and Engineering Research Council of Canada (NSERC) and the University of Alberta for the structural study at the University of Alberta. In addition M.C. thanks NSERC for partial funding of the diffractometer and A.D.H. thanks NSERC and the Izaak Walton Killam Foundation for postdoctoral fellowships. We thank also the MIT Mass Spectrometry Facility (supported by NIH Division of Research Resources, Grant No. RR00317; K. Biemann, principal investigator) for mass spectra.

Registry No. **1**, 115796-06-0; **2**, 115796-07-1; **3**, 115796-08-2; **4**, 115796-11-7; **5**, 115796-09-3; **6**, 115796-10-6; **7**, 115796-12-8; **8**, 115796-13-9; **9**, 115796-14-0; dicobaltoctacarbonyl, 10210-68-1; diiron nonacarbonyl, 15321-51-4; iron, 7439-89-6; cobalt, 7440-48-4.

Supplementary Material Available: Tables of anisotropic thermal parameters, idealized hydrogen parameters, and weighted least-squares planes (19 pages); listings of observed and calculated structure amplitudes (74 pages). Ordering information is given on any current masthead page.

Fluxional Behavior of Iron Complexes of 1,2-Cycloheptadiene: The Role of the Allyl Cation

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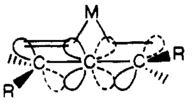
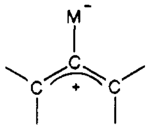
The fluxional behavior of two iron complexes of 1,2-cycloheptadiene—$(\eta^5\text{-}C_5H_5)(CO)_2Fe(\eta^2\text{-}1,2\text{-cycloheptadiene})$fluoroborate (**5**) and its Ph_3P-substituted relative **13**—has been studied. At this time, we report evidence for (1) fluxionality of **5** by a Vrieze–Rosenblum mechanism (E_a = 13.9 kcal/mol), a mechanism where the chirality of the allene moiety is retained, (2) fluxionality of **13** by the same mechanism with an activation barrier about 3–4 kcal/mol higher than that for **5**, (3) accessibility of an allyl cation mechanism in the latter case with E_a = ca. 23 kcal/mol, and (4) circumstantial evidence for accessibility of an allyl cation (E_a between 14.2 and 22 kcal/mol) from **5**.

The fluxionality of transition-metal complexes of allenes in which the metal migrates between the double bonds has piqued the curiosity of chemists since Ben-Shoshun and Pettit[1] first observed this behavior in the tetracarbonyliron complex of tetramethylallene. Although, to date, there are not enough examples to make sweeping generalities, examples of Pt(0),[2] Ni(0),[3] and Pt(II)[4] complexes have been reported that do not show this behavior on the NMR time scale at moderate temperatures (typically near room temperature), Pd(0)[5] complexes have been found that show fluxionality on this time scale but by a dissociation–recombination mechanism, and Fe(II)[6] cationic and Pt(II)[7] neutral complexes have been found that undergo intramolecular fluxionality at rates that are rapid enough to be detected by ^1H NMR.

Two mechanisms have been considered for the intramolecular fluxional process. Their transition states are pictured in **1**[6,7b] and **2**.[8] To distinguish between these is relatively straightforward, because **1** retains the chirality of the allene ligand during the fluxionality process while it would ultimately be lost if it went via transition state **2**.[9] Thus, Rosenblum's[6] finding that the Fp$^+$ [Fp = dicarbonyl(η^5-cyclopentadienyl)iron] complex of optically active 1,2-cyclononadiene did not racemize under conditions where fluxionality was rapid is inconsistent with the second mechanism for the fluxional behavior of Fp$^+$ complexes of allenes. The second transition state **2** has been invoked only once, when Cope[8] suggested it as a way to explain the mutarotation of **3** (Am = active amine). However, Rosenblum[6] has challenged this mechanism by pointing out that the racemization could be equally well

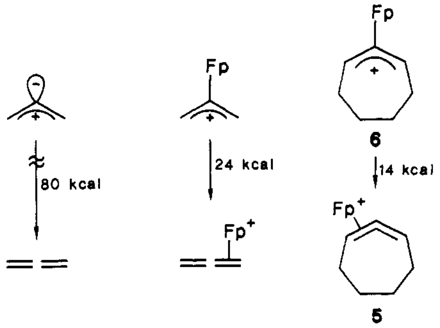


1



2

Scheme I



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[1] Ben-Shoshan, R.; Pettit, R. *J. Am. Chem. Soc.* **1967**, *89*, 2231.

[2] (a) Otsuka, S.; Nakamura, A.; Tani, K. J. *Organomet. Chem.* **1968**, *14*, 30. (b) Winchester, W. R.; Jones, W. M. *Organometallics* **1985**, *4*, 2228.

[3] Otsuka, S.; Tani, K.; Yamagata, T. *J. Chem. Soc., Dalton Trans.* **1973**, 2491.

[4] (a) Briggs, J. R.; Crocker, C.; McDonald, W. S.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1981**, 121. (b) Clark, H. C.; Manzer, L. E. *J. Am. Chem. Soc.* **1985**, *95*, 3812.

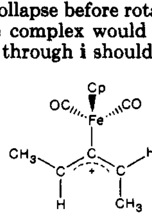
[5] Otsuka, S.; Nakamura, A. *Adv. Organomet Chem.* **1976**, *14*, 245.

[6] Foxman, B.; Marten, D.; Rosan, A.; Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 2160.

[7] (a) Vrieze, K.; Volger, H. C.; Gronert, M.; Pratt, A. P. *J. Organomet. Chem.* **1969**, *10*, 19. (b) Vrieze, K.; Volger, H. C.; Pratt, A. P. *J. Organomet. Chem.* **1970**, *21*, 467.

