (identical with that observed in **2**) consistent with the doubly bridging carbonyl structure found in **2**, while the last two molecules with weaker electron-withdrawing substituents ( $R = R' = CF_3$  and  $R = C_6Cl_5$ ,  $R' = C_6H_5$ ) possess carbonyl bands at  $1710$  and  $1680\text{ cm}^{-1}$ , respectively, in accord with the triply bridging carbonyl structure exemplified in **1**.<sup>31-33</sup> Of course, it is expected that the two mixed acetylene substituents in the latter molecule will produce unsymmetrical acetylene and carbonyl linkages to the normally equivalent Rh(2) and Rh(3) atoms.

It is reasonable to assume for this family of  $Rh_3(\eta^5-C_5H_5)_3(CO)(RC_2R')$  complexes in which the total molecular environment is assumed to depend only on the nature of the acetylene R and R' substituents (i.e., crystal packing forces are not considered to be a main factor) that the minimization of the total molecular energy, which determines which geometry is preferred for a given pair of substituents, is influenced particularly by the energy of the highest occupied molecular orbital (HOMO) resulting from its composition due to the electron distribution within the carbonyl and acetylene ligands.

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**Registry No.** **1**:  $1^1/2C_6H_6$ , 60840-37-1; **2**, 12679-42-4.

**Supplementary Material Available:** Listings of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

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- (27) Molecular orbital calculations<sup>28</sup> have shown that only three carbon monoxide MO's possess the appropriate symmetry and energy to interact strongly with the valence metal orbitals—viz., the highest occupied MO (HOMO) of representation  $5\sigma$ , which is an electron-pair donor orbital, and the two lowest unoccupied doubly degenerate MO's (LUMO's) of  $\pi^*$  (or  $2\pi^*$ ) representation, which form partial  $\pi$  bonds by back-donation from the filled metal d orbitals. The fact that the overlap populations show that the  $5\sigma$  and  $2\pi^*$  MO's of carbon monoxide are both antibonding in character results<sup>28</sup> in a strengthening of the C—O bond upon increased electron donation from the  $5\sigma$  orbital to the metal but in a weakening of the C—O bond upon increased back-bonding of electron density from the metal to the  $\pi^*$  orbitals.
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## Crystal Structures of Aquotris(salicylato)samarium(III) and Aquotris(salicylato)americium(III)<sup>1</sup>

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Two isostructural compounds  $(C_7H_5O_3)_3Sm \cdot H_2O$  and  $(C_7H_5O_3)_3Am \cdot H_2O$  are monoclinic, space group  $P2_1/c$ , and have unit-cell dimensions:  $a = 13.641$  (3) Å,  $b = 6.752$  (1) Å,  $c = 24.202$  (7) Å,  $\beta = 113.24$  (2)° and  $a = 13.69$  (2) Å,  $b = 6.762$  (2) Å,  $c = 24.14$  (1) Å,  $\beta = 112.89$  (5)°, respectively;  $Z = 4$ . Heavy-atom methods were used to determine the structure from x-ray diffraction data. Refinement of parameters by least-squares methods was carried out using 3280 observations on the Sm compound and 1401 on the Am. The  $R_F$  values obtained were 0.037 and 0.055 for the two refinements. There are no discrete molecules of the complex in the crystal; instead each metal ion is linked to six different salicylato ions through a variety of dentation modes in which both the carboxylate and phenolic oxygen atoms participate. Cross-linking of metal ions produces endless chains along the  $b$  axis and only van der Waals contacts exist between the chains. A total of eight oxygen atoms from the salicylato ligands plus one from a water molecule comprise the metal coordination. There is also evidence for some hydrogen bonding among the ligands. The bonding pattern within the salicylato ions is the same for all three independent ligands. It is characterized by equivalence of bond lengths to carboxylate oxygen atoms, by distortion of the benzene ring from hexagonal symmetry, by a short C-C bond to the carboxyl group, and by a short C-O bond to the hydroxyl group. Except for the carboxyl group, which is ionized, the molecular shape is the same as for salicylic acid. Analogous compounds containing La and Nd were shown to have this structure also.

