

Syntheses, Properties, and X-ray Crystal Structures of Iron and Ruthenium Compounds with the η^5 -C₅Me₄CF₃ Ligand. Compounds of the Type [(η^5 -C₅Me₄CF₃)M(μ -CO)(CO)]₂ (M = Fe, Ru)

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(Trifluoromethyl)tetramethylcyclopentadiene, HC₅Me₄CF₃ (Cp[†]H), reacts with Ru₃(CO)₁₂ in refluxing *n*-decane to produce [(η^5 -C₅Me₄CF₃)Ru(μ -CO)(CO)]₂ (**1**). In chlorinated hydrocarbon solutions, **1** reacts with the solvents in the presence of visible light to produce [(η^5 -C₅Me₄CF₃)Ru(CO)₂(Cl)] (**3a**). Compound **1** reacts with iodine in refluxing CH₂Cl₂ to produce [(η^5 -C₅Me₄CF₃)Ru(CO)₂(I)] (**3b**). The X-ray crystal structure of compound **3b** is presented. Compound **3b** reacts with triphenylphosphine in refluxing ethanol to produce [(η^5 -C₅Me₄CF₃)Ru(CO)(PPh₃)(I)] (**4**). The HC₅Me₄CF₃ ligand reacts with Fe(CO)₅ in refluxing heptane to produce [(η^4 -HC₅Me₄CF₃)Fe(CO)₃] (**5**). Compound **5** represents a new mode of coordination (η^4) for HC₅Me₄CF₃. The spectroscopic properties of compound **1** and its previously reported iron analog, [(η^5 -C₅Me₄CF₃)Fe(μ -CO)(CO)]₂ (**2**), are compared with those of their η^5 -C₅H₅ and η^5 -C₅Me₅ "parent" analogs of the type [(η^5 -C₅R₅)M(μ -CO)(CO)]₂ (M = Fe, Ru). Compounds **1** and **2** were characterized by single-crystal X-ray crystallography and found to be in the *trans* configuration with respect to the η^5 -C₅Me₄CF₃ rings. Overall, the spectroscopic and X-ray structural data of **1** and **2** support the previous conclusions that the η^5 -C₅Me₄CF₃ ligand is electronically equivalent to η^5 -C₅H₅ and sterically equivalent to η^5 -C₅Me₅. Compounds **1** and **3b** represent important synthons for subsequent ruthenium chemistry with the η^5 -C₅Me₄CF₃ ligand.

Introduction

Cyclopentadienyl (η^5 -C₅H₅) and pentamethylcyclopentadienyl (η^5 -C₅Me₅) ligands represent two of the most widely used ancillary ligands for transition-metal organometallic compounds. The substitution of η^5 -C₅Me₅ for η^5 -C₅H₅ in organometallic compounds usually results in major changes in both the physical and chemical properties of their respective derivatives.¹ However, this substitution simultaneously alters both the steric and electronic environment around the transition-metal center. Unfortunately, the dissection of steric and electronic effects of the η^5 -C₅Me₅ ligand has not been accomplished. Alternatively, the recently

discovered (trifluoromethyl)tetramethylcyclopentadienyl ligand^{2ab} (η^5 -C₅Me₄CF₃) exhibits electronic properties equivalent to those of η^5 -C₅H₅ but retains the steric equivalence of η^5 -C₅Me₅.² Besides being convenient starting materials, compounds of the type [(η^5 -C₅R₅)M(μ -CO)(CO)]₂ (where M = Fe,^{3ab} Ru,^{3c,d} R = H,^{3a,c} Me^{3b,d}) and their derivatives represent some of the more widely studied iron and ruthenium organometallic systems. Therefore, entry of the η^5 -C₅Me₄CF₃ ligand into organometallic iron and ruthenium chemistry is realized by the syntheses of [(η^5 -C₅Me₄CF₃)M(μ -CO)(CO)]₂ (M = Fe,^{2b,c} Ru).

Herein we report the syntheses, properties, and X-ray crystal structures of [(η^5 -C₅Me₄CF₃)M(μ -CO)(CO)]₂ (M = Ru (**1**), Fe^{2b,c} (**2**)) and compare these new compounds with their parent iron and ruthenium compounds. In

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Table 1. Infrared Carbonyl Stretching Frequencies of $[(\eta^5\text{-Cp}^*)\text{M}(\mu\text{-CO})(\text{CO})_2]$ ($\eta^5\text{-Cp}^* = \eta^5\text{-C}_5\text{H}_5$, $\eta^5\text{-C}_5\text{Me}_4\text{CF}_3$, $\eta^5\text{-C}_5\text{Me}_5$; $\text{M} = \text{Fe}$, Ru) Complexes^a

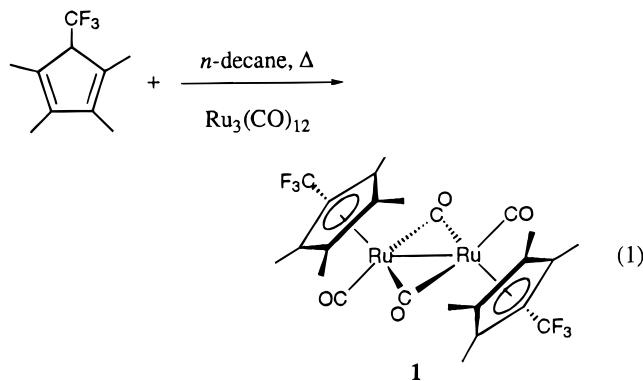
compd	$\nu(\text{CO})$, cm^{-1}	ref
<i>trans</i> - $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})(\text{CO})_2]$	1968, 1768 ^b	7a,b
$[(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{Ru}(\mu\text{-CO})(\text{CO})_2]$ (1)	1958, 1776	this work
<i>trans</i> - $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\mu\text{-CO})(\text{CO})_2]$	1925, 1744	8
<i>trans</i> - $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-CO})(\text{CO})_2]$	1955, 1773	2c
$[(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{Fe}(\mu\text{-CO})(\text{CO})_2]$ (2)	1952, 1776	2c
<i>trans</i> - $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\mu\text{-CO})(\text{CO})_2]$	1922, 1747	2c

^a CH_2Cl_2 solvent. ^b CHCl_3 solvent.

addition, we report the syntheses of half-sandwich derivatives $[(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{Ru}(\text{CO})_2(\text{I})]$ (**3b**), $[(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{Ru}(\text{CO})(\text{PPh}_3)(\text{I})]$ (**4**), and $[(\eta^4\text{-HC}_5\text{Me}_4\text{CF}_3)\text{Fe}(\text{CO})_3]$ (**5**). The crystal structure of **3b** is also presented. Compound **5** represents a new mode of coordination for $\text{HC}_5\text{Me}_4\text{CF}_3$.

Results and Discussion

Preparation and Properties of $[(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{M}(\mu\text{-CO})(\text{CO})_2]$ ($\text{M} = \text{Fe}$, Ru). Treatment of $\text{Ru}_3(\text{CO})_{12}$ with 3 equiv of $\text{HC}_5\text{Me}_4\text{CF}_3$ ^{2a} in refluxing *n*-decane results in the formation of the ruthenium carbonyl dimer $[(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{Ru}(\mu\text{-CO})(\text{CO})_2]$ (**1**) in 84% yield (eq 1). Compound **1** is readily soluble in halocarbon



solvents, but such solutions must be protected from visible light since a secondary reaction occurs (*vide infra*). The ^1H NMR spectrum of **1** in benzene- d_6 shows a quartet at 1.84 ppm ($^5J_{\text{HF}} = 0.97$ Hz) for the methyl hydrogens in the 2,5-position next to the CF_3 group and a singlet at 1.32 ppm for the methyl hydrogens in the 3,4-position (see Experimental Section for numbering scheme). The most notable features of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in benzene- d_6 include the single "averaged" resonance (*vide infra*) for the CO ligands at 224.46 ppm and the quartet at 125.69 ppm ($^1J_{\text{CF}} = 271.1$ Hz) for the CF_3 carbon. The ^1H NMR data for **1** compares with those for the iron analog $[(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{Fe}(\mu\text{-CO})(\text{CO})_2]$ (**2**),^{2c} which shows a quartet at 1.84 ppm ($^5J_{\text{HF}} = 1.2$ Hz) and a singlet at 1.59 ppm (in chloroform-*d*). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** in chloroform-*d* shows a similar broad, averaged resonance for the CO ligands at 240.8 ppm, while the resonance for the CF_3 group appears as a quartet at 124.9 ppm ($^1J_{\text{CF}} = 272$ Hz). The IR spectrum of **1** in dichloromethane shows $\nu(\text{CO})$ bands at 1958 and 1776 cm^{-1} for the terminal and bridging carbonyls, respectively, while in Nujol the $\nu(\text{CO})$ bands appear at 1955 and 1767 cm^{-1} with ^{13}CO satellites at 1918 and 1738 cm^{-1} . The IR data for both **1** and **2** are summarized in Table 1 along with those of the $\eta^5\text{-C}_5\text{H}_5$ and $\eta^5\text{-C}_5\text{Me}_5$ parent analogs.

