

$P(OMe)_3$  suggested a nonzero dependence on phosphite concentration, we were not able to fit our data to any reasonable rate equation. Similar nonzero dependence on phosphite concentration has been observed previously in substitution reactions of  $Ru_3(CO)_{12}$ <sup>29</sup> and  $Co_4(CO)_{12}$ .<sup>30</sup>

### Summary

Although the field of metal cluster chemistry has been growing at a very rapid rate, a need still exists for fundamental reactivity studies of cluster systems. In this work, a series of phosphine- and phosphite-substituted derivatives of  $H_2FeRu_3(CO)_{13}$  has been prepared and characterized. A kinetic study of the reaction of  $H_2FeRu_3(CO)_{13}$  with  $PPh_3$  has revealed that the substitution reaction proceeds via a  $[PPh_3]$ -independent pathway, presumably involving CO dissociation in the rate-determining step producing an unsaturated  $H_2FeRu_3(CO)_{12}$  intermediate.

<sup>1</sup>H and <sup>31</sup>P NMR spectra have further shown that the monosubstituted clusters exist in two isomeric forms of  $C_s$  and  $C_1$  symmetries, each of which has the phosphorus ligand bound to a Ru atom. The  $C_s/C_1$  isomer ratio is dependent on ligand size, ligand basicity, and the solvent employed. Large ligands, regardless of basicity, give only the  $C_s$  isomer. With smaller ligands, basicity becomes the controlling factor, with the more basic ligands preferring the  $C_1$  isomer. The disubstituted  $H_2FeRu_3(CO)_{11}L_2$  clusters possess a phosphine or phosphite ligand in each of the substitution sites established for the monosubstituted derivatives.

The fluxional properties of the substituted clusters, in which the phosphines exchange substitution sites by an intramolecular

process involving a subtle rearrangement of the cluster framework, and the reactions of  $H_2FeRu_3(CO)_{13}$  with alkynes are discussed in the following two papers.<sup>11,12</sup>

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**Registry No.**  $H_2FeRu_3(CO)_{13}$ , 32036-04-7;  $H_2FeRu_3(CO)_{12}(PPh_3)$ , 74128-12-4;  $H_2FeRu_3(CO)_{11}(PPh_3)_2$ , 78248-92-7;  $H_2FeRu_3(CO)_{10}(PPh_3)_3$ , 78249-48-6;  $H_2FeRu_3(CO)_{12}(PMePh_2)$  ( $C_s$  isomer), 78249-49-7;  $H_2FeRu_3(CO)_{12}(PMePh_2)$  ( $C_1$  isomer), 78249-50-0;  $H_2FeRu_3(CO)_{12}(PMe_2Ph)$  ( $C_s$  isomer), 78128-11-3;  $H_2FeRu_3(CO)_{12}(PMe_2Ph)$  ( $C_1$  isomer), 78128-07-7;  $H_2FeRu_3(CO)_{12}(PMe_3)$  ( $C_s$  isomer), 78248-89-2;  $H_2FeRu_3(CO)_{12}(PMe_3)$  ( $C_1$  isomer), 78248-90-5;  $H_2FeRu_3(CO)_{11}(PMe_3)_2$ , 78249-51-1;  $H_2FeRu_3(CO)_{12}(P(i-Pr)_3)$ , 78249-52-2;  $H_2FeRu_3(CO)_{12}(PEt_2Ph)$  ( $C_s$  isomer), 78249-53-3;  $H_2FeRu_3(CO)_{12}(PEt_2Ph)$  ( $C_1$  isomer), 78249-54-4;  $H_2FeRu_3(CO)_{11}(PEt_2Ph)_2$ , 78265-04-0;  $H_2FeRu_3(CO)_{12}(P(OEt)_2Ph)$  ( $C_s$  isomer), 78265-06-2;  $H_2FeRu_3(CO)_{12}(P(OEt)_2Ph)$  ( $C_1$  isomer), 78249-55-5;  $H_2FeRu_3(CO)_{12}(P(OMe)_3)$  ( $C_s$  isomer), 78265-85-7;  $H_2FeRu_3(CO)_{12}(P(OMe)_3)$  ( $C_1$  isomer), 78249-56-6;  $H_2FeRu_3(CO)_{11}(P(OMe)_3)_2$ , 78248-91-6;  $H_2FeRu_3(CO)_{10}(P(OMe)_3)_3$ , 78265-86-8;  $H_2FeRu_3(CO)_{12}(P(OEt)_3)$  ( $C_s$  isomer), 78249-57-7;  $H_2FeRu_3(CO)_{12}(P(OEt)_3)$  ( $C_1$  isomer), 78249-58-8;  $H_2FeRu_3(CO)_{11}(P(OEt)_3)_2$ , 78248-86-9;  $H_2FeRu_3(CO)_{10}(P(OEt)_3)_3$ , 78248-87-0;  $PPh_3$ , 603-35-0.

**Supplementary Material Available:** Table A (crystal structure analysis report) and Table B (structure factor amplitudes) (30 pages). Ordering information is given on any current masthead page.

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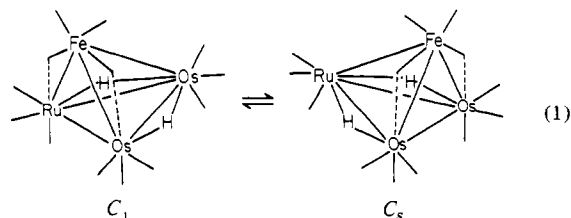
## Ligand Site Exchange Induced by Intrametallic Rearrangement Processes in $H_2FeRu_3(CO)_{13-x}(PR_3)_x$ ( $x = 1, 2$ )

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The fluxional processes which occur in  $H_2FeRu_3(CO)_{12}L$  ( $L = PMe_2Ph, PMe_3$ ) and  $H_2FeRu_3(CO)_{11}L_2$  ( $L = PMe_3, PPh_3, P(OMe)_3, P(OEt)_3$ ) have been studied by a combination of variable-temperature <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR spectroscopy. The fluxional processes are basically the same as those which have been shown to occur in the unsubstituted  $H_2FeRu_3(CO)_{13}$  cluster and involve bridge-terminal CO exchange localized on Fe, cyclic exchange of the carbonyls about the triangular face of the cluster which possesses the bridging CO's, and rearrangement of the metal framework with a corresponding shift of the hydrides and carbonyls. The intrametallic rearrangement process is of profound importance in these substituted derivatives since it leads to exchange of the substitution sites. For the monosubstituted derivatives, this exchange leads to the facile  $C_s \rightleftharpoons C_1$  isomerization observed, and for the disubstituted derivative it renders the phosphorus donor ligands equivalent on the time scale of the NMR measurements.

