Inorg. Chem. **1990**, *29*, 3923–3925 **3923**

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Structure and Bonding in Transition-Metal Carbonyls and Nitrosyls. 4. Molecular Structure of Ruthenium Pentacarbonyl Determined by Gas-Phase Electron Diffraction

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Received February 28, 1990

The molecular structure of ruthenium pentacarbonyl has been investigated by gas-phase electron diffraction. The effect of single–double multiple scattering on the structural parameters was taken into account. The diffraction data are consistent with a molecule of trigonal-bipyramidal symmetry with the axial Ru—C bonds slightly shorter than the equatorial. With assumption of D_{3h} symmetry for the molecule, values for some of the more important distance (r/Å) and root-mean-square amplitude (l_α/Å) parameters with estimated uncertainties (2σ) are $\langle r_\alpha(\text{Ru—C})\rangle = [2r(\text{Ru—C}_{ax}) + 3r_\alpha(\text{Ru—C}_{eq})]/5 = 1.953\ (3)$, $\Delta r_\alpha(\text{Ru—C}) = r_\alpha(\text{Ru—C}_{ax}) - r_\alpha(\text{Ru—C}_{eq}) = -0.021\ (21)$, $\langle r_\alpha(\text{C}\equiv\text{O})\rangle = 1.126\ (2)$, $\Delta r_\alpha(\text{C}\equiv\text{O}) = 0$ (assumed), $r_g(\text{Ru—C}_{ax}) = 1.950\ (9)$, $r(\text{Ru—C}_{eq}) = 1.969\ (3)$, $r_g(\text{C}\equiv\text{O}) = 1.143\ (2)$, $l(\text{Ru—C}_{eq}) = l(\text{Ru—C}_{ax}) - 0.002 = 0.070\ (5)$, and $l(\text{C}\equiv\text{O}) = 0.042\ (3)$. The multiple scattering from the molecule was found to be small. The quality of the fit was improved by allowance for the effect of multiple scattering, but the parameter values changed only slightly.

Introduction

The relative lengths of the axial and equatorial bonds in metal pentacarbonyls are of considerable interest. In $Os(CO)_5$, a molecule of D_{3h} symmetry, we found from an electron-diffraction investigation that the axial bonds were slightly longer (0.047 (46) Å) than the equatorial.[2] In the case of its congener $Fe(CO)_5$, however, the matter is uncertain. Several electron-diffraction investigations[3–6] led to the conclusion that the axial bonds in $Fe(CO)_5$ are shorter, but a recent study by low-temperature X-ray diffraction indicates that there is no significant difference.[7]

Ruthenium pentacarbonyl (Figure 2), the remaining member of this family, was first reported by Manchot and Manchot in 1936.[8] An early IR study[9] suggested that $Ru(CO)_5$ was probably trigonal bipyrimidal in the gas phase and in heptane solution; a more recent IR study[10] of ^{13}CO-enriched $Ru(CO)_5$ in liquid xenon was also consistent with a D_{3h} structure. The bonding and the relative lengths of the Ru—C axial and equatorial bonds have been discussed in an ab initio theoretical investigation.[11] As a part of our systematic studies of metal carbonyls, we have investigated the molecular structure of $Ru(CO)_5$ by the gas-phase electron-diffraction technique.

Experimental Section

The sample of $Ru(CO)_5$ was prepared at Simon Fraser University.[12] Solid $Ru_3(CO)_{12}$ was heated at 150 °C under CO (~200 atm) for 9 h. The bomb was cooled to −78 °C, CO pumped away, and the $Ru(CO)_5$ transferred at room temperature to a glass vessel at −190 °C. A U-tube with P_2O_5, cooled to 0 °C, formed part of the transfer line. The $Ru(CO)_5$ was transported under 1 atm of CO at −78 °C. All manipulations were carried out in the strict absence of light.

The diffraction experiments were carried out at Oregon State University with the apparatus at room temperature. A modified power supply that provided a 60-kV accelerating potential was used. The nominal electron wavelength, calibrated in separate experiments against CO_2 ($r_a(\text{C=O}) = 1.1646$ Å, $r_a(\text{O··O}) = 2.3244$ Å), was 0.05 Å. Other experimental conditions were an r^3 sector, 8 × 10 in Kodak projector slide plates (medium contrast) developed for 10 min in D-19 developer diluted 1:2, beam currents of 0.39–0.51 μA, nominal camera distances of 750 and 300 mm for the long and "middle" cameras, exposure times of 165–240 and 240–300 s for the long and middle distances, respectively, and ambient apparatus pressure during exposure of 1.9×10^{-6} Torr.

