

Preparation, Crystal Structure, and Low-Temperature ^1H NMR Study of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-C}_5\text{H}_5)$. Reaction of $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-C}_5\text{H}_5)$ ($\text{R} = \text{Me}, \text{H}$) with Bis(trifluoromethyl)ketene

Michael E. Wright, Gregory O. Nelson,¹ and Richard S. Glass*

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

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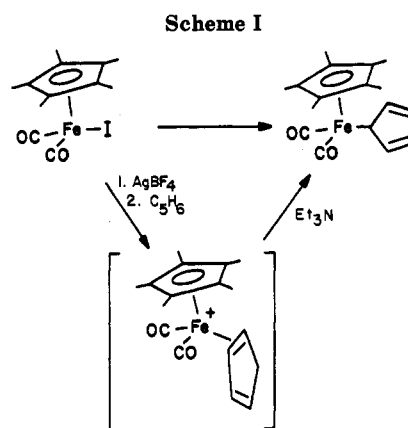
Sequential reaction of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{I}$ with silver tetrafluoroborate, cyclopentadiene, and finally triethylamine affords the new compound $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-C}_5\text{H}_5)$ (**2**) in 75% yield. Reaction of **2** with dimethyl fumarate in dichloromethane gives the [3 + 2] cycloadduct dimethyl 7-syn-[$(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2$]bicyclo[2.2.1]hept-5-ene-2-endo,3-exo-dicarboxylate in 90% yield. Competitive cycloaddition of the $\eta^1\text{-C}_5\text{H}_5$ moiety in $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-C}_5\text{H}_5)$ (**1**) and **2** with dimethyl fumarate reveals **2** to be ca. 5 times more reactive. Reaction of **1** and **2** with bis(trifluoromethyl)ketene produces the unexpected and unique 2:1 adducts $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2][1,3\text{-bis}[(\text{CF}_3)_2\text{CHCO}]$ cyclopentadienyl] (**4**, $\text{R} = \text{H}$; **5**, $\text{R} = \text{Me}$). The molecular and crystal structure for **2** is presented. Complex **2** crystallizes in the monoclinic space group $P2_1/n$ with $a = 8.591$ (2) Å, $b = 36.347$ (13) Å, $c = 10.119$ (3) Å, $\beta = 92.71$ (2)°, and $Z = 8$. The structural parameters are refined to convergence with $R_1 = 0.063$ and $R_2 = 0.084$ for 2563 reflections having $I > 3\sigma(I)$. A low-temperature ^1H NMR study reveals that the $\eta^1\text{-C}_5\text{H}_5$ ligand in **2** possesses increased fluxionality relative to analogue **1**. The increased fluxionality of the $\eta^1\text{-C}_5\text{H}_5$ ring in **2** is attributed to a combination of electronic and steric differences of the $\eta^5\text{-C}_5\text{Me}_5$ ligand relative to the $\eta^5\text{-C}_5\text{H}_5$ group.

Introduction

Metal-allyl complexes have attracted considerable attention as reagents for organic syntheses in recent years.² For example, $\text{Fp}(\eta^1\text{-C}_5\text{H}_5)$ [$\text{Fp} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$] (**1**) reacts with a variety of olefins and alkynes to yield synthetically useful [3 + 2] cycloadducts.³ Recently we have demonstrated the utility of **1** as a synthetic equivalent of methyl 1,3-cyclopentadiene-5-carboxylate by the stereospecific replacement of the iron moiety in the cycloadducts by a carbomethoxy group.^{3c}

Substitution of a phosphite for a carbon monoxide ligand enhances the reactivity of the η^1 -allyl complex $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})[\text{P}(\text{OCH}_2)_3\text{CH}](\eta^1\text{-C}_3\text{H}_5)$ by ca. 900-fold in cycloaddition reactions.⁴ This tremendous activation by electron donation encouraged us to prepare and study yet another mode of electron donation, that being through the η^5 -cyclopentadienyl ligand. In this paper full details on the synthesis and crystal structure of the new complex $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-C}_5\text{H}_5)$ (**2**) are reported as is the reaction of **2** and **1** with bis(trifluoromethyl)ketene and dimethyl fumarate. A competitive reaction of **1** and **2** with dimethyl fumarate reveals a mild increase in reactivity of **2** over **1** in the cycloaddition reaction.

The fluxional behavior of σ -bonded cyclopentadienyl ligands to a variety of metals is also of interest and is well documented.⁵ The fluxionality of **1** was studied by Cotton and co-workers⁶ and is in fact the first example where



NMR line-shape analysis was used to determine a mechanism for a fluxional process. To investigate the effect of the $\eta^5\text{-C}_5\text{Me}_5$ ligand on the fluxionality of the $\eta^1\text{-C}_5\text{H}_5$ ring in **2**, a variable-temperature ^1H NMR study has been conducted.

Results and Discussion

Preparation of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-C}_5\text{H}_5)$ (2**).** Attempts to synthesize $\text{Fp}'(\eta^1\text{-C}_5\text{H}_5)$ [$\text{Fp}' = (\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2$] (**2**) from the reaction of $\text{Fp}'\text{I}$ with either NaC_5H_5 or TiC_5H_5 were unsuccessful. However, treatment of $\text{Fp}'\text{I}$ with silver tetrafluoroborate,⁷ cyclopentadiene, and finally triethylamine^{3b} produces **2** in 75% yield (Scheme I). The reaction sequence is conveniently performed without isolation of the cationic iron-cyclopentadiene intermediate. Of the bases tried triethylamine affords **2** in the highest yields. Final purification of **2** is readily accomplished by medium-pressure chromatography on activity grade III alumina eluting with benzene.

