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Synthesis and Spectroscopic Characterization of $H_3CoRu_3(CO)_{12}$. Crystal and Molecular Structure of the C_{3v} Isomer

by

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The reaction of $HCoRu_3(CO)_{13}$ with H_2 in refluxing hexane gives the new cluster $H_3CoRu_3(CO)_{12}$ in 75% yield. Infrared and ^1H NMR spectra indicate that the cluster exists in two isomeric forms. The structure of one isomer has over

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determined by single-crystal x-ray diffraction. It crystallized in the triclinic space group $P\bar{1}$ with a = 9.204(2) Å, b = 13.615(4) Å, c = 8.318(2) Å, α = 100.49(2)°, β = 111.51(2)°, γ = 81.78(2)°, V = 950.1 $Å^3$ and Z = 2. The structure was determined by the heavy-atom method and refined to R_1 = 2.3% and R_2 = 3.6%. The $CoRu_3$ core of the molecule defines a distorted tetrahedron with three carbonyls terminally bound to each metal atom. The hydride ligands were located by difference Fourier techniques and bridge the three Ru-Ru bonds. The overall symmetry of the cluster is approximately C_{3v}. Spectral evidence indicates that the second isomer contains a bridging CO ligand and three non-equivalent hydrogens. The interconversion of the two isomers and the various hydrogen exchange processes have been monitored by ^1H NMR spectroscopy and the exchange mechanisms are discussed.

C sub 3V

H(1)

Comparison across a series of isoelectronic mixed-metal clusters with systematic metal variation can often provide valuable insight into the factors which affect bonding, stereochemistry, and stereochemical nonridgidity.[2,3] Mixed-metal clusters involving metals of neighboring groups are especially interesting since the change in the number of electrons contributed by each metal is usually accompanied by a change in the number of hydride ligands so as to maintain the proper electron count. The clusters $Co_4(CO)_{12}$,[4,5] $HCo_3Os(CO)_{12}$,[6] $H_2Co_2Os_2(CO)_{12}$,[7] $H_3CoOs_3(CO)_{12}$,[8] and $H_4Os_4(CO)_{12}$[9-11] constitute a Co-Os series of this type.

For the analogous Co-Ru series only $Co_4(CO)_{12}$, $HCo_3Ru(CO)_{12}$,[12,13] and $H_4Ru_4(CO)_{12}$[9,14] have been previously described. We recently reported the high-yield preparation of $HCoRu_3(CO)_{13}$[15] and have since found that treatment of this cluster with H_2 cleanly yields $H_3CoRu_3(CO)_{12}$, one of the remaining members of the Co-Ru series. Described herein are details of the synthesis of this compound, its spectroscopic characterization, and the crystal and molecular structure of one isomer.

A

Experimental

Synthesis of $H_3CoRu_3(CO)_{12}$. $HCoRu_3(CO)_{13}$ (181 mg, 0.248 mmol), prepared according to the literature procedure,[15] was dissolved in 125 ml of hexane, and the solution was deoxygenated by stirring under an N_2 purge for 10 min. The N_2 purge was replaced with an H_2 purge and the solution was refluxed for 2 h during which time the color changed from dark-red to orange. The hexane was removed under an N_2 purge to yield a red-orange solid which was recrystallized by slow evaporation of solvent from a hexane solution to give 131 mg (75% yield) of red crystals of $H_3CoRu_3(CO)_{12}$. Anal. Calcd. for $H_3CoRu_3(CO)_{12}$: C, 20.55%; H, 0.43%. Found: C, 20.79%; H, 0.42% (Galbraith Laboratories).

Spectroscopy. Unless otherwise specified, all ^1H NMR spectra were obtained on a JEOL PFT 100 Mhz Fourier transform spectrometer equipped with a Nicolet 1080 computer. The CD_2Cl_2 solvent was dried over P_2O_5 and distilled under vacuum directly into the 10 mm NMR tubes containing the samples, and these were sealed under vacuum. Infrared spectra were recorded using 0.5 mm NaCl solution IR cells on a Perkin Elmer 580 grating infrared spectrophotometer.

Crystallographic Summary. Pertinent crystal and intensity data are listed in Table I.[16] The data were collected and treated in the usual manner.[17] The Patterson function was automatically interpreted for the metal atom tetrahedron and yielded the carbonyl atom framework directly (R_1 = 21.4%).[18] The data were then corrected for absorption with an absorption coefficient of μ = 32.11 cm^{-1}, range of transmission of 0.43 - 0.74, and defining faces $\pm$[($\bar{1}01$, 0.05 mm), ($\bar{1}10$, 0.16 mm), (010, 0.18 mm)]. After a preliminary refinement series, a difference fourier map clearly revealed the presence of the three bridging hydride atoms along the base of the Ru_3 triangle. The structure was refined by full/block diagonal minimization of $\Sigma w_i(|F_o| - |F_c|)^2$ with final convergence to $R_1 = 2.3\%$ and $R_2 = 3.6\%$,[18] and an esd of an observation at unit weight = 1.13[19] with a data/parameter ratio of 11.7. In the final refinement cycle, the non-hydrogen atoms were allowed anisotropic thermal parameters whereas the hydrogen atoms were refined isotropically. Atomic scattering factors for the non-hydrogen atoms were taken from Cromer,[20] and the hydrogen scattering factors were those of Stewart et al.[21] The refinement also included terms for anomalous dispersion for Ru and Co.[22] There were no outstanding features on the final difference Fourier map. The refined positional and thermal parameters are listed in Tables II and III, and a summary of bond lengths and angles with errors estimated from the full variance-covariance matrix is given in Tables IV and V. A listing of the observed and calculated structure factor amplitudes is included in the Supplementary Material as Table A. Ordering information is available on any current masthead page.

Results

Synthesis and Spectroscopic Characterization of $H_3CoRu_3(CO)_{12}$.