We have previously reported that the mixed-metal clusters  $H_2FeRu_3(CO)_{13}$ ,  $H_2FeRu_2Os(CO)_{13}$ , and  $H_2FeRuOs_2(CO)_{13}$  undergo a variety of fluxional processes including one that involves a subtle shift in the metal framework, as illustrated in (1) for the  $C_1 \rightleftharpoons C_s$  isomerization of  $H_2FeRuOs_2(CO)_{13}$ .<sup>1,2</sup> The mono- and disubstituted  $H_2FeRu_3(CO)_{13-x}L_x$  clusters, in which L is a tertiary phosphine or phosphite and whose preparation was described in the preceding paper,<sup>3</sup> are also

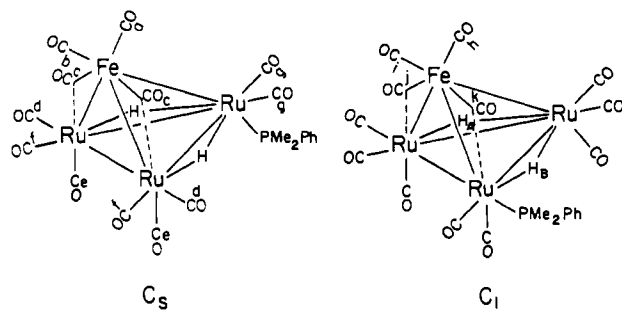


fluxional and undergo a similar intrametallic rearrangement process. This process is of critical importance for these substituted derivatives since it interchanges the two substitution sites which the ligands L occupy. For the monosub-

(1) Geoffroy, G. L.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1977**, *99*, 6775.

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

(3) Fox, J. R.; Gladfelter, W. L.; Wood, T. G.; Smegal, J. A.; Foreman, T. K.; Geoffroy, G. L. *Inorg. Chem.*, companion paper in this issue.



**Figure 1.** Structures of the  $C_1$  and  $C_s$  isomers of  $H_2FeRu_3(CO)_{12}(PMe_2Ph)$  showing the carbonyl and hydride labeling schemes.

stituted derivatives this process leads to rapid interconversion of the two substitutional isomers via rearrangement of the metal framework and accompanying ligands around the ligand L. Full details of the  $^1H$ ,  $^{13}C$ , and  $^{31}P$  NMR spectra of these derivatives and their interpretation are given herein.

### Experimental Section

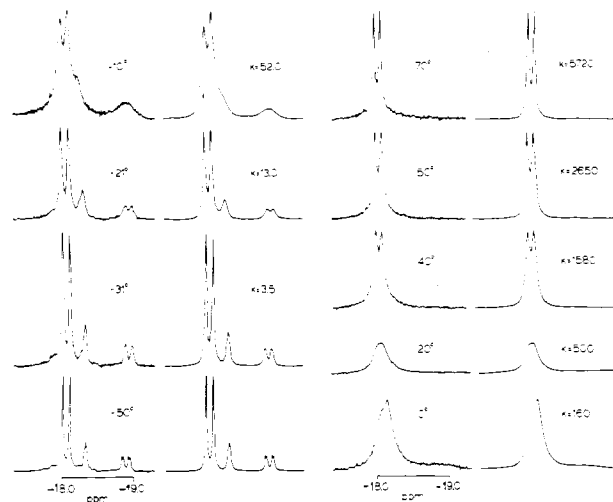
All the  $H_2FeRu_3(CO)_{13-x}(PR_3)_x$  ( $x = 1, 2$ ) derivatives were prepared as described in the preceding paper.<sup>3</sup>  $^{13}C$ -enriched  $H_2FeRu_3(CO)_{12}(PMe_2Ph)$  was prepared by allowing  $PMe_2Ph$  to react with  $\sim 25\%$  enriched  $H_2FeRu_3(CO)_{13}$ . The latter was prepared by stirring a hexane solution of  $H_2FeRu_3(CO)_{13}$  under an atmosphere of 90% enriched  $^{13}C$  (Monsanto Research Corp., Mound Laboratory) for 140 h at 45–50 °C.

NMR spectra were recorded with use of 10-mm NMR tubes containing  $\sim 3$  mL of sample solution. The sample used for the  $^{13}C$  NMR study contained  $[Cr(acac)_3]$  (0.05 M) as a shiftless relaxation agent. The lock substance in each case was deuterated solvent. Spectra were recorded on JEOL PS-100 FT and Bruker WH 200 NMR spectrometers, and heteronuclear decoupling was accomplished by using a broad-band noise decoupler. All reported  $^1H$  and  $^{13}C$  chemical shifts are relative to  $Me_4Si$ .  $^{31}P$  NMR chemical shifts are relative to  $H_3PO_4$  with downfield chemical shifts reported as positive. Line shape analyses were conducted with use of the program DNMR3.<sup>4</sup>

### Results

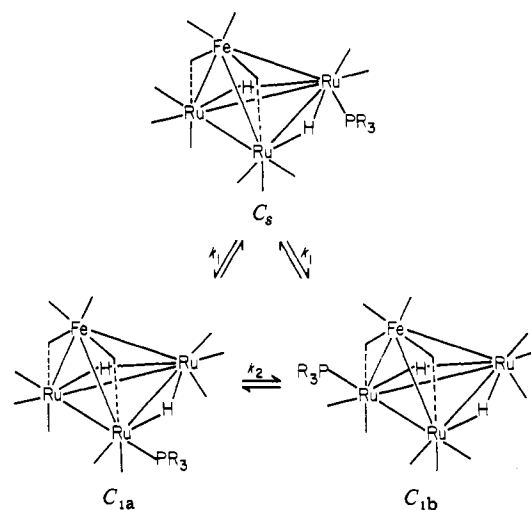
**A. Monosubstituted Derivatives.** As discussed in the preceding paper,<sup>3</sup> careful analysis of the low-temperature limiting  $^1H$  NMR and IR spectra indicate that the monosubstituted  $H_2FeRu_3(CO)_{12}L$  derivatives can exist in the  $C_s$  and  $C_1$  isomeric forms shown in Figure 1. The distribution between the isomers for a given ligand is dependent on both the ligand's size and its basicity as well as on the solvent in which the compound is dissolved. Polar solvents favor the  $C_s$  isomer and only for  $H_2FeRu_3(CO)_{12}(PMe_2Ph)$  and  $H_2FeRu_3(CO)_{12}(PMe_3)$  are the ligand effects sufficient to yield enough of the  $C_1$  isomer for it to be detected in the NMR experiments which require the use of polar solvents due to limited compound solubility. Thus, only these two monosubstituted derivatives show temperature-variant  $^1H$  and  $^{31}P$  NMR spectra.

**1.  $H_2FeRu_3(CO)_{12}(PMe_2Ph)$ .  $^{31}P$  NMR Spectra.** The  $^{31}P\{^1H\}$  NMR spectrum of  $H_2FeRu_3(CO)_{12}(PMe_2Ph)$  at  $-60$  °C in  $CD_2Cl_2/CHCl_3F$  solution shows three singlets at  $\delta$  33.4, 8.0, and 4.8 with relative intensities 1.0/13.2/7.7. The latter two resonances are attributed to the  $C_s$  ( $\delta$  8.0) and  $C_1$  ( $\delta$  4.8) isomers shown in Figure 1, whereas the weak  $\delta$  33.4 resonance is believed to be due to a third isomer with the phosphine bound to Fe.<sup>3</sup> The  $\delta$  33.4 resonance does not change with temperature, but the  $\delta$  8.0 and 4.8 singlets coalesce upon



**Figure 2.** Experimental and computer-simulated variable-temperature  $^1H$  NMR spectra of  $H_2FeRu_3(CO)_{12}(PMe_2Ph)$  in  $CDCl_3$  solution.