Attempts to improve the yield of **1** using norbornene as a hydrogen acceptor^{4,5} in the reaction of $\text{HC}_5\text{Me}_4\text{CF}_3$ with $\text{Ru}_3(\text{CO})_{12}$ were unsuccessful. In contrast, our group⁵ and Paquette and co-workers⁴ have successfully used this approach for the preparation of other Fe and Ru dicarbonyl cyclopentadienyl complexes. In this case, reaction of $\text{HC}_5\text{Me}_4\text{CF}_3$ and $\text{Ru}_3(\text{CO})_{12}$ resulted in the formation of reasonable amounts of the triply bridging alkene adduct $[(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-C}_7\text{H}_8)]$ (**A**), which was characterized by ^1H , ^{13}C , and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy and by X-ray crystallography. This compound was also recently reported by Johnson, Braga, and co-workers;⁶ however we include the complete characterization data for this compound in the Experimental Section.

Analysis of the data in Table 1 shows that the $\nu(\text{CO})$ stretching frequencies for **1** and **2** are similar to those of their $\eta^5\text{-C}_5\text{H}_5$ analogs. In contrast, the IR stretching frequencies of the ruthenium and iron $\eta^5\text{-C}_5\text{Me}_5$ analogs are significantly different (>30 cm^{-1}) compared to those of **1** and **2**. Other physical measurements, including X-ray photoelectron spectroscopy (XPS)^{2b} and electrochemical^{2c} data, reported for compound **2** reflect the same trends. These comparisons indicate that the $\eta^5\text{-C}_5\text{H}_5$ and $\eta^5\text{-C}_5\text{Me}_4\text{CF}_3$ ligands are electronically similar.

The IR spectral data for **1** and **2** (Table 1) show that both compounds exist as the *trans* isomers, containing bridging carbonyl ligands in solution. The sterically similar compounds $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\mu\text{-CO})(\text{CO})_2]$,⁹ $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\mu\text{-CO})(\text{CO})_2]$,¹⁰ and $(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{Ru}(\mu\text{-CO})(\text{CO})_2$ ¹¹ all exist in the thermodynamically preferred *trans* configurations in the solid and solution states, and the last species does not isomerize to the *cis* configuration in solution, presumably due to unfavorable steric interactions.^{3c,11} Moreover, compounds **1** and **2** crystallize as the *trans* isomers (*vide infra*). This contrasts with the behavior of $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\mu\text{-CO})(\text{CO})_2]$ ($\text{M} = \text{Fe}$, Ru), which have been shown to exist as mixtures of all four possible isomers in solution: *cis* and *trans*, with bridging and nonbridging CO ligands.^{3a,c,4b} Only two $\nu(\text{CO})$ bands are observed for both **1** and **2**, whereas the $\eta^5\text{-C}_5\text{H}_5$ analogs have complex IR spectra in the carbonyl regions with multiple bands. However, the room-temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of both **1** and **2** each show only one averaged CO resonance at 224 and 240 ppm, respectively. The $^{13}\text{C}\{^1\text{H}\}$ NMR data of **1** and **2** are similar to those of the reported iron and ruthenium $\eta^5\text{-C}_5\text{H}_5$ analogs.¹² The ruthenium compound $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\mu\text{-}^{13}\text{CO})(^{13}\text{CO})_2]$ showed one average CO resonance at ~ 225 ppm^{12a} (in carbon disulfide) while the iron analog showed one CO resonance at ~ 240 ppm (in

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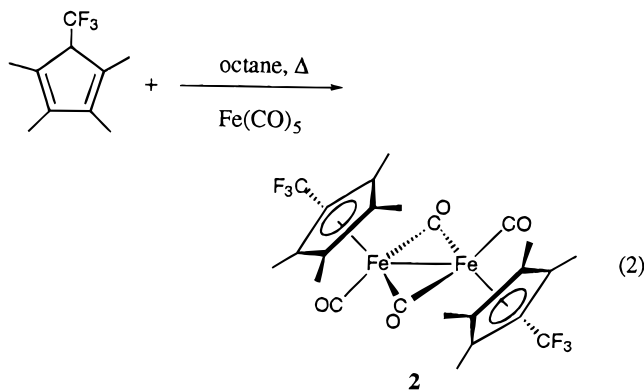
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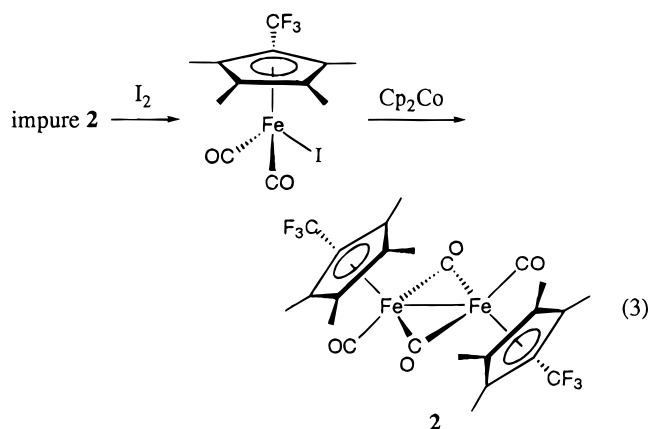
dichloromethane-*d*₂).^{12c} A similar phenomenon was also observed for [PCpRu(μ -CO)(CO)]₂,⁵ which also showed one averaged CO resonance at 224.5 ppm. Therefore, the ¹³C NMR data suggest that compounds **1** and **2** are dynamic in solution and undergo a bridged-to-non-bridged equilibrium¹² that is rapid on the NMR time scale.

Compound **1** is a red crystalline compound that is air-stable indefinitely in the solid state. However, solutions of **1** are photosensitive, even in room lighting, and must be handled accordingly. If a solution of **1** in chloroform is exposed to room lighting, it will completely convert to the dicarbonyl chloride compound [(η^5 -C₅Me₄CF₃)Ru(CO)₂(Cl)] (**3a**) in less than 24 h. The conversion of **1** into **3a** can be monitored by IR spectroscopy (dichloromethane), as the ν (CO) bands for **1** disappear and new bands for **3a** appear at 2063 and 2014 cm⁻¹, which indicates the presence of only terminal carbonyl ligands. This reaction is slower in dichloromethane than in chloroform and dramatically slower if the halocarbon solutions are protected from light. Solutions of **1** in benzene-*d*₆ also show minimal decomposition if unprotected from light, but the decomposition products remain unidentified. The ruthenium peralkylated cyclopentadienyl carbonyl dimer [(η^5 -C₅Me₄Et)Ru(μ -CO)(CO)]₂ displays the exact same behavior as observed for **1**, gradually reacting in chlorocarbons to form [(η^5 -C₅Me₄Et)Ru(CO)₂(Cl)].¹¹ Similar to **1**, the reactions of [(η^5 -C₅Me₄Et)Ru(μ -CO)(CO)]₂ in chloroform were accelerated by visible light and were slower in dichloromethane than in chloroform solutions.

The synthesis of [(η^5 -C₅Me₄CF₃)Fe(μ -CO)(CO)]₂ (**2**) has been published;^{2b,c} however, it is important to highlight some subtle differences between the two procedures. Initially it was found^{2b} that treatment of Fe(CO)₅ with 3 equiv of HC₅Me₄CF₃ in refluxing octane produced **2** in 34% yield (eq 2). Unfortunately, this



procedure produced a trace impurity that was not easily removed. During a subsequent study^{2c} the trace impurity was found to be problematic and electrochemically active. The "impurity" was identified as [(η^5 -C₅Me₅)(CO)Fe(μ -CO)₂Fe(CO)(η^5 -C₅Me₄CF₃)] by mass spectrometry. Pure samples of **2** were then prepared by oxidizing "impure" **2** with I₂ to make [(η^5 -C₅Me₄CF₃)Fe(CO)₂(I)] followed by purification and reduction to **2** with cobaltocene (eq 3). Unlike the ruthenium analog **1**, com-



ound **2** is stable in halocarbon solutions and does not exhibit any sensitivity to visible light. It is noteworthy that compound **2** was previously prepared using a rather circuitous method as detailed in reference 13.

X-ray Crystal Structures of 1 and 2. The molecular structures of **1** and **2** are shown in Figures 1 and 2, respectively. Selected bond distances and angles are listed in Tables 2 and 3, respectively. Crystallographic data and details of structure determination and refinement are given in Table 8. A comparative listing of bond distances for **1**, **2**, and their η^5 -C₅H₅ and η^5 -C₅Me₅ analogs is given in Table 4. The analyses of both **1** and **2** reveal a distorted octahedral geometry at each metal with two mutually trans η^5 -C₅Me₄CF₃ ligands and two terminal and two symmetrically bridging carbonyl ligands. There is a crystallographic center of symmetry located midway between the metal atoms. The CF₃ groups are oriented *anti* with respect to one another in accordance with the center of symmetry. Compounds **1** and **2** are isostructural and isomorphous.

