Synthesis, Stereoisomerism, and Fluxional Behavior of Cationic Alleneiron Complexes[1]

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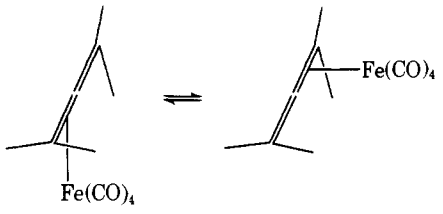
Abstract: The exchange reaction involving the dicarbonyl (η^5-cyclopentadienyl) isobutyleneiron cation (**2**) and allenes provides an efficient route to the corresponding allene complexes (**4–10**). For those allene complexes which are capable of existing in stereoisomeric forms the syn isomers may be obtained stereospecifically by protonation of dicarbonyl (η^5-cyclopentadienyl)-η^1-propargyliron complexes. The *syn*-3-methylalleneiron complex (**5**) undergoes unimolecular nondissociative isomerization to the anti isomer on heating in nitromethane ($K_{eq}^{50°C} = 1.95$, $\Delta H^{\ddagger} = 21.2 \pm 1.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = -5.2 \pm 3$ eu). Activation energy barriers for rotation about the metal-olefin bond in a number of these alleneiron complexes have been determined. The principal contributor to the rotational barrier is shown to be the *syn*-3 substituent. Above 10 °C the tetramethylalleneiron complex undergoes a rapid fluxional motion involving exchange of the ligand coordination site. Two dissociative mechanisms for this process have been considered and each may be shown to be inoperative. Of the two nondissociative mechanisms, a stepwise process involving the intermediacy of a η^1-2-allyliron cation has also been excluded, since fluxional motion does not result in the racemization of a chiral alleneiron complex. A concerted 1,2-shift mechanism is in accord with all the experimental results.

The number of organometallic complexes of transition metals, which undergo a rapid permutation among equivalent structures related to one another through a change in the locus of metal-ligand bonding, is now so considerable that the phenomenon may be regarded as commonplace among this class of compound.[2]

Allene complexes of iron[3] and platinum[4,5] represent the simplest π-complexes exhibiting such fluxional behavior. Of these, tetramethylalleneiron tetracarbonyl was the first to be recognized as a member of this class.[3] At room temperature its ^{1}H NMR spectrum exhibits a single methyl proton resonance due to rapid exchange of metal-olefin bonding among the four equivalent sites, through a formal orthogonal 1,2-shift of the metal atom (**1a** $\rightleftarrows$ **1b**). When exchange is frozen out at lower temperatures, three singlet resonances with the expected 1:1:2 pattern of relative intensities are observed.

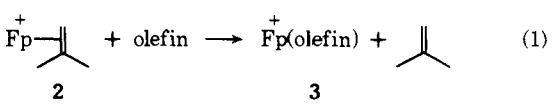


1a **1b**

The present paper provides an account of the preparation and stereochemistry of several new alleneiron complexes. The metal-olefin rotational barrier has been determined for some of these and the mechanism of fluxional change has been elucidated.

Results and Discussion

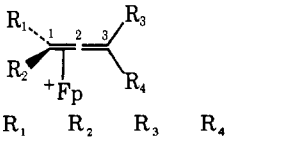
Synthesis of Complexes. We have previously shown that cationic dicarbonyl η^5-cyclopentadienyl (olefin) iron complexes (**3**) may be prepared by employing the readily available isobutylene complex (**2**) as a partner in the exchange reaction shown in eq 1. (In structure **2** and hereafter, the symbol Fp stands for the η^5-$C_5H_5Fe(CO)_2$ radical.)



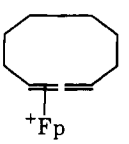
(1)

2 **3**

The reaction is particularly well suited to the preparation of complexes of terminal olefins and has now been found to be equally effective with allenes. In practice, **2** is heated briefly at 65 °C in dichloroethane solution in the presence of 2 molar equivalents of allene, and the product is isolated, generally in excellent yield, by cooling the solution and precipitating the product with ether. Allene complexes **4–10** were prepared in this way.



