α-Eliminations of Carbon Induced by Manganese and Iron: Expansion of Cyclopropanes to Manganacyclobutenes, Manganacyclopentenones, and Ferracyclopentenones

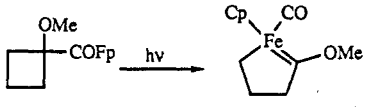
Donna J. Crowther, Z. Zhang, G. J. Palenik, and W. M. Jones*

Department of Chemistry, University of Florida, Gainesville, Florida 32611-2046

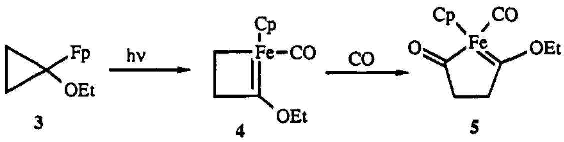
Received June 24, 1991

Reaction of $(CO)_5Mn^-$ with the acid chlorides of α-ethoxycyclopropanecarboxylic acid and 7-methoxy-7-norcaranecarboxylic acid gives the acyl complexes **21** and **34**. The former is inert to either heat or light. However, treatment with 2 equiv of trimethylamine oxide gives the π-allyl complex **23**. Thermolysis of **34** gives the rearranged acyl carbene complex **35**. Location of the ethoxy substituent on the terminal carbon of **23** and formation of **35** are taken as evidence for α-elimination of carbon induced by manganese. The stereochemistry of **34** is based on a single-crystal X-ray of the corresponding dicarbonyl(η^5-cyclopentadienyl)iron analogue **36**. Photolysis of **36** gives the isomeric acyliron carbene complexes **37** and **38**. The structure of each has been confirmed by single-crystal X-rays. The crystal structures of **36**–**38** are discussed.

Under nonforcing conditions, rearrangements of carbon from a saturated carbon to a transition metal to give isolable carbene complexes (α-eliminations) are unknown.[1] However, we have recently found that alkoxy-substituted cyclopropyl[3] and cyclobutyl complexes of carbonyl(η^5-cyclopentadienyl)iron[4] undergo α-eliminations to give ferracyclopentenones and ferracyclopentenes, respectively. For example, photolysis of **1** cleanly leads to **2** while **3** proceeds via **4** to **5**. Furthermore, from the kinetics of the carbene migratory insertion in **2**,[4c] it has been possible to show that the reason for the absence of such reactions in unperturbed carbonyl(η^5-cyclopentadienyl)iron complexes is thermodynamic rather than kinetic in origin; in other words, conversion of **6** to **7** is energetically uphill.



1 2

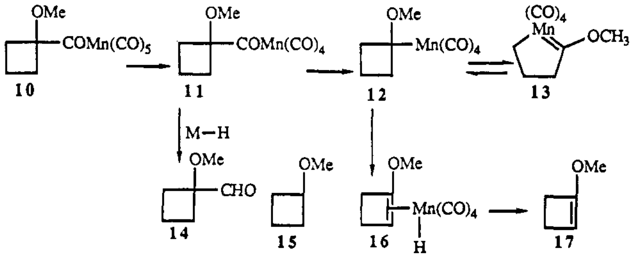


3 4 5

6 7

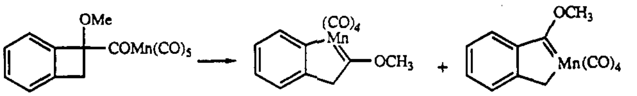
Some years ago, Hoffmann made the interesting prediction that the interconversion of **8** and **9** should be approximately thermoneutral,[5,6] a forecast that encouraged us to look for α-eliminations in pentacarbonylmanganese complexes. In view of our success with **1**, work on pentacarbonylmanganese was begun with **10**. However, as recently reported,[8] the principal products from either thermal or photochemical decarbonylation were the aldehyde **14** and 1-methoxycyclobutene. It was suggested that this may be due to irreversible dissociation of **16** which precluded observation of carbene **13**.

8 9



10 11 12 13 14 15 16 17

Consistent with this was the finding that α-elimination occurs when dissociation of the π-complex is retarded by benzannelation; for example, thermolysis of **18** gives the two carbene complexes **19** and **20**.[8,9]



18 19 20

It has been previously noted that β-hydrogen elimination is retarded in cyclopropyl σ-complexes.[10] Furthermore, as mentioned above, α-alkoxycyclopropyl σ-complexes of carbonyl(η^5-cyclopentadienyl)iron undergo α-elimination to give ferracyclobutenes.[3] These observations suggested α-alkoxycyclopropyl as a ligand that might undergo α-

---

[1] One example of α-elimination of carbon induced by nickel to give a transient carbene complex under nonforcing conditions has been reported by Grubbs.[2]

[2] Miyashita, A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 7418.

[3] (a) Lisko, J. R.; Jones, W. M. *Organometallics* **1985**, *4*, 944. (b) Conti, N. J.; Jones, W. M. *Organometallics* **1988**, *7*, 1666. (c) Conti, N. J.; Crowther, D. J.; Tivakornpannarai, S.; Jones, W. M. *Organometallics* **1990**, *9*, 175.

[4] (a) Stenstrom, Y.; Jones, W. M. *Organometallics* **1986**, *5*, 178. (b) Stenstrom, Y.; Klauck, G.; Koziol, A.; Palenik, G. J.; Jones, W. M. *Organometallics* **1986**, *5*, 2155. (c) Stenstrom, Y.; Koziol, A.; Palenik, G. J.; Jones, W. M. *Organometallics* **1987**, *6*, 2079.

[5] Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7418.

[6] More recent calculations[7] predict the conversion of **8** to **9** to be significantly endothermic.

[7] Ziegler, T.; Versluis, L.; Tschinke, V. *J. Am. Chem. Soc.* **1986**, *108*, 612.

[8] Crowther, D. J.; Tivakornpannarai, S.; Jones, W. M. *Organometallics* **1990**, *9*, 739.

[9] α-Elimination to give **19** and **20** is presumably favored by increased strain relief as well as retardation of π-complex dissociation.

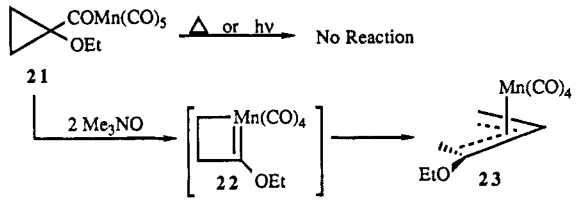
[10] Phillips, R. L.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1732.

0276-7333/92/2311-0622$03.00/0

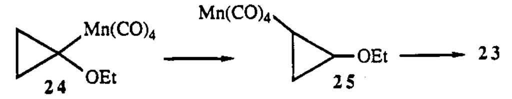
elimination of carbon if bonded to tetracarbonylmanganese. We therefore undertook a study of this system. The results are reported herein.

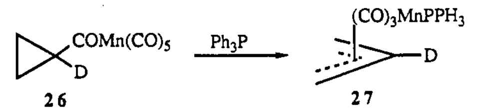
Results and Discussion

(Cyclopropanecarbonyl)pentacarbonylmanganese complexes were prepared by reaction of the $Mn(CO)_5^-$ with the appropriate acyl chlorides. The parent α-ethoxycyclopropyl acyl complex **21** showed the same rather remarkable stability reported by Stone[11] for its unsubstituted analogue; it was inert to both thermolysis (heat at 50–70 °C for 3 days) and photolysis (irradiation with a 450-W medium-pressure Hg Hanovia lamp through quartz or Pyrex in benzene-d_6, CD_3CN, or acetone-d_6 for up to 3 days).

