Acknowledgment. This work was supported in part by the U.S. National Science Foundation under Grant DMR 810-2940 and by the Center for Computer and Information Services of Rutgers University for the computational aspects of the study. This support is herewith gratefully acknowledged. We are also indebted to detailed discussions with Profs. G. Alonzo and R. Barbieri and Mr. J. E. Phillips concerning the bonding implications of the Mössbauer data presented in this work.

Registry No. I, 66585-96-4; II, 87333-59-3; III, 82112-71-8; IV, 88375-64-8; V, 88376-10-7; VI, 88326-03-8; VII, 88326-04-9; VIII, 88375-65-9; IX, 82094-65-3.

Synthesis and Spectra of $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$ and $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$. Crystal Structure of $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$

Leh-Yeh Hsu,, Wen-Liang Hsu, Deng-Yang Jan, Alan G. Marshall,* and Sheldon G. Shore*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

Received September 21, 1983

From the reaction of $H_2Os_3(CO)_{10}$ with $(\eta^5\text{-}C_5H_5)Rh(CO)_2$, the trinuclear cluster $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$ and the tetranuclear cluster $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$ have been obtained in 45% and 42% yields, respectively. The crystal structure of $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$ has been determined. Crystal parameters: space group $P\bar{1}$ (C_i^1, No. 2), $a = 9.128$ (2) Å, $b = 13.077$ (3) Å, $c = 8.224$ (2) Å, $\alpha = 106.94$ (2)°, $\beta = 113.51$ (2)°, $\gamma = 80.95$ (2)°, $V = 860.1$ (4) Å^3, $Z = 2$, mol wt = 800.5, $\rho_{\text{calcd}} = 3.090$ g cm^{-3}, $\mu_{\text{calcd}} = 157.37$ cm^{-1} for Mo Kα. The structural analysis is based upon 4497 independent reflections with $I > 3.0\sigma(I)$ collected on a CAD4 diffractometer at −80 °C over the range $4° \leq 2\theta \leq 60°$. Final $R_F = 0.057$ and $R_{wF} = 0.073$. In the crystalline state $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$ has approximate C_s symmetry. The molecule consists of an Os_2Rh triangle with four terminal CO groups bound to each Os atom and a terminal CO and a $\eta^5\text{-}C_5H_5$ group bound to the Rh atom. Carbon-13 NMR spectra in solution are consistent with the solid-state structure. The tetranuclear cluster $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$ was identified by means of FT-ICR mass spectrometry. It produces IR and NMR (^1H and ^{13}C) spectra that correspond very well to the solution spectra of the isoelectronic analogue $H_2(\eta^5\text{-}C_5H_5)CoOs_3(CO)_{10}$. These compounds are probably isostructural.

Introduction

Through the reaction of the electronically unsaturated cluster $H_2Os_3(CO)_{10}$ with metal carbonyls, we have prepared a number of new tetranuclear bimetallic clusters that contain an Os_3[1,2] unit. Among the compounds prepared in this way is $H_2(\eta^5\text{-}C_5H_5)CoOs_3(CO)_{10}$ which was obtained as the only identified product from reaction 1 in toluene.

$$H_2Os_3(CO)_{10} + (\eta^5\text{-}C_5H_5)Co(CO)_2 \xrightarrow{90\ °C} H_2(\eta^5\text{-}C_5H_5)CoOs_3(CO)_{10} \quad (1)$$

In the present investigation we have examined the analogous reaction between $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ with $H_2Os_3(CO)_{10}$. In this case not only was the tetranuclear cluster $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$ obtained (42% yield)[2] but also the trinuclear compound $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$ was also produced (45% yield). The preparation and spectra of these compounds and the crystal structure of $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$ are described and discussed below.

Experimental Section

Preparation of $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$ and $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$. The starting materials $H_2Os_3(CO)_{10}$[3] and $(\eta^5\text{-}C_5H_5)Rh(CO)_2$[4] were prepared according to published methods. Toluene was distilled from CaH_2 before use.

Both $H_2Os_3(CO)_{10}$ (130 mg, 0.15 mmol) and $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ (100 mg, 0.45 mmol) were placed in a 50-mL flask containing 20 mL of toluene. After the system was degassed, the mixture was stirred under vacuum at 90 °C for 3 days. A TLC spot check at this time indicated the complete consumption of $H_2Os_3(CO)_{10}$. Then toluene was removed under reduced pressure at room temperature on a rotary evaporator to leave a reddish brown residue. The residue was dissolved in a minimum amount of CH_2Cl_2 and chromatographed on a thin-layer plate (2 mm silica gel). Elution with 1:4 benzene/hexane gave four bands. In order of decreasing R values, the bands were orange, brownish green, pink, and brown. The last two bands were not characterized due to the small quantities available.