Competitive Reaction of **1 and **2** with Dimethyl Fumarate.** Treatment of $\text{Fp}'(\eta^1\text{-C}_5\text{H}_5)$ with 1.5 equiv of

(1) Presently located at Research Laboratories, Tennessee Eastman Co., Kingsport, TN 37662.

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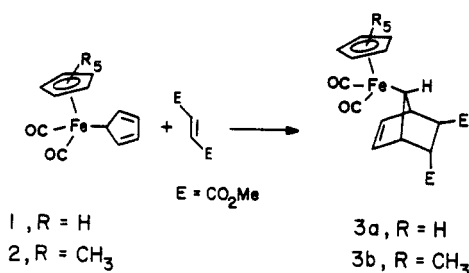
(4) Rosenblum, M.; Waterman, P. S. *J. Organomet. Chem.* 1980, 187, 267.

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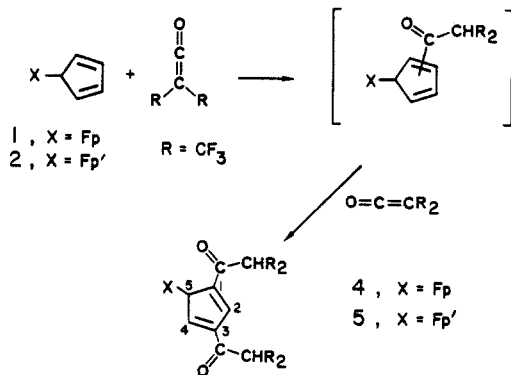
(6) Bennett, M. J.; Cotton, F. A.; Davison, A.; Faller, J. W.; Lippard, S. J.; Morehouse, S. M. *J. Am. Chem. Soc.* 1966, 88, 4371.

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Scheme II



Scheme III



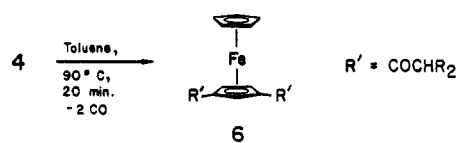
dimethyl fumarate in dichloromethane for 1 h gives **3b** as a yellow oil in 90% isolated yield. The H(7) resonance in the ¹H NMR spectrum for **3b** is 1.2 ppm upfield from the H(7) absorption in the spectrum for **3a**.^{3c} Aside from this difference the methyl esters and the signals of the remaining bicyclo[2.2.1]hept-5-ene ring protons are very similar in appearance and chemical shifts. A deuteriochloroform solution containing a ca. 50:50 mixture of complexes **1** and **2** is treated with 2 equiv of dimethyl fumarate. The progress of the reaction is monitored by ¹H NMR spectroscopy for the initial 50% of reaction. Adduct **3b** forms ca. 5 times faster than **3a**. Thus, complex **2** is approximately 5 times more reactive than **1** in the cycloaddition reaction with dimethyl fumarate.

Reaction of 1 and 2 with Bis(trifluoromethyl)ketene. Bis(trifluoromethyl)ketene is slowly bubbled into a dichloromethane solution containing Fp(η¹-C₅H₅) at 0 °C. The color of the solution changes from orange to deep red over ca. 10 min. The ketene is passed through the solution for an additional 10 min. Toluene is added to the mixture, and the dichloromethane is removed under reduced pressure. Light purple microcrystals precipitate from the solution after standing at -25 °C for 24 h.

The product from the reaction of **1** and the ketene is clearly not a [3 + 2] cycloadduct but arises from the addition of 2 equiv of the ketene to the η¹-C₅H₅ ring (Scheme III). Complex **4** is likely derived from the following sequence of events. The first equiv of ketene adds to the η¹-C₅H₅ ring that is followed by proton transfer and finally migration of the Fp moiety. This intermediate complex then reacts with the second equivalent of ketene that is followed by proton transfer. Similar behavior of this type (addition, proton transfer) is seen in the reaction of alkyl-substituted ketenes with Fp(η¹-C₅H₅)^{2b} and also in the reaction of **1** with *p*-toluenesulfonyl isocyanate.^{3b,8}

Conversion of **4** to the ferrocene derivative **6** is easily accomplished by heating the sample in toluene at 90 °C

for 20 min. The ¹H NMR spectrum of **6** gives an unre-



solved triplet at δ 5.45 (1 H), a doublet (*J* = 1.2 Hz) at 5.26 (2 H), and a singlet at 4.42 (5 H) for the cyclopentadienyl protons. These data are consistent with the ¹H NMR spectra for 1,3-diacylferrocene derivatives.⁹ It then follows that the acyl groups in **4** must be in a 1,3-substitution pattern.

The IR metal-carbonyl stretching frequencies of the product in dichloromethane appear at 2057 and 2017 cm⁻¹ and the ketone-carbonyl band at 1636 cm⁻¹. The metal-carbonyl bands are quite high for a Fp(η¹-alkyl)^{3b} compound and suggests that the iron-carbon bond in **4** has considerable ionic character. The low ketone-carbonyl band at 1636 cm⁻¹ is also consistent with the η¹-ring having considerable negative charge. The single heptet at δ 4.72 (*J*_{F-H} = 7.6 Hz) for the two CH(CF₃)₂ methine protons requires that the iron group is rapidly migrating partially or entirely around the η¹-ring. A ¹H NMR spectrum at 203 K of **4** does not show any significant broadening of the heptet at δ 4.72 or the η¹-ring proton resonances. Presumably then the energy barrier for the fluxional process is very small.¹⁰ As a consequence, it is not possible to determine a mechanism for the rearrangement. However, consecutive 1,2 shifts is the likely pathway.

