

priority than the one that is chelated by this ylide. Making this assignment gives both methine carbons an *S* configuration. There is also a helical axis of chirality collinear with the molecular twofold axis. The helix is left-handed and therefore *M*.

The solvate molecule in both structures does not associate with the uranium dimer. This can be seen in the stereoviews of the two structures in Figure 3 and 4. In structure I the closest interatomic contact of the diethyl ether solvate within the asymmetric unit is a 4.45 Å distance to a phenyl carbon. The closest contact to the dimer in an adjacent cell is 3.55 Å to a cyclopentadienyl carbon. In structure II the pentane molecule would not be expected to interact with the dimer and

is not found to do so. The closest contact is 3.88 Å with a cyclopentadienyl carbon. Both of the solvate molecules are poorly determined with high thermal parameters. As a result their structural parameters are characterized by large errors and are of little merit.

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**Registry No.** I, 67771-71-5; II, 71685-94-4; (C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>UCl, 1284-81-7.

**Supplementary Material Available:** Listings of structure factor amplitudes and cyclopentadienyl and phenyl C-C bond distances and angles (Tables VIII-XI) (27 pages). Ordering information is given on any current masthead page.

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## Synthesis and Spectroscopic Characterization of H<sub>3</sub>CoRu<sub>3</sub>(CO)<sub>12</sub>. Crystal and Molecular Structure of the C<sub>3v</sub> Isomer

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The reaction of HCoRu<sub>3</sub>(CO)<sub>13</sub> with H<sub>2</sub> in refluxing hexane gives the new cluster H<sub>3</sub>CoRu<sub>3</sub>(CO)<sub>12</sub> in 75% yield. Infrared and <sup>1</sup>H NMR spectra indicate that the cluster exists in two isomeric forms. The structure of one isomer has been determined by single-crystal X-ray diffraction. It crystallizes in the triclinic space group *P* $\bar{1}$  with *a* = 9.204 (2) Å, *b* = 13.615 (4) Å, *c* = 8.318 (2) Å,  $\alpha$  = 100.49 (2)°,  $\beta$  = 111.51 (2)°,  $\gamma$  = 81.78 (2)°, *V* = 950.1 Å<sup>3</sup>, and *Z* = 2. The structure was determined by the heavy-atom method and refined to *R*<sub>1</sub> = 2.3% and *R*<sub>2</sub> = 3.6%. The CoRu<sub>3</sub> 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<sub>3v</sub>. Spectral evidence indicates that the second isomer contains a bridging CO ligand and three nonequivalent hydrogens. The interconversion of the two isomers and the various hydrogen-exchange processes have been monitored by <sup>1</sup>H NMR spectroscopy, and the exchange mechanisms are discussed.

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 nonrigidity.<sup>2,3</sup> 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<sub>4</sub>(CO)<sub>12</sub>,<sup>4,5</sup> HCo<sub>3</sub>Os(CO)<sub>12</sub>,<sup>6</sup> H<sub>2</sub>Co<sub>2</sub>Os<sub>2</sub>(CO)<sub>12</sub>,<sup>7</sup> H<sub>3</sub>CoOs<sub>3</sub>(CO)<sub>12</sub>,<sup>8</sup> and H<sub>4</sub>Os<sub>4</sub>(CO)<sub>12</sub><sup>9-11</sup> constitute a Co-Os series of this type.

For the analogous Co-Ru series only Co<sub>4</sub>(CO)<sub>12</sub>, HCo<sub>3</sub>-Ru(CO)<sub>12</sub>,<sup>12,13</sup> and H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub><sup>9,14</sup> have been previously