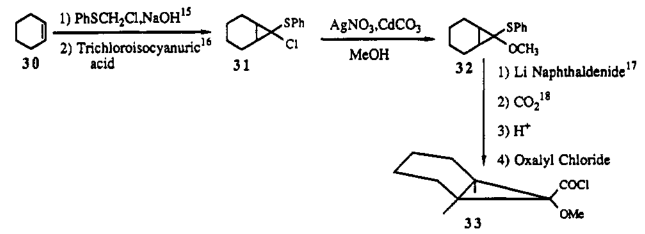


However, it was found that **21** does react with trimethylamine oxide; treatment with 2 equiv gave a low yield (12% isolated) of the π-allyl complex **23**. The substitution pattern in **23** is significant, because, by analogy with its iron counterpart,[3c] it is the pattern expected from opening of the metallacyclobutene **22** rather than the 16-electron σ-complex **24**. An alternative path to **23** via the rearranged β-ethoxycyclopopyl complex **25** can also be envisaged although it is unlikely for a number of reasons. First, evidence against this process for the carbonyl(η^5-cyclopentadienyl)iron counterpart is compelling.[2c] Second, cyclopropanes are normally reluctant to undergo β-hydrogen elimination due to ring strain.[12] Third, treatment of **26** with triphenylphosphine gave the π-allyl complex **27** with no detectable deuterium scrambling.[13] The latter result is obviously not demanding because the substituents in **24** and **26** are different and the mechanism of the conversion of **26** to **27** is unknown. However, it is quite likely that, at some point, the mechanism of **26** to **27** includes a cyclopropyl substituent σ-bonded to a 16-electron manganese where a conversion analogous to **24** to **25** would be possible. Absence of the carbene product **22** and its carbonyl insertion product (the metallacyclopentenone corresponding to **5**) from the reaction of **21** with amine oxide is expected in view of the known reactivity of carbene complexes with this kind of oxidizing agent.[14]



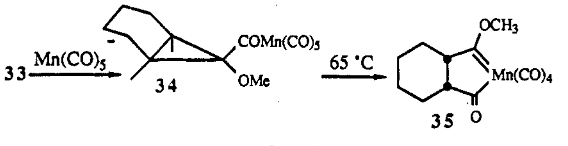


Scheme I

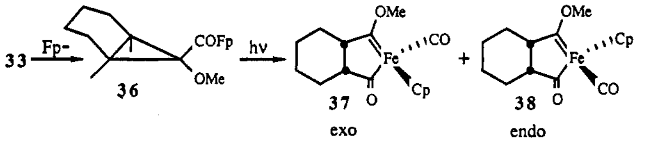


Steric compression due to eclipsing between a metal with its attendant ligands and a *cis*-alkyl group on a cyclopropane should be relieved upon α-elimination (**28** → **29**).

Furthermore, incorporation of the *cis*-alkyl groups into a 6-membered ring should inhibit opening of the cyclopropane ring to give the centrally substituted π-allyl complex.[3c] The bicyclic acid chloride **33** was therefore prepared as shown in Scheme I. Its stereochemical assignment is based on an X-ray crystal structure of an iron derivative that is discussed below. Reaction of **33** with $(CO)_5Mn^-$ in THF gave the acyl complex **34**. Thermolysis of a solution of **34** in benzene-d_6 at 65 °C led to slow, steady gas evolution. Monitoring with ^{13}C NMR showed conversion to three new materials in a ratio of about 75:20:5. Complete reaction required 48 h. The major product was separated from the crude mixture by crystallization. Based on its ^1H and ^{13}C NMR spectra (resonances at 357.5 ppm (carbene carbon) and 266.0 ppm (acyl carbonyl carbon)) and its high-resolution mass spectrum, there is little question but that this is the acyl carbene complex **35**. The cis fusion is presumed based on molecular models which suggest that this is less strained than the trans-fused isomer, and the results are discussed below. To date, attempts to prepare a crystal suitable for X-ray analysis have failed. The predominant minor product could not be separated from either residual starting material or the third product, but low-field resonances at 362.1 and 268.7 ppm are indicative of an acyl carbene complex (possibly a stereoisomer of **35**).



Our inability to unequivocally confirm the stereochemistry of the manganese carbene complex **35** by NMR or X-ray suggested the preparation of model carbenes for comparison. The iron complex **36** was therefore prepared for photolysis. This complex formed crystals suitable for X-ray analysis which permitted unequivocal assignment of the stereochemistry pictured in **33** to the acid chloride used in the synthesis of both the iron and manganese cyclopropylacyl complexes. Photolysis of a benzene-d_6



---

(11) Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Organomet. Chem.* **1969**, *20*, 161.

(12) (a) Phillips, R. L.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1732. (b) Lehmkuhl, H.; Grundke, J.; Mynott, R. *Ber.* **1983**, *116*, 176.

(13) Stone[11] has reported that **26** is inert to most decarbonylation conditions including treatment with amine oxides. However, it was found to react with triphenylphosphine to give the π-allyl complex. The role of the phosphine is unknown, but at some point, the mechanism presumably includes a cyclopropyl substituent σ-bonded to a 16-electron manganese. We have not found this reaction to be general; for instance, reaction of **21** with triphenylphosphine leads only to CO substitution.

(14) Cf. Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1.

(15) Boche, G.; Scheider, D. R. *Tetrahedron Lett.* **1975**, 4247.

(16) Mura, A. G.; Bennet, D. A.; Cohen, T. *Tetrahedron Lett.* **1975**, 4433.

(17) Cohen, T.; Matz, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 6902.

(18) Lisko, J. R.; Jones, W. M. *Organometallics*, **1985**, *3*, 612.

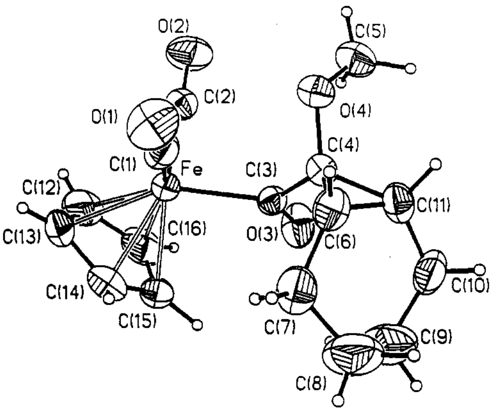


Figure 1. View of $FeC_{16}H_{18}O_4$ compound **36** showing the atomic numbering and thermal ellipsoids.

solution of **36** for 3 days at room temperature monitoring with ^{13}C NMR showed about 75% conversion to a mixture consisting of almost exclusively unreacted starting material and two isomeric acyl carbene complexes **37** and **38** (50% and 25% by NMR; 34% and 10% isolated, respectively). Each isomer showed resonances in the ^{13}C NMR with chemical shifts expected of carbene (351.9 and 347.9 ppm for major and minor isomer, respectively) and acyl carbonyl (267.9 and 226.6 ppm) carbons. Structures **38** and **39** are assigned to these two isomers. These assignments are based on the single-crystal X-ray studies given below.