Complex **2** reacts very rapidly with bis(trifluoromethyl)ketene in a similar fashion as **1**. Two equivalents of the ketene add to the η¹-C₅H₅ ligand in a 1,3 manner. The IR bands for the metal-carbonyl groups in **5** occur at 2040 and 2004 cm⁻¹ which is again consistent with an iron center possessing cationic character. The resonance at δ 5.42 (2 H) in the ¹H NMR spectrum of **5** is easily assigned to the H(4) and H(5) protons. The equivalence of these protons indicates that the iron moiety in **5** is at least rapidly migrating between carbons 4 and 5 of the η¹-ring if not all of the ring carbons.¹⁰

Crystal and Molecular Structure and Low-Temperature ¹H NMR Study of (η⁵-C₅Me₅)Fe(CO)₂(η¹-C₅H₅) (2). Complex **2** displays two sharp singlet ¹H NMR resonances at δ 5.80 (5 H) and 1.78 (15 H) at 298 K. As expected the η¹-C₅H₅ ring in **2** is clearly fluxional. Several organometallic complexes containing a fluxional η¹-C₅H₅ ring are known; however, to our knowledge this is the first example with a η⁵-C₅Me₅ ligand.¹¹ To investigate the effects of the η⁵-C₅Me₅ ligand on the fluxional behavior of the η¹-ring, the ¹H NMR spectrum of **2** was measured at various temperatures between 238 and 303 K and analyzed.¹² This analysis shows that complex **2** has a lower

(9) (a) Toma, S.; Pariciova, M.; Solcaniova, E.; Lesko, K. *Collect. Czech. Chem. Commun.* 1978, 43, 295. (b) Hisatome, M.; Tachikawa, O.; Sasho, M.; Yamakawa, K. *J. Organomet. Chem.* 1981, 217, C17.

(10) The -COCH(CF₃)₂ substituents are expected to lower the energy barrier for the fluxional process by stabilizing the developing negative charge in the cyclopentadienyl ring. The fluxional process likely involves a π-bonded η²-[C₅H₅]⁻ ligand. See discussion on the mechanism for the fluxional process in Fp(η¹-C₅H₅) and Fp'(η¹-C₅H₅) later in this paper.

(11) For examples where η¹-C₅Me₅ ligands are present see: Davison, A.; Rakita, P. E. *Inorg. Chem.* 1970, 9, 289.

(12) Fast exchange approximations were employed in analysis of the η¹-C₅H₅ resonances of both **1** and **2**. The energies of activation determined for **1** and **2** are 11.1 ± 0.2 and 9.6 ± 0.2 kcal/mol, respectively, in carbon disulfide/toluene-*d*₈ (3/1, v/v).¹³ Although our value of *E*_a for **1** is somewhat larger than that determined using ¹H NMR spectroscopy by Cotton and Marks (9.6 ± 0.1 kcal/mol)¹⁴ and Campbell and Green (8.5 ± 0.8 kcal/mol in acetone-*d*₆ as solvent),¹⁵ the difference between **1** and **2** determined by us should be quantitatively valid.

(8) The crystal structure of the adduct formed in the reaction of **1** with this isocyanate has been completed in our laboratory. The details will be published elsewhere: Wright, M. E.; Hoover, J. F.; Dobrzynski, E.; Glass, R. S., submitted for publication.

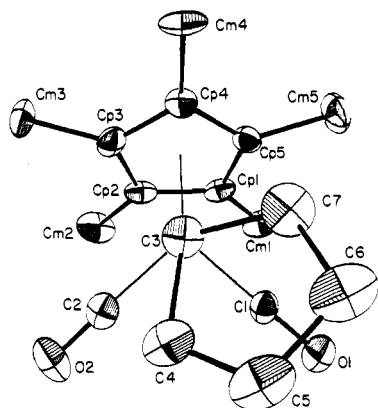


Figure 1. ORTEP drawing of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-C}_5\text{H}_5)$ (**2**) viewing head-on down the C3-Fe bond. The Fe atom is hidden directly behind the C3 ring carbon. Non-hydrogen atoms are represented by thermal ellipsoids drawn to encompass 30% of the electron density.

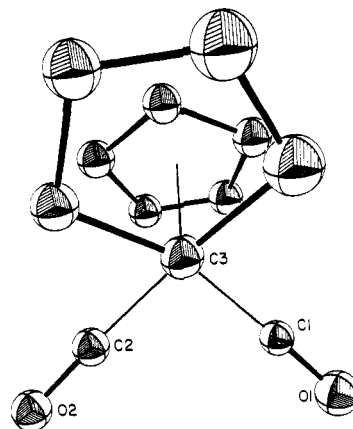


Figure 2. ORTEP drawing of $(\eta^1\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{Me}_5)$ (**1**) looking head-on down the C3-Fe bond. The Fe atom is hidden directly behind the C3 ring carbon. Non-hydrogen atoms are represented by thermal spheres drawn to encompass 30% of the electron density.

Table I. Selected Bond Lengths (Å) and Angles (deg) in Crystalline $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-C}_5\text{H}_5)$ ^a

Bond Lengths			
Fe1-C1	1.731 (11)	C3-C4	1.466 (17)
Fe1-C2	1.763 (12)	C4-C5	1.361 (20)
Fe1-C3	2.146 (10)	C5-C6	1.477 (22)
C1-O1	1.152 (15)	C6-C7	1.356 (20)
C2-O2	1.161 (15)	C7-C3	1.469 (17)
Bond Angles			
C1-Fe1-C2	96.5 (6)	Fe1-C3-C4	109.9 (8)
C1-Fe1-C3	89.3 (6)	Fe1-C3-C7	107.2 (8)
C2-Fe1-C3	90.3 (6)	C3-C4-C5	108.8 (10)
Fe1-C1-O1	177.6 (8)	C4-C5-C6	109.9 (11)
Fe1-C2-O2	176.4 (10)	C5-C6-C7	105.9 (11)
		C6-C7-C3	111.4 (10)

^a The numbers in parentheses are the estimated standard deviations in the last significant digit(s).

