

## Reaction of Tetranuclear Mixed-Metal Clusters with Carbon Monoxide

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Reaction of the mixed-metal tetranuclear clusters  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ ,  $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$ ,  $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$ ,  $\text{HCoRu}_3(\text{CO})_{13}$ ,  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}\text{L}$  ( $\text{L} = \text{PMe}_2\text{Ph}$ ,  $\text{PPh}_3$ ),  $[\text{HFeRu}_3(\text{CO})_{13}]^-$ , and  $[\text{CoRu}_3(\text{CO})_{13}]^-$  with CO under relatively mild conditions ( $P(\text{CO}) = 1 \text{ atm}$ ,  $t = 0-80^\circ\text{C}$ ) results in their fragmentation to give trimeric and monomeric products. The fragmentation reactions are generally quite selective:  $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$ , for example, reacts with CO to give  $\text{Ru}_3\text{Os}(\text{CO})_{12}$ ,  $\text{Fe}(\text{CO})_5$ , and  $\text{H}_2$  with no  $\text{RuOs}_2(\text{CO})_{12}$ ,  $\text{FeRu}_2(\text{CO})_{12}$ , or  $\text{FeRuOs}(\text{CO})_{12}$  detected in the product mixture. This reaction and the corresponding fragmentation of  $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$  provide a convenient means of separating and isolating the mixed-metal trimers  $\text{Ru}_2\text{Os}(\text{CO})_{12}$  and  $\text{RuOs}_2(\text{CO})_{12}$ . The reactivity of a particular cluster toward CO is greatly dependent on its metal composition and/or its structure. For example,  $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$  reacts slowly over a period of several days while the breakdown of  $\text{HCoRu}_3(\text{CO})_{13}$  is complete within 1 h. The tetrahydride clusters  $\text{H}_4\text{FeRu}_3(\text{CO})_{12}$  and  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  first react with CO to displace  $\text{H}_2$  and form the corresponding dihydride clusters which subsequently fragment under the reaction conditions. Kinetic measurements indicate that the fragmentation of  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  to produce  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{Fe}(\text{CO})_5$ , and  $\text{H}_2$  proceeds largely by a second-order,  $[\text{CO}]$ -dependent path with activation parameters  $\Delta H^\ddagger = 20.0 \pm 2.0 \text{ kcal/mol}$  and  $\Delta S^\ddagger = -25.4 \pm 5.8 \text{ cal/(mol K)}$ . Likewise, fragmentation of  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$  to form  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{Ru}(\text{CO})_5$ , and  $\text{H}_2$  proceeds via a second-order,  $[\text{CO}]$ -dependent path with  $\Delta H^\ddagger = 12.5 \pm 0.5 \text{ kcal/mol}$  and  $\Delta S^\ddagger = -36.6 \pm 1.6 \text{ cal/(mol K)}$ .

## Introduction

Transition metal cluster compounds are being investigated as catalysts for a variety of reactions involving carbon monoxide. These include the reduction of CO to produce hydrocarbons,<sup>1</sup> alcohols,<sup>2</sup> and ethylene glycol,<sup>3</sup> hydroformylation and related olefin reactions,<sup>4,5</sup> and the water-gas shift reaction.<sup>5,6</sup> With the interest in chemistry of this type so intense, it is essential that the basic reactivity patterns of clusters with CO be understood. A number of reactions of clusters with CO have been mentioned in the literature,<sup>7</sup> and detailed kinetic studies of the reactions of CO with  $\text{Ru}_3(\text{CO})_{12}$ <sup>8</sup> and  $\text{Co}_4(\text{C-O})_{12}$ <sup>9</sup> have been published. However, no comprehensive, comparative study is yet available, and, importantly, the ease with which clusters fragment in the presence of CO does not appear to be generally appreciated.

In order to further the understanding of how clusters interact with CO, we have examined the reactivity of a series of tetranuclear mixed-metal clusters with carbon monoxide and report the results of those studies herein. We have found that all the clusters examined in this work fragment in the presence of CO, generally to produce trimers and monomers, but that the rate of fragmentation is greatly dependent on the metal composition and/or the structure of the cluster. Kinetic data for the reactions of CO with  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  and  $\text{H}_2\text{Ru}_4(\text{C-}$

$\text{O})_{13}$  are also presented along with the corresponding mechanistic implications.

## Experimental Section

**Reactions of Tetranuclear Clusters with Carbon Monoxide.** The clusters  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ ,<sup>10</sup>  $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$ ,<sup>10</sup>  $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$ ,<sup>10</sup>  $\text{HCoRu}_3(\text{CO})_{13}$ ,<sup>11</sup>  $[\text{PPN}][\text{CoRu}_3(\text{CO})_{13}]$  ( $\text{PPN} = (\text{Ph}_3\text{P})_2\text{N}^+$ ),<sup>11</sup>  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ ,<sup>12</sup>  $\text{H}_4\text{FeRu}_3(\text{CO})_{12}$ ,<sup>12</sup>  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}\text{L}$  ( $\text{L} = \text{PMe}_2\text{Ph}$ ,  $\text{PPh}_3$ ),<sup>13</sup>  $[\text{PPN}][\text{HFeRu}_3(\text{CO})_{13}]$ ,<sup>14</sup> and  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ <sup>15</sup> were prepared by published procedures. A 5-mL aliquot of a concentrated solution ( $>10^{-3} \text{ M}$ ) of the cluster whose reaction with CO was to be studied was placed in a 25-mL Schlenk tube equipped with a serum cap. Hexane was used as the solvent for the neutral compounds, while the anionic clusters were dissolved in either THF or  $\text{CH}_2\text{Cl}_2$ . Hexane and  $\text{CH}_2\text{Cl}_2$  were used as received, whereas the THF was dried over sodium benzophenone ketyl immediately prior to use. The solution was degassed via three freeze-pump-thaw cycles, placed under an atmosphere of carbon monoxide, and immersed in a temperature-controlled water bath. The course of the reactions was monitored by infrared spectroscopy and by analytical liquid chromatography. Products of the reactions were separated by liquid chromatography and identified by mass spectrometry, by infrared spectroscopy, and by comparison of chromatographic retention times to those of standard samples.