[8] Cope, A. C.; Moore, W. R.; Bach, R. D.; Winkler, H. S. *J. Am. Chem. Soc.* **1970**, *92*, 1243.

[9] Chirality is not necessarily lost when **2** is formed. For instance, *i* is chiral, and if it were to collapse before rotation around the carbon iron bond, the resulting allene complex would not necessarily be racemic. However, multiple passes through **i** should lead to racemization.



i

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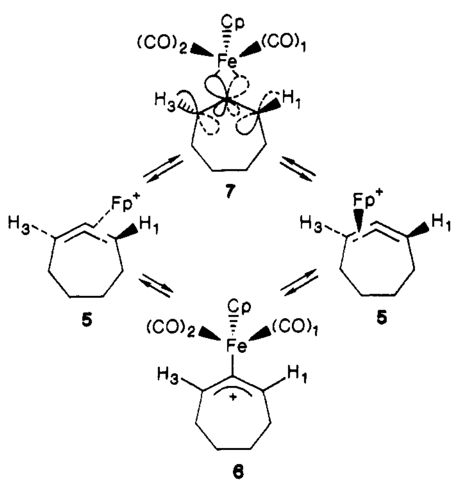
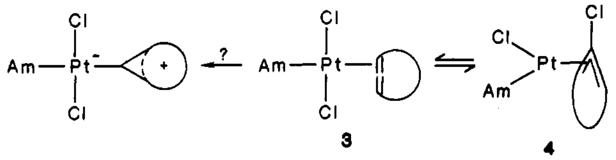
Scheme II



explained by a mechanism via **4**, a type of intermediate that is not available to Fp systems.



From recent EHMO calculations,[10] it was found that complexing Fp^+ [Fp = (η^5-cyclopentadienyl)dicarbonyliron] to allene should have a dramatic effect (reduction from 80 to 24 kcal/mol) on the energy required to force it into a planar configuration (Scheme I). Even taking into account that absolute numbers derived from EHMO calculations are not reliable, a difference of this magnitude leaves little question but that the impact of complexing Fp^+ to an allene should be significant. These calculations led to the second interesting prediction that this energy gap should be further reduced (to 14 kcal/mol), if the complexed allene were incorporated into a seven-membered ring. Again, this absolute number must be used with great caution, but the direction makes sense and suggests that where Rosenblum's Fp^+ complex of 1,2-cyclononadiene did not isomerize to a planar form under his reaction conditions, a complex such as **6** might be accessible under relatively mild conditions. We were therefore intrigued to find an abnormally low activation energy (E_a = 13.9 kcal/mol)[11] for fluxionality of **5** and wondered if, perhaps, unlike the acyclic and large ring Fp^+ allene complexes studied by Rosenblum, the ring strain in **5** might have caused this process to change from a Vrieze–Rosenblum mechanism to what we will hereinafter refer to as an allyl cation mechanism, i.e., fluxionality via **6**. We therefore undertook a more careful study of the fluxionality process of **5** as well as a phosphine-substituted congener.

At this time, we report evidence for (1) fluxionality of **5** by the Vrieze–Rosenblum mechanism (Scheme II), (2) fluxionality of **13** by the same mechanism ($E_a \simeq$ 17–18 kcal/mol), (3) accessibility of an allyl cation mechanism in the latter case with E_a = ca. 23 kcal/mol, and (4) circumstantial evidence for accessibility of an allyl cation (E_a between 14.2 and ca. 22 kcal/mol) from **5**.

Mechanism of the Fluxionality Process of 5 with E_a = 13.9 kcal/mol. The two reasonable mechanisms for the fluxionality of **5** (the Vrieze–Rosenblum mechanism and the allyl cation mechanism) are given in Scheme II. In both processes, H-1 and H-3 become equivalent. Coalescence of these hydrogens in the ^1H NMR simply tells us that the metal moiety rapidly migrates; it says nothing about the mechanism. However, the situation is different for the carbonyl ligands on the iron. Due to the chirality of the allene ligand, the two carbonyl groups in **5** are diastereotopic and are therefore not equivalent in the ^{13}C NMR spectrum. And, indeed, the two ligands show different resonances (207.2 and 210.2 ppm).[11] Since this relationship is retained in **7**, fluxionality by the Vrieze–Rosenblum mechanism should not lead to coalescence. However, in **6**, since the chirality of the allene is lost, the two carbonyls become enantiotopic and should now show identical chemical shifts. Thus, if the fluxiooality process with E_a = 13.9 kcal/mol goes via **6**, the ^{13}C resonances of the two carbonyls should coalesce at 13 °C (C-1 and C-3 should coalesce at ca. 55 °C). If, on the other hand, the process goes *via* **7**, then the resonances of only C-1 and C-3 should show any change with temperature; the two carbonyls should remain unchanged. In fact, when the temperature is raised, C-1 and C-3 had disappeared into the base line by 30 °C, while the carbonyl resonances showed no significant change up to 60 °C.[12] Thus, the fluxionality process with E_a = 13.9 kcal/mol must occur by the Vrieze–Rosenblum mechanism; i.e., the stereochemical integrity of the allene ligand must be retained during this process.

Attempts To Detect a Higher Energy Allyl Cation Fluxionality Mechanism for 5. Although the mechanism of the fluxional behavior of **5** with E_a = 13.9 kcal/mol clearly retains the allene chirality, it is possible that a higher energy process via **6** may be superimposed on the normal lower energy mechanism. We therefore undertook to see if such a mechanism could be detected. In principal, this could be accomplished for **5** either by NMR as described above or by classical racemization techniques. Both, however, have severe limitations. In the case of the NMR, thermal instability limits us to 60 °C, and therefore, if the reaction via **6** has a barrier greater than about 16 kcal/mol, coalescence of the carbonyl carbon resonances will not be observed. Racemization studies also have very real practical limitations, in that definitive results would only be obtained if racemization were slow enough to permit isolation of a resolved allene but fast enough to be observed below ca. 60 °C. Thus, unless the activation energy for reaching **6** falls into a relatively narrow range (ca. 24–27 kcal/mol), either racemization of the allene complex will not be observed or it will occur so rapidly that only racemic material will be detected which, of course, is a negative result. In point of fact, from the results reported below, we believe that the latter actually obtains for the Fp^+ complex **5**.

