

Synthesis and Reactivity of Ferrocenecarboxylate Ruthenium(II) Complexes. Catalytic Synthesis of a Ferrocenecarboxylic Enol Ester

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Received May 20, 1998

Summary: New ferrocenecarboxylate ruthenium(II) complexes were obtained from the reaction of $[\text{RuClH}(\text{CO})(\text{PPh}_3)_3]$ with ferrocenecarboxylic acid or its sodium salt. The reaction of alkenyl complexes $[\text{Ru}(\text{O}_2\text{C}(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5))(\text{CR}'=\text{CRH})(\text{CO})(\text{PPh}_3)_2]$ with CO and catalytic synthesis of the phenylethyleneferrocenecarboxylic ester have been studied.

Introduction

Insertion reactions into metal–hydrogen bonds are very important steps in catalytic reactions such as hydrogenation and isomerization of alkenes and alkynes.² The hydride–ruthenium bond is highly reactive toward alkynes and usually leads to η^1 -alkenyl compounds in mild conditions via insertion reactions.³ The reaction of the ruthenium hydride $[\text{RuClH}(\text{CO})(\text{PPh}_3)_2\text{L}]$ ($\text{L} = \text{PPh}_3$ or Py) with alkynes results in the formation of alkenyl complexes. If $\text{L} = \text{PPh}_3$, the alkenyl compounds $[\text{RuCl}(\eta^1\text{-CR}'=\text{CRH})(\text{CO})(\text{PPh}_3)_2]$ are coordinatively unsaturated⁴ and highly reactive toward small molecules such as alkynes, CO,⁵ CO_2 ,⁶ CS_2 ,⁷ and bidentate coor-

inating ligands as carboxylates,⁸ dithiocarboxylates, or xanthates.⁹ The reaction of $[\text{Ru}(\eta^1\text{-CR}'=\text{CRH})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ complexes ($\text{R} = \text{Me}$ or Ph) with CO led to the formation of hexacoordinated complexes containing an η^2 -alkeneacyl ligand, whereas when $\text{R} = \text{R}' = \text{CO}_2\text{Me}$, a simple CO coordination to the metal occurred. A $\eta^2 \rightarrow \eta^1$ conversion was also observed when a carboxylate ligand was added to the acyl compound.⁵ These results suggested that both steric and electronic effects might play a significant role in the CO–alkenyl coupling. To examine the effects of the coordination of carboxylates to the coordinatively unsaturated $[\text{RuCl}(\eta^1\text{-CR}'=\text{CRH})(\text{CO})(\text{PPh}_3)_2]$ complexes, we synthesized complexes with carboxylates.⁸ Here we present a study of the coordination ability of the ferrocenecarboxylate anion coordinated to mononuclear ruthenium(II) complexes and the reactivity of this complex with CO. The catalytic addition of ferrocenecarboxylic acid to phenylacetylene using ruthenium(I) and ruthenium(II) complexes as catalyst precursors was also undertaken. We chose this particular acid because of its size and the strong inductive effect of the ferrocene unit.¹⁰ Various examples of the coordination of the ferrocenecarboxylate ligand have been reported, but they were restricted by the low solubility of compounds.¹¹ Examples of both η^2