	R_1	R_2	R_3	R_4
4,	H	H	H	H
5,	H	H	H	Me
6,	H	H	Me	H
7,	H	Me	H	Me
8,	H	Me	Me	H
9,	H	H	Me	Me
10,	Me	Me	Me	Me



11

The stability of these complexes in solution is significantly greater than that of simple Fp(olefin)$^+$ complexes. Prolonged heating in nitromethane solutions, under conditions which generally lead to extensive decomposition of the latter cations, left the allene complexes unscathed. Thus, the tetramethylallene complex (**10**) may be heated in nitromethane solution to 95 °C without apparent decomposition, while the isobutylene complex (**2**) is decomposed within several minutes at 95 °C in this solvent. The factors responsible for increased stability in these complexes are not easily identified, but may in part derive from secondary back-bonding interactions between filled metal d orbitals and the π^* orbital associated with the noncoordinated double bond. Such interactions have been invoked[6] to account for the shorter metal-central carbon compared with metal-terminal carbon bond distances in rhodium, palladium, and platinum allene complexes.[7] Alternatively, increased bond strength as well as the unsymmetrical character of metal-olefin bonding in these allene complexes may derive from differences in hybridization at the two carbon centers. Very similar distortions in metal-olefin bonding are observed in a platinum-vinyl alcohol complex,[8] and have been inferred for Fp-vinyl alcohol and ether cationic complexes from spectral data.[9] These distortions undoubtedly reflect π-orbital charge displacement due to interactions with oxygen.

Stereoisomerism. Since π-orbitals in the allene ligand remain orthogonal in the complex,[6,7b,10] those complexes with a single

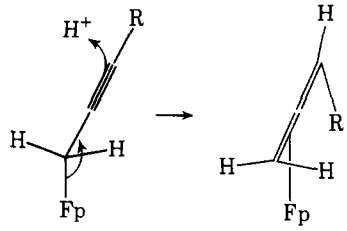
Table I. Rate Data For The Equilibration of Complex **5**

Temp, °C	$k \times 10^3$, s^{-1}	Temp, °C	$k \times 10^3$, s^{-1}
35	0.38 ± 0.01	45[a]	1.25 ± 0.04
40[a]	0.70 ± 0.02	50[a]	1.97 ± 0.05
	$\Delta H^{\ddagger}$ = 21.2 ± 1.5 kcal/mol		
	$\Delta S^{\ddagger}$ = −5.2 ± 3 eu		

[a] Average of two separate runs.

substituent at C(3) are capable of existing in two isomeric forms. These are designated as syn and anti depending on whether the substituent at C(3) is directed toward or away from the metal. Steric interactions between a syn 3-methyl substituent and the organometallic residue are relatively small, since the exchange reaction, carried out with either methylallene or with 1,3-dimethylallene affords 2:1 mixtures of stereoisomers (**5, 6** and **7, 8**), in which the predominant isomer is assigned the anti configuration.

A more stereospecific route to syn-3-substituted complexes is provided by protonation of (η^1-propargyl) Fp complexes (**12**). These substances are in turn available by metalation of the corresponding substituted propargyl halides.[11] Protonation of **12a** or **12b** yields a single stereoisomer assigned syn structures **5**[12] and **13**.[13] The stereospecificity of this reaction is readily accounted for in terms of protonation at C(3), concerted with trans periplanar participation of the organometallic group (eq 2), and is closely related to the stereospecificity ex-



(2)

12a, R = Me
b, R = Ph

5, R = Me
13, R = Ph

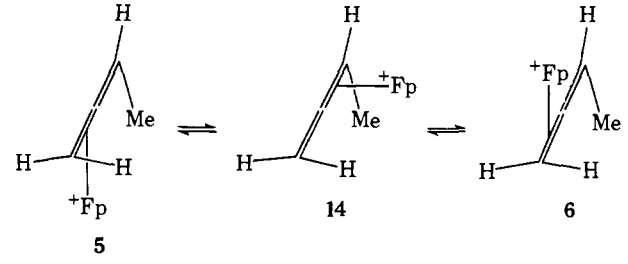
hibited in (3 + 2) cycloaddition reactions of (η^1-allyl)Fp complexes.[14,15]

On heating in nitromethane solution the syn complex (**5**) is partially isomerized to the less crowded, thermodynamically favored anti isomer (**6**). The proportion of anti/syn isomers at equilibrium ($K_{eq}^{50°C}$ = 1.95) is close to that observed in the direct preparation of these isomers by the exchange reaction.

