Rearrangements of Cyclopropanes σ Bonded to Iron: α-Eliminations to Carbene Complexes and Ring Opening to π-Allyl Complexes

Nicholas J. Conti, Donna J. Crowther, Supanna Tivakornpannarai, and W. M. Jones*

Department of Chemistry, University of Florida, Gainesville, Florida 32611

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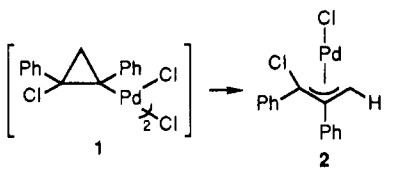
A number of α- and β-substituted cyclopropyl σ-complexes of dicarbonyl(η^5-cyclopentadienyl)iron have been photolyzed and their products examined. Under these conditions, the α-ethoxycyclopropane complex **6c** undergoes loss of CO to give a 16-electron iron intermediate that rapidly and reversibly undergoes α-elimination to give the first example of a 1-ferracyclobutene (**8c**). This complex has been identified by NMR but was too unstable for isolation and complete characterization. Treatment of the ferracyclobutene with CO or Ph_3P gives the ring-expanded ferracyclopentenones **9c** and **9d**. In the absence of added ligand, the ferracyclobutene opens to give the two isomeric π-allyl complexes **10c** (via **7c**) and **11c**. The 16-electron σ-complex **7c** irreversibly opens to the centrally substituted π-allyl complex **10c** in a slow competition with α-elimination to **8c**. Support for the assumption that these conversions (except carbon monoxide extrusion) are thermally induced was obtained by thermolysis of the phosphine-substituted σ-complex **6d**. Photolysis of dicarbonyl(η^5-cyclopentadienyl)(α-(phenylthio)cyclopropyl)iron **6e** gives the three-membered chelate **12** (or its dimer) which, upon warming, opens quantitatively to the centrally substituted π-allyl complex **10e**. When a mixture of *cis*- and *trans*-dicarbonyl(η^5-cyclopentadienyl)(2-fluorocyclopropyl)iron is photolyzed, the cis isomer remains unchanged but the trans isomer cleanly reacts to give a mixture of stereoisomers of the terminally substituted π-allyl complex **10h**. It is proposed that the syn isomer (fluorine and central hydrogen cis) is initially formed which rapidly photoisomerizes to a mixture of exo and endo anti isomers. Photolysis of a mixture of *cis*- and *trans*-dicarbonyl(η^5-cyclopentadienyl)(2-methylcyclopropyl)iron also shows preferential reaction of the trans isomer which opens to give the photostable syn isomer of **10g**. Both preferential reaction of *trans*-**6h** and stereospecific opening of *trans*-**7g** are consistent with a disrotatory ring opening of the cyclopropane in which the breaking cyclopropane bond assists in weakening the carbon–iron bond in much the same way a solvolysis reaction is assisted. The mechanism of the opening of the metallocyclobutene **8c** to the π-allyl complex **11c** is briefly discussed.

The discovery of unimolecular rearrangements of cyclopropyl σ complexes of transition metals antedates this paper by some 20 years: Mushak and Battiste suggested that **1** rearranges to the π-allyl complex **2**. Since the

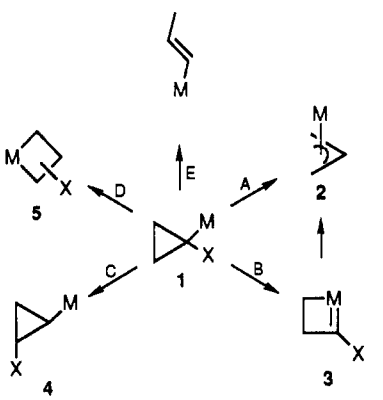


1 **2**

original report, occasional investigations of this rearrangement have been published[2] and alternate pathways for the rearrangement of metal–cyclopropyl complexes have appeared. These include single examples of reactions C,[2c] D,[2f] and E[4] (Scheme I).

We became interested in this chemistry with our serendipitous discovery[3] that photolysis of a derivative of **6b** (X = OCH_3) (Scheme II) induces α-elimination of carbon to ultimately give **9b** [R, (R) = Me]. Our interest in the unimolecular rearrangements of cyclopropyl complexes grew when we found that the opening of **7c** to **10c** competes with the α-elimination and that **8c** also opens to a π-allyl complex, **11c**, which provides a new mechanistic

Scheme I



5 **1** **2** **4** **3**

route to this kind of product.[5]

At this time we communicate a complete report of our work on reactions A and B (Scheme I) involving a number of cyclopropanes σ bonded to the 16-electron carbonyl(η^5-cyclopentadienyl)iron moiety.

Results

Syntheses and General Information. Dicarbonyl(η^5-cyclopentadienyl)iron complexes of cyclopropanes **6c,e,g,h** (L = CO) were prepared by direct substitution of Fp^- [Fp = dicarbonyl(η^5-cyclopentadienyl)iron] for halide (bromide for **6c**, **6g**, and **6h** and iodide for **6e**). The two stereoisomers of the 2-methyl-substituted cyclopropanes **6g** were also prepared by photodecarbonylation of a mixture of acyl complexes which, in turn, were prepared by

(1) Mushak, P.; Battiste, M. A. *J. Organomet. Chem.* **1969**, *17*, 46.
(2) (a) Bruce, M. I.; Igbal, M. Z.; Stone, F. G. A. *J. Organomet. Chem.* **1969**, *20*, 161. (b) Phillips, R. L.; Puddephatt, R. J. *J. Organomet. Chem.* **1977**, *136*, C52. (c) Phillips, R. L.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1732. (d) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 3252. (e) Hughes, R. P.; Lambert, J. M. J.; Rheingold, A. L. *Organometallics* **1985**, *4*, 2055. (f) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7346.
(3) Lisko, J. R.; Jones, W. M. *Organometallics* **1985**, *4*, 944.
(4) Young, W. J.; Simms, B. L.; Ibers, J. A. *J. Organomet. Chem.* **1984**, *272*, 295.

(5) A preliminary report of some of this work has appeared: Conti, N. J.; Jones, W. M. *Organometallics* **1988**, *7*, 1666.

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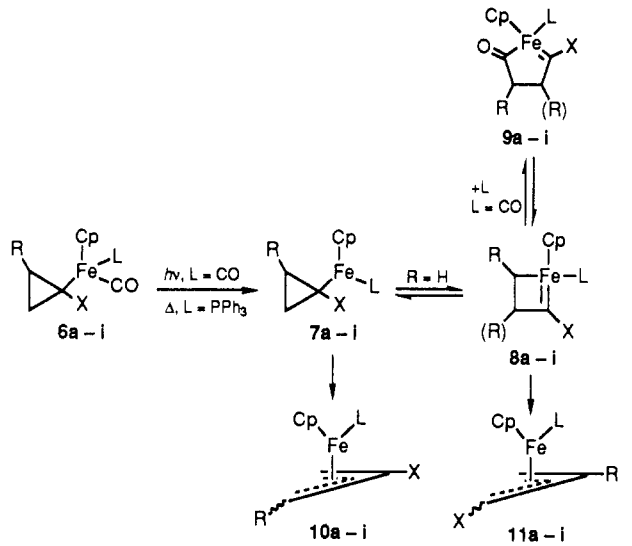
Scheme II



a, R = H, X = H, L = CO; **b**, R = H, X = OMe, L = CO; **c**, R = H, X = OEt, L = CO; **d**, R = H, X = OEt, L = PPh_3; **e**, R = H, X = SPh, L = CO; **f**, R = H, X = SPh, L = PPh_3; **g**, R = Me, X = H, L = CO; **h**, R = F, X = H, L = CO; **i**, R = OEt, X = H, L = CO

reaction of the acyl chlorides with KFp. Preparation of *cis*- and *trans*-2-fluorocyclopropyl σ-complexes **6h** from reaction of the bromides with KFp was interesting in that *cis*-2-fluorobromocyclopropane was nearly inert (very slow conversion to Fp_2 and unidentified organic materials) while the trans isomer reacted readily to give a mixture of the two stereoisomers of **6h** in a ratio of 82:18 (by NMR) with the trans isomer dominant.

Stereochemical assignments to the fluorine-substituted cyclopropyl complexes are based on F–H coupling constants by using ^{19}F NMR.[6] The predominant isomer (assigned the trans stereochemistry) showed a multiplet in which there are three large couplings (70.8, 29.3, and 19.5 Hz) for the geminal and cis F–H interactions and one small coupling (4.9 Hz) for the trans F–H splitting. The multiplet of the cis isomer contains two large (geminal and cis) and two small (trans) couplings. Loss of stereochemistry in the substitution reaction probably results from a single electron-transfer mechanism, but this was studied no further.

Assignment of the trans stereochemistry to the predominant isomer from reaction of KFp with 2-methylbromocyclopropane is based on its independent synthesis from photodecarbonylation of the corresponding 2-methylacyl complex.

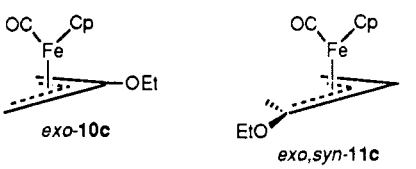
Carbonyl(η^5-cyclopentadienyl)(1-ethoxycyclopropyl)-(triphenylphosphine)iron was prepared by photolysis of **6c** in the presence of 1 equiv of Ph_3P in benzene-d_6 for 2 h. The reaction was followed by ^{13}C NMR which showed the conversion to be quantitative.

Photolyses were typically carried out in NMR tubes containing ca. 1.5 M solutions of substrate dissolved in benzene-d_6 using a 450-W medium-pressure mercury lamp in a Pyrex photolysis finger. Reaction progress was normally monitored by ^{13}C NMR.

Dicarbonyl(η^5-cyclopentadienyl)(α-ethoxycyclopropyl)iron (6c) and Carbonyl(η^5-cyclopentadienyl)(triphenylphosphine)(α-ethoxycyclopropyl)iron (6d): Photolysis, Thermolysis, and Chemistry of Photolysis Products. Photolysis of a yellow solution of **6c** in benzene-d_6 led to rapid darkening to a deep red solution within a few minutes. Flash chromatography of the solution after 6 h of photolysis gave the acylcarbene complex **9c** as a red crystalline solid. The reaction was monitored at intervals over a 6-hour period by using ^{13}C NMR and a pulse delay of 35 s with ferrocene as an internal standard. Control experiments verified that ferrocene is photostable under these conditions and that no chemistry occurred in the absence of the light source. At the outset, only the resonances of the Cp carbons of **6c** (δ 87.1 ppm) and ferrocene were present. After 2 h, a new Cp was present at δ 82.8 ppm. A resonance at δ 335.0 ppm indicative of Fe=C was also detected.[8] When CO was bubbled through this solution (presumed to contain **8c**) for 1 h, the resonances at δ 82.8 and 335.0 ppm were replaced by those of **9c** [δ 87.5, 270.0 (acyl carbon), and 342.0 ppm]. A solution similarly prepared and treated with triphenylphosphine gave, within 5 min, the phosphine analogue **9d** [δ 293.3 (acyl) and 341.0 ppm (carbene)]. This acyl carbene complex **9d** was independently prepared by photolysis of **9c** in the presence of Ph_3P. Finally, rapid, low-temperature (−50 °C) flash chromatography of a very concentrated solution of **6c** that had been photolyzed for 2 h gave a very unstable red solid. ^1H and ^{13}C NMR spectral data were consistent with the assignment of structure **8c** to this material, but it was too unstable for further characterization.