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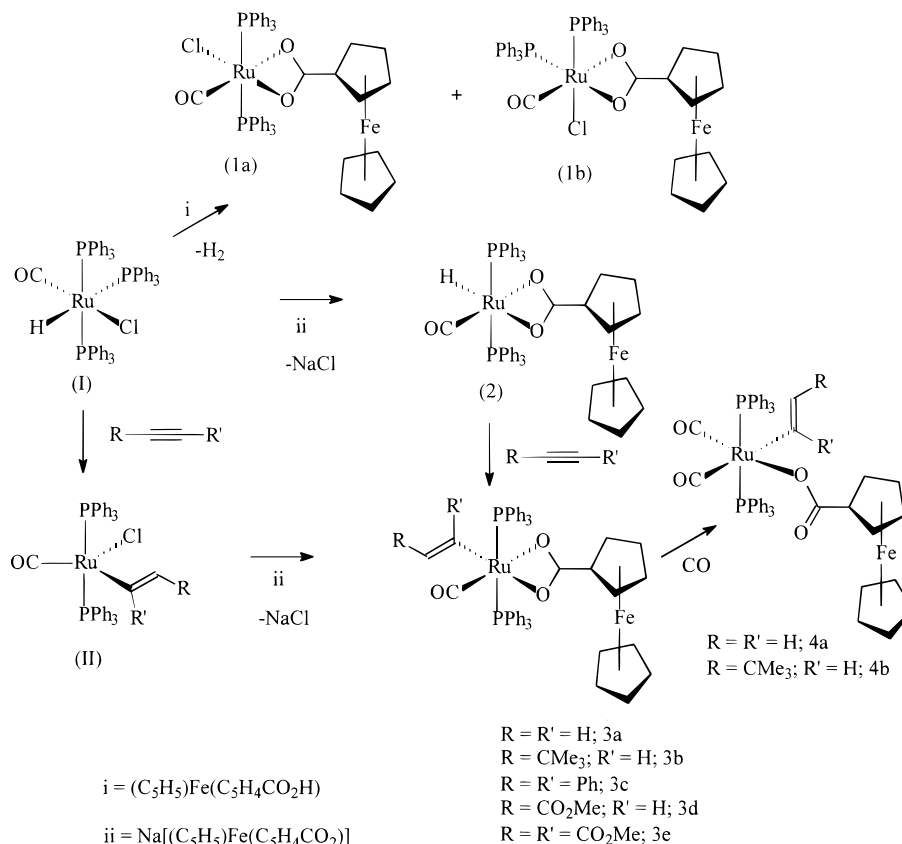
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Scheme 1



and η^1 coordination of the ferrocenecarboxylate ligand have been found in mononuclear and dinuclear copper(II) complexes.^{11d-e}

Results and Discussion

Synthesis of Complexes. The summary of reactions performed is shown in Scheme 1. A mixture of products (**1a** and **1b**) was prepared by reaction of $[\text{RuClH}(\text{CO})(\text{PPh}_3)_3]$ (**I**) with a solution of ferrocenecarboxylic acid in methanol at room temperature. Both complexes **1a** and **1b** have the same formula $[\text{Ru}(\text{O}_2\text{C}(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5))\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ and have the carboxylate ligand η^2 -coordinated to ruthenium. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1a** indicates a trans arrangement of phosphines, whereas two doublets with $^2J_{\text{PP}} = 22.9$ Hz in the spectrum of **1b** suggest a cis arrangement of PPh_3 ligands.¹² It is interesting to note that the ^1H NMR spectrum of **1b** shows a doubling of the signals of the ferrocenyl group. A possible reason for this pattern is the presence of two different arrangements of the bulky ferrocenyl group, which cannot rotate around the $\text{O}_2\text{C}-\text{C}_5\text{H}_4$ bond. The same complex $[\text{RuClH}(\text{CO})(\text{PPh}_3)_3]$ (**I**) reacted with the sodium salt of the ferrocenecarboxylic acid dissolved in methanol to give the complex **2**, of formula $[\text{Ru}(\text{O}_2\text{C}(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5))\text{H}(\text{CO})(\text{PPh}_3)_2]$. A triplet resonance at $\delta -16.2$ ppm with $^2J_{\text{HP}} = 21.6$ Hz in the ^1H NMR spectrum and a singlet at $\delta 43.9$ ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR of **2** indicate that the hydride ligand is in a cis position with respect to the PPh_3 ligands, which are mutually trans.^{4,12} A strong IR band of $\nu(\text{Ru}-$

$\text{H})^{12}$ was observed at 1995 cm^{-1} , and two C—O stretching frequencies at 1496 and 1397 cm^{-1} are consistent with the structure proposed.¹³