These structures differ in the endo–exo relationship of the cyclopentadienyl ligand with respect to the tetramethylene bridge. To determine if ring-fusion isomerization could be induced, the major isomer **37** was treated with a solution of CD_3ONa in CD_3OD. Based on both ^{13}C and ^1H NMR, the proton exchange α to the carbene carbon occurred rapidly at -60 °C[19] (to the exclusion of exchange α to the carbonyl) but no ring isomerization occurred. When the solution was warmed to 40 °C, slow exo–endo isomerization occurred, reaching equilibrium consisting of a 70:30 mixture of **37** and **38** after about 24 h, but no new product could be detected to which a trans fusion could be assigned. Interestingly, exo–endo isomerization was also found to occur upon photolysis of pure **37** (30 h; 2:1 mixture of **37** and **38**), but neither isomerization nor deuterium exchange was observed when **37** was heated to 40 °C in deuterated methanol for 7 days in the absence of methoxide or to 45 °C for 3 days in acetone-d_6 containing deuterated acetic acid. Decarbonylation followed by iron inversion appears reasonable for the photoinduced isomerization of **37** to **38**. The role of base in the inversion is unknown.

X-ray Crystal Structures of 36–38

The atomic numbering and thermal ellipsoids for **36–38** are shown in Figures 1–3. The driving force for the conversion of **36** to **37** and **38** is the relief of ring strain. The ring-puckering parameters[20,21] given in Table I illustrate the changes in ring distortions. In **36**, the total puckering amplitude Q is much less than that calculated for either **37** or **38**. The small torsion angle of -3.42° for C(7)–C(6)–C(11)–C(10) and the flattening of the 6-membered ring in **36** is a consequence of the cyclopropane ring fusion at the C(6)–C(11) bond. A consideration of the ϕ_2–θ angles suggests that **36** is best described as being halfway between a half-chair and half-boat conformation. In contrast, both **37** and **38** are close to the ideal chair conformation at 0° or 180°. The major isomer **37** is slightly more distorted than the minor isomer **38**.

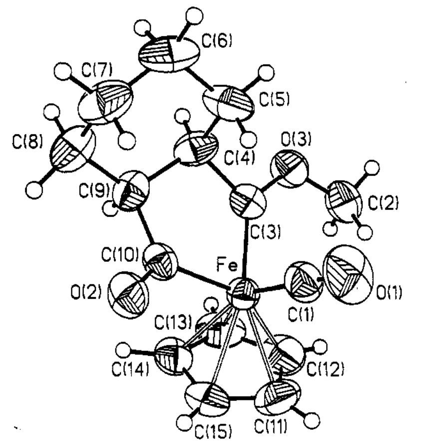


Figure 2. View of $FeC_{15}H_{18}O_3$ compound **37** showing the atomic numbering and thermal ellipsoids.

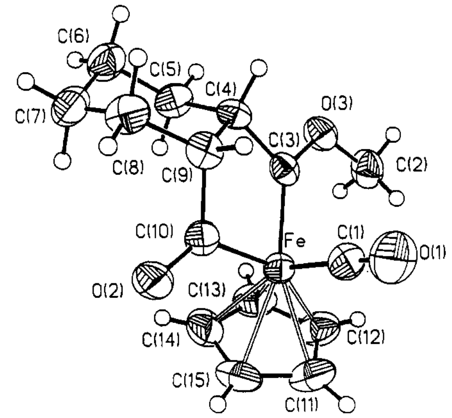


Figure 3. View of $FeC_{15}H_{18}O_3$ compound **38** showing the atomic numbering and thermal ellipsoids.

Table I. Summary of Geometrical Calculations for Compounds 37–39

(a) Ring Puckering Parameters for the 6-Membered Rings in Compounds 37–39[a]

	37	38	39
Q (Å)	0.402	0.534	0.536
Φ_2 (deg)	-50.9	120.0	-33.0
Θ (deg)	130.9	8.9	168.6

(b) Least-Squares Plane Data for Compounds 38 and 39

atom	38	39	atom	38	39
Fe	0.001(1)	0.001(1)	O(3)	-0.014(2)	-0.006(2)
C(2)	0.038(4)	0.019(3)	C(4)	0.022(3)	0.013(3)
C(3)	-0.026(3)	-0.018(3)			

[a] Following the notation in ref 20 and 21. Q is the total puckering amplitude with Φ_2 and Θ as phase amplitudes. Q, Φ_2, and Θ can be viewed as polar coordinates which map out the various conformations of a 6-membered ring.

The Fe atom is 1.742, 1.756, and 1.750 Å from the plane of the Cp ring in **36–38**, respectively. These values are somewhat longer than the mean value of 1.721 Å or the average value of 1.706 (39) Å reported in a recent compilation.[22] However, the presence of the CO groups may

---

[19] Cf.: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 128.

[20] Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354–1358.

[21] Nardelli, M. *Acta Crystallogr., Sect. C* **1983**, *C39*, 1141–1142.

[22] Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1–S83.

account for the longer values in our complexes. This point is under investigation.

One of the more interesting features is the shortness of the C(3)–O(3) and Fe–C(3) bonds in both **38** and **39** and the planarity of the C(4)–C(3)–O(3)–C(2)–Fe grouping (Table I). The Fe–C(3) bond is 1.994 (4) Å in **37** but 1.844 (3) Å in **38** and 1.854 (3) Å in **39**. The shortening of the Fe–C(3) bond is accompanied by or is a consequence of the short C(3)–O(3) bond of 1.314 (4) Å in both compounds. In contrast, the O(3)–CH_3 bond lengths of 1.431, 1.441, and 1.439 Å are close to the value reported for an aryl alkyl ether of 1.424 Å.[23] The result is that canonical forms involving C═O must be invoked in describing these structures. This can be rationalized by assuming that two electrons are donated from C to Fe, formally a double bond which accounts for the extremely short FeC(3) bond lengths. The planarity of the grouping is also explainable on this basis. A survey of transition metal–Cp–CO–$COCH_3$ complexes in the Cambridge Structural Database[22,23] suggests that this grouping has short Tr–C and C–O distances when planarity is present but not under other conditions. A more detailed analysis of the various structural features in complexes of this type will be published elsewhere.

Experimental Section

All solvents used were reagent grade. Both THF and diethyl ether were distilled over NaK/benzophenone. Those solvents used for column chromatography were degassed with N_2 for 1 h. The alumina used in chromatography was Fischer-certified neutral and was degassed on a vacuum line 12 h prior to use. The silica gel used was Alpha Products, 59-μm pore size, and was degassed for 12 h prior to use. Synthesis of all organometallic compounds was performed on a Schlenk line by standard procedures. Other manipulations were performed in a glovebox under a nitrogen atmosphere. Microanalysis was performed by Atlanta Microlabs. Mass spectral analysis was performed by this department. Proton and carbon NMR spectra were measured on a Varian 300FX. All infrared spectra were recorded on either a Perkin-Elmer 137 or a Perkin Elmer 1640 spectrometer. Melting points were determined on a Thomas Hoover melting point apparatus.

