Organometallics **1985**, *4*, 1069–1072 1069

Transition-Metal Complexes of Small-Ring Allenes: Synthesis of (η^5-C_5H_5)Fe(CO)$_2$(1,2-cycloheptadiene)OSO_2CF_3 and -BF_4^-

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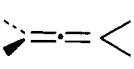
(η^5-C_5H_5)Fe(CO)$_2$(1,2-cycloheptadiene)OSO_2CF_3, the first example of a M(II) complex of a seven-membered-ring allene, has been synthesized by reaction of trimethylsilyl triflate with (η^5-C_5H_5)(CO)$_2$Fe-(7-methoxycycloheptene) in methylene chloride at −78 °C. The complex is fluxional (E_a = 13.9 kcal/mol) and reacts with Na_2CO_3/ethanol to give the ethyl ether **23** of expected regiochemistry. The triflate salt of the allene complex decomposes at room temperature in the presence of triphenylmethane to give π-complexes of 1,3-cycloheptadiene and cycloheptene. The corresponding fluoroborate salt (prepared from (η^5-C_5H_5)Fe(CO)$_2$(7-methoxycycloheptene) and trimethyloxonium fluoroborate) is stable to these conditions, thus implicating the triflate ion in these reactions.

Introduction

Just as the perpendicular form of acyclic allenes (**1**) is lower energy than any of the possible planar forms,[1] Fp^+ (Fp = η^5-$C_5H_5Fe(CO)_2$) complexes of allenes also prefer perpendicular structures over planar forms such as **4**.[2,3] In sharp contrast, although cycloheptatetraene **5** is apparently lower energy than its planar isomer **6**[4] (which corresponds to **2**), the corresponding Fp^+ complex exists exclusively as structure **8**[5] (analogous to **4**). The two most likely reasons for this change in structural preference upon going from **3**/**4** to **7**/**8** are tropylium resonance and ring strain.[6] Regarding the latter, it has been recognized for many years that incorporation of an allene into a relatively small ring should impose a greater strain on the linear, perpendicular ground state than on a bent planar valence isomer, thus reducing the energy gap separating them.[7] Since this should also be true, although to a lesser extent,[8] for metal complexes of allenes, incorporation of the allene into a seven-membered ring as in **7** should raise its energy relative to the cationic form **8**.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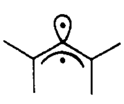
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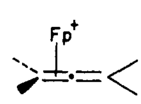

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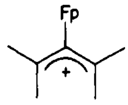

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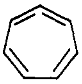
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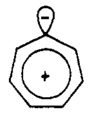

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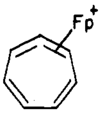

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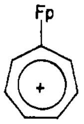

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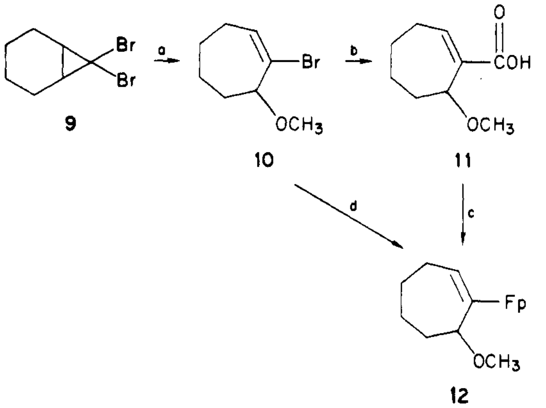
To qualitatively assess the importance of ring strain in the **7**/**8** system, we thought it would be interesting to synthesize an Fp^+ complex of 1,2-cycloheptadiene and determine its structural preference. At this time we report the synthesis of the Fp^+ complex of 1,2-cycloheptadiene[10] and our finding that it prefers an allene structure with an activation barrier separating it from a planar form of at least 13.9 kcal/mol.

Scheme I



(a) CH_3OH, $AgNO_3$; (b) (1) BuLi, (2) CO_2, (3) H^+; (c) (1) $SOCl_2$, (2) NaFp, (3) $h\nu$; (d) (1) BuLi, (2) FpCl

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[1] Cf. Seeger, R.; Krishnan, R.; Pople, J. A.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1977**, *99*, 7103. Roth, W. R.; Ruf, G.; Ford, P. W. *Chem. Ber.* **1974**, *107*, 48.

[2] For reviews of Transition Metal-Allene Complexes, see: Bowden, F. L.; Giles, R. *Coord. Chem. Rev.* **1976**, *20*, 81. Shaw, B. L.; Stringer, A. J. *Inorg. Chim. Acta Rev.* **1973**, *7*, 1.