$H_3CoRu_3(CO)_{12}$ is conveniently prepared by heating hexane solutions of $HCoRu_3(CO)_{13}$ under an H_2 atmosphere, eq. 1. Analogous reactions have been employed by Kaesz and coworkers[9] to prepare $H_4Ru_4(CO)_{12}$ and $H_4FeRu_3(CO)_{12}$

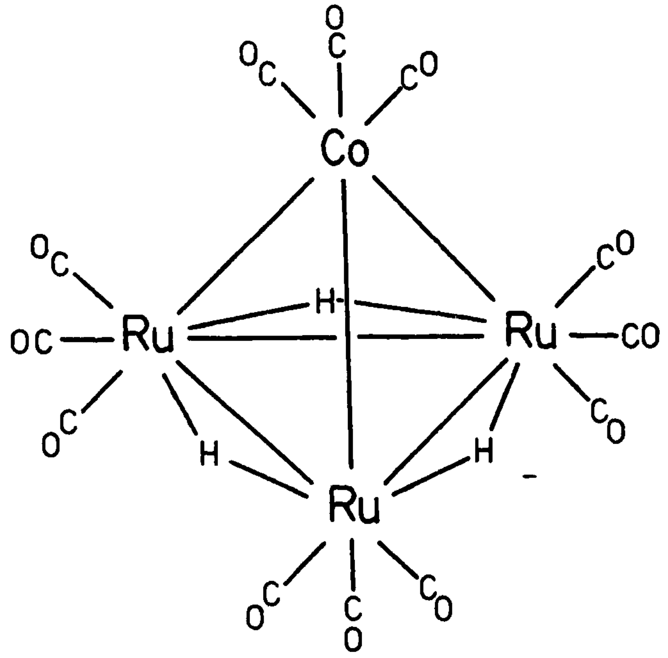
$$HCoRu_3(CO)_{13} + H_2 \xrightarrow{\Delta} H_3CoRu_3(CO)_{12} + CO \qquad (1)$$

from $H_2Ru_4(CO)_{13}$ and $H_2FeRu_3(CO)_{13}$, respectively. $H_3CoRu_3(CO)_{12}$ appears to be indefinitely stable in both the solid state and in solution. This contrasts sharply to $H_3CoOs_3(CO)_{12}$ which is reported to be air-sensitive.[5] $H_3CoRu_3(CO)_{12}$ was characterized by chemical analysis, by its ^1H NMR, infrared, and mass spectra, and one isomer of the compound by a complete single-crystal x-ray structure determination. Pertinent spectral data is summarized in Table VI along with corresponding data for $H_3CoOs_3(CO)_{12}$ for comparison.

The mass spectrum of $H_3CoRu_3(CO)_{12}$ shows a parent ion centered at m/e = 704 with the expected isotopic distribution and with fragment ions corresponding to loss of each of the twelve carbonyl ligands. The infrared spectrum is shown in Figure 1 and displays eleven distinct bands in the terminal region and a single weak, broad band in the bridging carbonyl region at 1878 cm^{-1}.

The ^1H NMR spectrum of $H_3CoRu_3(CO)_{12}$ at room temperature shows one sharp singlet at δ -17.1 ppm. However, as shown in Figure 2, upon cooling to -80°C the singlet develops into three separate singlets at δ -14.2, -17.2, and -18.7 ppm with relative intensities 1 to 0.85 to 2, respectively. At -80°C the downfield singlet at δ -14.2 ppm is clearly broader ($\sim$10 hz) than the remaining two ($\sim$6-7 hz). At -100°C using a 360 Mhz instrument,[23] the upfield singlet at δ -18.7 ppm is broadened almost into the baseline whereas the other two singlets remain unchanged, Figure 3.

Crystal and Molecular Structure of $H_3CoRu_3(CO)_{12}$. The ^1H NMR spectra imply that two isomers of $H_3CoRu_3(CO)_{12}$ are present in solution (see Discussion section). One of these isomers has been characterized by a complete single-crystal x-ray diffraction study and has the structure shown in Figure 4 and depicted in 1 below.



1 (C_{3v})

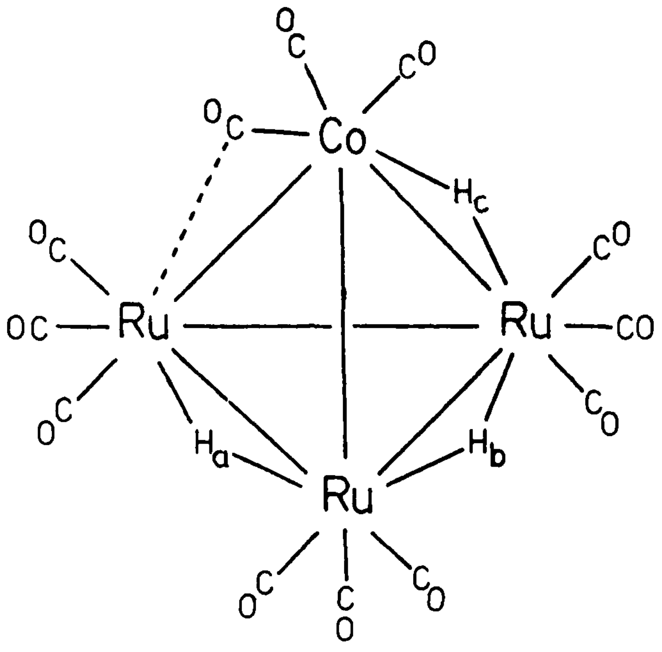
The $CoRu_3$ core of the cluster defines a distorted tetrahedron with approximate C_{3v} symmetry. The three hydride ligands were located by difference Fourier techniques and bridge the three Ru-Ru bonds, consistent with the near C_{3v} symmetry of this isomer. The structure is quite similar to that found for $H_3CoOs_3(CO)_{12}$, except that in the latter case the hydride ligands were not located.[8] The Ru-Ru distances of $H_3CoRu_3(CO)_{12}$ average 2.90 A°. These compare well to hydride-bridged Ru-Ru distances found in other clusters: $H_2Ru_4(CO)_{13}$ (2.93 A°),[24] $[H_3Ru_4(CO)_{12}]^-$ (C_2 isomer, 2.92 A°; C_{3v} isomer, 2.94 A°).[25] They differ significantly from unbridged Ru-Ru distances: $H_2Ru_4(CO)_{13}$ (2.78 A°),[24] $[H_3Ru_4(CO)_{12}]^-$ (C_2 isomer, 2.80 A°; C_{3v} isomer, 2.79 A°),[25] $[CoRu_3(CO)_{13}]^-$ (2.83 A°).[15] As illustrated in the ORTEP drawing, Figure 4, the three bridging hydrides are not coplanar with the Ru_3 triangle but instead lie below it.

Discussion

The substitution of CO by H_2 has been shown by Kaesz and coworkers[9] to be a valuable method for preparing metal hydride clusters. With $HCoRu_3(CO)_{13}$ the reaction proceeds smoothly to give an excellent yield of $H_3CoRu_3(CO)_{12}$, eq. 1. Although the mechanism of these various reactions is currently unknown, they likely proceed via a simple, direct substitution of CO by H_2 on the intact metal cluster.

The complexity of the infrared spectrum, Figure 1, and the observed low-temperature ^{1}H NMR pattern, Figure 2, indicate that two different isomeric forms of $H_3CoRu_3(CO)_{12}$ are present in solution, one of which is the structurally characterized C_{3v} isomer. The presence of a weak, broad band at 1878 cm^{-1} in the IR spectrum implies the presence of a bridging or semi-bridging CO in the second isomer.

