Inorg. Chem. 1981, 20, 3230-3237

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Reaction of $H_2FeRu_3(CO)_{13}$ with Alkynes. Preparation and Characterization of Isomeric $FeRu_3(CO)_{12}(RC\equiv CR')$ Clusters. A Definitive Structural Characterization of the μ_4-η^2-Bonding Mode for Substituted Alkynes

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Received January 27, 1981

$H_2FeRu_3(CO)_{13}$ reacts with a series of alkynes to form isomeric $FeRu_3(CO)_{12}(RC\equiv CR')$ clusters (R, R′ = Ph; R, R′ = Me; R = Ph, R′ = Me) which are conveniently separated by chromatography on silica gel. The reaction of $H_2FeRu_3(CO)_{13}$ with $PhC\equiv CPh$ produces two isomers of $FeRu_3(CO)_{12}(PhC\equiv CPh)$ in an overall yield of 65%. Reaction with $MeC\equiv CMe$ and $PhC\equiv CMe$ produces two and three isomers, respectively, of $FeRu_3(CO)_{12}(MeC\equiv CMe)$ and $FeRu_3(CO)_{12}(PhC\equiv CMe)$ in 40–41% total yield in each case. The isomeric products have been fully characterized by elemental analysis and by their IR, ^1H NMR, and mass spectra, and the two isomers of $FeRu_3(CO)_{12}(PhC\equiv CPh)$ by complete single-crystal X-ray diffraction studies. Each isomer crystallizes in the $P2_1/c$-C_{2h}^5 space group with $a = 9.526$ (3) Å, $b = 16.925$ (5) Å, $c = 17.037$ (4) Å, $\beta = 91.10$ (2)°, and $Z = 4$ for isomer **1a** and with $a = 9.699$ (1) Å, $b = 16.785$ (2) Å, $c = 17.054$ (2) Å, $\beta = 90.60$ (1)°, and $Z = 4$ for **1b**. The structures were refined to $R_1 = 0.028$ and $R_2 = 0.032$ for 4983 independent reflections having $I > 3.0\sigma(I)$ for **1a** and to $R_1 = 0.026$ and $R_2 = 0.028$ for 6901 independent reflections having $I > 3.0\sigma(I)$ for **1b**. In each isomer, the alkyne ligand has been incorporated into the cluster core to generate *closo*-$FeRu_3C_2$ cluster frameworks. The isomers differ only in the arrangement of the metal atoms with isomer **1a** having the Fe atom cis to both alkyne carbons (axial isomer) whereas in isomer **1b**, the Fe is cis to one carbon and trans to the other (equatorial isomer). Spectroscopic evidence indicates analogous structures for the other alkyne derivatives. The structural isomers interconvert at elevated temperatures, and for each alkyne the axial isomer is the more thermodynamically stable. However, the equatorial isomers form first during the syntheses of the compounds.

Mixed-metal clusters have proven extremely useful for elucidating important features of the reactivity and molecular dynamics of cluster complexes, primarily because of the asymmetry which is inherent within their metal framework.[2] The fluxional processes which occur in $H_2FeRu_3(CO)_{13}$, $H_2FeRu_2Os(CO)_{13}$, and $H_2FeRuOs_2(CO)_{13}$, for example, have been clearly resolved because of their mixed-metal character,[3,4] and the specific substitution sites in a series of $H_2FeRu_3(CO)_{13-x}L_x$ (L = PR_3, $P(OR)_3$) clusters were determined by NMR spectroscopy as a consequence of the low symmetry of these derivatives.[5]

Since alkynes have been shown to react with clusters to produce compounds with a variety of alkyne bonding modes,[6-22] we were curious as to the effect that the mixed-metal character of a cluster would have on the mode of alkyne bonding. We have thus investigated the reactions of $H_2FeRu_3(CO)_{13}$ with a series of internal alkynes and have found that the mixed-metal character manifests itself in the formation of isomeric $FeRu_3(CO)_{12}(RC\equiv CR)$ products. Details of the preparation, characterization, and interconversion of these isomeric derivatives are reported herein.

Experimental Section

$H_2FeRu_3(CO)_{13}$ was prepared according to literature procedures.[23] $PhC\equiv CPh$ (Aldrich Chemical Co.), $MeC\equiv CMe$ (Chemical Samples Co.), $PhC\equiv CMe$ (Aldrich Chemical Co.), and 1-hexene (Aldrich Chemical Co.) were obtained from commercial sources and used as received. All solvents were deaerated by an N_2 purge prior to use but were otherwise used as obtained.

Preparation of $FeRu_3(CO)_{12}(PhC\equiv CPh)$ (1a,b). $H_2FeRu_3(CO)_{13}$ (0.135 g, 0.186 mmol) and diphenylacetylene (0.105 g, 0.59 mmol) were refluxed in hexane (60 mL) under an N_2 atmosphere for 15 min, during which time the color changed from light red to dark brown. The solution was cooled and the solvent volume reduced to 20 mL for chromatography on the previously described low-pressure liquid chromatography apparatus[23] using silica gel (Woelm, 0.032–0.063 mm) and hexane as the eluting solvent. The first band to elute was faint yellow and contained a mixture of $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$. Unreacted $PhC\equiv CPh$ eluted next, followed by a small red band of unreacted $H_2FeRu_3(CO)_{13}$. A brown band of **1a** and a red-brown band of **1b** then eluted in that order. A final faint red band was tentatively identified as $Ru_2(CO)_8(PhC\equiv CPh)_2$ by its mass spectral data: *m/e* 784 for the parent ion and stepwise loss of eight carbonyls.

The $FeRu_3(CO)_{12}(PhC\equiv CPh)$ isomers were recrystallized by evaporating the solvent from the chromatography fractions, dissolving the residual air-stable black solids in the minimum volume of hot hexane (15 mL), and allowing the hexane to slowly evaporate over a period of several days to yield black, prismatic crystals, which were washed with small portions of cold hexane. Anal. Calcd for $FeRu_3(CO)_{12}(PhC\equiv CPh)$, **1a**: C, 35.75; H, 1.14. Found: C, 35.90; H, 1.18. Calcd for $FeRu_3(CO)_{12}(PhC\equiv CPh)$, **1b**: C, 35.75; H, 1.14.

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(1) (a) The Pennsylvania State University. (b) University of Nebraska.
(2) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1980**, *18*, 207.
(3) Geoffroy, G. L.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1977**, *99*, 6775.
(4) Gladfelter, W. L.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 2579.
(5) Fox, J. R.; Gladfelter, W. L.; Wood, T. G.; Smegal, J. A.; Foreman, T. K.; Geoffroy, G. L.; Tavanaiepour, I.; Day, V. W.; Day, C. S. *Inorg. Chem.*, companion paper in this issue.
(6) King, R. B. *Prog. Inorg. Chem.* **1972**, *15*, 343.
(7) Jackson, W. G.; Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Schorpp, K. T. *J. Organomet. Chem.* **1975**, *87*, C27.
(8) Jackson, W. G.; Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Schorpp, K. T. *J. Organomet. Chem.* **1975**, *88*, C17.
(9) Demming, A. J.; Hasso, S.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1614.
(10) Pierpont, C. G. *Inorg. Chem.* **1977**, *16*, 636.
(11) Dodge, R. P.; Schomaker, A. *J. Orgnomet. Chem.* **1965**, *3*, 274.
(12) Todd, L. J.; Yamamoto, T.; Garber, A. R.; Wilkinson, J. R.; Rausch, M. O.; Gardner, S. A., Abstracts, 6th International Conference on Organometallic Chemistry, Amherst, Mass., 1973; No. 2.
(13) Sappa, E.; Gambino, O.; Milone, L.; Cetini, G. *J. Organomet. Chem.* **1972**, *39*, 169.
(14) Krüerke, U.; Hübel, W. *Chem. Ber.* **1961**, *94*, 2829.
(15) Johnson, B. F.; Lewis, J.; Schorpp, K. T., *J. Organomet. Chem.* **1975**, *91*, C13.
(16) Johnson, B. F.; Lewis, J.; Reichert, B.; Schorpp, K. T.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1417.
(17) Tilney-Bassett, J. F. *J. Chem. Soc.* **1963**, 4784.
(18) Dahl, L. F.; Smith, D. L. *J. Am. Chem. Soc.* **1962**, *84*, 2450.
(19) Canty, A. J.; Johnson, B. F.; Lewis, J. *J. Organomet. Chem.* **1972**, *43*, C35.
(20) Booth, B. L.; Else, M. J.; Fields, R.; Haszeldine, R. N. *J. Organomet. Chem.* **1971**, *27*, 119.
(21) Mason, R.; Thomas, F. M. *J. Organomet. Chem.* **1972**, *43*, C39.
(22) Jackson, R.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Sankey, S. W. *J. Organomet. Chem.* **1980**, *193*, C1.
(23) Geoffroy, G. L.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1977**, *99*, 7565.

0020-1669/81/1320-3230$01.25/0

Found: C, 35.77; H, 1.18 (Galbraith Laboratories). Yields based on the amount of reacted $H_2FeRu_3(CO)_{13}$ were 17% for **1a** (16.0 mg) and 48% for **1b** (46.3 mg).

