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Syntheses, Properties, and X-ray Crystal Structures of Iron and Ruthenium Compounds with the η^5-$C_5Me_4CF_3$ Ligand. Compounds of the Type $[(\eta^5\text{-}C_5Me_4CF_3)M(\mu\text{-}CO)(CO)]_2$ (M = Fe, Ru)

Luis P. Barthel-Rosa,[†] John R. Sowa, Jr.,*[,‡] Paul G. Gassman,[§] Jean Fischer,[‖]
Bayrn M. McCarty,[⊥] Seth L. Goldsmith,[⊥] Michael T. Gibson,[⊥] and
John H. Nelson*[,†]

Department of Chemistry/216, University of Nevada—Reno, Reno, Nevada 89557-0020,
Department of Chemistry, Kolthoff Hall, University of Minnesota,
Minneapolis, Minnesota 55455, and Laboratoire de Cristallochimie (URA 424 du CNRS),
Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex, France

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(Trifluoromethyl)tetramethylcyclopentadiene, $HC_5Me_4CF_3$ ($Cp^{\ddagger}H$), reacts with $Ru_3(CO)_{12}$ in refluxing *n*-decane to produce $[(\eta^5\text{-}C_5Me_4CF_3)Ru(\mu\text{-}CO)(CO)]_2$ (**1**). In chlorinated hydrocarbon solutions, **1** reacts with the solvents in the presence of visible light to produce $[(\eta^5\text{-}C_5Me_4CF_3)Ru(CO)_2(Cl)]$ (**3a**). Compound **1** reacts with iodine in refluxing CH_2Cl_2 to produce $[(\eta^5\text{-}C_5Me_4CF_3)Ru(CO)_2(I)]$ (**3b**). The X-ray crystal structure of compound **3b** is presented. Compound **3b** reacts with triphenylphosphine in refluxing ethanol to produce $[(\eta^5\text{-}C_5Me_4CF_3)Ru(CO)(PPh_3)(I)]$ (**4**). The $HC_5Me_4CF_3$ ligand reacts with $Fe(CO)_5$ in refluxing heptane to produce $[(\eta^4\text{-}HC_5Me_4CF_3)Fe(CO)_3]$ (**5**). Compound **5** represents a new mode of coordination (η^4) for $HC_5Me_4CF_3$. The spectroscopic properties of compound **1** and its previously reported iron analog, $[(\eta^5\text{-}C_5Me_4CF_3)Fe(\mu\text{-}CO)(CO)]_2$ (**2**), are compared with those of their η^5-C_5H_5 and η^5-C_5Me_5 “parent” analogs of the type $[(\eta^5\text{-}C_5R_5)M(\mu\text{-}CO)(CO)]_2$ (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-$C_5Me_4CF_3$ rings. Overall, the spectroscopic and X-ray structural data of **1** and **2** support the previous conclusions that the η^5-$C_5Me_4CF_3$ ligand is electronically equivalent to η^5-C_5H_5 and sterically equivalent to η^5-C_5Me_5. Compounds **1** and **3b** represent important synthons for subsequent ruthenium chemistry with the η^5-$C_5Me_4CF_3$ ligand.

Introduction

Cyclopentadienyl (η^5-C_5H_5) and pentamethylcyclopentadienyl (η^5-C_5Me_5) ligands represent two of the most widely used ancillary ligands for transition-metal organometallic compounds. The substitution of η^5-C_5Me_5 for η^5-C_5H_5 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-C_5Me_5 ligand has not been accomplished. Alternatively, the recently discovered (trifluoromethyl)tetramethylcyclopentadienyl ligand[2ab] (η^5-$C_5Me_4CF_3$) exhibits electronic properties equivalent to those of η^5-C_5H_5 but retains the steric equivalence of η^5-C_5Me_5.[2] Besides being convenient starting materials, compounds of the type $[(\eta^5\text{-}C_5R_5)M(\mu\text{-}CO)(CO)]_2$ (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-$C_5Me_4CF_3$ ligand into organometallic iron and ruthenium chemistry is realized by the syntheses of $[(\eta^5\text{-}C_5Me_4CF_3)M(\mu\text{-}CO)(CO)]_2$ (M = Fe,[2b,c] Ru).

Herein we report the syntheses, properties, and X-ray crystal structures of $[(\eta^5\text{-}C_5Me_4CF_3)M(\mu\text{-}CO)(CO)]_2$ (M = Ru (**1**), Fe[2b,c] (**2**)) and compare these new compounds with their parent iron and ruthenium compounds. In

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[†] University of Nevada—Reno.

[‡] Current address: Department of Chemistry, Seton Hall University, South Orange, NJ 07079.

[§] Deceased April 21, 1993.

[‖] Université Louis Pasteur.

[⊥] NSF-REU Summer Undergraduate Participant.

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Table 1. Infrared Carbonyl Stretching Frequencies of $[(\eta^5\text{-Cp}')M(\mu\text{-CO})(CO)]_2$ (η^5-Cp′ = η^5-C_5H_5, η^5-$C_5Me_4CF_3$, η^5-C_5Me_5; M = Fe, Ru) Complexes[a]

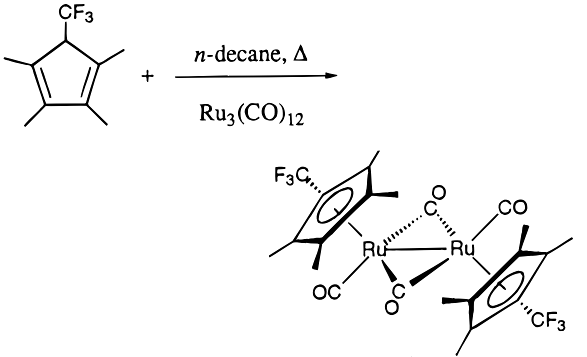
compd	ν(CO), cm^{-1}	ref
trans-$[(\eta^5\text{-}C_5H_5)Ru(\mu\text{-CO})(CO)]_2$	1968, 1768[b]	7a,b
$[(\eta^5\text{-}C_5Me_4CF_3)Ru(\mu\text{-CO})(CO)]_2$ (**1**)	1958, 1776	this work
trans-$[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-CO})(CO)]_2$	1925, 1744	8
trans-$[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-CO})(CO)]_2$	1955, 1773	2c
$[(\eta^5\text{-}C_5Me_4CF_3)Fe(\mu\text{-CO})(CO)]_2$ (**2**)	1952, 1776	2c
trans-$[(\eta^5\text{-}C_5Me_5)Fe(\mu\text{-CO})(CO)]_2$	1922, 1747	2c