The phosphine-substituted σ-complex **6d** is photostable. However, thermolysis at 75 °C in benzene for 47 h cleanly converted it to **9d** (89% isolated) as determined by ^1H and ^{13}C NMR.

The crude product from photolysis of **6c** showed resonances in the ^{13}C NMR spectrum (most notable at δ 79.8, 133.8, and 221.3 ppm and δ 79.8, 99.9, and 222.2 ppm) that could not be attributed to either **8c** or **9c**. These increased in intensity with prolonged photolysis. Repeated column chromatography of the photolysis mixture with these resonances at a maximum intensity yielded two yellow solids. These materials were fully characterized by spectroscopy and were assigned structures **10c** and **11c**. These



exo-**10c** *exo,syn*-**11c**

assignments were aided by the prior work of Rosenblum, who prepared three of the stereoisomers of **11b**.[7] Comparison of the chemical shifts of the protons and carbons of the allyl ligands of **10c** and **11c** showed them to be in the exo orientation (stereoisomer with central carbon cis to Cp). In the case of **11c** coupling between the central and terminal protons (α to ethoxy) indicated that the ethoxy group is syn to the proton on the central carbon of the allyl ligand. Examination of the NMR spectra showed no sign of the anti isomer. Furthermore, compounds **10c** and **11c** did not interconvert upon prolonged irradiation nor did any of the anti isomer of **11c** appear.

When a benzene-d_6 solution of the acyl carbene complex **9c** was photolyzed for 2 h, the ^{13}C NMR spectrum of the product mixture showed the presence of **6c**, **8c**, **10c**, **11c**, and Fp_2. Integrals of the Cps showed that **8c** was present in approximately twice the concentration of **6c**. The yield of the π-allyl complexes was comparable to the σ complex;

(6) Emsley, J. W. *Fluorine Coupling Constants*; Pergamon Press: New York, 1977; Chapter 4.

(7) Fish, R. W.; Giering, W. P.; Martin, D.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *105*, 101.

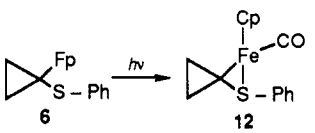
(8) Cf. Stenstrom, Y.; Klauck, G.; Koziol, A.; Palenik, G. J.; Jones, W. M. *Organometallics* **1986**, *5*, 2155 and references cited therein.

however, an excess of **11c** over **10c** was discernible. After 6 h of irradiation, the concentrations of all other compounds had increased at the expense of **8c** and **9c**.

A 1.9 M benzene-d_6 solution of **6c** was photolyzed in the presence of 2 atm of ^{13}CO. After 3 h, the mixture was chromatographed and **6c** reisolated. Analysis by ^{13}C NMR and mass spectroscopy showed less than 1% labeled CO had been incorporated into **6c**.

A benzene-d_6 solution of the σ-complex **6c** was photolyzed in the presence of 5 atm of CO and the reaction was monitored by ^{13}C NMR. The course of the reaction was not greatly altered, but the following effects (relative to photolysis without exogenic CO) were discernible. The yield of the acyl carbene complex **9c** was enhanced. A pronounced decrease in the initial buildup of the concentration of the alkylcarbene complex **8c** was noted. A similar attenuation in the formation of the π-allyl complexes **10c** and **11c** was also observed, the effect on the latter being noticeably greater than on the former. Consistent with lack of ^{13}CO incorporation, only a slight change in the rate of disappearance of the σ-complex **6c** was detected.

Photolysis of Dicarbonyl(η⁵-cyclopentadienyl)(α-(phenylthio)cyclopropyl)iron. Photolysis of a benzene-d_6 solution of **6e** for 6 h at ambient temperature gave **12** (or a dimer) as a bright yellow solid. When a benzene

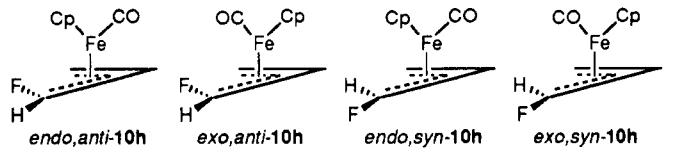


6 **12**

solution of **12** was treated with 1 equivalent of Ph_3P, the phosphine-substituted complex **6f** was formed quantitatively. Bubbling CO through a solution of **12** in benzene-d_6 cleanly regenerated the starting material **6e**. Complex **12** was fully characterized spectroscopically. IR, ^1H NMR, ^{13}C NMR, MS, and elemental analysis along with its reactivity are consistent with the sulfur chelate depicted in **12**. Attempts to grow a single crystal suitable for X-ray to confirm the structure of **12** have thus far been unsuccessful.

A benzene-d_6 solution of **12** was heated at 75 °C for 20 h. The reaction was monitored by FT-IR, ^1H NMR, and ^{13}C NMR. Two compounds appeared at the expense of **12**, **6e**, and the π-allyl complex **10e**. The latter was completely characterized by spectra and analysis. A brown, insoluble, intractable solid was also obtained. Neither **9e** nor **11e** could be detected.

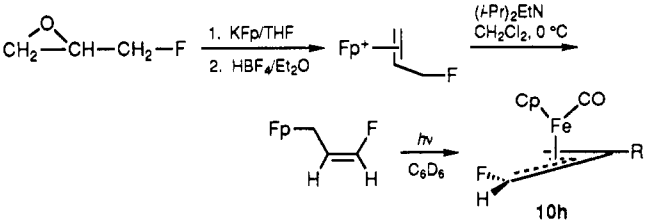
Photolysis of *cis*- and *trans*-Dicarbonyl(η⁵-cyclopentadienyl)(2-fluorocyclopropyl)iron. A mixture of *cis*-**6h** (18%) and *trans*-**6h** (82%) was photolyzed in benzene-d_6 at 10 °C for 3 days. The course of the reaction was monitored by ^{19}F NMR using $FCCl_3$ (a passive spectator under the conditions of the reaction) as an internal standard. As the irradiation continued, the signal from the trans isomer decreased while the cis isomer remained essentially unchanged. A mixture of three isomeric π-allyl complexes [*endo,anti*-**10h** (^{19}F signal at δ −189 ppm), *exo,anti*-**10h** (^{19}F signal at δ −172 ppm), and *endo,syn*- or *exo,syn*-**10h** (^{19}F NMR signal at δ −169 ppm)] was formed.



endo,anti-**10h** *exo,anti*-**10h** *endo,syn*-**10h** *exo,syn*-**10h**

During the course of the photolysis, the syn isomer rapidly reached steady state while the exo, anti isomer grew in more rapidly than did the endo, anti. However, upon

Scheme III



continued photolysis, *endo,anti*-**10h** continued to increase, apparently at the expense of its exo isomer. After 3 days, the steady state had been reached with *endo,anti*-**10h**, *exo,anti*-**10h**, and the syn isomer present in a ratio of 70:25:5, respectively.

The major isomer from the photolysis was assigned the endo, anti structure based on NMR coupling constants[6] and the independent synthesis shown in Scheme III (which is patterned after the Rosenblum's elegant synthesis of the corresponding methoxy-, chlorine-, and bromine-substituted complexes).[9] The ^{19}F NMR of *endo,anti*-**10h** shows a doublet of doublets at δ −189 ppm with couplings of 71.4 and 14.45 Hz. These correspond to $^2J_{FH}$ coupling and $^3J_{FH}$ trans olefinic coupling, respectively. The coupling of the proton residing on the fluorine substituted carbon supports the structure assignment. It has a coupling constant of 3.9 Hz.

When this isomer was heated in benzene-d_6 at 84 °C, it was transformed cleanly to a single new substance that isomerized back to the starting material upon photolysis at 10 °C. From this result and its ^1H and ^{19}F (−172 ppm) NMR, this single new substance was assigned the exo, anti structure.

The third isomer in the product mixture that showed a ^{19}F NMR signal at δ −169 ppm was assigned the syn stereochemistry based on characteristic ^1H and ^{19}F NMR coupling constants. Since only one syn isomer was obtained, assignment of an exo or endo configuration was not possible. However, when photolysis of this isomer was carried out at 10 °C, within 30 min, both of the anti isomers were cleanly formed.

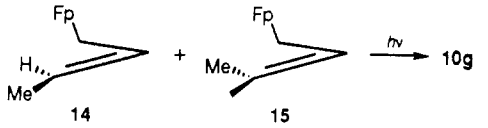
Photolysis of *cis*- and *trans*-Dicarbonyl(η⁵-cyclopentadienyl)(2-methylcyclopropyl)iron. We were unable to isolate geometrically pure *trans*-**13**, *trans*-**6g**, or the corresponding anti complexes of **10g**. However, the acyl

trans-**13** *cis*-**13**

complex **13** heavily enriched in the trans isomer (86:14) was obtained and was therefore photolyzed to study the stereochemistry of the ring-opening process. The mixture was photolyzed in benzene-d_6 for 40 h (monitored by ^{13}C NMR) and found to give a mixture that contained *exo,syn*-**10g** and *endo,syn*-**10g** as the predominant iron-containing products; no *anti*-π-allyl complex was detectable (less than 5%). Similarly, a 70:30 mixture of the trans and cis isomers of **6g** was photolyzed for 24 h to give a mixture of *syn*- and *anti*-**10g** in a ratio of 86:14 along with unreacted cyclopropyl σ complexes in a ratio of roughly 1:1. Stereochemical assignments to the π-allyl complexes are based on proton coupling constants (see Experimental Section), literature analogy, and alternate synthesis. The latter was effected by photolysis of a 63:37 mixture of **14**

(9) Cutler, A.; Ehntholt, D.; Lennon, P.; Nicholas, K.; Marten, D.; Madhavarao, S.; Rghu, S.; Rosan, A.; Rosenblum, M. *J. Am. Chem. Soc.* **1975**, *97*, 3149.

and **15** (prepared from crotyl chloride and KFp) in benzene-d_6 at 15 °C. This reaction was quite clean and gave a 63:37 mixture of *syn*- (as exo and endo isomers) and *anti*-**10g**.