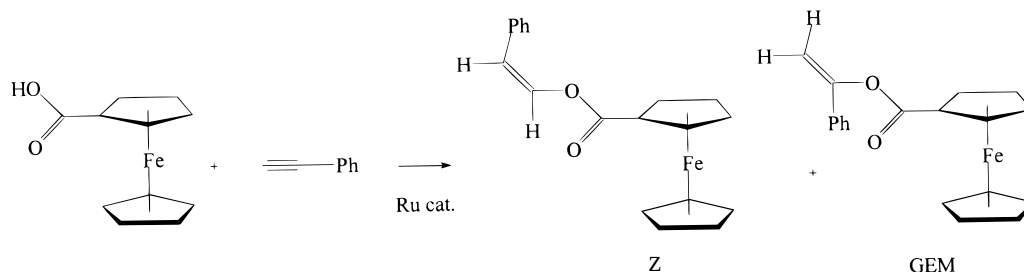
The coordinatively unsaturated complex $[\text{RuCl}(\text{CR}'=\text{CRH})(\text{CO})(\text{PPh}_3)_2]$ (**II**) is also highly reactive toward the ferrocenecarboxylate ligand. Complexes of type **II** reacted with the sodium salt of ferrocenecarboxylic acid dissolved in methanol to give hexacoordinated complexes $[\text{Ru}(\text{O}_2\text{C}(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5))(\text{CR}'=\text{CRH})(\text{CO})(\text{PPh}_3)_2]$, where $\text{R} = \text{R}' = \text{H}$ (**3a**); $\text{R} = \text{CMe}_3$, $\text{R}' = \text{H}$ (**3b**); $\text{R} = \text{R}' = \text{Ph}$ (**3c**); $\text{R} = \text{CO}_2\text{Me}$, $\text{R}' = \text{H}$ (**3d**); and $\text{R} = \text{R}' = \text{CO}_2\text{Me}$ (**3e**). IR spectra of complexes **3a–3e** show $\Delta = \nu(\text{OCO})_{\text{asym}} - \nu(\text{OCO})_{\text{sym}}$ values of ca. 100 cm^{-1} , which confirms the η^2 -coordination of the carboxylate ligand.¹³ The chemical shifts of the vinyl protons are similar to those of unsaturated complexes of type **II** and to other carboxylate complexes, indicating a trans arrangement of hydrogens in monosubstituted alkenyl groups ($\text{R}' = \text{H}$). The $^{31}\text{P}\{^1\text{H}\}$ spectra of complexes **3a–3e** show a singlet at $33\text{--}36$ ppm and are consistent with two mutually trans PPh_3 ligands.^{4,12} Hexacoordinated alkenyl ferrocenecarboxylate complexes **3a–3e** were also prepared from the reaction of the hydride compound $[\text{Ru}(\text{O}_2\text{C}(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5))\text{H}(\text{CO})(\text{PPh}_3)_2]$ (**2**) with the corresponding alkyne in refluxing dichloromethane.

When complexes **3a** and **3b** were reacted with CO at room temperature in dichloromethane solution, the compounds of formula $[\text{Ru}(\text{O}_2\text{C}(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5))(\text{CR}'=$

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Scheme 2



CRH)(CO)₂(PPh₃)₂] (R = R' = H (**4a**); R = CMe₃, R' = H (**4b**)) were formed. Two IR bands of $\nu(\text{C}(\text{O}))$ together with $\Delta = \nu(\text{OCO})_{\text{asym}} - \nu(\text{OCO})_{\text{sym}}$ values of 222 and 237 cm⁻¹, respectively, indicated the coordination of two mutually cis CO ligands⁵ and an η^1 -ferrocenecarboxylate ligand.¹⁴ The remaining coordination sites of the ruthenium atom in complexes **4a** and **4b** are completed by an alkenyl ligand and two PPh₃ ligands in a trans arrangement. The vinyl protons of these complexes show chemical shifts and coupling similar to those in complexes **3a** and **3b**. The ³¹P{¹H} NMR spectra of compounds **3a** and **3b** display singlets at 32.1 and 29.7 ppm, respectively.

Catalytic Synthesis of Ferrocenecarboxylate Enol Esters. Enol esters can be obtained from the addition of carboxylic acids to alkynes in the presence of a ruthenium complex.¹⁵ Enol esters are also intermediates for the conversion of amino acids into amides and peptides.¹⁶ The synthesis of ferrocenoyl amino acids has recently been reported.¹⁷ We have found that the addition of ferrocenecarboxylic acid to phenylacetylene in the presence of a ruthenium catalyst gives stereoisomers of phenylethyleneferrocenecarboxylic ester **5** (Scheme 2). The reaction of ferrocenecarboxylic acid (1 equiv) with a small excess of phenylacetylene in refluxing toluene for 20 h with [Ru₂(HCO₂)₂(CO)₄(PPh₃)₂] (0.005 equiv) as a catalyst led to the Z isomer of **5** (100%) in 80% yield. When we used the mononuclear Ru(II) complex **1a** [Ru(O₂C(C₅H₄)Fe(C₅H₅))Cl(CO)(PPh₃)₂] as a catalyst, the same reaction afforded a mixture of *gem* (1%) and *Z* (99%) isomers in 83% yield. Dinuclear [Ru₂(RCO₂)₂(CO)₄(PPh₃)₂] complexes¹⁸ and arene [RuCl₂(arene)(PR₃)] complexes¹⁹ have been shown to be active catalysts in the addition of carboxylic acids to terminal alkynes. Phosphine-containing dinuclear ruthenium(I) complexes are generally more regioselective than mononuclear compounds, and Markovnikov addition (isomer GEM) is more common than the formation of *Z* and *E* isomers. An opposite isomeric relationship was observed when Ru₃(CO)₁₂ was used as catalyst,^{15b} which suggests that coordinated PPh₃ ligands are essential for the regioselectivity of this reaction. In

our case ferrocenecarboxylic acid seems to induce the formation of the *Z* isomer as the major product in both reactions.