[a] CH_2Cl_2 solvent. [b] $CHCl_3$ solvent.

addition, we report the syntheses of half-sandwich derivatives $[(\eta^5\text{-}C_5Me_4CF_3)Ru(CO)_2(I)]$ (**3b**), $[(\eta^5\text{-}C_5Me_4CF_3)Ru(CO)(PPh_3)(I)]$ (**4**), and $[(\eta^4\text{-}HC_5Me_4CF_3)Fe(CO)_3]$ (**5**). The crystal structure of **3b** is also presented. Compound **5** represents a new mode of coordination for $HC_5Me_4CF_3$.

Results and Discussion

Preparation and Properties of $[(\eta^5\text{-}C_5Me_4CF_3)M(\mu\text{-CO})(CO)]_2$ (M = Fe, Ru). Treatment of $Ru_3(CO)_{12}$ with 3 equiv of $HC_5Me_4CF_3$[2a] in refluxing *n*-decane results in the formation of the ruthenium carbonyl dimer $[(\eta^5\text{-}C_5Me_4CF_3)Ru(\mu\text{-CO})(CO)]_2$ (**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 ($^5J_{HF}$ = 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 $^{13}C\{^1H\}$ 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 ($^1J_{CF}$ = 271.1 Hz) for the CF_3 carbon. The ^1H NMR data for **1** compares with those for the iron analog $[(\eta^5\text{-}C_5Me_4CF_3)Fe(\mu\text{-CO})(CO)]_2$ (**2**),[2c] which shows a quartet at 1.84 ppm ($^5J_{HF}$ = 1.2 Hz) and a singlet at 1.59 ppm (in chloroform-*d*). The $^{13}C\{^1H\}$ 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 ($^1J_{CF}$ = 272 Hz). The IR spectrum of **1** in dichloromethane shows ν(CO) bands at 1958 and 1776 cm^{-1} for the terminal and bridging carbonyls, respectively, while in Nujol the ν(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 η^5-C_5H_5 and η^5-C_5Me_5 parent analogs.



(1)

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Attempts to improve the yield of **1** using norbornene as a hydrogen acceptor[4,5] in the reaction of $HC_5Me_4CF_3$ with $Ru_3(CO)_{12}$ were unsuccessful. In contrast, our group[5] and Paquette and co-workers[4] have successfully used this approach for the preparation of other Fe and Ru dicarbonyl cyclopentadienyl complexes. In this case, reaction of $HC_5Me_4CF_3$ and $Ru_3(CO)_{12}$ resulted in the formation of reasonable amounts of the triply bridging alkene adduct $[(\mu\text{-H})_2Ru_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_7H_8)]$ (**A**), which was characterized by ^1H, ^{13}C, and $^{13}C\{^1H\}$ 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 ν(CO) stretching frequencies for **1** and **2** are similar to those of their η^5-C_5H_5 analogs. In contrast, the IR stretching frequencies of the ruthenium and iron η^5-C_5Me_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 η^5-C_5H_5 and η^5-$C_5Me_4CF_3$ 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 $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-CO})(CO)]_2$,[9] $[(\eta^5\text{-}C_5Me_5)Fe(\mu\text{-CO})(CO)]_2$,[10] and $(\eta^5\text{-}C_5Me_4Et)Ru(\mu\text{-CO})(CO)]_2$[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 $[(\eta^5\text{-}C_5H_5)M(\mu\text{-CO})(CO)]_2$ (M = 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 ν(CO) bands are observed for both **1** and **2**, whereas the η^5-C_5H_5 analogs have complex IR spectra in the carbonyl regions with multiple bands. However, the room-temperature $^{13}C\{^1H\}$ NMR spectra of both **1** and **2** each show only one averaged CO resonance at 224 and 240 ppm, respectively. The $^{13}C\{^1H\}$ NMR data of **1** and **2** are similar to those of the reported iron and ruthenium η^5-C_5H_5 analogs.[12] The ruthenium compound $[(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}^{13}CO)(^{13}CO)]_2$ 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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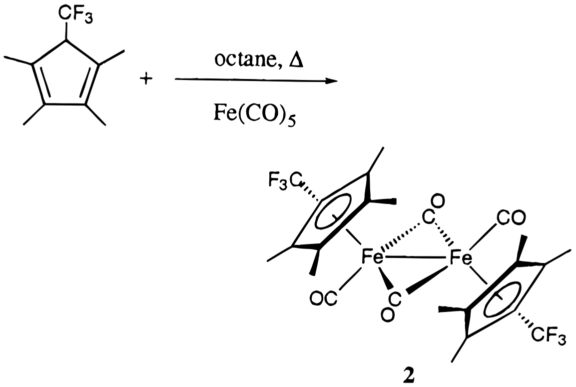
dichloromethane-d_2).[12c] A similar phenomenon was also observed for [PCpRu(μ-CO)(CO)]$_2$,[5] which also showed one averaged CO resonance at 224.5 ppm. Therefore, the ^{13}C NMR data suggest that compounds **1** and **2** are dynamic in solution and undergo a bridged-to-nonbridged equilibrium[12] that 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-$C_5Me_4CF_3$)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-C_5Me_4Et)Ru(μ-CO)-(CO)]$_2$ displays the exact same behavior as observed for **1**, gradually reacting in chlorocarbons to form [(η^5-C_5-Me_4Et)Ru(CO)$_2$(Cl)].[11] Similar to **1**, the reactions of [(η^5-C_5Me_4Et)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-$C_5Me_4CF_3$)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 $HC_5Me_4CF_3$ 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-C_5Me_5)-(CO)Fe(μ-CO)$_2$Fe(CO)(η^5-$C_5Me_4CF_3$)] by mass spectrometry. Pure samples of **2** were then prepared by oxidizing "impure" **2** with I$_2$ to make [(η^5-$C_5Me_4CF_3$)Fe(CO)$_2$(I)] followed by purification and reduction to **2** with cobaltocene (eq 3). Unlike the ruthenium analog **1**, compound **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.