Our attempts to detect the allyl cation mechanism by chirality studies took two tacks. In the first, the carboxylic acid **8** in Scheme III was partially resolved as its quinine salt. The optical purity of the acyl complex **9** was determined (50% ee) by NMR, using the chiral shift reagent $Eu(hfc)_3$ {hfc = [3-[(heptafluoropropyl)hydroxymethylene]-*d*-camphorate}.

Decarbonylation of the acyl complex, followed by methoxy abstraction with trimethylsilyl triflate, gave the allene complex. Within experimental limits, this material

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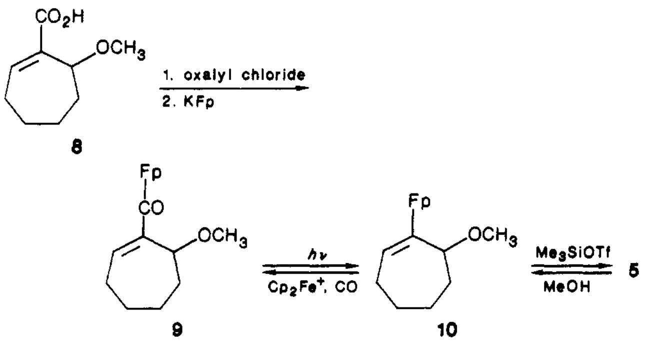
[10] Winchester W. R. Ph.D. Thesis, University of Florida, 1985.

[11] Manganiello, F. J.; Oon, S. M.; Radcliffe, M. D.; Jones, W. M. *Organometallics* **1985**, *4*, 1069.

[12] In a previous paper, it was reported that the triflate salt of **5** decomposes in solution at room temperature. We have since found that the triflate ion must contribute to this instability, since the fluoroborate salt is stable in solution to 60 °C.

Scheme III

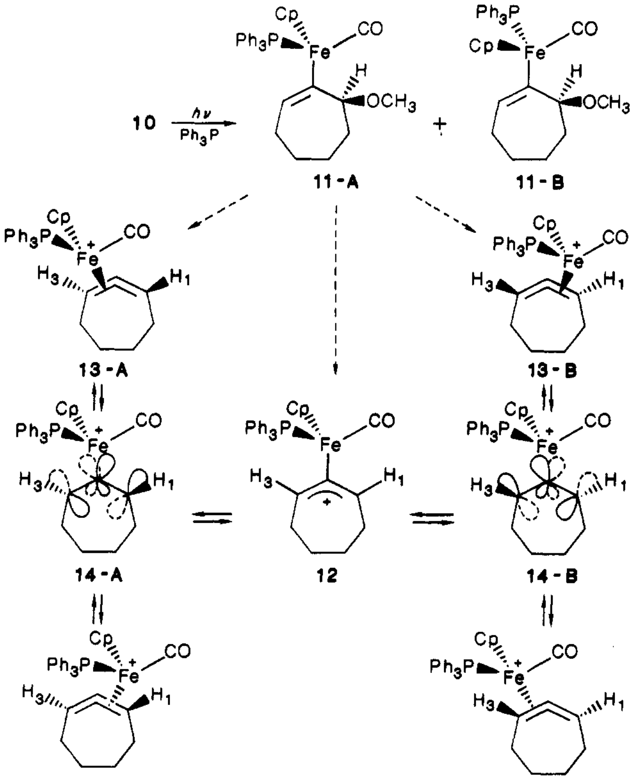


showed no rotation. However, the absence of rotation is less meaningful in this complex than we would like due to light absorption. Furthermore, its ^{1}H NMR was unaffected by Eu(hfc)$_3$. The π-complex was therefore converted back to its methyl ether (also unaffected by Eu(hfc)$_3$) which was, in turn, converted to the corresponding acyl complex **9**, as shown. A ^{1}H NMR study of this complex, using Eu(hfc)$_3$ shift reagent, showed complete racemization.[13]

In principle, loss of activity from the allene could have occurred during the methoxy abstraction step (i.e., an initially formed allyl cation could then collapse to the allene), or the allene itself could racemize via the allyl cation mechanism.[14] With an eye to distinguishing between these two possibilities, we attempted to produce an enantiomeric excess of one allene complex by partially destroying the racemate with an optically active base. For this purpose, in separate experiments, **5** was permitted to react with 0.5 equiv of (*S*)-2-methylbutanol and (−)-menthol. In the case of the primary alcohol, the corresponding ether was isolated, as well as unreacted allene. In the case of the more hindered secondary alcohol, menthol, although decomposition occurred and unreacted allene could be isolated, no ether was detected. In neither case did the allene complex show any detectable rotation. As with the other chirality study, this is once again a negative result that is consistent with, but does not demand, racemization of the allene complex.

Evidence for an Allyl Cation. Although not at all definitive, the results discussed above suggest the accessibility of the allyl cation complex **6**, quite probably originating from the transition state of the normal fluxional process. Furthermore, these results suggest an activation barrier for cation formation that happens to be too high to be detected by ^{13}C NMR but too low to yield to optical activity studies. In hopes of slowing the racemization step enough to experimentally observe epimerization of the allene moiety, the triphenylphosphine-substituted complex **13** was prepared.