Preparation of $FeRu_3(CO)_{12}(MeC{\equiv}CMe)$ (2a,b). $H_2FeRu_3(CO)_{13}$ (0.246 g, 0.336 mmol) and dimethylacetylene (0.5 mL, 0.345 g, 6.38 mmol) were heated in isooctane (150 mL) in a 300-mL Carius tube at 83 °C under an N_2 atmosphere for 15 min, during which time the solution changed color from red to dark brown. Chromatography of the concentrated solution on silica gel using hexane as the eluting solvent gave in order of elution a yellow band of $Ru_3(CO)_{12}$, a faint red band containing a trace of $FeRu_2(CO)_{12}$, a very intense brown band of **2a**, a faint red band of unreacted $H_2FeRu_3(CO)_{13}$, and a brown band of **2b**. The overall synthetic yield of the two isomers of $FeRu_3(CO)_{12}(MeC{\equiv}CMe)$ was 40% (**2a**, 63.5 mg, 25%; **2b**, 38.1 mg, 15%). Recrystallization was carried out as described above, and black air-stable crystals of each isomer were obtained. Anal. Calcd for $FeRu_3(CO)_{12}(MeC{\equiv}CMe)$, **2a**: C, 25.65; H, 0.81. Found: C, 25.28; H, 0.71. Calcd for $FeRu_3(CO)_{12}(MeC{\equiv}CMe)$, **2b**: C, 25.65; H, 0.81. Found: C, 25.50; H, 0.89 (Galbraith Laboratories).

Preparation of $FeRu_3(CO)_{12}(PhC{\equiv}CMe)$ (3a–c). $H_2FeRu_3(CO)_{13}$ (0.265 g, 0.363 mmol) dissolved in isooctane (200 mL) was brought to reflux under an N_2 atmosphere, and phenylmethylacetylene (0.2 mL, 0.188 g, 1.62 mmol) in isooctane (20 mL) was slowly added (over a 30-min period) via a pressure-equalizing dropping funnel, during which time the solution color changed from red to dark brown. Chromatography of the concentrated solution on silica gel using hexane as the eluting solvent gave in order of elution a yellow band of $Ru_3(CO)_{12}$, several small bands of trace amounts of unidentified compounds, a red band of unreacted $H_2FeRu_3(CO)_{13}$, an intense brown band of **3a**, and a very intense brown band containing both **3b** and **3c**. Although this latter mixture of isomers was rechromatographed several times, **3b** and **3c** could not be separated. The overall synthetic yield of the three isomers of $FeRu_3(CO)_{12}(PhC{\equiv}CMe)$ was 41% (**3a**, 29.8 mg, 10%; **3b,c**, 90.8 mg, 31%). Recrystallization from hexane yielded black, air-stable crystals of **3a** and the mixture of **3b** and **3c**. Anal. Calcd for $FeRu_3(CO)_{12}(PhC{\equiv}CMe)$, **3a**: C, 31.09; H, 0.99. Found: C, 31.10; H, 1.16. Calcd for $FeRu_3(CO)_{12}(PhC{\equiv}CMe)$, **3b,c**: C, 31.09; H, 0.99. Found: C, 30.94; H, 1.07 (Galbraith Laboratories).

$H_2FeRu_3(CO)_{13}$-Catalyzed Isomerization of 1-Hexene. $H_2FeRu_3(CO)_{13}$ (7.8 mg, 0.01 mmol) was dissolved in neat 1-hexene (20 mL, previously distilled over P_2O_5 under N_2) in a 50-mL three-necked flask equipped with a reflux condenser. The solution was refluxed at 63 °C for 2 h under an N_2 atmosphere. The extent of isomerization of the 1-hexene and the cis/trans ratio of the 2-hexenes were measured with a Varian Aerograph Model 1440 gas chromatograph equipped with a 7-ft SE-30 column having a temperature of 30 °C.

Spectral Measurements. Mass spectra were obtained with an AEI-MS-902 mass spectrometer (source voltage 70 eV, probe temperature 150 °C). Infrared spectra were recorded on a Perkin-Elmer 580 grating infrared spectrophotometer using 0.5-mm NaCl solution IR cells. ^1H NMR spectra were obtained in $CDCl_3$ solution with either a Varian A-60A or a JEOL PS-100-FT spectrometer.

Crystallographic Summary. The crystals employed in this study were cut from larger crystals and ground to spheres 0.24 mm (**1a**) and 0.40 mm (**1b**) in diameter. Pertinent crystal and intensity data are listed in Table I, and complete details of the crystallographic analyses are found in ref 24.[25] Intensity data for both compounds were reduced, without absorption corrections because of the spherical nature of the crystals, to relative squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections. Of the 9044 reflections examined for **1b**, 6901 were considered observed by applying the rejection criterion $I < 3\sigma(I)$ where $\sigma(I)$ is the standard deviation in intensity computed from $\sigma^2(I) = C_t + k^2B$ where C_t is the total count from scanning, k is the ratio of scanning time to total background time (in this case, $k = 1$), and B the total background count. For **1a**, of the 6333 examined reflections, 4983 were considered observed by the same rejection criterion.

Table I. Data for the X-ray Diffraction Study of Isomers 1a and **1b** of $FeRu_3(CO)_{12}(PhC{\equiv}CPh)$

Crystal Parameters

	1a	1b
space group	$P2_1/c\text{-}C_{2h}^5$	$P2_1/c\text{-}C_{2h}^5$
a, Å	9.526 (3)	9.699 (1)
b, Å	16.925 (5)	16.785 (2)
c, Å	17.037 (4)	17.054 (2)
β, deg	91.10 (2)	90.60 (1)
Z	4	4
calcd density, g/cm³	2.112	2.089
obsd density, g/cm³	2.115	2.092

Measurement of Intensity Data

diffractometer: $P\bar{1}$
radiation: Mo Kα (λ 0.710 73 Å)
monochromator: graphite crystal
scan method: ω; fixed background; bkgd/scan time = 1.0
scan speed fixed: 3°/min: 1a, 1b, $2\theta < 43°$. 2°/min: 1a, $43° < 2\theta < 50.7°$; 1b, $43° < 2\theta < 63.7°$. 1°/min: 1a, 50.7 $50.7° < 2\theta < 55°$
scan range: 1°
takeoff angle: 4°
std reflctns: 6/300, no variation
data limits: 1a, $0° \leqslant 2\theta \leqslant 55°$; 1b, $0° \leqslant 2\theta \leqslant 63.7°$
unique data: 1a, 6333; 1b, 9044
nonzero data: 1a, 4983; 1b, 6901 ($I > 3\sigma(I)$)

The structure of **1b** was solved first by direct methods. The four metal atoms were located on an E map calculated from a trial set of phases, and the remaining nonhydrogen atoms were located by using standard difference Fourier techniques. Atomic positions for the 10 phenyl hydrogen atoms were generated by using idealized sp² hybridization for the phenyl carbons and a C–H bond length of 0.95 Å. The structure was refined by full-matrix least-squares procedures with minimization of the function $\sum w(|F_o| - K^{-1}|F_c|)^2$, where w is the weight assigned each reflection and K is the scale factor, which puts F on an absolute basis, using the atomic form factors compiled by Cromer and Mann[26] and anomalous dispersion corrections[27] to the scattering factors of the metals in all structure factor calculations. Metal atom occupancies included as variables gave values of 1.00 for Ru at M_{a1} and M_{b1}, whereas those for Ru at M_{a2} and Fe at M_{b2} were consistent with 27% Fe at M_{a2} and 73% Fe at M_{b2}. The atomic scattering factors for the latter pair of metal sites were recalculated to reflect these percentages and were utilized with fixed metal site occupancies of 1.00 in the final structure factor calculations. The final cycles of empirically weighted full-matrix least-squares refinement, which employed mixed scattering factors for M_{a2} and M_{b2}, anisotropic thermal parameters for nonhydrogen atoms, isotropic thermal parameters for the hydrogen atoms, and a least-squares refinable extinction coefficient[28] (final value of 2.77×10^{-7}), converged to final values of 0.026 and 0.028 for R_1 and R_2, respectively.[29]

Since **1a** and **1b** are isomorphous, the atomic coordinates for the nonhydrogen atoms of **1b** were used as the starting point for the refinement of **1a**. The initial refinement results indicated that M_{a1} was probably the Fe site in **1a**. Metal atom site occupancies were included as variables and gave values of 1.00 for Ru at M_{a2} and M_{b2} whereas those for Ru at M_{b1} and Fe at M_{a1} were consistent with 63% Fe at M_{a1} and 37% Fe at M_{b1}. Refinement as above gave final values of 0.028 and 0.032 for R_1 and R_2, respectively. A listing of the observed and calculated structure factor amplitudes is included as Tables A and B in the supplementary material.

Results

Preparation and Characterization of Isomeric $FeRu_3(CO)_{12}(RC{\equiv}CR')$ Clusters. $H_2FeRu_3(CO)_{13}$ rapidly reacts with PhC≡CPh, MeC≡CMe, and PhC≡CMe at elevated

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(24) Tavanaiepour, I. Ph.D. Dissertation, University of Nebraska, 1980.

(25) Computer programs employed in this study with an IBM 360-65 or 370-158 computer: MAGTAPE, SCALUP, and SCTFT4, data reduction programs by V. W. Day; FORDAP, Fourier and Patterson synthesis program; FAME, a Wilson plot and normalized structure factor program by R. Dewar and A. Stone; MULTAN, direct-methods program by P. Main, M. M. Woolfson, and G. Germain; ORFLSE, full-matrix least-squares refinement program, a highly modified version of Busing, Martin, and Levy's original ORFLS; ORFFE, bond lengths and angles with standard deviations by Busing, Martin, and Levy; ORTEP2, thermal ellipsoid plotting program by C. K. Johnson.

(26) Cromer, D. T.; Mann, J. L. *Acta Crystallogr.* **1968**, *A24*, 321.

(27) Cromer, D. T., *Acta Crystallogr.* **1965**, *18*, 17.

(28) Zachariasen, W. H. *Acta Crystallogr.* **1967**, *23*, 558.

(29) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|]^{1/2}$.