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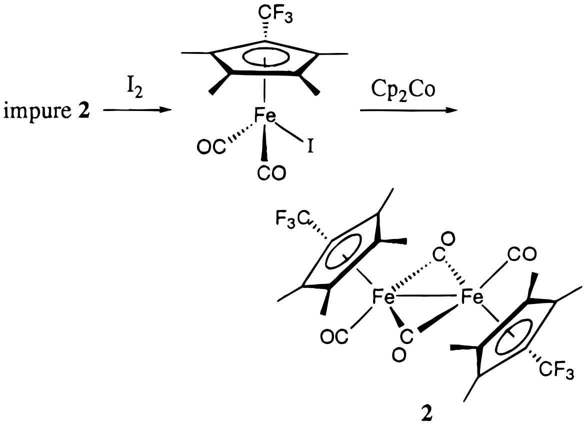

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(3)

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-C_5H_5 and η^5-C_5Me_5 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-$C_5Me_4CF_3$ ligands and two terminal and two symmetrically bridging carbonyl ligands. There is a crystallographic center of symmetry located midway between the metal atoms. The CF$_3$ groups are oriented *anti* with respect to one another in accordance with the center of symmetry. Compounds **1** and **2** are isostructural and isomorphic.

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-C_5-Me_5 analog than to those of the η^5-C_5H_5 analog. The Ru−Ru distance of 2.735(2) Å in the η^5-C_5H_5 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-C_5Me_5 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-C_5Me_5 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-C_5H_5 and the η^5-C_5-Me_5 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 CF$_3$ group on the η^5-$C_5Me_4CF_3$ ring which is in close proximity to the terminal CO ligand. However, it is noted that the overall electron-withdrawing effect of the CF$_3$ group in **1** and **2** is approximately balanced by the electron-donating effect of the four methyl groups on the C$_5$ ring,

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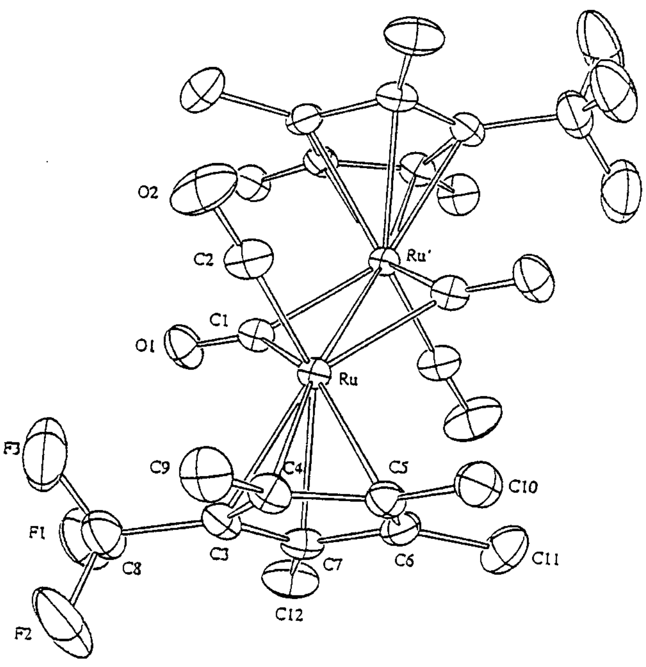

Figure 1. Structural drawing of $[(\eta^5\text{-}C_5Me_4CF_3)Ru(\mu\text{-}CO)(CO)]_2$ (**1**) showing the atom-numbering scheme (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

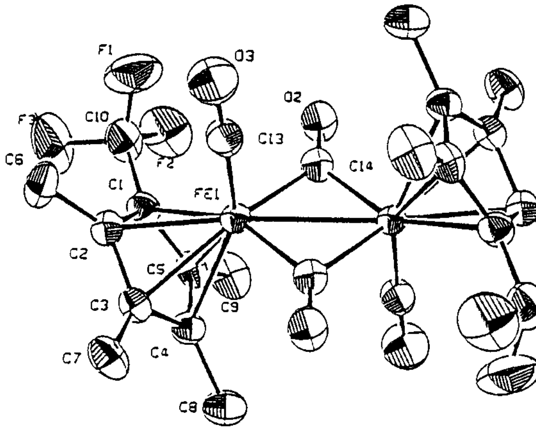

Figure 2. Structural drawing of $[(\eta^5\text{-}C_5Me_4CF_3)Fe(\mu\text{-}CO)(CO)]_2$ (**2**) showing the atom-numbering scheme (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $[(\eta^5\text{-}C_5Me_4CF_3)Ru(\mu\text{-}CO)(CO)]_2$ (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*-$[(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}CO)(CO)]_2$ (1968, 1768 cm^{-1}) and *trans*-$[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)(CO)]_2$ (1955, 1773 cm^{-1})).

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $[(\eta^5\text{-}C_5Me_4CF_3)Fe(\mu\text{-}CO)(CO)]_2$ (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−*C*−CF_3) are closer to the metal atoms than to the ring carbons bound to the CH_3 groups (metal−*C*−CH_3). The Ru−*C*(CF_3) bond distance of 2.230(2) Å is shorter than the four Ru−*C*(CH_3) carbon distances, which range from 2.238(2) to 2.311(3) Å. The Fe−*C*(CF_3) bond distance of 2.085(4) Å is also shorter than the remaining Fe−*C*(CH_3) distances of 2.119(4)−2.167(4) Å. In each case, the largest observed distance differential between the metal−*C*(CF_3) carbon distance and the longest metal−*C*(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 $[(\eta^5\text{-}C_5Me_4CF_3)Fe(\eta^5\text{-}C_5H_5)]$, where the Fe−*C*($CF_3$) carbon distance of 2.007(6) Å is shorter than the remaining Fe−*C*(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 η^5-$C_5Me_4CF_3$ and η^5-C_5Me_5 ligands are very similar.