The orange band was identified as $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$ (55 mg, 45% yield based on $H_2Os_3(CO)_{10}$) from a single-crystal X-ray structure determination. Single crystals of $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$ were obtained by crystallization from CH_2Cl_2/hexane at −15 °C: IR $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$ in cyclohexane (ν_{CO}) 2095 (m), 2051 (s), 2020 (s), 1998 (m-w), 1968 (w) cm^{-1}.

The brownish green band was identified as $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$ (60 mg, 42% yield based on $H_2Os_3(CO)_{10}$) from an analysis of its FT-ICR mass spectrum and comparison of its IR spectrum with that of $H_2(\eta^5\text{-}C_5H_5)CoOs_3(CO)_{10}$:[1] IR ($H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$ in cyclohexane (ν_{CO}) 2085 (m), 2063 (vs), 2042 (vs), 2010 (vs), 2000 (s(sh)), 1982 (m), 1972 (m), 1819 (m) cm^{-1}.

Infrared and NMR Spectra. Infrared spectra of solutions in matched cells were recorded on a Perkin-Elmer 457 spectrometer and were calibrated by using polystyrene as a standard. Proton and carbon-13 NMR spectra were obtained on a Bruker WH-300 spectrometer at 300.13 and 75.4 mHz, respectively. Chemical shifts are referred to $Si(CH_3)_4$ (^1H, τ 10.00; δ (^{13}C) 0.00).

Carbon-13 enriched samples of $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$ and $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$ for ^{13}C NMR spectra were prepared from enriched $H_2Os_3(CO)_{10}$ (ca. 25% ^{13}C) using the preparative procedures described above. A known amount of $Os_3(CO)_{12}$ was enriched by stirring it in refluxing toluene under a known amount

---

[1] Plotkin, J. S.; Alway, D. G.; Weisenberger, C. R.; Shore, S. G. *J. Am. Chem. Soc.* **1980**, *102*, 6157.

[2] Shore, S. G.; Hsu; W.-L., Weisenberger, C. R.; Caste, M. L.; Churchill, M. R.; Bueno, C. *Organometallics* **1982**, *1*, 1405.

[3] Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3942.

[4] Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 2158.

0276-7333/84/2303-0591$01.50/0

Table I. Positional Parameters of Non-Hydrogen Atoms

atom	*x*	*y*	*z*
Os(1)	0.10714 (3)	0.18130 (3)	0.39588 (4)
Os(2)	0.35686 (3)	0.18141 (2)	0.27169 (4)
Rh	0.29763 (8)	0.35658 (5)	0.52711 (8)
O	0.055 (1)	0.4611 (7)	0.249 (1)
O(11)	−0.1315 (8)	0.2472 (7)	0.0469 (9)
O(12)	0.3383 (9)	0.1064 (7)	0.7367 (9)
O(13)	0.002 (1)	−0.0488 (7)	0.228 (1)
O(14)	−0.1233 (9)	0.279 (1)	0.594 (1)
O(21)	0.1296 (9)	0.2790 (7)	−0.0447 (9)
O(22)	0.6035 (9)	0.1076 (6)	0.6075 (9)
O(23)	0.327 (1)	−0.0427 (6)	0.019 (1)
O(24)	0.6240 (8)	0.2578 (6)	0.2160 (9)
C	0.148 (1)	0.4171 (8)	0.350 (1)
C(1)	0.345 (1)	0.4072 (9)	0.827 (1)
C(2)	0.343 (1)	0.4973 (8)	0.768 (1)
C(3)	0.473 (1)	0.4839 (8)	0.705 (1)
C(4)	0.555 (1)	0.384 (1)	0.731 (1)
C(5)	0.471 (2)	0.3362 (9)	0.804 (1)
C(11)	−0.039 (1)	0.2247 (8)	0.178 (1)
C(12)	0.258 (1)	0.1378 (8)	0.610 (1)
C(13)	0.038 (1)	0.0374 (8)	0.287 (1)
C(14)	−0.037 (1)	0.241 (1)	0.519 (1)
C(21)	0.210 (1)	0.2440 (8)	0.078 (1)
C(22)	0.508 (1)	0.1351 (7)	0.485 (1)
C(23)	0.337 (1)	0.0392 (7)	0.110 (1)
C(24)	0.531 (1)	0.2303 (7)	0.240 (1)

of CO (95% ^{13}C, 1 atm pressure) for 4 days at 110 °C. Extent of ^{13}CO enrichment of the $Os_3(CO)_{12}$ was determined by mass spectral comparison of the ^{13}C content of the residual CO gas above the solution with that of the original CO gas. The enriched $Os_3(CO)_{12}$ was then converted into $H_2Os_3(CO)_{10}$.