The equilibration of **5** in nitromethane solution exhibits first-order kinetics over at least 3 half-lives and may be followed conveniently by monitoring the integrated intensities of cyclopentadienyl ring proton resonances for each isomer. Rate data obtained in this manner are summarized in Table I, together with derived activation parameters.

The isomerization reaction is intramolecular since, when carried out in the presence of excess allene, none of the allene complex (**4**) is formed.

Complex **14**, which is a necessary intermediate in a sequence involving successive 1,2-shifts of the Fp group, is not detected



5 14 6

Table II. Activation Energies ($\Delta G^{\ddagger}$) in Dicarbonyl η^5-Cyclopentadienyliron Allene Cations

Complex	Allene rotation, kcal mol^{-1}	1,2-Shift, kcal mol^{-1}
4	<8	
5	10.8	23.1
7		18
9	11.3	
10	12.7	16.3

in the isomerization reaction nor is it present to any appreciable extent in the equilibrium mixture. Its relatively lower thermodynamic stability is not unexpected in view of the effect of alkyl substituents in reducing the thermal stability of Fp(olefin)$^+$ complexes and of metal olefin complexes in general.[16] This effect is no doubt the consequence of steric interactions between substituents on the coordinated double bond and the organometallic group. Such interactions are clearly manifest in the crystal structure of the tetramethylallene complex (**10**) where large angle distortions are induced by the relatively short contact between a methyl group at C(1) and the proximate carbonyl ligand.[10] It is not surprising, therefore, that the exchange reaction with 1,1-dimethylallene gives only the distal substituted allene complex (**9**). Its structure is evidenced by its NMR spectrum which exhibits high-field vinyl proton resonances at τ 6.98 and two separate methyl proton resonances close to those observed in **5** and **6**. A similar structure has been established for a Pt(1,1-dimethylallene)$(PPh_3)_2$ complex.[4,17]

Dynamic Behavior. The syn → anti isomerization reaction, which is relatively slow for **5** ⇄ **6** at room temperature, becomes significantly more facile with increasing alkyl substitution of the allene ligand. At the same time such substitution raises the energy barrier associated with rotation of the allene about the iron-olefin bond. Both these effects are most clearly evident in the tetramethylallene complex (**10**). At −60 °C, the ^{1}H NMR spectrum of this substance exhibits four sharp methyl proton singlets at τ 7.65, 7.85, 8.00, and 8.30 (Figure 1a), consistent with a relatively rigid nonrotating structure. Conformations such as **10a** ≡ **10b** (Figure 2) are in accord with the spectral data, the high-field signals being assigned to methyl groups on the coordinated olefin and the remaining signals at τ 7.85 and 7.65 to *anti*- and *syn*-methyl groups, respectively. In the stereoisomeric complexes **6** and **5** these resonances are at τ 7.85 and 7.70, respectively.