As shown in Table 4, the Ru–Ru bond distance in **1** of 2.7613(4) Å and the Ru–Cp'(centroid) distance of 1.924 Å are the longest distances in the ruthenium series, although they are closer to those of the η^5 -C₅Me₅ analog than to those of the η^5 -C₅H₅ analog. The Ru–Ru distance of 2.735(2) Å in the η^5 -C₅H₅ compound is the shortest in the ruthenium series. Also for compound **1**, the terminal and bridging CO distances of 1.865(3) and 2.044(3) Å are the same within experimental error as those of the η^5 -C₅Me₅ compound: 1.866(3) and 2.041(3) Å, respectively. The Fe–Fe bond distance in **2** of 2.563(1) Å and the Fe–Cp'(centroid) distance of 1.766 Å are the longest in the iron series, although they are nearly the same within experimental error as those of the η^5 -C₅Me₅ analog: 2.560(1) and 1.764 Å, respectively. In the structure of **2**, the terminal CO has a slightly shortened Fe–C bond distance of 1.733(5) Å compared to both the η^5 -C₅H₅ and the η^5 -C₅Me₅ analogs, which have distances of 1.748(6) and 1.753 Å, respectively. This shortening of the Fe–C bond distance is likely caused by the CF₃ group on the η^5 -C₅Me₄CF₃ ring which is in close proximity to the terminal CO ligand. However, it is noted that the overall electron-withdrawing effect of the CF₃ group in **1** and **2** is approximately balanced by the electron-donating effect of the four methyl groups on the C₅ ring,

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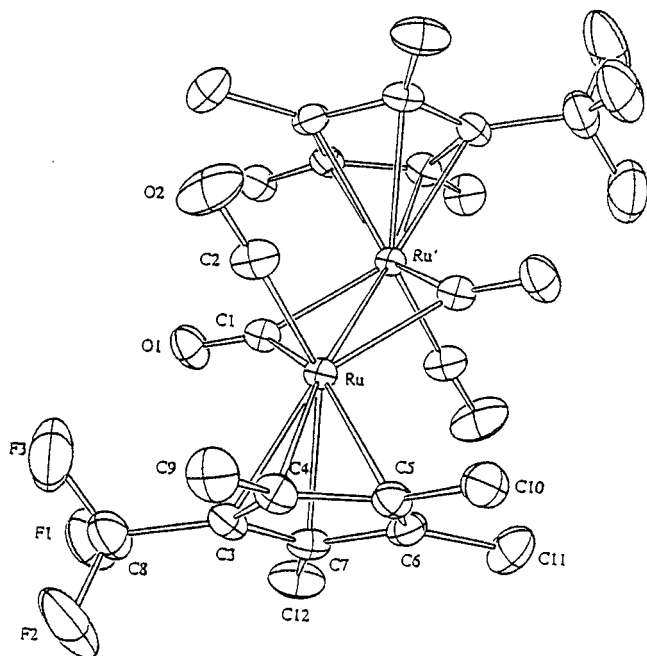


Figure 1. Structural drawing of $[(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{Ru}(\mu\text{-CO})(\text{CO})_2]$ (**1**) showing the atom-numbering scheme (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

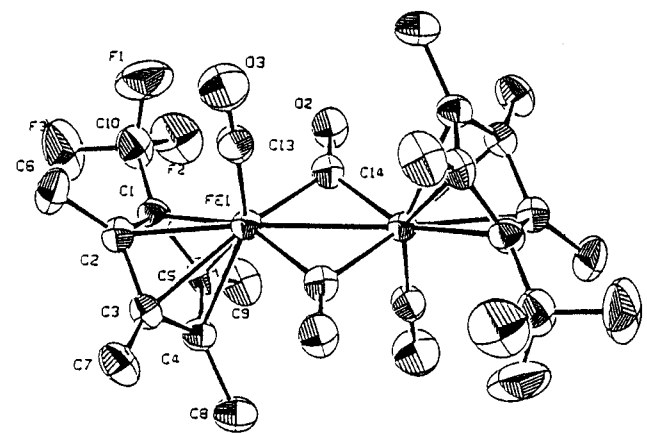


Figure 2. Structural drawing of $[(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{Fe}(\mu\text{-CO})(\text{CO})_2]$ (**2**) showing the atom-numbering scheme (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $[(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{Ru}(\mu\text{-CO})(\text{CO})_2]$ (1**)**

Bond Distances (Å)			
Ru–Ru'	2.7613(4)	Ru–C(5)	2.297(3)
Ru–C(1)	2.045(3)	Ru–C(6)	2.311(3)
Ru–C(1')	2.042(3)	Ru–C(7)	2.308(3)
Ru–C(2)	1.865(3)	C(3)–C(8)	1.488(4)
C(1)–O(1)	1.170(4)	F(1)–C(8)	1.365(5)
C(2)–O(2)	1.134(4)	F(2)–C(8)	1.282(5)
Ru–C(3)	2.230(2)	F(3)–C(8)	1.327(7)
Ru–C(4)	2.238(2)		
Bond Angles (deg)			
C(1)–Ru–C(1)'	95.0(1)	Ru'–Ru–C(1)	47.44(8)
C(1)–Ru–C(2)	92.1(1)	Ru'–Ru–C(1)'	47.54(8)
C(1)–Ru–C(2)	93.1(1)	Ru–C(1)–O(1)	137.2(2)
Ru'–Ru–C(2)	93.90(9)	Ru–C(2)–O(2)	176.5(3)
Ru'–C(1)–Ru	85.0(1)		

because the CO stretching frequencies of **1** (1958, 1776 cm^{-1}) and **2** (1952, 1776 cm^{-1}) are similar to those of the C_5H_5 complexes (*trans*- $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})(\text{CO})_2]$ (1968, 1768 cm^{-1}) and *trans*- $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-CO})(\text{CO})_2]$ (1955, 1773 cm^{-1})).

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $[(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{Fe}(\mu\text{-CO})(\text{CO})_2]$ (2**)**

Bond Distances (Å)			
Fe(1)–Fe(1)'	2.563(1)	Fe–C(3)	2.170(4)
Fe–C(14)	1.925(4)	Fe–C(4)	2.179(4)
Fe–C(14)'	1.911(4)	Fe–C(5)	2.167(4)
Fe–C(13)	1.733(5)	C(1)–C(10)	1.481(6)
C(14)–O(2)	1.186(5)	F(1)–C(10)	1.348(6)
C(13)–O(3)	1.164(5)	F(2)–C(10)	1.328(6)
Fe(1)–C(1)	2.085(4)	F(3)–C(10)	1.331(5)
Fe(1)–C(2)	2.119(4)		
Bond Angles (deg)			
C(14)–Fe(1)–C(14)'	96.2(2)	Fe(1)–Fe(1)–C(14)	47.8(1)
C(14)–Fe(1)–C(13)	93.0(2)	Fe(1)–Fe(1)–C(14)'	48.3(1)
C(14)–Fe(1)–C(13)	94.4(2)	Fe(1)–C(14)–O(2)	137.8(3)
Fe(1)–Fe(1)–C(13)	95.5(1)	Fe(1)–C(13)–O(3)	177.0(4)
Fe(1)–C(14)–Fe(1)	83.8(2)		

One notable feature common to both structures **1** and **2** is that the carbon atoms in the C_5 rings bound to the CF_3 groups (metal– $\text{C}-\text{CF}_3$) are closer to the metal atoms than to the ring carbons bound to the CH_3 groups (metal– $\text{C}-\text{CH}_3$). The Ru– $\text{C}(\text{CF}_3)$ bond distance of 2.230(2) Å is shorter than the four Ru– $\text{C}(\text{CH}_3)$ carbon distances, which range from 2.238(2) to 2.311(3) Å. The Fe– $\text{C}(\text{CF}_3)$ bond distance of 2.085(4) Å is also shorter than the remaining Fe– $\text{C}(\text{CH}_3)$ distances of 2.119(4)–2.167(4) Å. In each case, the largest observed distance differential between the metal– $\text{C}(\text{CF}_3)$ carbon distance and the longest metal– $\text{C}(\text{CH}_3)$ carbon distance is 0.08 Å. This shortening is attributed to the electron-withdrawing effect of the CF_3 group. A similar effect is also observed in the recently reported^{2c} crystal structure of $[(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$, where the Fe– $\text{C}(\text{CF}_3)$ carbon distance of 2.007(6) Å is shorter than the remaining Fe– $\text{C}(\text{CH}_3)$ distances, which range from 2.041(7) to 2.061(8) Å. Overall, however, the X-ray crystallographic studies of **1** and **2** suggest that the structural effects of the $\eta^5\text{-C}_5\text{Me}_4\text{CF}_3$ and $\eta^5\text{-C}_5\text{Me}_5$ ligands are very similar.