Table I. Data for the X-ray Diffraction Study of H<sub>3</sub>CoRu<sub>3</sub>(CO)<sub>12</sub>

| Crystal Parameters  |                         |
|---|-------------------------|
| cryst system: triclinic   | <i>a</i> = 9.204 (2) Å  |
| space group: <i>P</i> $\bar{1}$   | <i>b</i> = 13.615 (4) Å |
| <i>V</i> = 950.1 Å <sup>3</sup>   | <i>c</i> = 8.318 (2) Å  |
| <i>Z</i> = 2  | $\alpha$ = 100.49 (2)°  |
| calcd density = 2.451 g cm <sup>-3</sup>  | $\beta$ = 111.51 (2)°   |
| temp = 22 °C  | $\gamma$ = 81.78 (2)°   |
| Measurement of Intensity Data   |                         |
| diffractometer: Syntex P1   |                         |
| radiation: Mo K $\alpha$ ( $\lambda$ 0.710 73 Å)                                |                         |
| monochromator: graphite crystal   |                         |
| scan method: $\theta$ -2 $\theta$ (fixed background; background/scan time = 67) |                         |
| scan speed: variable, 2-24°/min   |                         |
| scan range: 2°  |                         |
| takeoff angle: 4°   |                         |
| std reflectns: 2/50, 1% variation   |                         |
| data limits: 3° $\leq$ 2 $\theta$ $\leq$ 50°                                    |                         |
| unique data: 3347   |                         |
| nonzero data: 3089 ( <i>I</i> $\geq$ 2 $\sigma$ ( <i>I</i> ))                   |                         |
| <i>p</i> = 0.055  |                         |

described. We recently reported the high-yield preparation of HCoRu<sub>3</sub>(CO)<sub>13</sub><sup>15</sup> and have since found that treatment of this cluster with H<sub>2</sub> cleanly yields H<sub>3</sub>CoRu<sub>3</sub>(CO)<sub>12</sub>, one of the remaining members of the Co-Ru series. Described herein are details of the synthesis of this compound, its spectroscopic

- (1) (a) The Pennsylvania State University. (b) The University of Wisconsin.
- (2) Such comparison has been made by utilizing the series M<sub>x</sub>M'<sub>4-x</sub>(CO)<sub>12</sub> (M, M' = Co, Rh, Ir): Martinengo, S.; Chini, P.; Albano, V. G.; Cariati, F.; Salvatori, T. *J. Organomet. Chem.* **1973**, *59*, 379. Chini, P.; Heaton, B. T. *Top. Curr. Chem.* **1977**, *71*, 1.
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Table II. Final Atomic Coordinates ( $\times 10^4$ ) and Hydrogen Thermal Parameters

| atom  | x          | y          | z          | $B_{iso}, \text{\AA}^2$ |
|-------|------------|------------|------------|-------------------------|
| 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)   | -503 (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)                |

characterization, and the crystal and molecular structure of one isomer.

### Experimental Section

**Synthesis of  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$ .**  $\text{HCoRu}_3(\text{CO})_{13}$  (181 mg, 0.248 mmol), prepared according to the literature procedure,<sup>15</sup> was dissolved in 125 mL of hexane, and the solution was deoxygenated by stirring under an  $\text{N}_2$  purge for 10 min. The  $\text{N}_2$  purge was replaced with an  $\text{H}_2$  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  $\text{N}_2$  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  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$ . Anal. Calcd for  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$ : C, 20.55; H, 0.43. Found: C, 20.79; H, 0.42 (Galbraith Laboratories).

**Spectroscopy.** Unless otherwise specified, all  $^1\text{H}$  NMR spectra were obtained on a JEOL PFT 100-MHz Fourier transform spectrometer equipped with a Nicolet 1080 computer. The  $\text{CD}_2\text{Cl}_2$  solvent was dried over  $\text{P}_2\text{O}_5$  and distilled under vacuum directly into the 10-mm NMR tubes containing the samples, and these were sealed under vacuum. Infrared spectra were recorded by 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.<sup>16</sup> The data were collected and treated in the usual manner.<sup>17</sup> The Patterson function was automatically interpreted for the metal atom tetrahedron and yielded the carbonyl atom framework directly ( $R_1 = 21.4\%$ )<sup>18</sup> The data were then corrected for absorption with an absorption coefficient of  $\mu = 32.11 \text{ cm}^{-1}$ , a range of transmission of 0.43–0.74, and defining faces  $\pm[(101, 0.05 \text{ mm}), (110, 0.16 \text{ mm}), (010, 0.18 \text{ mm})]$ . After a preliminary refinement series, a difference Fourier map clearly revealed the presence of the three bridging hydride atoms along the base of the  $\text{Ru}_3$  triangle.