**Kinetic Experiments.** Stock solutions of  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  and  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$  ( $[\text{cluster}] = 6 \times 10^{-4} \text{ M}$ ) were prepared with heptane as solvent, chosen because the solubility of carbon monoxide in that solvent has been accurately determined.<sup>16</sup> A 5-mL aliquot of the stock solution was pipetted into a 25-mL degassable Pyrex 1-cm path length spectrophotometer cell and degassed via freeze-pump-thaw techniques. The desired pressure of CO was admitted by using a Hg manometer ( $\pm 1 \text{ mmHg}$ ), and the spectrophotometer cell was immersed in a temperature-controlled water bath. The actual CO concentration in solution was calculated by assuming ideal gas behavior; thus the pressure of CO in the cell and hence the CO concentration in solution

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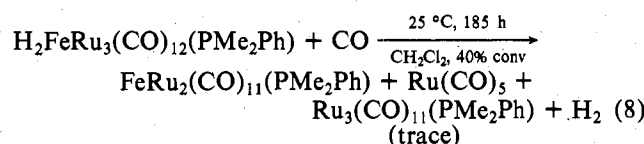
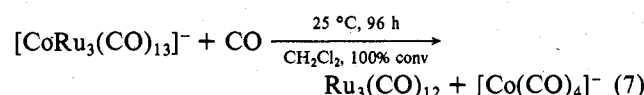
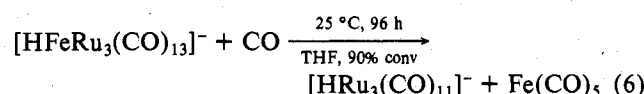
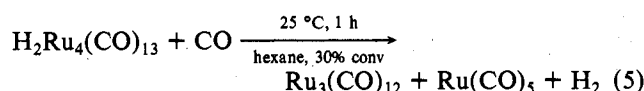
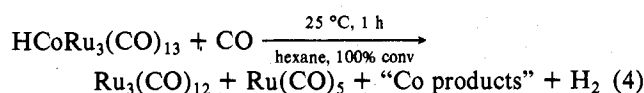
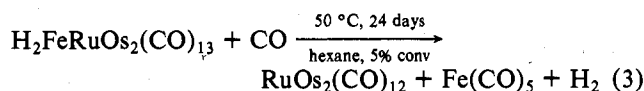
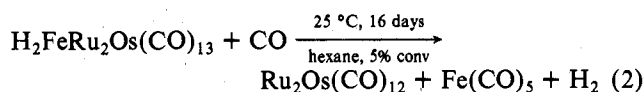
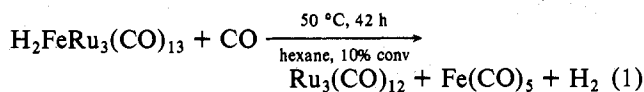
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increase with increasing temperature. For the experiments with CO pressures greater than 1 atm, a Parr model 4751 128-mL pressure reactor was used. The course of the reaction was monitored by following the disappearance of the absorbance of the tetranuclear cluster at 540 nm with the use of a Cary 17 spectrophotometer. The errors in the rate constants and the activation parameters are reported as 95% confidence limits,  $\lambda = ts$ , where  $s$  is the standard error,  $t$  is the appropriate correction factor for  $(N - 2)$  degrees of freedom, and  $N$  is the number of measurements.<sup>17</sup>

**Spectral Measurements and Analytical Liquid Chromatography.** Infrared spectra were recorded on a Perkin-Elmer 580 grating infrared spectrophotometer using 0.5-mm NaCl solution IR cells. Electron-impact mass spectra were obtained with an AEI MS9 mass spectrometer with a source voltage of 70 eV and probe temperatures ranging from 100 to 200 °C. Analytical liquid chromatography was conducted with the use of a unit assembled in this laboratory consisting of a Waters Associates M-6000A pump, a 25-cm  $\mu$ -Porasil chromatography column, and a Du Pont Model 830 detector, injector, and recorder.

## Results

**CO-Induced Cluster Fragmentation.** Each of the tetranuclear clusters shown in eq 1-8 was observed to fragment under



a CO atmosphere, generally to produce monomer and trimer products. The specific reactions observed under the given experimental conditions are given. The products of these various reactions were identified by their infrared and mass spectra and by comparison of liquid chromatography retention times to those of standard samples. The formation of H<sub>2</sub> was verified for the reactions shown in eq 1, 4, and 5 by mass spectral analysis of the gases above the reaction solutions. By analogy, the formation of H<sub>2</sub> in the remaining reactions is assumed since it is necessary to balance the observed stoichiometry.