Because of the similarity of the $\eta^5\text{-C}_5\text{Me}_4\text{CF}_3$ and $\eta^5\text{-C}_5\text{Me}_5$ ligands, this study confirms previous arguments that the *trans* geometry of $[(\eta^5\text{-C}_5\text{R}_5)\text{M}(\mu\text{-CO})(\text{CO})_2]$ complexes^{3b,c,11} are favored over the *cis* geometry for steric reasons. However, it is interesting to note that flash photolysis studies of *trans*- $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\mu\text{-CO})(\text{CO})_2]$ produced equal amounts of the *cis* and *trans* isomers.¹⁶ The energy of activation for the isomerization of the *cis* to the *trans* isomer was measured to be 68 ± 5 kcal mol^{-1} , as compared to the value for *cis*- $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-CO})(\text{CO})_2]$ of 54 ± 8 kcal mol^{-1} . The authors state that "it is not yet clear whether the higher activation barrier {for $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\mu\text{-CO})(\text{CO})_2]$ is due to steric or electronic factors".¹⁶ It is possible that future studies of **2** will help resolve some of these questions. In addition, the reported complex $[(\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{NMe}_2))\text{Fe}(\mu\text{-CO})(\text{CO})_2]$ was shown by IR spectroscopy to occur as the *trans* isomer and smaller amounts of the *cis* isomer in polar solvents in spite of the bulky substituted cyclopentadienyl ligand.¹⁷ Although steric factors account for the thermodynamic predominance of the *trans* isomer of substituted $\eta^5\text{-C}_5\text{R}_5$ iron dicarbonyl derivatives, steric and electronic factors may both be important in determining the kinetics of isomerization.

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Table 4. Comparison of M–M, M–Cp', and M–CO Bond Distances (Å) in *trans*-[(η^5 -Cp')M(μ -CO)(CO)]₂ (η^5 -Cp' = η^5 -C₅H₅, η^5 -C₅Me₄CF₃, η^5 -C₅Me₅; M = Fe, Ru) Complexes

compd	M–M	M–Cp' ^a	M–CO terminal	M–CO bridging ^b	ref
[(η^5 -C ₅ H ₅)Ru(μ -CO)(CO)] ₂	2.735(2) ^c	1.915	1.855(14)	1.986(13)	14
[(η^5 -C ₅ Me ₄ CF ₃)Ru(μ -CO)(CO)] ₂ (1)	2.7613(4)	1.924	1.865(3)	2.044(3)	<i>d</i>
[(η^5 -C ₅ Me ₅)Ru(μ -CO)(CO)] ₂	2.752(2)	1.917	1.866(3)	2.041(3)	9
[(η^5 -C ₅ H ₅)Fe(μ -CO)(CO)] ₂	2.534(2)	1.754	1.748(6)	1.914(5)	15a
[(η^5 -C ₅ Me ₄ CF ₃)Fe(μ -CO)(CO)] ₂ (2)	2.563(1)	1.766	1.733(5)	1.918(4)	<i>d</i>
[(η^5 -C ₅ Me ₅)Fe(μ -CO)(CO)] ₂	2.560(1)	1.764	1.753(3)	1.929(3)	10

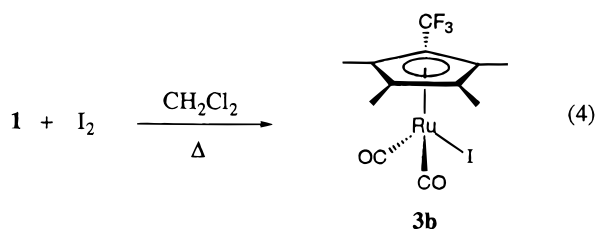
^a M–Cp' = metal–centroid of cyclopentadienyl ring distance. ^b Average distances. ^c Standard deviations are given in parentheses. ^d This work.

Table 5. Infrared Carbonyl Stretching Frequencies of [(η^5 -Cp')M(CO)₂(I)] (η^5 -Cp' = η^5 -C₅H₅, η^5 -C₅Me₄CF₃, η^5 -C₅Me₅; M = Fe, Ru) Complexes^a

compd	ν (CO), cm ⁻¹	ref
[(η^5 -C ₅ H ₅)Ru(CO) ₂ (I)]	2048, 1997	18
[(η^5 -C ₅ Me ₄ CF ₃)Ru(CO) ₂ (I)] (3b)	2060, 1998	this work
[(η^5 -C ₅ Me ₅)Ru(CO) ₂ (I)]	2030, 1981	19

^a CH₂Cl₂ solvent.

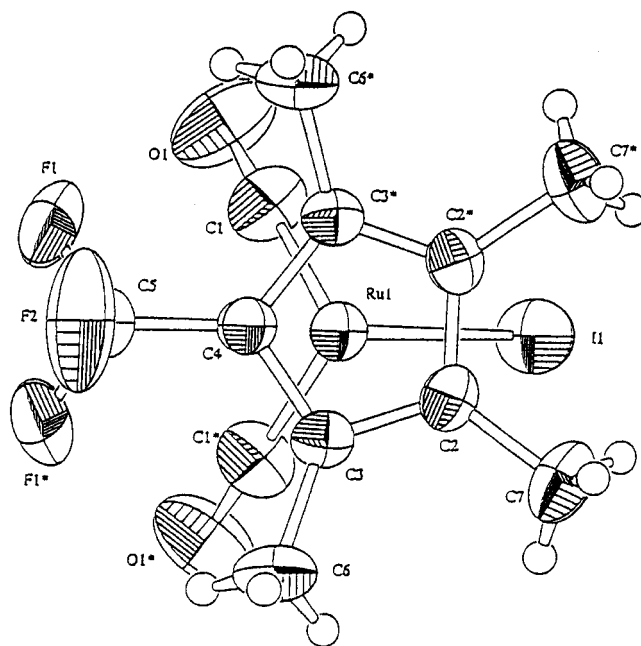
Preparation of [(η^5 -C₅Me₄CF₃)Ru(CO)₂(I)] (3b**).** Treatment of **1** with I₂ in refluxing dichloromethane (in the absence of light) leads to the formation of the dicarbonyliodoruthenium complex **3b** in 89% yield (eq 4). The ¹H NMR spectrum of **3b** shows a quartet at 2.23



ppm (⁵J_{HF} = 0.95 Hz) for the 2,5-methyl hydrogens and a singlet at 2.14 ppm for the 3,4-methyl hydrogens. The notable features of the ¹³C{¹H} NMR spectrum of **3b** in chloroform-*d* include the resonance at 195.43 ppm for the carbonyl ligands and a quartet for the unique CF₃ carbon at 124.21 ppm (¹J_{CF} = 271.5 Hz). The IR spectral data for **3b** are listed in Table 5 along with those of the η^5 -C₅H₅ and η^5 -C₅Me₅ analogs for comparison.

Analysis of the data in Table 5 shows that the ν (CO) stretching frequencies for **3b** are similar to those of the η^5 -C₅H₅ analog. Compound **3b** was also characterized by X-ray crystallography to extend the structural database for the η^5 -C₅Me₄CF₃ ligand.

A view of the molecular structure of **3b** is shown in Figure 3. Selected bond distances and angles are given in Table 6. The analysis reveals a distorted octahedral geometry about ruthenium with one η^5 -C₅Me₄CF₃, two *cis*-CO ligands, and one iodide completing the ruthenium coordination sphere. The average Ru–C(carbonyl) bond distance is 1.881(6) Å, and the Ru–I bond distance is 2.6989(8) Å. The distance from the ruthenium to the centroid of the η^5 -C₅Me₄CF₃ ligand is 1.878 Å, which is shorter than the Ru– η^5 -C₅Me₄CF₃ centroid distance in **1** (1.917 Å). Similar to what was observed in the structures of **1** and **2**, the metal–C(CF₃) carbon distance in **3b** is shorter than the remaining metal–C(CH₃) carbon distances. The Ru–C(CF₃) bond distance of 2.152(6) Å is significantly shorter than the Ru–C(CH₃) and Ru–C(CH₃) bond distances of 2.249(4) and 2.264(4) Å, respectively. In comparison, the largest metal to

**Figure 3.** Structural drawing of [(η^5 -C₅Me₄CF₃)Ru(CO)₂(I)] (**3b**) showing the atom-numbering scheme (50% probability ellipsoids).**Table 6.** Selected Bond Distances (Å) and Bond Angles (deg) for [(η^5 -C₅Me₄CF₃)Ru(CO)₂(I)] (**3b**)

Bond Distances (Å)			
Ru(1)–I(1)	2.6989(8)	C(3)–C(4)	1.439(6)
Ru(1)–C(1)	1.881(6)	C(2)–C(3)	1.409(6)
Ru(1)–C(2)	2.264(4)	C(2)–C(2)*	1.442(9)
Ru(1)–C(3)	2.249(4)	C(4)–C(5)	1.496(10)
Ru(1)–C(4)	2.152(6)	F(1)–C(5)	1.312(5)
		F(2)–C(5)	1.301(8)
Bond Angles (deg)			
C(1)–Ru(1)–C(1)*	91.5(3)	C(3)–C(4)–C(3)*	108.7(6)
I(1)–Ru(1)–C(1)	89.0(2)	C(2)–C(3)–C(4)	107.0(4)
Ru(1)–C(1)–O(1)	177.4(5)	C(2)*–C(2)–C(3)	108.5(3)
I(1)–Ru(1)–C(4)	155.7(2)	C(3)–C(4)–C(5)	125.1(3)