Scheme IV



It is generally accepted that the bond between a transition metal and an alkene results from a combination of a σ bond from the olefin HOMO into a vacant metal orbital and a π back-bond from the metal into the olefin LUMO.[16] In contrast, the carbon–metal bond in **6** should have a strong σ-bond component, but the node on the central carbon should essentially eliminate back-bonding. We therefore reasoned that substitution of a phosphine for CO in **5** should retard the allyl cation forming step (by stabilizing the ground state) and thereby possibly push the activation barrier into an experimentally observable range.

We therefore undertook to prepare a phosphine substituted σ complex corresponding to **10**, from which an allene complex could be prepared. This was accomplished by photolysis of **10** in the presence of triphenylphosphine. This gave an air-stable mixture of diastereoisomers **11-A** and **11-B** in ca. 60:40 ratio[17] which, upon treatment with trimethylsilyl triflate, gave the desired allene complex as a 60:40 mixture of diastereomers (**13-A** and **13-B**).[18]

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(13) We recognize that a sequence that involves this many steps with a material that is not 100% optically pure to begin with could lose its activity by racemization at any stage or by selective crystallization in a recrystallization step. However, in this particular sequence, there are no recrystallizations; none of the steps prior to the allene-forming reaction (**8** to **10**) nor the one following σ bond formation (**10** to **9**) involves a bond to the asymmetric center and therefore should not lead to racemization (e.g., the activity of **10** was independently shown to be retained upon conversion to **9**), and the only crystallization was precipitation of the allene complex from the crude reaction mixture. In this case, the filtrate was carefully examined for allene residue; none was found. We are therefore confident that the racemization involves the allene in some way.

(14) Re-formation of the methyl ether **10** could result either from trapping an allyl cation or, more likely, by the well-documented backside displacement of Fp$^+$ from the allene.[15] The former is unlikely, because all attempts to trap the allyl cation by (4 + 2) cycloaddition reactions failed.

(15) Lennon, P.; Rosan, A. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 8426 and references therein.

(16) (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C79. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2339.

(17) Diastereomeric ratios of σ- and allene complexes are based on ^{1}H NMR methoxy and cyclopentadiene intensities, respectively. We were unable to assign stereochemistries to the individual diastereoisomers of either the ethers or the allenes. A 60:40 ratio simply means the mixture contained 60% of the diastereoisomer with the lower field methoxy resonance (for the ethers) or cyclopentadienyl resonance (for the allenes).

Attempts to separate (or enrich) **11-A** from **11-B** by recrystallization failed. Furthermore, even though the acyl complexes corresponding to **11-A** and **11-B** (prepared by carbonylation) could be separated into individual diastereoisomers by recrystallization from 33% ethyl acetate/pentane, decarbonylation back to the σ complex led to complete isomerization. Decarbonylation was unusually difficult. Neither photolysis nor chemical decarbonylation with trimethylamine oxide, iodosobenzene, or the dimer of chlorobis(triphenylphosphine)rhodium was successful. Decarbonylation was finally accomplished by using simultaneous photolysis and sonication. Partial separation of **11-A** from **11-B** was finally achieved by chromatography of the 60:40 mixture of σ complexes on neutral alumina (II). This gave a small amount of a material (10%) that showed 80:20 enrichment. The composition of this mixture was unchanged after several weeks in the refrigerator. A solution in methylene chloride or chloroform was stable for at least 1 day at room temperature.

The 60:40 mixture of **13-A** and **13-B** showed well-separated sets of vinyl hydrogens for each isomer, neither of which showed any broadening in the ^{1}H NMR spectrum up to about 60 °C, the temperature at which the complex began to show decomposition. From this, it is clear that substitution of a phosphine for CO has raised the activation energy for the fluxional process from 13.9 to at least 15.3 kcal/mol, although it says nothing about accessibility of the allyl cation.

While studying the fluxionality of **5**,[11] we found efficient spin saturation transfer between vinyl hydrogens at about 50 °C below the temperature of vinyl hydrogen coalescence. We therefore applied this technique to **13**. At 60 °C, it was found that blind irradiation of the high-field allene hydrogen (e.g., H-1 of **13-B**, which was hidden under the saturated hydrogens) of the major diastereoisomer led to saturation of the low-field allene hydrogen on the same isomer, while leaving the intensity of both H-1 and H-3 of the minor isomer unaffected. Likewise, irradiation of H-1 (the high-field hydrogen) on the minor isomer led to saturation of its low-field counterpart (approximately half-saturation at 40 °C), while leaving the major isomer unaffected.

From these results, we can reach two important conclusions. First, it is clear that the allene is fluxional, and even though it was not possible to accurately determine an activation barrier for this process, it must be in the range of 17–18 kcal/mol.[23] In other words, substitution of a phosphine ligand for CO has increased the activation barrier to fluxionality by some 3–4 kcal/mol. Second, we detected no spin transfer between diastereomers; i.e., saturation of the uncomplexed vinyl hydrogen of one diastereomer had no effect on either vinyl hydrogen of the other. From this we conclude that, as with the dicarbonyl complex, fluxionality is occurring by the Vrieze–Rosenblum mechanism and the allyl cation complex must lie more than 17–18 kcal/mol above the allene complex.

To study the interconversion of the two allene diastereoisomers, separation of **13-A** from **13-B** was required. Unfortunately, all attempts to separate, or even effect enrichment, by standard purification methods failed.[24] However, it was found that enrichment could be accomplished by changing the solvent used for preparing the allene from a benzene/pentane mixture (which gave the 60:40 mixture) to pure pentane, which gave a product that was enriched (80:20) in one of the diastereoisomers. Although not as pure as we would have preferred, this mixture was adequate to study the isomerization of **13**. This was carried out in the following way. First, a 60:40 mixture of diastereoisomers was dissolved in deuteriochloroform and warmed to 60 °C. The composition of the mixture did not show significant change over a period of 3 h. Thus, either this is the equilibrium mixture or isomerization is slow. We then dissolved a sample of the 80:20 mixture in deuteriochloroform and recorded its proton NMR spectrum. In this case, even at room temperature, the composition changed to eventually reach equilibrium (about 60:40).[26] At 30 °C, this equilibration showed satisfactory first-order kinetics with a rate constant of 3.3×10^{-4}. Assuming a preexponential of 10^{13}, this corresponds to an activation barrier of about 23 kcal/mol.