Crystal Structure Determination of (η^5-C_5H_5)$RhOs_2(CO)_9$. A prismatic specimen of approximate dimensions 0.40 × 0.35 × 0.2 mm was mounted on the tip of a thin glass fiber for X-ray examination and data collection. All data were collected on a CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Unit cell paramters were obtained by least-squares refinement of the angular settings from 25 reflections, well distributed in reciprocal space and lying in a 2θ range of 15–30°. Crystal parameters: space group $P\bar{1}$ (C_i^1, No. 2), a = 9.128 (2) Å, b = 13.077 (3) Å, c = 8.224 (2) Å, α = 106.94 (2)°, β = 113.51 (2)°, γ = 80.95 (2)°, V = 860.1(4) Å^3, Z = 2, mol wt 800.5, ρ_{calcd} = 3.090 g cm^{-3}, μ_{calcd} = 157.37 cm^{-1} for Mo Kα radiation. Intensity data were collected in the ω–2θ scan mode with a 2θ range of 4–60°. Six standard reflections were monitored and showed no significant decay. The data were corrected for Lorentz and polarization effects. An absorption correction was also applied on the basis of the Gaussian integration formula with grid 10 × 4 × 12 points. The maximum and minimum transmission coefficients are 0.125 and 0.028, respectively. All crystallographic computations were carried out by using the "Structure Determination Package" (SDP).[5]

Statistical distributions of reflection intensities indicated that the space group is likely to be centrosymmetric, $P\bar{1}$, rather than noncentric $P1$. Furthermore, the three-dimensional Patterson synthesis also suggests that the true space group is $P\bar{1}$. Therefore, there is one molecule per asymmetric unit. Of a total of 5895 reflections measured, 4497 independent reflections with intensities $I \geq 3.0\sigma(I)$ were used in the structure refinement.

The structure was solved by a combination of Patterson and Fourier synthesis techniques. Analytical atomic scattering factors were used throughout the structure refinement with both the real and imaginary components of anomalous dispersion included for all atoms. The positions of the two Os atoms and the Rh atom were determined from the Patterson function. Then, the positions of the oxygen and carbon atoms were determined from a Fourier synthesis, which was phased on the three metal atoms. The coordinates of hydrogens in the cyclopentadienyl ring were calculated with d(C–H) = 0.95 Å and B(H) = 4.0 Å^2. Full-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$ was carried out by using anisotropic thermal parameters. The weights were taken as $w = [\sigma(I)^2 + (kI)^2]^{-1/2}$ where k = 0.06 was chosen to make $w\Delta F^2$ uniformly distributed in $|F_o|$. The full-matrix least-squares refinement for all non-hydrogen atoms converged with $R_F = \sum||F_o| - |F_c|| / \sum|F_o|$ and $R_{wF} = \sum w^{1/2}||F_o| - |F_c|| / \sum w^{1/2}|F_o|$ equal to 0.057 and 0.073, respectively, and GOF = 2.00. Final atomic positional parameters for non-hydrogen atoms are given in Table I.

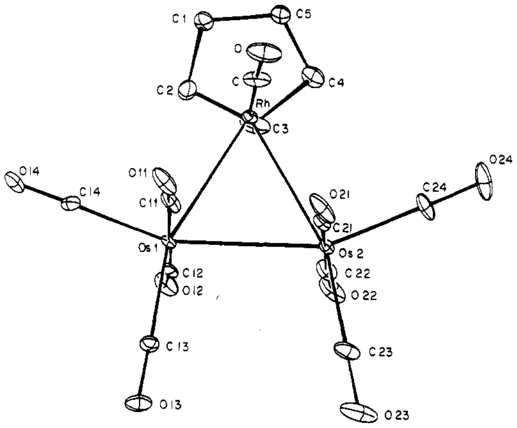

Figure 1. Geometry and labeling of atoms for the (η^5-C_5H_5)$RhOs_2(CO)_9$ molecule (ORTEP-II diagram: 20% probability ellipsoids).

Mass Spectrum of H_2(η^5-C_5H_5)$RhOs_3(CO)_{10}$. Useful mass spectra of H_2(η^5-C_5H_5)$RhOs_3(CO)_{10}$ could not be obtained as a probe sample on a conventional double-focusing instrument (Kratos MS-30). Raising the probe temperature to give sufficient vapor pressure for observation of high-mass peaks resulted in pyrolytic fragmentation. Furthermore, in order to scan above m/z 600, it was necessary to cut the accelerating voltage in half (thereby reducing signal-to-noise ratio by a factor of 4). Because Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry[6,7] typically requires about 1000-fold lower sample pressure than conventional mass spectrometry (e.g., ca. 10^{-8} vs. 10^{-5} torr), FT-ICR was chosen for mass analysis.[8]

Results and Discussion

The clusters H_2(η^5-C_5H_5)$RhOs_3(CO)_{10}$ and (η^5-C_5H_5)$RhOs_2(CO)_9$ were obtained from reaction 2 in toluene at 90 °C by using a threefold excess of (η^5-C_5H_5)$Rh(CO)_2$.

$$H_2Os_3(CO)_{10} + (\eta^5\text{-}C_5H_5)Rh(CO)_2 \xrightarrow[\text{toluene}]{90\ °C} (\eta^5\text{-}C_5H_5)RhOs_2(CO)_9 + H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10} \quad (2)$$