^b Atoms are labeled in agreement with Figure 1.

energy of activation for the fluxional process than **1**¹² by about 1.5 kcal/mol. This result is discussed below in light of the structural and electronic differences between **1** and **2**. By line-shape analysis of the spectra for **2** the mechanism of the rearrangement process appears analogous to that previously assigned for **1**, that is, consecutive 1,2 shifts.

To lend further insight into the increased fluxionality of **2** relative to **1**, the molecular structure of **2** is determined by a single-crystal X-ray study. Related crystal structures have been reported for $(\text{C}_5\text{H}_5)_3\text{Ti}$,¹⁶ $(\text{C}_5\text{H}_5)_3\text{MoNO}$,¹⁷ $(\text{C}_5\text{H}_5)_4\text{Ti}$,¹⁸ and $(\text{C}_5\text{H}_5)_3\text{Sb}$,¹⁹ which all possess a σ -bonded cyclopentadienyl ligand. Complex **2** is found to crystallize in the space group $P2_1/n$ (an alternate setting of $P2_1/c$, No. 14) with two molecules per asymmetric unit. The two

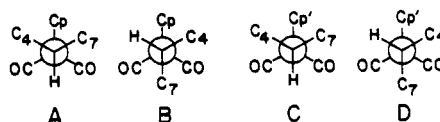


Figure 3. Newman projection formulas of **1** and **2** viewed down the C3-Fe bond. In A-D, the C3 atoms is at the front and the Fe atom with its coordination sphere is depicted as the rear. For clarity, $\eta^5\text{-C}_5\text{H}_5$ and $\eta^5\text{-C}_5\text{Me}_5$ are represented as Cp and Cp', respectively.

crystallographically independent molecules are structurally identical within the precision of the X-ray study (applying $\geq 3\sigma$ as a significant difference). An ORTEP drawing of one of the molecules of **2** in the asymmetric unit and the labeling scheme employed is shown in Figure 1. Selected geometric parameters for **2** are given in Table I. A complete listing of anisotropic thermal parameters and bond lengths and angles for **2** can be found in Tables A-D of the supplementary material.

A comparison of the ORTEP views for **2** and **1**²⁰ shown in Figures 1 and 2, respectively, reveals a major difference in the orientation of the $\eta^1\text{-C}_5\text{H}_5$ ligand with respect to the $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2$ unit. The only major geometric difference found between **1** and **2** is this rotation of 120° about the C(3)-Fe bond. Possible staggered (or minimum energy) conformational isomers about the C(3)-Fe bond for **1** and **2** are shown in Figure 3 as Newman projection formulas. For clarity, the $\eta^5\text{-C}_5\text{R}_5$ (Cp, R = H; Cp', R = Me) ligand attachment to the iron is represented by a single "bond" to the center of the five-membered ring. This simplification permits the iron to have pseudotetrahedral geometry.

The C(4) and C(7) carbons are expected to be found in the sterically least hindered position relative to the other ligands on the metal.²¹ On the basis of this assumption, the observed rotamer A in the crystal structure of **1** indicates that Cp poses a smaller steric demand than the CO ligands. In contrast, rotamer D for complex **2** that is observed in the crystalline state suggests that Cp' has a larger steric interaction with the $\eta^1\text{-C}_5\text{H}_5$ ring than does CO. This comparison shows that the steric requirements of the ligands attached to the iron are in the order Cp' > CO > Cp, as probed by the η^1 -cyclopentadienyl ring. Four metal-carbonyl bands at 2022, 2016, 1973, and 1966 cm^{-1} are

(13) The effect of different solvents on the energy barrier for the fluxional process requires comment. The energies of activation determined by us for **1** in carbon disulfide/toluene- d_8 (3/1, v/v) and acetone- d_6 are similar: 11.1 ± 0.2 and 10.3 ± 0.2 kcal/mol, respectively. However, the E_a for **2** in carbon disulfide/toluene- d_8 (3/1, v/v) differs enormously from that in deuteriochloroform: 9.6 ± 0.2 and 14.2 ± 0.2 kcal/mol, respectively. Further studies on the effect of solvent on the fluxional process are in progress.

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(15) Campbell, C. H.; Green, M. L. H. *J. Chem. Soc. A*. **1970**, 1318.

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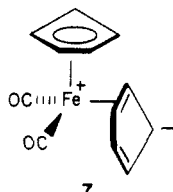
(19) Birkhahn, M.; Krommes, P.; Massa, W.; Lorberth, J. *J. Organomet. Chem.* **1981**, *208*, 161.

(20) The ORTEP drawings of **1** use atomic coordinates and isotropic thermal parameters from the structure determination by Cotton and co-workers (see ref 6) with permission from the authors.

(21) Reger, D. L.; Coleman, C. *J. Inorg. Chem.* **1979**, *18*, 3155.

found for 1 in cyclohexane by high-resolution infrared spectroscopy.¹⁴ The four bands are a consequence of the two unique rotamers of 1, A and B, which exist in rapid equilibrium in solution. However, for complex 2 only two metal-carbonyl infrared bands are found in the high-resolution (0.7 cm⁻¹) spectrum. This implies that 2 does not exist in both rotamers C and D, but rather only D which is observed in the crystal structure.