The two resonances at δ -14.2 and δ -18.7 ppm in the -80°C ^{1}H NMR spectrum have an intensity ratio of 1:2 which suggests that they arise from a single isomer in which two of the hydrogens are equivalent (δ -18.7 ppm) but different from the third (δ -14.2 ppm) under the kinetic limitations of this experiment. However, as shown in Figure 3, the δ -18.7 ppm resonance is considerably broadened when the spectrum is recorded at -100°C using a 360 Mhz spectrometer. Thus, this resonance must be due to two inequivalent hydrogens which rapidly exchange. The low-temperature limiting spectrum, if it could be reached, should show three separate singlets of equal intensity for the three inequivalent hydrogens of this second isomer. The most reasonable structure for this isomer which is consistent with the observed ^{1}H NMR and infrared spectra is that shown in 2 with its C_1 symmetry label.

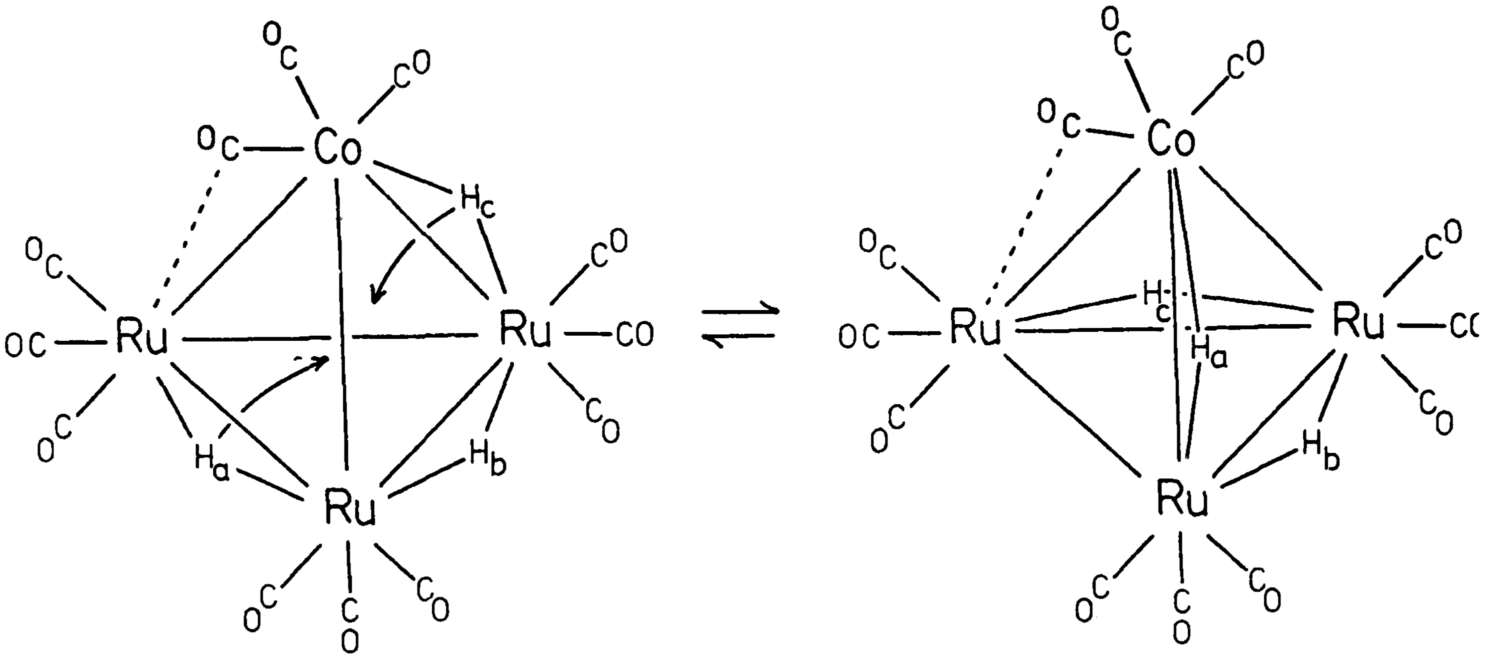


2 (C_1)

The semibridging carbonyl formation is preferred as this gives each metal the requisite eighteen electrons[26] as well as being consistent with the IR spectrum (ν_{CO} = 1878 cm^{-1}).

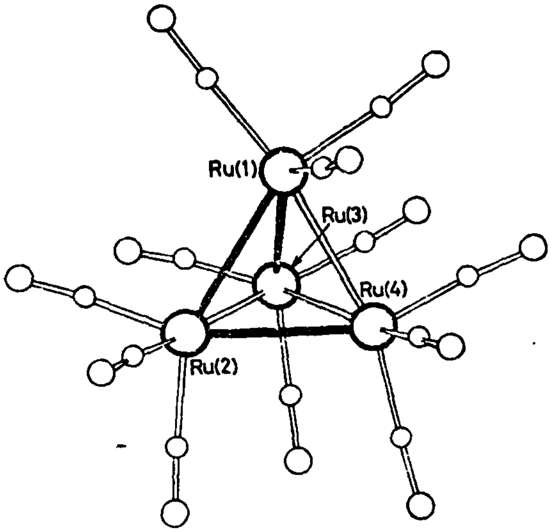
Assignment of the observed resonances to specific hydrogens in the C_1 isomer is difficult because of the lack of resolution of H-H coupling and the unknown quadrupolar broadening effect of the ^{59}Co nucleus in this cluster. On the basis of the observed linewidths and the reasonable exchange mechanisms, we tentatively attribute the δ -14.2 ppm resonance to H_b and the δ -18.7 ppm resonance to the rapidly exchanging H_a and H_c. We suggest that the exchange of H_a and H_c occurs simply by movement of these two hydrogens to the adjacent unbridged metal-metal bonds as shown in Scheme I. Such movement interconverts the two enantiomers of the C_1 isomer. If H-H coupling were resolved in the -80°C, 100 Mhz spectrum, we would expect the resonance due to H_b to be a triplet while that due to the rapidly exchanging H_a and H_c would be a doublet. Although this coupling was not resolved, the observed linewidths are consistent with our assignment since the δ -14.7 ppm linewidth (10.1 hz) is greater than that of the δ -18.7 ppm resonance (7.0 hz).

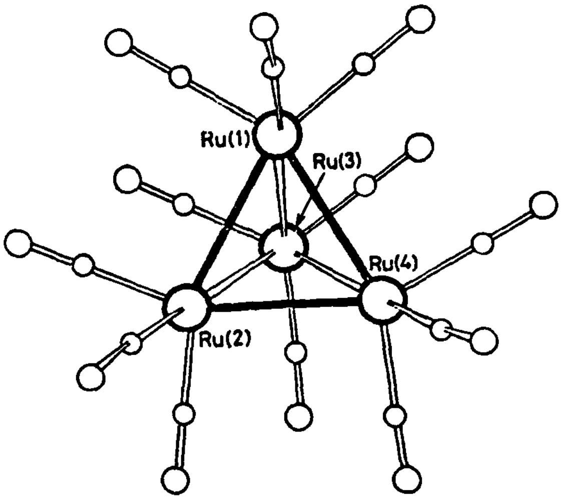
Scheme I



The remaining resonance at δ -17.2 ppm in the -80°C ^1H NMR spectrum is logically attributed to the structurally characterized C_{3v} isomer in which the three hydrogen ligands are equivalent. Such an assignment is consistent with the observation that this resonance has the smallest linewidth since no H-H coupling is present.