[3] For an excellent study of the isomerization of Fp^+ allene complexes see: Foxman, B.; Marten, D.; Rosan, A.; Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 2160.

[4] Random, L.; Schaefer, H. F. III; Vincent, M. A. *Nouv. J. Chim.* **1980**, *4*, 411. Waali, E. E. *J. Am. Chem. Soc.* **1981**, *103*, 3604. Dewar, M. J. S.; Landman, D. *J. Am. Chem. Soc.* **1977**, *99*, 2435. Tyner, R. L.; Jones, W. M.; Ohrn, Y.; Sabin, J. R. *J. Am. Chem. Soc.* **1974**, *96*, 3765.

[5] Riley, P. E.; Davis, R. E.; Llison, N. T.; Jones, W. M. *Inorg. Chem.* **1982**, *21*, 1321; *J. Am. Chem. Soc.* **1980**, *102*, 2458. To date, the 7/8 pair of complexes have been prepared only by hydride abstraction. Such a reaction could lead directly to **8** which would not convert to a lower energy form (**7**) at room temperature. This appears highly unlikely since **16** is prepared by a similar kind of reaction so there clearly cannot be a high activation barrier separating **18** from **16** and EHMO calculations place **8** 37 kcal/mol below **7**.[17] These calculations will be reported in detail elsewhere.

[6] The change in structural preference in going from **5**/**6** to **7**/**8** must be due primarily to a heterolytic bond strength in **8** (including back-bonding) that is greater than the π-bond strength of **7**. Further, this difference must be greater than the difference in heat of formation of **5** and **6**. It is also necessary that the difference in bond strengths of **3** and **4** (the latter without back-bonding) be less than the difference in heat of formation of **1** and **2**.

[7] For general discussion, see: Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978; pp 128–131. See also: Schmidt, M. W.; Angus, R. O., Jr.; Johnson, R. P. *J. Am. Chem. Soc.* **1982**, *104*, 6838.

[8] This would be expected to be less important in complexes than in free allenes because of the distortion that is induced by the complexing. For instance, in one Fp^+ allene complex for which a structure has been determined by single-crystal X-ray diffraction the central bond angle is 145.7°.[9].

[9] Foxman, B. M. *J. Chem. Soc., Chem. Commun.* **1975**, 221.

[10] Pt(0) complexes of both 1,2-cyclooctadiene and 1,2-cycloheptadiene have been reported.[11] To our knowledge, the cycloheptadiene complex reported herein is the first M(II) complex of an allene in a ring smaller than nine members.[3]

[11] Visser, J. P.; Ramakers, J. E. *J. Chem. Soc., Chem. Commun.* **1972**, 178.

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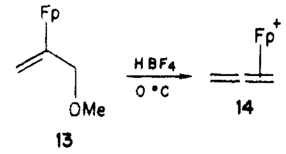
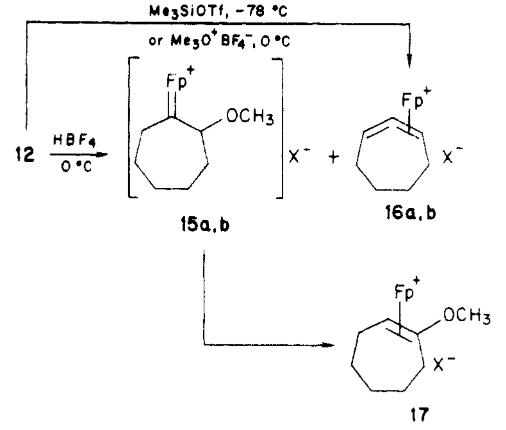
Results and Discussion

The precursor to **16** was prepared by the sequence of reactions outlined in Scheme I. Taking as an analogy Rosenblum's observation that reaction of **13** with protonic acid gives **14**,[12] our first attempts to prepare the allene



complex were by reaction of **12** with $HBF_4{\cdot}Et_2O$. However, from the ^{1}H NMR spectrum of the crude reaction mixture, it was clear that this gave, in addition to methoxy abstraction (ca. 40%), a substantial amount (ca. 38%) of what is presumed to be **17** (identified from crude ^{1}H NMR and iodide-induced hydrolysis to cycloheptanone). This difference in behavior of the cyclic and acyclic systems may be due to trans assistance by iron in the latter which would be inhibited in the seven-membered ring.