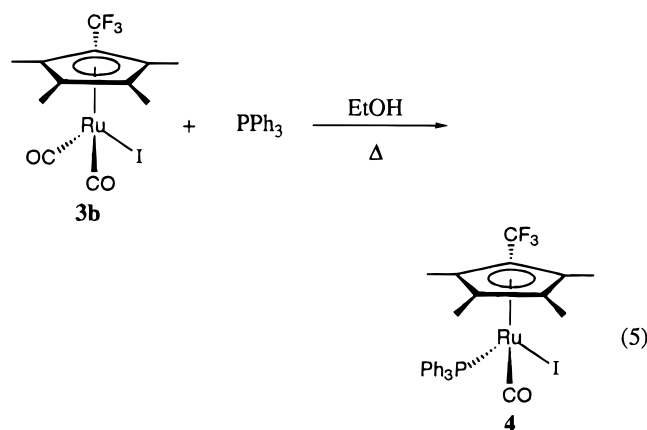
ring-carbon distance differential in **3b** (0.11 Å) is greater than the largest differential (0.08 Å) observed for **1** or **2**. The CF₃ group is *anti* or "staggered" with respect to the iodo ligand and lies on the crystallographically imposed mirror plane. To the best of our knowledge, the crystal structures of the η^5 -C₅H₅ and η^5 -C₅Me₅ iodo analogs of **3b** are not known; however, the structures of [PCpRu(CO)₂(I)]⁵ and [(η^5 -C₅Me₄Et)Ru(CO)₂(Br)]²⁰ are suitable for comparison. The average Ru–C(CO) bond distance in the [PCpRu(CO)₂(I)] compound of 1.91(1) Å is longer than the Ru–C(CO) distance in **3b** of 1.881(6) Å, while the Ru–C(CO) distance in the η^5 -C₅Me₄Et compound of 1.892(14) Å is the same within experimental error. The Ru–I bond distance in **3b** of 2.6989(8) Å is very similar to the Ru–I bond distance of

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2.708(1) Å in the [PCpRu(CO)₂(I)] compound. In the η^5 -C₅Me₄Et compound, the ethyl group is *anti* to the bromide and lies on the mirror plane of the molecule, which is similar to what is observed for the CF₃ group in **3b**.

Compound **3b** may represent a convenient starting point for other derivatives of the type [(η^5 -C₅Me₄CF₃)-Ru(CO)(L)(I)], where L is a neutral, two-electron-donor ligand. The utility of [(η^5 -C₅H₅)Ru(CO)₂(I)],^{3c,21,22} [(η^5 -C₅Me₅)Ru(CO)₂(I)],^{3d} and [(η^5 -C₅Me₄Et)Ru(CO)₂(I)]²³ as starting materials for such derivatives has been established.

Preparation of [(η^5 -C₅Me₄CF₃)Ru(CO)(PPh₃)(I)] (4). Treatment of **3b** with 1.5 equiv of PPh₃ in refluxing ethanol displaces one carbonyl ligand and affords compound **4** in 70% yield (eq 5). In an attempt to displace



both carbonyl ligands, the reaction was carried out with a large excess of PPh₃ in the presence of 2 equiv of (CH₃)₃NO; however, compound **4** was the only tractable product. Compound **4** is chiral at ruthenium, and the ¹H NMR spectrum in chloroform-*d* shows four resonances for the inequivalent methyl groups. The methyl hydrogens in the 2,5-positions appear as broad resonances at 2.15 and 1.56 ppm with unresolved fluorine and phosphorus coupling. The methyl hydrogens in the 3,4-positions appear as doublets at 1.74 (⁴J_{HP} = 1.5 Hz) and 1.51 ppm (⁴J_{HP} = 1.0 Hz). The ³¹P{¹H} NMR spectrum of **4** shows a quartet at 46.7 ppm (⁴J_{PF} = 2.3 Hz). The IR spectrum of **4** in dichloromethane shows a ν (CO) stretching frequency at 1953 cm⁻¹ that is broadened, which is similar to the ν (CO) stretching frequency of 1962 cm⁻¹ that is observed for [(η^5 -C₅H₅)Ru(CO)(PPh₃)(I)] in CS₂.²² One noteworthy fact about the preparation of compound **4** is that the CF₃ group was not esterified to the ethyl ester (CO₂Et) by the action of refluxing ethanol. This contrasts with the reported example of η^5 -C₅Me₄CF₃ esterification observed when [(η^5 -C₅Me₄CF₃)RhCl₂]₂ was reacted with diphenylvinylphosphine in refluxing ethanol.²⁴

Failure to displace both CO ligands from **3b** is not surprising, since this is usually difficult for complexes of the type [(η^5 -C₅R₅)M(CO)₂(X)] (R = H, Me₄Et; M =

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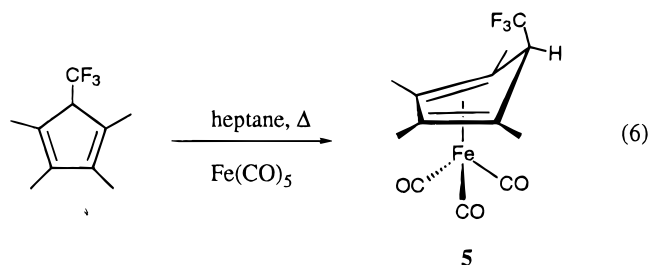
Table 7. Infrared Carbonyl Stretching Frequencies of [(η^4 -HCp')Fe(CO)₃] (η^4 -Cp' = η^4 -HC₅H₅, η^4 -HC₅Me₄CF₃, η^4 -HC₅Me₅) Complexes^a

compd	ν (CO), cm ⁻¹	ref
[(η^4 -HC ₅ H ₅)Fe(CO) ₃]	2048, 1981, 1974	27b
[(η^4 -HC ₅ Me ₄ CF ₃)Fe(CO) ₃] (5)	2040, 1975, 1969	this work
[(η^4 -HC ₅ Me ₅)Fe(CO) ₃]	2031, 1964, 1955 ^b	28b

^a Hexane solution. ^b Methylcyclohexane solution.

Ru; X = Cl, Br, I).^{23,25} However, at least *one* example has been reported where compounds of the type [(η^5 -C₅H₅)Ru(L)₂(H)] (L = chelating phosphine) were prepared from [(η^5 -C₅H₅)Ru(CO)₂(H)].²⁵ Therefore, the range of possible derivatives from **1** and **2** may be somewhat limited, especially if ancillary carbonyl ligands are not desirable. Regardless, compounds **1** and **3b** represent important synthons for subsequent ruthenium chemistry, since the η^5 -C₅Me₄CF₃ analog of [(η^5 -C₅Me₅)RuCl₂]₂²⁶ is not known. We have previously shown that treatment of RuCl₃·xH₂O with HC₅Me₄CF₃ affords the ruthenocene [(η^5 -C₅Me₄CF₃)₂Ru] as the sole product.^{2b}

Preparation of [(η^4 -HC₅Me₄CF₃)Fe(CO)₃] (5). During the course of preparing **2** in refluxing octane (eq 3), a trace byproduct was isolated and subsequently identified as the iron tricarbonyl diene compound [(η^4 -HC₅Me₄CF₃)Fe(CO)₃] (**5**). Treatment of iron pentacarbonyl with HC₅Me₄CF₃ in refluxing heptane results in the formation of **5** in 13% yield (eq 6). The most notable



feature in the ¹H NMR spectrum of **5** in chloroform-*d* is a quartet at 3.19 ppm (³J_{HF} = 6.5 Hz) for the proton geminal to the CF₃ group. This proton is probably *endo* with respect to the metal due to steric reasons. However, a crystal structure of an iron substituted η^4 -cyclopentadiene tricarbonyl complex, [(η^4 -C₅(1-H)(1-CF₃)(2-CF₃)(3-OCH₃)(4-H)(5-OCH₂CH₃)]Fe(CO)₃, with a CF₃ group in the *endo* position was recently reported.^{27a} Only one isomer of **5** is observed by ¹H NMR spectroscopy at room temperature and at temperatures up to 80 °C (in toluene-*d*₆). The IR spectral data for **5** are listed in Table 7 along with those of the η^4 -HC₅H₅ and η^4 -HC₅Me₅ analogs for comparison. The infrared spectrum for **5** in hexanes (Table 7) shows three ν (CO) bands at 2040, 1975, and 1969 cm⁻¹, as expected for iron η^4 -diene tricarbonyl complexes.^{27b} The carbonyl stretching frequencies of **5** are lower in value than those of the [(η^4 -HC₅H₅)Fe(CO)₃] analog.^{27b} This indicates that the η^4 -HC₅Me₄CF₃ ligand in **5** is slightly more electron donating than the η^4 -HC₅H₅ ligand in its analogous iron complex. In contrast, the ν (CO) values for all of the η^5 -C₅Me₄CF₃ metal complexes discussed above are more similar to those of their η^5 -C₅H₅ metal analogs, because

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the effects of the methyl and trifluoromethyl groups are more evenly distributed through resonance in the planar η^5 -C₅Me₄CF₃ coordinated ligand than in **5**.