Description of the Molecular Structure of Complex 3a. The structure of **3a** (Figure 1) consists of [Ru(O₂C(C₅H₄)Fe(C₅H₅))(CH=CH₂)(CO)(PPh₃)₂] molecules separated by van der Waals distances. Selected bond lengths and angles are collected in Table 1. The Ru atom has a distorted octahedral coordination with two PPh₃ ligands occupying trans positions (P1–Ru–P2 = 175.9 (5)°). The rest of the ligands, η^2 -ferrocenecarboxylate, η^1 -vinyl, and CO, complete the coordination to the metal. The ferrocenecarboxylate ligand is unsymmetrically η^2 -bonded to metal with Ru–O77 and Ru–O78 distances of 2.192(3) and 2.269(3) Å, respectively. These distances are shorter than others found in acetate and formate mononuclear complexes of Ru(II).⁸ The C=C bond length of 1.159(11) Å and the C≡O bond length of 1.088(6) Å are short, whereas the Ru–alkenyl and Ru–CO bond lengths are longer than those in related complexes.⁸ These significant differences may arise from the particular nature of this carboxylate ligand. The ferrocenyl system is a strong donor group, which makes the ferrocenecarboxylic acid weaker than benzoic acid and aminoferrocene more basic than aniline.¹⁰ The strong inductive quality of this ligand explains why the Ru–carboxylate and O₂–C(C₅H₄) bonds are short, but this property is not reflected in the structural parameters of C≡O or vinyl ligands. The Ru–CO and Ru–vinyl distances are long

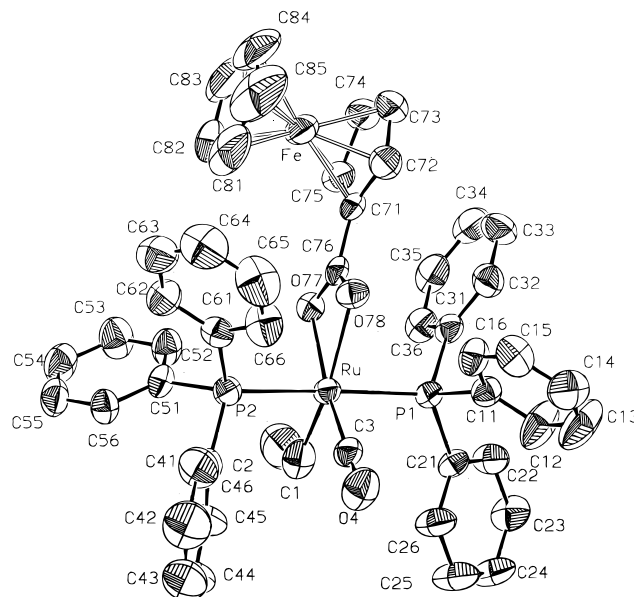


Figure 1. Molecular structure of [Ru(O₂C(C₅H₄)Fe(C₅H₅))(CH=CH₂)(CO)(PPh₃)₂] (**3a**).

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Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Complex 3a

Ru—C(3)	1.850(6)	Ru—C(1)	2.073(7)
Ru—O(77)	2.192(3)	Ru—O(78)	2.269(3)
Ru—P(2)	2.377(2)	Ru—P(1)	2.3845(14)
Fe—C(81)	2.009(5)	Fe—C(75)	2.012(6)
Fe—C(82)	2.013(5)	Fe—C(71)	2.017(5)
Fe—C(85)	2.026(5)	Fe—C(74)	2.030(6)
Fe—C(72)	2.034(6)	Fe—C(73)	2.039(6)
Fe—C(83)	2.032(5)	Fe—C(84)	2.041(5)
C(76)—O(77)	1.283(6)	C(76)—O(78)	1.263(6)
C(71)—C(76)	1.463(7)	C(1)—C(2)	1.159(11)
C(3)—O(4)	1.088(6)		
C(3)—Ru—C(1)	91.5(2)	O(77)—Ru—P(2)	93.53(9)
C(3)—Ru—O(77)	169.5(2)	O(78)—Ru—P(2)	95.05(10)
C(1)—Ru—O(77)	98.8(2)	C(3)—Ru—P(1)	87.8(2)
C(3)—Ru—O(78)	110.9(2)	C(1)—Ru—P(1)	91.8(2)
C(1)—Ru—O(78)	157.1(2)	O(77)—Ru—P(1)	89.96(9)
O(77)—Ru—O(78)	58.65(13)	O(78)—Ru—P(1)	84.93(10)
C(3)—Ru—P(2)	88.4(2)	P(2)—Ru—P(1)	175.90(5)
C(1)—Ru—P(2)	89.8(2)	O(78)—C(76)—O(77)	118.3(4)