Table II. Spectral Data for $FeRu_3(CO)_{12}(RC{\equiv}CR')$ Clusters

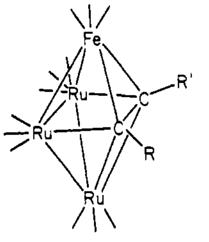
cluster	color	ν_{CO},[a] cm^{-1}	m/e[b]	^1H NMR, δ (rel intens)
$FeRu_3(CO)_{12}(PhC{\equiv}CPh)$ (1a)	brown	2095 m, 2064 s, 2049 s, 2036 s, 2024 m, 2016 m, 1998 m, 1986 w, 1976 w, 1962 vw	875,[d] 847 (vw), 819, 791, 763, 735, 707, 679, 651, 623, 595, 567, 539	7.5 m
$FeRu_3(CO)_{12}(PhC{\equiv}CPh)$ (1b)	red-brown	2097 m, 2073 s, 2064 w, 2050 s, 2028 s, 2019 m, 2016 m, 2002 w, 1978 w, 1969 w, 1944 w	875,[d] 847 (vw), 819, 791, 763, 735, 707, 679, 651, 623, 595, 567, 539	7.5 m
$FeRu_3(CO)_{12}(MeC{\equiv}CMe)$ (2a)	brown	2095 m, 2063 s, 2046 s, 2033 s, 2015 m, 2001 w, 1990 w, 1977 w	751,[d] 723 (vw), 695, 667, 639, 611, 583, 555, 527, 499, 471, 443, 415	3.17 s
$FeRu_3(CO)_{12}(MeC{\equiv}CMe)$ (2b)	red-brown	2097 w, 2086 w, 2082 s, 2047 s, 2026 s, 2018 m, 1997 w, 1979 w, 1965 w, 1947 w	751,[d] 723 (vw), 695, 667, 639, 611, 583, 555, 527, 499, 471, 443, 415	3.12 s (1) 3.24 s (1)
$FeRu_3(CO)_{12}(PhC{\equiv}CMe)$ (3a)	brown	2097 m, 2063 s, 2048 s, 2035 s, 2019 m, 2015 m, 1999 vw, 1991 w, 1977 w, 1965 vw	813,[d] 785 (vw), 757, 729, 701, 673, 645, 617, 589, 561, 533, 505, 477	3.91 s (3) 7.5 s (5)
$FeRu_3(CO)_{12}(PhC{\equiv}CMe)$ (3b/3c)	red-brown	2098 w, 2074 s, 2050 s, 2029 (sh), 2025, 2020 (sh), 1999 w, 1979 w, 1966 w, 1944 w	813,[d] 785 (vw), 757, 729, 701, 673, 645, 617, 589, 561, 533, 505, 477	3.86 s (1.0) 4.00 s (1.82) 7.5 m

[a] Hexane solution. [b] Mass position of the most intense peak in the isotopic envelope. [c] $CHCl_3$ solution. [d] Parent ion.

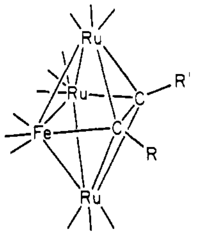
temperatures to give a series of isomeric $FeRu_3(CO)_{12}(RC{\equiv}CR')$ clusters according to eq 1. With $PhC{\equiv}CPh$ and

$$H_2FeRu_3(CO)_{13} + RC{\equiv}CR' \rightarrow FeRu_3(CO)_{12}(RC{\equiv}CR') + H_2 + CO \quad (1)$$

$MeC{\equiv}CMe$, two isomers of $FeRu_3(CO)_{12}(PhC{\equiv}CPh)$, **1a** and **1b**, and $FeRu_3(CO)_{12}(MeC{\equiv}CMe)$, **2a** and **2b**, are respectively obtained. Reaction with the unsymmetrical alkyne $PhC{\equiv}CMe$ produces three isomers of $FeRu_3(CO)_{12}(PhC{\equiv}CMe)$, **3a**, **3b**, and **3c**. The structures of these various derivatives, as indicated by the crystallographic and spectroscopic results are as shown here. Except for the **3b**/**3c** mixture, all of these isomers are readily separated by chromatography on silica gel. The mixture of **3b** and **3c** has thus far eluded separation by repeated chromatography and fractional crystallization. The formation of molecular hydrogen as indicated in eq 1 was verified by GC mass spectral analysis of the gases released upon reaction of $H_2FeRu_3(CO)_{13}$ with $PhC{\equiv}CPh$ in a closed system. Gas chromatography and mass spectral analysis of the reaction mixtures failed to show any evidence for the formation of $PhCH{=}CHPh$ or $PhCH_2CH_2Ph$, which could be derived by hydrogenation of $PhC{\equiv}CPh$.



1a: R = R' = Ph
2a: R = R' = Me
3a: R = Ph; R = Me



1b: R = R' = Ph
2b: R = R' = Me
3b: R = Me; R' = Ph
3c: R = Ph; R = Me

Each of these clusters has been characterized be elemental analysis and by their IR, ^1H NMR, and mass spectra, Table II. The mass spectrum of each compound shows the parent ion, fragment ions corresponding to loss of the 12 carbonyl ligands, and mass peaks attributable to the corresponding $FeRu_3(RC{\equiv}CR')^+$ ions. In each case the calculated isotopic distribution for the parent ion is in excellent agreement with that observed experimentally.

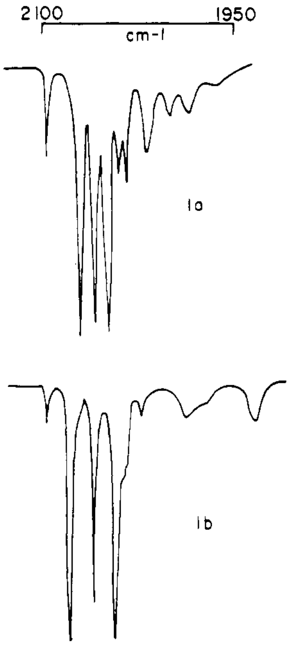


Figure 1. Carbonyl-region infrared spectra of $FeRu_3(CO)_{12}(PhC{\equiv}CPh)$ (**1a**,**b**), measured in hexane solution.

The carbonyl region infrared spectra of the two isomers of $FeRu_3(CO)_{12}(PhC{\equiv}CPh)$, **1a** and **1b**, are shown in Figure 1 and are representative of all the derivatives. Each cluster shows three characteristic intense bands in the 2080–2020-cm^{-1} region. The positions of these bands indicate structural correspondences for the isomers of the different compounds. For example, the spectra of **1a**, **2a**, and **3a** are virtually identical (**1a**: 2064, 2049, 2036 cm^{-1}; **2a**: 2063, 2046, 2033 cm^{-1}; **3a**: 2063, 2048, 2035 cm^{-1}). Likewise, the spectra of **1b**, **2b**, and the mixture of **3b** and **3c** are similar (**1b**: 2073, 2050, 2028 cm^{-1}; **2b**: 2072, 2047, 2026 cm^{-1}; **3b**,**c**: 2074, 2050, 2025 cm^{-1}). The significance of these similarities is presented in the Discussion.

Interconversion of Isomeric $FeRu_3C_2$ Clusters. An intriguing observation is the interconversion of the isomers of the $FeRu_3(CO)_{12}(RC{\equiv}CR')$ clusters upon heating. In refluxing hexane, **1b** readily isomerizes to **1a**, but the reverse isomerization of **1a** to **1b** is not nearly as facile (eq 2).[30] Prolonged

$$\underset{\mathbf{1a}}{FeRu_3(CO)_{12}(PhC{\equiv}CPh)} \underset{\substack{70\ °C,\ 15\ min,\\ >80\%\ isomerzn}}{\overset{\substack{70\ °C,\ 8\ h,\\ <10\%\ isomerzn}}{\rightleftarrows}} \underset{\mathbf{1b}}{FeRu_3(CO)_{12}(PhC{\equiv}CPh)} \quad (2)$$

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(30) The percent isomerization in each case was estimated from the relative intensities of the IR bands of each isomer.

heating of either isomer (8 h) gives a 9:1 **1a**/**1b** equilibrium mixture. The **1b** → **1a** isomerization occurs more slowly in concentrated solutions than in dilute solutions and also more slowly under an atmosphere of carbon monoxide than under an N_2 atmosphere.

The $FeRu_3(CO)_{12}(MeC{\equiv}CMe)$ and $FeRu_3(CO)_{12}(PhC{\equiv}CMe)$ clusters also isomerize upon heating as indicated in eq 3 and 4.[28] We were unable to distinguish by IR spectroscopy

$$\underset{\textbf{2a}}{FeRu_3(CO)_{12}(MeC{\equiv}CMe)} \underset{\substack{70\ ^\circ C,\ 8\ h,\\ 15\%\ isomerzn}}{\overset{\substack{70\ ^\circ C,\ 8\ h,\\ 10\%\ isomerzn}}{\rightleftarrows}} \underset{\textbf{2b}}{FeRu_3(CO)_{12}(MeC{\equiv}CMe)} \quad (3)$$

$$\underset{\textbf{3a}}{FeRu_3(CO)_{12}(PhC{\equiv}CMe)} \underset{\substack{70\ ^\circ C,\ 8\ h,\\ >60\%\ isomerzn}}{\overset{\substack{70\ ^\circ C,\ 24\ h,\\ 10\%\ isomerzn}}{\rightleftarrows}} \underset{\textbf{3b,c}}{FeRu_3(CO)_{12}(PhC{\equiv}CMe)} \quad (4)$$

and thin-layer chromatography whether **3a** selectively converts to **3b** or **3c** or whether a **3b**/**3c** mixture is formed. Isomerization to **3a** also occurred when a mixture of **3b** and **3c** was heated in isooctane at 70 °C under N_2 for 2 h in the presence of excess $PhC{\equiv}CPh$, but no $FeRu_3(CO)_{12}(PhC{\equiv}CPh)$, which might have resulted from alkyne interchange, was detected.