- (16) All crystallographic programs used in the structural determination and least-squares refinement were written by J.C.C. The absorption correction program (J. F. Blount) uses the Gaussian integration method of Busing and Levy. Plots were made by using ORTEP (C. K. Johnson).  
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 (18)  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| \times 100\%$ ,  $R_2 = [\sum w_i |F_o|^2 - |F_c|^2 / \sum w_i |F_o|^2]^{1/2} \times 100\%$ .

Table III. Anisotropic Thermal Parameters for Nonhydrogen Atoms<sup>a</sup>

| 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)  |

<sup>a</sup> 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  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$ 

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

The structure was refined by full/block diagonal minimization of  $\sum w_i(|F_o| - |F_c|)^2$  with final convergence to  $R_1 = 2.3\%$  and  $R_2 = 3.6\%$ <sup>18</sup> and an esd of an observation at unit weight = 1.13<sup>19</sup> with a data/parameter ratio of 11.7. In the final refinement cycle, the nonhydrogen atoms were allowed anisotropic thermal parameters whereas the hydrogen atoms were refined isotropically. Atomic scattering factors for the nonhydrogen atoms were taken from Cromer,<sup>20</sup> and the hydrogen scattering factors were those of Stewart et al.<sup>21</sup> The refinement also included terms for anomalous dispersion for Ru and Co.<sup>22</sup> There

- (19) The standard deviation of an observation at unit weight is defined as  $[\sum w_i |F_o| - |F_c|]^2 / (m - n)]^{1/2}$ , where  $m$  is the number of observations and  $n$  is the number of parameters fitted to the data set.  
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Table V. Selected Bond Angles (Deg) in  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$ 

|                   |            |                   |            |
|-------------------|------------|-------------------|------------|
| 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)-O(1)      | 175.8 (4)  |
| Ru(3)-Ru(2)-Co    | 57.12 (5)  | Co-C(2)-O(2)      | 177.8 (4)  |
| Ru(1)-Co-Ru(2)    | 65.74 (5)  | Co-C(3)-O(3)      | 176.1 (4)  |
| Ru(1)-Co-Ru(3)    | 65.41 (4)  | Ru(1)-C(4)-O(4)   | 177.4 (4)  |
| Ru(2)-Co-Ru(3)    | 65.69 (5)  | Ru(1)-C(5)-O(5)   | 178.9 (4)  |
| Ru(1)-Ru(3)-Ru(2) | 60.22 (5)  | Ru(1)-C(6)-O(6)   | 176.6 (4)  |
| Ru(1)-Ru(2)-Ru(3) | 59.74 (5)  | Ru(3)-C(7)-O(7)   | 177.9 (5)  |
| Ru(1)-Ru(1)-Ru(3) | 60.05 (5)  | Ru(3)-C(8)-O(8)   | 178.8 (4)  |
| Co-Ru(1)-C(6)     | 167.4 (1)  | Ru(3)-C(9)-O(9)   | 177.6 (4)  |
| Co-Ru(2)-C(10)    | 169.5 (1)  | Ru(2)-C(10)-O(10) | 178.4 (4)  |
| Co-Ru(3)-C(7)     | 171.9 (1)  | Ru(2)-C(11)-O(11) | 178.0 (4)  |
| Ru(1)-Co-C(2)     | 159.1 (1)  | Ru(2)-C(12)-O(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  $^1\text{H}$  NMR Data for  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$  and  $\text{H}_3\text{CoOs}_3(\text{CO})_{12}$ 

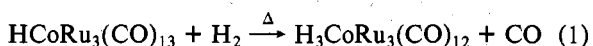
| cluster   | $\nu_{\text{CO}}, \text{cm}^{-1}$   | $\delta$   |
|---|---|--|
| $\text{H}_3\text{CoRu}_3(\text{CO})_{12}^a$     | 2111 vw, 2088 s, 2080 m,<br>2068 s, 2052 vs, 2041 m,<br>2036 m, 2027 m,<br>2012 w, 2002 w, 1878 w, br | -17.2 ( $\text{CD}_2\text{Cl}_2$ , 30 °C),<br>-14.2, -17.2, -18.7 ( $\text{CD}_2\text{Cl}_2$ , -80 °C) |
| $\text{H}_3\text{CoOs}_3(\text{CO})_{12}^{b,c}$ | 2076 vs, 2066 m, 2049 w,<br>2030 vs, 2025 vs, 2012 w,<br>2005 s, 2000 sh,<br>1982 w                   | -19.1 ( $\text{CD}_2\text{Cl}_2$ , -85 °C) →<br>+30 °C   |

<sup>a</sup> Hexane solution. <sup>b</sup> Reference 8. <sup>c</sup> Cyclohexane solution.