The endo–exo isomers of *syn*-**10g** are unstable to column chromatography, photolysis, or simply standing at room temperature. When the crude reaction mixture from **14** to **15** (containing both endo and exo isomers of *syn*-**10g**) was passed down an alumina column, only the exo, syn and exo, anti isomers were recovered in the same ratio as the total syn/anti mixture introduced into the column. Photolysis of this mixture led to regeneration of the endo isomer from the syn complex but not from the anti. Finally, simply standing at room temperature for 36 h led to essentially complete conversion of the endo, syn complex to its more stable exo, syn isomer. Under none of these conditions was any syn to anti conversion detected. To test this further, a very careful study was made of the photolysis of a 63:37 mixture of *syn*- and *anti*-**10g**. To determine conditions for accurate area measurements, T_{-1} studies were carried out on this mixture by using the standard program employed with a Varian 300XL NMR spectrophotometer. The mixture was photolyzed and monitored by using ^{13}C NMR by measuring areas under the four allyl peaks (the Cp resonances are coincidental). Within experimental error, the ratios of all four pairs of peaks were invariant for up to 72 h of photolysis at 34 °C. From this, it is clear that photolysis of the *anti*-allyl complex does not lead to its syn isomer; therefore, the virtually exclusive formation of the syn isomer from photolysis of the 86:14 mixture of *trans*- and *cis*-**6g** and the high predominance from the 70:30 mixture cannot be explained by initial formation of the *anti*-π-allyl complex followed by isomerization to its syn isomer.

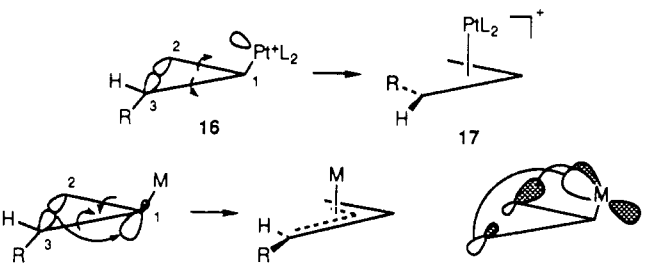
Discussion

Rearrangements A and B in Scheme I [M = Cp(CO)Fe] appear to be independent of both the first reactant (acyl or sigma complex) and the method of initiating the reaction (photolysis or heat). This leaves little question but that the initiation is simply generation of an electron-deficient σ complex (Scheme II) and that the rearrangements that follow are induced by heat rather than light.

Once the 16-electron σ complex is formed, its immediate fate depends on the substituents on the cyclopropane ring. If the cyclopropane ring is unsubstituted or substituted with a cis β-fluorine or a cis β-methyl group, the principal reaction of the 16-electron intermediate is simply recapture of CO. However, when the ring is substituted with a trans β-fluorine, a trans β-methyl, an α-phenylthio, or an α-alkoxy rearrangement occurs. We believe that the role of these substituents in the ensuing rearrangements is quite different. The trans β-fluorine and trans β-methyl are believed to accelerate ring opening to the π-allyl complex. This will be discussed in more detail below. The α-phenylthio and α-alkoxy may play more than one role in the reactions that follow. Since both have potential coordinate atoms,[10] one role that they may play is the relatively trivial one of simply retarding back-reaction with CO in the solvent cage and, in this way, permitting additional thermal chemistry to occur. The strongest support for this contention was the isolation and characterization of the chelate **12** (or its dimer) which, upon warming, undergoes ring opening to **10e**. Both α-alkoxy and α-phenylthio may also accelerate ring opening to the π-allyl complex (vide infra). Finally, the α-alkoxy influences the α-elimination (rearrangement B in Scheme I) by stabilizing the resulting carbene (**8**), an effect that would most certainly also be felt in the transition state for its formation. It would appear that neither an α-phenylthio nor an α-phenyl[11] substituent is a strong enough electron donor to induce α-elimination of a cyclopropyl carbon in a carbonyl(cyclopentadienyl)iron complex. α-Phenylthio does induce this reaction in the corresponding benzocyclobutenyl system.[8]

Rearrangements A and B in Scheme I include two different paths to π-allyl complexes, one presumably a single-step ring opening and the other requiring at least two steps.

Two reasonable mechanistic pathways can be postulated for the single-step ring-opening process.



In one, first suggested by Puddephatt[2] for the opening of **16**, a vacant metal orbital inserts into the C2–C3 bond of the cyclopropane in much the same way electron-deficient metals insert into cyclopropanes to give metallocyclobutanes.[12] In the second mechanism which, to our knowledge, has not been previously suggested but which finds analogy in the iron carbonyl induced ring opening of methylenecyclopropanes,[13] the interaction of the breaking C2–C3 cyclopropane bond (HOMO) with the LUMO of the carbon–iron bond assists in its cleavage in much the same way it assists in a traditional solvolysis reaction.[14a] In addition, in this case, it is possible that this opening process might be assisted by a filled metal "d" orbital mixing with the C2–C3 antibonding orbital as depicted in **19**. In this case, the role of the vacant orbital on the metal way be to simply avoid a 20-electron product.

To distinguish between these mechanisms for the carbonyl(cyclopentadienyl)iron case, advantage was taken of the fact that even though both of these mechanisms require disrotatory ring openings,[14b] the direction of their disrotation is different. Thus, the finding that the π-allyl complex from ring opening of the *trans*-2-methylcyclopropyl complex **6g** is the syn isomer of **10g** and that the anti isomer of **10g** does not isomerize under the reaction conditions points clearly to the second or "solvolysis" mechanism.

(10) Sulfur would be expected to chelate more tightly than oxygen. Cf. Lotz, S.; van Rooyen, P. H.; van Dyk, M. M. *Organometallics* **1987**, *6*, 499.

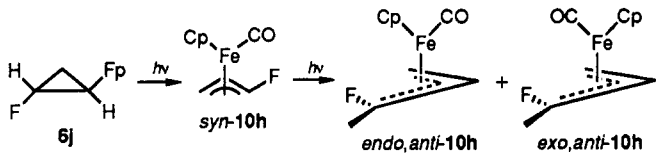
(11) Trace, R.; Jones, W. M. *J. Organomet. Chem.*, in press.

(12) For lead references, see: (a) Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1449. (b) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4202.

(13) Pinhas, A. R.; Samuelson, A. G.; Risemberg, R.; Arnold, E. V.; Clardy, J.; Carpenter, B. K. *J. Am. Chem. Soc.* **1981**, *103*, 1668 and references cited.

(14) (a) Cf. LeNoble, W. J. *Highlights of Organic Chemistry*; Marcel Dekker: New York, 1974; p 469. (b) Although none of the results reported here preclude a conrotatory ring opening, we have found that photolysis of the Fp complex of 1-fluoro-*trans*-2,3-dimethylcyclopropane give exclusively the syn–anti π-allyl complex, a result that requires a disrotatory process (unpublished results of T. Omrcen-Vondracek, University of Florida).

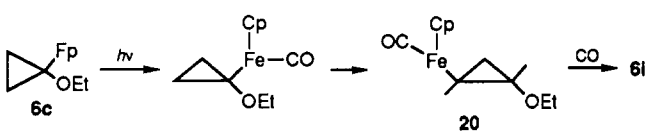
Consistent with this conclusion is the observation that only *trans*-2-fluorocyclopropyl complex rearranges; the cis isomer behaves like the unsubstituted cyclopropyl σ complex in that it is essentially inert to the photochemical conditions that led to rearrangement of its trans isomer. In other words, it would appear that the trans fluorine accelerates the ring-opening process relative to the cis and it is suggested that photolysis of *trans*-**6h** initially gives the syn isomer of **10h** which then isomerizes to the observed anti products. The accelerating effect of the trans



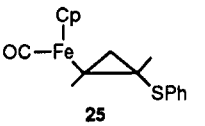
fluorine on the related opening of cyclobutenes has been treated theoretically by Houk[15] and has been experimentally confirmed by Dolbier for both electrocyclic opening of 3-fluorocyclobutenes[16] and solvolysis of 2-fluorobromocyclopropanes. The *trans*-2-methyl substituent may play a similar role although it is more difficult to rule out steric acceleration (and possibly deceleration in the cis isomer) in this case.

Insofar as the opening of **7** to **10** resembles a solvolysis reaction, α substituents might also influence the rate of the ring-opening process. This may therefore be part of the reason that ring opening occurs when the ring is substituted with an α-methoxy, an α-phenylthio, or an α-phenyl substituent but not when it is unsubstituted. However, due to the node on the central carbon of the LUMO of a π-allyl cation, it is not surprising that the effect of α substituents is modest and we therefore suspect that the primary role of these substituents in the processes leading to the π-allyl complexes is to prevent back-reaction with CO (vide supra).

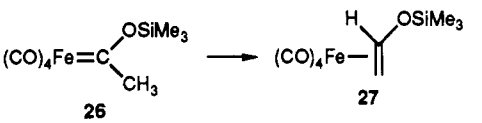
The terminally substituted π-allyl complex **11c** could originate from either opening of the metallocyclobutene or rearrangement of **6c** to **20**[8] followed by rapid ring opening (accelerated by the electron-donating alkoxy) by the mechanism discussed above. A number of observa-



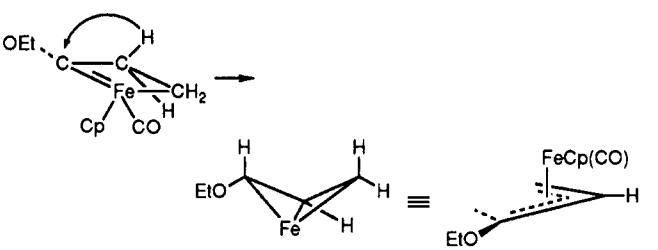
tions argue against the latter. First, photolysis of **6c** in the presence of added CO gave no detectable σ-complex **6i**. Second, photolysis of **6c** and **9c** gave different relative amounts of the two π-allyl complexes with **6c** giving relatively more of the centrally substituted product and **9c** more of the terminally substituted isomer. This is consistent with **8c** as the progenitor of **11c** if contraction of **8c** to **7c** is slow relative to its ring opening. It is not consistent with rearrangement via **6i**. Third, the amount of **10c** relative to **11c** increased with added CO. This is consistent with **8c** as the progenitor of **11c** if its reaction with CO to give **9c** (which is essentially irreversible) is competitive with its ring opening. This is not consistent with isomerization to **20** as the key step in the formation of **11c**. Finally, photolysis of **6e** gave none of the terminally substituted π-allyl complex which would be expected if **25** were formed.