Extended heating (>24 h) of all of the $FeRu_3C_2$ clusters results not only in isomerization but also in decomposition. Most of the decomposition products have not been identified, but in the case of the $FeRu_3(CO)_{12}(PhC{\equiv}CPh)$ isomers, mass spectral evidence indicated the formation of $Ru_3(CO)_9(PhC{\equiv}CPh)$ (m/e 737 for parent ion, stepwise loss of nine CO ligands).

Attempted Preparation of Other Derivatives. Although the reaction of $H_2FeRu_3(CO)_{13}$ with $PhC{\equiv}CPh$, $MeC{\equiv}Me$, and $PhC{\equiv}CMe$ proceeds smoothly to give the series of $FeRu_3(CO)_{12}(RC{\equiv}CR)$ products, other alkynes did not exhibit similar reactivity. Complex mixtures of products resulted from the reactions of $H_2FeRu_3(CO)_{13}$ with $HC{\equiv}CH$,[31a] t-$BuC{\equiv}C$-t-Bu,[31b] and $PhC{\equiv}CH$,[31c] but no evidence for isomeric $FeRu_3(CO)_{12}(RC{\equiv}CR)$ clusters was obtained. In an attempt to form M_4N_2 and M_4CN analogues of the M_4C_2 clusters, reactions of $H_2FeRu_3(CO)_{13}$ with azobenzene and acetonitrile were investigated. No reaction was observed when $H_2FeRu_3(CO)_{13}$ was heated in the presence of azobenzene in refluxing hexane or isooctane solution, but $H_4Ru_4(CO)_{12}$ along with several unidentified compounds resulted from refluxing $H_2FeRu_3(CO)_{13}$ for 1 h in neat acetonitrile.

$H_2FeRu_3(CO)_{13}$-Catalyzed Isomerization of 1-Hexene. The reaction of $H_2FeRu_3(CO)_{13}$ with 1-hexene was investigated in an attempt to prepare cluster–olefin complexes, but none could be isolated. Instead, it was found that $H_2FeRu_3(CO)_{13}$ readily catalyzes the isomerization of 1-hexene to give a mixture of *cis*- and *trans*-2-hexene. When the reaction was carried out in refluxing neat 1-hexene with a cluster concentration of 5×10^{-4} M, approximately 60% of the 1-hexene was isomerized to *cis*- and *trans*-2-hexene after 2 h, giving a turnover number for the catalysis of approximately 4500 mol of hexene/mol of $FeRu_3$ per hour. The cis/trans ratio was 1.0/3.25. No 3-hexenes were detected in these experiments.

IR analysis of the solid obtained following evaporation of the olefin mixture showed that the bulk of the $H_2FeRu_3(CO)_{13}$ (>95%) was recovered unchanged, although thin-layer chromatography on silica gel indicated the presence of a very small amount of another compound. However, insufficient amount of this material was obtained to allow its characterization.

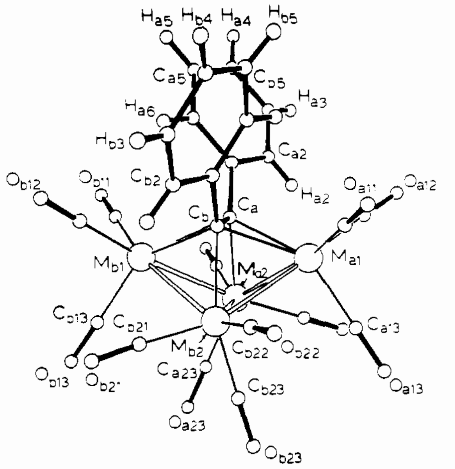

Figure 2. Perspective drawing, adapted from an ORTEP plot, of the **1a** and **1b** isomers of $FeRu_3(CO)_{12}(PhC{\equiv}CPh)$.

Crystal and Molecular Structures of 1a and 1b. The structures of both isomers of $FeRu_3(CO)_{12}(PhC{\equiv}CPh)$ have been determined by X-ray diffraction. The final atomic coordinates from the X-ray structural analysis of **1a**, **1b**, and the previously reported $Ru_4(CO)_{12}(PhC{\equiv}CPh)$,[16] which is isomorphous with **1a** and **1b**, are compared in Table C of the supplementary material. Refined anisotropic thermal parameters for nonhydrogen atoms of **1a** and **1b** are given in Table D. The numbering scheme used to designate atoms of **1a** and **1b** is as follows. The halves of the molecule related by the pseudo-C_2 axis, which passes through the midpoints of the acetylenic C_a–C_b and M_{a2}–M_{b2} bonds (Figure 2), are distinguished from one another by a subscripted a or b. Metal atoms are designated by M and the remaining atoms by their respective atomic symbols. Metal atoms and their carbonyl groups in the same half of the molecule are distinguished from one another by a first numerical subscript. A second numerical subscript is used to distinguish between carbonyl ligands bonded to the same metal. A perspective view of the structures which illustrates this numbering scheme is shown in Figure 2. Covalent bond lengths and angles determined for **1a** and **1b** are compared with those reported[16] for $Ru_4(CO)_{12}(PhC{\equiv}CPh)$ in Tables III and IV, respectively.

The two isomers of $FeRu_3(CO)_{12}(PhC{\equiv}CPh)$ are isomorphous, differing only in their distribution of the metal atoms. Isomer **1a** has the Fe atom located in an "axial" position cis to both carbon atoms (M_{a1} or M_{b1}, Figure 2) whereas in isomer **1b** the Fe atom is located in an "equatorial" position cis to one carbon atom and trans to the other (M_{a2} or M_{b2}). The axial and equatorial labels will be used from here on to differentiate these two isomers. Both structures are disordered with respect to the specific location of the Fe atoms. The best refinement was achieved for **1a** by varying the metal site occupancies and the final values obtained were 63% Fe for M_{a1} and 37% Fe for M_{b1}. For **1b**, the values were 27% Fe for M_{a2} and 73% Fe for M_{b2}.

The distorted octahedral structures that these clusters adopt is fully consistent with Wade's[32] skeletal electron counting

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(31) (a) $H_2FeRu_3(CO)_{13}$ was heated in a refluxing hexane solution that was continuously purged with C_2H_2. Mass spectral evidence suggested the formation of a small amount of $FeRu_4(CO)_{15}C$ (parent ion m/e 896; stepwise loss of 15 CO ligands) and $FeRu_2(CO)_{10}(C_2H_2)$ (parent ion m/e 566; stepwise loss of 10 CO ligands), but these could not be isolated in sufficient quantities to characterize. (b) Reaction between t-$BuC{\equiv}C$-t-Bu and $H_2FeRu_3(CO)_{13}$ in refluxing hexane gave at least three products, which were not fully characterized but definitely were shown not to be $FeRu_3C_2$ clusters by infrared and mass spectral analyses. (c) When $H_2FeRu_3(CO)_{13}$ was treated with $C_6H_5C{\equiv}CH$ in refluxing hexane, the solution darkened considerably. Evaporation of solvent gave a brown tar, from which no characterizable compounds could be obtained.

(32) Wade, K., *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

Table III. Bond Lengths (Å) in Crystalline $M'M_3(CO)_{12}(PhC{\equiv}CPh)$ Complexes ($M' = Fe, Ru; M = Ru$)[a,b]