and C≡O and C=C are short compared with other related ruthenium(II) carboxylate complexes.⁸ The C76 atom lies on the C₅H₄ plane, and the planar O₂C group forms an angle of 5.20° with this plane. The RuO₂C plane forms a dihedral angle of 13.1° with the C₅H₄ ring. These angles indicate that ligands coordinating to ruthenium have moved the ferrocenyl group away, thus minimizing steric repulsions, although the PPh₃ ligands remain in trans positions. The Fe—C₅H₄ distances range from 2.012(6) through 2.039(6) Å, while Fe—C₅H₅ distances are between 2.009(7) and 2.041(7) Å. The ferrocenyl group adopts a staggered conformation that deviates from the eclipsed conformation by 19.0°. Both staggered and eclipsed conformations have been reported in other complexes.¹¹

Experimental Section

All reactions were performed under an N₂ atmosphere. All the solvents were distilled and dried before use. NMR spectra were recorded on a Bruker AC-250 (¹H, 250 MHz; ¹³C, 62 MHz; ³¹P, 102 MHz) spectrometer in CDCl₃ or CD₃CO solutions. IR spectra were recorded on a Perkin-Elmer FT 1710 spectrophotometer in KBr disks or with CH₂Cl₂ solutions. Elemental analyses were obtained by the staff of the Chemical Analysis Service of the University Autònoma de Barcelona. The [RuClH(CO)(PPh₃)₃]²⁰ and [Ru(CR'=CRH)Cl(CO)(PPh₃)₂]⁴ complexes were prepared by using previously published procedures. Ferrocenecarboxylic acid was purchased commercially. Sodium ferrocenecarboxylate was prepared by reacting ferrocenecarboxylic acid with sodium methoxide in methanol.

[Ru(O₂C(C₅H₄)Fe(C₅H₅))Cl(CO)(PPh₃)₂] (1). Ferrocenecarboxylic acid (330 mg, 14 mmol) dissolved in methanol (5 mL) was added to a solution of [RuClH(CO)(PPh₃)₃] (100 mg, 11 mmol) in dichloromethane (15 mL), and the resulting mixture was stirred for 6 h. The solvent was evaporated, the residue was extracted with dichloromethane (10 mL) and chromatographed on a silica column. Complex **1a** was eluted with dichloromethane and **1b** with a 4:1 dichloromethane–ethyl acetate mixture. Both fractions were separately evaporated to dryness and crystallized in dichloromethane–methanol mixtures, and the resulting orange solids were filtered off. Yields were 27% and 41% for **1a** and **1b**, respectively.

(1) Analysis: Found (calc) for C₄₈H₃₉O₃ClP₂FeRu·CH₂Cl₂: C, 58.93 (58.67); H, 4.25 (4.12). **(1a)** IR (cm⁻¹): 1946 (C=O),

1479 (OCO)_{asym}, 1401 (OCO)_{sym}. ³¹P{¹H} NMR(CDCl₃) δ: 29.18 (s) ppm. ¹H NMR (CDCl₃): δ 7.60–7.20 (m, 30 H), 3.83 (br s, 2 H), 3.79 (br s, 2 H), 3.46 (s, 5 H) ppm. **(1b)** IR (cm⁻¹): 1950 (C=O), 1476 (OCO)_{asym}, 1415 (OCO)_{sym}. ³¹P{¹H} NMR(CDCl₃): δ 44.17 (d, ²J_{PP} = 22.9 Hz), 42.04 (d, ²J_{PP} = 22.9 Hz) ppm. ¹H NMR (CDCl₃): δ 7.60–7.20 (m, 60 H), 4.39 (br s, 2 H), 4.26 (s, 5 H), 4.19 (s, 5 H), 4.14 (br s, 2 H), 4.05 (br s, 2 H), 3.99 (br s, 2 H) ppm.