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 (Table A).

## Results

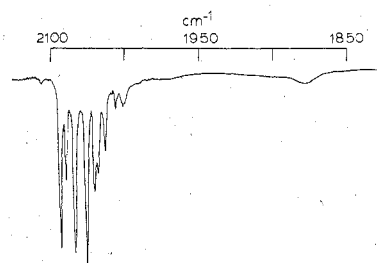
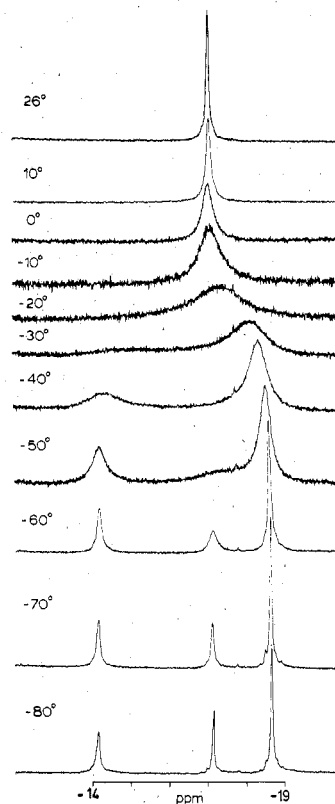
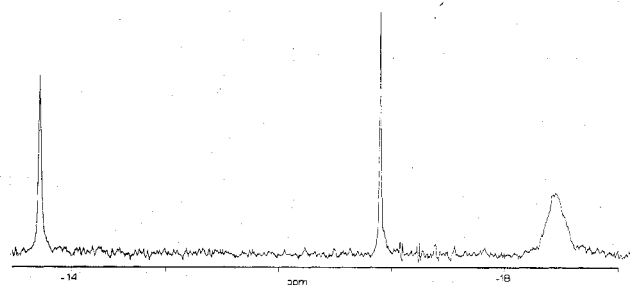
**Synthesis and Spectroscopic Characterization of  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$ .**  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$  is conveniently prepared by heating hexane solutions of  $\text{HCoRu}_3(\text{CO})_{13}$  under an  $\text{H}_2$  atmosphere (eq 1). Analogous reactions have been employed



by Kaesz and co-workers<sup>9</sup> to prepare  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  and  $\text{H}_4\text{FeRu}_3(\text{CO})_{12}$  from  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$  and  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ , respectively.  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$  appears to be indefinitely stable both in the solid state and in solution. This contrasts sharply to  $\text{H}_3\text{CoOs}_3(\text{CO})_{12}$  which is reported to be air sensitive.<sup>5</sup>  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$  was characterized by chemical analysis and by its  $^1\text{H}$  NMR, infrared, and mass spectra and one isomer of the compound by a complete single-crystal X-ray structure determination. Pertinent spectral data are summarized in Table VI along with corresponding data for  $\text{H}_3\text{CoOs}_3(\text{CO})_{12}$  for comparison.

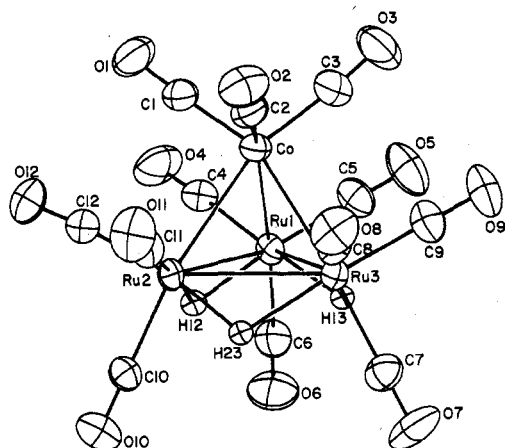
The mass spectrum of  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$  shows a parent ion centered at  $m/e$  704 with the expected isotopic distribution and with fragment ions corresponding to the loss of each of the 12 carbonyl ligands. The infrared spectrum is shown in Figure 1 and displays 11 distinct bands in the terminal region and a single weak, broad band in the bridging carbonyl region at  $1878 \text{ cm}^{-1}$ .