Despite the fact that there are numerous possible product distributions, especially for the clusters containing three dif-

ferent metals, for most of the clusters studied the breakdown proceeds to give a specific trimer-monomer pair. For example, H<sub>2</sub>FeRu<sub>2</sub>Os(CO)<sub>13</sub> reacts with CO to form only Ru<sub>2</sub>Os(CO)<sub>12</sub> and none of the RuOs<sub>2</sub>, FeRu<sub>2</sub>, or FeRuOs trimers; furthermore, Fe(CO)<sub>5</sub> is the only monomeric product observed. The major exceptions to this specificity are the neutral hydridocobalt clusters HCoRu<sub>2</sub>Os(CO)<sub>13</sub> and HCoRuOs<sub>2</sub>(CO)<sub>13</sub>. The reactions of these clusters with CO give a very complex product mixture which we were unable to quantitatively analyze but which did show extensive scrambling in the fragmentation products: both Ru<sub>2</sub>Os(CO)<sub>12</sub> and RuOs<sub>2</sub>(CO)<sub>12</sub> were observed in each case. The reaction of HCoRu<sub>3</sub>(CO)<sub>13</sub> with CO is somewhat puzzling. In our early experiments, a compound shown by mass spectrometry to be H<sub>2</sub>Co<sub>2</sub>Ru<sub>2</sub>(CO)<sub>12</sub> was detected along with Ru<sub>3</sub>(CO)<sub>12</sub> in the product mixture. However, this compound was not seen in later experiments in which samples were more rigorously degassed and instead infrared evidence for Co<sub>2</sub>(CO)<sub>8</sub> was obtained. The latter may arise through the initial formation of HCo(CO)<sub>4</sub>.

The reactions of CO with H<sub>2</sub>FeRu<sub>3</sub>(CO)<sub>13</sub> and H<sub>2</sub>FeRu<sub>3</sub>(CO)<sub>12</sub>(PMe<sub>2</sub>Ph) present an interesting comparison. Substitution of PMe<sub>2</sub>Ph for CO completely alters the fragmentation pattern: H<sub>2</sub>FeRu<sub>3</sub>(CO)<sub>13</sub> gives Ru<sub>3</sub>(CO)<sub>12</sub> and Fe(CO)<sub>5</sub> (eq 1) whereas H<sub>2</sub>FeRu<sub>3</sub>(CO)<sub>12</sub>(PMe<sub>2</sub>Ph) yields FeRu<sub>2</sub>(CO)<sub>11</sub>(PMe<sub>2</sub>Ph) and Ru(CO)<sub>5</sub> (eq 8) although a trace amount of Ru<sub>3</sub>(CO)<sub>11</sub>(PMe<sub>2</sub>Ph) was separated from the latter reaction mixture. The trimeric products were identified by mass spectrometry. In a separate study, we have demonstrated that H<sub>2</sub>FeRu<sub>3</sub>(CO)<sub>12</sub>(PMe<sub>2</sub>Ph) exists in two isomeric forms of C<sub>1</sub> and C<sub>s</sub> symmetries with the C<sub>s</sub> isomer slightly predominant in CH<sub>2</sub>Cl<sub>2</sub> solution.<sup>13</sup> To determine if the two isomeric forms of the monosubstituted derivatives behave differently in their reactions with CO, we briefly examined the reactivity of H<sub>2</sub>FeRu<sub>3</sub>(CO)<sub>12</sub>(PPh<sub>3</sub>) which exists almost entirely in the C<sub>s</sub> form.<sup>13</sup> Under a CO pressure of 1 atm, the fragmentation products of this cluster were tentatively identified as Ru<sub>3</sub>(CO)<sub>11</sub>(PPh<sub>3</sub>) and Fe(CO)<sub>5</sub> with a trace of FeRu<sub>2</sub>(CO)<sub>11</sub>(PPh<sub>3</sub>) and Ru(CO)<sub>5</sub>. However, in a separate experiment employing a CO pressure of 200 psi, the predominant trimer product was FeRu<sub>2</sub>(CO)<sub>11</sub>(PPh<sub>3</sub>).

The reactivity of a particular cluster toward CO is greatly dependent on its metal composition, as illustrated by comparison of the percent conversions shown in eq 1-5. At room temperature, H<sub>2</sub>FeRu<sub>3</sub>(CO)<sub>13</sub>, H<sub>2</sub>FeRu<sub>2</sub>Os(CO)<sub>13</sub>, and H<sub>2</sub>FeRuOs<sub>2</sub>(CO)<sub>13</sub> react slowly over a period of several days, whereas the reaction with H<sub>2</sub>Ru<sub>4</sub>(CO)<sub>13</sub> and HCoRu<sub>3</sub>(CO)<sub>13</sub> is complete within minutes. The reaction rate increases with increasing temperature; for example, 80% of H<sub>2</sub>FeRu<sub>3</sub>(CO)<sub>13</sub> is converted to products after 90 h at 70 °C compared to 20% conversion when the reaction is conducted at 50 °C. The rate of the reaction is also solvent dependent. The rate of the reaction of H<sub>2</sub>FeRu<sub>3</sub>(CO)<sub>13</sub> with CO at 70 °C in a 15/1 2-ethoxyethanol/water mixture, the solvent system employed in several of the studies which use this cluster as a water-gas shift reaction catalyst,<sup>6</sup> is approximately 8 times as fast as in hexane solution under similar conditions.