These air-stable compounds were easily separated from each other by thin-layer chromatography. They appeared to form concurrently, both being detected by TLC within a few hours of the start of the reaction. A reaction pathway that involves consecutive formation of these products does not appear to contribute importantly to this system, since a mixture of H_2(η^5-C_5H_5)$RhOs_3(CO)_{10}$ plus (η^5-C_5H_5)Rh(CO)$_2$ at 90 °C in toluene does not produce (η^5-C_5H_5)$RhOs_2(CO)_9$, while a mixture of $H_2Os_3(CO)_{10}$ plus (η^5-

---

(5) SDP (developed by B. A. Frenz and Associated, Inc., College Station, TX 77840) was used to process X-ray data, apply corrections, solve and refine the structure, produce drawings, and print tables.

(6) (a) Comisarow, M. B.; Marshall, A. G. *Chem. Phys. Lett.* **1974**, *22*, 568. (b) Comisarow, M. B.; Marshall, A. G. *Ibid.* **1974**, *26*, 489.

(7) Wilkins, C. L.; Gross, M. L. *Anal. Chem.* **1981**, *53*, 1661A.

(8) FT-ICR data acquisition parameters are as follows: (a) Sample: pressure = 1.1 × 10^{-8} torr; vacuum chamber temperature = 100 °C; probe temperature = 100 °C. (b) timing sequence: quench pulse = 1.0 ms; delay after quench = 1.0 ms; electron beam = 50.0 ms; delay = 1.0 ms; duration of frequency sweep = 0.2 ms; delay = 200 µs; data acquisition time = 832 ms (65 536 time-domain data points); The total duty cycle (quench to quench) was 885 ms. (c) Electron beam: accelerating potential = 50 eV, filament current = 3.5 amp, emission current = 280 nA. (d) Cell trapping voltage = 0.100 V. (e) Mass scale: frequency sweep from 39.4 to 78.8 kHz (bandwidth = 39.4 kHz) to give a detected mass range from 600 to 1200 amu; time-domain data padded with 64K zeroes before Fourier transformation. (f) Magnetic field strength: 3.075 T.

Table II. Interatomic Distances (Å) and Esd's of $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$

(A) Metal-Metal Distances			
Rh-Os(1)	2.7850 (7)	Rh-Os(2)	2.7673 (6)
Os(1)-Os(2)	2.8455 (4)		
(B) Metal-(C_5H_5) and Carbon-Carbon of (C_5H_5) Distances			
Rh-C(1)	2.234 (8)	C(1)-C(2)	1.395 (11)
Rh-C(2)	2.222 (6)	C(2)-C(3)	1.443 (10)
Rh-C(3)	2.245 (7)	C(2)-C(4)	1.426 (12)
Rh-C(4)	2.285 (9)	C(4)-C(5)	1.442 (13)
Rh-C(5)	2.260 (7)	C(5)-C(1)	1.393 (13)
(C) Metal-Carbonyl Distances			
Rh-C	1.833 (7)	Os(2)-C(21)	1.928 (8)
Os(1)-C(11)	1.940 (8)	Os(2)-C(22)	1.943 (8)
Os(1)-C(12)	1.928 (8)	Os(2)-C(23)	1.932 (6)
Os(1)-C(13)	1.919 (7)	Os(2)-C(24)	1.932 (7)
Os(1)-C(14)	1.908 (7)		
(D) Carbon-Oxygen Distances			
C-O	1.142 (0)	C(21)-O(21)	1.156 (9)
C(11)-O(11)	1.157 (0)	C(22)-O(22)	1.147 (9)
C(12)-O(12)	1.158 (0)	C(23)-O(23)	1.107 (9)
C(13)-O(13)	1.133 (0)	C(24)-O(24)	1.081 (9)
C(14)-O(14)	1.157 (9)		

$C_5H_5)RhOs_2(CO)_9$ produces a detectable amount (by TLC) of $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$ only in a period of 2 days. Under the conditions of reaction 2, $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ might form trimeric and tetrameric[23] intermediates that react with $H_2Os_3(CO)_{10}$. In a study separate from the present report we are examining possible reactions of these trimers and tetramers.

$(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$. The molecular structure of $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$ is shown in Figure 1. Bond distances and bond angles are listed in Tables II and III, respectively. The $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$ molecule has approximate C_s symmetry in the solid state. The cluster consists of an $RhOs_2$ unit, an isoceles triangle in which each osmium atom is linked to four terminal carbonyl ligands and the rhodium atom is linked to one.