[Ru(O₂C(C₅H₄)Fe(C₅H₅))H(CO)(PPh₃)₂] (2). Sodium ferrocenecarboxylate (500 mg, 20 mmol) dissolved in methanol (5 mL) was added to a solution of [RuClH(CO)(PPh₃)₃] (200 mg, 20 mmol) in dichloromethane (15 mL). After 2 h of stirring, the solvent was evaporated, and the resulting residue was extracted with dichloromethane (10 mL). The orange complex **2** was precipitated with hexane and filtered off (65% yield).

(2) Analysis: Found (calc) for C₄₈H₄₀O₃P₂FeRu: C, 65.35 (65.30); H, 4.52 (4.46)%. IR (cm⁻¹): 1995 (Ru—H), 1924 (C=O), 1496 (OCO)_{asym}, 1397 (OCO)_{sym}. ³¹P{¹H} NMR (CO(CD₃)): δ 43.9 (s) ppm. ¹H NMR (CDCl₃): δ 7.80–7.20 (m, 30 H), 4.07 (br s, 2 H), 3.94 (br s, 2 H), 3.55 (s, 5 H), -16.2 (t, ²J_{PH} = 21.6 Hz, 1 H) ppm.

[Ru(O₂C(C₅H₄)Fe(C₅H₅))(CR'=CRH)(CO)(PPh₃)₂] (R = R' = H (3a**); R = CMe₃, R' = H (**3b**); R = R' = Ph (**3c**); R = CO₂Me, R' = H (**3d**); and R = R' = CO₂Me (**3e**)).** **(a) Synthesis from Alkenyl Complexes [Ru(CR'=CRH)Cl(CO)(PPh₃)₂].** Sodium ferrocenecarboxylate (1.1 equiv) dissolved in methanol was added to a solution of the alkenyl complex in dichloromethane, and the mixture was stirred for 3 h. The solvent was evaporated, and the residue was extracted with dichloromethane. Orange-yellow complexes (**3a–3e**) were precipitated with hexane, filtered off, and dried. Yields were **3a**, 97%; **3b**, 95%; **3c**, 98%; **3d**, 80%, and **3e**, 70%.

(b) Synthesis from [Ru(O₂C(C₅H₄)Fe(C₅H₅))H(CO)(PPh₃)₂] (2). To a solution of **2** in dichloromethane was added the corresponding alkyne (1.2 equiv), and the resulting mixture was refluxed for 2 h. After cooling to room temperature, mixtures of complexes (**3a–3e**) and the hydride complex (**2**) were precipitated with hexane, filtered off, and dried. Yields were **3a**, 42%; **3b**, 60%; **3c**, 60%; **3d**, 70%; and **3e**, 60%.

(3a) Analysis: Found (calc) for C₅₀H₄₂O₃P₂FeRu·0.7 CH₂Cl₂: C, 62.61 (62.83); H, 4.78 (4.48). IR (cm⁻¹): 1897 (C=O), 1541 (C=C), 1498 (OCO)_{asym}, 1401 (OCO)_{sym}. ³¹P{¹H} NMR(CDCl₃): δ 35.7 (s) ppm. ¹H NMR (CDCl₃): δ 7.80–7.20 (m, 31 H), 5.00 (dd, ³J_{HH} = 9.2 Hz, ⁴J_{PH} = 2.1 Hz, 1 H), 4.52 (dd, ³J_{HH} = 16.5 Hz, ⁴J_{PH} = 1.8 Hz, 1 H), 4.01 (br s, 2 H), 3.83 (br s, 2 H), 3.40 (s, 5 H) ppm. ¹³C{¹H} NMR (CDCl₃): δ 206.0 (t, ³J_{CP} = 15.6 Hz, CO), 185.3 (C=O), 156.7 (t, ²J_{CP} = 10.8 Hz, CH=), 134.9–127.3 (Ph), 119 (t, ²J_{CP} = 3.32 Hz, =CH₂), 68.7, 68.6, 68.4 (C₅H₄), 68.3 (C₅H₅) ppm.