These two isomers are directly analogous to the two structurally characterized isomers of $[H_3Ru_4(CO)_{12}]^-$ of C_2 and C_{3v} symmetries shown in 3 and 4, respectively, with the hydride bridged Ru-Ru bonds represented by the solid lines.[25] The principal structural difference between 2 and 3 is the presence of the semibridging carbonyl in 2. Structurally similar isomers have been suggested for $[H_3Os_4(CO)_{12}]^-$,[27] and the C_{3v} isomer of $H_3CoRu_3(CO)_{12}$ is isostructural to $H_3CoOs_3(CO)_{12}$.[8]



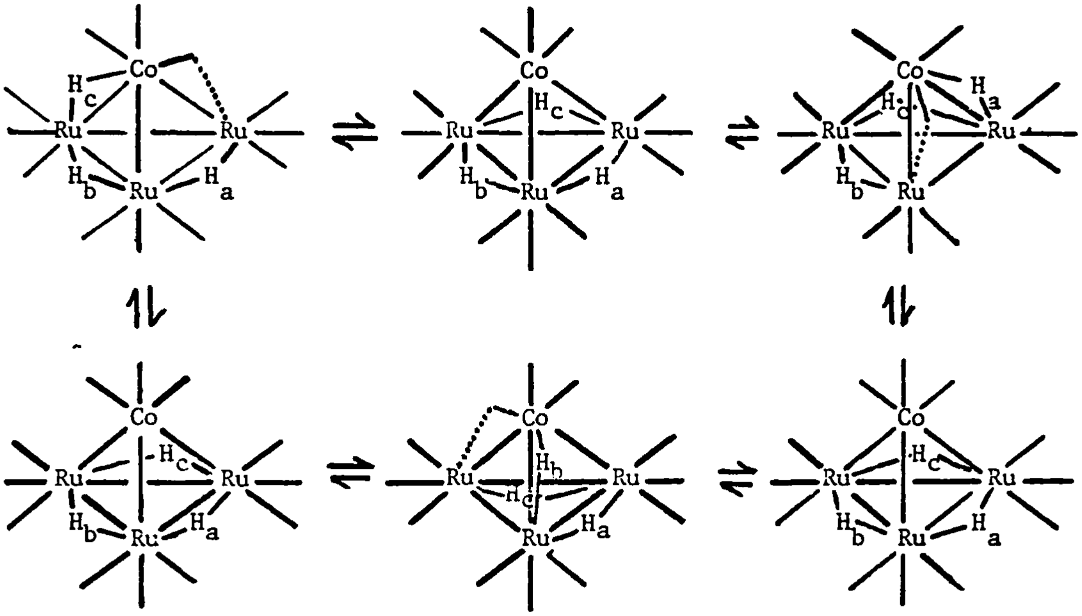


$\underline{3}$ (C_2) (reproduced with permission of ref. 25) $\underline{4}$ (C_{3v})

In the ^{1}H NMR spectrum of the isomeric mixture, as the temperature is raised above -80°C, the resonances broaden, coalesce, and form a single resonance at 26°C, Figure 2. Thus, as the temperature is raised, the two isomers interconvert and at 26°C all hydrogens see an equivalent environment on the NMR time scale. The mechanism that we propose to account for the $C_1 \rightleftarrows C_{3v}$ isomerization and total exchange of all hydrogens is qualitatively similar to that suggested by Kaesz and coworkers[28] for hydrogen exchange and isomerization in $[H_3Ru_4(CO)_{12}]^-$ and is shown in Scheme II.

It is apparent from this scheme that complete exchange of the three hydrogens of the C_1 isomer occurs only after three $C_1 \rightleftarrows C_{3v}$ isomerizations. Accordingly, we find that the resonance at δ -17.2 ppm due to the C_{3v} isomer broadens faster than those due to the C_1 isomer, Figure 2. Note that the exchange process also involves interconversion of the semi-bridging carbonyl and a terminal carbonyl on Co concomitant with the shift of one of the hydrogen ligands. It is also apparent from the spectral changes shown in Figures 2 and 3 that the $C_1 \rightleftarrows C_{3v}$ equilibrium

Scheme II



shifts to the left as the temperature is raised. Analysis of the -70°C, -80°C, and -100°C (360 MHz) spectra give the thermodynamic parameters $\Delta H = 160$ cal/mole and $\Delta S = -1.7$ cal/mole-K for the $C_1 \rightleftarrows C_{3v}$ isomerization.

Acknowledgments

We thank Mr. Price Stiffler of the International Engineering Corp. for allowing us use of their Harris/7 computer to complete the refinement of the $H_3CoRu_3(CO)_{12}$ structure and Dr. George McDonald of The University of Pennsylvania for obtaining the -100°C, 360 Mhz ^1H NMR spectrum. This work was supported in part by the Office of Naval Research. GLG gratefully acknowledges the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Grant (1978-1983) and the Alfred P. Sloan Foundation for a research fellowship (1978-1980).

Table I. Data for the X-ray Diffraction Study of $H_3CoRu_3(CO)_{12}$

Crystal Parameters

crystal system = triclinic

space group = $P\bar{1}$

a = 9.204(2) Å

b = 13.615(4) Å

c = 8.318(2) Å

α = 100.49(2)°

β = 111.51(2)°

γ = 81.78(2)°

V = 950.1 $Å^3$

Z = 2

calcd density = 2.451 g cm^{-3}

temp = 22°C

Measurement of Intensity Data

diffractometer = Syntex $P\bar{1}$

radiation = MoK_α (λ 0.71073)

monochromator = graphite crystal

scan method = θ-2θ; fixed background; background/scan time = .67

scan speed = variable, 2-24°/min

scan range = 2°

take-off angle = 4°

standard reflections = 2/50, 1% variation

data limits = $3° \leq 2\theta \leq 50°$

unique data = 3347

non-zero data = 3089 ($I \geq 2\sigma(I)$)