The Os(1)-Os(2) distance in $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$, 2.8455 (4) Å, is shorter than the corresponding distance in $Os_3(CO)_{12}$ (2.8824 (5)-2.8737 (5) Å)[9] and $H_2Os_3(CO)_{11}$ (2.9097 (7)-2.8574 (7) Å)[9] but is longer than the unbridged Os-Os distance in the unsaturated cluster (46 valence electrons) $H_2Os_3(CO)_{10}$ (2.817 (1)-2.812 (1) Å).[10] The Os(1)-Rh and Os(2)-Rh distances, 2.785 (1) and 2.769 (1) Å, are longer than the Rh-Os distances observed in H_2(acetonylacetonate)$RhOs_3(CO)_{10}$ (2.743 (2)-2.690 (2) Å)[11a] and in $H_3(\eta^6\text{-}C_6H_5CH_3)RhOs_3(CO)_9$ (2.703 (1)-2.702 (1) Å).[11b] The Os-Os distance in H_2(acetonylacetonate)$RhOs_3(CO)_{10}$ (2.809 (1) Å[11a]) is also shorter than that bond distance in $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$.

The Rh-C distance, 1.832 (10) Å, for the carbonyl bound to rhodium in $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$ is longer than the corresponding distance observed in H_2(acetonylacetonate)$RhOs_3(CO)_{10}$, 1.78 (1) Å.[11a] Of the remaining carbonyl groups, distances given in Table II reveal that mutually trans axial carbonyl ligands have longer Os-C distances, 1.941 (4) Å (average),[12] than equatorial carbonyl Os-C distances, 1.922 (3) Å (average), which are trans to a metal. This pattern has also been observed in $Os_3(CO)_{12}$,[9] $Ru_3(CO)_{12}$,[13] and $H_2Os_3(CO)_{10}$.[10] This difference has been accounted for[9,10,13] in terms of the expected greater competition for back-donated π-electron density between the trans axial carbonyl groups than the competition involving an axial carbonyl group and the metal to which it is trans.

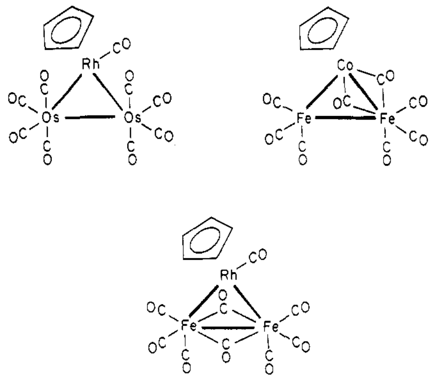

Figure 2. Structures of $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$, $(\eta^5\text{-}C_5H_5)CoFe_2(CO)_9$, and $(\eta^5\text{-}C_5H_5)RhFe_2(CO)_9$.

The dihedral angle between the $\eta^5\text{-}C_5H_5$ ring and the $RhOs_2$ plane is 49.9 (4)°, while the angle between the carbon of the CO group bound to Rh and the $RhOs_2$ plane is 90.0 (3)°. Large differences that occur in the cyclopentadienyl carbon-Rh distances are consistent with observations of other cyclopentadienyl cluster complexes.[17,23] The presence of a CO group in conjunction with a cyclopentadienyl group on the metal appears to cause "slippage" or slight displacement of the cyclopentadienyl group.

It is of interest to compare the molecular structure of $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$ with the proposed structures (based on IR and Mössbauer spectra) of $(\eta^5\text{-}C_5H_5)RhFe_2(CO)_9$[14] and $(\eta^5\text{-}C_5H_5)CoFe_2(CO)_9$[14] (Figure 2). The latter two compounds have two bridging carbonyl ligands, while the title compound possesses only terminal carbonyls. Such differences in carbonyl configurations are well-known for clusters of metals in the same triad (e.g., $Fe_3(CO)_{12}$[15] and $Os_3(CO)_{12}$[13]) and have been related to differences in intermetal bond distances. The distances associated with the largest metal in the triad are believed to be too long to conveniently accommodate bridging carbonyls.[23]

The $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$ molecule is highly fluxional in solution at 25 °C in THF/THF-d_8. A single sharp ^{13}C NMR signal is observed at 184.8 ppm. As the temperature is lowered, this signal initially broadens and descends to the base line, but upon further decrease in temperature to -85 °C, two signals arise from the base line. A very weak and broad signal at 196.7 ppm is assigned to the CO bound to rhodium,[16] while a stronger but still broad signal at 188.4 ppm is probably due to the unresolved terminal carbonyls on osmium. At -95 °C, the lowest temperature attained, the exchange limiting condition has not been achieved. The proton NMR spectrum consists of a single sharp signal at τ 4.48 which is due to C_5H_5 protons.

$H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$. The FT-ICR positive ion mass spectrum of $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$ run as an ordinary probe sample is shown in Figure 3. The most

---

[9] Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

[10] Churchill, M. R.; Hollander, F. J. Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2697.

[11] (a) Farrugia, L. J.; Howard, J. A. K.; Mitprachachon; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1981**, 171. (b) Shore, S. G.; Hsu, W.-L.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 655.