(3b) Analysis: Found (calc) for C₅₄H₅₀O₃P₂FeRu·0.5 CH₂Cl₂: C, 64.14 (64.92); H, 5.39 (5.10). IR (cm⁻¹): 1917 (C(O), 1512 (C=C), 1492 (OCO)_{asym}, 1392 (OCO)_{sym}. ³¹P{¹H} NMR(CDCl₃): δ 35.6 (s) ppm. ¹H NMR (CDCl₃): δ 7.80–7.20 (m, 30 H), 6.22 (dd, ³J_{HH} = 16.0 Hz, ³J_{PH} = 2.1 Hz, 1 H), 4.87 (dd, ³J_{HH} = 16.0 Hz, ⁴J_{PH} = 1.8 Hz, 1 H), 4.01 (br s, 2 H), 3.83 (br s, 2 H), 3.40 (s, 5 H), 0.85 (s, 9 H) ppm.

(3c) Analysis: Found (calc) for C₆₂H₅₀O₃P₂FeRu·CH₂Cl₂: C, 65.83 (65.98); H, 4.92 (4.57). IR (cm⁻¹): 1928 (C(O), 1516 (C=C), 1496 (OCO)_{asym}, 1396 (OCO)_{sym}. ³¹P{¹H} NMR(CDCl₃): δ 35.7 (s) ppm. ¹H NMR (CDCl₃): δ 7.80–7.00 (m, 40 H), 5.30 (s, 1 H), 3.93 (br s, 2 H), 3.76 (br s, 2 H), 3.40 (s, 5 H) ppm.

(3d) Analysis: Found (calc) for C₅₂H₄₄O₅P₂FeRu·2CH₂Cl₂: C, 57.23 (57.01); H, 4.39 (4.22). IR (cm⁻¹): 1924 (C(O), 1699 (C=O), 1556 (C=C), 1496 (OCO)_{asym}, 1396 (OCO)_{sym}. ³¹P{¹H} NMR(CDCl₃): δ 35.7 (s) ppm. ¹H NMR (CDCl₃): δ 9.56 (d, ³J_{HH} = 14.4 Hz, 1 H), 7.80–7.00 (m, 30 H), 5.26 (d, ³J_{HH} = 14.4 Hz, 1 H), 3.93 (br s, 2 H), 3.76 (br s, 2 H), 3.40 (s, 5 H), 3.37 (s, 3 H) ppm.

(20) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttey, M. F. *Inorg. Synth.* **1974**, *15*, 48.

(**3e**) Analysis: Found (calc) for $C_{54}H_{46}O_7P_2FeRu$: C, 63.72 (63.25); H, 4.39 (4.22). IR (cm^{-1}): 930 (C≡O), 1713 (C=O), 1561 (C=C), 1503 (OCO)_{asym}, 1395 (OCO)_{sym}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 33.3 (s) ppm. 1H NMR ($CDCl_3$): δ 7.80–7.00 (m, 30 H), 4.32 (s, 1 H), 3.93 (br s, 2 H), 3.76 (br s, 2 H), 3.51 (s, 3 H), 3.40 (s, 5 H), 3.36 (s, 3 H) ppm.

[$Ru(O_2C(C_5H_4)Fe(C_5H_5))(CR'=CRH)(CO)_2(PPh_3)_2$] (**R** = **R'** = **H** (**4a**); **R** = **CMe₃**, **R'** = **H** (**4b**)). CO was bubbled into a solution of [$Ru(O_2C(C_5H_4)Fe(C_5H_5))(CR'=CRH)(CO)(PPh_3)_2$] complexes in dichloromethane at room temperature, and the progress of the reaction was monitored by IR spectroscopy. The reaction was complete in 4 h. Yellow complexes **4a** and **4b** were precipitated with hexane, filtered off, and dried. Yields were 70% for both complexes.

(**4a**) Analysis: Found (calc) For $C_{51}H_{42}O_4P_2FeRu$: C, 65.06 (65.32); H, 4.45 (4.51). IR (cm^{-1}): 1944, 1917 (C≡O), 1577 (C=C), 1618, 1396 (OCO). $^{31}P\{^1H\}$ ($CDCl_3$): δ 32.1 (s) ppm. 1H NMR ($CDCl_3$): δ 7.8–7.2 (m, 31 H), 5.68 (d, $^3J_{HH}$ = 8.0 Hz, 1 H), 4.80 (d, $^3J_{HH}$ = 15 Hz, 1 H), 3.94 (br s, 2 H), 3.75 (br s, 2 H), 3.37 (s, 5 H) ppm.