p = 0.055

Table II. Final atomic coordinates (x 10^4) and hydrogen thermal parameters

Atom	x	y	z	$B_{(iso)}$
Ru(1)	4470.6 (3)	2400.3 (2)	2040.6 (4)	
Ru(2)	1201.9 (3)	2206.5 (2)	-116.5 (4)	
Ru(3)	2419.5 (3)	1629.9 (2)	3354.3 (4)	
Co	2108.0 (6)	3531.2 (4)	2787.2 (6)	
O(1)	1977 (5)	5196 (2)	936 (5)	
O(2)	-927 (4)	4083 (3)	3252 (5)	
O(3)	4071 (5)	4476 (3)	6207 (5)	
O(4)	5077 (5)	3995 (2)	293 (5)	
O(5)	6960 (4)	3063 (3)	5539 (5)	
O(6)	6543 (5)	781 (3)	678 (5)	
O(7)	2994 (5)	-603 (3)	3646 (6)	
O(8)	-694 (4)	1882 (3)	3929 (5)	
O(9)	4266 (5)	2211 (3)	7194 (4)	
O(10)	732 (5)	473 (3)	-3096 (5)	
O(11)	-2221 (4)	2550 (3)	-371 (5)	
O(12)	849 (5)	3697 (3)	-2570 (5)	
C(1)	2045 (5)	4529 (3)	1606 (6)	
C(2)	243 (5)	3852 (3)	3077 (6)	
C(3)	3318 (6)	4076 (3)	4894 (6)	
C(4)	4832 (5)	3422 (3)	955 (6)	
C(5)	6025 (5)	2823 (4)	4246 (6)	
C(6)	5821 (5)	1388 (3)	1216 (6)	
C(7)	2769 (5)	215 (3)	3504 (6)	
C(8)	468 (5)	1798 (3)	3727 (6)	
C(9)	3579 (5)	2016 (3)	5760 (6)	
C(10)	891 (5)	1105 (3)	-1991 (5)	
C(11)	-935 (5)	2439 (3)	-275 (5)	
C(12)	981 (5)	3165 (3)	-1612 (6)	
H(12)	3111 (64)	1919 (41)	-26 (74)	5.8 (13)
H(13)	3983 (69)	1445 (43)	3199 (76)	6.6 (15)
H(23)	1290 (70)	1170 (44)	852 (77)	5.9 (13)

Table III. Anisotropic thermal parameters for non-hydrogen atoms[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ru(1)	1.93(1)	2.53(1)	2.30(1)	-0.24(1)	0.61(1)	0.24(1)
Ru(2)	2.12(1)	2.38(1)	1.96(1)	-0.26(1)	0.31(1)	0.23(1)
Ru(3)	2.22(1)	2.48(1)	2.27(1)	-0.15(1)	0.62(1)	0.57(1)
Co	2.55(2)	2.16(2)	2.46(2)	-0.03(2)	0.75(2)	0.00(2)
O(1)	6.5 (2)	3.3 (1)	5.9 (2)	0.2 (1)	2.5 (2)	1.7 (1)
O(2)	4.2 (2)	5.1 (2)	6.9 (2)	0.5 (1)	3.2 (2)	0.8 (2)
O(3)	6.4 (2)	6.2 (2)	3.7 (2)	-0.9 (2)	0.2 (1)	-1.6 (1)
O(4)	7.5 (2)	3.4 (1)	6.3 (2)	-0.8 (1)	3.7 (2)	1.1 (1)
O(5)	3.8 (2)	8.4 (2)	3.5 (2)	-0.9 (2)	0.3 (1)	-0.6 (2)
O(6)	4.8 (2)	4.7 (2)	6.6 (2)	0.8 (1)	2.9 (2)	0.0 (1)
O(7)	6.8 (2)	3.2 (2)	9.6 (3)	0.3 (1)	2.2 (2)	2.6 (2)
O(8)	3.2 (1)	5.1 (2)	6.3 (2)	-0.1 (1)	2.3 (1)	1.2 (1)
O(9)	5.3 (2)	7.6 (2)	2.8 (2)	-0.8 (2)	0.4 (1)	0.3 (1)
O(10)	7.8 (2)	4.1 (2)	4.0 (2)	-0.6 (2)	0.8 (2)	-0.8 (1)
O(11)	2.5 (1)	6.9 (2)	6.3 (2)	-0.2 (1)	1.3 (1)	1.4 (2)
O(12)	7.2 (2)	4.2 (2)	4.5 (2)	-0.4 (1)	1.8 (2)	2.1 (1)
C(1)	4.0 (2)	2.8 (2)	3.5 (2)	0.0 (1)	1.6 (2)	0.3 (1)
C(2)	4.1 (2)	2.6 (2)	3.7 (2)	0.3 (1)	1.6 (2)	0.6 (1)
C(3)	4.2 (2)	3.4 (2)	3.5 (2)	-0.1 (2)	1.1 (2)	0.0 (2)
C(4)	3.3 (2)	2.8 (2)	3.3 (2)	-0.3 (1)	1.3 (1)	0.0 (1)
C(5)	2.5 (2)	4.4 (2)	3.3 (2)	-0.5 (1)	0.7 (1)	-0.1 (2)
C(6)	2.6 (2)	3.3 (2)	3.8 (2)	-0.2 (1)	1.1 (1)	0.4 (1)
C(7)	3.2 (2)	3.5 (2)	4.3 (2)	-0.1 (1)	0.9 (2)	0.8 (2)
C(8)	3.0 (2)	3.1 (2)	3.5 (2)	-0.1 (1)	1.2 (1)	1.2 (1)
C(9)	3.2 (2)	4.5 (2)	2.9 (2)	-0.3 (2)	1.1 (2)	0.4 (2)
C(10)	3.4 (2)	3.1 (2)	2.8 (2)	-0.5 (1)	0.3 (1)	0.3 (1)
C(11)	3.3 (2)	3.7 (2)	2.8 (2)	-0.3 (1)	0.5 (1)	0.6 (1)
C(12)	3.8 (2)	3.1 (2)	3.0 (2)	-0.1 (1)	1.1 (1)	0.5 (1)

[a] The anisotropic thermal parameters are of the form:
$\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table IV. Selected bond lengths (Å) in $H_3CoRu_3(CO)_{12}$