### Introduction

Previous work with salicylato complexes of trivalent lanthanides and actinides has been concerned with their formation in solution, their stability constants, and their solubility products. The first solid compounds of the type being considered here were obtained<sup>2,3</sup> from slightly acid solutions and were assigned the formula  $(C_7H_5O_3)_3La \cdot 1.5H_2O$  and  $(C_7H_5O_3)_3Pu \cdot 1.5H_2O$ . Later studies<sup>4,5</sup> showed that, in slightly basic solutions, two-thirds of the phenolic H atoms could be ionized from the ligands and two complex compounds involving the divalent salicylato ion were made:  $NaLa(C_7H_4O_3)(C_7H_5O_3)_2$  and  $NaLa(C_7H_4O_3)_2$ . Solution studies<sup>6,7</sup> of  $Nd^{3+}$  ions with salicylato (*o*-hydroxybenzoate) and *p*-hydroxybenzoate ions showed differences in solubility which were attributed, respectively, to cyclic and linear attachment of the ligands. A recent study<sup>8</sup> of the stability constants of salicylato complexes of several lanthanide elements assumes that there are no polynuclear species in solution. An understanding of all these observations should be enhanced by knowledge of the structure of the complex molecule and we undertook the determination described here for this purpose.

The study of complexation of lanthanide and actinide elements by salicylato ions is important also because the bonding in such complexes can serve as a very simple model for the interaction of these elements with humic materials in the natural environment. These materials are products of plant decomposition and are characterized chemically as complex polymers containing benzene rings with varying numbers of carboxyl and hydroxyl groups attached in a wide variety of combinations.<sup>9</sup> The salicylato ion,  $(C_7H_5O_3)^-$ , contains both the carboxylic and hydroxy functional groups, and complexes

with it must show bonding typical of the more complicated, natural materials.

Only a few crystal structures containing the salicylato ion have been determined. In all of these the metal is copper; in two cases the salicylato ion is linked to it through the carboxyl group, one<sup>10</sup> in monodentate and one<sup>11</sup> in bidentate fashion; in the third<sup>12</sup> some ions are linked to (different) metal ions by both the carboxylic and phenolic O atoms. A precise description of the structure of salicylic acid itself is available also.<sup>13</sup>

### Experimental Section

**Preparation of Compounds.** Aquotris(salicylato)samarium(III) was made by reaction of  $SmCl_3$  and  $Na(C_7H_5O_3)$  in aqueous ethanol. To increase crystal size of the product the components were allowed to diffuse together through a separate layer of aqueous ethanol. Colorless needles up to several millimeters in length were obtained. Analysis for salicylate was carried out by converting the ion to salicylic acid on a Dowex 50 resin column, eluting with 1:1 aqueous ethanol, and titrating the eluate with standard base. The equivalent weight found was 187.5; that calculated for  $(C_7H_5O_3)_3Sm \cdot H_2O$  is 193.2.

Aquotris(salicylato)americium(III) was made by diffusion together of aqueous solutions of  $Na(C_7H_5O_3)$  and  $Am(NO_3)_3$  over a period of a few days. The latter solution was prepared from  $^{243}AmO_2$  by dissolution in concentrated  $HNO_3$ . Pale yellow-pink needles were formed. No elemental analysis was done because the x-ray diffraction pattern showed isomorphism with the Sm analogue.

Aquotris(salicylato)lanthanum(III) was prepared in the manner described by Zvyagintsev and Sudarikov.<sup>2</sup> At a pH between 3 and 7,  $La(NO_3)_3$  and  $Na(C_7H_5O_3)$  were mixed to yield fine, white needles of the compound. No attempt was made at increasing crystal size because these were adequate for identification purposes.

Aquotris(salicylato)neodymium(III) was made as pale violet crystals by diffusing together neutral solutions of  $NdCl_3$  and  $Na(C_7H_5O_3)$ .