Interestingly, the reactions of H<sub>2</sub>FeRu<sub>2</sub>Os(CO)<sub>13</sub> and H<sub>2</sub>FeRuOs<sub>2</sub>(CO)<sub>13</sub> with CO provide a means for separating Ru<sub>2</sub>Os(CO)<sub>12</sub> and RuOs<sub>2</sub>(CO)<sub>12</sub>. A mixture of these trimers with Ru<sub>3</sub>(CO)<sub>12</sub> and Os<sub>3</sub>(CO)<sub>12</sub> results from their synthesis,<sup>18</sup> and this mixture has proven extremely difficult to separate by normal chromatography and fractional crystallization techniques.<sup>18,19</sup> The tetranuclear clusters H<sub>2</sub>FeRu<sub>2</sub>Os(CO)<sub>13</sub> and H<sub>2</sub>FeRuOs<sub>2</sub>(CO)<sub>13</sub> are prepared from this trimer mixture,

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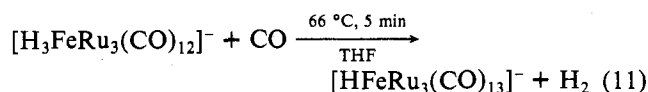
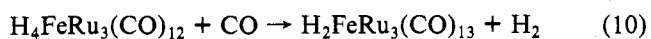
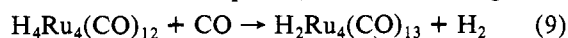
Table I. Kinetic Data for the Reactions of  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  and  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$  with CO

cluster <sup>a</sup>	temp, °C	$10^{-2} \times [\text{CO}]^b$ , M	$k_{\text{obsd}}$ , s <sup>-1</sup>	$k_2^c$ , M <sup>-1</sup> s <sup>-1</sup>
$\text{H}_2\text{FeRu}_3(\text{CO})_{13}$	50	1.33	$6.14 \times 10^{-7}$	$4.62 \times 10^{-5}$
	60	1.38	$1.66 \times 10^{-6}$	$1.20 \times 10^{-4}$
	70	1.42	$5.25 \times 10^{-6}$	$3.00 \times 10^{-4}$
	80	1.46	$1.17 \times 10^{-5}$	$8.01 \times 10^{-4}$
	90	1.50	$2.44 \times 10^{-5}$	$1.63 \times 10^{-3}$
$\text{H}_2\text{Ru}_4(\text{CO})_{13}$	0	1.13	$6.02 \times 10^{-6}$	$5.33 \times 10^{-4}$
	10	1.17	$1.47 \times 10^{-5}$	$1.26 \times 10^{-3}$
	20	1.21	$3.28 \times 10^{-5}$	$2.71 \times 10^{-3}$
	30	1.25	$7.05 \times 10^{-5}$	$5.70 \times 10^{-3}$

<sup>a</sup> [Cluster] =  $6 \times 10^{-4}$  M; heptane solution. <sup>b</sup> The concentration of CO in solution at various temperatures and pressures was estimated by using known CO solubilities in heptane<sup>16</sup> and extrapolating with use of the ideal gas law and Henry's law. <sup>c</sup> The values of  $k_2$  at 70 °C for  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  and at 30 °C for  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$  were obtained from least-squares analysis of the data in Table II. Since the value of  $k_1$  is almost negligible in comparison to  $k_2$  at a given temperature, the other  $k_2$  values were calculated simply by dividing  $k_{\text{obsd}}$  by [CO].

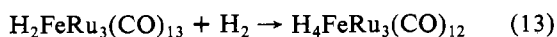
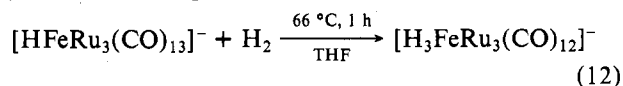
and they are easily separated by liquid chromatography.<sup>10</sup> The separate reactions shown in eq 2 and 3 thus provide pure  $\text{Ru}_2\text{Os}(\text{CO})_{12}$  and  $\text{RuOs}_2(\text{CO})_{12}$ .

For comparative purposes, the polyhydride clusters  $\text{H}_4\text{FeRu}_3(\text{CO})_{12}$ ,  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ , and  $[\text{H}_3\text{FeRu}_3(\text{CO})_{12}]^-$  were also studied. As illustrated in eq 9–11, these first undergo sub-



stitution of CO for  $\text{H}_2$  to form the corresponding di- and monohydride clusters, and these then undergo their characteristic fragmentation. The reactivity of the two tetrahydride clusters is vastly different: after 68 h at 25 °C in hexane solution, >90% of  $\text{H}_4\text{FeRu}_3(\text{CO})_{12}$  had been converted to products whereas after 100 h at 50 °C only ~30% of  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  had disappeared. In the latter case, the initially formed  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$  was detected by IR spectroscopy and by analytical liquid chromatography, but its concentration did not build up since it rapidly reacts with CO to produce  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{Ru}(\text{CO})_5$ , and  $\text{H}_2$ , eq 5.