In principle, equilibration of the diastereoisomers of **13** could occur by epimerization of either the metal center or the organic ligand. Under thermal conditions, the most likely mechanism for racemization of the metal center would be by phosphine dissociation.[27] This process was therefore examined in the following ways. First, a mixture of **13** was treated with an excess of triphenyl phosphite in deuteriochloroform. No exchange was observed at room temperature over 95 h, despite the fact that the triphenyl phosphite substituted complex would be expected to be thermodynamically favored over its triphenylphosphine substituted relative.[28] Second, the rate of isomerization was unaffected by the addition of triphenylphosphine. We therefore conclude that the iron center does not epimerize under the isomerization conditions.

Epimerization of the bound allene ligand probably occurs through the allyl cation form **12**. It is not known whether this represents an energy minimum or a transition state, nor is it known whether it is also on the path from **11** to **13**. However, it is an interesting species because of its relationship to the normal transition state for the fluxionality of the allene complex. In its simplest form, **12** can be viewed simply as a valence isomer of **14** that lies at only a few kilocalories per mole (in the range of 5–6) higher energy. This suggests a very low barrier to rotation about the partial double bonds in **14**.

Experimental Section

Proton magnetic resonance spectra were obtained with either a Perkin-Elmer EM 360 or a JEOL FX-100 spectrometer and carbon magnetic resonance spectra were obtained with a JEOL FX-100 spectrometer. All chemical shifts are reported in units of δ, with reference to trimethylsilane. Infrared spectra were recorded on a Perkin-Elmer 283B spectrophotometer. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA. All melting points were measured with a Thomas-Hoover melting point apparatus and are uncorrected. All solutions were

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[18] This is apparently an equilibrium mixture of the two diastereoisomers. This was shown by both equilibrating an enriched mixture of the isomers (vide infra) and by the surprising observation that methoxy abstraction from a 60:40 mixture of diastereoisomers,[11] using only 0.5 equiv of trimethylsilyl triflate, gave a 60:40 mixture of allene complexes but a 10:90 mixture of unreacted σ complexes. Furthermore, treatment of the 10:90 mixture of ethers with 1 equiv of the methoxy-abstracting agent gave virtually no allene complex at all. In other words, only one isomer of **11** gives the allene complex as a 60:40 mixture of diastereoisomers;[19] the other decomposes to products of unknown structures.

[19] On the basis of EHMO calculations of Seeman and Davies,[20] X-ray crystal structures of similar types of complexes,[21] and MMX calculations[22] it appears that only one of the diastereoisomers of **11** has an exposed methoxy group; in the other, the methoxy is shielded by one of the phenyl rings of the triphenylphosphine ligand.

[20] Seeman, J. I.; Davies, S. G. *J. Am. Chem. Soc.* **1985**, *107*, 6522.

[21] (a) Baird, G. J.; Bandy, J. A.; Davies, S. G.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1983**, 1202. (b) Baird, G. J.; Davies, S. G.; Jones, R. H.; Prout, K.; Warner, P. J. *J. Chem. Soc., Chem. Commun.* **1984**, 745.

[22] Unpublished results of P. K. Hanna, University of Florida.

[23] This barrier is based on half-saturation transfer at +40 °C and T_1 between 0.1 and 0.5 s. Unfortunately, neither the temperature nor T_1 could be determined with very much accuracy. The temperature at half-saturation is not accurate because not only are the allenic hydrogen resonances quite broad (which reduced the accuracy of the area determinations) but also only the minor isomer could be used for this purpose because H-1 of the major isomer is hidden under the saturated hydrogens of the cycloheptadiene ring. Second, and of less importance, the broad allenic hydrogen resonances also reduced the accuracy of T_1 measurements. The T_1 range is a conservative estimate.

[24] A crystal of one diastereoisomer that was suitable for X-ray analysis[25] was obtained by very slow crystallization from methylene chloride. However, we were unable to obtain enough of a single material by this method for spectral studies.

[25] Oon, S. M.; Koziol, A. E.; Jones, W. M.; Palenik, G. J. *J. Chem. Soc., Chem. Commun.* **1987**, 491.

[26] "Equilibrium" compositions varied from 65:35 to 60:40. Although this appeared to be outside the error range for the NMR, we found no clear pattern and assume that this has little, if any, significance.

[27] It is unlikely that epimerization of the metal center would occur as a result of dissociation of the organic ligand, since allenes are apparently quite tightly bound to Fp.[6]

[28] This expectation was based on Tolman's cone angles for $(PhO)_3P$ and Ph_3P[29] and our own observation that **11** readily undergoes thermally induced exchange with $(PhO)_3P$.