Above temperatures of −60 °C, the high field doublet broadens and finally collapses at −25 °C, due to averaging of Me(1) and Me(2) through rotation about the metal-olefin bond (Figure 2 a ⇌ c ⇌ b). The activation free energy for this process, calculated from the coalescence temperature, is 12.3 kcal mol^{-1}. This is well within the range of rotational barriers observed for a number of neutral metal-olefin complexes of rhodium,[18,19] platinum,[20] manganese,[21] chromium,[21] and iron.[22] Significant contributions to the rotational barrier in **10** are undoubtedly made by steric interactions of the *syn*-methyl group at C(3) and the two methyl groups at C(1) of the allene ligand, with carbonyl and cyclopentadienyl ligands. Of these, the former would appear to be the more important. This is suggested by a comparison of the free energies of activation for allene rotation in complexes **4, 5, 9,** and **10** (Table II), determined from NMR coalescence temperatures. Thus, the principal increment to the rotational barrier in the parent complex (**4**) is associated with a *syn*-methyl substitution at C(3). Further substitution at this center as in **9** results in only a small increase in rotational barrier and even the addition of two methyl groups at C(1) in **10** does not greatly increase the barrier. A comparison of the estimated maximum barrier for

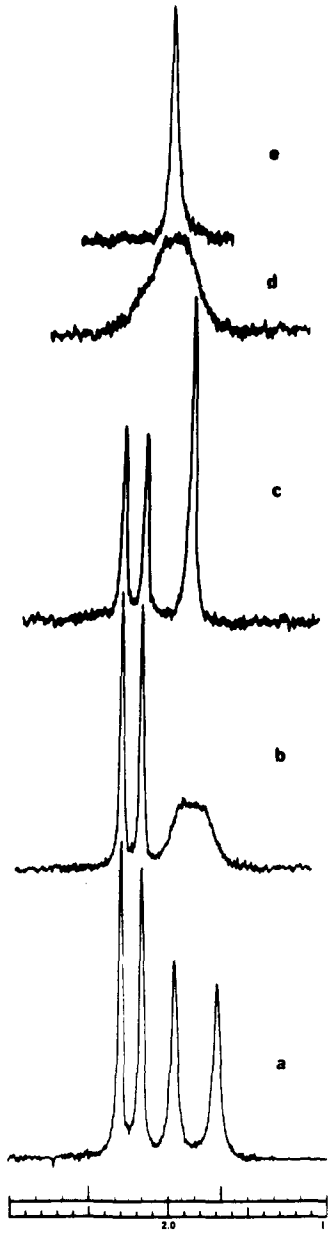


Figure 1. Methyl proton resonances in complex **10** taken in CD_2Cl_2–CD_3NO_2: (a) −60 °C; (b) −25 °C; (c) 10 °C; (d) 45 °C; (e) 95 °C.

4 with rotational barriers of ethylene in neutral Rh,[18,19] Pt,[20] chromium,[21] and iron[22] complexes (12–15 kcal mol^{-1}) suggests that the electronic component of the rotational barrier, which is dependent on metal → ligand back-bonding interactions, is less important for the cationic iron complexes than for neutral complexes. A similarly small olefin rotational barrier (7.5–9.5 kcal mol^{-1}) has been observed in cationic ethylene complexes of osmium[23] and iron.[24]

Progressive narrowing of the high field absorption in **10** in the range of −25 to 10 °C, due to rotational averaging of methyl groups at C(1), is not accompanied by any significant change in the appearance of the lower field doublet (Figure 1c). Above this temperature exchange of *syn*- and *anti*-methyl groups with one another and with the C(1) methyl groups becomes more important, as is seen in the broadening and final coalescence of these resonances at 45 °C. Such exchange clearly requires migration of the organometallic Fp radical between the two olefinic bonds of the allene.

Mechanism of the 1,2-Shift. We consider four generalized mechanisms for proton exchange in **10**, of which two are dissociative (eq 3 and 4) and two are nondissociative (eq 5 and 6).