Preparation of α-Ethoxycyclopropanecarboxylic Acid. A solution of α-ethoxycyclopropyl bromide[24] (2.0 g, 5.4 mmol) in 20 mL of diethyl ether was cooled to −78 °C before the gradual addition (20 min) of 10.7 mL of 1.7 M *tert*-butyllithium (in hexane, 8.1 mmol). After an additional 20 min, CO_2 was bubbled in for 10 min. The reaction mixture was warmed to room temperature. The reaction was acidified with 35% HCl to pH 1 and extracted several times with diethyl ether, and the extracts were dried over $MgSO_4$. Rotovapping the extracts gave 1.15 g of viscous carboxylic acid (72%). Further purification by Kugelrohr distillation at 0.1 mm from 84 to 92 °C gave 0.77 g (48%) of colorless product: ^1H NMR (C_6D_6 ppm, δ) 10.2 (s, COOH), 3.7 (q, OCH_2), 1.65–1.05 (m, ring H and Me); ^{13}C NMR (C_6D_6, δ) 180.5 (CO_2H), 65.7 (α-ring C), 17.2 (β-ring C), 15.5 (CH_3).

Preparation of α-Ethoxycyclopropanecarbonyl Chloride. The general synthesis of an acid chloride from the corresponding carboxylic acid is illustrated for the title compound. To a 250-mL round-bottom flask containing a magnetic stir bar and α-ethoxycyclopropanecarboxylic acid (5.5 g, 42 mmol) was slowly added oxalyl chloride (16 g, 126 mmol). The reaction was allowed to stir for 12 h under N_2. The excess oxalyl chloride was removed at 10 mm at 25 °C. The acid chloride was purified by Kugelrohr distillation at 10 mm from 62 to 80 °C (3.0 g, 48%): ^1H NMR (C_6D_6, δ) 3.7 (q, OCH_2), 1.7–0.8 (m, ring H and CH_3); ^{13}C NMR (C_6D_6, δ) 175.7 (COCl), 67.2 (α-C), 65.7 (OCH_2), 18.8 (β-C), 15.1 (CH_3).

Preparation of (α-Ethoxycyclopropanecarbonyl)Mn$(CO)_5$ (21). α-Ethoxycyclopropanecarbonyl chloride (2.7 g, 16.2 mmol) in 20 mL of THF was gradually added (30 min) to a slurry of $KMn(CO)_5$[25] (3.8 g, 16.2 mmol) in 50 mL of THF. After 24 h, the solvent was removed under vacuum. The crude orange residue was extracted several times with a 1:3 methylene chloride/hexane mixture and filtered through Celite/medium glass frit. The orange-yellow residue obtained after rotovapping off solvents was subjected to column chromatography (silica gel, fluorescent indicator, quartz column). The complex **21** was eluted as a colorless band with 10:90 ethyl acetate/hexane to give 1.6 g of oily product (32%). Crystallization from hexane (−40 °C) yielded white crystals (1.0 g, 20%): mp 36 °C; ^1H NMR (C_6D_6, δ) 3.18 (s, OCH_2), 1.15–0.7 (m, 7 H); ^{13}C NMR (C_6D_6, δ) 257.2 (acyl CO), 210.2 (MCO), 80.2 (α-ring C), 65.1 (OCH_2), 15.1 (CH_3), 14.8 (β-ring C); IR (CCl_4) 2114, 2050, 2027, 2009, 1629 cm^{-1}. Anal. Calcd for $MnC_{11}H_9O_7$: C, 42.87; H, 2.93. Found: C, 42.30; H, 2.85.

Attempted Thermal or Photolytic Decarbonylation of 21. Solutions of **21** in benzene-d_6 were subjected to photolysis with both quartz and pyrex filters at 28 °C without any detectable reaction (^1H or ^{13}C NMR). Similarily, thermolysis from 50 to 70 °C did not result in any decarbonylation. Very minute amounts of $Mn_2(CO)_{10}$ were detected by TLC.

Reaction of 21 with Trimethylamine Oxide. A solution of **21** (0.6 g, 1.95 mmol) in 2 mL of CD_3CN was cooled to −40 °C. To this was added in small portions Me_3NO (0.32 g, 4.3 mmol). The ensuing decarbonylation was quite vigorous. Besides $Mn_2(CO)_{10}$, the only detectable product was **23**. The remainder consisted of an orange intractable material. Complex **23** was isolated from the reaction mixture by column chromatography (silica gel, 20:80 ethyl acetate/hexane) as a bright yellow viscous oil (0.13 g, 12%): ^1H NMR (C_6D_6, δ) 4.6 (d, ═C*H*OEt), 4.3 (m, 2-allylic), 3.2 (m, OCH_2), 1.7 (dd, syn, 3-allylic), 0.9 (t, CH_3), 0.6 (dd, anti, 3-allylic); ^{13}C NMR (C_6D_6, δ) 110.0 (2-allylic), 76.3 (═CHOEt), 68.4 (OCH_2), 25.5 (3-allylic), 14.5 (CH_3); IR (CCl_4) 2048, 1965, 1942 cm^{-1}; MS (EI) 252 (M^+).

Preparation of (α-Deuteriocyclopropanecarbonyl)Mn$(CO)_5$ (27). α-Deuteriocyclopropanecarboxylic acid was made by a literature method[26] and its acid chloride synthesized as described above. Purification was achieved by Kugelrohr distillation at 60 mm from 52 to 72 °C. The title complex **27** was prepared according to the method of Stone.[27] ^2H NMR (C_6D_6 benzene as ref, δ) 2.2 (CD); ^1H NMR (C_6D_6, δ) 2.2 (CH, 95% deuterated), 1.4–0.8 (m, CH_2); ^{13}C NMR (C_6D_6, δ) 252.0 (acyl CO), 210.3 (MCO), 40.4 (J_{CD} = 35.3 Hz, CD), 11.1 (CH_2).

Determination of the Deuterium Position in the π-Allyl Product from Thermolysis of PPh_3 and 27. Equivalent amounts of **27** and PPh_3 were refluxed in cyclohexane for 12 h as previously described by Stone et al.[27] The cyclohexane was removed under a vacuum and the crude reaction mixture analyzed by ^2H NMR (benzene). A single resonance at 3.95 ppm indicated the only product was the 2-deuterio-π-allyl complex. In the ^{13}C NMR spectrum, a triplet was observed at 93.6 ppm.

Preparation of 7-Chloro-7-(phenylthio)bicyclo[4.1.0]heptane (31). To a solution of trichloroisocyanuric acid (5.1 g, 21.9 mmol) in 50 mL of CCl_4 cooled to 0 °C was slowly added (1 h) a precooled solution of 5-(phenylthio)bicyclo[4.1.0]heptane[28] (8.5 g, 41.7 mmol). After 12 h, the reaction mixture was filtered through a medium glass frit and the solvents were removed under reduced pressure. Chromatography on silica gel with 50:50 methylene chloride/hexane resulted in elution of a product which gave a ^{13}C NMR consistent with nearly pure title compound (7.6 g, 77%) as a mixture of isomers. This material was used for the following preparation without further purification. ^{13}C NMR ($CDCl_3$, δ) (major product) 140–125 (aromatics), 54.4 (quart, C for both isomers), 28.3 and 25.1 (CH of two isomers) 20.4, 19.7 (CH_2).

Preparation of 7-Methoxy-7-(phenylthio)bicyclo[4.1.0]heptane (32). A slurry of **31** (4.2 g, 17.6 mmol) and $CdCO_3$ (3.9

---

(23) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1–S19.

(24) (a) Gadwood, R. *Tetrahedron Lett.* **1984**, 5851. (b) Ruhlmann, K. *Synthesis* **1971**, 236.

(25) Gladysz, J.; Williams, G.; Tam, W.; Johnson, D.; Parker, D.; Selover, J. *Inorg. Chem.* **1979**, *18*, 553.

(26) Silverman, R. B.; Hoffman, S. J. *J. Labelled Compd. Radiopharm.* **1981**, *18*, 781.