Opening of the metallocyclobutene **8c** to the π-allyl complex **11c** is simply a special case of the well-documented rearrangement of carbene complexes to their isomeric π complexes[18] (e.g. **26** to **27**). The mechanism



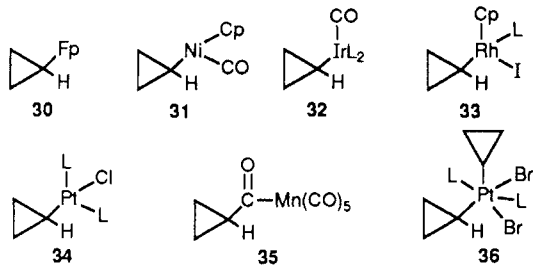
of the latter has been pictured as a simple hydride migration to the electron-deficient carbene carbon to give a carbocation that undergoes the necessary conformational changes to give the final π complex. However, although Brookhart[19] has provided evidence for substantial positive charge on the β-carbon in the transition state for the rearrangement of cationic Fp complexes, it is unlikely that a free carbocation is formed in the rearrangement of **8** to **11** since this would require a highly endothermic path from a cation stabilized by both methoxy and Fp to one that is only stabilized by two alkyl groups. To avoid this, it is likely that, as suggested by Gladysz,[18] hydride transfer and carbon–metal bond formation are concerted although probably not using the "d" orbital that back-bonds to the carbene carbon since the stereochemistry of the π-allyl complex would require a symmetry forbidden [$\sigma^2a + \pi^2a$] process. Exclusive formation of the *syn*-π-allyl complex is consistent with this mechanism.



The nature of the metal and its attendant ligands most certainly also influence the rearrangements in Scheme I. Unfortunately, of the variety of rearrangements in Scheme I, only the opening to π-allyl complexes has been studied for more than a single metal, and, even in this case, very little in the way of significant generalities has emerged. For instance, while photolysis of **30**, thermolysis or photolysis of **31**,[20] or thermolysis of **32**[21] gives no π-allyl products, treatment of **33**[2f] or **34**[2c] with silver ion, **35**[2a] with triphenylphosphine, or thermolysis of **36**[2c] leads to the ring-opened product.

The one obvious generality that appears to have emerged from these results (including the ones reported herein) was first articulated by Ibers,[21] who observed that a metal with 16 or less electrons is a necessary but not sufficient condition for ring opening of (an unsubstituted) cyclopropane

(15) Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2099.
(16) Dolbier, W. R., Jr.; Koroniak, H.; Burton, D. J.; Heinze, P. L.; Bailey, A. R.; Shaw, G. S.; Hansen, S. W. *J. Am. Chem. Soc.* **1987**, *109*, 219 and references cited therein.
(17) Dolbier, W. R., Jr.; Phanstiel, O., IV *Tetrahedron Lett.* **1988**, *29*, 53.
(18) Cf. Hatton, W. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6157 and references cited therein.
(19) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258.
(20) Brown, J. M.; Mertis, K. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1993.
(21) Jones, N. L.; Ibers, J. A. *Organometallics* **1983**, *2*, 490.



to a π-allyl complex. From the results reported herein, a second generality may be emerging: electron donors α or β and trans to the metal (at least for iron and tetracarbonylmanganese)[22] accelerate the ring-opening process. This needs to be checked for other metals.

With regard to α-eliminations of carbon in cyclopropane systems, from the work in these laboratories, both 16 (or less) electrons and the presence of a strong electron donor on the α-carbon are requirements for α-elimination of a cyclopropane carbon by iron and manganese.[23] Whether or not a strong electron donor on the α-carbon will be a requirement for other metals remains to be seen.

Experimental Section

Hexane, diethyl ether, and tetrahydrofuran were distilled from benzophenone ketyl. Methylene chloride was distilled from P_2O_5 and was degassed prior to use. Benzene was distilled from SilicaPent under nitrogen. The silica gel used was M.C.B. 230–400 mesh. All chromatographic separations were accomplished by the low-pressure flash column method of Still.[23] Low-temperature columns were run by using a triple-jacketed column in which 2-propanol (cooled with dry ice) was recirculated through the innermost jacket, the section was a sealed vacuum jacket, and a continuous stream of dry nitrogen was flushed through the outermost jacket. The silica gel used was degassed overnight (0.25 Torr, 25 °C) prior to use. NMR spectra was taken on a Varian EM-360 (60 MHz), JEOL FX-100 (100 MHz), Varian XL-200 (200 MHz), or Varian XL-300 (300 MHz) spectrometer. All spectra were recorded at room temperature unless specified as otherwise. Infrared data was recorded on either a Perkin-Elmer 137 or a Nicolet 5DXB FTIR spectrometer. Atlantic Microlab, Inc., or the University of Florida Chemical Analysis Service performed C, H analyses. Melting points (uncorrected) were obtained by using a Thomas-Hoover apparatus. All solution containing transition-metal complexes, as well as organometallic solids, were manipulated under inert atmosphere (Schlenk line or glovebox) conditions.

Synthesis of 1-Bromo-1-ethoxycyclopropane. 1-Ethoxy-1-((trimethylsilyl)oxy)cyclopropane was prepared by the method of Ruhlman.[24] The cyclopropyl bromo ether was prepared by the method of Goadwood.[25] The overall yield from ethyl 2-chloropropionate was 57.6%: ^{1}H NMR (60 MHz, $CDCl_3$) 3.72 (q, 2 H, OCH_2), 1.27 (t, 3 H, CH_3), 1.0–0.3 ppm (m, 4 H, CH_2) (lit.[25] 3.69, 1.31, 1.1–0.5 ppm).

Synthesis of Dicarbonyl(η^5-cyclopentadienyl)(1-ethoxycyclopropyl)iron (6c). To a stirred suspension of KFp (1.31 g, 6.1 mmol) was added 1-bromo-1-ethoxycyclopropane (1.00 g, 5.1 mmol) at −78 °C via cannula under nitrogen. The mixture was allowed to stir at low temperature for 1 h followed by a warming to room temperature. The mixture was then allowed to stir at ambient temperature for an additional 2 h; after which time, a brown, pasty solid was filtered from the reaction vessel. The residual brown paste was chromatographed on silica gel by using 10% ethyl acetate/hexanes (v/v) as the eluent. A yellow band was collected which yielded 0.74 g (46.6%) of a reddish orange oil: IR ($CHCl_3$) 1999, 1943 cm^{-1}; ^{1}H NMR (60 MHz, C_6D_6) 4.4 (s, 5 H, Cp), 3.4 (q, 2 H, OCH_2), 1.1 (t, 3 H, CH_3), 1.0–0.4 ppm (m, 4 H, CH_2); ^{13}C NMR (75 MHz, C_6D_6) 217.6 (M − CO), 87.1 (Cp), 63.4 (OCH_2), 60.6 (Fe–C), 19.6 (CH_2), 15.9 ppm (CH_3); mass spectrum, m/e 262 (M^+), 234 (−CO), 206 (−2CO), 186 (Cp_2Fe^+), 177 (Fp^+), 149 ($CpFeCO^+$), 85 ($C_3H_4OEt^+$). Anal. Calcd for $C_{12}H_{14}FeO_3$: C, 54.98; H, 5.39. Found: C, 54.84; H, 5.42.

Synthesis of Carbonyl(η^5-cyclopentadienyl)(1-ethoxycyclopropyl)(triphenylphosphine)iron (6d). An NMR tube was charged with dicarbonyl(η^5-cyclopentadienyl)(1-ethoxycyclopropyl)iron (0.255 g, 0.97 mmol), triphenylphosphine (0.255 g, 0.98 mmol), some boiling chips, and 1.5 mL of C_6D_6. The photolysis was carried out in the apparatus and manner previously described. The sample was irradiated for 2 h; at which time, the red solution was poured into 10 mL of hexanes. The solution was cooled to −35 °C. After several hours, 0.45 g (68.8%) of red powder had precipitated from the solution. This was recrystallized from cold hexanes to produce analytical samples: mp 97–99 °C; IR (C_6D_6) 1911.8 cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6) 7.6–6.9 (m, 15 H, PPh_3), 4.36 (d, 5 H, $^4J_{PH}$ = 1.5 Hz, Cp), 3.20 (m, 2 H, OCH_2), 1.00 (t, 3 H, CH_3), 0.54–0.21 ppm (m, 4 H, CH_2); ^{13}C NMR (50 MHz, C_6D_6) 222.4 (d, $^2J_{PC}$ = 34.2 Hz, M–CO), 137.6 (d, $^2J_{PC}$ = 39.1 Hz, C_i), 133.4 (d, $^3J_{PC}$ = 9.8 Hz, C_m), 131.4 (d, $^4J_{PC}$ = 7.4 Hz, C_p), 127.6 (d, $^2J_{PC}$ = 17.1 Hz, C_o), 85.4 (Cp), 60.9 (OCH_2), 53.7 (d, $^1J_{PC}$ = 29.3 Hz, C–OEt), 20.1, 17.9 9 (CH_2), 16.2 ppm (CH_3); mass spectrum (chemical ionization), m/e 497 (MH^+), 468 (−CO), 383 ($CpFePPh_3^+$), 234 (−PPh_3), 206 (−PPh_3, −CO), 186 (Cp_2Fe^+). Anal. Calcd for $C_{29}H_{29}FeO_2P$: C, 70.17; H, 5.89. Found: C, 69.34; H, 5.73.

Preparation of 1-Carbonyl-1-(η^5-cyclopentadienyl)-5-ethoxyferracyclopent-5-en-2-one (9c). An NMR tube was charged with dicarbonyl(η^5-cyclopentadienyl)(1-ethoxycyclopropyl)iron (0.55 g, 2.1 mmol), a few boiling stones, and 0.6 mL of C_6D_6. The tube was fitted with a rubber septum and irradiated with a 450-W medium-pressure Hg lamp in the cell of a sonicator at 25 °C. After 6 h, the solvent was removed in vacuo and the residue was chromatographed on silica gel by using 10% ethyl acetate/hexanes (v/v) as the eluent. A faint yellow band and a red band (Fp_2) were eluted from the column. A red band remained atop the column. It was brought down with pure ethyl acetate. Upon removal of the solvent from the ethyl acetate fraction, 0.05 g of a red crystalline material weighing 0.131 g (23.8%) was obtained: mp 71–72 °C; IR (CCl_4) 1950, 1646 cm^{-1}; ^{1}H NMR (60 MHz, C_6D_6) 4.5 (s, 5 H, Cp), 4.0 (q, 2 H, OCH_2), 2.3 (m, 3 H, CH_2), 1.1 ppm (t, 3 H, CH_3); ^{13}C NMR (75 MHz, C_6D_6) 342.0 (M=C), 270.0 [M(CO)R], 216.9 (M–CO), 87.5 (Cp), 74.8 (OCH_2), 53.1, 49.3 (CH^2), 14.8 ppm (CH_3); mass spectrum, m/e 262 (M^+), 234 (−CO), 206 (−2CO), 186 (Cp_2Fe^+), 177 (Fp^+), 149 ($CpFeCO^+$). Anal. Calcd for $C_{12}H_{14}FeO_3$: C, 54.98; H, 5.39. Found: C, 54.96; H, 5.43.

Photolysis of Dicarbonyl(η^5-cyclopentadienyl)(1-ethoxycyclopropyl)iron in the Presence of Carbon Monoxide. A benzene (0.5 mL) solution of the title compound (0.007 g, 0.27 mmol) was placed in an NMR tube with some boiling chips and ferrocene (0.10 mmol). The tube was cooled in liquid nitrogen, charged with CO (2 atm at room temperature), and flame sealed. Another tube was prepared with exactly the same amount of benzene, σ complex, and ferrocene. This tube was sealed under nitrogen. The tubes were subjected to photolysis in a merry-go-round apparatus that was immersed in the cell of a sonicator. The relative concentrations of the reactants and products were followed by comparison of the ratio of the ^{13}C NMR integrals of the signals corresponding to the Cp group to that of the internal standard. The relative concentrations of the σ complex, the centrally and terminally substituted π-allyls, the alkylcarbenes, and the acylcarbene are recorded in Table I.