The mechanism established for the fluxional process of the η^1 -C₅H₅ ring is 1,2 shifts of the metal group around the five-membered carbon ring.^{6,12,22} The 1,2 shifts likely involve the σ -bonded η^1 -C₅H₅ ligand rearranging to a π -bonded ligand, η^2 -[C₅H₅⁻], and then back to the σ -bonded ligand.⁶ In the present system a π -bonded complex would be a zwitterion with a positively charged iron and an allylic anion depicted as 7.



The relative ease of the rearrangement process has been interpreted in terms of the concept of "hard" and "soft" bases.²³ σ -Bonded organic groups are harder than corresponding π -bonded moieties due to the greater polarizability of the π -electron cloud compared with the more localized σ -orbitals.²⁴ Applying these principles, it appears reasonable that the iron center is "softer" with the η^5 -C₅Me₅ ligand and would tend to favor the π -bonded complex. This factor could stabilize the zwitterion intermediate (or transition state) and hence lower the energy barrier for the rearrangement.

Another factor that might contribute to a lower barrier for forming the π -bonded complex is the orientation of the η^1 -C₅H₅ ring. In 2 the η^1 -C₅H₅ ligand is positioned such that it can "slide" into a π -bonded compound with the η^2 -[C₅H₅⁻] group positioned in the most stable rotamer.²⁵ Whereas for complex 1, the η^1 -Cp ring exists in two rotamers,¹⁴ only one of these would lead to the more stable η^2 -Cp rotamer.

Summary and Conclusions

The study presented here has demonstrated that only mild activation of the η^1 -C₅H₅ ring in the cycloaddition reaction occurs as a result of substituting the η^5 -C₅Me₅ ligand for η^5 -C₅H₅. However, the η^5 -C₅Me₅ substitution does induce a significant difference in the orientation of the η^1 -C₅H₅ ligand in the crystal structure relative to that previously found in 1. The more facile rearrangement of the Fp' group around the η^1 -C₅H₅ ligand is likely an effect of this structural difference, but there is also clearly an electronic variation between the η^5 -C₅Me₅ and η^5 -C₅H₅ ligands that may in part have an effect on the fluxional process.

The reactions of both 1 and 2 with bis(trifluoromethyl)ketene afford the unique products 4 and 5, whose unusual spectra suggest considerable ionic character in the iron-carbon bond. Continuing studies on the preparation

and reactivity of related η^1 -cyclopentadienyl complexes are currently under way in our laboratory.

Experimental Section

General Data. All manipulations of complexes and solvents were carried out using standard Schlenk techniques under an atmosphere of purified argon or nitrogen. Solvents were degassed and purified by distillation under nitrogen from standard drying agents.²⁶ Spectroscopic measurements utilized the following instrumentation: ¹H NMR, Bruker WM 250 FT (at 250 MHz); ¹³C NMR, Bruker WM 250 FT (at 62.9 MHz); IR, Perkin-Elmer 983; NMR chemical shifts are reported in δ vs. Me₄Si assigning the CDCl₃ resonance in ¹³C spectra to be at 77.00 ppm. ¹³C NMR spectra are run with ¹H decoupling, and resonances may be assumed to be singlets unless multiplicity is specified. The (η^5 -C₅H₅)Fe(CO)₂(η^1 -C₅H₅) (1) is prepared by a literature method.²⁷ The (η^5 -C₅Me₅)Fe(CO)₂I is prepared from the dimer [(η^5 -C₅Me₅)Fe(CO)₂]₂.²⁸ The alumina (Woelm N32-63) for the medium-pressure chromatography is purchased from Universal Scientific and deactivated to grade III. Medium-pressure chromatography utilizes a column 15 × 500 mm unless otherwise specified. NMR solvents are routinely degassed by three consecutive freeze-pump-thaw cycles and stored under nitrogen.

Preparation of (η^5 -C₅Me₅)Fe(CO)₂(η^1 -C₅H₅) (2). A mixture of (η^5 -C₅Me₅)Fe(CO)₂I (0.70 g, 1.9 mmol) and silver tetrafluoroborate (0.48 g, 2.5 mmol) in dichloromethane (30 mL) was stirred for 30 min. The mixture was filtered through a medium glass-fritted funnel covered with ca. 2 cm of Celite. Freshly distilled cyclopentadiene (0.5 mL, 6.0 mmol) was added to the purple filtrate and the solution stirred for 15 min. The mixture was cooled to 0 °C and triethylamine (0.5 mL, 3.6 mmol) was added by syringe. The mixture was stirred at 0 °C for an additional 15 min. Benzene (30 mL) was added and the mixture filtered through Celite. The solvent was removed under reduced pressure to give a red-orange solid. The residue was dissolved in dichloromethane (ca. 2 mL) and column chromatographed (alumina III, benzene, 2.5 × 8 cm). The orange band first off the column was collected and the solvent removed under reduced pressure. An orange band remained at the top portion of the column and was not collected. The solid from the first band was dissolved in benzene (ca. 2 mL) and placed on a medium-pressure chromatography column (alumina III, benzene). A faint red band eluted first off the column was identified as [(η^5 -C₅Me₅)Fe(CO)₂]₂ by IR spectroscopy. The second, major orange band was identified as pure 2 (0.42 g, 75%): ¹H NMR (CDCl₃) δ 5.80 (s, 5, C₅H₅), 1.75 (s, 15, C₅CH₃); ¹³C NMR (CDCl₃) δ 217.37 (C=O), 112.29 (bs, C₅H₅), 95.16 (C₅Me₅), 9.67 (C₅CH₃); IR (CH₂Cl₂) ν (C=O) 1996, 1944 cm⁻¹. Anal. Calcd for C₁₇H₂₀FeO₂: C, 65.40; H, 6.46. Found: C, 65.25; H, 6.45.