Because of the similarity of the η^5-$C_5Me_4CF_3$ and η^5-C_5Me_5 ligands, this study confirms previous arguments that the *trans* geometry of $[(\eta^5\text{-}C_5R_5)M(\mu\text{-}CO)(CO)]_2$ 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*-$[(\eta^5\text{-}C_5Me_5)Fe(\mu\text{-}CO)(CO)]_2$ 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*-$[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)(CO)]_2$ of 54 ± 8 kcal mol^{-1}. The authors state that "it is not yet clear whether the higher activation barrier {for $[(\eta^5\text{-}C_5Me_5)Fe(\mu\text{-}CO)(CO)]_2$} 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 $[\{\eta^5\text{-}C_5Me_4(SiMe_2NMe_2)\}Fe(\mu\text{-}CO)(CO)]_2$ 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 η^5-C_5R_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-C_5H_5 , η^5-$C_5Me_4CF_3$, η^5-C_5Me_5; M = Fe, Ru) Complexes

compd	M–M	M–Cp′[a]	M–CO terminal	M–CO bridging[b]	ref
[(η^5-C_5H_5)Ru(μ-CO)(CO)]$_2$	2.735(2)[c]	1.915	1.855(14)	1.986(13)	14
[(η^5-$C_5Me_4CF_3$)Ru(μ-CO)(CO)]$_2$ (**1**)	2.7613(4)	1.924	1.865(3)	2.044(3)	*d*
[(η^5-C_5Me_5)Ru(μ-CO)(CO)]$_2$	2.752(1)	1.917	1.866(3)	2.041(3)	9
[(η^5-C_5H_5)Fe(μ-CO)(CO)]$_2$	2.534(2)	1.754	1.748(6)	1.914(5)	15a
[(η^5-$C_5Me_4CF_3$)Fe(μ-CO)(CO)]$_2$ (**2**)	2.563(1)	1.766	1.733(5)	1.918(4)	*d*
[(η^5-C_5Me_5)Fe(μ-CO)(CO)]$_2$	2.560(1)	1.764	1.753(3)	1.929(3)	10

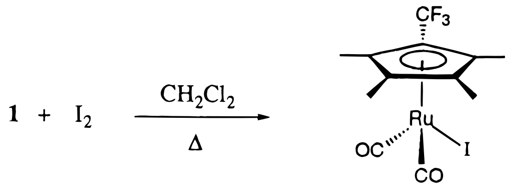
[a] M-Cp′ = metal–centroid of cyclopentadienyl ring distance. [b] Average distances. [c] Standard deviations are given in parentheses. [d] This work.

Table 5. Infrared Carbonyl Stretching Frequencies of [(η^5-Cp′)M(CO)$_2$(I)] (η^5-Cp′ = η^5-C_5H_5, η^5-$C_5Me_4CF_3$, η^5-C_5Me_5; M = Fe, Ru) Complexes[a]

compd	ν(CO), cm^{-1}	ref
[(η^5-C_5H_5)Ru(CO)$_2$(I)]	2048, 1997	18
[(η^5-$C_5Me_4CF_3$)Ru(CO)$_2$(I)] (**3b**)	2060, 1998	this work
[(η^5-C_5Me_5)Ru(CO)$_2$(I)]	2030, 1981	19

[a] CH_2Cl_2 solvent.

Preparation of [(η^5-$C_5Me_4CF_3$)Ru(CO)$_2$(I)] (3b). Treatment of **1** with I_2 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 $^{13}C\{^1H\}$ NMR spectrum of **3b** in chloroform-*d* include the resonance at 195.43 ppm for the carbonyl ligands and a quartet for the unique CF_3 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-C_5H_5 and η^5-C_5Me_5 analogs for comparison.



(4)

3b

Analysis of the data in Table 5 shows that the ν(CO) stretching frequencies for **3b** are similar to those of the η^5-C_5H_5 analog. Compound **3b** was also characterized by X-ray crystallography to extend the structural database for the η^5-$C_5Me_4CF_3$ ligand.

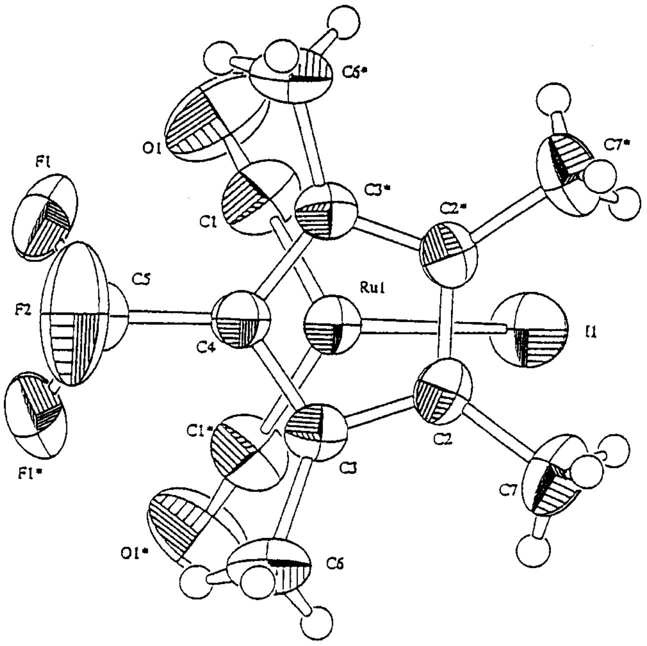


Figure 3. Structural drawing of [(η^5-$C_5Me_4CF_3$)Ru(CO)$_2$-(I)] (**3b**) showing the atom-numbering scheme (50% probability ellipsoids).