	compd				compd		
bond[c]	M′ = Fe **1b**[d]	M′ = Fe **1a**[e]	M′ = Ru **2**	bond[c]	M′ = Fe **1b**[d]	M′ = Fe **1a**[e]	M′ = Ru **2**
$M_{a1}-M_{a2}$	2.712 (1)	2.681 (1)	2.74 (1)	$C_{a1}-C_{a2}$	1.392 (4)	1.398 (5)	1.39 (2)
$M_{a1}-M_{b2}$	2.646 (1)	2.649 (1)	2.71 (1)	$C_{a1}-C_{a6}$	1.398 (4)	1.397 (5)	1.38 (2)
$M_{b1}-M_{b2}$	2.680 (1)	2.700 (1)	2.74 (1)	$C_{a2}-C_{a3}$	1.387 (4)	1.393 (6)	1.40 (2)
$M_{b1}-M_{a2}$	2.688 (1)	2.681 (1)	2.71 (1)	$C_{a3}-C_{a4}$	1.370 (5)	1.379 (7)	1.36 (2)
				$C_{a4}-C_{a5}$	1.369 (5)	1.366 (7)	1.36 (2)
$M_{a2}-M_{b2}$	2.780 (1)	2.849 (1)	2.85 (1)	$C_{a5}-C_{a6}$	1.386 (4)	1.379 (5)	1.42 (2)
				$C_{b1}-C_{b2}$	1.395 (4)	1.401 (5)	1.39 (2)
$M_{a1}\cdots M_{b1}$	3.910 (1)	3.775 (1)	3.93 (1)	$C_{b1}-C_{b6}$	1.399 (4)	1.405 (5)	1.39 (2)
				$C_{b2}-C_{b3}$	1.378 (4)	1.382 (5)	1.39 (2)
$M_{a1}-C_a$	2.235 (1)	2.160 (3)	2.24 (1)	$C_{b3}-C_{b4}$	1.373 (6)	1.375 (7)	1.37 (2)
$M_{a1}-C_b$	2.234 (2)	2.163 (3)	2.24 (1)	$C_{b4}-C_{b5}$	1.376 (6)	1.371 (7)	1.34 (2)
$M_{b1}-C_a$	2.259 (3)	2.204 (3)	2.26 (1)	$C_{b5}-C_{b6}$	1.390 (4)	1.389 (6)	1.40 (2)
$M_{b1}-C_b$	2.237 (2)	2.185 (3)	2.25 (1)				
				$C_{a11}-O_{a11}$	1.127 (4)	1.136 (5)	1.16 (2)
$M_{a2}-C_a$	2.136 (2)	2.166 (3)	2.16 (1)	$C_{a12}-O_{a12}$	1.128 (4)	1.135 (5)	1.15 (2)
$M_{b2}-C_b$	2.105 (3)	2.188 (3)	2.16 (1)	$C_{a13}-O_{a13}$	1.135 (4)	1.144 (5)	1.17 (2)
				$C_{a21}-O_{a21}$	1.150 (4)	1.132 (6)	1.14 (2)
$M_{a1}-C_{a11}$	1.898 (3)	1.830 (4)	1.88 (1)	$C_{a22}-O_{a22}$	1.130 (4)	1.130 (5)	1.15 (2)
$M_{a1}-C_{a12}$	1.916 (4)	1.851 (4)	1.91 (2)	$C_{a23}-O_{a23}$	1.128 (5)	1.123 (6)	1.16 (2)
$M_{a1}-C_{a13}$	1.890 (3)	1.804 (5)	1.87 (2)	$C_{b11}-O_{b11}$	1.134 (4)	1.129 (5)	1.14 (2)
$M_{a2}-C_{a21}$	1.863 (4)	1.906 (5)	1.89 (2)	$C_{b12}-O_{b12}$	1.125 (4)	1.134 (5)	1.14 (2)
$M_{a2}-C_{a22}$	1.872 (4)	1.903 (5)	1.89 (2)	$C_{b13}-O_{b13}$	1.130 (4)	1.127 (5)	1.14 (2)
$M_{a2}-C_{a23}$	1.887 (4)	1.930 (5)	1.90 (2)	$C_{b21}-O_{b21}$	1.144 (4)	1.138 (5)	1.14 (2)
$M_{b1}-C_{b11}$	1.903 (3)	1.867 (4)	1.89 (1)	$C_{b22}-O_{b22}$	1.141 (4)	1.134 (5)	1.16 (2)
$M_{b1}-C_{b12}$	1.923 (3)	1.872 (4)	1.92 (1)	$C_{b23}-O_{b23}$	1.142 (4)	1.130 (5)	1.14 (2)
$M_{b1}-C_{b13}$	1.900 (3)	1.849 (5)	1.88 (2)				
$M_{b2}-C_{b21}$	1.811 (3)	1.906 (5)	1.90 (2)	$C_{a2}-H_{a2}$	0.93 (3)	0.96 (4)	...[f]
$M_{b2}-C_{b22}$	1.824 (3)	1.904 (4)	1.89 (2)	$C_{a3}-H_{a3}$	0.90 (4)	0.99 (5)	...[f]
$M_{b2}-C_{b23}$	1.811 (4)	1.923 (4)	1.90 (2)	$C_{a4}-H_{a4}$	0.91 (4)	0.94 (5)	...[f]
				$C_{a5}-H_{a5}$	1.0 (4)	0.91 (5)	...[f]
C_a-C_b	1.460 (3)	1.458 (4)	1.46 (2)	$C_{a6}-H_{a6}$	0.95 (3)	0.96 (5)	...[f]
				$C_{b2}-H_{b2}$	0.93 (3)	0.93 (4)	...[f]
C_a-C_{a1}	1.505 (3)	1.504 (4)	1.53 (2)	$C_{b3}-H_{b3}$	0.91 (4)	0.97 (6)	...[f]
C_b-C_{b1}	1.501 (3)	1.499 (4)	1.52 (2)	$C_{b4}-H_{b4}$	0.89 (4)	0.96 (4)	...[f]
				$C_{b5}-H_{b5}$	0.91 (4)	0.97 (5)	...[f]
				$C_{b6}-H_{b6}$	0.96 (4)	0.97 (5)	...[f]

[a] Figures in parentheses are the estimated standard deviations in the last significant digit. [b] The three compounds crystallize isomorphously. [c] Atoms are labeled in agreement with Table C and Figure 2. [d] For **1b**, metal sites M_{a1} and M_{b1} were 100% Ru, M_{a2} was 27% Fe and 73% Ru, and M_{b2} was 73% Fe and 27% Ru. [e] For **1a**, metal sites M_{a2} and M_{b2} were 100% Ru, M_{a1} was 63% Fe and 37% Ru, and M_{b1} was 37% Fe and 63% Ru. [f] Atomic positions for hydrogens of **2** were calculated by using idealized geometry and a C–H bond length of 0.95 Å.

rules, which predict a *closo*-M_4C_2 structure with six vertices.[33] Other clusters with analogous M_4C_2 frameworks have been structurally characterized.[16,18,21,22,34] The alkyne can be best viewed as a four-electron donor to the cluster framework. Each framework carbon can be considered to be sp^2 hybridized with the three hybride orbitals bonding the other carbon, the R (or R′) group, and the equatorial cis metal. The remaining two carbon electrons would occupy a π-bonding orbital between the carbon atoms, but this electron pair is equally shared with the two axial metals via overlap with the metal d orbitals. Such an interaction has been previously described as a bent μ-type bond.[18]

The metal atoms of **1a** and **1b** can be described as having a "butterfly" configuration with dihedral angles of 112.7 and 117.0°, respectively, about the "hinge" of the butterfly. Corresponding angles of 115.5 and 118° were observed in $Ru_4(CO)_{12}(PhC{\equiv}CPh)$[16] and $Co_4(CO)_{10}(EtC{\equiv}CEt)$,[18] respectively. Within the octahedral $FeRu_3C_2$ framework of **1a** and **1b** the two acetylenic carbons (C_a and C_b) are coplanar with M_{a2} and M_{b2} to within 0.01 Å. Each of the metals in **1a** and **1b** is terminally bonded to three carbonyl ligands. The average M–C–O angles of 177.6 (6,11,23,12)°[35] in **1a** and 177.4 (8,15,48,12)° in **1b** and C–O distances of 1.133 (5,4,11,12) Å in **1a** and 1.134 (4,6,16,12) Å in **1b** are typical values for this formally two-electron donating ligand.

Perhaps the most significant feature of the data presented in Tables III, IV, C, and D is the approximately 5-fold increase in precision for the structural analysis of **1a** and **1b** relative to $Ru_4(CO)_{12}(PhC{\equiv}CPh)$[16] despite the disordering of Fe among the metal sites in **1a** and **1b**. The bond distances involving the cluster metals in **1a** and **1b** are in complete accord with the crystallographically determined metal-site occupancies. The carbonyl M–C distances in **1b** for M_{a1} and M_{b1} that are 100% Ru are the longest and comparable to those in $Ru_4(CO)_{12}(PhC{\equiv}CPh)$, whereas those for M_{b2}, which has the highest percentage of Fe (73%), are the shortest. Analogous results obtain for **1a**, and a similar comparison can be made for the M–M and acetylenic M–C bonds. Average bond lengths involving pure Ru metal sites in **1a** and **1b** are carbonyl Ru–C 1.912 (5,7,18,6) Å[35] in **1a** and 1.905 (3,10,18,6) Å in **1b**, acetylenic Ru–C 2.177 (3,11,11,2) Å in **1a** and 2.241 (2,9,18,4) Å in **1b**, and Ru-Ru 2.849 (1) Å in **1a**. The average phenyl C–C bond lengths of 1.386 (6,11,20,12) Å in **1a** and 1.384 (4,9,15,17) Å in **1b** are normal values for these bonds.

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(33) Fe(8) + 3Ru(24) + 2C(8) + 12CO(24) + $2C_6H_5(2)$ = 66 valence electrons; 52 electrons required for ligand bonding and nonbonding orbitals [Fe(12) + 3Ru(36) + 2C(4)]; 66 − 52 = 14 = $2n + 2$ for n = 6.

(34) Stuntz, G. F.; Shapley, J. R.; Pierpont, C. G. *Inorg. Chem.* **1978**, *17*, 2596.

(35) The first number in parentheses following an average value for a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively; the fourth number is the number of individual values included in the average.

Each of the six-membered phenyl rings in both compounds are coplanar to within 0.01 Å. The average C–H bond lengths of 0.96 (5,2,5,10) Å in **1a** and 0.93 (4,3,7,10) Å in **1b** are typical X-ray values for these bonds and in excellent agreement with high-precision X-ray structural studies of other compounds.[36]

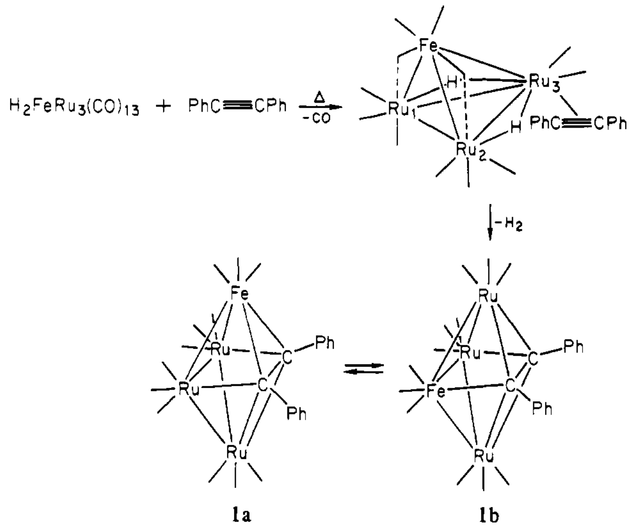
Discussion

$H_2FeRu_3(CO)_{13}$ readily reacts with diphenylacetylene, dimethylacetylene, and phenylmethylacetylene to produce isomeric $FeRu_3(CO)_{12}(RC{\equiv}CR)$ products according to the stoichiometry shown in eq 1. The isomeric $FeRu_3(CO)_{12}(RC{\equiv}CR)$ clusters have been characterized by their IR and mass spectra and by elemental analysis, all of which are consistent with the formulations given. The absence of hydride ligands in the formulations is supported by the lack of hydride resonances in their ^1H NMR spectra and the evolution of H_2 during the course of the reactions. The two isomers of $FeRu_3(CO)_{12}(PhC{\equiv}CPh)$ have been further characterized by complete single-crystal X-ray diffraction analysis, and their structures are shown in Figure 2.