[29] Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953, 2956. Some of Tolman's cone angles have recently been challenged. See: Stahl, L., Ernst, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 5673.

appropriately dried and degassed before use. Reactions were carried out by using Schlenk line techniques under dinitrogen or in a Vacuum Atmosphere glovebox. Degassed Fisher certified neutral alumina (80–200 mesh), Brockman Activity 1, to which 3% water was added, was used for chromatography. Photolysis was carried out by using a 450-W low-pressure Hg Hanovia lamp in a Pyrex well. (*S*)-(−)-2-Methylbutanol was obtained from Aldrich and used as received. Menthol and triphenylphosphine were recrystallized from absolute ethanol and dried in vacuo. 7-Methoxycycloheptene-1-carboxylic acid and (η^5-C_5H_5)-$(CO)_2$Fe(η^2-1,2-cycloheptadiene)OTf/BF_4 were prepared by published procedures.[11]

Preparation of Dicarbonyl(η^5-cyclopentadienyl)(η^1-7-methoxy-1-cycloheptenyl)iron (10). The synthesis of this compound was reported previously.[11] An improved synthesis follows: *n*-Butyllithium (6 mL, 9.6 mmol, 1.6 M in hexane) was added, dropwise, to 20 mL of a cold (−78° C) THF solution containing 1-bromo-7-methoxycycloheptene (2.24 g, 11 mmol). The mixture was allowed to stir for 1 h at −78 °C, after which a 5-mL THF solution of Fp chloride (2.1 g, 10 mmol) was added. The mixture was allowed to warm to room temperature and was transferred into a 100-mL round-bottom flask containing 8 g of alumina. The solvent was removed in vacuo, and the products coated on the alumina were chromatographed on a 3 × 1 in. alumina column eluting with hexane. The yellow colored band was collected, giving 2.08 g (63%) of the air-sensitive product: IR (neat) 2010 s, 1920 s cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz, δ) 5.80 (t, H2, 1 H), 4.75 (s, Cp, 5 H), 3.80 (m, H7, 1 H), 3.30 (s, OMe, 3 H), 2.50–0.80 (m, CH_2's, 8 H). The previous procedure[11] starting with 1-bromo-7-methoxycycloheptene gave **10** in an overall yield of only 7%.

Resolution of 7-Methoxycycloheptene-1-carboxylic Acid (8). Preparation of Optically Active Dicarbonyl(η^5-cyclopentadienyl)(η^1-7-methoxy-1-cycloheptenyl)iron (10). A one-to-one molar amount of **8** and (−)-quinine was dissolved in hot absolute ethanol to a concentration of 1 g of **8** to 3 mL of ethanol. The solution was filtered and allowed to stand at room temperature. A white translucent solid crystallized within 2 days. The solid was filtered, washed with ethanol, and air-dried to give a white solid. mp 160–162 °C. The diastereomeric salt was dissolved in hot dilute aqueous HCl. The solution was cooled and extracted with diethyl ether. The combined diethyl ether layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo to give optically active **8** as a clear yellow oil. **10** was prepared from optically active **8** according to published procedures.[11] Enantiomeric excess of 50% was determined by ^1H NMR integration of the cyclopentadienyl resonances of a $CDCl_3$ solution of **9**, to which 10 mol % of $Eu^{III}(hfc)_3$ was added. Since photolytic decarbonylation of **9** to **10** does not involve the chiral center, it is reasonable to assume that the enantiomeric excess of 50% is maintained in **10**.

Reaction of Methanol with Dicarbonyl(η^5-cyclopentadienyl)(η^2-1,2-cycloheptadiene)iron Triflate (5). To a solid mixture of **5** (0.15 g, 0.35 mmol) and 0.10 g (0.94 mmol) of sodium carbonate was added 10 mL of dried, degassed methanol at room temperature. The mixture was stirred for 2 h at room temperature. Methanol was removed in vacuo and the residue eluted through a 2 × 1 in. alumina column with hexane. A single yellow band was collected to give 0.032 g (30%) of **10** as a brown oil: IR (neat) 2010, 1920 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz, δ) 5.80 (t, H_2 1 H), 4.75 (s, Cp, 5 H), 3.80 (m, H7, 1 H), 3.30 (s, OMe, 3 H), 2.50–0.80 (m, CH_2's, 8 H).

Preparation of Dicarbonyl(η^5-cyclopentadienyl)(η^1-7-methoxycycloheptene-1-carbonyl)iron (9) via Carbonylation of Dicarbonyl(η^5-cyclopentadienyl)(η^1-7-methoxy-1-cycloheptenyl)iron (10). A cold (−78 °C) 10-mL methylene chloride solution of **10** (0.08 g, 0.26 mmol) and ferrocenium tetrafluoroborate (0.01 g, 0.037 mmol) in a thick wall glass reactor was charged with 55 psi of carbon monoxide gas. The reaction mixture was allowed to react for 1 h, after which the carbon monoxide gas was vented. The solvent was removed in vacuo and the residue eluted through a 1 × 1 in. alumina column. The first band (yellow), ferrocene, was eluted with hexane. The second band (yellow), **9**, was eluted with methylene chloride. **9** was obtained in quantitative yield: IR (neat) 2010, 1960 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz, δ) 6.45 (m, H2, 1 H), 4.90 (s, Cp, 5 H), 4.20 (m, H7, 1 H), 3.20 (s, OMe, 3 H), 2.90–1.00 (m, CH_2's, 8 H).

Partial Decomposition of Racemic Dicarbonyl(η^5-cyclopentadienyl)(η^2-1,2-cycloheptadiene)iron Tetrafluoroborate (5) by (*S*)-(−)-2-Methylbutanol and (−)-Menthol. (a) (*S*)-(−)-2-Methylbutanol. (*S*)-(−)-2-Methylbutanol (0.02 mL, 0.18 mmol) was added to a room-temperature suspension of **5** (0.10 g, 0.36 mmol) in 20 mL of diethyl ether. The mixture was allowed to stir overnight at room temperature. The remaining solid **5** was then collected via filtration and washed with diethyl ether. Approximately 0.06 g of **5** was recovered and was found to have a negligible optical rotation: $[\alpha]^{546}_{\mathrm{roomtemp}}$ −0.7 (*c* 0.001, CH_2Cl_2).