[12] The error estimate shown in brackets for the average distance $\bar{d}$ was obtained from the expression $[\sum^n_i{=}1(di - d)^2/(n^2 - 1)]^{1/2}$.

[13] Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

[14] (a) Knight, J.; Mays, M. J. *J. Chem. Soc. A* **1970**, 654. (b) Howell, J. A. S.; Matheson, T. W.; Mays, M. J. *J. Organomet. Chem.* **1975**, *88*, 363.

[15] (a) Wei, C. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 1351. (b) Cotton, F. A.; Troup, J. M. *Ibid.* **1974**, *96*, 4155.

[16] Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1.

Table III. Bond Angles (deg) and Esd's of $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$

	(A) Metal-Metal Angles		
Os(1)-Rh-Os(2)	61.65 (1)	Rh-Os(2)-Os(1)	59.46 (1)
Rh-Os(1)-Os(2)	58.89 (1)		
	(B) Metal-Metal-Carbon Angles		
Os(1)-Rh-C	89.1 (2)	Os(2)-Os(1)-C(14)	156.5 (3)
Os(2)-Rh-C	92.7 (2)	Rh-Os(2)-C(21)	89.6 (2)
Rh-Os(1)-C(11)	94.7 (2)	Os(1)-Os(2)-C(21)	90.2 (2)
Os(2)-Os(1)-C(11)	87.4 (2)	Rh-Os(2)-C(22)	84.4 (2)
Rh-Os(1)-C(12)	84.4 (2)	Os(1)-Os(2)-C(22)	89.1 (2)
Os(2)-Os(1)-C(12)	90.6 (2)	Rh-Os(2)-C(23)	158.3 (2)
Rh-Os(1)-C(13)	160.5 (2)	Os(1)-Os(2)-C(23)	98.9 (2)
Os(2)-Os(1)-C(13)	102.8 (3)	Rh-Os(2)-C(24)	101.0 (2)
Rh-Os(1)-O(14)	98.0 (3)	Os(1)-Os(2)-C(24)	160.4 (2)
	(C) Carbon-Metal-Carbon Angles		
C(11)-Os(1)-C(12)	178.1 (3)	C(21)-Os(2)-C(22)	173.4 (3)
C(11)-Os(1)-C(13)	90.7 (3)	C(21)-Os(2)-C(23)	92.5 (3)
C(11)-Os(1)-C(14)	91.0 (3)	C(21)-Os(2)-C(24)	88.3 (3)
C(12)-Os(1)-C(13)	89.6 (3)	C(22)-Os(2)-C(23)	94.1 (3)
C(12)-Os(1)-C(14)	90.8 (3)	C(22)-Os(2)-C(24)	90.2 (3)
C(13)-Os(1)-C(14)	100.7 (4)	C(23)-Os(2)-C(24)	100.6 (3)
	(D) Metal-Carbon-Oxygen Angles		
Rh-C-O	175.0 (7)	Os(2)-C(21)-O(21)	175.2 (7)
Os(1)-C(11)-O(11)	176.7 (7)	Os(2)-C(22)-O(22)	176.0 (6)
Os(1)-C(12)-O(12)	173.9 (7)	Os(2)-C(23)-O(23)	179.1 (6)
Os(1)-C(13)-O(13)	177.3 (6)	Os(2)-C(24)-O(24)	177.3 (6)
Os(1)-C(14)-O(14)	178.5 (9)		

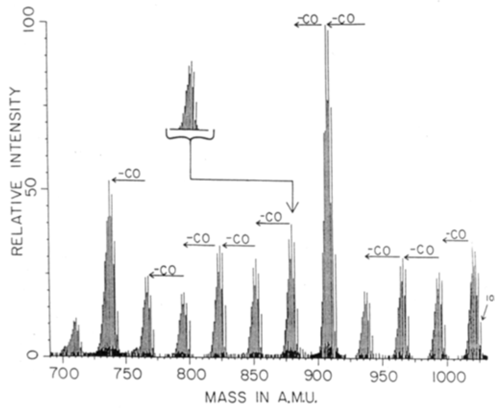

Figure 3. Fourier transform mass spectrum of $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$.

striking features of the spectrum are as follows: (a) the prominent parent ion cluster is sufficiently resolved to give the molecular formula (e.g., the parent ion peak shown by the arrow in Figure 3 corresponds to $^1H_2(\eta^5\text{-}^{12}C_5{}^1H_5)^{103}Rh^{192}Os_3(^{12}C^{16}O)_{10}$ (*m/z* 1026); (b) major peaks corresponding to loss of *each* of the 10 carbonyls are clearly visible, further confirming the molecular formula of the parent neutral compound; and (c) the cluster centered near *m/z* 710 corresponds to loss of $H_2(\eta^5\text{-}C_5H_5)Rh(CO)_5$ from the parent. A theoretical stick plot for the $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_5{}^+$ mass cluster is shown as the inset in Figure 3.