Synthesis of 1-(η^5-Cyclopentadienyl)-1-(triphenylphosphine)-5-ethoxyferracyclopent-5-en-2-one (9d). An NMR tube was charged with 1-carbonyl-1-(η^5-cyclopentadienyl)-5-ethoxyferracyclopent-5-en-2-one (0.07 g, 0.27 mmol), triphenylphosphine (0.08 g, 0.28 mmol), some boiling chips, and 1.5 mL of C_6D_6. The photolysis was carried in the apparatus and manner previously described. After 2 h of irradiation, the red solution was chromatographed on silica gel by using a low-temperature column. The eluent was 50% ethyl acetate/hexanes (v/v). A red band was collected that yielded 0.11 g (82.1%) of a red solid: mp 148–149 °C; IR (C_6D_6) 1615 cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6) 7.6–6.9 (m, 15 H, PPh_3), 4.48 (d, 5 H, $^4J_{PH}$ = 1.35 Hz, Cp), 4.10 (m, 2 H, OCH_2), 2.10 (m, 4 H, CH_2), 1.06 (t, 3 H, CH_3); mass

(22) Unpublished results of D. J. Crowther, University of Florida.
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(25) Gadwood, R. C. *Tetrahedron Lett.* **1984**, *25*, 5851.

Table I. Effect of Added CO on Products from Photolysis of 6c[a]

time, h	6c[b]	6c/CO[c]	8c[b]	8c/CO[c]	9c[b]	9c[c]	10c[b]	10c/CO[c]	11c[b]	11c/CO[c]	Fp dimer[b]	Fp dimer/CO[c]
0.00	1.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.00	0.33	0.43	0.33	0.01	0.21	0.33	0.04	0.02	0.04	0.01	0.04	0.03
4.00	0.16	0.30	0.05	0.02	0.28	0.41	0.17	0.07	0.14	0.02	0.09	0.07
6.00	0.09	0.20	0.03	0.03	0.23	0.41	0.16	0.05	0.22	0.03	0.11	0.07
8.00	0.05	0.17	0.03	0.01	0.18	0.40	0.19	0.07	0.21	0.04	0.12	0.08

[a] All data are given as concentration relative to the initial concentration of the starting sigma complex (taken as 1.00). [b] No added CO. [c] 2 atm of added CO.

spectrum, *m/e* 262 (PPh_3^+), 234 (-PPh_3), 186 (Cp_2Fe), 121 ppm ($CpFe^+$). Anal. Calcd for $C_{29}H_{29}FeO_2P$: C, 70.17; H, 5.89. Found: C, 69.98; H, 5.91.

Characterization of 1-Carbonyl-1-(η^5-cyclopentadienyl)-2-ethoxyferracyclobut-1-ene (8c). A large sample (approximately 1 gm) of dicarbonyl(η^5-cyclopentadienyl)(1-ethoxycyclopropyl)iron was dissolved in benzene-d_6 and photolyzed in a sonicator cavity. The reaction was monitored every 30 min via ^{13}C NMR. When the spectrum indicated a maximum intensity for the singlet at 82.8 ppm (after 2 h), the contents of the tube were subjected to low-temperature (-50 °C) flash chromatography on silica gel (4 in. × 25 mm) using 10% (v/v) ethyl acetate in hexane as the eluent. A yellow band followed by a red band progressed down the column. The polarity of the eluent was increased to speed the red band down the column as it decomposed to a brown material during its solution. A red oil was obtained upon evaporation of the solvent in vacuo at 0 °C: ^{13}C NMR (75 MHz, C_6D_6) 335.0 (M=C), 224.0 (CO), 82.8 (Cp), 79.4 (OCH_2), 61.6, 56.8 (CH_2), 12.5 ppm (CH_3); ^1H NMR (60 MHz, C_6D_6) 4.3 (s, Cp), 4.0 (m, OCH_2), 2.5-1.7 (m, CH_2), 0.9 ppm (t, CH_3).

Synthesis of Carbonyl(η^5-cyclopentadienyl)(*exo*-η^3-2-ethoxypropenyl)iron (10c). An NMR tube was charged with dicarbonyl(η^5-cyclopentadienyl)(1-ethoxycyclopropyl)iron (0.55 g, 2.1 mmol) along with some boiling chips and 0.6 mL of C_6D_6. The tube was fitted with a rubber septum and irradiated in the cell of a sonicator under nitrogen at room temperature. It was found that the yield of the title compound was dependent upon the time of irradiation; hence yields varied. For maximum yield, the photolysis was continued for 6 h. The solvent was removed in vacuo, and the residual material was chromatographed on silica gel using 10% ethyl acetate/hexanes (v/v) as the eluent. A yellow band was collected. After solvent removal, the yellow material was rechromatographed on silica by using 2% ethyl acetate/hexanes (v/v) as the eluent. The first yellow band was collected. Upon removal of the solvent in vacuo, 0.01 g (18.3%) of a yellow solid was obtained: mp 130-132 °C; IR (CCl_4) 1945 cm^{-1}; ^1H NMR (100 MHz, C_6D_6) 4.27 (s, 5 H, Cp), 3.37 (q, 2 H, J = 6.9 Hz, OCH^2), 3.12 (d, 2 H, $J_{H_sH_a}$ = 1.2 Hz, H_s), 1.06 (t, 3 H, J = 6.9 Hz, CH_3), 0.69 ppm (d, 2 H, $J_{H_sH_a}$ = 1.2 Hz, H_a); ^{13}C NMR (25 MHz, C_6D_6) 221.3 (M-CO), 133.8 (C-OEt), 79.8 (Cp), 62.7 (OCH_2), 14.7 ppm (CH_3); mass spectrum, *m/e* 234 (M^+), 206 (-CO), 186 (Cp_2Fe^+), 121 ($CpFe^+$), high-resolution calcd for $C_{11}H_{14}FeO_2$ 234.03428, found 234.036114, deviation +7.8 ppm.

Synthesis of Carbonyl(η^5-cyclopentadienyl)(*exo*-η^3-*syn*-1-ethoxypropenyl)iron (11c). The title compound was prepared by the same method as was carbonyl(η^5-cyclopentadienyl)(η^3-2-ethoxypropenyl)iron with the following modification: the second yellow band of the ultimate chromatographic column was collected. Upon removal of the solvent in vacuo, 0.01 g (11.9%) of a yellow solid was recovered: mp 128-129 °C; IR (CCl_4) 1940 cm^{-1}; ^1H NMR (100 MHz, C_6D_6) 4.49 (m, 1 H, H_c), 4.26 (s, 5 H, Cp), 3.83 (d, 1 H, $J_{H_sH_a}$ = 7.8 Hz, H_a), 3.48 (q, 2 H, J = 7.2 Hz, OCH_2), 2.41 (dd, 1 H, $J_{H_sH_c}$ = 7.5 Hz, $J_{H_sH_a}$ = 2.1 Hz, H_s), 1.16 (t, 3 H, J = 7.1 Hz, CH_3), 0.33 ppm (dd, 1 H, $J_{H_aH_c}$ = 10.9 Hz, $J_{H_aH_s}$ = 2.1 Hz, H_a); ^{13}C NMR (25 MHz, C_6D_6) 222.2 (M-CO), 99.9 (C-OEt), 79.8 (Cp), 67.8 (OCH_2), 61.0 (CH), 22.4 (CH_2), 15.1 ppm (CH_3); mass spectrum, *m/e* 234 (M^+), 206 (-CO), 186 (Cp_2Fe^+), 177 (Fp^+), 149 ($CpFeCO^+$), 121 ($CpFe^+$); high-resolution calcd for $C_{11}H_{14}FeO_2$ 234.03428, found 234.03428, deviation +2.9 ppm.

Thermolysis of Carbonyl(η^5-cyclopentadienyl)(1-ethoxycyclopropyl)(triphenylphosphine)iron. The title compound (0.255 g, 0.97 mmol) was placed in an NMR tube along with some boiling stones and 1.6 mL of C_6D_6. The tube was fitted with a rubber septum and was placed in an oil bath maintained at 75 °C. The contents of the tube were kept under a blanket of nitrogen with an oil bubbler serving as a pressure release. The tube was heated for 47 h after which time the contents were emptied into hexanes. When the solution was chilled to -35 °C, 0.189 g (78.9%) of **9d** precipitated from the solution as a red solid.

Photolysis of 1-Carbonyl-1-(η^5-cyclopentadienyl)-5-ethoxyferracyclopent-5-en-2-one. A benzene-d_6 solution of the title compound (0.07 g, 0.27 mmol) was photolyzed in an NMR tube under a nitrogen blanket while being sonicated. The course of the reaction was monitored via ^{13}C NMR. At the end of 2 h, the following resonances were detected in the Cp region of the spectrum: 87.5 (ferracyclopentenone), 82.8 (ferracyclobutene), 79.8 (π-allyls), 87.1 ppm (σ complex). The presence of the ferracyclobutene was supported by the observation of the carbenic resonance at δ 335.0 ppm. The identity of the π-allyls and the σ complex was confirmed by repeated flash chromatography columns using 10% EtOAc/hexanes as the eluent. The compounds were isolated, and their ^1H NMR and ^{13}C NMR spectra were identical with those of authentic samples synthesized independently. The compounds were isolated. The contents of the tube were subjected to flash chromatography on silica gel using 10% (v/v) ethyl acetate in hexane as the eluent. Significantly, a yellow band was collected that upon removal of solvent in vacuo yielded a small amount of the σ-complex dicarbonyl(η^5-cyclopentadienyl)(1-ethoxycyclopropyl)iron based on comparison of its IR, ^1H NMR, and ^{13}C NMR spectra with those of an authentic sample.

Synthesis of Dicarbonyl(η^5-cyclopentadienyl)(1-(phenylthio)cyclopropyl)iron (6e). To a stirred suspension of KFp (1.56 g, 7.2 mmol) in 10 mL of THF at -78 °C was added 1-iodo-1-(phenylthio)cyclopropane (2.0 g, 7.2 mmol) via a steel cannula under nitrogen. The mixture was allowed to stir at low temperature for 1 h followed by warming to room temperature. The material was allowed to stir at ambient temperature for an additional 2 h. A brown solid was filtered from the mixture, and the remaining material was chromatographed on silica gel by using 10% ethyl acetate/hexanes (v/v) as the eluent. A yellow band was collected that yielded 1.09 g (46.4%) of an amber oil upon in vacuo removal of the solvent: IR (C_6D_6) 2010.3, 1955.0 cm^{-1}; ^1H NMR (60 MHz, C_6D_6) 7.5-6.8 (m, 5 H, SPh), 4.0 (s, 5 H, Cp) 0.7 ppm (m, 4 H, CH_2); ^{13}C NMR (50 MHz, C_6D_6) 216.4 (M-CO) 139.6, 131.6, 128.7, 126.4 (SPh), 87.8 (Cp), 20.6 (CH_2), 10.7 ppm (C-SPh); mass spectrum (chemical ionization), *m/e* 327 (MH^+), 298 (-CO), 271 (-2CO), 217 ($FpC_3H_4^+$), 189 [$CpFe(CO)C_3H_4^+$], 177 (Fp^+), 149 ($CpFeCO^+$). Anal. Calcd for $C_{16}H_{14}FeO_2S$: C, 58.91; H, 4.33. Found: C, 58.51; H, 4.55.