Table 6. Selected Bond Distances (Å) and Bond Angles (deg) for [(η^5-$C_5Me_4CF_3$)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)

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-$C_5Me_4CF_3$, 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-$C_5Me_4CF_3$ ligand is 1.878 Å, which is shorter than the Ru-η^5-$C_5Me_4CF_3$ centroid distance in **1** (1.917 Å). Similar to what was observed in the structures of **1** and **2**, the metal–*C*(CF_3) carbon distance in **3b** is shorter than the remaining metal–*C*(CH_3) carbon distances. The Ru–*C*(CF_3) bond distance of 2.152(6) Å is significantly shorter than the Ru–*C*(CH_3) and Ru–*C*(CH_3) bond distances of 2.249(4) and 2.264(4) Å, respectively. In comparison, the largest metal to ring-carbon distance differential in **3b** (0.11 Å) is greater than the largest differential (0.08 Å) observed for **1** or **2**. The CF_3 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-C_5H_5 and η^5-C_5Me_5 iodo analogs of **3b** are not known; however, the structures of [PCpRu(CO)$_2$(I)]^5 and [(η^5-C_5Me_4Et)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-C_5Me_4Et 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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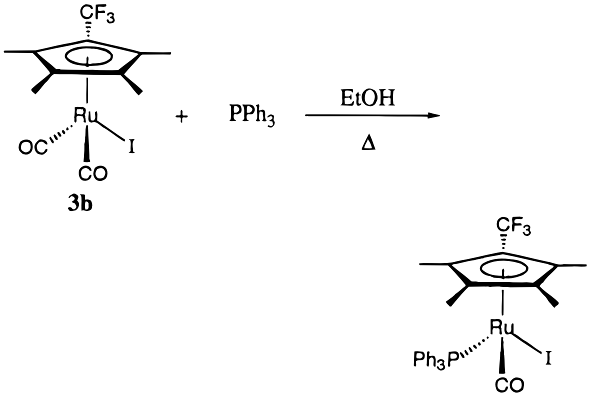
2.708(1) Å in the [PCpRu(CO)$_2$(I)] compound. In the η^5-C_5Me_4Et compound, the ethyl group is *anti* to the bromide and lies on the mirror plane of the molecule, which is similar to what is observed for the CF_3 group in **3b**.

Compound **3b** may represent a convenient starting point for other derivatives of the type [(η^5-$C_5Me_4CF_3$)Ru(CO)(L)(I)], where L is a neutral, two-electron-donor ligand. The utility of [(η^5-C_5H_5)Ru(CO)$_2$(I)],[3c,21,22] [(η^5-C_5Me_5)Ru(CO)$_2$(I)],[3d] and [(η^5-C_5Me_4Et)Ru(CO)$_2$(I)][23] as starting materials for such derivatives has been established.

Preparation of [(η^5-$C_5Me_4CF_3$)Ru(CO)(PPh$_3$)(I)] (4). Treatment of **3b** with 1.5 equiv of PPh$_3$ 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 PPh$_3$ in the presence of 2 equiv of $(CH_3)_3NO$; however, compound **4** was the only tractable product. Compound **4** is chiral at ruthenium, and the ^{1}H 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 ^{31}P{^{1}H} 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-C_5H_5)Ru(CO)(PPh$_3$)(I)] in CS_2.[22] One noteworthy fact about the preparation of compound **4** is that the CF_3 group was not esterified to the ethyl ester (CO_2Et) by the action of refluxing ethanol. This contrasts with the reported example of η^5-$C_5Me_4CF_3$ esterification observed when [(η^5-$C_5Me_4CF_3$)RhCl$_2$]$_2$ was reacted with diphenylvinylphosphine in refluxing ethanol.[24]



3b

4

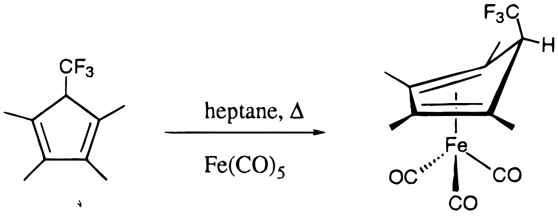
(5)

Failure to displace both CO ligands from **3b** is not surprising, since this is usually difficult for complexes of the type [(η^5-C_5R_5)M(CO)$_2$(X)] (R = H, Me$_4$Et; M = Ru; X = Cl, Br, I).[23,25] However, at least *one* example has been reported where compounds of the type [(η^5-C_5H_5)Ru(L)$_2$(H)] (L = chelating phosphine) were prepared from [(η^5-C_5H_5)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-$C_5Me_4CF_3$ analog of [(η^5-C_5Me_5)RuCl$_2$]$_2$[26] is not known. We have previously shown that treatment of $RuCl_3 \cdot xH_2O$ with $HC_5Me_4CF_3$ affords the ruthenocene [(η^5-$C_5Me_4CF_3$)$_2$Ru] as the sole product.[2b]

Table 7. Infrared Carbonyl Stretching Frequencies of [(η^4-HCp′)Fe(CO)$_3$] (η^4-Cp′ = η^4-HC_5H_5, η^4-$HC_5Me_4CF_3$, η^4-HC_5Me_5) Complexes[a]

compd	ν(CO), cm^{-1}	ref
[(η^4-HC_5H_5)Fe(CO)$_3$]	2048, 1981, 1974	27b
[(η^4-$HC_5Me_4CF_3$)Fe(CO)$_3$] (**5**)	2040, 1975, 1969	this work
[(η^4-HC_5Me_5)Fe(CO)$_3$]	2031, 1964, 1955[b]	28b

[a] Hexane solution. [b] Methylcyclohexane solution.