### Scheme I



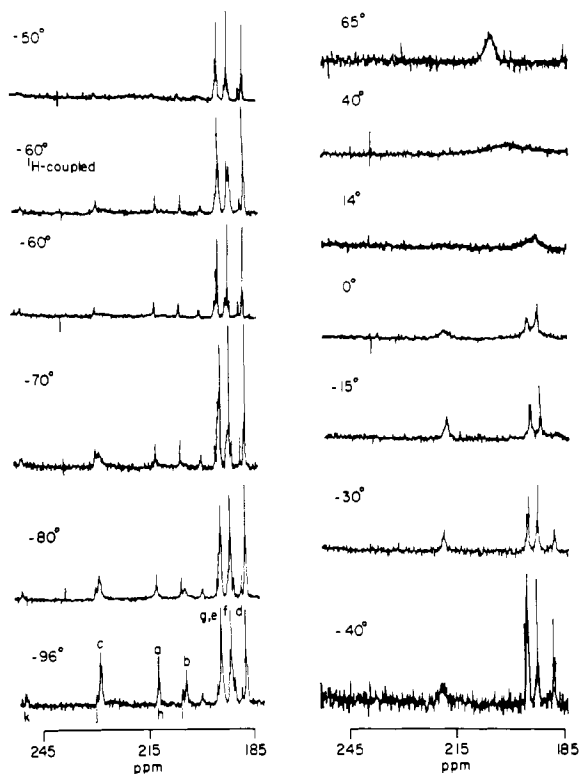
warming ( $T_c \approx 20$  °C) and by 40 °C have sharpened into a single resonance at  $\delta$  7.0, indicating the interconversion of the  $C_s$  and  $C_1$  isomers within this temperature range.

**$^1H$  NMR Spectra.** The  $^1H$  NMR spectrum of  $H_2FeRu_3(CO)_{12}(PMe_2Ph)$  in  $CDCl_3$  solution, at  $-50$  °C, Figure 2, shows an intense doublet at  $\delta$   $-18.07$  ( $J_{P-H} = 10.3$  Hz), a poorly resolved multiplet at  $\delta$   $-18.35$ , and a doublet of doublets at  $\delta$   $-18.93$  ( $J_{P-H_B} = 9.7$  Hz;  $J_{H_A-H_B} = 2.6$  Hz). The intense doublet is attributed to the two equivalent hydrogens of the  $C_s$  isomer, the multiplet at  $\delta$   $-18.35$  to  $H_A$ , and the doublet of doublets to  $H_B$  of the  $C_1$  isomer.<sup>3</sup> Computer simulation of the  $-50$  °C spectrum gave  $J_{P-H_A} = 1.8$  Hz and  $J_{H_A-H_B} = 2.6$  Hz for the  $\delta$   $-18.35$  multiplet.

As the temperature is raised, the  $^1H$  NMR resonances broaden, coalesce at  $\sim 20$  °C, and sharpen to a doublet at  $\delta$   $-18.18$  ( $J_{P-H} = 8.6$  Hz) at 70 °C (Figure 2). The latter implies that at this temperature the cluster undergoes rapid  $C_1 \rightleftharpoons C_s$  isomerization and that the two hydrogens experience an average chemical environment during the time of the  $^1H$  NMR measurement.

The  $^1H$  NMR spectral changes shown in Figure 2 have been computer simulated with use of the model shown in Scheme I, in which  $k_1$  represents the forward rate of the  $C_1 \rightleftharpoons C_s$  isomerization and  $k_2$  is the rate of interconversion of the  $C_1$  enantiomers. The excellent agreement shown in Figure 2 between the experimental and computer-simulated spectra could only be obtained by assuming that  $k_2 = 0$ . Thus,  $hy-$

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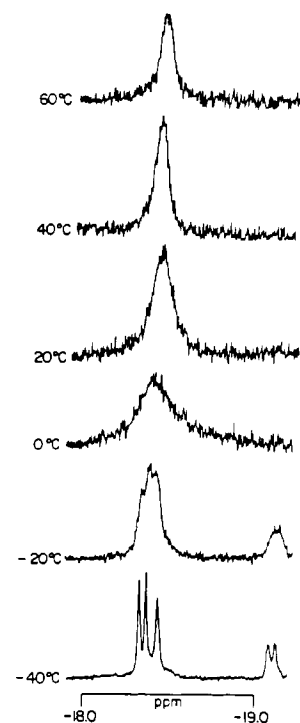


**Figure 3.** Variable-temperature  $^{13}\text{C}$  NMR spectra of  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$  in  $\text{CDCl}_3$  solution.

*drogen exchange occurs only through the isomerization process.*

**$^{13}\text{C}$  NMR Spectra.** The variable-temperature  $^{13}\text{C}$  NMR spectra of  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$  in a 2:1  $\text{CD}_2\text{Cl}_2/\text{CHCl}_2\text{F}$  solution in the  $-96$  to  $+65$   $^\circ\text{C}$  temperature range are shown in Figure 3. The carbonyl resonances in the low-temperature limiting spectrum have been assigned according to the labeling scheme shown in Figure 1. Assignment of the individual resonances is aided by comparison to the assignments given for  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  for which the resonances of the carbonyls bound to Ru occur in the  $\delta$  185–195 region whereas those bound to Fe have  $\delta > 200$ .<sup>1,2</sup> Furthermore, the  $C_s$  isomer is in greater abundance than the  $C_1$  isomer in  $\text{CD}_2\text{Cl}_2/\text{CHCl}_2\text{F}$  solution, and hence the more intense resonances can be attributed to the  $C_s$  isomer. The resonance at 228.5 ppm is logically attributed to the bridging carbonyls c of the  $C_s$  isomer. The nonequivalent carbonyls a and b terminally bound to Fe give rise to the 212.8 and 204.8 ppm resonances, but these cannot be individually assigned.  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ , for comparison, shows these three resonances at 229, 211, and 203 ppm, respectively.<sup>1,2</sup>

Two clearly resolved peaks at 192.0 and 187.8 ppm and two overlapping resonances at 195.1 and 194.7 ppm in the Ru carbonyl region are attributable to the  $C_s$  isomer. The peaks at 195.1 and 192.0 ppm broaden considerably when the hydrides are allowed to couple with the  $^{13}\text{C}$  nuclei, and hence the carbonyls which give rise to these resonances must be trans to hydrogens, i.e., f or g.<sup>1,2</sup> For the 192.0 ppm resonance,  $J_{\text{C-H}} = 13$  Hz. The resonances at 194.7 and 187.8 ppm are attributed to carbonyls e and d, but they cannot be individually assigned. However, carbonyl e is trans to the bridging CO and is expected to give rise to the downfield (194.7 ppm) resonance.<sup>1</sup> When the sample is warmed to  $-50$   $^\circ\text{C}$ , rapid exchange of carbonyls d and e occurs, and the corresponding resonances collapse into the base line. The remaining peaks due to carbonyls f and g have an intensity ratio of 1:1. However, the 195.1 ppm resonance clearly shows phosphorus-carbon coupling ( $J_{\text{P-C}} = 8$  Hz); it thus must be assigned



**Figure 4.** Variable-temperature  $^1\text{H}$  NMR spectra of  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_3)$  in  $\text{CDCl}_3$  solution.