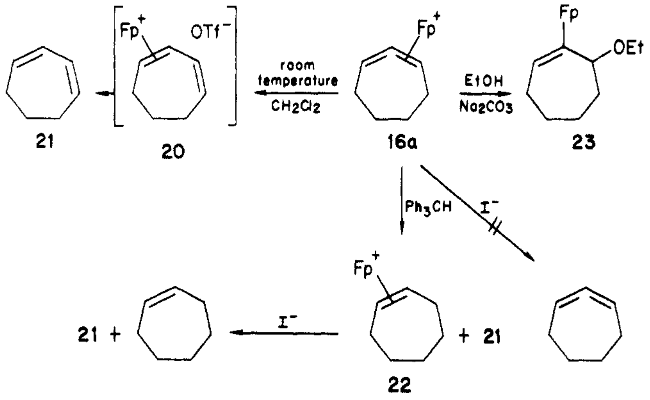


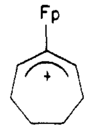
a, $X^- = OSO_2CF_3$, b, $X^- = BF_4$

Where protonation of **12** failed to lead to clean methoxy abstraction, trimethylsilyl triflate[13] worked quite well. Thus, addition of 1 equiv of Me_3SiOTf to a cold (−78 °C) CH_2Cl_2 solution of **12** followed by addition of cold ether gave **16a** in 71% yield. This allene complex is a light yellow solid that decomposes in solution in 3–4 h at room temperature (vide infra) but as a solid is indefinitely stable if kept under N_2 in the freezer. In solution, it is fluxional showing well-separated vinyl proton resonances (δ 4.45 and δ 6.66) at −40 °C which coalesce at 29 °C. This corresponds to an activation barrier of 13.9 kcal/mol. Rapid exchange of the two allene hydrogens was also demonstrated by spin saturation transfer.[14] Thus, at −20 °C irradiation of H3 in **16a** led to complete saturation of H1, saturation at −40 °C showed partial diminution of H1, and saturation at −60 °C left H1 unchanged.

The activation barrier for this exchange process is lower than has been observed for Fp^+ complexes of methylallene, 1,1-dimethylallene, tetramethylallene, and cyclononadiene (23.1, 18.0, 16.3, and greater than 16.4 kcal/mol, respectively). The lower barrier could be due to a change in mechanism via **18** or ring-strain-induced distortion of the orbitals on the central carbon of the allene that would lead to more favorable bonding in the transition state[15] as depicted in **19**. The chemistry of the complex (vide infra) favors the latter view.

Scheme II





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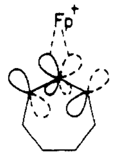

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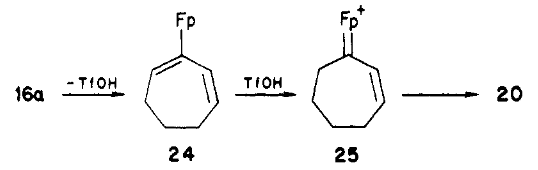
Some chemistry of **16a** is summarized in Scheme II. Its reaction with ethanol and base is typical of other Fp^+ allene complexes, in both types of product and regiochemistry.[16] Its failure to yield the free allene when treated with NaI is also not unusual although its failure to yield the allene when treated with Na^+Fp^- is different from the cyclononadiene complex.[3] Its thermal chemistry differs from other Fp^+ allene complexes in that it rather rapidly converts to 1,3-cycloheptadiene (from NMR experiments apparently via the unstable Fp^+ π-complex). That this rearrangement is probably induced by the triflate counterion was shown by preparing the tetrafluoroborate **16b** from reaction of **12** with $Me_3O^+BF_4^-$. This salt was found to be remarkably stable showing no decomposition after 16 h at 40 °C in CH_2Cl_2. A reasonable mechanism for cycloheptadiene formation from **16a** is shown in eq 1:



(1)

EHMO calculations[17] suggest that **16** and **18** might be rather close in energy. We therefore undertook to design experiments to see if the allyl cation valence isomer of **16** could be trapped. Our first attempt with triphenylmethane appeared to be successful when it was found that warming a solution of **16a** to room temperature in the presence of this hydride donor followed by workup with NaI gave a mixture of 1,3-cycloheptadiene (51%) and cycloheptene (34%). In the absence of the hydride source only the diene was formed. However, the fluoroborate salt of 1,2-cycloheptadiene was found to be completely stable to triphenylmethane (no reaction in 3 h at 40 °C). From this it is clear that the triflate ion is required for the re-

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(12) Lennon, P.; Madhavaro, M.; Rasan, A.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *108*, 93.