(27) Bruce, M.; Iqbal, M.; Stone, F. G. A. *J. Organomet. Chem.* **1969**, *20*, 161.

(28) Lisko, J. Ph.D. Dissertation, University of Florida, 1984.

g, 22 mmol) in 100 mL of MeOh was cooled to 0 °C under nitrogen with stirring (magnetic). To this was added portions of $AgBF_4$ (4.1 g, 21 mmol) over a 30-min period. After 6 h, the reaction mixture was filtered over a Celite/medium glass frit, and the MeOH was removed at 20 mm at 40 °C. Column chromatography (silica gel, 50:50 hexane/ethyl acetate) gave known **32**[29] as one predominant isomer (2.7 g, 65%): ^{13}C NMR ($CDCl_3$, δ) (major resonances) 135.4, 128.5, 127.3, 125.0, 53.4, 23.6. 20.8, 19.6.

Preparation of *endo*-7-Methoxybicyclo[4.1.0]heptane-7-carboxylic Acid Chloride (33). A dark green solution of naphthyl anion was obtained by stirring together Li, cut into small pieces, (0.27 g, 38.4 mmol) and naphthalene (4.9 g, 38.4 mmol) in 150 mL of THF. The solution was cooled to −78 °C, and **32** (3.0 g, 12.8 mmol) in 10 mL of THF was added by cannula. The reaction mixture was carefully warmed to −5 °C and maintained at this temperature for 10 min. The reaction was then cooled down to −78 °C, and CO_2 was bubbled through for 15 min, resulting in an immediate color change to orange. After the mixture was warmed to 28 °C, water (50 mL) was slowly added followed by saturated $NaHCO_3$ solution. The reaction mixture was extracted three times with diethyl ether (50 mL) to remove naphthalene. The aqueous layer was acidified with 35% HCl to a pH 1 and extracted with diethyl ether, and the extracts were dried with $MgSO_4$. The ether was rotovapped to give a white solid that showed a ^{13}C NMR consistent with the crude carboxylic acid (1.2 g, 57%) (exo isomer). This material was used in the following reaction without further purification: ^{13}C NMR ($CDCl_3$, δ) (major resonances) 175.4 (CO), 67.5 (quant C), 56.0 (OMe), 26.2 (CH), 20.3, 17.4 (CH_2).

The acid chloride **33** was synthesized using neat oxalyl chloride and worked up as previously described. Kugelrohr distillation from 110 to 135 °C gave **33** (45%) that was used without further purification for the following reactions.

Preparation of (7-Methoxy[4.1.0]heptane-7-carbonyl)-pentacarbonylmanganese (34). A solution of **33** (1.3 g, 6.9 mmol) in THF (20 mL) was added to a slurry of $KMn(CO)_5$ (1.65 g, 6.9 mmol) in 40 mL of THF, via cannula, at 25 °C. After 24 h, the solvents were removed under vacuum. The orange-yellow residue was extracted with 10:90 ethyl ether/hexane and filtered through Celite. After removal of solvents, the oily residue was chromatographed on silica gel with a 10:90 ethyl acetate/hexane mixture, eluting the desired acyl complex as a bright yellow band. After the chromatography fraction was rotovapped, complex **34** was found to be a bright yellow oil (1.0 g, 40%): ^1H NMR (C_6D_6, δ) 3.0 (s, OCH_3), 1.75, 1.66 (m, CH), 1.4–1.1 (m, CH_2); ^{13}C NMR (C_6D_6, δ) 259.8 (acyl CO), 210.4 (MCO), 83.0 (COMe), 56.1 (OMe), 26.8 (CH), 21.3, 18.6 (CH_2); IR (CCl_4) 2110, 2022, 2007, 1628 cm^{-1}; MS (EI) 348 (M^+). Anal. Calcd for $C_{14}H_{13}O_7Mn$: C, 48.29; H, 3.76. Found: C, 48.44; H, 3.80.

Thermolysis of Complex 34 To Give Isomeric Acyl Carbene Complex 35. A solution of acyl complex **34** (0.35 g, 1.0 mmol) in 0.8 mL of C_6D_6 was heated at 65 °C under a N_2 atmosphere, which resulted in a slow and steady evolution of CO. The reaction was monitored by ^{13}C NMR which showed that two acyl carbene complexes, **35** (75%) and **36** (20%), as well as an unidentified compound (5%) were products from rearrangement of **34**. After 48 h, the contents of the NMR tube were chromatographed on silica gel. A 15:85 ethyl acetate/hexane mixture eluted **35** and **36** together. Complex **35** could be selectively recrystallized from an ethyl acetate/hexane solution cooled to −30 °C. Complex **35**: ^1H NMR (C_6D_6, δ) 3.88 (s, OMe), 2.3 (m, CH), 1.8–0.6 (m, CH_2); ^{13}C NMR (C_6D_6, δ) 357.5 (=COMe), 266.0 (acyl CO), 217 to 212 (MCO), 75.9, 69.7, 68.7 (OMe, CH), 28.5, 27.5, 25.4, 25.3 (CH_2); IR (CCl_4) 2066, 2011, 1972, 1950, 1660 cm^{-1}; MS, *m/e* 320.0107 (theoretical 320.0092). Complex **36**: ^1H NMR (C_6D_6, δ) 3.84 (s, OMe); ^{13}C NMR (C_6D_6, δ) 362.1 (=COMe), 268.7 (acyl CO), 68.4, 63.9.

Preparation of (*endo*-7-Methoxybicyclo[4.1.0]heptane-7-carbonyl)dicarbonyl(η^5-cyclopentadienyl)iron (36). A solution of **33** (1.3 g, 6.9 mmol) in 15 mL of THF was added via cannula to a slurry of KFp (1.55 g, 6.9 mmol) in 40 mL of THF. After 12 h, the THF was removed under vacuum and the residue was chromatographed on alumina. Complex **36** was eluted as a bright yellow band with a 5:95 ethyl acetate/hexane solvent mixture. The compound was recrystallized from hexane to yield 0.8 g (77%) of yellow needlelike crystals. Crystals suitable for X-ray diffraction were precipitated from dilute hexane solutions of **36** cooled to −30 °C: mp 120 °C; ^1H NMR (C_6D_6, δ) 4.31 (s, Cp), 3.09 (s, OMe), 1.83 (m, CH_2), 1.43 (m, CH), 1.25 (m, CH_2); ^{13}C NMR (C_6D_6, δ) 256.1 (acyl CO), 216.0 (M-CO), 87.0 (Cp), 82.2 (COMe), 55.6 (OMe), 25.3 (CH), 21.6, 19.1 (CH_2); IR (CCl_4) 2019, 1966, 1635 cm^{-1}; MS (EI) 330 (M^+). Anal. Calcd for $C_{16}H_{18}O_4Fe$: C, 58.21; H, 5.49. Found: C, 58.10; H, 5.52.