5

(6)

Preparation of [(η^4-$HC_5Me_4CF_3$)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-$HC_5Me_4CF_3$)Fe(CO)$_3$] (**5**). Treatment of iron pentacarbonyl with $HC_5Me_4CF_3$ in refluxing heptane results in the formation of **5** in 13% yield (eq 6). The most notable feature in the ^{1}H 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 CF_3 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-C_5(1-H)(1-CF_3)(2-CF_3)(3-OCH_3)(4-H)(5-OCH_2CH_3)]Fe(CO)$_3$, with a CF_3 group in the endo position was recently reported.[27a] Only one isomer of **5** is observed by ^{1}H NMR spectroscopy at room temperature and at temperatures up to 80 °C (in toluene-d_8). The IR spectral data for **5** are listed in Table 7 along with those of the η^4-HC_5H_5 and η^4-HC_5Me_5 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-HC_5H_5)Fe(CO)$_3$] analog.[27b] This indicates that the η^4-$HC_5Me_4CF_3$ ligand in **5** is slightly more electron donating than the η^4-HC_5H_5 ligand in its analogous iron complex. In contrast, the ν(CO) values for all of the η^5-$C_5Me_4CF_3$ metal complexes discussed above are more similar to those of their η^5-C_5H_5 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-$C_5Me_4CF_3$ coordinated ligand than in **5**.

Compound **5** is an air-stable, sublimable solid, whereas the related derivatives $[(\eta^4\text{-}HC_5H_5)Fe(CO)_3]$[27b] and $[(\eta^4\text{-}HC_5Me_5)Fe(CO)_3]$[28] are air-sensitive, oily liquids. In the case of **5**, the electron-withdrawing nature and steric bulk of the η^4-$HC_5Me_4CF_3$ 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 CF_3 group is *endo* with respect to the metal center; however, no further attempts were made at characterization.

The previously reported $[(\eta^4\text{-}HC_5H_5)Fe(CO)_3]$ and $[(\eta^4\text{-}HC_5Me_5)Fe(CO)_3]$ complexes are believed to be intermediates in the preparation of $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)(CO)]_2$ and $[(\eta^5\text{-}C_5Me_5)Fe(\mu\text{-}CO)(CO)]_2$, 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.

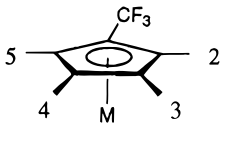
Summary

The chemistry of iron and ruthenium carbonyl dimers of the type $[(\eta^5\text{-}C_5R_5)M(\mu\text{-}CO)(CO)]_2$ (M = Fe, Ru; R = H, Me) is vast.[3] The compounds $[(\eta^5\text{-}C_5Me_4CF_3)Ru(\mu\text{-}CO)(CO)]_2$ (**1**) and $[(\eta^5\text{-}C_5Me_4CF_3)Fe(\mu\text{-}CO)(CO)]_2$ (**2**) represent suitable precursors to other iron and ruthenium compounds containing the sterically demanding, electron-withdrawing η^5-$C_5Me_4CF_3$ 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-C_5Me_5 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 $[(\eta^5\text{-}C_5Me_4CF_3)Ru(CO)_2(Cl)]$ (**3a**). Compound **1** reacts with I_2 to produce $[(\eta^5\text{-}C_5Me_4CF_3)\text{-}Ru(CO)_2(I)]$ (**3b**), which in turn reacts with PPh_3 to form $[(\eta^5\text{-}C_5Me_4CF_3)Ru(CO)(PPh_3)(I)]$ (**4**) in reasonable yield. The compound $[(\eta^4\text{-}HC_5Me_4CF_3)\text{-}Fe(CO)_3]$ (**5**) is prepared from $Fe(CO)_5$ and represents a new mode of coordination for the $HC_5Me_4CF_3$ ligand. Overall, the IR spectroscopic data for **1** and **2** and their η^5-C_5H_5 analogs are very similar, and the X-ray crystallographic data for **1** and **2** suggest that the structural effects of η^5-$C_5Me_4CF_3$ and η^5-C_5Me_5 are very similar. These comparisons support the general conclusion[2a,b] that the η^5-$C_5Me_4CF_3$ ligand is electronically equivalent to η^5-C_5H_5 and sterically equivalent to the η^5-C_5Me_5 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. $HC_5Me_4CF_3$[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 CaF_2 cells, and solid-state spectra were conducted on NaCl windows. ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and ^{19}F 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 Me_4Si, while phosphorus chemical shifts are relative to external 85% H_3PO_4 (aq) with positive values downfield of the respective reference. Fluorine chemical shifts are relative to external $CFCl_3$ 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 $[(\eta^5\text{-}C_5Me_4CF_3)Ru(\mu\text{-}CO)(CO)]_2$ (1). A 50-mL Schlenk flask was charged with $Ru_3(CO)_{12}$ (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% $HC_5Me_4CF_3$ (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 $Ru_3(CO)_{12}$. The product was then purified by chromatography. The crude product was dissolved in a minimal amount of CH_2Cl_2 (about 75 mL), and enough Florisil was added to make a slurry and adsorb the product (~10 g). The CH_2Cl_2 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 $Ru_3(CO)_{12}$. Typically, 125−300 mL of hexanes was required to obtain colorless fractions. The column was then eluted with CH_2Cl_2 which gave a red-orange band that contained **1**, followed by a black band that was discarded. Typically about 400−600 mL of CH_2Cl_2 was required to completely remove **1** from the column. Solutions of **1** in CH_2Cl_2 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 CH_2Cl_2 and filtering the solution into hexanes that was twice the volume of CH_2Cl_2. 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 CH_2Cl_2, faster in $CHCl_3$, and in all cases greatly accelerated if unprotected from visible light. Mp: 218 °C dec. Anal. Calcd for $C_{24}H_{24}F_6O_4Ru_2$: C, 41.62; H, 3.49. Found: C, 41.39; H, 3.51.



^1H NMR (C_6D_6): δ 1.84 (q, $^5J_{HF}$ = 0.97 Hz, 6H, 2,5-CH_3), 1.32 (s, 6H, 3,4-CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 224.46 (br s, CO),

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[28] (a) Balakrishnan, P. V.; Maitlis, P. M. *J. Chem. Soc. A* **1971**, 1715. (b) Zou, C.; Wrighton, M. S.; Blaha, J. P. *Organometallics* **1987**, *6*, 1452.