(13) Brookhart, M.; Tucker, J. *J. Am. Chem. Soc.* **1981**, *103*, 979.

(14) Faller, J. W. "Determination of Organic Structure by Physical Methods"; Nachod, F. C., Zuckermn, J. J., Eds.; Academic Press: New York, 1976; Vol. 5. Larrabee, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 1510. Mann, B.; Taylor, B.; Taylor, N.; Wood, R. *J. Organomet. Chem.* **1978**, *162*, 137. Karel, K.; Albright, T.; Brookhart, M. *Organometallics* **1982**, *3*, 419.

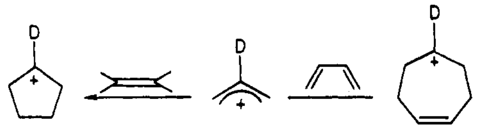
(15) Cf. Vrieze, K.; Volger, H. C.; Pratt, A. P. *J. Organomet. Chem.* **1970**, *21*, 467. Vrieze, K.; Volger, H. C.; Gonert, M.; Pratt, A. P. *J. Organomet. Chem.* **1969**, *16*, P19.

(16) Lichtenberg, D.; Wojcicki, A. *J. Organomet. Chem.* **1975**, *94*, 311; *J. Am. Chem. Chem.* **1972**, *94*, 8271.

(17) Unpublished results of W. R. Winchester, University of Florida.

duction which, in turn, requires a more complex mechanism than simple isomerization to **18**.

Allyl cations with electron-donating groups at C2 can sometimes be trapped with dienes and substituted alkenes.[18] One driving force for these cycloadditions is presumably localization of the positive charge on the carbon bearing the donor group (eq 2). Since the iron in **18** should be an effective donor, we tested the reaction of **16b** with furan, cyclopentadiene, and tetramethylethylene. In no case did any reaction occur at room temperature.



(2)

From the above results and the fluxional behavior of **16**, the following conclusions can be drawn about the interconversion of **16** and **18**. (1) The energy separating **16** from **18** must be at least 13.9 kcal/mol, the activation barrier for fluxional behavior, and (2) if the allyl cation form is accessible at room temperature, it is not trapped by triphenylmethane, tetramethylethylene, or dienes. Indeed, there is a real chance that **18** does not represent an energy minimum at all; it could simply be a transition state (not necessarily the lowest energy one) for fluxional behavior. This latter point is subject to test by chirality studies that are currently in progress.

Experimental Section

All solvents were appropriately dried and degassed prior to use under an atmosphere of dinitrogen. Reactions were carried out under Schlenk conditions with a dinitrogen atmosphere or in a Vacuum Atmosphere's glovebox. Thoroughly degassed Fisher certified neutral alumina, Brockman Activity I to which 3% water had been added, was used for chromatography. Proton magnetic resonance spectra were obtained with a JEOL FX-100 or a JEOL PMX-60 spectrometer and references to tetramethylsilane (all chemical shifts are reported in units of δ). Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer. Elemental analyses were performed by Atlantic Microlab; Atlanta, GA. All melting points were measured with a Thomas-Hoover melting point apparatus and are uncorrected. Mass spectra were obtained on an AEI MS 30 spectrometer. Photolyses were carried out by using a 450-W low-pressure Hg Hanovia lamp in a Pyrex well. Transfer needles were ordered from Aldrich (stainless-steel, double-tip noncoring deflective 20 and 18 guage). GLPC analyses were carried out by using a Varian Aerograph Model 90-P gas chromatograph with thermal conductivity detector and a 20 ft × 0.125 in. column packed with 80–100 mesh Chromosorb (white, acid washed, dimethyldichlorosilane) coated with 20% SE-30.