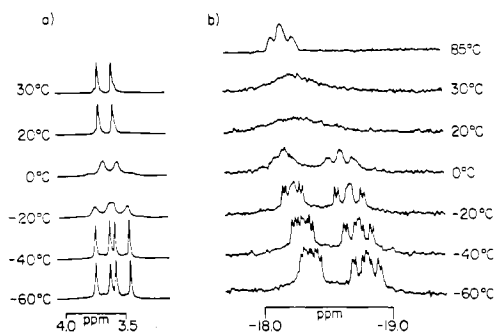
to carbonyl g, which is cis to the  $\text{PMe}_2\text{Ph}$  ligand (Figure 1). The 192.0 ppm resonance is assigned to carbonyl f.

For the  $C_1$  isomer, the terminal carbonyls h and i bound to Fe appear at 205.7 and 212.6 ppm but cannot be separately identified. One of the bridging carbonyls, j, appears at 228.7 ppm, similar to carbonyl c in the  $C_s$  isomer. The other, however, appears at 249.7 ppm, which is over 20 ppm downfield from the usual position for a semibridging Fe–Ru carbonyl.<sup>1,2</sup> This peak is assigned to carbonyl k which is bound to the same metal as the phosphine. The position of this resonance is more reminiscent of symmetrically bridging carbonyls rather than semibridging carbonyls. In  $\text{Fe}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})_2$ ,<sup>5</sup> for example, the terminal carbonyls are at 211 ppm, in exactly the same region that the CO's terminally bound to Fe appear in these  $\text{FeRu}_3$  clusters. However, the resonances due to the bridging carbonyls in  $\text{Fe}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})_2$  are at 275 ppm.<sup>5</sup> Thus, carbonyl k appears to shift from a semibridging position to more nearly full bridging to assist in delocalizing the excess electron density that is present on  $\text{Ru}_1$  due to the phosphine ligand.<sup>3</sup> The increased back-bonding causes a significant downfield shift in its  $^{13}\text{C}$  NMR resonance.<sup>6</sup> The resonances attributable to the terminal carbonyls bound to Ru in the  $C_1$  isomer are too poorly resolved to allow definitive assignments.

As the temperature is raised, the carbonyl resonances broaden in well-defined patterns, coalesce, and begin to sharpen, presumably into a single resonance. The 65  $^\circ\text{C}$  spectrum shows a broad singlet at  $\delta$  201.2 (Figure 3).

**2.  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_3)$ .** The  $-40$   $^\circ\text{C}$   $^1\text{H}$  NMR spectrum of  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_3)$  in  $\text{CDCl}_3$  solution, Figure 4, is similar to that of  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$  except that H–H coupling is not fully resolved. The doublet at  $\delta$   $-18.24$  ( $J_{\text{P-H}} = 11.0$  Hz) is attributable to the  $C_s$  isomer, the broad singlet at  $\delta$   $-18.39$  to  $\text{H}_A$ , and the doublet at  $\delta$   $-19.20$  ( $J_{\text{P-H}_B} = 9.2$  Hz) to  $\text{H}_B$  of the  $C_1$  isomer.<sup>3</sup> As the temperature is raised, the spectra broaden, coalesce at  $\sim 20$   $^\circ\text{C}$ , and by 40  $^\circ\text{C}$  have

(5) Bullitt, J. G.; Cotton, F. A.; Marks, T. J. *Inorg. Chem.* **1972**, *11*, 671.  
(6) (a) Mahnke, H.; Sheline, R. K.; Spiess, H. W. *J. Chem. Phys.* **1974**, *61*, 55. (b) Bodner, G. M.; Todd, L. J. *Inorg. Chem.* **1974**, *13*, 1335.



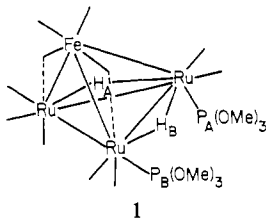
**Figure 5.** Variable-temperature  $^1\text{H}$  NMR spectra of  $\text{H}_2\text{FeRu}_3(\text{CO})_{11}(\text{P}(\text{OMe})_3)_2$  in  $\text{CDCl}_3$  solution.

sharpened to a broad singlet at  $\delta -18.34$ . Although qualitatively similar to the spectral changes associated with  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$ , the absence of a well-defined doublet in the 60  $^\circ\text{C}$  spectrum suggests that the exchange processes for this derivative may be more complicated. Variable-temperature  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR spectra were not obtained for this compound.

**B. Disubstituted Derivatives.** Although variable-temperature  $^1\text{H}$  NMR spectra were obtained for the disubstituted  $\text{H}_2\text{FeRu}_3(\text{CO})_{11}\text{L}_2$  clusters with  $\text{L} = \text{P}(\text{OMe})_3$ ,  $\text{P}(\text{OEt})_3$ ,  $\text{PPh}_3$ , and  $\text{PMe}_3$ , the resolution is greatest for the  $\text{P}(\text{OMe})_3$  derivative. Hence, full variable-temperature  $^{31}\text{P}$  NMR spectra were obtained for this compound, and its spectra are discussed in detail in the following paragraphs. The variable-temperature  $^1\text{H}$  NMR spectra obtained for the other disubstituted derivatives are given as Figures A–C of the supplementary material. Their interpretation is similar to that given below for the  $\text{P}(\text{OMe})_3$  derivative.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{H}_2\text{FeRu}_3(\text{CO})_{11}(\text{P}(\text{OMe})_3)_2$  at  $-60^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$  solution shows a pair of equal-intensity singlets at  $\delta 148.7$  and  $138.5$ . As the temperature is raised to  $0^\circ\text{C}$ , these two resonances broaden, coalesce ( $T_c \approx 0^\circ\text{C}$ ), and then sharpen to a  $\delta 141.5$  singlet at  $25^\circ\text{C}$ . These observations indicate the presence of two inequivalent  $\text{P}(\text{OMe})_3$  ligands at the low-temperature limit, which eventually become equivalent at higher temperatures due to fluxional processes occurring in the molecule.

The  $^1\text{H}$  NMR spectrum of  $\text{H}_2\text{FeRu}_3(\text{CO})_{11}(\text{P}(\text{OMe})_3)_2$  at  $-60^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$  solution consists of a pair of eight-line multiplets in the hydride region centered at  $\delta -18.53$  and  $-18.87$  (Figure 5b). This spectrum implies the structure shown in **1** with the presence of two nonequivalent hydride



ligands, each of which is split by the other hydride and also by the two nonequivalent phosphorus atoms.<sup>3</sup> Computer simulation of the low-temperature limiting spectrum gave the following coupling constants.  $\text{H}_A$ ,  $\delta -18.53$ :  $J_{\text{H}_A-\text{P}_A} = 6.3$  Hz,  $J_{\text{H}_A-\text{P}_B} = 3.2$  Hz,  $J_{\text{H}_A-\text{H}_B} = 1.9$  Hz.  $\text{H}_B$ ,  $\delta -18.87$ :  $J_{\text{H}_B-\text{P}_A} = 6.0$  Hz,  $J_{\text{H}_B-\text{P}_B} = 9.2$  Hz.