Preparation of 3b. A dichloromethane (20-mL) solution containing dimethyl fumarate (0.20 g, 1.4 mmol) and 2 (0.31 g, 1.0 mmol) was stirred at 25 °C for 1 h. The solvent was removed under reduced pressure to give a yellow solid. The residue was dissolved in a minimum of benzene (ca. 2 mL) and placed on a medium-pressure chromatography column (alumina III, benzene). The yellow band was collected and the solvent removed under reduced pressure to afford pure 3b (0.41 g, 90%): ¹H NMR (CDCl₃) δ 6.17 (dd, 1, *J* = 3.1, 5.5 Hz, H-5), 5.91 (dd, 1, *J* = 2.9, 5.5 Hz, H-6), 3.70, 3.62 (s, s, 6, CO₂CH₃), 3.37 (dd, 1, *J* = 4.1 Hz, H-2), 3.16 (m, 1, H-1), 3.02 (m, 1, H-4), 2.80 (d, 1, *J* = 4.4 Hz, H-3), 1.78 (s, 1, H-7), 1.69 (s, 15, C₅CH₃); ¹³C NMR (CDCl₃) δ 219.36, 219.14 (C=O), 175.33, 173.71 (C=O), 137.86, 135.16 (HC=), 95.08 (C₅Me₅), 58.38, 56.34 (CH), 51.61, 51.41 (CO₂CH₃), 50.15, 49.14, 48.53 (CH), 9.11 (C₅CH₃); IR (CH₂Cl₂) ν (C=O) 1984, 1926, ν (C=O) 1729 cm⁻¹. Anal. Calcd for C₂₃H₂₈FeO₆: C, 60.54; H, 6.19. Found: C, 60.32; H, 6.23.

Competitive Reaction of 1 and 2 with Dimethyl Fumarate. A deuteriochloroform solution containing 1 (ca. 50 mg, 0.2 mmol) and 2 (ca. 65 mg, 0.2 mmol) was treated with dimethyl fumarate (60 mg, 0.40 mmol). The change in the η^5 -ring signals for both the disappearance of 1 and 2 and the formation of 3a and 3b were

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Table II. Summary of Crystallographic Data for $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-C}_5\text{H}_5)$ (2)

formula	$\text{C}_{17}\text{H}_{20}\text{FeO}_2$
fw, amu	312.19
<i>a</i> , <i>b</i> , <i>c</i> , Å	8.519 (2), 36.347 (13), 10.119 (3)
β , deg	92.71
<i>V</i> , Å ³	3156 (2)
ρ calcd, g/cm ⁻³	1.31
space group, <i>Z</i>	$P2_1/n$, 8
cryst size, mm	0.42 × 0.30 × 0.17
radiation	Mo K α
μ , cm ⁻¹	9.52
scan method	ω
2 θ limits, deg	4.0–45.0
total data	4485
observed data	2563
$I \geq 3\sigma(I)$	
no. of variables	362
<i>R</i> ₁	0.063
<i>R</i> ₂	0.084
GOF ^a	2.6

^a Goodness-of-fit (GOF) = $\{\sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV})\}^{1/2}$, where NO is the number of observations and NV is the number of variables.

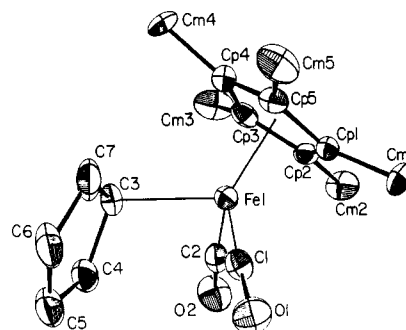
monitored by integration of the ¹H NMR spectra. After 50% of **2** had reacted to produce **3b** only 10% of **1** had been converted to **3a**.

Preparation of 4 and 5. Bis(trifluoromethyl)ketene is slowly bubbled into a dichloromethane (25 mL) solution containing **1** (0.50 g, 2.1 mmol) at 0 °C for 20 min. Toluene (25 mL) was added, and the total volume of the mixture was reduced to ca. 30 mL under reduced pressure. The mixture was then set aside at -25 °C for 24 h to allow complete precipitation. The purple microcrystals were collected, washed with cold toluene (2 × 10 mL), and dried under reduced pressure to afford analytically pure **4** (0.88 g, 70%): ¹H NMR (CD₂Cl₂) δ 7.56 (s, 1, C₅H₃), 6.21 (s, 2, C₆H₃), 5.09 (s, 5, C₅H₅), 4.72 (heptet, 2, *J*_{F-H} = 7.6 Hz, CH(CF₃)₂); ¹³C NMR (CD₂Cl₂) δ 210.62 (C=O), 177.85 (C=O), 85.73 (C₅H₅); IR (CH₂Cl₂) ν (C=O) 2057, 2017, ν (C=O) 1636 cm⁻¹. Anal. Calcd for C₂₀H₁₀F₁₂FeO₄: C, 40.16; H, 1.69. Found: C, 39.98; H, 1.72.

Complex **5** was prepared in a similar manner in 80% yield: ¹H NMR (CDCl₃) δ 7.29 (s, 1, C₅H₃), 5.42 (s, 2, C₅H₃), 4.54 (heptet, 2, *J*_{F-H} = 7.7 Hz, CH(CF₃)₂), 1.90 (s, 15, C₅CH₃); ¹³C NMR (CDCl₃) δ 211.13 (C=O), 176.68 (C=O), 97.37 (C₅Me₅), 53.19 [heptet, CH(CF₃)₂], 9.47 (C₅Me₅); IR (CH₂Cl₂) ν (C=O) 2040, 2004, and ν (C=O) 1625 cm⁻¹. Anal. Calcd for C₂₅H₂₀F₁₂FeO₄: C, 44.94; H, 3.02. Found: C, 45.07; H, 3.03.