The cluster $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$ is isoelectronic with $H_2(\eta^5\text{-}C_5H_5)CoOs_3(CO)_{10}$, the structure of which has been determined by X-ray crystallography.[17] These compounds are believed to be isostructural. Infrared spectra of the two clusters are strikingly similar (Figure 4). Infrared data for $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$ are given in the Experimental Section, while IR data for $H_2Co(\eta^5\text{-}C_5H_5)CoOs_3(CO)_{10}$ are given elsewhere.[1]

Low-temperature proton and carbon-13 NMR spectra of $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$ (Figure 5) are in accord with the proposed structure. Under slow-exchange conditions the ^1H NMR spectrum reveals the presence of two nonequivalent bridging hydrogens while the ^{13}C NMR spectrum shows that this compound contains 10 distinct carbonyl groups.

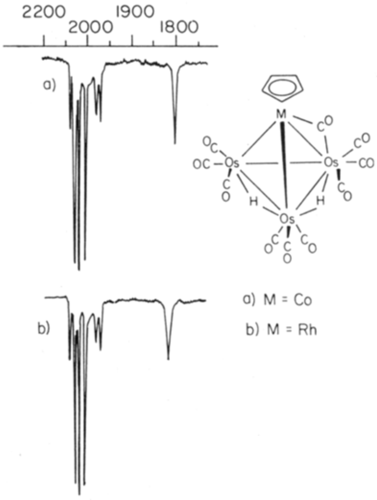

Figure 4. Infrared spectra of $H_2(\eta^5\text{-}C_5H_5)CoOs_3(CO)_{10}$ and $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$.

At −60 °C, the ^1H NMR spectrum of $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$ in toluene-d_8 consists of a sharp signal of relative area 5 (τ 4.93), assigned to $\eta^5\text{-}C_5H_5$ and two sharp singlets, at τ 27.57 and 30.78, each of relative area 1, assigned to bridging hydrogens H_B and H_A. Assignments of these hydrogens are based upon the observation that in related compounds, for which unambiguous assignments can be made, bridging hydrogens cis to a carbonyl bridge have chemical shifts larger than τ 30 (e.g., $H_2Fe_2Os_3(CO)_{13}$,[18] τ 30.7; $HCoOs_3(CO)_{13}$,[19] τ 30.3) while hydrogens bridging osmium atoms that are not cis to a bridge carbonyl have chemical shifts smaller than τ 30 (e.g., $H_3CoOs_3(CO)_{12}$, τ 29.1;[20] $H_3(\eta^5\text{-}C_5H_5)WOs_3(CO)_{12}$, τ 28.8[21]). The

---

[17] Churchill, M. R.; Bueno, C.; Kennedy, S.; Bricker, J. C.; Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1982**, *21*, 627.

[18] Churchill, M. R.; Bueno, C.; Hsu, W.-L.; Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1982**, *21*, 1958.

[19] Hsu, W.-L.; Shore, S. G., unpublished results.

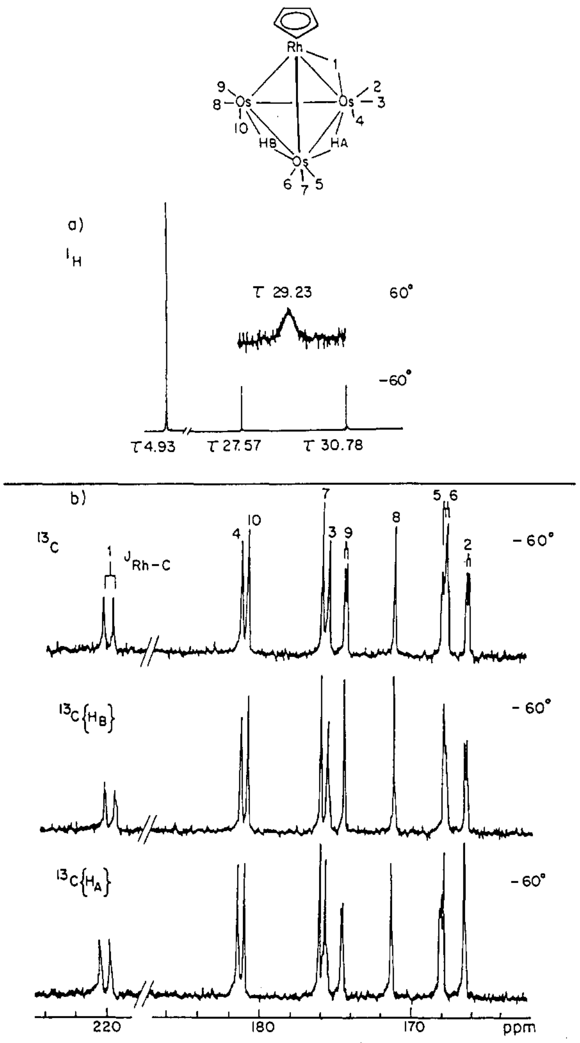

Figure 5. NMR spectra of $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$.