Compound **5** is an air-stable, sublimable solid, whereas the related derivatives $[(\eta^4\text{-HC}_5\text{H}_5)\text{Fe}(\text{CO})_3]^{27b}$ and $[(\eta^4\text{-HC}_5\text{Me}_5)\text{Fe}(\text{CO})_3]^{28}$ are air-sensitive, oily liquids. In the case of **5**, the electron-withdrawing nature and steric bulk of the η^4 -HC₅Me₄CF₃ ligand protects the metal center from oxidation. Complex **5** cannot be deprotonated with excess 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU); however, deprotonation is observed with lithium diisopropylamide in THF. Reprotonation with excess methanol gives an unstable compound that has the same CO stretching frequencies as the original complex. It is likely that this compound is the isomer where the CF₃ group is *endo* with respect to the metal center; however, no further attempts were made at characterization.

The previously reported $[(\eta^4\text{-HC}_5\text{H}_5)\text{Fe}(\text{CO})_3]$ and $[(\eta^4\text{-HC}_5\text{Me}_5)\text{Fe}(\text{CO})_3]$ complexes are believed to be intermediates in the preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-CO})(\text{CO})_2]$ and $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\mu\text{-CO})(\text{CO})_2]$, respectively.^{27b,c,28} Thus, it is likely that complex **5** is also an intermediate in the preparation of **2**. Purified samples of **5** were heated under an argon atmosphere in refluxing octane solvent, but only trace quantities of **2** were observed. Stronger thermolysis^{27c} or photolysis^{28b} conditions may be required to affect this conversion.

Summary

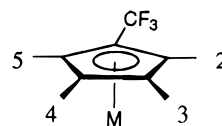
The chemistry of iron and ruthenium carbonyl dimers of the type $[(\eta^5\text{-C}_5\text{R}_5)\text{M}(\mu\text{-CO})(\text{CO})_2]$ (M = Fe, Ru; R = H, Me) is vast.³ The compounds $[(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{Ru}(\mu\text{-CO})(\text{CO})_2]$ (**1**) and $[(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{Fe}(\mu\text{-CO})(\text{CO})_2]$ (**2**) represent suitable precursors to other iron and ruthenium compounds containing the sterically demanding, electron-withdrawing η^5 -C₅Me₄CF₃ ligand. Compounds **1** and **2** both crystallize as the *trans* isomers with bridging carbonyl ligands. The crystal structures of **1** and **2** compare favorably with those of the η^5 -C₅Me₅ analogs, providing strong evidence that the steric bulk of the ligand controls the overall *trans* geometry of these complexes. Compound **1** is sensitive to visible light in aerated solvents and reacts with chloroform or dichloromethane to form $[(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{Ru}(\text{CO})_2(\text{Cl})]$ (**3a**). Compound **1** reacts with I₂ to produce $[(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{Ru}(\text{CO})_2(\text{I})]$ (**3b**), which in turn reacts with PPh₃ to form $[(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{Ru}(\text{CO})(\text{PPh}_3)(\text{I})]$ (**4**) in reasonable yield. The compound $[(\eta^4\text{-HC}_5\text{Me}_4\text{CF}_3)\text{-Fe}(\text{CO})_3]$ (**5**) is prepared from Fe(CO)₅ and represents a new mode of coordination for the HC₅Me₄CF₃ ligand. Overall, the IR spectroscopic data for **1** and **2** and their η^5 -C₅H₅ analogs are very similar, and the X-ray crystallographic data for **1** and **2** suggest that the structural effects of η^5 -C₅Me₄CF₃ and η^5 -C₅Me₅ are very similar. These comparisons support the general conclusion^{2a,b} that the η^5 -C₅Me₄CF₃ ligand is electronically equivalent to η^5 -C₅H₅ and sterically equivalent to the η^5 -C₅Me₅ ligand.

Experimental Section

A. Reagents and Physical Measurements. All chemicals were reagent grade and were used as received from

commercial sources (Aldrich or Fisher Scientific) or synthesized as described below. Solvents were dried by standard procedures and stored over Linde type 4 Å molecular sieves. All syntheses were conducted in Schlenk glassware under a nitrogen atmosphere. HC₅Me₄CF₃^{2a} and **2**^{2c} were synthesized by literature procedures. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points were obtained using a Mel-Temp melting point apparatus and are uncorrected. Solution infrared spectra were obtained on Perkin-Elmer 599 or Paragon 1000 PC-FT spectrometers in sealed CaF₂ cells, and solid-state spectra were conducted on NaCl windows. ¹H, ¹³C{¹H}, ³¹P{¹H}, and ¹⁹F NMR spectra were recorded at 499.8, 125.7, 202.4, and 470.3 MHz, respectively, on a Varian Unity Plus 500 FT-NMR spectrometer. Proton and carbon chemical shifts are relative to internal Me₄-Si, while phosphorus chemical shifts are relative to external 85% H₃PO₄ (aq) with positive values downfield of the respective reference. Fluorine chemical shifts are relative to external CFCl₃ with negative values upfield of the reference. NMR data for **A** were obtained on General Electric GN and QE 300 MHz spectrometers. NMR data for **2** were obtained on Varian VXR-300 or Bruker NR 300 MHz spectrometers, IR data were obtained on a Mattson Sirius 100 FTIR spectrophotometer, and mass spectra were obtained with a Finnigan 4000 mass spectrometer as described in the Experimental Section of ref 2c.

B. Syntheses. Preparation of $[(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{Ru}(\mu\text{-CO})(\text{CO})_2]$ (1**).** A 50-mL Schlenk flask was charged with Ru₃(CO)₁₂ (0.57 g, 0.89 mmol) and 25 mL of freshly distilled *n*-decane. This mixture was degassed, flushed with nitrogen, and subsequently charged with 98% HC₅Me₄CF₃ (0.52 g, 2.73 mmol). The clear red solution was refluxed for 6 h and gradually turned dark brown. The reaction solution was then stored at -25 °C for 24 h. The solution was filtered, and the resulting orange-brown solid was washed with 3 × 5 mL portions of cold hexanes. The crude product was dried *in vacuo* (0.1 mmHg) to give 0.78 g of **1** in 84% yield based on Ru₃(CO)₁₂. The product was then purified by chromatography. The crude product was dissolved in a minimal amount of CH₂Cl₂ (about 75 mL), and enough Florisil was added to make a slurry and adsorb the product (~10 g). The CH₂Cl₂ was removed *in vacuo*, and the adsorbed crude product was added to a dry-packed 2 × 35 cm column of Florisil. The column was eluted with hexanes, which gave a yellow band containing unreacted Ru₃(CO)₁₂. Typically, 125–300 mL of hexanes was required to obtain colorless fractions. The column was then eluted with CH₂Cl₂ which gave a red-orange band that contained **1**, followed by a black band that was discarded. Typically about 400–600 mL of CH₂Cl₂ was required to completely remove **1** from the column. Solutions of **1** in CH₂Cl₂ were protected from light. The solvent was removed *in vacuo* resulting in an orange-brown solid which contained 0.39 g (42%) of pure **1**. Compound **1** was recrystallized by dissolving the orange-brown residue in a minimal amount of CH₂Cl₂ and filtering the solution into hexanes that was twice the volume of CH₂Cl₂. The vessel was sealed, wrapped in aluminum foil, and stored at -25 °C for 24 h. The resulting clear red-orange crystals were collected on a medium-porosity glass frit and washed with 2 × 5 mL portions of cold hexanes. Compound **1** is air-stable indefinitely in the solid state, but in aerated halocarbon solutions **1** is sensitive to visible light. The reactions are slow in CH₂Cl₂, faster in CHCl₃, and in all cases greatly accelerated if unprotected from visible light. Mp: 218 °C dec. Anal. Calcd for C₂₄H₂₄F₆O₄Ru₂: C, 41.62; H, 3.49. Found: C, 41.39; H, 3.51.



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¹H NMR (C₆D₆): δ 1.84 (q, ⁵J_{HF} = 0.97 Hz, 6H, 2,5-CH₃), 1.32 (s, 6H, 3,4-CH₃). ¹³C{¹H} NMR (C₆D₆): δ 224.46 (br s, CO),

125.69 (q, $^1J_{CF} = 271.14$ Hz, CF₃), 105.28 (q, $^4J_{CF} = 0.75$ Hz, 3,4-CCH₃), 104.48 (q, $^3J_{CF} = 1.42$ Hz, 2,5-CCH₃), 89.36 (q, $^2J_{CF} = 35.87$ Hz, CCF₃), 10.30 (q, $^4J_{CF} = 2.10$ Hz, 2,5-CH₃), 8.70 (s, 3,4-CH₃). ^{19}F NMR (C₆D₆): $\delta -52.59$ (sep, $^5J_{HF} = 0.97$ Hz). IR (CH₂Cl₂): $\nu(\text{CO})$ 1958, 1776 cm⁻¹. IR (Nujol): $\nu(\text{CO})$ 1955, 1767 cm⁻¹ (^{13}CO satellites 1918, 1738). ^1H NMR (CDCl₃): δ 2.05 (q, $^5J_{HF} = 1.2$ Hz, 6H, 2,5-CH₃), 1.72 (s, 6H, 3,4-CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃): δ 224.15 (br s, CO), 124.51 (q, $^1J_{CF} = 271.15$ Hz, CF₃), 104.76 (q, $^4J_{CF} = 0.75$ Hz, 3,4-CCH₃), 103.92 (q, $^3J_{CF} = 1.51$ Hz, 2,5-CCH₃), 88.83 (q, $^2J_{CF} = 35.95$ Hz, CCF₃), 10.02 (q, $^4J_{CF} = 2.10$ Hz, 2,5-CH₃), 8.60 (s, 3,4-CH₃).