As the temperature is raised, the  $^1\text{H}$  NMR resonances broaden, coalesce at  $\sim 10^\circ\text{C}$ , and sharpen to a well-resolved triplet at  $\delta -18.12$  ( $J_{\text{P-H}} = 5.0$  Hz) at  $85^\circ\text{C}$  in toluene- $d_8$  solution. Again, the  $85^\circ\text{C}$  spectrum implies that the hydrogens and phosphorus atoms undergo rapid exchange at this temperature to in effect give two equivalent hydrogen ligands which are split by two equivalent phosphorus atoms during

the time of the  $^1\text{H}$  NMR measurement.

In the organic spectral region, the low-temperature limiting spectrum at  $-60^\circ\text{C}$  consists of a pair of equal-intensity doublets at  $\delta 3.70$  ( $J_{\text{P-H}} = 12.0$  Hz) and  $\delta 3.53$  ( $J_{\text{P-H}} = 12.0$  Hz) (Figure 5a), which are attributed to the methyl protons of two inequivalent  $\text{P}(\text{OMe})_3$  ligands. These doublets coalesce at about  $-10^\circ\text{C}$  and then sharpen to a single doublet at  $\delta 3.61$  ( $J_{\text{P-H}} = 12.0$  Hz) at  $20^\circ\text{C}$ .

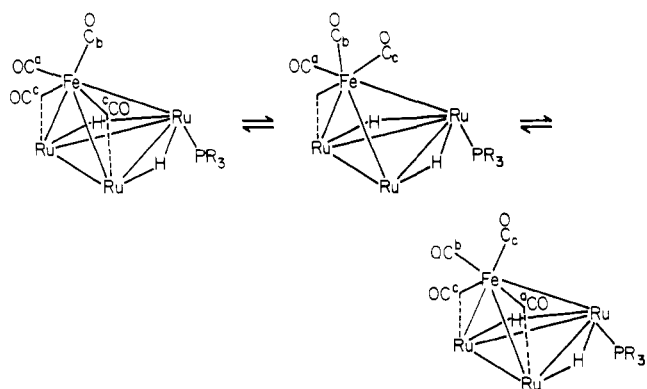
## Discussion

The variable-temperature NMR spectra reported herein clearly demonstrate that the phosphorus donor ligands in these substituted  $\text{H}_2\text{FeRu}_3(\text{CO})_{13-x}\text{L}_x$  ( $x = 1, 2$ ) derivatives undergo rapid exchange of ligand substitution sites. For the disubstituted derivatives, as evidenced by the data presented for  $\text{H}_2\text{FeRu}_3(\text{CO})_{11}(\text{P}(\text{OMe})_3)_2$ , this fast exchange renders the two ligands equivalent on the time scale of the NMR measurements at  $\sim 80^\circ\text{C}$ . For the monosubstituted derivatives this fast site exchange leads to the facile  $C_s \rightleftharpoons C_1$  isomerization observed for which computer simulation of the  $20^\circ\text{C}$   $^1\text{H}$  NMR spectrum gives a rate constant of  $500\text{ s}^{-1}$ . This is an incredibly fast rate of isomerization when it is considered that two different substitutional isomers interconvert, especially since the phosphorus ligands are bound to different Ru atoms in two distinctly different environments in the two isomers. The question then arises as to how this rapid interconversion occurs. The first clue is the presence of the doublet in the high-temperature limiting  $^1\text{H}$  NMR spectrum of  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$  and the triplet in the corresponding spectrum of  $\text{H}_2\text{FeRu}_3(\text{CO})_{11}(\text{P}(\text{OMe})_3)_2$ . These imply that P–H coupling is maintained throughout the interconversion, and hence *the fast site exchange must occur solely by an intramolecular process*. It cannot involve dissociation–reassociation of the ligand L. In order to properly address the question of how this rapid site exchange occurs, we must consider all the fluxional processes of these molecules, beginning with the lowest activation energy process.

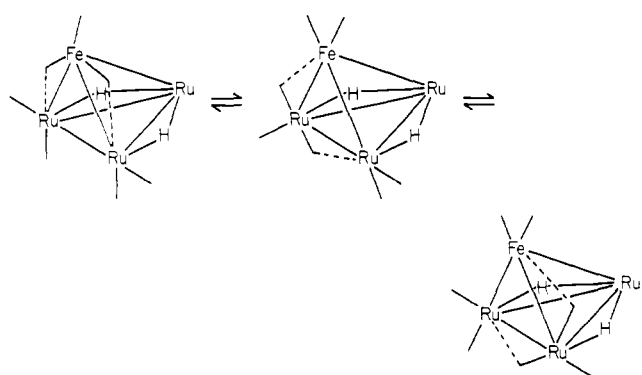
The NMR spectral data described herein indicate that the fluxional processes of these substituted  $\text{H}_2\text{FeRu}_3(\text{CO})_{13-x}\text{L}_x$  derivatives are basically the same as those which occur in  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ . Detailed  $^{13}\text{C}$  and  $^1\text{H}$  NMR studies of the latter, in conjunction with companion studies of  $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$  and  $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$ , have demonstrated the occurrence of three distinctly different processes which give rise to total exchange of the hydrides and carbonyl ligands.<sup>1,2</sup> The first of these involves bridge–terminal interchange of the four carbonyl ligands localized on Fe. For  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ , this process begins to occur at  $-60^\circ\text{C}$ . The  $^{13}\text{C}$  NMR spectra of  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$ , Figure 3, indicate that a similar process occurs in both the  $C_s$  and  $C_1$  isomers of this derivative. In the  $C_s$  isomer, carbonyls a–c bound to iron undergo exchange in the  $-96$  to  $-70^\circ\text{C}$  temperature range, with an activation energy slightly less than that of the comparable process in  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ . As in  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ , this exchange likely involves the breaking of one bridging Ru–CO bond followed by a trigonal twist of the  $\text{Fe}(\text{CO})_3$  group and re-formation of the bridging CO bond (Scheme II). As the temperature is raised to  $-40^\circ\text{C}$ , a new resonance grows in at 217.5 ppm, which is presumably the average Fe–CO resonance. Its calculated position is 218.7 ppm.

A similar process also occurs in the  $C_1$  isomer, but in a higher temperature range ( $-60$  to  $-40^\circ\text{C}$ ), as the bridging and terminal carbonyls h–k bound to Fe broaden into the base line. That this process occurs at a higher temperature for the  $C_1$  isomer is presumably due to the increased bridging nature of one of the carbonyls in this isomer (vide supra).<sup>3</sup> During this exchange process, the Ru–C bond of the bridging CO must be broken, and it is precisely this bond which is proposed to be strengthened to assist in delocalizing the excess electron

Scheme II



Scheme III



density on the  $\text{PMe}_2\text{Ph}$ -substituted atom.