Conversion of 4 to 6. A suspension of **4** (ca. 20 mg) in toluene (2 mL) was heated at 90 °C for 20 min. The sample was cooled to 25 °C and filtered through a pipet column (0.5 × 2 cm) of alumina III eluting with toluene. The orange band was collected and the solvent removed under vacuum to give **6**: ¹H NMR (CDCl₃) δ 5.45 (ca. t, 1, H-2), 5.26 (d, 2, *J* = 1.2 Hz, H-4,5), 4.44 (heptet, 2, *J* = 7.4 Hz, CH(CF₃)₂), 4.42 (s, 5, C₅H₅); IR (CH₂Cl₂) ν (C=O) 1695 cm⁻¹.

Crystal Structure of 2. Orange, air-stable crystals of **2** were obtained from cooling an ether solution of **2** to -78 °C. A single crystal of **2** was mounted on a glass fiber in the air using epoxy cement and then a glass capillary was placed over the crystal and sealed with epoxy cement. This crystal was inspected by rotation photographs taken on the Syntex P₂₁ diffractometer using Mo K α (λ = 0.71073 Å) radiation with a graphite monochromator. The ω -scan peak profiles of several reflections showed an average half-width of 0.20°. The standard Syntex P₂₁ centering (25 random reflections), indexing, and data collection programs were employed. A summary of data collection and refinement parameters is presented in Table II, and complete details of the structure determination can be found in Table E in the supplementary material. Final atomic coordinates for the two crystallographically unique molecules of **2** are presented in Tables III and IV. Standard Lorentz and polarization corrections have been applied to the data. With the modest size of the crystal and the low linear absorption coefficient of 9.5 cm⁻¹, no absorption correction was deemed necessary. During data collection three standard reflections were measured every 297 reflections. The

**Figure 4.** ORTEP perspective drawing and labeling scheme for molecule 1 of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-C}_5\text{H}_5)$ (**2**) with non-hydrogen atoms represented by thermal ellipsoids drawn to encompass 30% of the electron density.**Table III. Final Atomic Coordinates for Molecule 1 of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-C}_5\text{H}_5)$ (**2**)^a**

atom type ^b	<i>x</i>	<i>y</i>	<i>z</i>
Fe1	0.3360 (2)	0.56667 (4)	0.4231 (2)
Cp1	0.2950 (14)	0.5678 (3)	0.6258 (11)
Cp2	0.4043 (13)	0.5967 (3)	0.5948 (12)
Cp3	0.3227 (15)	0.6209 (3)	0.4979 (12)
Cp4	0.1644 (14)	0.6075 (3)	0.4779 (12)
Cp5	0.1522 (13)	0.5751 (3)	0.5516 (12)
Cm1	0.3221 (16)	0.5384 (3)	0.7264 (13)
Cm2	0.5682 (14)	0.6030 (4)	0.6569 (15)
Cm3	0.3854 (16)	0.6565 (3)	0.4414 (17)
Cm4	0.0371 (14)	0.6258 (3)	0.3967 (13)
Cm5	0.0004 (14)	0.5532 (4)	0.5669 (14)
C1	0.3278 (12)	0.5191 (3)	0.4183 (11)
O1	0.3233 (9)	0.5191 (3)	0.4197 (9)
C2	0.5267 (14)	0.4874 (2)	0.3677 (11)
O2	0.6552 (10)	0.5729 (3)	0.3376 (9)
C3	0.2433 (12)	0.5683 (3)	0.2225 (10)
C4	0.3437 (15)	0.5472 (4)	0.1372 (12)
C5	0.2642 (19)	0.5170 (4)	0.0914 (12)
C6	0.1059 (18)	0.5168 (4)	0.1423 (13)
C7	0.0965 (14)	0.5474 (4)	0.2181 (12)

^a The numbers in parentheses are the estimated standard deviations in the last significant digit(s).
^b Atoms are labeled in agreement with Figure 4.

Table IV. Final Atomic Coordinates for Molecule 2 of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-C}_5\text{H}_5)$ (2**)^a**

atom type ^b	<i>x</i>	<i>y</i>	<i>z</i>
Fe2	0.8966 (2)	0.68536 (5)	0.9206 (2)
Cp6	0.9856 (15)	0.6884 (3)	1.1163 (12)
Cp7	0.8481 (15)	0.6672 (4)	1.1123 (12)
Cp8	0.8698 (16)	0.6356 (4)	1.0284 (14)
Cp9	1.0226 (16)	0.6367 (4)	0.9860 (12)
Cp10	1.0960 (14)	0.6699 (4)	1.0381 (13)
Cm6	1.1097 (20)	0.7207 (4)	1.2019 (16)
Cm7	0.7017 (16)	0.6744 (5)	1.1908 (15)
Cm8	0.7549 (21)	0.6043 (4)	1.0042 (18)
Cm9	1.0987 (20)	0.6070 (4)	0.9050 (16)
Cm10	1.2677 (15)	0.6782 (5)	1.0287 (17)
C8	0.9483 (15)	0.7301 (3)	0.8933 (13)
O8	0.9816 (12)	0.7610 (26)	0.8786 (10)
C9	0.6992 (16)	0.6915 (3)	0.8777 (12)
O9	0.5655 (11)	0.6954 (3)	0.8554 (10)
C10	0.9396 (14)	0.6726 (3)	0.7196 (10)
C11	0.8428 (15)	0.6935 (4)	0.6279 (12)
C12	0.9294 (22)	0.7185 (4)	0.5612 (14)
C13	1.0918 (19)	0.7131 (4)	0.6054 (15)
C14	1.1009 (16)	0.6848 (4)	0.6953 (13)

^a The numbers in parentheses are the estimated standard deviations in the last significant digit(s).
^b Atoms are labeled in agreement with Figure 5.

intensities remained constant within experimental error throughout the entire data collection.