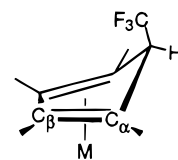
Reaction of 1 in CDCl₃: Formation of $[(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{-Ru}(\text{CO})_2(\text{Cl})]$ (3a). In an NMR tube, a CDCl₃ solution of **1** was allowed to stand in visible light for 48 h. The red solution darkened, and some brown solid precipitated. The solution was filtered, and the solvent was removed *in vacuo*. The residue was dissolved in CDCl₃ for spectroscopic characterization. No further attempts were made to purify the product **3a**. ^1H NMR (CDCl₃): δ 2.12 (q, $^5J_{HF} = 1.2$ Hz, 6H, 2,5-CH₃), 1.92 (s, 6H, 3,4-CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃): 195.67 (s, CO), 124.33 (q, $^1J_{CF} = 271.53$ Hz, CF₃), 105.74 (q, $^3J_{CF} = 1.38$ Hz, 2,5-CCH₃), 103.06 (q, $^4J_{CF} = 0.50$ Hz, 3,4-CCH₃), 80.55 (q, $^2J_{CF} = 36.83$ Hz, CCF₃), 10.55 (q, $^4J_{CF} = 2.26$ Hz, 2,5-CH₃), 9.24 (s, 3,4-CH₃). IR (CDCl₃): $\nu(\text{CO})$ 2063, 2014 cm⁻¹.

Preparation of $[(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{Ru}(\text{CO})_2(\text{I})]$ (3b). Under a nitrogen atmosphere a Schlenk flask was charged with 30 mL of CH₂Cl₂, I₂ (1.28 g, 5.0 mmol), and **1** (0.25 g, 0.36 mmol). The deep red solution was purged with nitrogen and refluxed for 1.5 h. The reaction solution was transferred to a separatory funnel and washed with three 80 mL portions of 1.61 M aqueous sodium thiosulfate to remove excess iodine. The orange CH₂Cl₂ layer was separated and dried with magnesium sulfate. The solution was filtered, and the solvent was removed *in vacuo* to produce an orange solid which was dried *in vacuo* (0.1 mmHg) to give 0.25 g of **3b** in 74% yield. Compound **3b** was recrystallized from boiling ethanol to give orange needles. It is air-stable in solution and the solid state. Mp: 154–157 °C. Anal. Calcd for C₁₂H₁₂F₃IO₂Ru: C, 30.46; H, 2.56. Found: C, 30.35; H, 2.42. ^1H NMR (CDCl₃): δ 2.23 (q, $^5J_{HF} = 0.95$ Hz, 6H, 2,5-CH₃), 2.14 (s, 6H, 3,4-CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃): δ 195.43 (q, $^4J_{CF} = 1.09$ Hz, CO), 124.21 (q, $^1J_{CF} = 271.51$ Hz, CF₃), 104.79 (q, $^3J_{CF} = 1.42$ Hz, 2,5-CCH₃), 102.04 (q, $^4J_{CF} = 0.75$ Hz, 3,4-CCH₃), 82.66 (q, $^2J_{CF} = 36.77$ Hz, CCF₃), 11.08 (q, $^4J_{CF} = 2.14$ Hz, 2,5-CH₃), 10.59 (s, 3,4-CH₃). ^{19}F NMR (CDCl₃): $\delta -54.34$ (sep, $^5J_{HF} = 0.95$ Hz). IR (CH₂Cl₂): $\nu(\text{CO})$ cm⁻¹ 2060, 1998. IR (Nujol): $\nu(\text{CO})$ 2040, 1984 cm⁻¹.

Preparation of $[(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{Ru}(\text{CO})(\text{PPh}_3)(\text{I})]$ (4). Under a nitrogen atmosphere, to a suspension of **3b** (0.4 g, 0.84 mmol) in 45 mL of absolute ethanol was added triphenylphosphine (0.47 g, 1.8 mmol). The reaction mixture was refluxed for 48 h and the solution gradually turned from orange to red. The reaction mixture was then cooled to room temperature, and the solvent was removed *in vacuo*. A 60 mL glass frit funnel was used as a column and attached to a 1000 mL Erlenmeyer flask equipped with a side arm. A 2.5 cm layer of silica gel (grade 12, 28–300 mesh, Aldrich) was covered with a 0.5 cm layer of Celite and firmly packed with a spatula and suction. The crude reaction product was dissolved in a minimal amount of CH₂Cl₂ and loaded onto the column, and the residual solvent was removed with suction. All subsequent solvents were eluted with suction. The column was eluted with (1) 250 mL of hexanes and (2) 350 mL of CH₂Cl₂, and all solvents were removed *in vacuo*. By $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, fractions 1 and 2 both contained the product and were combined and dried to give 0.41 g of **4** in 69% yield. Compound **4** was recrystallized from boiling ethanol to give deep red crystals which are air-stable in solution and the solid state. Mp: 186–188 °C. Anal. Calcd for C₂₉H₂₇F₃IO₂RPu: C, 49.23; H, 3.85. Found: C, 49.18; H, 3.73. ^1H NMR (CDCl₃): δ 7.56–7.35 (m, 15H, Ph), 2.15 (br m, 3H, 2- or 5-CH₃), 1.74 (d, $^4J_{PH} = 1.5$ Hz, 3H, 3- or 4-CH₃), 1.56 (br m, 3H, 2- or 5-CH₃), 1.51 (d, $^4J_{PH} = 1.0$ Hz, 3- or 4-CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃): δ

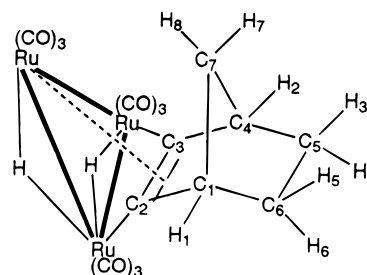
203.82 (dq, $^2J_{PC} = 21.3$ Hz, $^4J_{CF} = 1.3$ Hz, CO), 134.24 (d, $^2J_{PC} = 10.6$ Hz, C_o), 130.10 (d, $^4J_{CP} = 2.4$ Hz, C_p), 127.94 (d, $^3J_{CP} = 10.2$ Hz, C_m), C_i not observed, 125.35 (q, $^1J_{CF} = 271.9$ Hz, CF₃), 101.23 (dq, $^2J_{PC} = 3.3$ Hz, $^3J_{CF} = 1.6$ Hz, 2- or 5-CCH₃), 99.73 (br s, 3- or 4-CCH₃), 99.09 (dq, $^2J_{PC} = 3.5$ Hz, $^4J_{CF} = 0.75$ Hz, 3- or 4-CCH₃), 98.44 (dq, $^2J_{PC} = 3.1$ Hz, $^3J_{CF} = 1.45$ Hz, 2- or 5-CCH₃), 81.48 (qd, $^2J_{CF} = 35.5$ Hz, $^2J_{PC} = 2.9$ Hz, CCF₃), 11.43 (q, $^4J_{CF} = 1.0$ Hz, 2- or 5-CH₃), 10.45 (d, $^3J_{CP} = 0.88$ Hz, 3- or 4-CH₃), 10.10 (q, $^4J_{CF} = 2.0$ Hz, 2- or 5-CH₃), 9.55 (s, 3- or 4-CH₃). ^{19}F NMR (CDCl₃): $\delta -53.38$ (m). IR (CH₂Cl₂): $\nu(\text{CO})$ 1953 cm⁻¹. IR (Nujol): $\nu(\text{CO})$ 1936 (sh 1949 w, 1966 m) cm⁻¹.

Preparation of $[(\eta^4\text{-HC}_5\text{Me}_4\text{CF}_3)\text{Fe}(\text{CO})_3]$ (5). Under an argon atmosphere, 40 mL of predistilled heptane was charged with Fe(CO)₅ (2.0 g, 10 mmol, filtered through glass wool) and HC₅Me₄CF₃ (2.0 g, 10.5 mmol). The solution was purged with argon and heated to reflux for 48 h. After it was cooled to room temperature, the heptane solution was filtered and the solvent was removed under high vacuum. The resulting yellow oil was sublimed onto a water-cooled sublimation probe (25 °C, 0.01 mmHg). The yellow oil was resublimed, and the sublimate was recrystallized from hexanes at -78 °C to give 0.42 g of **5** in 13% yield as a yellow waxy solid. Mp: 128–129 °C. Anal. Calcd for C₁₃H₁₃F₃FeO₃: C, 47.30; H, 3.97. Found: C, 47.15; H, 4.00.