The  $^1\text{H}$  NMR spectrum of  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$  at room temperature shows one sharp singlet at  $\delta$  -17.1. However, as shown in Figure 2, upon cooling of the solution to -80 °C, the singlet develops into three separate singlets at  $\delta$  -14.2, -17.2,

Figure 1. Infrared spectrum of  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$  in hexane solution.Figure 2. 100-MHz  $^1\text{H}$  NMR spectra of  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$  in  $\text{CD}_2\text{Cl}_2$  solution.Figure 3.  $^1\text{H}$  NMR spectrum of  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$  at -100 °C and 360 MHz. The use of the 60/40  $\text{CHCl}_2\text{F}/\text{CD}_2\text{Cl}_2$  solvent system resulted in chemical shifts in this spectrum slightly different from those shown in Figure 2.

and -18.7 with relative intensities 1:0.85:2, respectively. At -80 °C the downfield singlet at  $\delta$  -14.2 is clearly broader ( $\sim 10$  Hz) than the remaining two ( $\sim 6$ -7 Hz). At -100 °C with the use of a 360-MHz instrument,<sup>23</sup> the upfield singlet at  $\delta$  -18.7 is broadened almost into the base line whereas the other

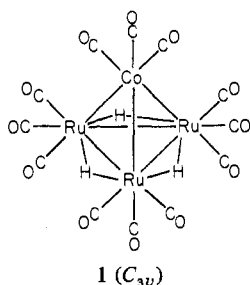
(23) The spectrum was obtained by Dr. George McDonald on a Bruker WH 360/180 spectrometer at the Middle Atlantic NMR Facility (supported by NIH Grant RR542 at the University of Pennsylvania).



**Figure 4.** ORTEP plot of  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$  showing the atom-numbering scheme.

two singlets remain unchanged (Figure 3).

**Crystal and Molecular Structure of  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$ .** The  $^1\text{H}$  NMR spectra imply that two isomers of  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$  are present in solution (see Discussion). 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. The  $\text{CoRu}_3$  core of the cluster defines a dis-



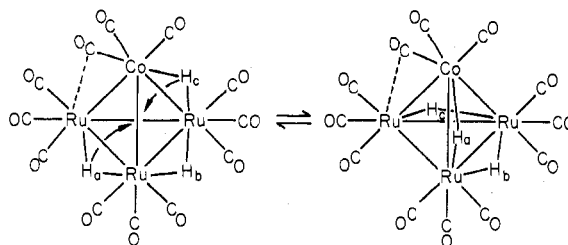
torted tetrahedron with approximate  $C_{3v}$  symmetry. The three hydride ligands were located by difference Fourier techniques and bridge the three Ru–Ru bonds, consistent with the near  $C_{3v}$  symmetry of this isomer. The structure is quite similar to that found for  $\text{H}_3\text{CoOs}_3(\text{CO})_{12}$ , except that in the latter case the hydride ligands were not located.<sup>8</sup> The Ru–Ru distances of  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$  average 2.90 Å. These compare well to hydride-bridged Ru–Ru distances found in other clusters:  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$  (2.93 Å),<sup>24</sup>  $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$  ( $C_2$  isomer, 2.92 Å;  $C_{3v}$  isomer, 2.94 Å).<sup>25</sup> They differ significantly from unbridged Ru–Ru distances:  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$  (2.78 Å),<sup>24</sup>  $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$  ( $C_2$  isomer, 2.80 Å;  $C_{3v}$  isomer, 2.79 Å),<sup>25</sup>  $[\text{CoRu}_3(\text{CO})_{13}]^-$  (2.83 Å).<sup>15</sup> As illustrated in the ORTEP drawing, Figure 4, the three bridging hydrides are not coplanar with the  $\text{Ru}_3$  triangle but instead lie below it.