Ru(1)-Co	2.678 (2)	0(1)-C(1)	1.131 (5)
Ru(2)-Co	2.674 (2)	0(2)-C(2)	1.131 (6)
Ru(3)-Co	2.672 (2)	0(3)-C(3)	1.143 (6)
		0(4)-C(4)	1.122 (5)
Ru(1)-Ru(2)	2.904 (2)	0(5)-C(5)	1.130 (5)
Ru(1)-Ru(3)	2.890 (1)	0(6)-C(6)	1.119 (5)
Ru(2)-Ru(3)	2.900 (2)	0(7)-C(7)	1.124 (6)
		0(8)-C(8)	1.129 (5)
Co-C(1)	1.799 (4)	0(9)-C(9)	1.128 (5)
Co-C(2)	1.802 (5)	0(10)-C(10)	1.121 (5)
Co-C(3)	1.786 (5)	0(11)-C(11)	1.146 (6)
		0(12)-C(12)	1.135 (5)
Ru(1)-C(4)	1.916 (4)		
Ru(1)-C(5)	1.916 (4)	Ru(1)-H(12)	1.788 (56)
Ru(1)-C(6)	1.925 (4)	Ru(1)-H(13)	1.939 (56)
Ru(3)-C(7)	1.926 (5)	Ru(2)-H(12)	1.721 (55)
Ru(3)-C(8)	1.907 (4)	Ru(2)-H(23)	1.726 (57)
Ru(3)-C(9)	1.905 (5)	Ru(3)-H(13)	1.474 (58)
Ru(2)-C(10)	1.925 (4)	Ru(3)-H(23)	1.982 (60)
Ru(2)-C(11)	1.906 (5)		
Ru(2)-C(12)	1.903 (4)		

Table V. Selected bond angles in $H_3CoRu_3(CO)_{12}$

Ru(1)-Ru(2)-Co	57.19 (5)	C(11)-Ru(2)-H(12)	176.4 (18)
Ru(2)-Ru(1)-Co	57.07 (5)	C(12)-Ru(2)-H(23)	168.4 (20)
Ru(1)-Ru(3)-Co	57.39 (4)	C(8)-Ru(3)-H(13)	174.8 (23)
Ru(3)-Ru(1)-Co	57.20 (4)	C(9)-Ru(3)-H(23)	177.2 (17)
Ru(2)-Ru(3)-Co	57.19 (5)	Co-C(1)-0(1)	175.8 (4)
Ru(3)-Ru(2)-Co	57.12 (5)	Co-C(2)-0(2)	177.8 (4)
Ru(1)-Co-Ru(2)	65.74 (5)	Co-C(3)-0(3)	176.1 (4)
Ru(1)-Co-Ru(3)	65.41 (4)	Ru(1)-C(4)-0(4)	177.4 (4)
Ru(2)-Co-Ru(3)	65.69 (5)	Ru(1)-C(5)-0(5)	178.9 (4)
Ru(1)-Ru(3)-Ru(2)	60.22 (5)	Ru(1)-C(6)-0(6)	176.6 (4)
Ru(1)-Ru(2)-Ru(3)	59.74 (5)	Ru(3)-C(7)-0(7)	177.9 (5)
Ru(2)-Ru(1)-Ru(3)	60.05 (5)	Ru(3)-C(8)-0(8)	178.8 (4)
Co-Ru(1)-C(6)	167.4 (1)	Ru(3)-C(9)-0(9)	177.6 (4)
Co-Ru(2)-C(10)	169.5 (1)	Ru(2)-C(10)-0(10)	178.4 (4)
Co-Ru(3)-C(7)	171.9 (1)	Ru(2)-C(11)-0(11)	178.0 (4)
Ru(1)-Co-C(2)	159.1 (1)	Ru(2)-C(12)-0(12)	176.5 (4)
Ru(2)-Co-C(3)	158.7 (2)	Ru(1)-H(12)-Ru(2)	111.7 (30)
Ru(3)-Co-C(1)	155.9 (1)	Ru(1)-H(13)-Ru(3)	115.1 (35)
C(5)-Ru(1)-H(12)	175.7 (18)	Ru(2)-H(23)-Ru(3)	102.7 (29)
C(4)-Ru(1)-H(13)	175.3 (18)		

Table VI. Infrared and ^{1}H NMR data for $H_3CoRu_3(CO)_{12}$ and $H_3CoOs_3(CO)_{12}$

Cluster	ν_{CO} (cm^{-1})	δ (ppm)
$H_3CoRu_3(CO)_{12}$	[a]2111 vw, 2088 s, 2080 m, 2068 s, 2052 vs, 2041 m, 2036 m, 2027 m, 2012 w, 2002 w, 1878 w, br	-17.2 (CD_2Cl_2, +30°C) -14.2, -17.2, -18.7 (CD_2Cl_2, -80°C)
$H_3CoOs_3(CO)_{12}$[b]	[c]2076 vs, 2066 m, 2049 w, 2030 vs, 2025 vs, 2012 w, 2005 s, 2000 sh, 1982 w	-19.1 (CD_2Cl_2, -85°C → +30°C)

[a] Hexane solution.

[b] Ref. 8.

[c] Cyclohexane solution.

References and Notes

1. a) The Pennsylvania State University
   b) The University of Wisconsin; present address, Nicolet XRD Corporation, Cuppertino, CA 95014

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19. The standard deviation of an observation at unit weight is defined as

$$[\Sigma w_i\left||F_o|-|F_c|\right|^2/(m-n)]^{1/2}$$

where m is the number of observations and n is the number of parameters fitted to the data set.

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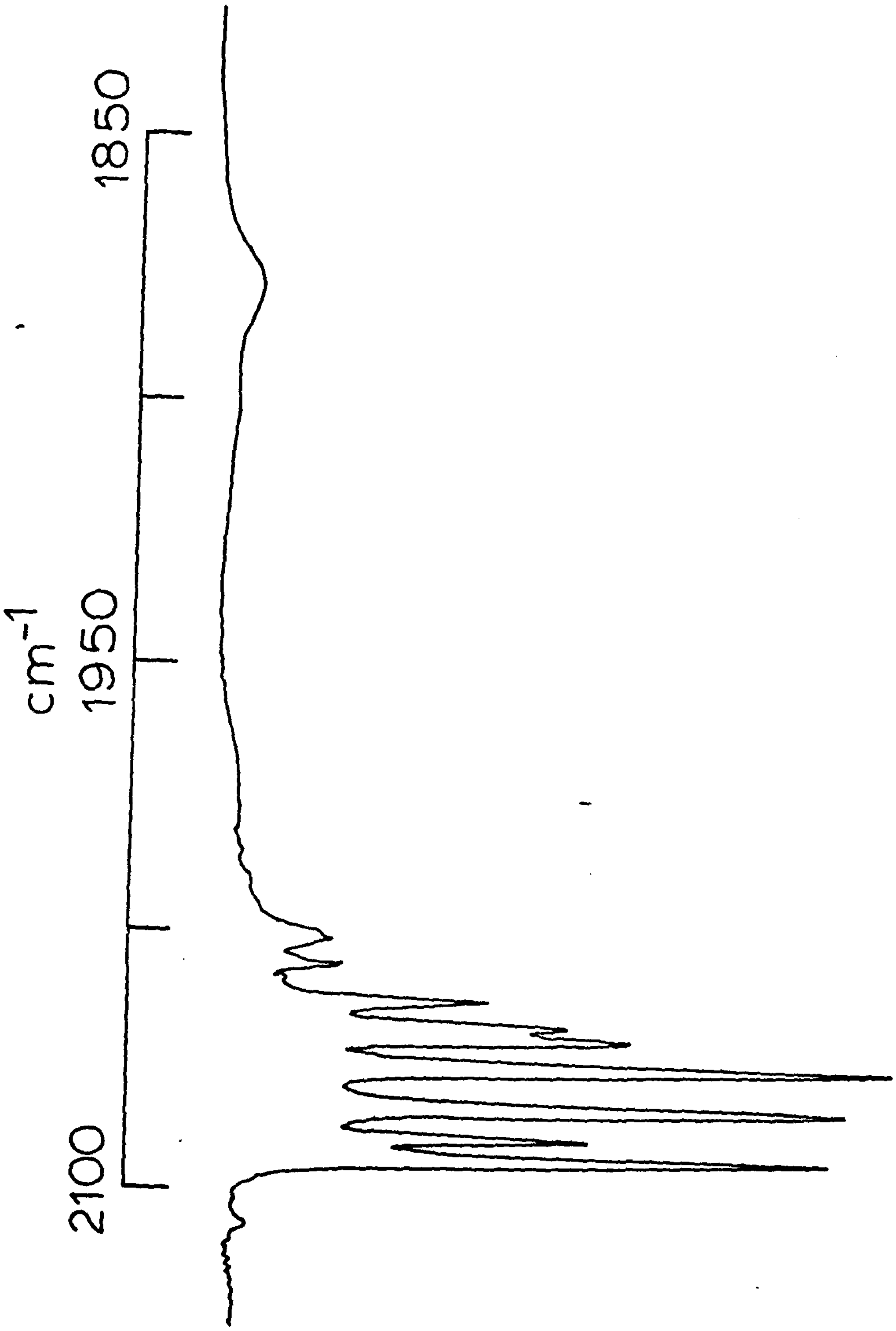
Figure Captions