Synthesis of Carbonyl(η^5-cyclopentadienyl)(η^1-(phenylthio)cyclopropyl)iron (12). An NMR tube was charged with dicarbonyl(η^5-cyclopentadienyl)(1-(phenylthio)cyclopropyl)iron (0.276 g, 0.662 mmol) along with some boiling chips and 0.6 mL of C_6D_6. The sample was photolyzed in the apparatus and manner previously described. After 2 h of irradiation, the contents of the tube were poured into 5 mL of hexanes. The liquid was allowed to evaporate to dryness at -35 °C over the course of several days. A dirty yellow solid was obtained that could be further purified by low-temperature recrystallization from hexanes. A yellow solid weighing 0.052 g (19.8%) was obtained. Alternatively, the reaction mixture was stripped of its solvent in vacuo and chromatographed on silica gel by using 5% ethyl acetate/hexanes (v/v) as the eluent. A yellow band was collected that yielded trace amounts of the title compound as determined from its spectral characteristics: mp 110 °C dec; IR (C_6D_6) 1921.6 cm^{-1}; ^1H NMR (200 MHz, C_6D_6)

7.7–6.8 (m, 5 H, SPh), 3.98 (s, 5 H, Cp), 1.2–0.8 ppm (m, 4 H, CH_2); ^{13}C NMR (50 MHz, C_6D_6) 218.7 (M–CO), 133.2, 129.1, 128.3, 127.2 (SPh), 79.8 (Cp) 49.6 (C–SPh), 14.7, 10.9 ppm (CH_2); mass spectrum (chemical ionization), *m/e* 299 (MH^+), 270 (–CO), 186 (Cp_2Fe^+), 149 ($CpFeCO^+$), 121 ($CpFe^+$). Anal. Calcd for $C_{15}H_{14}FeOS$: C, 60.42; H, 4.73. Found: C, 60.19; H, 4.12.

Synthesis of Carbonyl(η^5-cyclopentadienyl)(η^3-2-(phenylthio)propenyl)iron (10e). An NMR tube was charged with dicarbonyl(η^5-cyclopentadienyl)(1-(phenylthio)cyclopropyl)iron (0.216 g, 0.662 mmol) along with some boiling chips and 1.5 mL of C_6D_6. The sample was photolyzed in the apparatus and manner previously described. After 4 h of irradiation, the tube was immersed in an oil bath that was maintained at 75 °C. The contents were kept under a nitrogen blanket with an oil bubbler serving as a pressure release. The tube was heated for 21 h at which time the solvent was removed in vacuo and the residual material was chromatographed on silica gel by using 2% ethyl acetate/hexanes (v/v) as the eluent. The second yellow band was collected, and it was stripped of its solvent. The light yellow oil was rechromatographed on silica gel by using pure hexanes and the eluent. A yellow band was collected that yielded 0.04 g (19.4%) of a yellow solid: mp 133–134 °C; IR (C_6D_6) 1945.9 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) 7.3–6.8 (m, 5 H, SPh), 3.97 (s, 5 H, Cp), 2.77 (d, 2 H, J_{HH} = 1.7 Hz, H_s), 0.78 ppm (d, 2 H, J_{HH} = 1.7 Hz, H_a); ^{13}C NMR (75 MHz, C_6D_6) 222.3 (M–CO), 142.2 (C–SPh) 129.1, 128.4, 127.7, 125.8 (SPh), 80.9 (Cp) 42.1 ppm (CH_2); mass spectrum, *m/e* 298 (M^+), 270 (–CO), 186 (Cp_2Fe^+), 149 ($CpFeCO^+$); 121 ($CpFe^+$). Anal. Calcd for $C_{15}H_{14}FeOS$: C, 60.42; H, 4.73. Found: C, 60.22; H, 4.02.

Synthesis of Carbonyl(η^5-cyclopentadienyl)(1-(phenylthio)cyclopropyl)(triphenylphosphine)iron (6f). An NMR tube was charged with dicarbonyl(η^5-cyclopentadienyl)(1-(phenylthio)cyclopropyl)iron (0.216 g, 0.622 mmol) along with triphenylphosphine (0.17 g, 0.65 mmol), some boiling chips, and 1.5 mL of C_6D_6. The sample was irradiated in the apparatus and manner previously described. After 1 h of irradiation, a red solid began precipitating from the solution. The contents were poured into cold hexanes to suspend the solid. After the solution was filtered and washed three times with cold hexanes, 0.154 g (42.4%) of a red powder was obtained. The material was further purified by low-temperature recrystallization from a benzene/hexanes solvent system: mp 99–101 °C; IR (C_6D_6) 1921.5 cm^{-1}; ^1H NMR (200 MHz, C_6D_6) 7.75–6.90 (m, 15 H, PPh_3), 4.499 (s, 5 H, Cp), 1.21–0.88 ppm (m, 4 H, CH_2); ^{13}C NMR (50 MHz, C_6D_6) 222.7 (d, $^2J_{PC}$ = 32.1 Hz, M–CO), 137.4 (J_{PC} = 4.2 Hz), 136.7, 135.7, 134.5 (d, J_{PC} = 9.8 Hz) [PPh_3], 129.6, 128.3, 127.9, 126.9 (SPh), 86.3 (Cp), 17.1, 15.5 (CH_2), 7.7 ppm (d, $^2J_{PC}$ = 21.5 Hz); mass spectrum (chemical ionization), *m/e* 532 (–CO), 298 (–PPh_3), 270 (–PPh_3, –CO), 263 (PPh_3H^+), 186 (Cp_2Fe^+), 177 (Fp^+), 149 ($CpFeCO^+$). Anal. Calcd for $C_{33}H_{29}FeOPS$: C, 70.72; H, 5.22. Found: C, 70.41; H, 4.90.

Synthesis of *trans*- and *cis*-Dicarbonyl(η^5-cyclopentadienyl)(2-fluorocyclopropyl)iron (6h). To a stirred suspension of KFp (1.09 g, 5.04 mmol) at –78 °C in 10 mL of THF was added *trans*-1-bromo-2-fluorocyclopropane[26] via a steel cannula under nitrogen. The material was allowed to stir for 1 h at low temperature. It then was warmed to room temperature and allowed to stir for an additional 2 h. A brown solid was filtered from the mixture, and the filtrate was stripped of its solvent in vacuo. The residue was chromatographed on silica gel by using 10% ethyl acetate/hexanes as the eluent. A yellow band was collected, concentrated, and rechromatographed on silica gel by using pure hexanes. The first of two yellow bands was collected. Upon removal of its solvent in vacuo, 0.143 g (16.8%) of an amber oil (trans isomer) was obtained: IR (C_6D_6) 2016.3, 1962.1 cm^{-1}, ^1H NMR (300 MHz, C_6D_6) 4.32 (m, 1 H, J_{HF} = 70.8 Hz, CHF), 3.97 (s, 5 H, Cp), 1.1 (m, 2 H, CH_2), 0.21 ppm (m, 1 H, Fe–CH); ^{13}C NMR (75 MHz, C_6D_6) 216.4 (M–CO), 85.5 (Cp), 80.1 (d, J_{CF} = 225.1 Hz, CF), 15.4 (d, $^2J_{CF}$ = 12.7 Hz, CH_2), –5.8 ppm (Fe–C); ^{19}F NMR (282 MHz, C_6D_6) –191.21 ppm (m, $^2J_{HF_{gem}}$ = 70.8 Hz, $J_{HF_{cis}}$ = 29.3 Hz, $J_{HF_{cis}}$ = 19.5 Hz, $J_{HF_{trans}}$ = 4.9 Hz); mass spectrum, *m/e* 236 (M^+), 208 (–CO), 149 ($CpFeCO^+$), 121 ($CpFe^+$); high-resolution calcd for $C_{10}H_9FFeO_2$ 235.99359, found 235.99274, dev –3.64 ppm. Removal of the solvent from the second fraction afforded 0.031 g (3.6%) of an amber oil (cis isomer): IR (C_6D_6) 2010.3, 1953.8 cm^{-1}; ^1H NMR (300 MHz, C_6D_6), 4.31 (m, 1 H, J_{HF} = 71.4 Hz, CHF), 4.21 (s, 5 H, Cp), 1.10 (m, 2 H, CH_2), 0.25 ppm (m, 1 H, FeCH); ^{13}C NMR (75 MHz, C_6D_6) 216.7 (M–CO), 85.3 (Cp), 78.3 (d, J_{CF} = 311.8 Hz, CF), 14.3 (d, $^2J_{CF}$ = 10.0 Hz, CH_2), –5.1 ppm (FeC); ^{19}F NMR (282 MHz, C_6D_6) –199.2 ppm (m, $J_{HF_{gem}}$ = 71.4 Hz, $J_{HF_{cis}}$ = 25.0 Hz, $J_{HF_{trans}}$ = 6.0 Hz, $J_{HF_{trans}}$ = 5.2 Hz); mass spectrum, *m/e* 236 (M^+), 208 (–CO), 149 ($CpFeCO^+$), 121 ($CpFe^+$), high-resolution calcd for $C_{10}H_9FFeO_2$ 235.99359, found 235.99291, dev –2.88 ppm.