Three plates from the long and four from the middle camera were selected for analysis. The ranges of intensity data were $3.0 \le s/\text{Å}^{-1} \le 15.00$ (long) and $9.00 \le s/\text{Å}^{-1} \le 37$ (middle); the data interval was $s = 0.25$ Å^{-1}. Procedures for obtaining the total intensities ($s^4I_t(s)$) and the molecular intensities ($sI_m(s)$) have been described.[13–15] Figure 1 shows the total intensities from each plate and the calculated background curves. The total intensity data, the calculated backgrounds, and the averaged molecular intensity data are available as supplementary material.

Structure Analysis

Experimental radial distribution curves ($rD(r)$) were calculated in the usual way[13] by Fourier transformation of the function $I'(s) = sI_mZ_{Ru}Z_C(A_{Ru}A_C)^{-1}\exp(-0.0025s^2)$. Data in the unobserved or uncertain region $s \le 3$ Å^{-1} were taken from theoretical intensity calculations. The atomic scattering amplitudes $f = A/s^2$ and the phases η for all calculations were taken from tables.[16] The final curve is shown in Figure 2. The positions of the peaks of this curve are consistent with distances in a molecule of D_{3h}, not C_{4v}, symmetry. We therefore based our refinements on assumed symmetry D_{3h}.

The structure of $Ru(CO)_5$ with D_{3h} symmetry can be described in terms of the following four independent structural parameters: $\langle r(\text{Ru—C})\rangle = [2r(\text{Ru—C}_{ax}) + 3r(\text{Ru—C}_{eq})]/5$, $\Delta r(\text{Ru—C}) = r(\text{Ru—C}_{ax}) - r(\text{Ru—C}_{eq})$, and $\langle r(\text{C}\equiv\text{O})\rangle$ and $\Delta r(\text{C}\equiv\text{O})$ similarly defined. The 55 ($=n(n-1)/2$) atomic pairs generate 16 different interatomic distances and accordingly 16 vibrational amplitude parameters (l). The structure was specified with r_α-type distances from which the r_a type was obtained with use of the usual formula $r_a = r_\alpha + \delta r + K - l^2/r$. The centrifugal distortions δr and the perpendicular amplitude corrections K were calculated from a vibrational force field for $Fe(CO)_5$:[17] for $Ru(CO)_5$ only two infrared-active stretching frequencies (for C≡O) have been assigned,[9,10] and since the vibrational corrections required for the distance conversions in electron-diffraction work are usually not very sensitive to change in force field, use of force constants from $Fe(CO)_5$ seemed appropriate. Corrections for vibrational anharmonicity, which were estimated by the usual diatomic approximation,[18] were also included: the

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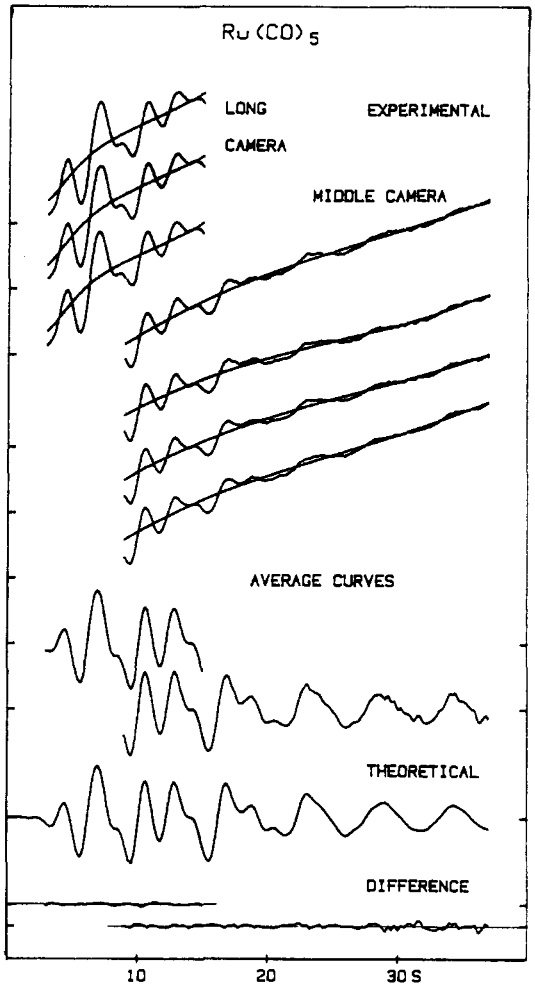