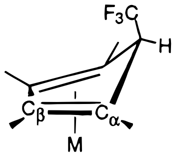
125.69 (q, $^1J_{CF}$ = 271.14 Hz, CF_3), 105.28 (q, $^4J_{CF}$ = 0.75 Hz, 3,4-CCH_3), 104.48 (q, $^3J_{CF}$ = 1.42 Hz, 2,5-CCH_3), 89.36 (q, $^2J_{CF}$ = 35.87 Hz, CCF_3), 10.30 (q, $^4J_{CF}$ = 2.10 Hz, 2,5-CH_3), 8.70 (s, 3,4-CH_3). ^{19}F NMR (C_6D_6): δ −52.59 (sep, $^5J_{HF}$ = 0.97 Hz). IR (CH_2Cl_2): ν(CO) 1958, 1776 cm^{-1}. IR (Nujol): ν(CO) 1955, 1767 cm^{-1} (^{13}CO satellites 1918, 1738). ^1H NMR ($CDCl_3$): δ 2.05 (q, $^5J_{HF}$ = 1.2 Hz, 6H, 2,5-CH_3), 1.72 (s, 6H, 3,4-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 224.15 (br s, CO), 124.51 (q, $^1J_{CF}$ = 271.15 Hz, CF_3), 104.76 (q, $^4J_{CF}$ = 0.75 Hz, 3,4-CCH_3), 103.92 (q, $^3J_{CF}$ = 1.51 Hz, 2,5-CCH_3), 88.83 (q, $^2J_{CF}$ = 35.95 Hz, CCF_3), 10.02 (q, $^4J_{CF}$ = 2.10 Hz, 2,5-CH_3), 8.60 (s, 3,4-CH_3).

Reaction of 1 in $CDCl_3$: Formation of [(η^5-$C_5Me_4CF_3$)-Ru(CO)$_2$(Cl)] (3a). In an NMR tube, a $CDCl_3$ 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 $CDCl_3$ for spectroscopic characterization. No further attempts were made to purify the product **3a**. ^1H NMR ($CDCl_3$): δ 2.12 (q, $^5J_{HF}$ = 1.2 Hz, 6H, 2,5-CH_3), 1.92 (s, 6H, 3,4-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 195.67 (s, CO), 124.33 (q, $^1J_{CF}$ = 271.53 Hz, CF_3), 105.74 (q, $^3J_{CF}$ = 1.38 Hz, 2,5-CCH_3), 103.06 (q, $^4J_{CF}$ = 0.50 Hz, 3,4-CCH_3), 80.55 (q, $^2J_{CF}$ = 36.83 Hz, CCF_3), 10.55 (q, $^4J_{CF}$ = 2.26 Hz, 2,5-CH_3), 9.24 (s, 3,4-CH_3). IR ($CDCl_3$): ν(CO) 2063, 2014 cm^{-1}.

Preparation of [(η^5-$C_5Me_4CF_3$)Ru(CO)$_2$(I)] (3b). Under a nitrogen atmosphere a Schlenk flask was charged with 30 mL of CH_2Cl_2, I_2 (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 CH_2Cl_2 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 $C_{12}H_{12}F_3IO_2Ru$: C, 30.46; H, 2.56. Found: C, 30.35; H, 2.42. ^1H NMR ($CDCl_3$): δ 2.23 (q, $^5J_{HF}$ = 0.95 Hz, 6H, 2,5-CH_3), 2.14 (s, 6H, 3,4-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 195.43 (q, $^4J_{CF}$ = 1.09 Hz, CO), 124.21 (q, $^1J_{CF}$ = 271.51 Hz, CF_3), 104.79 (q, $^3J_{CF}$ = 1.42 Hz, 2,5-CCH_3), 102.04 (q, $^4J_{CF}$ = 0.75 Hz, 3,4-CCH_3), 82.66 (q, $^2J_{CF}$ = 36.77 Hz, CCF_3), 11.08 (q, $^4J_{CF}$ = 2.14 Hz, 2,5-CH_3), 10.59 (s, 3,4-CH_3). ^{19}F NMR ($CDCl_3$): δ −54.34 (sep, $^5J_{HF}$ = 0.95 Hz). IR (CH_2Cl_2): ν(CO) cm^{-1} 2060, 1998. IR (Nujol): ν(CO) 2040, 1984 cm^{-1}.

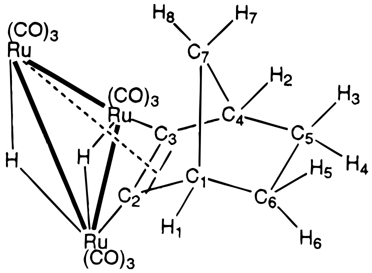
Preparation of [(η^5-$C_5Me_4CF_3$)Ru(CO)(PPh$_3$)(I)] (4). Under a nitrogen atmosphere, to a suspension of **3b** (0.4 g, 0.84 mmol) in 45 mL of absolute ethanol was added triphenylphosphine (0.47 g, 1.8 mmol). The reaction mixture was refluxed for 48 h and the solution gradually turned from orange 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 CH_2Cl_2 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 CH_2Cl_2, and all solvents were removed *in vacuo*. By $^{31}P\{^1H\}$ 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 $C_{29}H_{27}F_3IOPRu$: C, 49.23; H, 3.85. Found: C, 49.18; H, 3.73. ^1H NMR ($CDCl_3$): δ 7.56−7.35 (m, 15H, Ph), 2.15 (br m, 3H, 2- or 5-CH_3), 1.74 (d, $^4J_{PH}$ = 1.5 Hz, 3H, 3- or 4-CH_3), 1.56 (br m, 3H, 2- or 5-CH_3), 1.51 (d, $^4J_{PH}$ = 1.0 Hz, 3- or 4-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 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, CF_3), 101.23 (dq, $^2J_{PC}$ = 3.3 Hz, $^3J_{CF}$ = 1.6 Hz, 2- or 5-CCH_3), 99.73 (br s, 3- or 4-CCH_3), 99.09 (dq, $^2J_{PC}$ = 3.5 Hz, $^4J_{CF}$ = 0.75 Hz, 3- or 4-CCH_3), 98.44 (dq, $^2J_{PC}$ = 3.1 Hz, $^3J_{CF}$ = 1.45 Hz, 2- or 5-CCH_3), 81.48 (qd, $^2J_{CF}$ = 35.5 Hz, $^2J_{PC}$ = 2.9 Hz, CCF_3), 11.43 (q, $^4J_{CF}$ = 1.0 Hz, 2- or 5-CH_3), 10.45 (d, $^3J_{CP}$ = 0.88 Hz, 3- or 4-CH_3), 10.10 (q, $^4J_{CF}$ = 2.0 Hz, 2- or 5-CH_3), 9.55 (s, 3- or 4-CH_3). ^{19}F NMR ($CDCl_3$): δ −53.38 (m). IR (CH_2Cl_2): ν(CO) 1953 cm^{-1}. IR (Nujol): ν(CO) 1936 (sh 1949 w, 1966 m) cm^{-1}.