Table II. Summary of Crystal, Data Collection, and Refinement Parameters for Compounds 37–39

compound	**37**	**38**	**39**
formula	$C_{16}H_{18}O_4Fe$	$C_{15}H_{18}O_3Fe$	$C_{15}H_{18}O_3Fe$
formula weight	330.02	302.01	302.01
cryst syst	monoclinic	monoclinic	monoclinic
space group; Z	$P2_1/c$; 4	$P2_1/c$; 4	$P2_1/c$; 4
a (Å)	16.644 (5)	9.933 (4)	8.466 (2)
b (Å)	6.849 (1)	12.770 (5)	13.471 (3)
c (Å)	13.121 (5)	11.987 (3)	12.312 (2)
β (deg)	92.66 (3)	110.69 (2)	101.69 (2)
V (Å^3)	1494.2 (7)	1422.3 (8)	1375.0 (8)
$F(000)$	688	632	632
D (g·cm^{-3})	1.467	1.410	1.458
μ (cm^{-1})	10.18	10.58	10.94
transmissn, max	0.47	0.72	0.33
transmissn, min	0.44	0.65	0.26
cryst size (mm)	0.36 × 0.24 × 0.03	0.07 × 0.09 × 0.28	0.05 × 0.22 × 0.34
no. reflcns	2181	2024	2061
no. parameters	226	244	244
$R(F_o)$	0.036	0.029	0.028
$R_w(F_o)$	0.039	0.028	0.030
GOF	1.25	1.33	1.08
max Δ/σ final cycle	0.44	0.32	0.11
max peak final diff	0.55	0.23	0.27

Table III. Final Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $FeC_{16}H_{18}O_4$, Compound 37

	x	y	z	U[a]
Fe	6404 (1)	6815 (1)	3377 (1)	34 (1)
O(1)	6808 (2)	3970 (5)	1852 (2)	68 (1)
O(2)	5927 (2)	3931 (4)	4832 (2)	64 (1)
O(3)	7613 (2)	7970 (3)	4815 (2)	57 (1)
O(4)	7843 (1)	3482 (3)	4039 (2)	45 (1)
C(1)	6684 (2)	5083 (5)	2467 (2)	44 (1)
C(2)	6133 (2)	5055 (5)	4260 (3)	39 (1)
C(3)	7479 (2)	6872 (4)	4113 (2)	33 (1)
C(4)	8109 (2)	5386 (5)	3830 (2)	34 (1)
C(5)	7932 (3)	2990 (6)	5098 (3)	57 (1)
C(6)	8571 (2)	5561 (6)	2879 (3)	47 (1)
C(7)	8521 (2)	7352 (7)	2213 (3)	62 (1)
C(8)	9165 (4)	8823 (9)	2471 (4)	100 (2)
C(9)	9270 (4)	9281 (8)	3545 (4)	89 (2)
C(10)	9416 (3)	7586 (8)	4250 (3)	61 (1)
C(11)	9007 (2)	5712 (5)	3925 (2)	47 (1)
C(12)	5301 (3)	8305 (6)	3437 (5)	76 (2)
C(13)	5490 (2)	8146 (5)	2444 (4)	72 (1)
C(14)	6229 (3)	9112 (6)	2320 (3)	65 (1)
C(15)	6479 (2)	9882 (5)	3261 (3)	62 (1)
C(16)	5923 (3)	9377 (6)	3969 (4)	69 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Photolysis of Complex 36 To Give Anti Carbene Complex 37 and Syn Carbene Complex 38. A solution of complex **36** (0.3 g, 0.91 mmol) in 0.8 mL of C_6D_6 was photolyzed at room temperature using a water-cooled Pyrex filter and monitored by ^{13}C NMR. Reaction was observed to occur slowly, and it was necessary to photolyze for 3 days for ca. 75% conversion. The contents of the NMR tube were poured onto the top of a column packed with

---

[29] (a) Schollkopf, U.; Ruban, E.; Tonne, P.; Riedel, K. *Tetrahedron Lett.* **1970**, 5077. (b) Cohen, T.; Bhupathy, M.; Matz, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 520.

Table IV. Final Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $FeC_{15}H_{18}O_3$, Compound 38

	x	*y*	*z*	*U*^{a}
Fe	6098 (1)	8079 (1)	2437 (1)	42 (1)
O(1)	6960 (3)	9185 (2)	697 (2)	94 (1)
O(2)	6544 (2)	6215 (1)	1320 (2)	63 (1)
O(3)	8422 (2)	9057 (1)	4358 (2)	59 (1)
C(1)	6625 (3)	8736 (2)	1397 (3)	56 (1)
C(2)	7613 (4)	9991 (2)	4319 (3)	70 (1)
C(3)	7869 (3)	8282 (2)	3616 (2)	47 (1)
C(4)	9022 (3)	7462 (2)	3810 (2)	57 (1)
C(5)	10052 (3)	7802 (3)	3172 (3)	76 (1)
C(6)	11062 (3)	6913 (4)	3120 (4)	89 (2)
C(7)	10212 (4)	5972 (3)	2498 (3)	79 (2)
C(8)	9214 (4)	5578 (3)	3109 (4)	74 (2)
C(9)	8259 (3)	6450 (2)	3294 (2)	54 (1)
C(10)	6974 (3)	6774 (2)	2187 (2)	45 (1)
C(11)	3921 (3)	8575 (3)	1683 (3)	79 (1)
C(12)	4437 (4)	8880 (3)	2867 (4)	83 (2)
C(13)	4869 (3)	7985 (3)	3562 (3)	70 (1)
C(14)	4581 (3)	7124 (3)	2787 (3)	60 (1)
C(15)	3996 (3)	7495 (3)	1625 (3)	63 (1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table V. Final Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $FeC_{15}H_{18}O_3$, Compound 39

	x	*y*	*z*	*U*^{a}
Fe	4102 (1)	8389 (1)	2623 (1)	36 (1)
O(1)	3274 (3)	9470 (2)	4465 (2)	82 (1)
O(2)	3623 (2)	6547 (1)	3640 (2)	54 (1)
O(3)	1581 (2)	9311 (1)	966 (1)	43 (1)
C(1)	3601 (3)	9054 (2)	3725 (2)	50 (1)
C(2)	2637 (4)	10067 (2)	694 (2)	52 (1)
C(3)	2103 (3)	8635 (2)	1723 (2)	34 (1)
C(4)	725 (3)	7938 (2)	1773 (2)	34 (1)
C(5)	569 (3)	7248 (2)	759 (2)	45 (1)
C(6)	−455 (3)	6336 (2)	836 (2)	53 (1)
C(7)	228 (3)	5763 (2)	1888 (2)	57 (1)
C(8)	240 (3)	6402 (2)	2900 (2)	50 (1)
C(9)	1158 (3)	7366 (2)	2864 (2)	38 (1)
C(10)	2999 (3)	7268 (2)	3129 (2)	37 (1)
C(11)	6590 (3)	8765 (3)	3090 (3)	60 (1)
C(12)	6037 (3)	9094 (2)	2000 (2)	56 (1)
C(13)	5454 (3)	8270 (2)	1356 (3)	56 (1)
C(14)	5671 (3)	7424 (2)	2044 (3)	60 (1)
C(15)	6383 (3)	7731 (2)	3122 (2)	60 (1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

silica gel. The second red band eluted with a 10:90 ethyl acetate/hexane mixture (the first is Fp_2) was found to be the minor, syn isomer **38**. The compound was isolated as light red crystals (0.03 g, 10%). Crystals suitable for X-ray analysis were grown from a dilute hexane solution cooled to −30 °C: mp 162 °C; ^1H NMR (C_6D_6, δ) 4.36 (s, Cp), 3.80 (s, OMe), 2.44 (m, C*H*COMe), 2.24 (m, C*H*C=O), 1.44–1.00 (m, CH_2); ^{13}C NMR (C_6D_6, δ) 347.5 (=COMe), 266.6 (acyl CO), 217.4 (MCO), 87.2 (Cp), 66.0, 64.0, 61.7 (OMe and CH), 28.0, 24.2, 23.5, 23.1 (CH_2); IR (CCl_4) 1997, 1949, 1647 cm^{-1}. Anal. Calcd for $C_{15}H_{18}O_3Fe$: C, 59.63; H, 6.00. Found: C, 59.70; H, 6.04.