The  $[\text{H}_3\text{FeRu}_3(\text{CO})_{12}]^-$  anion is a new compound which we prepared in the course of this study by allowing  $[\text{HFeRu}_3(\text{CO})_{13}]^-$  to react with  $\text{H}_2$  in refluxing THF, eq 12, analogous to Kaesz's<sup>12</sup> published conversion of  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  into  $\text{H}_4\text{FeRu}_3(\text{CO})_{12}$ , eq 13. The reaction shown in eq 12 was



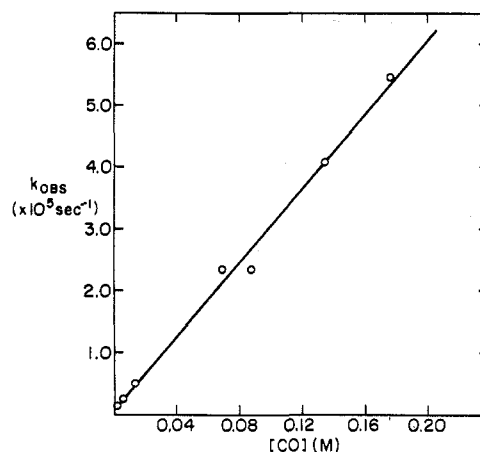
monitored by infrared spectroscopy. After 1 h of heating under an  $\text{H}_2$  purge, the infrared bands due to  $[\text{HFeRu}_3(\text{CO})_{13}]^-$  had completely disappeared and were replaced by the two strong bands at 2042 and 2019  $\text{cm}^{-1}$ , which we attribute to  $[\text{H}_3\text{FeRu}_3(\text{CO})_{12}]^-$ . These spectral changes were completely reversed by a 5-min exposure to CO, eq 11.

**Kinetics of the Reactions of  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  and  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$  with CO.** In order to resolve the mechanisms of the fragmentation reactions, we undertook a kinetic study of the reactions of  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  and  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$  with CO. For  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ , the reaction rate at 50, 60, 70, and 80 °C under pseudo-first-order conditions ( $[\text{FeRu}_3] = 6 \times 10^{-4}$  M,

Table II. Carbon Monoxide Pressure Dependence for the Reactions of  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  and  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$  with CO

cluster	temp, °C	$P_{\text{CO}}$ , mmHg	$[\text{CO}]^a$ , M	$k_{\text{obsd}}$ , s <sup>-1</sup>
$\text{H}_2\text{FeRu}_3(\text{CO})_{13}^b$	70	210	$3.55 \times 10^{-3}$	$1.41 \times 10^{-6}$
		420	$7.10 \times 10^{-3}$	$2.79 \times 10^{-6}$
		840	$1.42 \times 10^{-2}$	$5.25 \times 10^{-6}$
		4136	$6.97 \times 10^{-2}$	$2.36 \times 10^{-5}$
		5170	$8.88 \times 10^{-2}$	$2.32 \times 10^{-5}$
		7755	$1.36 \times 10^{-1}$	$4.07 \times 10^{-5}$
$\text{H}_2\text{Ru}_4(\text{CO})_{13}^c$	30	10340	$1.78 \times 10^{-1}$	$5.41 \times 10^{-5}$
		374	$6.30 \times 10^{-3}$	$3.15 \times 10^{-5}$
		544	$9.16 \times 10^{-3}$	$4.78 \times 10^{-5}$
		734	$1.24 \times 10^{-2}$	$6.60 \times 10^{-5}$

<sup>a</sup> Calculated from known CO solubilities in heptane<sup>16</sup> and extrapolating with use of the ideal gas law and Henry's law. <sup>b</sup>  $[\text{H}_2\text{FeRu}_3(\text{CO})_{13}] = 6 \times 10^{-4}$  M; heptane solution. <sup>c</sup>  $[\text{H}_2\text{Ru}_4(\text{CO})_{13}] = 6 \times 10^{-4}$  M; heptane solution.

Figure 1. Plot of  $k_{\text{obsd}}$  vs. [CO] for fragmentation of  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ .

$[\text{CO}] = 1.28 \times 10^{-2}$  M at 25 °C) was determined by monitoring the decrease in the absorbance at 540 nm due to the tetranuclear cluster ( $\epsilon_{540} = 900 \text{ M}^{-1} \text{ cm}^{-1}$ ). At high conversion, it was necessary to correct for contribution to the absorbance from  $\text{Ru}_3(\text{CO})_{12}$  ( $\epsilon_{540} = 50 \text{ M}^{-1} \text{ cm}^{-1}$ ). Infrared spectroscopy and analytical liquid chromatography did not show any evidence for the formation of any intermediates which might absorb at that wavelength. Absorbance data were used to obtain pseudo-first-order rate plots which were linear up to 90% conversion (>3 half-lives). The  $k_{\text{obsd}}$  values determined from these plots are listed in Table I.

To determine the reaction order with respect to carbon monoxide for  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ , we monitored the reaction at 70 °C with  $P_{\text{CO}}(\text{initial})$  allowed to vary from 0.28 to 13.6 atm. The  $k_{\text{obsd}}$  values shown in Table II were found to increase with increasing CO concentration. A plot of  $k_{\text{obsd}}$  vs. [CO], Figure 1, gave a straight line, and the data were fitted to the rate equation  $k_{\text{obsd}} = k_1 + k_2[\text{CO}]$ . Least-squares analysis gave  $k_1 \approx 5.7 \times 10^{-7} (\pm 3.5 \times 10^{-6}) \text{ s}^{-1}$  and  $k_2 = 3.0 \times 10^{-4} (\pm 3.8 \times 10^{-5}) \text{ M}^{-1} \text{ s}^{-1}$ . In essence, there are two parallel reaction paths, one which is CO dependent and the other which is not. However,  $k_1$  was determined by measuring the intercept of the plot shown in Figure 1 and within our experimental error it could be zero. Although we do not dismiss the first-order pathway entirely, our interpretation is that the CO-independent pathway is negligible. Under the conditions of these reactions, the fragmentation is essentially first order with respect to carbon monoxide and second order overall. Activation parameters for the second-order process, based on the standard state  $[\text{CO}] = 1 \text{ mol/L}$ , are set out in Table III.