The filtrate was passed down a $1^1/_2 \times 1/2$ in. alumina column, eluting with hexane. A single yellow band was collected to give the ether adduct which, unfortunately, showed no diastereotopism: IR ($CDCl_3$) 2015, 1955 cm^{-1}; ^1H NMR ($CDCl_3$, 100 MHz, δ) 5.05 (t, H2, 1 H), 4.80 (s, Cp, 5 H), 3.94 (d, H7, 1 H), 3.16 (dd, CH_2, 2 H), 2.32–0.08 (m, ring CH_2's, CH_3, CH_2, and CH, 17 H).

(b) (−)-Menthol. Diethyl ether (15 mL) was added to a solid mixture of **5** (0.10 g, 0.18 mmol) and (−)-menthol (0.015 g, 0.09 mmol) and was allowed to stir overnight at room temperature. The mixture turned dark brown. Filtration and washing with ether gave 0.04 g of unreacted allene which showed no detectable rotation. The solvent was removed, leaving behind an intractable residue.

Preparation of Carbonyl(η^5-cyclopentadienyl)(η^1-7-methoxycycloheptenyl)(triphenylphosphine)iron (11). A solution of **10** (1.10 g, 3.6 mmol) in 80 mL of a 1:1 pentane/benzene was photolyzed under a gentle stream of N_2 to remove CO gas. A 15-mL benzene solution of triphenylphosphine (1.0 g, 3.8 mmol) was added via syringe, at a rate of 1 mL/min. The reaction was photolyzed for 10 min more, after addition of triphenylphosphine, at which time the red reaction mixture was transferred to a 100-mL round-bottom flask containing 10 g of alumina. The solvent was removed in vacuo, and the products coated on alumina were chromatographed through a $2^1/_2 \times 1$ in. alumina column. Unreacted triphenylphosphine and **10** were eluted first with 100 mL of hexane. The product was then eluted as a red band with benzene. Solvent was removed in vacuo to give 0.96 g (48%) of **11** as a red oil: IR ($CDCl_3$) 1920 cm^{-1}; ^1H NMR ($CDCl_3$, 100 MHz, δ) diastereomer A 7.60–7.10 (m, C_6H_5, 15 H), 5.32 (dt, H2, 1 H), 4.46 (d, $^3J_{PH}$ = 0.98 Hz, Cp, 5 H), 3.90 (dd, H7, 1 H), 3.19 (s, OMe, 3 H), 2.30–0.80 (m, CH_2's, 8 H); diastereomer B 7.60–7.00 (m, C_6H_5, 15 H), 5.76 (dt, H2, 1 H), 4.43 (d, $^3J_{PH}$ = 0.98 Hz, Cp, 5 H), 3.60 (dd, H7, 1 H), 3.08 (s, OMe, 3 H), 2.30–0.80 (m, CH_2's, 8 H); ^{13}C NMR ($CDCl_3$, 25 MHz, δ) 211.6 (CO), 151.1 (Cl, $^1J_{PC}$ = 23.19 Hz), 141.7 (C2, $^3J_{PC}$ = 9.76 Hz), 136.8 (i-C, $^1J_{PC}$ = 39.06 Hz), 133.5 (m-C, $^3J_{PC}$ = 9.76 Hz), 127.8 (o-C, $^2J_{PC}$ = 8.54 Hz), 92.0 (C7), 84.4 (Cp), 55.8 (C8), 31.7, 27.9, 26.7, 25.8 (C3–C6). Anal. Calcd for $C_{32}H_{33}FeO_2P$: C, 71.65; H, 6.20. Found: C, 71.62; H, 6.22. **11** was obtained in a 60:40 diastereomeric composition determined by ^1H NMR integration of the methoxy resonances.

Preparation of Carbonyl(η^5-cyclopentadienyl)(η^2-1,2-cyclophetadiene)(triphenylphosphine)iron Triflate (13). To a solution of **11** (60:40) (0.15 g, 0.28 mmol) in 10 mL of a 1:1 pentane/benzene solvent mixture at room temperature was added, dropwise, trimethylsilyl triflate (0.10 mL, 0.4 mmol). The reaction mixture was allowed to stir for $^1/_2$ h, after which the solvent was removed. **13** was precipitated from the residue with ethyl acetate to give 0.10 g (56%) of an orange solid: mp 170–173 °C dec; IR (KBr) 1996 cm^{-1}, ^1H NMR ($CDCl_3$, 100 MHz, δ) diastereomer A 7.60–7.00 (b, C_6H_5, 15 H), 6.40 (m, H3, 1 H), 5.12 (d, $^3J_{PH}$ = 1.22 Hz, Cp, 5 H), 2.92 (m, H1, 1 H), 2.50–0.80 (m, CH_2's, 8 H), diastereomer B 7.60–7.00 (m, C_6H_5, 15 H), 6.15 (m, H3, 1 H), 5.32 (d, $^3J_{PH}$ = 1.22 Hz, Cp, 5H), 2.50–0.80 (m, CH_2's and H1, 9 H); ^{13}C NMR ($CDCl_3$, 25 MHz, δ) 217.94 (CO), 154.27 (C2, $^2J_{PC}$ = 20.75), 132.8–129.0 (C_6H_5), 126.71 (C3, $^3J_{PC}$ = 17.25 Hz), 90.4 (Cp), 32.11, 31.29, 28.75, 27.63 (C3–C6). Anal. Calcd for $C_{32}H_{30}F_3FeO_4PS$: C, 58.72; H, 4.62. Found: C, 58.74; H, 4.72. **13** was obtained in a 60:40 diastereomeric composition that was determined by ^1H NMR integration of the cyclopentadienyl resonances. An X-ray structure of the tetrafluoroborate salt of this complex is available.[25]

Enrichment of 11 by Column Chromatography. A 60:40 mixture of **11-A** and **11-B** was passed down an 8 × 1 in. alumina column eluting with a 1:1 benzene/pentane mixture. The tailing end of the broad red band was collected, and the diastereomeric ratio of 80:20 was determined by ^{1}H NMR integrated ratios of the cyclopentadienyl resonances. Only approximately 10% of the initial **11** was collected.