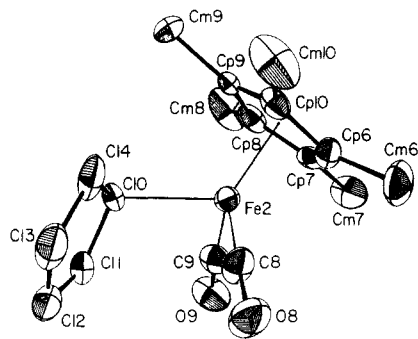


Figure 5. ORTEP drawing of $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-C}_6\text{H}_5)$ (**2**) molecule **2**, with non-hydrogen atoms represented by thermal ellipsoids drawn to encompass 30% of the electron density.

The structure is initially solved by direct methods using MULTAN (1978 version) program. The remaining non-hydrogen atoms were located by standard difference Fourier techniques. The structure is refined by using two molecular fragments due to the large number of parameters during refinement. The resulting structural parameters for **2** have been refined to convergence [$R_1 = 0.063$ and $R_2 = 0.084$ for 2563 reflections having $I > 3\sigma(I)$] using counter-weighted least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms. No effort was

made to locate the hydrogen atoms in the structure. The largest peak found in the final difference Fourier map was $0.49 \text{ e}/\text{\AA}^3$.

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Registry No. **1**, 12247-96-0; **2**, 92366-04-6; **3a**, 84500-51-6; **3b**, 92366-05-7; **4**, 92366-06-8; **5**, 92366-07-9; **6**, 92366-08-0; $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{I}$, 88363-26-2; dimethyl fumarate, 624-49-7; bis-(trifluoromethyl)ketene, 684-22-0.

Supplementary Material Available: Tables of anisotropic thermal parameters, bond lengths and angles, and structure factor amplitudes and a crystallographic report (21 pages). Ordering information is given on any current masthead page.

Synthesis, Structure, and Fluxional Properties of $(\eta^5\text{-C}_5\text{Me}_5)(\text{OC})_2\text{IrW}(\text{CO})_5$. A Compound with an Ir–W Dative Bond

Frederick W. B. Einstein, Roland K. Pomeroy,* Paul Rushman, and Anthony C. Willis

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

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The compound $(\eta^5\text{-C}_5\text{Me}_5)(\text{OC})_2\text{IrW}(\text{CO})_5$ (**1**) has been synthesized by the reaction of $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{CO})_2$ and $\text{W}(\text{CO})_5(\text{THF})$ in hexane. The structure of **1** has been solved by conventional crystallographic techniques: space group $P\bar{1}$ with $a = 9.057$ (2) \AA , $b = 9.560$ (3) \AA , $c = 12.695$ (2) \AA , $\alpha = 71.83$ (2) $^\circ$, $\beta = 83.07$ (2) $^\circ$, $\gamma = 68.62$ (2) $^\circ$, $Z = 2$; $R_F = 0.027$, $R_{wF} = 0.032$ for 3426 reflections with $I > 3\sigma(I)$ having $2\theta < 55^\circ$. It reveals that the 18-electron complex $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{CO})_2$ acts as a donor ligand toward the $\text{W}(\text{CO})_5$ fragment via an unbridged Ir–W dative bond of length 3.0539 (11) \AA . The ^{13}C NMR spectrum of the compound in $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ at -97°C was that expected from the solid-state structure. However, on warming the solution all the carbonyl resonances coalesced such that a single broad signal was observed at ambient temperature. A mechanism that involves an intermediate with bridging carbonyls is proposed to account for the carbonyl exchange. The donor–acceptor, metal–metal bond in $(\eta^5\text{-C}_5\text{Me}_5)(\text{OC})_2\text{IrW}(\text{CO})_5$ was weak since the compound reacted with the donor ligand L (L = CO, PPh_3 , or $\text{Os}(\text{CO})_4(\text{PMe}_3)$) to yield $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{CO})_2$ and $\text{W}(\text{CO})_5\text{L}$ (in solution at room temperature over a period of ca. 90 min).

Introduction

We have recently described the synthesis and structure of $(\text{Me}_3\text{P})(\text{OC})_4\text{OsW}(\text{CO})_5$ in which the 18-electron complex $\text{Os}(\text{CO})_4(\text{PMe}_3)$ acts as a ligand to the 16-electron fragment $\text{W}(\text{CO})_5$.¹ The osmium–tungsten donor–acceptor bond was unbridged which made it the first bond of this type to be structurally characterized where the transition-metal atoms were different. (The compound $(\text{O-C})_5\text{OsOs}(\text{CO})_3(\text{GeCl}_3)(\text{Cl})$, also synthesized in this laboratory, contains an unbridged Os–Os dative bond.²) In

solution $(\text{Me}_3\text{P})(\text{OC})_4\text{OsW}(\text{CO})_5$ was found to exist in two isomeric forms that were shown to be in dynamic equilibrium by ^1H NMR spin saturation transfer techniques.¹

The investigation of the ability of 18-electron complexes to act as ligands has been extended to $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{CO})_2$. This complex was chosen because it contained a five-coordinate metal atom that would be expected to readily expand its coordination number to six. Also, it is our experience that with neutral transition-metal donors the third-row metal forms much stronger dative bonds than its lighter congeners.

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