### Discussion

The substitution of CO by  $\text{H}_2$  has been shown by Kaesz and co-workers<sup>9</sup> to be a valuable method for preparing metal hydride clusters. With  $\text{HCoRu}_3(\text{CO})_{13}$  the reaction proceeds smoothly to give an excellent yield of  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$  (eq 1). Although the mechanism of these various reactions is currently unknown, they likely proceed via a simple, direct substitution of CO by  $\text{H}_2$  on the intact metal cluster.

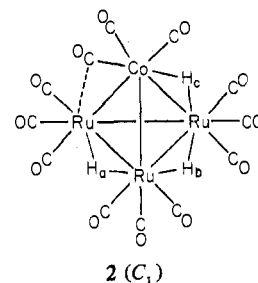
The complexity of the infrared spectrum, Figure 1, and the observed low-temperature  $^1\text{H}$  NMR pattern, Figure 2, indicate that two different isomeric forms of  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$  are present in solution, one of which is the structurally charac-

**Scheme I**



terized  $C_{3v}$  isomer. The presence of a weak, broad band at  $1878\text{ cm}^{-1}$  in the IR spectrum implies the presence of a bridging or semibridging CO in the second isomer.

The two resonances at  $\delta -14.2$  and  $-18.7$  in the  $-80^\circ\text{C}$   $^1\text{H}$  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 ( $\delta -18.7$ ) but different from the third ( $\delta -14.2$ ) under the kinetic limitations of this experiment. However, as shown in Figure 3, the  $\delta -18.7$  resonance is considerably broadened when the spectrum is recorded at  $-100^\circ\text{C}$  by 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  $^1\text{H}$  NMR and infrared spectra is that shown in 2 with its  $C_1$  symmetry label. The semi-



bridging carbonyl formation is preferred as this gives each metal the requisite 18 electrons<sup>26</sup> as well as being consistent with the IR spectrum ( $\nu_{\text{CO}} = 1878\text{ cm}^{-1}$ ).

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  $^{59}\text{Co}$  nucleus in this cluster. On the basis of the observed line widths and the reasonable exchange mechanisms, we tentatively attribute the  $\delta -14.2$  resonance to  $\text{H}_b$  and the  $\delta -18.7$  resonance to the rapidly exchanging  $\text{H}_a$  and  $\text{H}_c$ . We suggest that the exchange of  $\text{H}_a$  and  $\text{H}_c$  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  $-80^\circ\text{C}$ , 100-MHz spectrum, we would expect the resonance due to  $\text{H}_b$  to be a triplet while that due to the rapidly exchanging  $\text{H}_a$  and  $\text{H}_c$  would be a doublet. Although this coupling was not resolved, the observed line widths are consistent with our assignment since the  $\delta -14.7$  line width (10.1 Hz) is greater than that of the  $\delta -18.7$  resonance (7.0 Hz).

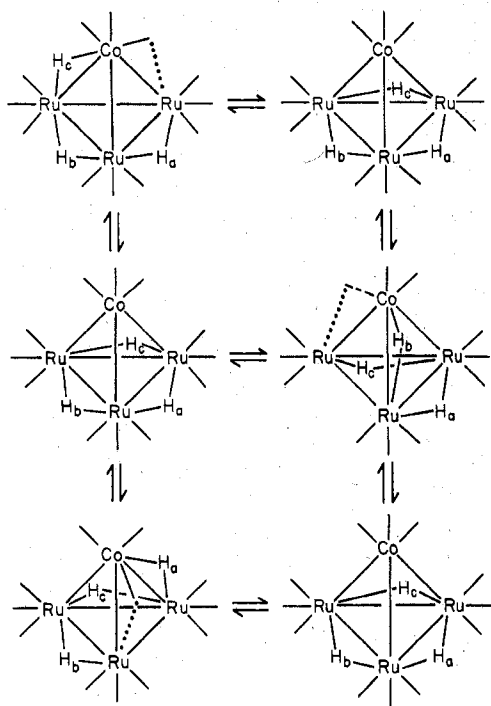
The remaining resonance at  $\delta -17.2$  in the  $-80^\circ\text{C}$   $^1\text{H}$  NMR spectrum is logically attributed to the structurally characterized  $C_{3v}$  isomer in which the three hydrogen ligands are

(24) Yawney, D. B. W.; Doedens, R. J. *Inorg. Chem.* **1972**, *11*, 838.