The third red band was eluted with a 40:60 ethyl acetate/hexane mixture and was identified as the major, anti isomer **37**. The compound was initially isolated as a dark red oil (0.1 g, 35%). X-ray-quality crystals were slowly grown from hexane solutions cooled to −30 °C (ca. 3 weeks) which resulted in the formation of dark red crystals: mp 76–77 °C; ^1H NMR (C_6D_6, δ) 4.27 (s, Cp), 3.81 (s, OMe), 2.60 (m, C*H*COMe), 2.35 (m, C*H*C=O), 1.48–1.21 (m, CH_2); ^{13}C NMR (C_6D_6, δ) 351.9 (=COMe), 267.9 (acyl CO), 217.8 (MCO), 85.8 (Cp), 67.8, 66.3 (OMe and CHC=O), 61.8 (CHCOMe), 27.0, 24.5, 24.3, 23.3 (CH_2); IR (CCl_4) 2006, 1951, 1674, 1652 cm^{-1}; MS (EI) 302 (M^+). Anal. Calcd for $C_{15}H_{18}O_3Fe$: C, 59.63; H, 6.00. Found: C, 59.50; H, 6.01.

Table VI. Distances and Angles for $FeC_{16}H_{18}O_4$, Compound 37

Distances (Å)			
Fe–C(1)	1.761 (3)	C(1)–O(1)	1.137 (4)
Fe–C(2)	1.745 (3)	C(2)–O(2)	1.139 (4)
Fe–C(3)	1.994 (3)	C(3)–O(3)	1.201 (4)
C(3)–C(4)	1.521 (4)	C(4)–O(4)	1.409 (4)
O(4)–C(5)	1.431 (5)	C(4)–C(6)	1.500 (4)
C(4)–C(11)	1.509 (4)	C(6)–C(7)	1.506 (6)
C(7)–C(8)	1.499 (8)	C(8)–C(9)	1.447 (8)
C(9)–C(10)	1.497 (7)	C(10)–C(11)	1.505 (6)
C(6)–C(11)	1.526 (5)	Fe–C(12)	2.105 (4)
Fe–C(13)	2.114 (4)	Fe–C(14)	2.108 (4)
Fe–C(15)	2.111 (4)	Fe–C(16)	2.093 (4)
C(12)–C(13)	1.358 (8)	C(13)–C(14)	1.413 (6)
C(14)–C(15)	1.389 (6)	C(15)–C(16)	1.385 (6)
C(16)–C(12)	1.425 (6)		
Angles (deg)			
Fe–C(1)–O(1)	174.9 (3)	Fe–C(2)–O(2)	177.4 (3)
Fe–C(3)–O(3)	121.0 (2)	Fe–C(3)–C(4)	118.9 (2)
O(3)–C(3)–C(4)	120.0 (3)	C(3)–C(4)–O(4)	110.2 (2)
C(4)–O(4)–C(5)	112.8 (2)	O(4)–C(4)–C(6)	114.5 (3)
C(3)–C(4)–C(6)	122.4 (3)	O(4)–C(4)–C(11)	116.1 (3)
C(3)–C(4)–C(11)	124.9 (3)	C(6)–C(4)–C(11)	61.0 (2)
C(4)–C(6)–C(11)	59.8 (2)	C(4)–C(11)–C(6)	59.2 (2)
C(4)–C(6)–C(7)	122.1 (3)	C(6)–C(7)–C(8)	113.4 (4)
C(7)–C(8)–C(9)	114.7 (5)	C(8)–C(9)–C(10)	116.2 (5)
C(9)–C(10)–C(11)	115.4 (4)	C(10)–C(11)–C(6)	120.1 (3)
C(11)–C(6)–C(7)	118.6 (3)	C(4)–C(11)–C(10)	125.6 (3)
C(1)–Fe–C(2)	94.0 (2)	C(1)–Fe–C(3)	94.7 (1)
C(2)–Fe–C(3)	86.9 (1)	C(12)–C(13)–C(14)	108.3 (4)
C(13)–C(14)–C(15)	107.6 (4)	C(14)–C(15)–C(16)	108.6 (3)
C(15)–C(16)–C(12)	107.1 (4)	C(16)–C(12)–C(13)	108.4 (4)

Table VII. Distances and Angles for $FeC_{15}H_{18}O_3$, Compound 38

Distances (Å)			
Fe–C(1)	1.731 (3)	Fe–C(3)	1.844 (2)
Fe–C(10)	1.951 (3)	Fe–C(11)	2.124 (3)
Fe–C(12)	2.152 (4)	Fe–C(13)	2.118 (4)
Fe–C(14)	2.093 (4)	Fe–C(15)	2.104 (3)
O(1)–C(1)	1.158 (4)	O(2)–C(10)	1.208 (3)
O(3)–C(2)	1.430 (4)	O(3)–C(3)	1.314 (3)
C(3)–C(4)	1.508 (4)	C(4)–C(5)	1.539 (5)
C(4)–C(9)	1.515 (4)	C(5)–C(6)	1.531 (6)
C(6)–C(7)	1.506 (6)	C(7)–C(8)	1.512 (6)
C(8)–C(9)	1.529 (5)	C(9)–C(10)	1.538 (3)
C(11)–C(12)	1.383 (5)	C(11)–C(15)	1.384 (5)
C(12)–C(13)	1.390 (5)	C(13)–C(14)	1.402 (5)
C(14)–C(15)	1.390 (5)		
Angles (deg)			
C(1)–Fe–C(3)	92.0 (1)	C(1)–Fe–C(10)	92.2 (1)
C(3)–Fe–C(10)	83.2 (1)	C(2)–O(3)–C(3)	120.7 (2)
Fe–C(1)–O(1)	179.0 (3)	Fe–C(3)–O(3)	133.0 (2)
Fe–C(3)–C(4)	119.2 (2)	O(3)–C(3)–C(4)	107.8 (2)
C(3)–C(4)–C(5)	109.3 (2)	C(3)–C(4)–C(9)	106.6 (2)
C(5)–C(4)–C(9)	111.3 (3)	C(4)–C(5)–C(6)	111.8 (3)
C(5)–C(6)–C(7)	110.5 (3)	C(6)–C(7)–C(8)	112.0 (3)
C(7)–C(8)–C(9)	112.0 (3)	C(4)–C(9)–C(8)	115.7 (3)
C(4)–C(9)–C(10)	105.4 (2)	C(8)–C(9)–C(10)	116.0 (2)
Fe–C(10)–O(2)	126.6 (2)	Fe–C(10)–C(9)	112.1 (2)
O(2)–C(10)–C(9)	121.1 (2)	Fe–C(11)–C(12)	72.2 (2)
Fe–C(11)–C(15)	70.1 (2)	C(12)–C(11)–C(15)	109.0 (3)
Fe–C(12)–C(11)	70.0 (2)	Fe–C(12)–C(13)	69.7 (2)
C(11)–C(12)–C(13)	107.9 (3)	Fe–C(13)–C(12)	72.3 (2)
Fe–C(13)–C(14)	69.6 (2)	C(12)–C(13)–C(14)	107.5 (3)
Fe–C(14)–C(13)	71.5 (2)	Fe–C(14)–C(15)	71.1 (2)
C(13)–C(14)–C(15)	108.2 (3)	Fe–C(15)–C(11)	71.7 (2)
Fe–C(15)–C(14)	70.2 (2)	C(11)–C(15)–C(14)	107.4 (3)