Figure 1. Intensity curves. The s^4I_t curves from each plate are shown superimposed on the final backgrounds and are magnified 10 times relative to the backgrounds. The average curves are $s[s^4I_t - \mathrm{Bkgd}]$ minus the contribution from multiple scattering. The difference curves are experimental minus theoretical for model A.

values of $\kappa/\text{Å}^3$ ($\times 10^6$) for the Ru—C, $C\equiv O$ and Ru·O distances were respectively 1.6, 0.90, and 2.0; the anharmonicities of other distances were ignored. As mentioned in a previous article,[2] multiple scattering plays a smaller role in trigonal-bipyramidal molecules such as $Os(CO)_5$ and $Ru(CO)_5$ than in octahedral molecules such as TeF_6.[19] The effect of multiple scattering will be less important in $Ru(CO)_5$ than in $Os(CO)_5$ because the osmium atom is heavier than ruthenium. However, we still felt it necessary to include the multiple-scattering correction because of the possible sensitivity of the axial and equatorial Ru—C bond lengths to even small effects. The calculation of the theoretical three-atom (multiple) scattering followed the equation given in the previous work.[2] Only triples containing the Ru atom were taken into account. The procedure for refinement of the structural parameters by our usual least-squares method[13,20] with consideration for multiple scattering has been described in detail elsewhere.[2]

Preliminary refinements showed that values for the parameters $\langle r$(Ru—C)$\rangle$ and $\langle r(C\equiv O)\rangle$ would be precisely determined but that the most interesting parameter Δr(Ru—C) would have a small value with a relatively large uncertainty. A source of the difficulty in the case of Δr(Ru—C) was high correlation between it and $\Delta r(C\equiv O)$ and between it and some of the individual amplitudes of vibration. Other high correlations were expected and found between some of the amplitudes themselves, particularly those associated with pairs of distances located under the same peak of the radial distribution curve such as $l(\mathrm{Ru{-}C_{ax}})$ and $l(\mathrm{Ru{-}C_{eq}})$. We handled the problem of the parameter Δr(Ru—C) by investigating the quality of fit obtained by assigning assumed values to $\Delta r(C\equiv O)$ and to *differences* between some of the troublesome amplitudes, each over plausible ranges: $-0.02 \le \Delta r(C\equiv O)/\text{Å} \le +0.02$; $-0.011 \le \Delta l(\mathrm{Ru{\cdot}O})/\text{Å} = l(\mathrm{Ru{\cdot}O})_{ax} - l(\mathrm{Ru{\cdot}O})_{eq} \le +0.012$; $-0.002 \le \Delta l(C\equiv O)/\text{Å} = l(C\equiv O)_{ax} - l(C\equiv O)_{eq} \le +0.002$; $-0.011 \le \Delta l(\mathrm{Ru{-}C})/\text{Å} = l(\mathrm{Ru{-}C})_{ax} - l(\mathrm{Ru{-}C})_{eq} \le +0.012$. Over 20 converged refinements were made throughout these parameter ranges.

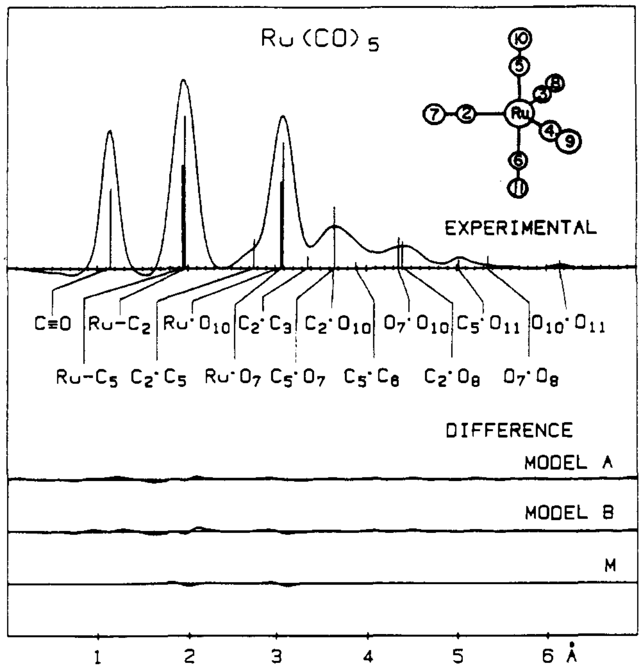

Figure 2. Radial distribution curves. The experimental curve was calculated from a composite of the average curves of Figure 1 with addition of theoretical data from model A for $a < 2.00$ Å^{-1} and with the convergence factor B equal to 0.0025 Å^2. The difference curves for models A and B are experimental minus theoretical; curve M is the contribution from multiple scattering.