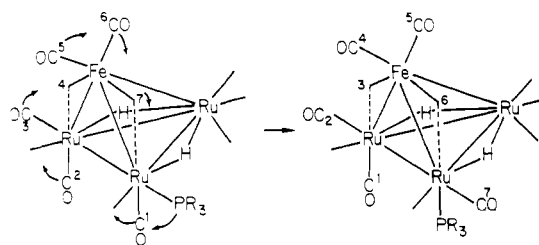
Although  $^{13}\text{C}$  NMR spectra were not obtained for  $\text{H}_2\text{FeRu}_3(\text{CO})_{11}(\text{P}(\text{OMe})_3)_2$ , there are no significant spectral changes observed in the  $^{31}\text{P}$  and  $^1\text{H}$  NMR spectra in the temperature range in which this Fe-localized process is expected to occur.

The next fluxional process which was shown to occur in  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  begins at  $-40^\circ\text{C}$  and involves exchange of the eight CO ligands that are approximately coplanar with the  $\text{FeRu}_2$  triangle which contains the bridging CO's.<sup>1,2</sup> This exchange is believed to occur by the CO's executing a cyclic motion about the  $\text{FeRu}_2$  face that contains the bridging CO's (Scheme III). This process is clearly evident for the  $C_3$  isomer of  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$  as the resonances corresponding to carbonyls d and e collapse in the  $-40$  to  $-15^\circ\text{C}$  temperature range. These presumably exchange with the Fe carbonyls by cyclic migration about the  $\text{FeRu}_2$  triangular face, and this is supported by the failure of the averaged Fe-CO resonance to sharpen into a singlet since these CO's are now also exchanging with carbonyls d and e.

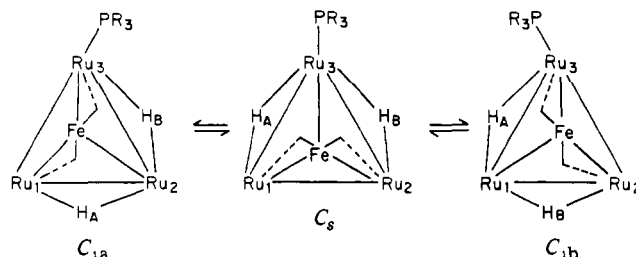
A similar CO-exchange process in the  $C_1$  isomer of  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$  and in  $\text{H}_2\text{FeRu}_3(\text{CO})_{11}(\text{P}(\text{OMe})_3)_2$  is hindered by the presence of a  $\text{PR}_3$  ligand in one of the sites that is coplanar with the  $\text{FeRu}_2$  triangle possessing the bridging CO's. A partial averaging of the resonances could still occur if the  $\text{PR}_3$  ligand were to move from its equatorial position to an axial position (Scheme IV). However, the low intensities of the  $^{13}\text{C}$  NMR resonances of the  $C_1$  isomer of  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$  and the unavailability of  $^{13}\text{C}$  NMR spectra of  $\text{H}_2\text{FeRu}_3(\text{CO})_{11}(\text{P}(\text{OMe})_3)_2$  do not allow us to address this point.

The final fluxional process which occurs in  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ ,<sup>1,2</sup> and also in these substituted derivatives, involves a subtle rearrangement of the cluster framework. This process has profound consequences in the substituted derivatives since it leads to exchange of the ligand substitution sites. This process is best illustrated for  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$  by

Scheme IV



Scheme V



considering the structures shown in Scheme V. It should first be recalled that the structure of  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  is that of a distorted tetrahedron: the Fe atom is closer to the two Ru atoms with which it shares the semibringing CO's and is further away from the unique Ru atom.<sup>7</sup> Consider first the  $C_3$  isomer in Scheme V in which the phosphine ligand is attached to the unique Ru atom,  $\text{Ru}_3$ . Following the demonstrated fluxional process for  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ ,<sup>1,2</sup> if the Fe atom moves away from  $\text{Ru}_2$  and closer to  $\text{Ru}_3$ , and the one hydride and the carbonyls shift appropriately, the  $C_{1a}$  enantiomer is generated. In order to bring the phosphine into the required equatorial position, rotation of the  $\text{Ru}(\text{CO})_2(\text{PMe}_2\text{Ph})$  unit must accompany the framework rearrangement. Likewise, starting from the  $C_3$  isomer, if the Fe atom moves away from  $\text{Ru}_1$  and toward  $\text{Ru}_3$  and the other hydride and the carbonyls shift appropriately, and the  $\text{Ru}(\text{CO})_2(\text{PMe}_2\text{Ph})$  unit rotates, the  $C_{1b}$  enantiomer is generated. Note that the phosphine remains attached to the same  $\text{Ru}_3$  atom throughout this exchange process but that the environment of  $\text{Ru}_3$  changes such that it is no longer the unique Ru. In essence, the phosphine appears to exchange positions, but the exchange proceeds by the phosphine staying attached to  $\text{Ru}_3$  with the cluster rearranging around the ligand.

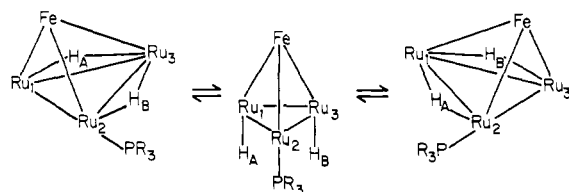
As illustrated in Scheme V, the  $C_3 \rightleftharpoons C_{1a}$  isomerization requires movement of only one of the hydride ligands,  $\text{H}_A$  in this case, in addition to the movement of the Fe atom and the shift in the bridging carbonyls. The corresponding  $C_3 \rightleftharpoons C_{1b}$  isomerization requires movement of only  $\text{H}_B$ . Thus,  $\text{H}_A$  and  $\text{H}_B$  in the  $C_1$  isomer can exchange positions via two successive isomerization processes.

The  $C_{1a}$  and  $C_{1b}$  enantiomers could also directly interconvert by a process involving movement of only one of the hydrogens. Thus, starting from the  $C_{1a}$  enantiomer in Scheme V, if  $\text{H}_B$  swings under the cluster to bridge the  $\text{Ru}_3$ - $\text{Ru}_1$  bond as the Fe atom swings away from  $\text{Ru}_1$  toward  $\text{Ru}_2$ , the  $C_{1b}$  enantiomer is generated. However, this process does not involve actual exchange of the two hydrogens since  $\text{H}_A$  remains fixed, bridging the  $\text{Ru}_1$ - $\text{Ru}_2$  vector in each of the two enantiomers. Thus, this process is not detectable in the hydride region of the  $^1\text{H}$  NMR spectra.<sup>8</sup> It should be detectable in the  $^{13}\text{C}$  NMR spectra, but the resolution is insufficient to allow a

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

(8) The two enantiomers of the  $C_1$  isomer are also distinguishable in the  $\delta_{\text{CH}_3}$  region of the  $^1\text{H}$  NMR spectrum as both apparently contribute to the  $\delta$  2.11 d ( $J_{\text{P-H}} = 10$  Hz) resonance. The  $C_3$  isomer shows a doublet at  $\delta$  1.96 ( $J_{\text{P-H}} = 9$  Hz).