The crystal structures of **2a**, **2b**, **3a**, **3b**, and **3c** have not been determined, but their structures can be confidently assigned on the basis of their spectral and chromatographic relationships to **1a** and **1b**. The similarities noted earlier in the IR spectra of **1a**, **2a**, and **3a**, coupled with the observation that each of these three isomers is brown and each elutes first upon separating their respective mixtures by chromatography, suggest that **2a** and **3a** are axial isomers with cluster frameworks similar to that of **1a**, with the iron atom cis to both carbon atoms. Consistent with this assignment is the observation of a single methyl resonance at 3.17 ppm in the ^1H NMR spectrum of **2a**, implying equivalent methyl groups in the bound $CH_3C{\equiv}CCH_3$ ligand. Likewise, the IR spectra of **1b**, **2b**, and the **3b**/**3c** mixture are similar, these clusters are all red-brown, and they all elute after **1a**, **2a**, and **3a** during their respective chromatographic separation. We thus suggest that **2b**, **3b**, and **3c** are equatorial isomers with structures analogous to **1b** with the Fe atom trans to one carbon atom and cis to the other. The ^1H NMR spectrum of **2b** shows two singlets at 3.12 and 3.24 ppm of equal intensity, implying nonequivalent methyl groups consistent with this structural assignment. The ^1H NMR spectrum of the **3b**/**3c** mixture shows two singlets at 3.86 and 4.00 ppm in a 1/1.82 intensity ratio. The methyl groups in these isomers are in different chemical environments since the methyl group in **3b** is attached to a carbon atom cis to Fe, whereas in **3c** the methyl group is attached to a trans carbon. The overall structural similarity of these two isomers is apparently responsible for their similar chromatographic behavior.

When $PhC{\equiv}CPh$ was allowed to react with $H_2FeRu_3(CO)_{13}$ for 15 min in refluxing hexane, the yield of **1b** was 2.9 times that of **1a**. However, the isomerization experiments indicate that **1b** readily isomerizes to **1a** but that the reverse process is not nearly as rapid. It thus appears that **1b** is initially formed during the course of the reaction and that it subsequently isomerizes to **1a** under the reaction conditions. Isomer **1b** is thus the kinetically preferred isomer, whereas **1a** is the more thermodynamically stable. The $FeRu_3(CO)_{12}(MeC{\equiv}CMe)$ and $FeRu_3(CO)_{12}(PhC{\equiv}CMe)$ systems are entirely analogous with the axial isomer being the more thermodynamically stable isomer for each of the alkynes.[37]

Scheme I



Although detailed kinetic mesurements have not been conducted for the reaction of $H_2FeRu_3(CO)_{13}$ with alkynes, it is quite likely that the reaction proceeds via the sequence of steps outlined in Scheme I. The first step presumably involves dissociation of CO from $H_2FeRu_3(CO)_{13}$ to generate $H_2FeRu_3(CO)_{12}$. This unsaturated species then rapidly adds an alkyne to give the substituted derivative shown in Scheme I. Kinetic measurements have shown that the substitution of PPh_3 for CO in $H_2FeRu_3(CO)_{13}$ proceeds by such a dissociative process.[5] Although rate data have not been obtained for the reaction with alkynes, qualitative experiments indicate that the reaction occurs on about the same time scale as PPh_3 substitution, consistent with the rate-limiting step being dissociation of CO. Initial substitution of the alkyne presumably occurs in an axial position on the unique Ru atom as this is the substitution site that large tertiary phosphine and phosphite ligands occupy.[5] From this site the alkyne could easily insert into a Ru–Ru bond to give the kinetically prepared equatorial isomer **1b**.

The reaction of $H_2FeRu_3(CO)_{13}$ with 1-hexene did not generate an isolable cluster–olefin complex. Instead, facile isomerization of the alkene to a mixture of *cis*- and *trans*-2-hexene occurred. Unlike the alkyne ligands, 1-hexene is incapable of acting as a four-electron donor to the cluster and is not incorporated into the framework of an M_4C_2 species. Olefin coordination and isomerization presumably occurs at a single metal center after initial CO dissociation from the cluster.

The mechanism of the cluster framework isomerization in which the isomeric $FeRu_3(CO)_{12}(RC{\equiv}CR)$ derivatives interconvert is not well understood at this point. However, the following qualitative conclusions can be derived. The absence of substantial decomposition during the early stages of the isomerization suggests that the process is entirely intramolecular. Furthermore, the lack of alkyne interchange during the isomerization process indicates that the isomer interconversion occurs without dissociation of the alkyne. The inhibition of the rate of isomerization in the presence of carbon monoxide and the concentration dependence both suggest that CO dissociation is an integral step in the process. The key

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(36) (a) Cotton, F. A.; Day, V. W.; Hazen, E. E., Jr.; Larsen, S. *J. Am. Chem. Soc.* **1973**, *95*, 4834. (b) Cotton, F. A.; Day, V. W.; Hazen, E. E., Jr.; Larsen, S.; Wong, S. T. K. *Ibid.* **1974**, *96*, 4471. (c) Baumgarten, H.. D.; McMahan, D. G.; Elia, V. J.; Gold, B. I.; Day, V. W.; Day, R. O. *J. Org. Chem.* **1976**, *41*, 3798. (d) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(37) In the original synthesis, the yield of **2a** was greater than that of **2b**. This reaction however was run at 83 °C, as opposed to 70 °C for the other alkynes. We believe these conditions accelerated the isomerization of **2b** initially formed from **2a**. For the phenylmethylacetylene clusters, the yield of the **3b**/**3c** mixture was greater than that of **3a**.

Table IV. Bond Angles (Deg) in Crystalline $M'M_3(CO)_{12}(PhC{\equiv}CPh)$ Complexes (M' = Fe, Ru; M = Ru)^{a,b}