Results

Evaluation of the refinement results led to the parameter values given in Table I for a pair of "best models", one (model A) derived with inclusion of the multiple-scattering corrections and one (model B) without them. Both the goodness-of-fit factor R and the standard deviations for most of the distances and amplitudes are smaller for model A, indications of a better fit for this model. The better fit provided by model A is also seen in a comparison of the radial distribution difference curves of Figure 2. Curve M shows the contribution of multiple scattering to the Ru—C and Ru·O peaks of the radial distribution curves; it is calculated from the Fourier transformation of the multiple-scattering intensity. Previous investigations of the effects of inclusions of multiple-scattering corrections have shown that the values for internuclear distances are rather insensitive to such corrections but that vibrational amplitude values may be significantly changed.[19,21,22] The first of these observations is also found in our investigation of $Ru(CO)_5$; the amplitude changes, however, are also quite small.

Our preferred model is A. Table II is the correlation matrix for this model.

Discussion

The average distances $\langle r_g(C\equiv O)\rangle$ in the group 8 gaseous pentacarbonyls of Fe, Ru, and Os are respectively 1.146 (2),[4] 1.142 (2),[2] and 1.142 (2) Å (this work). The bond lengths $r(C\equiv O_{ax})$ = 1.133 (2) Å and $r(C\equiv O_{eq})$ = 1.127 (2) Å have been reported for $Ru_3(CO)_{12}$[23] in the crystal. The r_α distance is more appropriate than r_g for comparison with distances obtained from X-ray crystallographic work, and our result $\langle r_\alpha(C\equiv O)\rangle$ = 1.126 (2) Å for $Ru(CO)_5$ is in good agreement with the X-ray result of 1.130 Å for the average carbonyl bond length in $Ru_3(CO)_{12}$. Our value of 1.953 (3) Å for $\langle r_\alpha$(Ru—C)$\rangle$ in $Ru(CO)_5$ is longer than the corresponding average of 1.931 (5) Å, in $Ru_3(CO)_{12}$. Since the

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Table I. Structural Results for Ruthenium Pentacarbonyl[a]

param[b]	model A				model B	
	r_α	r_g[c]	r_a[c]	l_α[d]	r_α	l_α
$\langle r(C\equiv O)\rangle$	1.126 (2)	1.143	1.141	0.042 (3)	1.126 (2)	0.042 (3)
$\langle r(Ru—C)\rangle$	1.953 (3)				1.952 (4)	
$\Delta r(Ru—C)$	−0.021 (21)			−0.019 (24)		
$Ru—C_{eq}$	1.961 (9)	1.969	1.966	0.070 (5)	1.959 (11)	0.073 (6)
$Ru—C_{ax}$	1.941 (13)	1.950	1.948	0.072	1.940 (14)	0.074
$C_2{\cdot}C_5$	2.759 (5)	2.767	2.760	0.152 (31)	2.758 (6)	0.154 (36)
$Ru{\cdot}O_{eq}$	3.088 (10)	3.102	3.100	0.072 (5)	3.085 (11)	0.075 (6)
$Ru{\cdot}O_{ax}$	3.067 (13)	3.084	3.083	0.073	3.066 (14)	0.076
$C_2{\cdot}C_3$	3.398 (16)	3.403	3.399	0.103 (30)	3.394 (15)	0.104 (33)
$C_5{\cdot}O_7$	3.647 (5)	3.660	3.650	0.192	3.645 (6)	0.193
$C_2{\cdot}O_{10}$	3.640 (8)	3.655	3.645	0.186	3.639 (8)	0.187
$C_5{\cdot}C_6$	3.881 (25)	3.886	3.879	0.160 (275)	3.881 (25)	0.161 (327)
$C_2{\cdot}O_8$	4.409 (17)	4.417	4.406	0.218 (60)	4.405 (16)	0.219 (67)
$O_7{\cdot}O_{10}$	4.352 (6)	4.367	4.338	0.354	4.350 (7)	0.355
$C_5{\cdot}O_{11}$	5.007 (26)	5.014	5.014	0.055 (23)	5.007 (25)	0.055 (26)
$O_7{\cdot}O_8$	5.348 (17)	5.356	5.342	0.270 (238)	5.352 (19)	0.268 (261)
$O_{10}{\cdot}O_{11}$	6.133 (26)	6.140	6.139	0.091 (85)	6.133 (41)	0.091 (95)
R[e]	0.0894				0.1007	

[a] D_{3h} symmetry. Distances (r) and amplitudes (l) in angstroms. Quantities in parentheses are estimated 2σ. For definitions see text. [b] The first three parameters used to define the geometry with $\Delta r(C\equiv O)$ assumed equal to zero. [c] Uncertainties estimated to be the same as for r_α. [d] Amplitudes in curly brackets were refined as a group with difference values calculated from a vibrational force field; see text. [e] $R = [\sum_i w_i\Delta_i^2/\sum_i w_i(s_iI_i(\text{obsd}))^2]^{1/2}$ where $\Delta_i = s_iI_i(\text{obsd}) - s_iI_i(\text{calcd})$.