Photolysis of *cis*- and *trans*-Dicarbonyl(η^5-cyclopentadienyl)(2-fluorocyclopropyl)iron. A mixture of the *trans*- (82.3%) and *cis*- (17.7%) dicarbonyl(η^5-cyclopentadienyl)(2-fluorocyclopropyl)iron complexes (0.167 g, 7.31 mmol) was placed in an NMR tube along with some boiling chips and ferrocene (0.05 g, 3.1 mmol) as an internal standard. The sample was photolyzed in the apparatus and manner previously described. The reaction was monitored over a 16-h period by ^{13}C and ^{19}F NMR. During this period, the trans σ complex decreased to a negligible concentration; the concentration of the cis σ complex did not change with time. At the end of 3 days of irradiation, the solvent was removed from the sample in vacuo and the residue was chromatographed on silica gel by using hexane as the eluent. The first four yellow bands were collected. Four compounds were isolated and were identified to be ferrocene, *exo,anti*-**10h**, *syn*-**10h**, and *endo,anti*-**10h**, respectively. *exo,anti*-**10h**: mp 128 °C; IR (C_6D_6) 1949.7 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) 4.86 (dd, 1 H, $J_{H_s'F}$ = 71.1 Hz, $J_{H_s'H_c}$ = 6.16 Hz, H_a'), 4.31 (m, 1 H, H_c), 4.05 (s, 5 H, Cp), 2.10 (d, 1 H, $J_{H_sH_c}$ = 7.7 Hz, H_s), 0.15 ppm (d, 1 H, $J_{H_aH_c}$ = 11.2 Hz, H_a); ^{13}C NMR (75 MHz, C_6D_6) 221.0 (M–CO), 108.9 (d, $J_{CF_{gem}}$ = 249.6 Hz, CF), 80.3 (Cp), 61.5 (d, $J_{CF_{syn}}$ = 13.9 Hz, CH), 22.9 ppm (d, $^3J_{CF}$ = 7.2 Hz, CH_2); ^{19}F NMR (282 MHz, C_6D_6) –172.88 ppm (dd, $J_{HF_{gem}}$ = 71.1 Hz, $J_{HF_{anti}}$ = 12.2 Hz); mass spectrum, *m/e* 208 (M^+), 180 (–CO), 149 ($CpFeCO^+$), 121 ($CpFe^+$). Anal. Calcd for C_9H_9FFeO: C, 51.96; H, 4.36. Found: C, 52.30; H, 4.30. *syn*-**10h**: mp 118.5–120 °C; ^1H NMR (300 MHz, C_6D_6) 5.691 (dd, 1 H, $J_{H_a'F}$ = 72 Hz, $J_{H_a'H_c}$ = 6.74 Hz, H_a'), 4.153 (m, 1 H, H_c), 4.15 (s, 5 H, Cp), 2.414 (d, 1 H, $J_{H_sH_c}$ = 8.6 Hz, H_s), 0.614 (d, 1 H, $J_{H_aH_c}$ = 12.0 Hz, H_a); ^{19}F NMR (282 MHz, C_6D_6) –169 ppm (dd, $J_{HF_{gem}}$ = 71.9 Hz, $J_{HF_{syn}}$ = 8.6 Hz). All spectroscopic data of the *endo,anti*-**10h** are the same as the authentic sample obtained from independent synthesis.

Synthesis of Dicarbonyl(η^5-cyclopentadienyl)(η^1-1-fluoropropenyl)iron. To a stirred suspension of $KCpFe(CO)_2$ (2.84 g, 13.15 mmol) in 100 mL of THF at 0 °C was added neat epifluorohydrin (0.9 g, 13.15 mmol). The mixture was stirred at 0 °C for 1 h and then added to 100 mL of anhydrous diethyl ether containing 3.5 mL of HBF_4 (57%) (1.59 g, 21.5 mmol) at 0 °C. Collection of the yellow solid and reprecipitation from acetone with diethyl ether followed by further reprecipitation from nitromethane gave the fluoroborate salt (3.8 g, 89%): mp 175 °C dec; FT IR (Nujol) 2073, 2037 cm^{-1}; ^1H NMR (300 MHz, CD_3NO_2) 5.971 (s, 5 H, Cp), 5.155 (m, 1 H, =CH), 4.893 (complex m, 2 H, CH_2F), 4.097 (d, 1 H, *J* = 9 Hz, cis $=CH_2$), 3.692 ppm (d, 1 H, *J* = 15 Hz, trans $=CH_2$); ^{13}C NMR (75 MHz, CD_3NO_2) 207.27 (M–CO), 91.01 (Cp), 84.291 (d, $^1J_{CF}$ = 170 Hz, CH_2F), 79.871 (d, $^2J_{CF}$ = 18.0 Hz, =CH), 52.615 ppm (d, $^3J_{CF}$ = 7.6 Hz, $=CH_2$) (cf. ref 7).

The fluoroborate salt (1.0 g, 3.09 mmol) was taken up in 10 mL of methylene chloride, and the mixture was cooled to 0 °C. Diisopropylethylamine (0.45 g, 3.17 mmol) was added, and after 10 min at 0 °C, solvent was removed and the brown oil was extracted several times with petroleum ether to give the title complex (0.250 g, 35%) as an amber oil: ^1H NMR (300 MHz, C_6D_6) 6.856 (d, 1 H, J_{HF} = 50 Hz, =CHF), 6.097 (m, 1 H, =CH), 5.136 (d, 1 H, *J* = 16.6 Hz, CH_2–M), 4.743 (d, 1 H, *J* = 10 Hz, CH_2–M), 4.077 ppm (s, 5 H, Cp); ^{13}C NMR (300 MHz, C_6D_6) 216.548 (M–CO), 148.302 (d, $^2J_{CF}$ = 14.7 Hz), 103.920 (d, $^3J_{CF}$ = 11.6 Hz), 96.985 (d, $^1J_{CF}$ = 228.6 Hz), 86.548 ppm (Cp). Elemental analysis of this complex could not be done due to its decomposition above 0 °C.

Synthesis of Carbonyl(η^5-cyclopentadienyl)(*endo*-η^3-*anti*-1-fluoropropenyl)iron (10h). A solution of the σ complex from the previous experiment (0.150 g, 0.635 mmol) in 0.6 mL

(26) Graciously provided by W. R. Dolbier, University of Florida.

of benzene-d_6 was placed in an NMR tube along with some boiling chips. The tube was fitted with a rubber septum and irradiated with a 450-W medium-pressure Hg lamp in the cell of a sonicator at 10 °C. The reaction was monitored over a 15-h period by ^{13}C NMR. After the end of 15 h of irradiation, the solvent was removed in vacuo and the residue was flash chromatographed over silica gel using 5% ethyl acetate/hexanes as the eluent. The first yellow band was collected. Upon removal of the solvent in vacuo, 0.061 g (46%) of a yellow solid was recovered: mp 115.5–116 °C; FT IR ($CDCl_3$) 1967.1 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) 7.432 (dd, 1 H, J_{HF} = 71.4 Hz, $J_{H_sH_c}$ = 3.9 Hz, =CHF), 4.503 (s, 5 H, Cp), 3.687 (m, 1 H, $=CH_c$), 3.128 (d, 1 H, J_{HH_c} = 7.6 Hz, $=CH_2$), 1.642 ppm (d, 1 H, J_{HH_c} = 11.4 Hz, $=CH_2$); ^{13}C NMR (75 MHz, C_6D_6) 219.459 (M–CO), 113.093 (d, $^1J_{CF}$ = 249.8 Hz, =CHF), 80.231 (Cp), 56.513 (d, $^2J_{CF}$ = 10.2 Hz, =CH), 36.482 ppm (d, $^3J_{CF}$ = 3.1 Hz, $=CH_2$); ^{19}F NMR (282 MHz, C_6D_6) −189.95 ppm (dd, $J_{HF_{gem}}$ = 71.35 Hz, $J_{HF_{anti}}$ = 14.65 Hz); mass spectrum, *m/e* 208 (M^+), 180 (−CO), 121 ($CpFeCO^+$). Anal. Calcd for C_9H_9FFeO: C, 51.96; H, 4.36. Found: C, 52.10; H, 4.33.

Thermal Isomerization of Carbonyl(η^5-cyclopentadienyl)(*endo*-η^3-*anti*-1-fluoropropenyl)iron. The complex was dissolved in benzene-d_6 in an NMR tube. The tube was fitted with a rubber septum and was heated at 84 °C in an oil bath. The reaction was monitored by ^1H and ^{19}F NMR periodically. After 20 h at 84 °C, it had transformed clearly to the *exo,anti*-**10h**. The half-life of isomerization was estimated to be 6 h.

Synthesis of *trans*- and *cis*-2-Methylcyclopropyl Bromides. The procedure of Applequist and Peterson[27] was followed to synthesize the title compounds, as a mixture of isomers. The isomeric composition obtained from their synthesis (using a *cis/trans* mixture of the silver salt of 2-methylcyclopropanecarboxylic acid) was not specified. In our hands, a 35/65 mixture of cis/trans isomers was procured.

Synthesis of Dicarbonyl(η^5-cyclopentadienyl)(2-methylcyclopropyl)iron (6g). A slurry of KFp (1.5 g, 6.9 mmol) was prepared in 25 mL of THF and cooled to −78 °C. A solution of 2-methylcyclopropyl bromide (1.2 g, 6.9 mmol) in 20 mL THF, also cooled to −78 °C, was slowly added by cannula. The reaction was allowed to stir and warm to room temperature over the course of 18 h. Removal of the solvents, extraction of the residue with hexanes, filtration over Celite, and removal of solvents resulted in a dark red semisolid. Column chromatography on neutral alumina, with hexane as eluent, gave a yellow band. Rotovapping gave the title compound as a red-yellow oil in 8% yield (3:1 trans:cis) (the major product from this reaction was FpBr). Even though the oil appeared pure by spectroscopic methods (^{13}C and ^1H NMR), small amounts of a blackish solid were invariably observed, even from freshly eluted solutions. Consequently, satisfactory elemental analysis could not be obtained. It was not possible to separate the cis from the trans isomer, and the mixture was used in subsequent experiments: IR (CCl_4) 2011, 1955 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) 4.17 (s, Cp of cis isomer), 4.12 (s, Cp of trans), 1.20 (d, Me of trans), 1.16 (d, Me of cis), +1.40 to −0.16 ppm (m); ^{13}C NMR (300 MHz, C_6D_6) 217.3 (M–CO), 85.4 (Cp of cis and trans), 22.1, 17.4, 17.2, −0.2 (due to trans isomer), 19.4, 15.4, 11.8, 0.4 ppm (due to cis isomer); mass spectrum, *m/e* 233 (M + 1).

Synthesis of 2-Methylcyclopropanecarboxylic Acid Chloride. To neat 2-methylcyclopropanecarboxylic acid,[28] (5.0 g, 50 mmol) was slowly added oxallyl chloride (12.9 mL, 150 mmol). The reaction was allowed to stir under N_2 for 12 h. Excess oxallyl chloride was removed at reduced pressure (30 mm, room temperature). The acid chloride was purified by Kugelrohr distillation at 30 mm and a cut taken from 45 to 55 °C yielded 60% of pure title compound.