Reaction of Anti-Carbene Complex 37 with CD_3ONa in CD_3OD. ^1H and ^{13}C NMR spectra at −60 °C were recorded of a solution of **37** (0.15 g, 0.5 mmol) in 0.7 mL of CD_3OD. The NMR tube was cooled to −100 °C, and 0.1 mL of 2% Na in CD_3OD was added via a syringe. Analysis indicated deuterium exchange on the carbon α to the carbene carbon. This was evident because a new triplet at 63.5 ppm had replaced the singlet in the ^{13}C

Table VIII. Distances and Angles for $FeC_{15}H_{18}O_3$, Compound 39

	Distances (Å)		
Fe–C(1)	1.748 (3)	Fe–C(3)	1.854 (2)
Fe–C(10)	1.944 (2)	Fe–C(11)	2.129 (3)
Fe–C(12)	2.164 (3)	Fe–C(13)	2.120 (3)
Fe–C(14)	2.085 (3)	Fe–C(15)	2.101 (3)
O(1)–C(1)	1.151 (4)	O(2)–C(10)	1.218 (3)
O(3)–C(2)	1.439 (3)	O(3)–C(3)	1.314 (2)
C(3)–C(4)	1.508 (3)	C(4)–C(5)	1.541 (3)
C(4)–C(9)	1.527 (3)	C(5)–C(6)	1.517 (4)
C(6)–C(7)	1.517 (4)	C(7)–C(8)	1.512 (4)
C(8)–C(9)	1.519 (4)	C(9)–C(10)	1.532 (3)
C(11)–C(12)	1.401 (4)	C(11)–C(15)	1.406 (5)
C(12)–C(13)	1.395 (4)	C(13)–C(14)	1.409 (4)
C(14)–C(15)	1.404 (4)		
	Angles (deg)		
C(1)–Fe–C(3)	92.1 (1)	C(1)–Fe–C(10)	86.7 (1)
C(3)–Fe–C(10)	83.7 (1)	C(2)–O(3)–C(3)	121.3 (2)
Fe–C(1)–O(1)	178.3 (2)	Fe–C(3)–O(3)	133.0 (2)
Fe–C(3)–C(4)	119.0 (1)	O(3)–C(3)–C(4)	108.0 (2)
C(3)–C(4)–C(5)	106.4 (2)	C(3)–C(4)–C(9)	107.5 (2)
C(5)–C(4)–C(9)	112.0 (2)	C(4)–C(5)–C(6)	113.2 (2)
C(5)–C(6)–C(7)	110.0 (2)	C(6)–C(7)–C(8)	110.6 (2)
C(7)–C(8)–C(9)	112.4 (2)	C(4)–C(9)–C(8)	115.1 (2)
C(4)–C(9)–C(10)	106.4 (2)	C(8)–C(9)–C(10)	115.1 (2)
Fe–C(10)–O(2)	126.8 (2)	Fe–C(10)–C(9)	113.5 (1)
O(2)–C(10)–C(9)	119.7 (2)	Fe–C(11)–C(12)	72.3 (2)
Fe–C(11)–C(15)	69.5 (2)	C(12)–C(11)–C(15)	108.7 (3)
Fe–C(12)–C(11)	69.6 (2)	Fe–C(12)–C(13)	69.3 (2)
C(11)–C(12)–C(13)	107.7 (3)	Fe–C(13)–C(12)	72.7 (2)
Fe–C(13)–C(14)	69.1 (2)	C(12)–C(13)–C(14)	108.3 (3)
Fe–C(14)–C(13)	71.8 (2)	Fe–C(14)–C(15)	71.1 (2)
C(13)–C(14)–C(15)	108.0 (3)	Fe–C(15)–C(11)	71.7 (2)
Fe–C(15)–C(14)	69.8 (2)	C(11)–C(15)–C(14)	107.3 (2)

spectrum and the ^1H NMR resonance at 2.25 ppm had disappeared. Warming the tube by increments of 10 °C did not result in any detectable changes until 40 °C. After 24 h at 40 °C, an equilibrium mixture of **37** (66%) and **38** (33%) was obtained.

A control experiment consisting of heating complex **37** in CD_3OD for up to 7 days did not result in isomerization of the anti carbene complex **37** to the syn isomer **38**. Deuterium exchange did occur, and a slight decomposition of **38** to Fp_2 and other unidentified compounds was observed.

Photolysis of Anti Carbene Complex 37. A solution of **37** (0.15 g, 0.5 mmol) in C_6D_6 was photolyzed with a Pyrex filter at 24 °C and spectrally monitored. After 30 h an equilibrium mixture of **37** (66%) and **38** (33%) was obtained.

Reaction of Anti Carbene Complex 37 with CD_3CO_2D in CD_3COCD_3. A solution of **37** (0.1 g, 0.33 mmol) in 0.7 mL of acetone-d_6 was cooled to −100 °C, and to this was added 0.05 mL of CD_3CO_2D. ^1H and ^{13}C NMR spectra recorded from −60 to +40 °C showed that complex **37** was completely stable under these conditions; no isomerization to complex **38** was detected. Neither did isomerization to **38** occur when complex **37** was simply heated in acetone-d_6 at 40 °C for 3 days.

X-ray Data Collection, Structure Determination, and Refinement for 36–38. Suitable single crystals for all three compounds were grown by slow solvent evaporation in a drybox at room temperature. Each crystal was mounted on the end of a thin glass fiber. All measurements were made with a Nicolet R3m diffractometer using graphite-monochromated Mo Kα radiation. In all three cases, a variable-speed θ–2θ scan, maximum speed 29.3°/min, was used to measure the intensity data. The 2θ scan range was 3.0–50.0°, with the background count taken for half the scan time at each end of the scan. Two standard reflections were measured after each 98 reflections and were used to correct for small changes in their intensity, 5, 4, and 3% for **36–38**, respectively. An absorption correction was determined by the ψ scan method.

The structures were solved using the Patterson function and successive Fourier syntheses. The refinement was by least squares using isotropic and then anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were located in a difference Fourier synthesis and were included in the calculation, but their parameters were not refined. No extinction parameter was refined for any of the three compounds. The relevant crystal data, data collection, and refinement parameters for the three compounds have been summarized in Table II.

The final positional parameters for the three compounds are given in Tables III–V. The distances and angles in the molecules are given in Tables VI–VIII. The molecules are illustrated in Figures 1–3, with the atomic numbering used in the analysis and the final thermal ellipsoids. All calculations were carried out on a Model 30 Desktop Eclipse, using the programs and data in the Nicolet SHELXTL program.[30]

Acknowledgment. This work was supported by the National Science Foundation to whom we are most grateful.

Supplementary Material Available: Tables of the hydrogen atom positions and thermal parameters for the non-hydrogen atoms (6 pages); listing of observed and calculated structure amplitudes for each compound (47 pages). Ordering information is given on any current masthead page.

---

(30) Sheldrick, G. M. *DESKTOP SHELXTL*; Nicolet X-ray Instruments: Madison, WI, 1986.