(25) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Nelson, W. J. *J. Chem. Soc., Chem. Commun.* **1978**, 920.

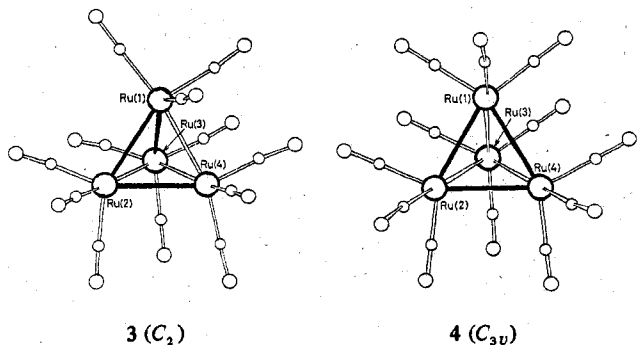
(26) This assumes that the bridging hydride contributes  $1/2$  electron to each metal and the semibridging carbonyl contributes  $1/2$  electrons to Co and  $1/2$  electron to Ru.

Scheme II



equivalent. Such an assignment is consistent with the observation that this resonance has the smallest line width since no H-H coupling is present.

These two isomers are directly analogous to the two structurally characterized isomers of  $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$  of  $C_2$  and  $C_{3v}$  symmetries shown in 3 and 4,<sup>27</sup> respectively, with the

3 ( $C_2$ )4 ( $C_{3v}$ )

(27) Reprinted with permission from ref 25. Copyright 1978 The Chemical Society.

hydride-bridged Ru-Ru bonds represented by the solid lines.<sup>25</sup> The principal structural difference between 2 and 3 is the presence of the semibridging carbonyl in 2. Structurally similar isomers have been suggested for  $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ ,<sup>28</sup> and the  $C_{3v}$  isomer of  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$  is isostructural to  $\text{H}_3\text{CoOs}_3(\text{CO})_{12}$ .<sup>8</sup>

In the  $^1\text{H}$  NMR spectrum of the isomeric mixture, as the temperature is raised above  $-80^\circ\text{C}$ , the resonances broaden, coalesce, and form a single resonance at  $26^\circ\text{C}$  (Figure 2). Thus, as the temperature is raised, the two isomers interconvert, and at  $26^\circ\text{C}$  all hydrogens see an equivalent environment on the NMR time scale. The mechanism that we propose to account for the  $C_1 \rightleftharpoons C_{3v}$  isomerization and total exchange of all hydrogens is qualitatively similar to that suggested by Kaesz and co-workers<sup>29</sup> for hydrogen exchange and isomerization in  $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$  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  $C_1 \rightleftharpoons C_{3v}$  isomerizations. Accordingly, we find that the resonance at  $\delta -17.2$  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 semibridging 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  $C_1 \rightleftharpoons C_{3v}$  equilibrium shifts to the left as the temperature is raised. Analysis of the  $-70$ ,  $-80$ , and  $-100^\circ\text{C}$  (360 MHz) spectra give the thermodynamic parameters  $\Delta H = 160$  cal/mol and  $\Delta S = -1.7$  cal/(mol K) for the  $C_1 \rightleftharpoons C_{3v}$  isomerization.

**Acknowledgment.** 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  $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$  structure and Dr. George McDonald of The University of Pennsylvania for obtaining the  $-100^\circ\text{C}$ , 360-MHz  $^1\text{H}$  NMR spectrum. This work was supported in part by the Office of Naval Research. G.L.G. 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).

**Registry No.** 1, 73926-32-6; 2, 73926-33-7;  $\text{HCoRu}_3(\text{CO})_{12}$ , 72275-15-1.

**Supplementary Material Available:** A listing of observed and calculated structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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