angle^c	compd		
	M' = Fe 1b^d	M' = Fe 1a^e	M' = Ru 2
$M_{a2}M_{a1}M_{b2}$	62.5 (1)	64.61 (2)	63.1 (1)
$M_{a2}M_{b1}M_{b2}$	62.39 (1)	63.92 (3)	63.1 (1)
$M_{a1}M_{a2}M_{b2}$	57.58 (1)	57.15 (2)	57.9 (1)
$M_{a1}M_{b2}M_{a2}$	59.91 (1)	58.24 (1)	59.0 (1)
$M_{b1}M_{a2}M_{b2}$	58.67 (1)	58.36 (1)	59.0 (1)
$M_{b1}M_{b2}M_{a2}$	58.94 (1)	57.71 (2)	57.9 (1)
$M_{a1}M_{a2}M_{b1}$	92.80 (1)	89.50 (2)	92.2 (1)
$M_{a1}M_{b2}M_{b1}$	94.48 (1)	89.77 (2)	92.2 (1)
$M_{a2}M_{a1}C_{a11}$	162.6 (1)	165.0 (1)	162.9 (4)
$M_{b2}M_{b1}C_{b11}$	160.8 (1)	163.4 (2)	162.3 (4)
$M_{b2}M_{a1}C_{a12}$	167.7 (1)	168.9 (2)	169.0 (4)
$M_{a2}M_{b1}C_{b12}$	166.0 (1)	167.7 (1)	166.6 (4)
$M_{a2}M_{a1}C_{a13}$	97.4 (1)	91.0 (1)	95.8 (6)
$M_{b2}M_{b1}C_{b13}$	94.3 (1)	89.3 (1)	92.1 (5)
$M_{b2}M_{a1}C_{a13}$	88.7 (1)	82.9 (1)	86.8 (4)
$M_{a2}M_{b1}C_{b13}$	94.3 (1)	90.3 (2)	92.7 (5)
$M_{a2}M_{a1}C_{a12}$	105.3 (1)	104.3 (1)	106.0 (4)
$M_{b2}M_{b1}C_{b12}$	106.6 (1)	105.4 (1)	105.7 (4)
$M_{b2}M_{a1}C_{a11}$	102.2 (1)	101.6 (1)	101.6 (4)
$M_{a2}M_{b1}C_{b11}$	98.9 (1)	99.7 (1)	99.5 (4)
$M_{a1}M_{a2}C_{a23}$	136.0 (1)	135.1 (2)	134.0 (5)
$M_{b1}M_{b2}C_{b23}$	123.9 (1)	125.1 (1)	125.3 (4)
$M_{b1}M_{a2}C_{a21}$	168.8 (1)	167.5 (2)	168.1 (5)
$M_{a1}M_{b2}C_{b21}$	162.3 (1)	157.7 (1)	160.1 (4)
$M_{a1}M_{a2}C_{a22}$	129.7 (1)	131.0 (2)	129.5 (4)
$M_{b1}M_{b2}C_{b22}$	141.2 (1)	142.0 (1)	141.7 (4)
$M_{b1}M_{a2}C_{a22}$	92.5 (1)	91.0 (1)	92.7 (4)
$M_{a1}M_{b2}C_{b22}$	87.1 (1)	87.5 (1)	87.3 (4)
$M_{a1}M_{a2}C_{a21}$	76.0 (1)	78.9 (1)	76.1 (5)
$M_{b1}M_{b2}C_{b21}$	75.4 (1)	77.5 (1)	76.3 (4)
$M_{b1}M_{a2}C_{a23}$	96.3 (1)	100.5 (2)	99.1 (5)
$M_{a1}M_{b2}C_{b23}$	101.9 (1)	108.5 (1)	105.4 (4)
$M_{b2}M_{a2}C_{a21}$	114.5 (1)	117.2 (1)	114.7 (5)
$M_{a2}M_{b2}C_{b21}$	122.8 (1)	125.1 (1)	123.7 (4)
$M_{b2}M_{a2}C_{a23}$	91.7 (1)	91.4 (2)	90.7 (5)
$M_{a2}M_{b2}C_{b23}$	84.2 (1)	88.3 (1)	87.7 (4)
$M_{b2}M_{a2}C_{a22}$	151.2 (1)	149.3 (1)	151.7 (4)
$M_{a2}M_{b2}C_{b22}$	145.4 (1)	143.5 (1)	144.5 (4)
$C_{a11}M_{a1}C_{a12}$	89.4 (1)	89.5 (2)	89.0 (6)
$C_{a11}M_{a1}C_{a13}$	90.1 (1)	92.8 (2)	90.8 (6)
$C_{a12}M_{a1}C_{a13}$	95.2 (1)	97.5 (2)	95.9 (6)
$C_{b11}M_{b1}C_{b12}$	91.1 (1)	90.9 (2)	90.9 (6)
$C_{b11}M_{b1}C_{b13}$	91.2 (1)	92.6 (2)	91.7 (6)
$C_{b12}M_{b1}C_{b13}$	95.2 (1)	96.9 (1)	95.5 (6)
$C_{a21}M_{a2}C_{a22}$	93.7 (2)	93.1 (2)	93.1 (6)
$C_{a21}M_{a2}C_{a23}$	92.7 (2)	91.1 (2)	90.8 (7)
$C_{a22}M_{a2}C_{a23}$	92.8 (2)	92.7 (2)	94.6 (6)
$C_{b21}M_{b2}C_{b22}$	91.8 (1)	91.3 (2)	91.8 (6)
$C_{b21}M_{b2}C_{b23}$	95.8 (2)	93.8 (2)	94.6 (6)
$C_{b22}M_{b2}C_{b23}$	93.4 (2)	91.4 (2)	91.4 (6)
$M_{a1}C_aC_b$	70.9 (1)	70.4 (2)	71.1 (6)
$M_{b1}C_bC_a$	71.9 (1)	71.3 (2)	71.6 (6)
$M_{b1}C_aC_b$	70.2 (1)	69.9 (2)	70.6 (6)
$M_{a1}C_bC_a$	71.0 (1)	70.2 (2)	70.8 (6)
$M_{a1}C_aM_{a2}$	76.6 (1)	76.6 (1)	77.1 (4)
$M_{b1}C_bM_{b2}$	76.2 (1)	76.3 (1)	76.9 (3)
$M_{b1}C_aM_{a2}$	75.4 (1)	75.7 (1)	75.6 (4)
$M_{a1}C_bM_{b2}$	75.1 (1)	75.0 (1)	75.9 (3)
$M_{a1}C_aM_{b1}$	120.9 (1)	119.8 (1)	121.8 (5)
$M_{a1}C_bM_{b1}$	122.0 (1)	120.5 (1)	122.2 (5)
$M_{a1}C_aC_{a1}$	122.9 (2)	123.8 (2)	122.6 (7)
$M_{b1}C_bC_{b1}$	122.2 (2)	123.8 (2)	122.7 (7)
$M_{b1}C_aC_{a1}$	115.9 (2)	116.1 (2)	115.3 (7)
$M_{a1}C_bC_{b1}$	115.6 (2)	115.5 (2)	114.8 (7)
$M_{a2}C_aC_{a1}$	124.6 (2)	124.0 (2)	123.3 (8)
$C_aM_{a1}C_{a11}$	119.8 (1)	121.6 (1)	120.2 (5)
$C_bM_{b1}C_{b11}$	123.5 (1)	124.8 (2)	124.5 (5)
$C_aM_{a1}C_{a12}$	98.3 (1)	97.6 (2)	99.0 (5)
$C_bM_{b1}C_{b12}$	93.7 (1)	93.7 (1)	94.2 (5)
$C_aM_{a1}C_{a13}$	147.0 (1)	142.3 (2)	145.6 (5)
$C_bM_{b1}C_{b13}$	143.9 (1)	141.2 (2)	142.3 (5)
$C_bM_{a1}C_{a11}$	91.8 (1)	92.3 (1)	92.1 (5)
$C_aM_{b1}C_{b11}$	93.5 (1)	94.5 (2)	94.6 (5)
$C_bM_{a1}C_{a12}$	126.5 (1)	126.6 (2)	126.9 (5)
$C_aM_{b1}C_{b12}$	119.8 (1)	120.4 (1)	120.5 (5)
$C_bM_{a1}C_{a13}$	138.3 (1)	135.6 (2)	137.1 (5)
$C_aM_{b1}C_{b13}$	144.6 (1)	141.8 (2)	143.3 (5)
$C_aM_{a2}C_{a21}$	116.0 (1)	115.2 (2)	115.5 (5)
$C_bM_{b2}C_{b21}$	108.2 (1)	106.3 (2)	107.3 (5)
$C_aM_{a2}C_{a22}$	91.8 (1)	91.9 (1)	92.3 (5)
$C_bM_{b2}C_{b22}$	98.1 (1)	99.0 (1)	98.7 (5)
$C_aM_{a2}C_{a23}$	150.6 (1)	153.0 (1)	152.4 (6)
$C_bM_{b2}C_{b23}$	152.9 (2)	157.0 (2)	155.5 (5)
$C_aM_{a1}M_{a2}$	50.0 (1)	51.8 (1)	50.2 (3)
$C_bM_{b1}M_{b2}$	49.7 (1)	51.9 (1)	50.2 (3)
$C_bM_{a1}M_{a2}$	72.2 (1)	75.0 (1)	72.4 (3)
$C_aM_{b1}M_{b2}$	71.6 (1)	74.3 (1)	72.3 (3)
$C_aM_{a1}M_{b2}$	72.7 (1)	76.0 (1)	73.3 (3)
$C_bM_{b1}M_{a2}$	72.6 (1)	74.6 (1)	72.9 (3)
$C_bM_{a1}M_{b2}$	50.2 (1)	52.9 (1)	50.8 (3)
$C_aM_{b1}M_{a2}$	50.2 (1)	51.5 (1)	50.6 (3)
$C_aM_{a2}M_{a1}$	53.3 (1)	51.6 (1)	52.6 (3)
$C_bM_{b2}M_{b1}$	54.1 (1)	51.8 (1)	53.4 (3)
$C_aM_{a2}M_{b1}$	54.4 (1)	52.8 (1)	53.9 (3)
$C_bM_{b2}M_{a1}$	54.7 (1)	52.1 (1)	53.0 (3)
$C_aM_{a2}M_{b2}$	71.3 (1)	71.7 (1)	71.4 (3)
$C_bM_{b2}M_{a2}$	72.4 (1)	71.1 (1)	71.1 (3)
$M_{a1}C_{a11}O_{a11}$	178.0 (8)	177.8 (7)	178 (1)
$M_{a1}C_{a12}O_{a12}$	177.1 (5)	176.2 (5)	177 (1)
$M_{a1}C_{a13}O_{a13}$	179.2 (5)	175.3 (4)	179 (1)
$M_{b1}C_{b11}O_{b11}$	178.8 (9)	177.9 (5)	177 (1)
$M_{b1}C_{b12}O_{b12}$	178.8 (11)	179.2 (10)	177 (1)
$M_{b1}C_{b13}O_{b13}$	179.0 (11)	178.8 (5)	177 (1)
$M_{a2}C_{a21}O_{a21}$	174.3 (5)	176.8 (4)	176 (1)
$M_{a2}C_{a22}O_{a22}$	179.4 (9)	179.8 (3)	177 (1)
$M_{a2}C_{a22}O_{a23}$	177.8 (9)	179.0 (5)	176 (1)
$M_{b2}C_{b21}O_{b21}$	172.6 (4)	175.4 (4)	174 (1)
$M_{b2}C_{b22}O_{b22}$	177.0 (5)	177.7 (7)	178 (1)
$M_{b2}C_{b23}O_{b23}$	176.7 (5)	177.6 (7)	176 (1)
$C_aC_{a1}C_{a2}$	120.9 (2)	120.4 (3)	120 (1)
$C_aC_{a1}C_{a6}$	121.6 (2)	122.2 (3)	121 (1)
$C_{a6}C_{a1}C_{a2}$	117.4 (2)	117.4 (3)	119 (1)
$C_{a4}C_{a2}C_{a3}$	121.2 (3)	120.8 (4)	119 (1)
$C_{a2}C_{a3}C_{a4}$	120.1 (3)	120.1 (4)	121 (1)
$C_{a3}C_{a4}C_{a5}$	120.0 (3)	119.8 (4)	121 (1)
$C_{a4}C_{a5}C_{a6}$	120.4 (3)	120.6 (4)	119 (1)
$C_{a1}C_{a6}C_{a5}$	120.9 (3)	121.3 (4)	121 (1)
$C_bC_{b1}C_{b2}$	120.1 (2)	120.3 (3)	119 (1)
$C_bC_{b1}C_{b6}$	122.0 (2)	122.1 (3)	120 (1)
$C_{b6}C_{b1}C_{b2}$	117.8 (2)	117.5 (3)	119 (1)
$C_{b1}C_{b2}C_{b3}$	121.1 (3)	120.8 (4)	120 (1)
$C_{b2}C_{b3}C_{b4}$	120.4 (3)	120.6 (4)	121 (1)
$C_{b3}C_{b4}C_{b5}$	119.8 (3)	119.9 (4)	119 (1)
$C_{b4}C_{b5}C_{b6}$	120.2 (3)	120.5 (4)	122 (1)
$C_{b5}C_{b6}C_{b1}$	120.6 (3)	120.6 (4)	119 (1)
$H_{a2}C_{a2}C_{a3}$	122 (2)	119 (2)	121
$H_{a2}C_{a2}C_{a1}$	116 (2)	121 (2)	121
$H_{a3}C_{a3}C_{a4}$	124 (3)	120 (3)	119
$H_{a3}C_{a3}C_{a2}$	116 (3)	120 (3)	119
$H_{a4}C_{a4}C_{a5}$	119 (3)	125 (3)	120
$H_{a4}C_{a4}C_{a3}$	121 (3)	115 (3)	120
$H_{a5}C_{a5}C_{a4}$	121 (2)	118 (3)	121
$H_{a5}C_{a5}C_{a6}$	118 (2)	122 (3)	121
$H_{a6}C_{a6}C_{a5}$	120 (2)	116 (3)	120
$H_{a6}C_{a6}C_{a1}$	119 (2)	123 (3)	120
$H_{b2}C_{b2}C_{b3}$	115 (2)	119 (2)	120