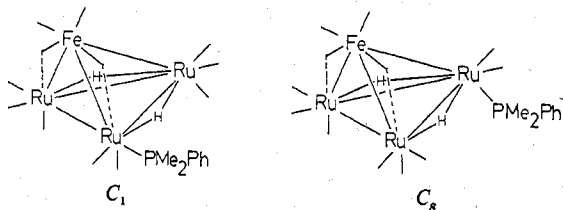
$\text{H}_2\text{Ru}_4(\text{CO})_{13}$  reacts much more rapidly with CO than does  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ . Hence it was necessary to monitor its re-

actions at 0, 10, 20, and 30 °C. Again, the reactions were monitored by measuring the decrease in absorbance at 540 nm ( $\epsilon_{540} = 900 \text{ M}^{-1} \text{ cm}^{-1}$ ). The  $k_{\text{obsd}}$  values obtained from linear pseudo-first-order rate plots are listed in Table I. The reaction order with respect to carbon monoxide was determined by monitoring the rate at 30 °C with  $P_{\text{CO}}(\text{initial})$  equal to 740, 545, and 375 mmHg. A plot of the  $k_{\text{obsd}}$  values shown in Table II vs.  $[\text{CO}]$  gave a straight line, and the data were fitted to the rate equation  $k_{\text{obsd}} = k_1 + k_2[\text{CO}]$ . Least-squares analysis gave  $k_1 = -4.0 \times 10^{-6} (\pm 1.8 \times 10^{-4}) \text{ s}^{-1}$  and  $k_2 = 5.7 \times 10^{-3} (\pm 6.1 \times 10^{-4}) \text{ M}^{-1} \text{ s}^{-1}$ . Again, the value of  $k_1$  is zero within experimental error and the reaction is essentially first order with respect to carbon monoxide concentration and second order overall. The activation parameters for the process, based on the standard state  $[\text{CO}] = 1 \text{ mol/L}$ , are given in Table III.

### Discussion

**Fragmentation Reactions.** All of the tetranuclear clusters we studied react with carbon monoxide under relatively mild conditions ( $P_{\text{CO}} = 1 \text{ atm}$ ,  $t = 0\text{--}80 \text{ }^\circ\text{C}$ ), generally to fragment to a trimer-monomer pair. With the exception of  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$ , each of the mixed-metal clusters gives a monomer containing a first-row transition metal and a trimer consisting of second- and third-row metals. Although specific metal-metal bond strengths in these clusters have not been determined, if we assume that the bonds involving first-row transition metals are weaker than those between second- and third-row metals,<sup>20</sup> then the formation of the observed products is consistent with breakage of the three weakest metal-metal bonds in the cluster framework. The absence of any Fe-containing trimers and the lack of Ru-Os scrambling during formation of  $\text{Ru}_2\text{Os}(\text{CO})_{12}$  and  $\text{RuOs}_2(\text{C}\text{-O})_{12}$  from  $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$  and  $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$ , respectively, suggest that this portion of the parent cluster remains intact throughout the conversion.

In the case of  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$ ,  $^1\text{H}$  NMR studies have shown that the two rapidly equilibrating  $C_1$  and  $C_s$  iso-



mers are present in solution at 25 °C.<sup>13</sup> In  $\text{CH}_2\text{Cl}_2$  solution at 25 °C, the  $C_s$  isomer is favored over the  $C_1$  isomer by a factor of  $\sim 3$  to 1. For  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PPh}_3)$  infrared and  $^1\text{H}$  NMR spectra show only the presence of the  $C_s$  isomer, which is evidently preferred for steric reasons.<sup>13</sup> Although we cannot precisely define the effect of phosphine substitution on the fragmentation pattern, the product distribution observed in the fragmentation reactions conducted at a CO pressure of 1 atm suggests that the two isomers break down in different fashions: the  $C_s$  isomer appears to give predominantly  $\text{Ru}_3(\text{CO})_{11}\text{L}$  and  $\text{Fe}(\text{CO})_5$  whereas the  $C_1$  isomer yields  $\text{FeRu}_2\text{-}$

$(\text{CO})_{11}\text{L}$  and  $\text{Ru}(\text{CO})_5$ . We cannot presently explain this reactivity difference nor do we understand the change in product distribution for  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PPh}_3)$  as the CO pressure is increased.

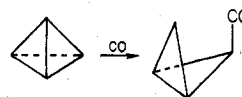
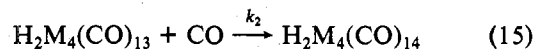
Molecular hydrogen is evolved in the fragmentation of the dihydride clusters which were studied. The hydride ligands in all the  $\text{H}_2\text{M}_4(\text{CO})_{13}$  clusters are known to occupy bridging positions,<sup>10,13,15,21</sup> but it is likely that at some point in the fragmentation process both hydrogen atoms migrate to the same metal atom and are then displaced by a molecule of CO. Consistent with such a notion is the fragmentation of  $[\text{HFeRu}_3(\text{CO})_{13}]^-$ , for which  $\text{H}_2$  loss is impossible and for which formation of  $[\text{HRu}_3(\text{CO})_{11}]^-$  is observed. The sole hydride ligand in  $[\text{HFeRu}_3(\text{CO})_{13}]^-$  bridges a Ru-Ru bond<sup>14</sup> and is retained in that position in the trimer product.<sup>22</sup> Interestingly, if  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  were to react in a similar fashion,  $\text{Fe}(\text{CO})_5$  and the unstable species  $\text{H}_2\text{Ru}_3(\text{CO})_{11}$  would be produced. Subsequent displacement of  $\text{H}_2$  by CO in the latter compound would generate the observed  $\text{Ru}_3(\text{CO})_{12}$ .<sup>23</sup>