Preparation of 1-Bromo-7-methoxycycloheptene (10). A mixture of 7,7-dibromobicyclo[4.1.0]heptane[19] (18 g, 0.071 mol) and silver nitrate (13 g, 0.076 mol) in dry methanol (150 mL) was refluxed for 5 h under a N_2 atmosphere. The precipitate which formed was removed by filtration, and 100 mL of CH_2Cl_2 and 200 mL of H_2O were added. The water layer was extracted with CH_2Cl_2 (2 × 100 mL) and the combined layers were washed with H_2O (50 mL) and dried over $MgSO_4$. The filtrate was concentrated and purified by vacuum distillation (51–53 °C at 0.4 torr) to give 14.5 g (55%) of a colorless liquid. An analytical sample was prepared by a second distillation taking a cut at 52 °C (0.4 torr): ^1H NMR ($CDCl_3$, 60 MHz, δ) 6.30 (t, H1, 1 H), 4.05 (m, H3, 1 H), 3.40 (s, OMe, 3 H), 1.75 (m, CH_2's) 1.20 (m, CH^2's);[3] IR (neat) 2920, 1700, 1650, 1450, 1365, 1310, 1200, 1160, 1120, 1095, 1050, 905, 890, 870, 850, 765, 730 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$, δ) 135.6 (C1), 125.7 (C2), 84.9 (C3), 56.6 (OMe), 29.6, 27.9, 23.8 (C4–C7); MS, *m/e* 171.9857 (M^+ calcd 171.9887). Anal. Calcd for $C_8H_{13}BrO$: C, 46.85; H, 6.39. Found: C, 46.91; H, 6.40. Substitution of silver perchlorate for silver nitrate increased the yield of **10** to 97%.

Preparation of 7-Methoxycycloheptene-1-carboxylic Acid and Acid Chloride. To a cold (−90 °C) dry solution of 1-bromo-7-methoxycycloheptene (3.314 g, 0.016 mol) in THF (30 mL) under N_2 atmosphere was added *n*-butyllithium (11.5 mL of a 1.6 M solution in hexane) dropwise during 10 min with stirring. The temperature was not allowed to exceed −80 °C. The mixture was stirred for 1.5 h at −80 °C after which the mixture was added slowly to dry ice (by means of a transfer needle) in a 500 mL of Erlenmeyer flask under a stream of N_2. This was stirred for 1 h at room temperature after which it was added to a mixture of CH_2Cl_2 (200 mL) and water (100 mL) and acidified with dilute H_2SO_4. The water layer was extracted two times with CH_2Cl_2 (200 mL) (do not use diethyl ether) followed by drying the organic layer over $MgSO_4$. Removal of the solvent in vacuo afforded 1.80 g (66%) of a white solid (mp 59–62 °C) which was used in the following reaction without further purification: ^1H NMR ($CDCl_3$, 60 MHz, δ) 11.6 (s, 1 H), 7.50 (t, H1, 1 H), 4.55 (d, H3, 1 H), 3.30 (s, OMe, 3 H), 2.70–0.60 (m, CH_2, 8 H); IR (neat) 2930, 2640, 1680, 1640, 1430, 1270, 1190, 1090, 1055, 1010, 900, 725, 705 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$, δ) 172.5 (CO), 150.4 (C1), 134.5 (C2), 55.8 (OMe), 29.3, 27.5, 25.8, 23.9 (C4–C7). Anal. Calcd for $C_9H_{13}O_3$: C, 63.49; H, 8.29. Found: C, 63.31; H, 8.40.

To a stirred solution of the acid described above (3.2550 g, 0.02 mol) in benzene (30 mL) at room temperature was added thionyl chloride (3.520 g, 0.03 mol) dropwise during 3 min under a N_2 atmosphere. The reaction mixture was allowed to stir for 2 h at room temperature at which time 2 drops of *N*,*N*-dimethylformamide was added followed by refluxing for 2 h after which the solvent was removed in vacuo to afford a brownish oil. Vacuum distillation (75–80 °C (0.0o torr)) gave 2.504 g (70%) of a colorless liquid: ^1H NMR ($CDCl_3$, 60 MHz, δ) 7.75 (t, H1, 1 H), 4.50 (d, H3, 1 H), 3.30 (s, OMe, 3 H), 2.30–0.50 (m, CH_2, 8 H); IR (neat) 3000, 1750, 1450, 1380, 1340, 1220, 1170, 1120, 1090, 1030, 960, 905, 865, 820, 780 cm^{-1}.