(**4b**) Analysis: Found (calc) For $C_{55}H_{50}O_4P_2FeRu$: C, 66.00 (66.47); H, 5.03 (5.07). IR (cm^{-1}): 1945, 1912 (C≡O), 1565 (C=C), 1631, 1394 (OCO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.7 (s) ppm. 1H NMR ($CDCl_3$): δ 7.66–7.13 (m, 30 H), 6.36 (d, $^3J_{HH}$ = 15.0 Hz, 1 H), 4.96 (d, $^3J_{HH}$ = 15.0 Hz, 1 H), 3.94 (br s, 2 H), 3.75 (br s, 2 H), 3.73 (s, 5 H), 0.56 (s, 9 H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 244.1 (t, $^2J_{CP}$ = 9.9 Hz, CO), 204.4 (t, $^2J_{CP}$ = 14.4 Hz, CO), 196.2 (t, $^2J_{CP}$ = 10.3 Hz, CH=), 180.1 (C=O), 139.6 (t, $^2J_{CP}$ = 2.11 Hz, =CH^tBu), 134.9–126.7 (Ph), 78.4, 69.1, 68.7 (C_5H_4), 68.12 (C_5H_5), 32 (CMe_3), 29.0 (CMe_3) ppm.

Catalytic Addition of Phenylacetylene to Ferrocene-carboxylic Acid. The catalytic reaction was carried out under an atmosphere of nitrogen. Phenylacetylene (0.05 mL, 44 mmol), ferrocenecarboxylic acid (0.1 g, 44 mmol), a ruthenium catalyst (0.005 equiv of [$Ru_2(HCO_2)_2(CO)_4(PPh_3)_2$] or [$Ru(O_2C(C_5H_4)Fe(C_5H_5))Cl(CO)(PPh_3)_2$]), and 15 mL of toluene were placed in a 50 mL round-bottomed flask fitted with a condenser coupled to a nitrogen line, and this mixture was stirred for 20 h at 111 °C. The progress of the reaction was

monitored by 1H NMR spectroscopy. After 20 h the mixture was cooled to room temperature and the solvent was evaporated. The ratio of isomers was determined by 1H NMR in $CDCl_3$ of the crude of reaction. The resulting orange oil contained the Z isomer ($Ru_2(HCO_2)_2(CO)_4(PPh_3)_2$ catalyst) or a mixture of Z (99%) + GEM (1%) isomers of the phenyl-ethyleneferrocenecarboxylic ester **5**.

(**5**) E + GEM isomers: IR (cm^{-1}): 1727 (C=O), 1658 (C=C). 1H NMR ($CDCl_3$): Z δ 7.30 (m, 5 H), 5.70 (d, $^3J_{HH}$ = 7.3 Hz, 1 H), 4.87 (m, 2 H), 4.45 (m, 2 H), 4.19 (d, $^3J_{HH}$ = 7.3 Hz, 1 H), 4.17 (s, 5 H) ppm; GEM: δ 7.30 (m, 5 H), 5.46 (d, $^2J_{HH}$ = 1.5 Hz, 1 H), 5.04 (d, $^2J_{HH}$ = 1.5 Hz, 1 H), 4.85 (m, 2 H), 4.41 (m, 2 H), 4.17 (s, 5 H) ppm.

X-ray Diffraction Study of 3a. **3a:** $C_{50}H_{42}O_3P_2RuFe \cdot 0.7CH_2Cl_2$, M_r = 969.14, monoclinic, space group $P2_1/n$ (No. 14), a = 10.069(1) Å, b = 21.610(2) Å, c = 20.822(2) Å, β = 99.34(1)°, V = 4470.6 Å³, Z = 4, D_c = 1.440 g cm⁻³, μ = 8.60 cm⁻¹; measurements, Enraf-Nonius CAD4; radiation, graphite monochromated Mo K α (λ = 0.710 69 Å), T = 293 K, data collection range $2^\circ < 2\theta < 50^\circ$, ω - 2θ scan, absorption correction based on ψ -scan measurements; solution, SHELXS-86 program; refinement on F^2 for all reflections, SHELXL-93 program; 7851 unique reflections, 4010 observed [$I > 2\sigma(I)$]; number of variables 460, hydrogen atoms in calculated positions with isotropic temperature factors fixed at 1.2 times U_{eq} of the corresponding carbon atoms. $R(F)$ = 0.050, $R_w(F^2)$ = 0.108 for the observed reflections.

Acknowledgment. We thank the Dirección General de Investigación Científica y Técnica for the financial support (Projects PB92-0628 and PB96-1146).

Supporting Information Available: Crystallographic data including complete tables of atomic coordinates, bond lengths and bond angles, and equivalent isotropic parameters for **3a** (11 pages). Ordering information is given on any current masthead page.

OM9804069