Synthesis of Dicarbonyl(η^5-cyclopentadienyl)((2-methylcyclopropyl)carbonyl)iron (13). To a slurry of KFp (3.6 g, 16.9 mmol) in 20 mL of THF was added 2-methylcyclopropanecarboxylic acid chloride (2.0 g, 16.9 mmol) dissolved in 20 mL of THF, via cannula at 0 °C. The reaction was stirred for 15 h and allowed to warm to room temperature. Hexane (100 mL) was added, the crude reaction was filtered over Celite, and the solvents were removed to give a red-yellow oil. Chromatography on neutral alumina with hexane resulted in the separation of a yellow band which gave a 35% yield of the title compound as a red-yellow oil. Subsequent analysis showed the acyl to be an 86/14 mixture of trans/cis isomers: IR (CCl_4) 2022, 1961, 1641 cm^{-1}; ^1H NMR (300 MHz, C_6D_6), 4.9 (s, Cp), 3.05 (m, cis FpCOCH), 2.75 (m, trans FpCOCH), 2.0–0.9 (m's); ^{13}C NMR (300 MHz, C_6D_6) 249.6 (MCOR), 215.27, 215.12 (M–CO), 86.3 (Cp), 49.0 (trans (CO)–CH), 46.1 (cis (CO)–CH), 19.43, 19.32, 18.0 (trans CHMe, CH_2, Me), 18.5, 15.6, 12.7 (cis CHMe, CH_2, Me); mass spectrum, *m/e* 261 (M + 1). Anal. Calcd for $C_{12}H_{12}FeO_3$: C, 55.42; H, 4.65. Found: C, 55.49; H, 4.70.

Photolysis of 13. In an NMR tube with boiling chips, 0.3 g of **13** in 0.7 mL benzene-d_6 was photolyzed at 15 °C over a period of 40 h. The crude reaction was analyzed by ^{13}C NMR which showed only the *syn*-crotyl, π-allyl complex **10h** to be formed, 36% (both exo and endo configurations), and the major products (59%) were *trans*- and *cis*-dicarbonyl(η^5-cyclopentadienyl)(2-methylcyclopropyl)iron (**6g**). About 3% of the reaction mixture was Fp_2.

Photolysis of Dicarbonyl(η^5-cyclopentadienyl)(2-methylcyclopropyl)iron (6g). A mixture of the cis (25%) and trans (75%) isomers (0.3 g, 1.3 mmol), Fp_2 (0.05 g, 0.11 mmol), and 0.6 mL of C_6D_6 were mixed in an NMR tube with graphite boiling chips and capped with a septum. The tube was immersed in a water bath and photolyzed at 34 °C for 48 h. It was observed (monitoring ^{13}C NMR) that the trans alkyl complex disappeared faster than the cis isomer, and this coincided with an increase in the amount of *exo,syn*- and *endo,syn*-η^3-allyl complexes. The exo, anti isomer was also observed to form. After 48 h of photolysis, a 50:50 ratio of cis/trans isomers (starting material) remained and a 14/86 ratio of anti:syn isomers of **10g** were present.

Independent Synthesis of *syn*- and *anti*-Carbonyl(η^5-cyclopentadienyl)(η^3-1-methylpropenyl)iron (10g). The title compounds were obtained as a 63:37 mixture of syn/anti η^3-allyls (predominantly exo) by photolysis of the corresponding η^1-allyls following a literature procedure.[29] The ^1H NMR spectrum agreed with the published spectrum. A small amount of the *endo,syn*-allyl was also observed (identification based on its thermal instability). The mixture of isomers was chromatographed on neutral alumina using hexane as eluent to give a mixture of exo, syn and exo, anti isomers. The endo, syn isomer did not survive the chromatography. However, photolysis, at 15 °C, of a C_6D_6 solution of the purified exo, syn and exo, anti mixture resulted in a decrease of the exo, syn isomer with a concomitant increase in the endo, syn isomer. After cessation of photolysis, the mixture was allowed to warm to room temperature and monitored periodically by ^{13}C NMR. The endo, syn isomer was observed to essentially disappear, while the relative amount of exo, syn isomer increased. At no time was any endo, anti isomer detected. ^{13}C NMR (300 MHz, C_6D_6); exo, syn isomer, 222.6 (M–CO), 79.6 (Cp), 75.4 (CH), 53.0 (CHMe), 29.5 (CH_2), 21.8 ppm (CH_3); exo, anti isomer, 222.6 (M–CO), 79.6 (Cp), 72.4 (CH), 50.3 (CHMe), 33.8 (CH_2), 18.4 ppm (CH_3); endo, syn isomer, 92.8 (CH), 82.5 (Cp), 55.1 (CHMe), 32.5 (CH_2), 22.4 ppm (CH_3).

Quantitative ^{13}C NMR Studies of *exo,syn*- and *exo,anti*-10g Interconversions. To determine if any interconversion from *anti*-**10g** to its syn isomer was occurring, quantitative ^{13}C was used to monitor a mixture of *syn*- and *anti*-**10g** subjected to photolysis. Careful T_1 studies had been performed on C_6D_6 solutions of exo, syn and exo, anti isomers employing the standard program available with the Varian VXR 300. For each isomer, four nonoverlapping resonances were observed in the region from 10 to 80 ppm. The Cp resonances were coincidental. Thus, the amount of an isomer could be monitored via four independent quantities. A solution containing only *exo,syn*- and *exo,anti*-**10g** (63.37; 0.4 g, 2 mmol) in 0.6 mL of C_6D_6 was photolyzed for 8 h at 34 °C. During this time, a small amount of the endo, syn isomer was formed (from the exo, syn isomer). Quantitative ^{13}C measurements were taken every 24 h for an additional 72 h of pho-

(27) Applequist, D. E.; Peterson, A. H. *J. Am. Chem. Soc.* **1960**, *82*, 2372.

(28) Obtained from Aldrich Chemicals as a 15:85 mixture of cis/trans isomers.

(29) Merour, J.; Charrier, C.; Roustan, J.; Benain, J. *C.R. Seances Acad. Sci., Ser. C* **1971**, *105*, 101.

tolysis. Within experimental error, the relative amounts of the three isomers remained constant.

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Registry No. **6c**, 114944-66-0; **6d**, 114944-67-1; **6e**, 123724-41-4; **6f**, 123724-44-7; *trans*-**6g**, 123724-50-5; *cis*-**6g**, 123807-09-0; *trans*-**6h**, 123724-45-8; *cis*-**6h**, 123807-06-7; **8c**, 114944-68-2; **9c**, 114944-69-3; **9d**, 114944-70-6; *exo*-**10c**, 114944-72-8; **10e**, 123724-43-6; *exo,syn*-**10g**, 35429-53-9; *exo,anti*-**10g**, 35429-52-8; *exo,anti*-**10h**, 123724-46-9; *endo,syn*-**10h**, 123807-07-8; *endo,anti*-**10h**, 123807-08-9; *exo,syn*-**10h**, 123807-11-4; *exo,syn*-**11c**, 114944-71-7; **12**, 123724-42-5; *trans*-**13**, 123724-51-6; *cis*-**13**, 123807-10-3; KFp, 60039-75-0; $[CpFe(CO)_2(\eta^2\text{-}CH_2{=}CHCH_2F)]BF_4$, 123724-49-2; dicarbonyl(η^5-cyclopentadienyl)(η^1-*cis*-1-fluoropropenyl)iron, 123724-47-0; 1-bromo-1-ethoxycyclopropane, 95631-62-2; 1-iodo-1-(phenylthio)cyclopropane, 123724-40-3; *trans*-1-bromo-2-fluorocyclopropane, 116577-38-9; *trans*-2-methylcyclopropyl bromide, 6142-48-9; epifluorohydrin, 503-09-3; *cis*-2-methylcyclopropyl bromide, 6142-60-5; 2-methylcyclopropanecarboxylic acid chloride, 60733-34-8; 2-methylcyclopropanecarboxylic acid, 29555-02-0; oxalyl chloride, 79-37-8.

Solid-State Structure and Fluxional Solution Behavior of the Ambident Organometallic Nucleophiles $(\eta^3\text{-}C_7H_7)M(CO)_3^-$ (M = Ru, Os)

Stephen T. Astley and Josef Takats*

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

John C. Huffman and William E. Streib

Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

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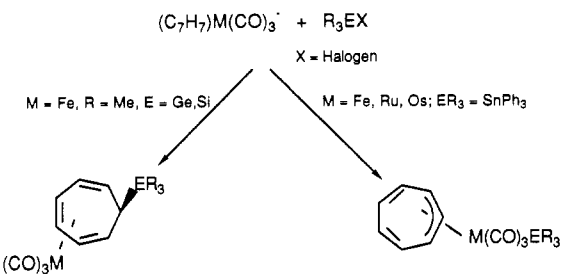
The cycloheptatrienyl carbonyl anions $(C_7H_7)M(CO)_3^-$ (M = Ru, **1b**; M = Os, **1c**) have been isolated and structurally characterized as their Ph_4As^+ salts. Both **1b** and **1c** crystallize in the centrosymmetric space group $P\bar{1}$ with two molecules per unit cell. For **1b**: a = 12.308 (4) Å, b = 12.017 (5) Å, c = 11.326 (4) Å, α = 71.18 (2)°, β = 80.93 (2)°, γ = 90.15 (2)°. For **1c**: a = 12.314 (2) Å, b = 12.025 (2) Å, c = 11.331 (2) Å, α = 71.12 (2)°, β = 80.87 (2)°, γ = 90.08°. The structures were refined to $R(F)$ = 0.0567 and 0.0268 and $R_w(F)$ = 0.0575 and 0.0278 for 3686 and 3905 reflections with $F > 3.0\sigma(F)$ for **1b** and **1c**, respectively. In both cases the seven-membered ring is coordinated to the metal in an η^3 fashion. The low-temperature-limiting ^1H and ^{13}C NMR spectra of **1c** have been obtained and show that the same bonding mode is also adopted in solution. A comparison of the spectroscopic, structural, and chemical properties for the series of complexes $(C_7H_7)M(CO)_3^-$ (M = Fe, Ru, Os) is made and explained in terms of increasing metal basicity upon descending the triad.

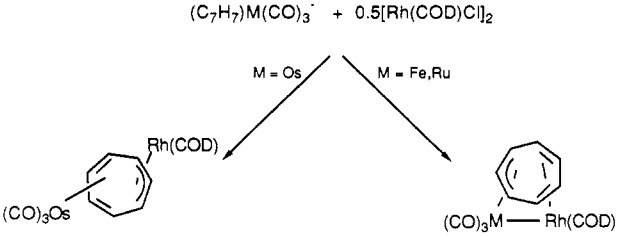
Introduction

Anionic complexes of the transition metals are generally highly reactive species and offer a simple route to the preparation of new metal–carbon[1] and metal–metal[2] bonds. We have for some time been involved in a systematic investigation of the chemistry of the anionic complexes $(C_7H_7)M(CO)_3^-$ (**1**) [M = Fe (**1a**), Ru (**1b**), Os (**1c**)]. The ambident nature of **1** manifests itself in an interesting and metal-dependent fashion. Thus the reaction with R_3SiCl and R_3GeBr gives ring-substituted complexes,[3] whereas Ph_3SnCl results in fluxional η^3-C_7H_7 complexes containing a M–Sn bond[4] (Scheme I). In accord with the reaction of Ph_3SnCl, transition-metal-based electrophiles were found to react with **1a** and **1b** to give cycloheptatrienyl-bridged heterobimetallic complexes[4b,5] where the two metals occupy the same face of the ring. However, recent discoveries indicated that the reaction of **1c** with [Rh(C-

Scheme I



Scheme II



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