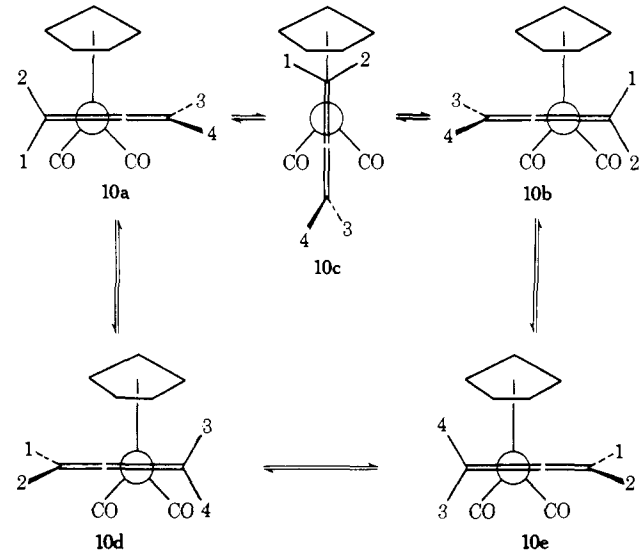
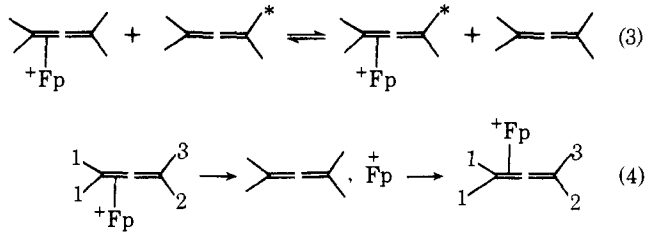
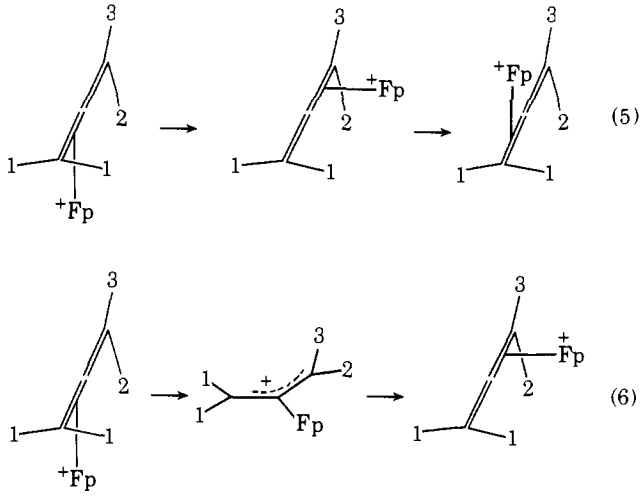


Figure 2.

Dissociative Exchange



Nondissociative Exchange



Of these, exchange through a dissociative intermolecular process (eq 3) can readily be discarded, since the NMR spectrum of complex **10**, taken in the presence of free allene, shows no exchange of complexed and uncomplexed ligand at temperatures at which methyl group exchange in **10** is rapid.

These results do not exclude proton exchange by a dissociative process involving rapid recombination within a solvent cage (eq 4). Such a process may, however, be excluded by examining the spectrum of **10** in the region of exchange coalescence. The dissociative mechanism (eq 4) provides a pathway for the exchange of *syn*- and *anti*-methyl groups (Me(2), Me(3)) which does not require concurrent exchange of Me(1) with either Me(2) or Me(3). By contrast, nondissociative exchange (eq 5 or 6) requires that exchange of Me(1) with Me(2) and Me(3) takes place with concurrent exchange of Me(2) and Me(3).