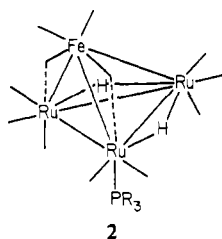
Scheme VI



definitive interpretation. We thus cannot comment further on the importance of this process for  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$ . However, such an exchange process has been demonstrated to occur for the  $\text{H}_2\text{FeRu}_{3-x}\text{Os}_x(\text{CO})_{13}$  ( $x = 1, 2$ ) clusters via their  $^{13}\text{C}$  NMR spectra.<sup>1,2</sup>

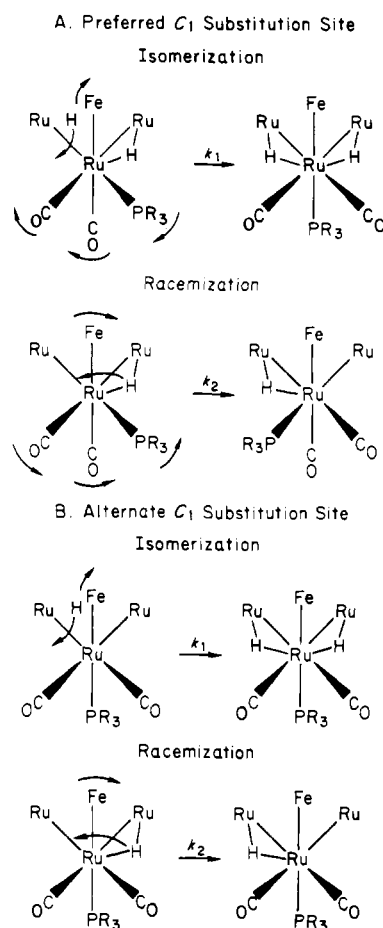
In principle,  $\text{H}_A$  and  $\text{H}_B$  could directly exchange through  $\text{C}_{1s} \rightleftharpoons \text{C}_{1s}$  racemization, presumably via the type of intermediate depicted in Scheme VI, but line shape analysis of the  $^1\text{H}$  NMR spectral changes have shown that this exchange mechanism does not occur in  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$  ( $k_2 = 0$ ; vide supra). However, a similar exchange process is operative in the related  $\text{H}_2\text{FeRu}_{3-x}\text{Os}_x(\text{CO})_{13}$  ( $x = 1, 2$ ) clusters.<sup>1,2</sup>

We were initially surprised that  $k_2$  was equal to zero, since in  $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$  and  $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$ , the analogous exchange process occurs with a rate constant of magnitude similar to that found for isomerization.<sup>2</sup> It is precisely this observation which causes us to favor substitution in the equatorial site indicated for the  $\text{C}_1$  isomer in Figure 1 rather than in the alternative axial substitution site, **2**, which is also

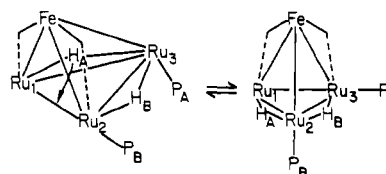


consistent with the low-temperature limiting  $^1\text{H}$  NMR spectra.<sup>3</sup> Specifically, if substitution were in the alternative site shown in **2**, we can offer no explanation of why  $k_2$  is zero. On the other hand, substitution in the preferred equatorial site requires a rotation of the  $\text{Ru}(\text{CO})_2(\text{PMe}_2\text{Ph})$  unit in each exchange process, and it must thus be unfavorable rotational constraints that yield  $k_2 = 0$ . Rotation of  $\text{PR}_3$ -substituted metal atoms has also been postulated to explain the high-temperature NMR spectra of  $\text{Os}_3(\text{CO})_{12-x}(\text{PR}_3)_x$  ( $x = 1, 2$ )<sup>9</sup> and  $\text{Ir}_4(\text{CO})_8(\text{PR}_3)_4$ .<sup>10-12</sup> Scheme VII clearly shows the stereochemical environments and the movements of the various atoms attached to the substituted Ru atom that occur during the intrametallic rearrangement processes in  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$ . The drawings at the top of Scheme VII show the twisting processes that would occur if the phosphine is substituted in the preferred equatorial site in the  $\text{C}_1$  isomer, whereas the bottom drawings illustrate the twisting motions that would be required for substitution in the alternate axial site. If substitution were in the alternative substitution site, no twisting of the  $\text{Ru}(\text{CO})_2(\text{PMe}_2\text{Ph})$  unit is required to occur during either process and thus we can see no reason for an appreciable activation barrier. On the other hand, substitution

Scheme VII



Scheme VIII



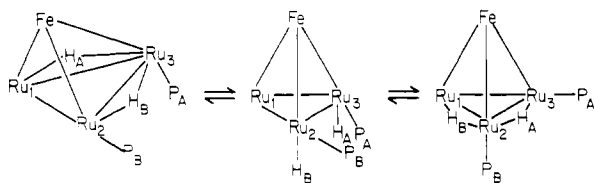
at the proposed site requires a twisting motion in the  $\text{C}_{1s} \rightleftharpoons \text{C}_{1s}$  racemization process in which the Fe atom is required to move in a direction opposite to the movement of the  $\text{Ru}(\text{CO})_3(\text{PMe}_2\text{Ph})$  unit, and this is apparently unfavorable. In the corresponding isomerization process, all atoms bound to Ru move in the same direction.

In the  $\text{H}_2\text{FeRu}_{3-x}\text{Os}_x(\text{CO})_{13}$  clusters previously studied, total exchange of all carbonyl ligands was postulated to occur through the cyclic exchange process coupled with the intrametallic rearrangement process.<sup>1,2</sup> Each time the cluster rearranged, the cyclic process would occur about a different triangular face, and through the commonality of the Fe CO's total exchange of all CO's occurred. Such a process, however, cannot account for the total CO exchange observed for  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$  (Figure 3), since the cyclic exchange process cannot obtain for the  $\text{C}_1$  isomer. In this case total exchange must occur via a process involving rotation of the Ru atoms, coupled with the intrametallic rearrangement and cyclic processes.

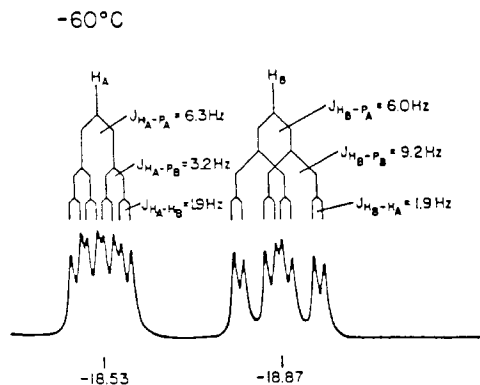
A similar intrametallic rearrangement process occurs for  $\text{H}_2\text{FeRu}_3(\text{CO})_{11}(\text{P}(\text{OMe})_3)_2$  and the other disubstituted derivatives, but here two different exchange processes can be resolved. The first process occurs in the  $-40$  to  $-20$  °C temperature range and causes the multiplets for  $\text{H}_A$  and  $\text{H}_B$  to each collapse into the pseudotriplet patterns seen in the  $-20$

- (9) Johnson, B. F. G.; Lewis, J.; Reichert, B. E.; Schorpp, K. T. *J. Chem. Soc., Dalton Trans.* **1976**, 1403.  
 (10) Cattermole, P. E.; Orrell, K. G.; Osborne, A. G. *J. Chem. Soc., Dalton Trans.* **1974**, 329.  
 (11) Stuntz, G. F.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, 99, 607.  
 (12) Albano, V.; Bellon, P.; Scattarin, V. *Chem. Commun.* **1967**, 730.