Preparation of Dicarbonyl(η^5-cyclopentadienyl)(η^1-7-methoxycycloheptene-1-carbonyl)iron. To a stirred suspension of potassium η^5-cyclopentadienyldicarbonylferrate (2.90 g, 0.01 mol) in THF (50 mL) at −78 °C was added a mixture of 7-methoxycycloheptene-1-carboxylic acid chloride (2.3120 g, 0.01 mol) in THF (30 mL) dropwise during 10 min under a N_2 atmosphere. This mixture was allowed to stir for 1 h at −78 °C followed by 1 h at room temperature at which time it was transferred to a 100-mL round-bottom flask containing 10 g of alumina (neutral, grade II). The solvent was removed in vacuo, and the products coated on the alumina were chromatographed on an alumina (neutral, grade II) column (1 in. × 8 in.) eluting with a mixture of hexane/CH_2Cl_2 (80/20). The first band (red) was bis[(dicarbonylcyclopentadienyl)iron]. This was followed immediately by a yellow band. Removal of the solvent in vacuo gave 1.102 g (27%) of a brownish, air-sensitive oil. An analytical sample was prepared by rechromatographing the brownish oil [$^1/_2$ in. × 2 in. column; elution with a mixture of hexane/CH_2Cl_2 (80/20); in a drybox] to afford a brown, air-sensitive oil: ^1H NMR ($CDCl_3$, 60 MHz, δ) 6.45 (m, H1, 1 H), 4.90 (s, Cp, 5 H), 4.20 (m, H3, 1 H), 3.20 (s, OMe, 3 H), 2.90–1.00 (m, CH_2's, 8 H); IR (neat) 3110, 2930, 2860, 2820, 2010, 1960, 1600, 1450, 1440, 1370, 1340, 1315, 1220, 1200, 1165, 1120, 1090, 1025, 1000, 970, 885, 830, 710, 680, 630, 570, 510 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$, δ) 252.7 (bridging CO), 214.2 (FeCO), 158.1 (C2), 144.4 (C1), 85.8 (Cp), 75.7 (C3), 55.8 (OMe), 29.7, 26.7, 26.1, 24.2 (C4–C7); MS, *m/e* 302.0588 (M^+ − CO, calcd 302.0604). Anal. Calcd for $C_{16}H_{18}FeO_4$: C, 58.21; H, 5.50. Found: C, 58.05; H, 5.68. The product from the first chromatography or a mixture of Fp_2 and the acyl complex was satisfactory for the next step.

Preparation of Dicarbonyl(η^5-cyclopentadienyl)(η^1-7-methoxycycloheptenyl)iron (12). A solution of dicarbonyl(η^5-cyclopentadienyl)(7-methoxycycloheptene-1-carbonyl)iron (1.102 g, 3.4 mmol) in acetone-d_6 (2 mL) was photolyzed under nitrogen for 3 h at 0 °C. The product was then coated on alumina

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[18] Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 819. Hoffmann, H. M. R.; Vathke-Ernst, H. *Chem. Ber.* **1981**, *114*, 2898. Klein, H.; Freyberger, G.; Mayr, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 49. Henning, R.; Hoffmann, H. M. R. *Tetrahedron Lett.* **1982**, *23*, 2305. Klein, H.; Mayr, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1027. van Tilborg, M. W. E. M.; van Doorn, R.; Nibbering, N. M. M. *Org. Mass Spectrom.* **1980**, *15*, 152.

[19] Adapted from: Fieser, L. "Organic Experiments", 4th ed.; Raytheon Education Company: Lexington, MA, 1979; p 312.

(neutral, grade II) and chromatographed on an alumina (neutral, grade II) column ($^1/_2$ in. × 2 in.) eluting with hexane. Only one yellow band was collected, and removal of the solvent gave 0.536 g (53%) of a brownish, air-sensitive oil. An analytical sample was prepared by rechromatographing the brown oil ($^1/_2$ in. × 1 in. column) eluting with hexane. Only one yellow band was collected and removal of the solvent gave 0.536 g (53%) of a brownish, air-sensitive oil. An analytical sample was prepared by rechromatographing the brown oil ($^1/_2$ in. × 1 in. column; eluting with hexane; in a drybox) to afford a brown, air-sensitive oil: ^{1}H NMR ($CDCl_3$, 60 MHz, δ) 5.80 (t, H1, 1 H), 4.75 (s, Cp, 5 H), 3.8 (m, H3, 1 H), 3.30 (s, OMe, 3 H), 2.50–0.80 (m, CH_2's, 8 H); IR (neat) 3110, 2930, 2980, 2850, 2820, 2010, 1920, 1785, 1585, 1440, 1365, 1330, 1265, 1235, 1205, 1145, 1100, 1070, 1050, 1020, 1000, 825, 800, 780, 720, 630, 575 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$, δ) 216.7 (FeCO's), 147.8 (C2), 140.7 (C1), 90.3 (C3), 85.4 (Cp), 56.1 (oMe), 31.7, 29.6, 27.5, 27.2 (C4–C7); MS, *m/e* 302.0670 (calcd M$^+$, 302.0605). Anal. Calcd for $C_{15}H_{18}FeO_3$: C, 59.63; H, 6.00. Found: C, 59.38; H, 6.10.