Table II. Correlation Matrix (×100) for Parameters of Model A[a]

	param	σ[b]	r_1	r_2	r_3	l_4	l_5	l_6	l_7	l_8	l_9	l_{10}	l_{11}	l_{12}	l_{13}
1	$\langle r(Ru—C)\rangle$	0.093	100	−16	−14	<1	−6	25	3	−20	−5	2	<1	−2	<1
2	$\Delta r(Ru—C)$	0.75		100	−4	<1	29	−6	16	−10	3	5	<1	5	<1
3	$\langle r(C\equiv O)\rangle$	0.057			100	<1	−1	10	3	−14	−3	3	<1	<1	<1
4	$l(C\equiv O)$	0.074				100	34	−13	33	−6	−1	5	5	<1	2
5	$l(Ru—C)$	0.15					100	−6	40	−8	<1	7	3	<1	<1
6	$l(C_2{\cdot}C_5)$	1.08						100	11	−3	−1	4	−2	−4	−2
7	$l(Ru{\cdot}O)$	0.16							100	−9	−1	6	4	<1	<1
8	$l(C_2{\cdot}C_3)$	1.02								100	44	−15	1	9	<1
9	$l(C_5{\cdot}C_6)$	9.71									100	−4	7	6	<1
10	$l(C_2{\cdot}O_8)$	2.09										100	−6	−18	1
11	$l(C_5{\cdot}O_{11})$	0.81											100	10	2
12	$l(O_7{\cdot}O_8)$	8.41												100	−4
13	$l(O_{10}{\cdot}O_{11})$	3.00													100

[a] Distances (r) and amplitudes (l) in angstroms. For numbering of atoms see Figure 2. For explanation about grouping of amplitudes see text. [b] Standard deviations (×100) from least squares.

ruthenium atom in $Ru_3(CO)_{12}$ has 6-fold coordination, it is not implausible that the Ru—C distances would differ from those in pentacoordinate $Ru(CO)_5$. The Ru—C bonds in each of these substances are seen to have a considerable amount of double-bond character, as follows. The sum of Pauling's covalent single-bond radii for C and Ru at 2.03 Å (1.26 Å + 0.77 Å)[24] is appreciably longer than the measured values. According to his bond order–bond length criterion $D'(n) = D(1) - 0.71 \log n$,[24] the amount of double-bond character is about 30%.

The average M—C distances in $Ru(CO)_5$ and $Os(CO)_5$ are the same to within experimental uncertainty ($\langle r_\alpha(Ru—C)\rangle = 1.953$ (3) Å, $\langle r_\alpha(Os—C)\rangle = 1.955$ (4) Å[2]), but that in $Fe(CO)_5$ is much smaller ($\langle r_g(Fe—C)\rangle = 1.824$ (3) Å).[25] The values obtained for $\Delta r(Ru—C) = r(Ru—C_{ax}) - r(Ru—C_{eq})$ in our many refinements were negative over all of the parameter space investigated. The magnitude of this parameter is sensitive to the value of $\Delta r(C\equiv O)$; e.g., the values are −0.025 (22) and −0.006 (22) Å with $\Delta r(C\equiv O)$ set respectively to +0.02 and −0.02 Å, but the magnitude is not very sensitive to the assumed amplitude differences. The value $\Delta r(Ru—C) = -0.021$ (21) Å from our preferred model is in excellent agreement with the result from the theoretical work (−0.013 Å).[11] It is noteworthy that for $Os(CO)_5$ the weight of the evidence indicated a different result for the difference between the axial and equatorial metal–carbon bonds: the axial Os—C bond appears to be longer than the equatorial one.

Acknowledgment. This work was supported by the National Science Foundation under Grants CHE84-11165 and CHE88-10070 to Oregon State University and by the Natural Sciences and Engineering Research Council of Canada in the form of an operating grant to R.K.P.

Supplementary Material Available: Tables III–VI, listing the total scattered intensities $s^4I_t(s)$, the calculated backgrounds from each plate, the averaged molecular intensities $sI_m(s)$ from each camera distance, and the calculated multiple scattering (10 pages). Ordering information is given on any current masthead page.

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