Scheme IX



$^{\circ}\text{C}$   $^1\text{H}$  NMR spectrum, Figure 5b. Consideration of the following coupling scheme for the  $-60^{\circ}\text{C}$  spectrum

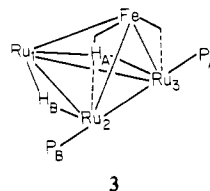


indicates that  $\text{H}_A\text{-H}_B$  coupling does not change in moving from  $-60$  to  $-20^{\circ}\text{C}$  but that all the  $J_{\text{P-H}}$  coupling constants approach a similar value; i.e., the two phosphorus atoms appear equivalent to  $\text{H}_A$  and  $\text{H}_B$ . The exchange mechanism that we believe accounts for these spectral changes is that shown in Scheme VIII. Beginning with the structure on the left, movement of the Fe atom away from  $\text{Ru}_2$  toward  $\text{Ru}_3$  accompanied by a shift in  $\text{H}_A$  and in the carbonyl ligands, and by rotation of the  $\text{Ru}(\text{CO})_2(\text{P}(\text{OMe})_3)$  units, would generate the structure on the right. Note that the two hydrogens have not exchanged positions and are still inequivalent but that this movement causes  $\text{P}_A$  and  $\text{P}_B$  to exchange environments. Support for this interpretation comes from consideration of the  $^1\text{H}$  NMR spectral changes in the  $\delta$  3.0–4.0 region where the  $\text{P}(\text{OMe})_3$  doublets appear (Figure 5a). Note that these resonances coalesce at  $\sim -10^{\circ}\text{C}$ , exactly in the temperature range where the metal hydride region spectral changes dictate the exchange process described above.

As the temperature is raised still higher, the hydride resonances broaden, coalesce, and sharpen into a triplet pattern which implies rapid intramolecular exchange of both hydrides and the two phosphorus atoms. Similar spectral changes have been observed for the substituted  $\text{H}_2\text{Ru}_4(\text{CO})_{13-x}(\text{P}(\text{OMe})_3)_x$  ( $x = 1, 2$ ) and  $\text{H}_4\text{Ru}_4(\text{CO})_{12-y}(\text{P}(\text{OMe})_3)_y$  ( $y = 1-4$ ) derivatives.<sup>13</sup> This rapid exchange is proposed to occur by an intrametallic rearrangement process but presumably proceeds through an intermediate such as that shown in Scheme IX in which both hydrides have opened up to terminal positions. Reformation of the bridges in the manner shown in Scheme IX with the necessary  $\text{Ru}(\text{CO})_2(\text{P}(\text{OMe})_3)$  group rotation exchanges the two hydrogen nuclei and the environments of the two phosphite ligands. The synchronous movement of  $\text{H}_A$  and  $\text{H}_B$  in Scheme IX is reminiscent of the motion of the four hydride ligands in  $\text{H}_4\text{Ru}_4(\text{CO})_{10}((\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)$ .

$\text{H}_3$ )<sub>2</sub>.<sup>14</sup> The migration of  $\text{H}_A$  to a terminal position on  $\text{Ru}_3$  could be a higher activation energy process than a similar movement to  $\text{Ru}_1$  because of the presence of the phosphite ligand on  $\text{Ru}_3$ , possibly because of the increased steric hindrance.

The shift in the metal framework described in Schemes VIII and IX is similar to that proposed for  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ <sup>1,2</sup> and  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$ . However, the  $^1\text{H}$  NMR spectral changes observed for  $\text{H}_2\text{FeRu}_3(\text{CO})_{11}(\text{P}(\text{OMe})_3)_2$  are consistent with movement of the Fe atom between positions only above the  $\text{Ru}_1\text{-Ru}_2$  and  $\text{Ru}_1\text{-Ru}_3$  edges but never above the  $\text{Ru}_2\text{-Ru}_3$  edge. Migration of the Fe atom to the latter position would generate structure 3, in which each of the phosphorus



ligands is bonded to a Ru atom, which is also ligated by a bridging CO. This isomer has never been detected in any of our experiments.

### Summary

The mono- and disubstituted phosphine and phosphite derivatives of  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  undergo a variety of fluxional processes including bridge-terminal CO interchange localized on Fe, cyclic exchange of the carbonyls about the triangular face of the cluster which possesses the bridging CO's, and rearrangement of the metal framework with a corresponding shift of the hydrides and carbonyls. For the monosubstituted derivatives, this latter process results in interconversion of the  $C_2$  and  $C_1$  isomers by interchanging the two distinct substitution sites that the phosphine ligand occupies by, in effect, the cluster rearranging around the phosphine. Similar fluxional processes also occur in  $\text{H}_2\text{FeRu}_3(\text{CO})_{11}(\text{P}(\text{OMe})_3)_2$  with the rearrangement of the metal framework and the accompanying shift of the other ligands, yielding the two  $\text{P}(\text{OMe})_3$  ligands equivalent at high temperatures on the NMR time scale.

**Acknowledgment.** This work was supported in part by the Office of Naval Research. We thank A. Freyer for assistance in obtaining some of the NMR spectra and the National Science Foundation's major equipment grant program for providing matching funds to purchase the JEOL 100-FT and Bruker WH 200 NMR spectrometers. G.L.G. gratefully acknowledges the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Award and the Alfred P. Sloan Foundation for a research fellowship.

**Registry No.**  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$  ( $C_2$  isomer), 78128-11-3;  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$  ( $C_1$  isomer), 74128-07-7;  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_2\text{Ph})$  (third isomer), 78265-05-1;  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_3)$  ( $C_2$  isomer), 78248-89-2;  $\text{H}_2\text{FeRu}_3(\text{CO})_{12}(\text{PMe}_3)$  ( $C_1$  isomer), 78248-90-5;  $\text{H}_2\text{FeRu}_3(\text{CO})_{11}(\text{P}(\text{OMe})_3)_2$ , 78248-91-6;  $\text{H}_2\text{FeRu}_3(\text{CO})_{11}(\text{PMe}_3)_2$ , 78249-51-1;  $\text{H}_2\text{FeRu}_3(\text{CO})_{11}(\text{PPh}_3)_2$ , 78248-92-7;  $\text{H}_2\text{FeRu}_3(\text{CO})_{11}(\text{P}(\text{OEt})_3)_2$ , 78248-86-9.

**Supplementary Material Available:** Figures A–C (variable-temperature  $^1\text{H}$  NMR spectra) (3 pages). Ordering information is given on any current masthead page.

(13) (a) Kaesz, H. D. "Organotransition-Metal Chemistry"; Plenum Press: New York, 1975; p 291. (b) Kaesz, H. D. *Chem. Br.* 1973, 9, 344. (c) Knox, A. A. R.; Kaesz, H. D. *J. Am. Chem. Soc.* 1971, 93, 4594.

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