The polyhydride clusters  $\text{H}_4\text{FeRu}_3(\text{CO})_{12}$ ,  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ , and  $[\text{H}_3\text{FeRu}_3(\text{CO})_{13}]^-$  are the only tetranuclear clusters studied which give other stable tetranuclear clusters as the initial products. Conversion of  $\text{H}_4\text{M}_4(\text{CO})_{12}$  into  $\text{H}_2\text{M}_4(\text{CO})_{13}$  can obviously occur, but the corresponding conversion of  $\text{H}_2\text{M}_4(\text{CO})_{13}$  into the hypothetical  $\text{M}_4(\text{CO})_{14}$  clusters does not obtain. Apparently clusters of these metals simply cannot accommodate 14 carbonyls, presumably for steric reasons,<sup>24</sup> and fragmentation of  $\text{H}_2\text{M}_4(\text{CO})_{13}$  rather than  $\text{H}_2$  displacement occurs in the presence of CO.

**Kinetics of Reactions of  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  and  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$  with Carbon Monoxide: Mechanistic Implications.** The rate law which best fits our kinetic data for fragmentation of both  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$  and  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  is that shown in eq 14.

$$-d[\text{cluster}]/dt = \{k_1 + k_2[\text{CO}]\}[\text{cluster}] \quad (14)$$

Under our conditions the first-order term is negligible and the reactions are essentially second order overall. The mechanism which we believe is most consistent with this rate law and with the activation parameters obtained, Table III, involves association of CO with the intact cluster concomitant with cleavage of one of the metal-metal bonds to give an  $\text{H}_2\text{M}_4(\text{CO})_{14}$  butterfly cluster as the first intermediate, eq 15. The acti-



vation profile envisaged for this process is shown in Scheme I.

This mechanism implies that attack of CO on the cluster is concerted with metal-metal bond breakage. The latter is necessary because the initial cluster is coordinatively and sterically saturated. A comparison of the activation parameters indicates that the relative degree of CO association and M-M bond cleavage in the transition state varies from  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$  to  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ . The larger value of  $\Delta H^\ddagger$  (20.0 kcal/mol) and the less negative  $\Delta S^\ddagger$  ( $-25.4 \text{ cal}/(\text{mol K})$ ) imply that in the transition state M-CO bond formation occurs to a lesser extent for  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  than for  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$  ( $\Delta H^\ddagger = 12.5$

(20) This assumption may or may not be valid. Connor has given the following order of average M-M bond energies within the Fe-Ru-Os triad: Fe-Fe, 19.2 kcal/mol < Ru-Ru, 28 kcal/mol < Os-Os, 31.1 kcal/mol (Connor, J. A.; Skinner, H. A.; Virmani, Y. *Symp. Faraday Soc.* 1973, No. 8, 18. See also Connor, J. A. *Top. Curr. Chem.* 1977, 71, 71). However, several studies have led to the conclusion that the Mn-Re bond in  $\text{MnRe}(\text{CO})_{10}$  is stronger than either of the metal-metal bonds in  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Re}_2(\text{CO})_{10}$  (Junk, G. A.; Svec, H. J. *J. Chem. Soc. A* 1970, 2102. Fawcett, J. P.; Poë, A. J. *J. Chem. Soc., Dalton Trans.* 1976, 2039. Fawcett, J. P.; Poë, A. J.; Twigg, M. V. *J. Chem. Soc. Chem. Commun.* 1973, 267) although the latter study indicated that the "kinetic" strength of the Mn-Re bond is slightly less than the corresponding Re-Re bond.

(21) Gilmore, C. J.; Woodward, P. J. *Chem. Soc. A* 1971, 3453.

(22) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Süß, G. *J. Chem. Soc., Dalton Trans.* 1979, 1356.

(23)  $\text{H}_2\text{Ru}_3(\text{CO})_{11}$  has recently been prepared and does in fact react with CO at 25 °C to give  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{H}_2$ ; Keister, J. B., paper presented at the 14th Middle Atlantic Regional Meeting of the American Chemical Society, Valley Forge, PA, April 23-25, 1980.

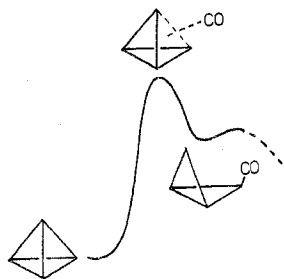
(24) Yawney, D. B. W.; Doedens, R. J. *Inorg. Chem.* 1972, 11, 838.