Preparation of [(η^4-$HC_5Me_4CF_3$)Fe(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 $HC_5Me_4CF_3$ (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 $C_{13}H_{13}F_3FeO_3$: C, 47.30; H, 3.97. Found: C, 47.15; H, 4.00.



^1H NMR ($CDCl_3$): δ 3.19 (q, $^3J_{HF}$ = 6.5 Hz, 1H, H), 2.13 (s, 6H, $CH_{3\alpha}$), 1.52 (s, 6H, $CH_{3\beta}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 211.98 (s, CO), 122.49 (q, $^1J_{CF}$ = 291.0 Hz, CF_3), 102.10 (q, $^4J_{CF}$ = 0.9 Hz, C_β=C), 65.41 (q, $^2J_{CF}$ = 24.2 Hz, CCF_3), 60.80 (q, $^3J_{CF}$ = 1.7 Hz, C=C_α), 15.27 (q, $^4J_{CF}$ = 0.8 Hz, $CH_{3\alpha}$), 11.57 (s, $CH_{3\beta}$). ^{19}F NMR ($CDCl_3$): δ −72.96 (d, $^3J_{HF}$ = 6.5 Hz). IR (cyclohexane): ν(CO) 2039, 1973, 1967 cm^{-1}. MS: *m/e* calcd for $C_{13}H_{13}FeO_3$ 330.016 62, found 330.014 13.

Spectroscopic Data for [(μ-H)$_2$Ru$_3$(CO)$_9$(μ_3-η^1:η^2:η^1-C_7H_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, $CDCl_3$): δ 3.19 (apparent tt, $^3J(H_1H_7)$ = $^3J(H_1H_8)$ = 2.0 Hz, $^3J(H_1H_5)$ = $^3J(H_1H_6)$ = 1.35 Hz, 2H, $H_{1,2}$), 1.90 (m, 2H, $H_{3,5}$), 1.35 (apparent dt, $^2J(H_7H_8)$ = 9.3 Hz, $^4J(H_4H_8)$ = $^4J(H_6H_8)$ = 3.9 Hz, 1H, H_8), 1.20 (m, $^2J(H_3H_4)$ = 4.50 Hz, $^4J(H_4H_8)$ = 3.9 Hz, $^3J(H_4H_5)$ = 2.4 Hz, 2H, $H_{4,6}$), 0.68 (m, $^2J(H_7H_8)$ = 9.3 Hz, $^3J(H_1H_7)$ = $^3J(H_2H_7)$ = 2.0 Hz, $^4J(H_3H_7)$ = $^4J(H_5H_7)$ = 2.1 Hz, 1H, H_7), −16.8 (broad, 1H, RuH), −20.2 (broad, 1H, RuH). ^{13}C NMR (75.58 MHz, $CDCl_3$): 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, C_7), 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 ($CDCl_3$): ν(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	$C_{24}H_{24}O_4F_6Ru_2$	$C_{24}H_{24}O_4F_6Fe_2$	$C_{12}H_{12}F_3O_2RuI$
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	$\theta/2\theta$	ω-2θ	ω-2θ
scan rate (deg/min in ω)	variable	16.5	16.0
scan width (deg)	$1.06 + 0.34 \tan \Theta$	$0.60 + 0.35 \tan \Theta$	$1.47 + 0.35 \tan \Theta$
$2\theta_{max}$ (deg)	54	51.9	45.0
no. of rflns collcd	3393	2621	1143
no. of unique rflns	3191	2515	1050
no. of observns ($I > 3\sigma(I)$) (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] $I > 2\sigma(I)$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{0.5}$.

[(η^5-$C_5Me_4CF_3$)Ru(μ-CO)(CO)]$_2$ (1). Red-orange crystals of **1** were grown by slow diffusion of hexanes into a saturated CH_2Cl_2 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 $B(H) = 1.3B_{eqv}(C)$ Å. Fourier difference maps revealed no significant maxima. Neutral atom scattering factor coefficients and anomalous dispersion coefficients were taken from a standard source.[30]

[(η^5-$C_5Me_4CF_3$)Fe(μ-CO)(CO)]$_2$ (2). Dark purple prismatic crystals of **2** were grown from a mixture of CH_2Cl_2 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-$C_5Me_4CF_3$)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

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[29] Molen, An Interactive Structure Solution Procedure; Enraf-Nonius, Delft, The Netherlands, 1990.

[30] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2b, Table 2.2A, Table 2.3.1.

[31] Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

[32] (a) Gilmore, C. *J. Appl. Crystallogr.* **1984**, *17*, 42. (b) Beurskens, P. T. DIRDIF; Technical Report 1984/1; Crystallographic Laboratory, Toernooiveld, 6525 Ed Nijmegen, The Netherlands. (c) TEXSAN: Crystal Structure Analysis Package; Molecular Structure Corp., The Woodlands, TX, 1985, 1992.

[33] Molecular Structure Corp., 3200 Research Forest Drive, The Woodlands, TX 77381.