H_B and H_A signals of $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$ broaden with increasing temperature and coalesce at room temperature. At 60 °C in toluene-d_8 a single broad band signal is observed at τ 29.13 (τ 29.18 (average) while the signal due to $(\eta^5\text{-}C_5H_5)$ is temperature independent. The H_A and H_B chemical shifts in $CDCl_3$ are within experimental error of those in toluene-d_8, while the chemical shift of $\eta^5\text{-}C_5H_5$ differs by close to 1 ppm (τ 4.05), as expected for a change from nonaromatic to aromatic solvent. We have also observed a similar solvent effect in the ¹H NMR spectrum of $H_2(\eta^5\text{-}C_5H_5)CoOs_3(CO)_{10}$, with the H_A and H_B signals (τ 30.89, 27.17) being essentially solvent independent in CD_2Cl_2 and toluene-d_8, while the $\eta^5\text{-}C_5H_5$ signal is τ 4.53 in CD_2Cl_2 and 5.33 in toluene-d_8.

Table IV. Carbon-13 NMR Data (75.4 MHz) for $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$ in CH_2Cl_2 at -60 °C

δ	assignt (see Figure 5)
222.3 (1 C, d, J_{Rh-C} = 50.8 Hz)	1
181.7 (1 C, s)	4
181.3 (1 C, s)	10
176.5 (1 C, s)	7
176.0 (1 C, s)	3
174.9 (1 C, d, J_{C-H} = 10.3 Hz)	9
171.6 (1 C, s)	8
168.4 (1 C, d, J_{C-H} = 12.6 Hz)	5
168.2 (1 C, d, J_{C-H} = 11.8 Hz)	6
166.8 (1 C, d, J_{C-H} = 10.3 Hz)	2

The room-temperature ¹³C NMR spectrum of ¹³CO-enriched $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$ in CD_2Cl_2 consists of braod indistinct signals. As the temperature is lowered, the spectrum resolves into 10 CO signals that are distinct at -60 °C (Figure 5, Table IV). The low-field doublet at 222.3 ppm is assigned to the edge-bridging carbonyl 18 with a coupling constant of J_{Rh-C} = 50.8 Hz which is consistent with an earlier observation.[4] The remaining carbonyl assignments are based upon the proton assignments and general observations of other cluster carbonyl spectra. The carbonyl groups 2, 6 are trans to H_A and 5, 9 are trans to H_B. By comparison of the ¹H-coupled spectrum (J_{CH} = 10–12 Hz) with the H_A decoupled and the H_B decoupled spectrum, 2 and 9 are assigned. H_A is cis to carbonyl 5 while H_B is cis to carbonyl 6. Assignments of these two groups are made by observing coupling with the cis hydrogen (J_{CH} = 2–3 Hz) when the trans hydrogen is decoupled. Assignment of the remaining five carbonyls cis to the bridging hydrogens is achieved in an analogous manner. Axial carbonyls in this type of cluster generally have resonances at lower field than equatorial carbonyls.[22] Thus the lower field terminal signals are assigned to 4, 10, and 7 with specific assignments based upon intensities in the ¹H-coupled and decoupled spectra. The remaining carbonyl signals 3 and 8 are assigned in the same way.

Acknowledgment. We thank the National Science Foundation for support of this work through Grant No. CHE 79-18148. NMR spectra were obtained at The Ohio State University Campus Chemical Instrument Center (funded in part by National Science Foundation Grant CHE 79-10019). FT/MS spectra were obtained from a Nicolet FT/MS-1000 instrument funded in part by NIH 1-R01-GM-31683-01, with the assistance of T.-C. L. Wang. We also wish to thank Dr. R. B. Cody, Jr., of Nicolet Analytical Instruments (5225-1 Verona Road, Madison, WI 53711) for advice on FT/MS conditions.

Registry No. $(\eta^5\text{-}C_5H_5)RhOs_2(CO)_9$, 88303-33-7; $H_2(\eta^5\text{-}C_5H_5)RhOs_3(CO)_{10}$, 82678-97-5; $H_2OS_3(CO)_{10}$, 41766-80-7; $(\eta^5\text{-}C_5H_5)Rh(CO)_2$, 12192-97-1.

Supplementary Material Available: Listing of anisotropic thermal parameters of non-hydrogen atoms, positional and isotropic thermal parameters of hydrogen atoms, and structure factor amplitudes (33 pages). Ordering information is given on any masthead page.

---

(20) Bhaduri, S.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Watson, D. J. *J. Chem. Soc., Chem. Commun.* **1978**, 260.

(21) Churchill, M. R.; Hollander, F. J.; Shapley, J. R.; Foose, D. S. *J. Chem. Soc., Chem. Commun.* **1978**, 534.

(22) Geoffroy, G. L.; Gladfelter, W. L. *Inorg. Chem.* **1980**, *19*, 2579.

(23) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1979**, *18*, 843.