Preparation of the Trifluoromethanesulfonate Salt of Dicarbonyl(η^5-cyclopentadienyl)(η^2-1,2-cycloheptadiene)iron (16a). In a dry Schlenk tube (equipped with a magnetic stirrer) a solution of dicarbonyl(η^5-cyclopentadienyl)(η^1-7-methoxy-1-cycloheptenyl)iron (0.597 g, 1.9 mmol) in CH_2Cl_2 (20 mL) was degassed and cooled to −78 °C. A cold (−78 °C) solution of $Me_3SiOSO_2CF_3$ (0.456 g, 2.0 mmol) in CH_2Cl_2 (4 mL) was added dropwise under a N_2 atmosphere. The reaction mixture was allowed to stire for 30 min at −78 °C at which time ca. 200 mL of cold (−78 °C) ether was added via cannula. The resulting yellow precipitate was filtered (under N_2), washed with ether, and dried in an inert atmosphere to give 0.54 g (65%) of light yellow solid: mp 77–79 °C dec (sealed capillary tube); ^{1}H NMR [acetone-d_6, −20 °C (stable in acetone only at low temperature), 100 MHz, δ] 6.55 (m, H3, 1 H), 5.95 (s, Cp, 5 H), 4.45 (m, H1, 1 H), 2.30 (m), 2.00 (m), 1.00 (m); IR (acetone-d_6) 2080, 2040 cm^{-1}; decoupled ^{13}C NMR (acetone-d_6 −20 °C, δ) 209.6, 206.6 (FeCO's), 150.1 (C2), 124.3 (C3), 91.9 (Cp), 42.6 (C1), other C's (C4–C7) under acetone; ^{1}H NMR [CD_3NO_2, −20 °C (stable in solution for at least 4 h at room temperature), 100 MHz, δ] 6.61 (m, H3, 1 H), 5.77 (s, Cp, 5 H), 4.34 (m, H1, 1 H), 2.4 (m), 2.01 (m), 0.95 (m); IR (CD_3NO_2) 2075, 2040 cm^{-1}; decoupled ^{13}C NMR (CD_3NO_2, −20 °C, δ) 210.2, 207.2 (FeCO's), 150.1 (C2), 125.8 (C3), 92.3 (Cp), 43.6 (C1), 30.7, 29.6, 29.4 (C4–C7). Anal. Calcd for $C_{15}H_{15}FeF_3O_5S$: C, 42.88; H, 3.63. Found: C, 42.63; H, 3.63.

Preparation of the Tetrafluoroborate Salt of Dicarbonyl(η^5-cyclopentadienyl)(η^2-1,2-cycloheptadiene)iron (16b). To a suspension of trimethyloxonium tetrafluoroborate (0.34 g, 2.3 mmol) in 12 mL of CH_2Cl_2 at 0 °C was added 0.7 g (2.3 mmol) of **12** in 4 mL of CH_2Cl_2. The mixture was stirred for 15 min at 0 °C and then for 15 min at room temperature. Filtration followed by addition of anhydrous ether to the filtrate gave a yellow solid which was purified by recrystallizing from CH_2Cl_2–ether; mp 145–148 °C dec (sealed tube). The ^{1}H NMR spectrum is identical with that of **16a**. The IR showed an intense BF_4^- absorption at 1050 cm^{-1}.

Reaction of 16 with Ethanol/Sodium Carbonate. Dicarbonyl(η^5-cyclopentadienyl)(η^1-7-ethoxy-1-cycloheptenyl)iron (23). To a mixture of 0.029 g (0.081 mmol) of **16b** and 0.10 g (0.94 mmol) of sodium carbonate in a Schlenk tube was added 3.5 mL of thoroughly degassed absolute ethanol. The mixture was stirred rapidly for 2 h at room temperature. The solvent was removed in vacuo and the residue passed through a 1 × $^1/_2$ in. alumina (II, neutral) column, eluting with hexane. A single yellow band was collected to give 0.020 g (77%) of pure ethyl ether **23** as a brown oil. The triflate gave 54% of the same material, both of which showed all properties identical with those of the title compound synthesized by the method used to make the methoxy derivative: ^{1}H NMR ($CDCl_3$, 60 MHz, δ) 5.81 (t, H1, 1 H), 4.80 (s, Cp, 5 H), 4.00 (m, H3, 1 H), 3.45 (q, OCH_2, 2 H), 1.55 (m, CH_2's and CH_3); IR (neat) 3100, 2990, 2920, 2850, 2005, 1950, 1580, 1440, 1370, 1345, 1260, 1190, 1180, 1080, 1000, 820, 630, 570 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$, δ) 216.8 (FeCO), 148.9 (C2), 140 (C1), 87.9 (C3), 85.3 (Cp), 63.4 (OCH_2), 31.7, 30.3, 27.6, 27.4 (C4–C7), 15.7 (CH_3); MS, *m/e* 316.0771 (calcd M$^+$ 316.0761), 288.0815 (calcd M$^+$ − CO 288.0812). Anal. Calcd for $C_{16}H_{20}FeO_3$: C, 60.78; H, 6.38. Found: C, 60.95; H, 6.43.