Figure 1. Infrared spectrum of $H_3CoRu_3(CO)_{12}$ in hexane solution.

Figure 2. 100 Mhz ^1H NMR spectra of $H_3CoRu_3(CO)_{12}$ in CD_2Cl_2 solution.

Figure 3. ^1H NMR spectrum of $H_3CoRu_3(CO)_{12}$ at -100°C and 360 Mhz. The use of the 60% $CHCl_2F$/40% CD_2Cl_2 solvent system resulted in chemical shifts in this spectrum slightly different from those shown in Figure 2.

Figure 4. ORTEP plot of $H_3CoRu_3(CO)_{12}$ showing the atom numbering scheme.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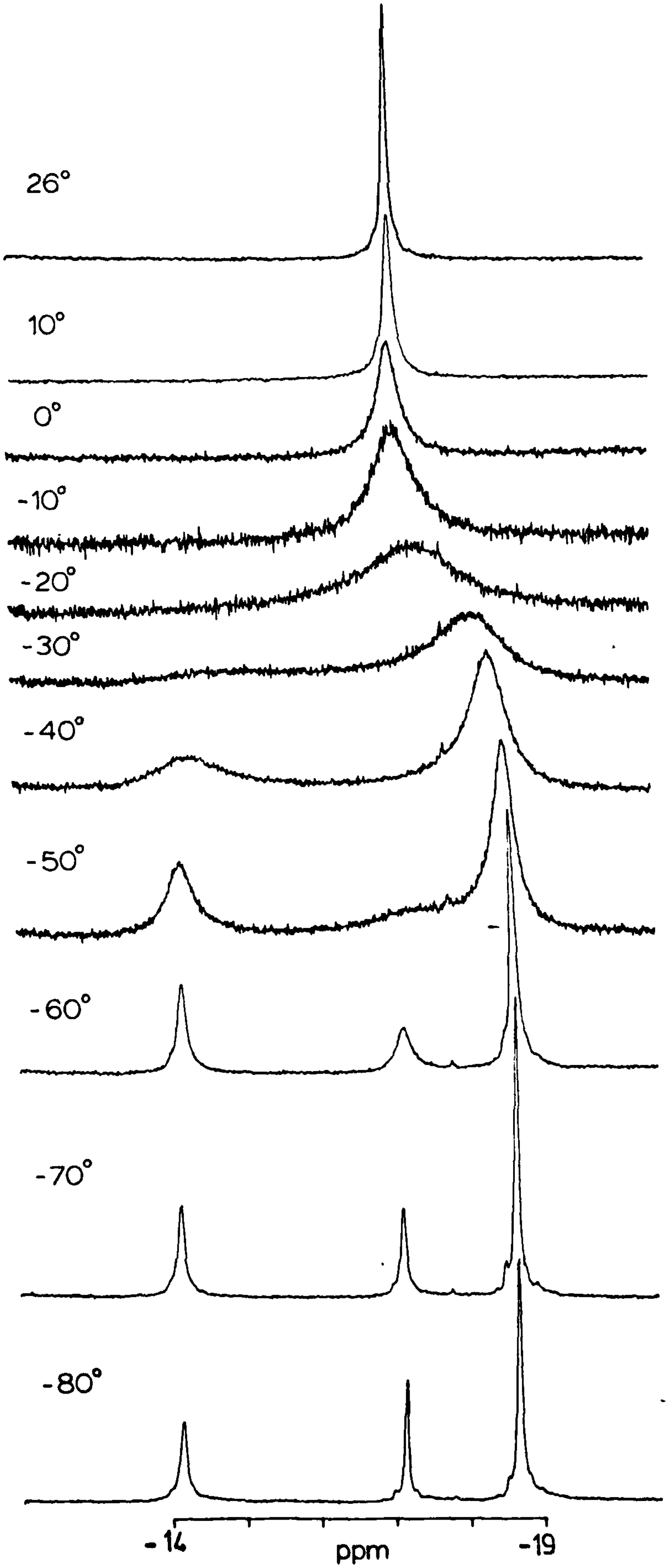
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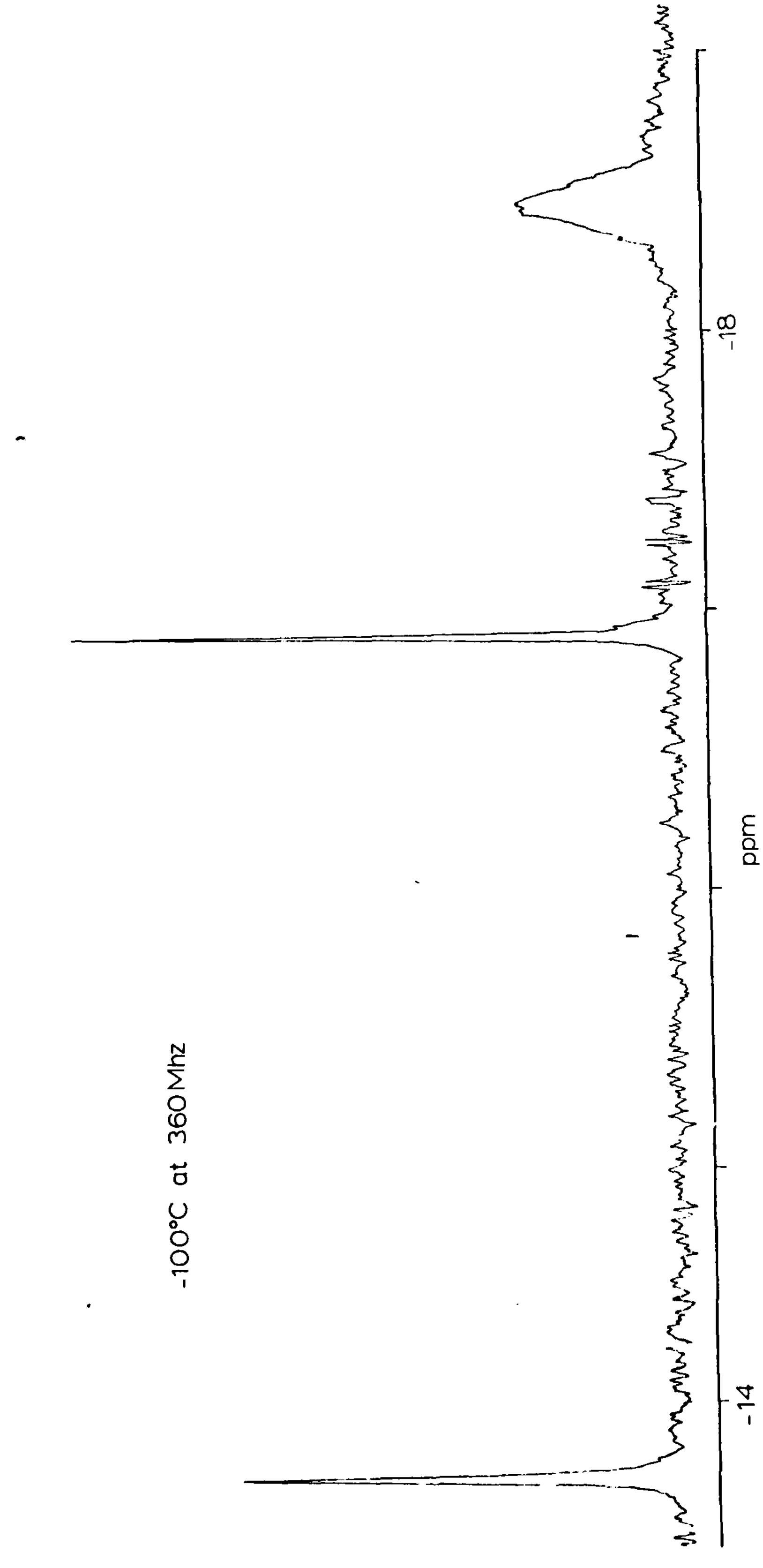
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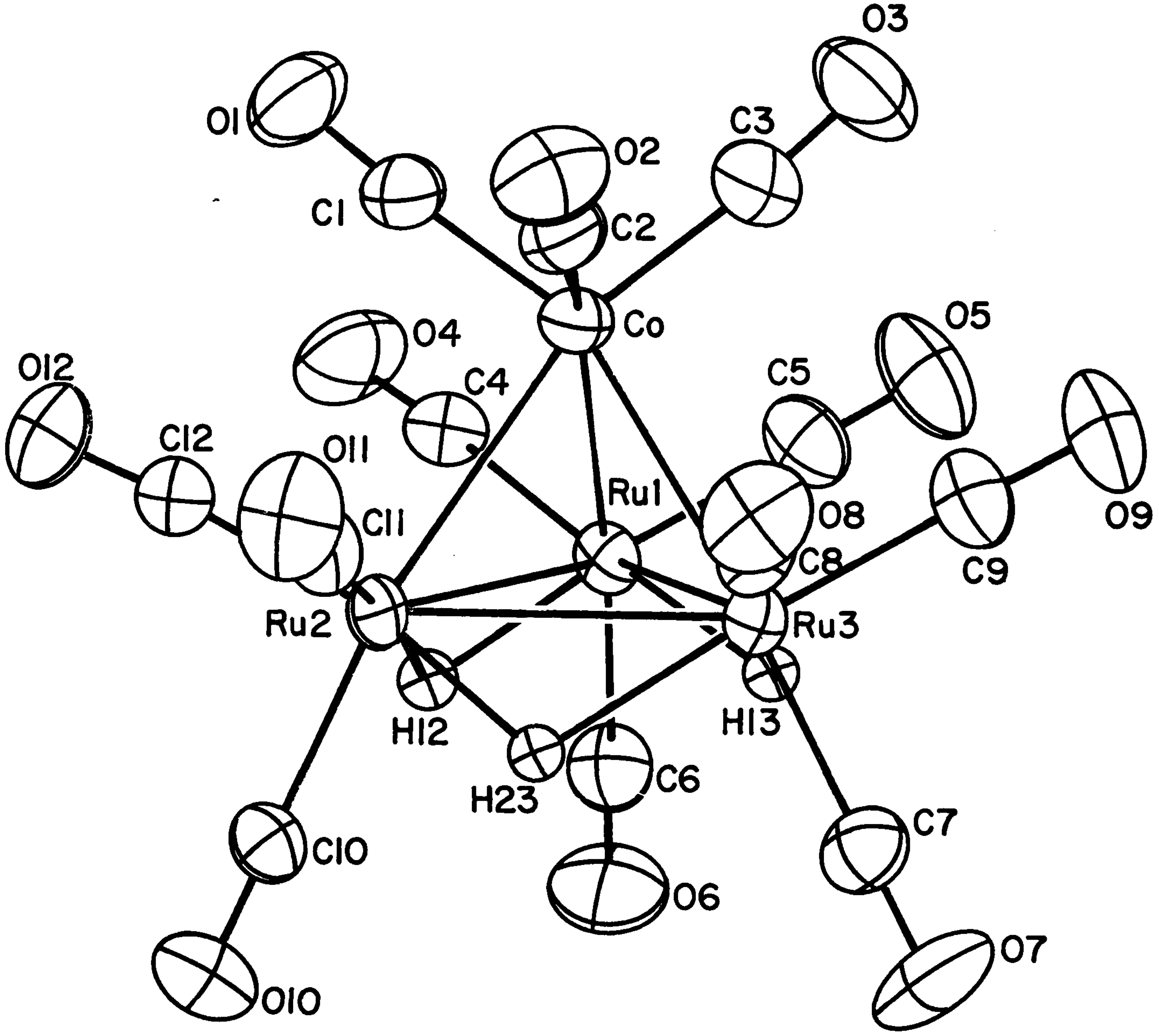
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