Reaction of Carbonyl(η^5-cyclopentadienyl)(η^1-7-methoxy-1-Cycloheptenyl)(triphenylphosphine)iron (11) with 0.5 Equiv of Trimethylsilyl Triflate. To a solution of a 60:40 mixture of **11-A** and **11-B** (0.63 g, 1.17 mmol) in 15 mL of a 1:1 pentane/benzene solvent mixture at room temperature was added, dropwise, trimethylsilyl triflate (0.11 mL, 0.6 mmol). The mixture was allowed to stir for $^1/_2$ h, after which the solvent was removed. **13** was precipitated from the residue with ethyl acetate to give 0.33 g (85% based on trimethylsilyl triflate) of an orange solid with a 60:40 diastereomeric composition. The solvent was removed from the filtrate, and the residue was chromatographed through a 1 × $^1/_2$ in. column with benzene. A red band was collected. Removal of solvent afforded 0.30 g of **11** with a 10:90 diastereomeric composition.

Reaction of Carbonyl(η^5-cyclopentadienyl)(η^1-7-methoxy-1-cycloheptenyl)(triphenylphosphine)iron (11) with Trimethylsilyl Triflate in Pentane. To a cold (0 °C) solution of a 60:40 mixture of **11-A** and **11-B** (0.20 g, 0.35 mmol) in 20 mL of pentane was added, dropwise, trimethylsilyl triflate (0.10 mL, 0.4 mmol). An orange precipitate was formed immediately and was collected via filtration. **13** was purified by dissolving the orange solid in a small amount of cold methylene chloride, followed by precipitation from ethyl acetate. The diastereomeric composition of 80:20 was determined by ^{1}H NMR integrated areas of the cyclopentadienyl resonances.

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Registry No. **5**, 87792-69-6; (±)-**8**, 115513-75-2; **8**, 95865-49-9; **9**, 95865-47-7; **10**, 95865-41-1; **11-A**, 115649-09-7; **11-B**, 115649-10-0; **13-A**, 115649-12-2; **13-B**, 115649-14-4; FpCl, 12107-04-9; Me_3SiOTf, 27607-77-8; (±)-1-bromo-7-methoxycycloheptene, 115513-74-1; methanol, 67-56-1; ferrocenium tetrafluoroborate, 1282-37-7.

Mono(cyclopentadienyl)zirconium(II) and -hafnium(II) Chemistry: Synthesis and Reactivity of $CpM(CO)_2(dmpe)Cl$ [M = Zr, Hf; Cp = Cyclopentadienyl; dmpe = 1,2-Bis(dimethylphosphino)ethane] via Mild-Condition Carbonylation Reaction of $CpM(dmpe)_2Cl$. The Crystal Structure of $CpZr(CO)_2(dmpe)Cl$

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The Na reduction of $CpMCl_3(THF)_2$ (M = Zr, Hf; Cp = cyclopentadienyl; THF = tetrahydrofuran) in the presence of a slight excess of dmpe [dmpe = 1,2-bis(dimethylphosphino)ethane] led to the formation of the two isostructural species $CpM(dmpe)_2Cl$ [M = Zr (**1**), 68%; M = Hf (**2**), 58%]. Easy replacement of one of the two coordinated dmpe by two molecules of CO was achieved by either a carbonylation reaction under mild conditions or CO abstraction from $[CpFe(CO)_2]_2$. The resulting carbonyl derivatives $CpM(CO)_2(dmpe)Cl$ [M = Zr (**3**), 73%; M = Hf (**4**), 63%] have been isolated and fully characterized. The close similarity in their spectroscopic properties suggested that the two complexes are isostructural. Compound **3** crystallizes in a monoclinic space group of $P2_1/a$ symmetry with a = 15.664 (10) Å, b = 7.208 (3) Å, c = 16.869 (9) Å, β = 112.89 (4)°, V = 1754 (2) Å^3, and Z = 4. The presence of a fast CO exchange in solution has been demonstrated for both **3** and **4** by using ^{13}CO. In agreement with its dynamic behavior in solution, an easy ligand-exchange reaction occurs between **3** and **1** forming the pyrophoric light green carbonyl derivative $[CpZr(CO)(dmpe)Cl]_2(dmpe)$ (**5**). Complex **5** can be more conveniently synthesized by carrying the carbonylation reaction on saturated solutions of **1** in ether. Easy ligand-exchange reactions of both **1** and **3** with butadiene afforded the new butadiene derivative $CpZr(\eta^4\text{-butadiene})(dmpe)Cl$ (**6**). Vigorous reaction of **3** with 2 equiv of ethylene (1 atm, room temperature) led instead to the evolution of 1 equiv of CO with formation of a yellow solid product, probably $CpZr[\eta^2\text{-}\overline{C(O)CH_2CH_2CH_2CH_2}]Cl\cdot{}^1/_2(dmpe)$ (**7**). Chemical degradation of **7** with 2 equiv of anhydrous HCl gave cyclopentanol in 75% yield.

Introduction

The coordination of CO in its intact form, which is the prerequisite for its activation,[1] has been reported in the chemistry of zirconium and hafnium in only few cases: $Cp'_2M(CO)L$ ($Cp' = C_5H_5, RC_5H_4, C_5Me_5$; L = CO, PR_3; M = Zr, Hf)[2] and $Cp'M(CO)_4^-$ ($Cp' = C_5H_5, C_5Me_5$; M = Zr, Hf)[3] in which the metal is in the oxidation state II and

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