Table III. Activation Parameters for the Reactions of  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  and  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$  with  $\text{CO}^{a,b}$

	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , cal/(mol K)	$\Delta G^\ddagger_{298}$ , kcal/mol
$\text{H}_2\text{FeRu}_3(\text{CO})_{13}$	$20.0 \pm 2.0$	$-25.4 \pm 5.8$	$27.6 \pm 2.6$
$\text{H}_2\text{Ru}_4(\text{CO})_{13}$	$12.5 \pm 0.5$	$-36.6 \pm 1.6$	$23.4 \pm 0.7$

<sup>a</sup> Based on the standard state  $[\text{CO}] = 1 \text{ M}$ . The Arrhenius plot of the experimental  $k_2$  values for  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  gave  $\Delta H^\ddagger = 20.0 \text{ kcal/mol}$ ,  $\Delta S^\ddagger = -16.7 \text{ cal/(mol K)}$ , and  $\Delta G^\ddagger_{298} = 25.0 \text{ kcal/mol}$ . These values were adjusted to the standard state by using the equations described by Pino et al. in ref 9. For  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ , the experimental values were  $\Delta H^\ddagger = 12.5 \text{ kcal/mol}$ ,  $\Delta S^\ddagger = -27.9 \text{ cal/(mol K)}$ , and  $\Delta G^\ddagger_{298} = \text{kcal/mol}$ . <sup>b</sup> See ref 17 for description of error calculations.

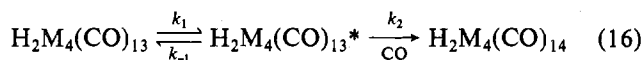
Scheme I



kcal/mol;  $\Delta S^\ddagger = -36.6 \text{ cal/(mol K)}$ ). This is consistent with the notion that Ru is larger than Fe and there is more room on the surface of intact  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$  to accommodate the incoming CO than in  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ .

The absence of any spectroscopic or chromatographic evidence for intermediates in the fragmentation reactions indicates that after the initial addition of CO in the rate-determining step, subsequent reaction must be extremely rapid. A similar conclusion has been drawn from a kinetic study of the fragmentation of  $\text{Co}_4(\text{CO})_{12}$  with CO in which the presumed  $\text{Co}_4(\text{CO})_{13}$  intermediate was believed to undergo rapid further fragmentation.<sup>9</sup>

An alternate mechanism, which cannot be eliminated on the basis of our data, involves a preequilibrium between the closed tetrahedral cluster and a coordinatively unsaturated butterfly cluster, which could subsequently add CO to give the same  $\text{H}_2\text{M}_4(\text{CO})_{14}$  intermediate proposed above, eq 16. The rate



law which this mechanism generates is shown in eq 17. This

$$\frac{-d[\text{cluster}]}{dt} = \frac{k_1 k_2 [\text{cluster}][\text{CO}]}{k_{-1} + k_2 [\text{CO}]} \quad (17)$$

rate equation predicts that the overall rate of cluster disappearance will become independent of CO concentration at sufficiently high values, i.e., when  $k_2[\text{CO}] \gg k_{-1}$ . However, as shown in Figure 1, the plot of  $k_{\text{obsd}}$  vs.  $[\text{CO}]$  is linear up to CO pressures of 13.6 atm. Although these data argue against the latter mechanism, it could well be that we had still not reached the CO concentration regime where  $k_{\text{obsd}}$  is independent of  $[\text{CO}]$ . However, the CO concentration at the high-pressure limit of 13.6 atm is about 300 times that of the cluster concentration and it is difficult to imagine that under these conditions CO would not add to every open cluster. Furthermore, if this alternate mechanism were operative,  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$  might be expected to react more slowly than  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  on the assumption that the Ru-Ru bonds are more robust than Fe-Ru bonds.<sup>20</sup> However, the exact opposite is observed.

**Acknowledgment.** We wish to thank Dr. Robert Minard and Ms. Karen Ann Smith for their assistance in obtaining mass spectra. This research was supported by the Department of Energy, Office of Basic Energy Sciences. G.L.G. gratefully acknowledges the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Grant and the Alfred P. Sloan Foundation for a Research Fellowship.

**Registry No.**  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ , 12375-24-5;  $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$ , 61863-84-1;  $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$ , 61816-94-2;  $\text{HCoRu}_3(\text{CO})_{13}$ , 72275-15-1;  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ , 36484-70-5;  $[\text{HFeRu}_3(\text{CO})_{13}]^-$ , 74128-10-2;  $[\text{CoRu}_3(\text{CO})_{13}]^-$ , 72152-10-4;  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$  ( $C_2$  form), 74128-11-3;  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PPh}_3)$ , 74128-12-4;  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ , 34438-91-0;  $\text{H}_4\text{FeRu}_3(\text{CO})_{12}$ , 11064-20-3;  $[\text{H}_3\text{FeRu}_3(\text{CO})_{12}]^-$ , 74331-36-5;  $\text{Ru}_3(\text{CO})_{12}$ , 15243-33-1;  $\text{Ru}_2\text{Os}(\text{CO})_{12}$ , 12389-47-8;  $\text{RuOs}_2(\text{CO})_{12}$ , 12389-50-3;  $[\text{HRu}_3(\text{CO})_{11}]^-$ , 60496-59-5;  $\text{FeRu}_2(\text{CO})_{11}(\text{PMe}_2\text{Ph})$ , 74128-09-9;  $\text{Ru}_3(\text{CO})_{11}(\text{PMe}_2\text{Ph})$ , 38686-57-6;  $\text{Ru}_3(\text{CO})_{11}(\text{PPh}_3)$ , 38686-52-1;  $\text{FeRu}_2(\text{CO})_{11}(\text{PPh}_3)$ , 74128-08-8;  $\text{Fe}(\text{CO})_5$ , 13463-40-6;  $\text{Ru}(\text{CO})_5$ , 16406-48-7;  $[\text{Co}(\text{CO})_4]^-$ , 14971-27-8; CO, 630-08-0;  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$  ( $C_1$  form), 74128-07-7.