Table IV (*Continued*)

	compd				compd		
angle[c]	M′ = Fe 1b[d]	M′ = Fe 1a[e]	M′ = Ru 2	angle[c]	M′ = Fe 1b[d]	M′ = Fe 1a[e]	M′ = Ru 2
$M_{b_2}C_bC_{b_1}$	124.9 (2)	124.3 (2)	124.9 (8)	$H_{b_2}C_{b_2}C_{b_1}$	124 (2)	120 (2)	120
				$H_{b_3}C_{b_3}C_{b_4}$	121 (2)	122 (3)	120
$C_aM_{a_1}C_b$	38.1 (1)	39.4 (1)	38.1 (4)	$H_{b_3}C_{b_3}C_{b_2}$	119 (2)	118 (3)	120
$C_aM_{b_1}C_b$	37.9 (1)	38.8 (1)	37.8 (4)	$H_{b_4}C_{b_4}C_{b_5}$	118 (3)	118 (3)	120
				$H_{b_4}C_{b_4}C_{b_3}$	123 (3)	122 (3)	120
$C_{a_1}C_aC_b$	127.0 (2)	126.9 (3)	128 (1)	$H_{b_5}C_{b_5}C_{b_4}$	125 (2)	122 (3)	119
$C_{b_1}C_bC_a$	126.8 (2)	127.0 (3)	126 (1)	$H_{b_5}C_{b_5}C_{b_6}$	115 (2)	118 (3)	119
				$H_{b_6}C_{b_6}C_{b_5}$	119 (2)	117 (3)	120
				$H_{b_6}C_{b_6}C_{b_1}$	120 (2)	122 (3)	120

[a] Figures in parentheses are the estimated standard deviations in the last significant digit. [b] The three compounds crystallize isomorphously. [c] Atoms are labeled in agreement with Table C and Figure 2. [d] For 1b, metal sites M_{a_1} and M_{b_1} were 100% Ru, M_{a_2} was 27% Fe and 73% Ru, and M_{b_2} was 73% Fe and 27% Ru. [e] For 1a, metal sites M_{a_2} and M_{b_2} were 100% Ru, M_{a_1} was 63% Fe and 37% Ru, and M_{b_1} was 37% Fe and 63% Ru.

Table V. Structural Comparisons for High-Precision Studies of Several μ_x-η^2-Bonded Alkyne Ligands[a]

compd[b]	x	C≡C, Å	≡C–C, Å	C≡C–C, deg	ref
$(CpNi)_2(HC{\equiv}CH)$	2	1.341 (6)			38
$(NiCOD)_2(C_6H_5C{\equiv}CC_6H_5)$	2	1.366 (6)	1.459 (4)	141.4 (2)	40, *c*
$(NiCOD)_2(CH_3C_6H_4C{\equiv}CC_6H_4CH_3)$	2	1.346 (4)	1.467 (4,4,4,2)	141.3 (3,10,10,2)	*c*
$Ni_4L_4(C_6H_5C{\equiv}CC_6H_5)_3$	3	1.343 (4,1,2,3)	1.488 (8,2,7,6)	133.2 (3,1,2,6)	39, *c*
$Ni_4L_4(CH_3C_6H_4C{\equiv}CC_6H_4CH_3)_3$	3	1.331 (9,10,15,3)	1.492 (9,2,8,6)	130.4 (6,13,30,6)	39
$FeRu_3(CO)_{12}(C_6H_5C{\equiv}CC_6H_5)$ (1b)	4	1.460 (3)	1.503 (3,2,2,2)	126.9 (2,1,1,2)	*d*
$FeRu_3(CO)_{12}(C_6H_5C{\equiv}CC_6H_5)$ (1a)	4	1.458 (4)	1.502 (4,3,3,2)	126.9 (3,1,1,2)	*d*

[a] See ref 35 for an explanation of the numbers in parentheses. [b] $Cp = \eta$-C_5H_5; COD = 1,5-cyclooctadiene; L = *tert*-butyl isocyanide. [c] Day, V. W., unpublished results. [d] This work.

intermediate thus appears to be $FeRu_3(CO)_{11}(RC{\equiv}CR)$.

Structural Consequences of the μ_4-η^2-Alkyne Bonding Mode. Considerable recent interest has been given to the activation of multiple-order bonds in small organic molecules.[38–40] It is well-known that these bonds can be activated by complexation to a single metal center and it has been proposed that simultaneous complexation to several metal centers could enhance this activation process.[41] A recent survey of structural studies of μ_x-η^2-bonded substituted alkynes (x = 1–4) revealed interesting trends for the acetylenic C≡C bond lengths in these complexes.[39] These data seemed to indicate that C≡C bonds were elongated from the 1.20 Å formal triple-bond value in free acetylene[42] to ~1.35 Å upon complexation to one, two, or three metal centers and to ~1.46 Å when complexed to four metal centers. Unfortunately, the precision obtained in most of the cited studies was not sufficiently high to make these differences statistically significant ($\geq 5\sigma$). Only five structural studies of the μ_4-η^2-bonded type have been reported prior to the present studies for the **1a** and **1b** isomers of $FeRu_3(CO)_{12}(PhC{\equiv}CPh)$.[16,18,21,22,24] With the exception of the $Os_4(CO)_{12}(C_2R_1R_2)$ clusters discussed in ref 22, the variation in bond lengths for these μ_4-η^2-bonded acetylene ligands was small, ranging from 1.43 to 1.46 Å. However, the average estimated standard deviation was large (0.02 Å). The values of 1.458 (4) and 1.460 (3) Å for the alkyne C–C bonds in **1a** and **1b**, respectively, are in excellent agreement with these previously reported values but 5–6 times more precise. The C–C bond lengths in $Os_4(CO)_{12}(HC{\equiv}CH)$ and $Os_4(CO)_{12}(HC{\equiv}CR)$ have been reported to be 1.55 (4) and 1.54 (3) Å, respectively,[22] and are thus significantly larger than all other reported values for μ_4-η^2-bonded alkynes.

The increased precision of this study enhances the reliability of comparisons such as those given in Table V, in which the structural parameters for the acetylenic carbon atoms in **1a** and **1b** are compared with those for high-precision studies of other μ_x-η^2-bonded alkyne ligands. These data clearly indicate a substantial (~0.15 Å) elongation of the acetylenic C≡C bond from the formal triple-bond value of 1.20 Å in free acetylene to ~1.35 Å when complexed to two or three metals. Another substantial (~0.10 Å or longer[22]) elongation occurs upon complexation to the fourth metal. The 1.460 Å average C≡C bond length is, in fact, nearly 0.14 Å longer than the normal ethylenic C=C double bond and only 0.028 Å shorter than a formal single bond between two sp^3-hybridized carbon atoms. Furthermore, the data for the ≡C—C bond indicate that p orbital contribution to the hybridization for the acetylenic carbon atoms increases with x. The ≡C—C bond length of diphenylacetylene steadily increases from 1.459 (4) Å for the μ_2-η^2-bonding to 1.503 (3,3,3,4) Å[35] for the μ_4-η^2-bonding mode. The C≡C—C angle also decreases from 141.4 (2)° for μ_2-η^2 bonding to 126.9 (2,1,1,4)° for μ_4-η^2 bonding.

Acknowledgment. This research was supported in part by the Office of Naval Research. G.L.G. gratefully acknowledges the Camille and Henry Dreyfus Foundation for the award of a Teacher-Scholar grant and the Alfred P. Sloan Foundation for the award of a research fellowship. The assistance of Alan Freyer and Dr. Robert Minard in obtaining NMR and mass spectra is appreciated.

Registry No. **1a**, 78248-93-8; **1b**, 78248-94-9; **2a**, 78248-95-0; **2b**, 78248-96-1; **3a**, 78248-97-2; **3b**, 78248-98-3; **3c**, 78248-99-4; $H_2FeRu_3(CO)_{13}$, 32036-04-7; 1-hexene, 592-41-6; $(NiCOD)_2(CH_3C_6H_4C{\equiv}CC_6H_4CH_3)$, 78249-00-0; *cis*-2-hexene, 7688-21-3; *trans*-2-hexene, 4050-45-7.

Supplementary Material Available: Tables A–D giving structure factors, final atomic coordinates, and thermal parameters (67 pages). Ordering information is given on any current masthead page.

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(38) Wang, Y.; Coppens, P. *Inorg. Chem.* **1976**, *15*, 1122.

(39) Thomas, M. G.; Muetterties, E. L.; Day, R. O.; Day, V. W. *J. Am. Chem. Soc.* **1976**, *98*, 4645.

(40) Day, V. W.; Abdel-Mequid, S. S.; Dabestani, S.; Thomas, M. G.; Pretzer, W. R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1976**, *98*, 8289.

(41) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1976**, *85*, 451.

(42) "Tables of Interatomic Distances and Configurations in Molecules and Ions"; The Chemical Society: London; Vol. 11, p M122.