Room-Temperature Decomposition of 16 in CH_2Cl_2. A solution of 0.281 g (0.7 mmol) of **11a** was dissolved in 15 mL of CH_2Cl_2 and allowed to remain at room temperature for 4 h. Removal of the solvent gave a brown oil which was dissolved in acetone. An excess of solid NaI was added. After 2 min the solution had turned to a purplish color. Bulb to bulb distillation gave a residue of FpI and a clear distillate that upon GLPC analysis was found to contain a trace of cycloheptene and 0.24 g (40%) of 1,3-cycloheptadiene. When this reaction was followed in the NMR using a solution of 0.010 g of the allene complex in CD_2Cl_2 in a sealed NMR tube, the mixture was found to rather rapidly give two new Cp resonances, one at δ 5.58 and a second at δ 5.19. After the first hour the resonance at δ 5.58 began to slowly subside, eventually reaching the base line. Concurrently, the resonance at δ 5.19 continued to grow reaching its maximum with total loss of the lower field resonance. The remainder of the spectrum was identical with that of pure 1,3-cycloheptadiene with a small unidentified resonance at δ 5.88. The Cp resonance at δ 5.19 exactly coincides with the Cp resonance resulting from addition of silver trifluoromethanesulfonate to a CD_2Cl_2 solution of FpCl and is presumably from FpOTF. The δ 5.58 resonance is assigned to the labile π-complex of 1,3-cycloheptadiene. Consistent with a very labile diene complex was our observation that 1,3-cycloheptadiene did not exchange with the Fp$^+$ π-complex of propene. The NMR experiment was repeated by using the tetrafluoroborate salt of 1,2-cycloheptadiene. No change was observed upon warming the solution to 40 °C for 16 h.

Room-Temperature Reaction of 16a with Triphenylmethane. To a cold (−78 °C) solution of 0.270 g (0.64 mmol) of **16a** in 20 mL of CH_2Cl_2 was added 10% excess (0.17 g) triphenylmethane. The mixture was stirred at −78 °C for 30 min followed by 3 h at room temperature. Solvent removal gave a brownish oil which was dissolved in acetone. Addition of NaI followed by bulb to bulb distillation gave a residue of FpI and a clear distillate. GLPC analysis of the distillate showed it to contain 0.031 g (51%) of 1,3-cycloheptadiene and 0.021 g (34%) of cycloheptene. In an NMR experiment, 0.0068 g (0.019 mmol) of the BF_4^- salt of the Fp 1,2-cycloheptadiene and 0.0054 g (0.022 mmol) of triphenylmethane were dissolved in CD_2Cl_2 and the NMR monitored while the mixture was warmed to 40 °C. There was no detectable change over a 3-h period.

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Registry No. **9**, 2415-79-4; **10**, 68861-56-3; **11**, 95865-49-9; **12**, 95865-41-1; **16+**, 87792-68-5; **16a**, 87792-69-6; **16b**, 95892-07-2; **17**, 95865-43-3; **18**, 95865-44-4; **20**, 95865-45-5; **21**, 4054-38-0; **22**, 46749-15-9; **23**, 95865-46-6; FpI, 12078-28-3; FpOTF, 95865-48-8; KFp, 60039-75-0; NaFp, 12152-20-4; FpCl, 12107-04-9; Fp-($CH_3CH{=}CH_2$), 38817-10-6; 7-methoxycycloheptene-1-carboxylic acid chloride, 95912-80-4; dicarbonyl(η^5-cyclopentadienyl)(η^1-7-methoxycycloheptene-1-carbonyl)iron, 95865-47-7; cycloheptene, 628-92-2; cycloheptanone, 502-42-1; triphenylmethane, 519-73-3; bis[(dicarbonylcyclopentadienyl)iron], 12154-95-9.