^1H NMR (CDCl₃): δ 3.19 (q, $^3J_{HF} = 6.5$ Hz, 1H, H), 2.13 (s, 6H, CH_{3o}), 1.52 (s, 6H, CH_{3β}). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃): δ 211.98 (s, CO), 122.49 (q, $^1J_{CF} = 291.0$ Hz, CF₃), 102.10 (q, $^4J_{CF} = 0.9$ Hz, C_β=C), 65.41 (q, $^2J_{CF} = 24.2$ Hz, CCF₃), 60.80 (q, $^3J_{CF} = 1.7$ Hz, C=C_o), 15.27 (q, $^4J_{CF} = 0.8$ Hz, CH_{3o}), 11.57 (s, CH_{3β}). ^{19}F NMR (CDCl₃): $\delta -72.96$ (d, $^3J_{HF} = 6.5$ Hz). IR (cyclohexane): $\nu(\text{CO})$ 2039, 1973, 1967 cm⁻¹. MS: *m/e* calcd for C₁₃H₁₃FeO₃ 330.016 62, found 330.014 13.

Spectroscopic Data for $[(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-C}_7\text{H}_8)]$ (A). See ref 6 for synthesis and X-ray crystal structure of **A**. The authors did not report complete details of ^1H or ^{13}C NMR data.



^1H NMR (300.16 MHz, CDCl₃): δ 3.19 (apparent tt, $^3J(\text{H}_1\text{H}_7) = ^3J(\text{H}_1\text{H}_8) = 2.0$ Hz, $^3J(\text{H}_1\text{H}_5) = ^3J(\text{H}_1\text{H}_6) = 1.35$ Hz, 2H, H_{1,2}), 1.90 (m, 2H, H_{3,5}), 1.35 (apparent dt, $^2J(\text{H}_7\text{H}_8) = 9.3$ Hz, $^4J(\text{H}_4\text{H}_8) = ^4J(\text{H}_6\text{H}_8) = 3.9$ Hz, 1H, H₈), 1.20 (m, $^2J(\text{H}_3\text{H}_4) = 4.50$ Hz, $^4J(\text{H}_4\text{H}_8) = 3.9$ Hz, $^3J(\text{H}_4\text{H}_5) = 2.4$ Hz, 2H, H_{4,6}), 0.68 (m, $^2J(\text{H}_7\text{H}_8) = 9.3$ Hz, $^3J(\text{H}_1\text{H}_7) = ^3J(\text{H}_2\text{H}_7) = 2.0$ Hz, $^4J(\text{H}_3\text{H}_7) = ^4J(\text{H}_5\text{H}_7) = 2.1$ Hz, 1H, H₇), -16.8 (broad, 1H, RuH), -20.2 (broad, 1H, RuH). ^{13}C NMR (75.58 MHz, CDCl₃): δ 192.44 (s, 3CO_{ax}), 189.95 (s, 6CO_{eq}), 157.54 (s, C_{2,3}), 53.52 (dd, $^1J_{CH} = 149.3$ Hz, $^2J_{CH} = 7.3$ Hz, C_{1,4}), 50.97 (tt, $^1J_{CH} = 133.8$ Hz, $^2J_{CH} = 6.3$ Hz, C₇), 27.12 (t of apparent tq, $^1J_{CH} = 129.0$ Hz, $^2J_{CH} = 5.2$ Hz, $^2J_{CH} = ^3J_{CH} = 2.6$ Hz, C_{5,6}). IR (CDCl₃): $\nu(\text{CO})$ 2120 m, 2100 s, 2070 vs, 2030 s, 2010 sh, 1990 sh cm⁻¹.

C. X-ray Data Collection and Processing for 1, 2, and 3b. Crystal data and details of data collection and refinement are given in Table 8. Other crystallographic data are included in the Supporting Information.

Table 8. Crystallographic Data for Compounds **1**, **2**, and **3b**

	1	2	3b
empirical formula	C ₂₄ H ₂₄ O ₄ F ₆ Ru ₂	C ₂₄ H ₂₄ O ₄ F ₆ Fe ₂	C ₁₂ H ₁₂ F ₃ O ₂ RuI
fw	692.6	602.14	473.20
cryst dimens (mm)	0.40 × 0.40 × 0.40	0.35 × 0.35 × 0.30	0.88 × 0.08 × 0.08
cryst syst	monoclinic	monoclinic	monoclinic
space group	P2 _{1/n}	P2 _{1/n}	P2 _{1/m}
a (Å)	8.541(2)	8.451(3)	7.2526(4)
b (Å)	9.804(2)	9.900(6)	12.1952(6)
c (Å)	15.103(4)	14.437(8)	8.647(1)
β (deg)	97.37(2)	94.76(3)	99.020(9)
V (Å ³)	1254.2(9)	1204(2)	755.3(1)
Z	2	2	2
D _{calc} (g/cm ⁻³)	1.834	1.661	2.080
μ(Mo Kα) (cm ⁻¹)	12.526	12.78	31.08
radiation (λ = 0.710 69 Å)	Mo Kα	Mo Kα	Mo Kα
temp (°C)	20	24	20
scan type	θ/2θ	ω-2θ	ω-2θ
scan rate (deg/min in ω)	variable	16.5	16.0
scan width (deg)	1.06 + 0.34 tan Θ	0.60 + 0.35 tan Θ	1.47 + 0.35 tan Θ
2θ _{max} (deg)	54	51.9	45.0
no. of rflns colld	3393	2621	1143
no. of unique rflns	3191	2515	1050
no. of observns (I > 3σ(I)) (N _o)	2805	1870 ^a	950
no. of variables (N _v)	163	163	119
N _o /N _v	17.63	11.47	7.98
R ^b , R _w ^c	0.028, 0.061	0.045, 0.056	0.024, 0.026
goodness of fit	1.45	1.42	3.42
max peak final diff map (e Å ⁻³)	0.56	0.34	0.68
min peak final diff map (e Å ⁻³)	-0.87	-0.36	-0.74
max shift/error final cycle	0.04	0.00	0.64

^a I > 2σ(I). ^b R = Σ||F_o - |F_c||/Σ|F_o|. ^c R_w = [(Σw(|F_o - |F_c||)²/ΣwF_o²)]^{0.5}.

[(η^5 -C₅Me₄CF₃)Ru(μ -CO)(CO)]₂ (**1**). Red-orange crystals of **1** were grown by slow diffusion of hexanes into a saturated CH₂Cl₂ solution that was protected from visible light at -25 °C. Data were collected using an Enraf-Nonius CAD4-F automatic diffractometer at room temperature. Three standard reflections measured every 1 h during the entire data collection period showed no significant trend. The raw data were converted to intensities and corrected for Lorentz and polarization factors. All calculations were performed on a VAX computer using the Enraf-Nonius VAX/Molen package.²⁹ The structure was solved by the heavy-atom method. After refinement of the non-hydrogen atoms, difference Fourier maps revealed maxima of residual electron density close to positions expected for hydrogen atoms. Hydrogen atoms were refined at calculated positions with a riding model in which the C-H vector was fixed at 0.95 Å with isotropic temperature factors such as B(H) = 1.3B_{eq}(C) Å. Fourier difference maps revealed no significant maxima. Neutral atom scattering factors and anomalous dispersion coefficients were taken from a standard source.³⁰

[(η^5 -C₅Me₄CF₃)Fe(μ -CO)(CO)]₂ (**2**). Dark purple prismatic crystals of **2** were grown from a mixture of CH₂Cl₂ and hexanes overnight at -15 °C. Data were collected on an Enraf-Nonius CAD-4 diffractometer and were corrected for Lorentz, polarization, and absorption using the DIFABS program.³¹ The structure was solved by direct methods, and the non-hydrogen atoms were refined anisotropically.³² Neutral atom scattering factors and anomalous dispersion coefficients were taken from a standard source.³⁰ All calculations were performed using the TEXSAN crystallographic software package.^{32c}

[(η^5 -C₅Me₄CF₃)Ru(CO)₂(I)] (**3b**). Orange needles of **3b** were grown from hot ethanol. Data were collected on a Rigaku AFC7R diffractometer with a 12 kW rotating-anode generator. An empirical absorption correction based on azimuthal scans of several different reflections was applied. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient 5.41429 × 10⁻⁶). The structure was solved by direct methods, and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically with a riding model. Neutral atom scattering factors and anomalous dispersion coefficients were taken from a standard source.³⁰ All calculations were performed using the TEXSAN crystallographic software package.^{32c}

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Supporting Information Available: For the compounds **1**, **2**, and **3b**, listings of crystal and refinement data, atomic coordinates and U values, bond lengths and angles, anisotropic displacement parameters, and H atom coordinates and isotropic displacement parameters (20 pages). Ordering information is given on any current masthead page.

OM961069B

(33) Molecular Structure Corp., 3200 Research Forest Drive, The Woodlands, TX 77381.

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