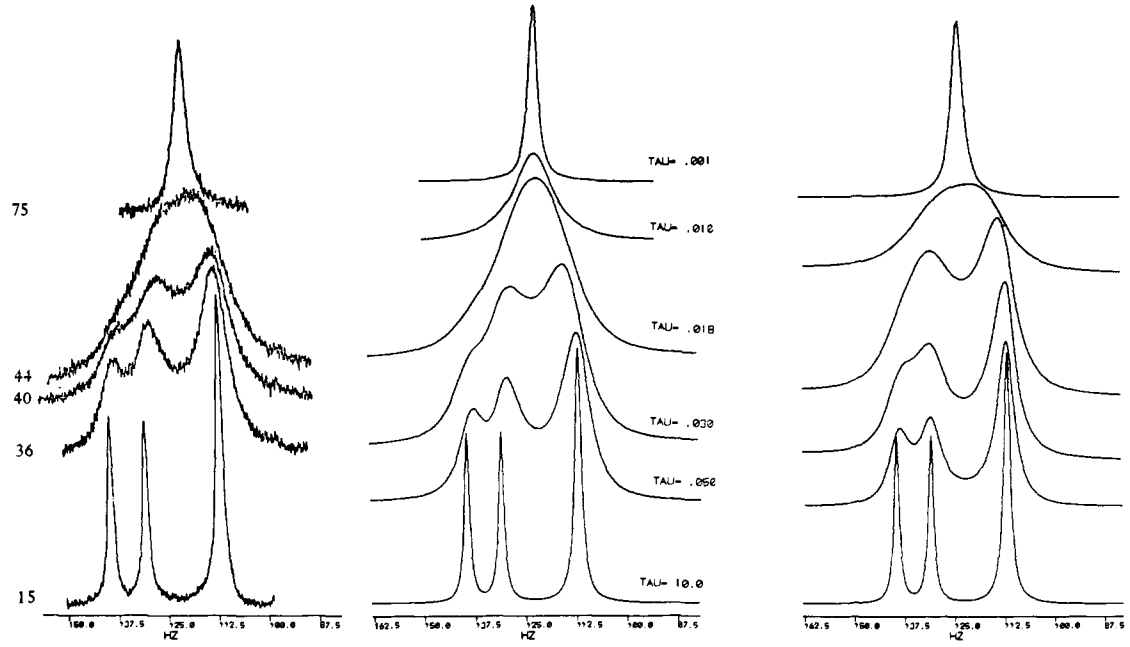
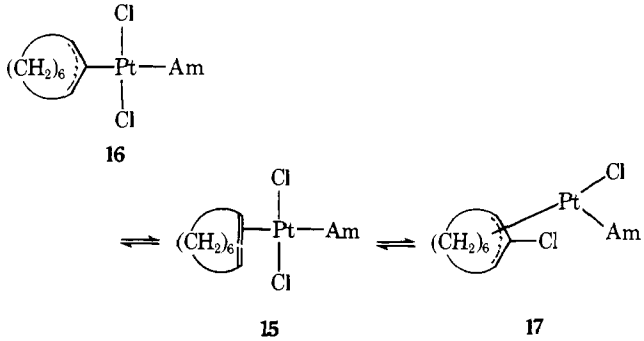


Figure 3. Observed and computed spectra for proton exchange in complex **10**. Experimental spectra at various temperatures (a). Computed spectra for several mean residence times for a nondissociative exchange mechanism (b) and for a dissociative exchange mechanism (c).

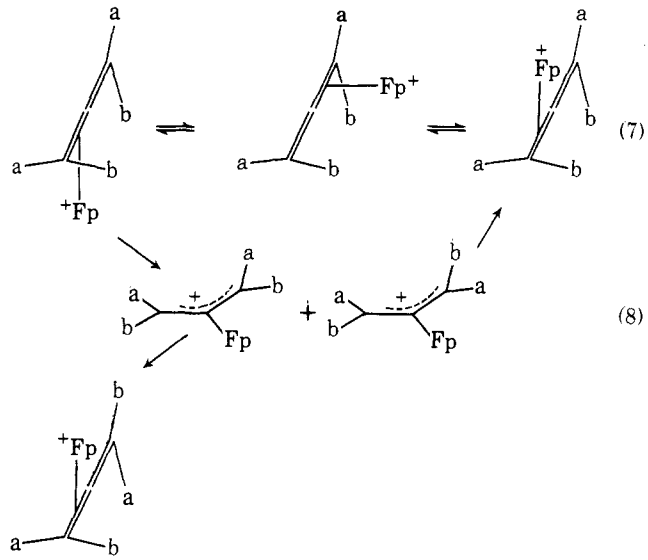
Figure 3 shows the experimental spectrum and those computed[25] for the nondissociative and for the dissociative mechanisms in the region of exchange coalescence for Me(1), Me(2), and Me(3). For the dissociative process (eq 4), exchange broadening and collapse of the low field doublet absorption (Me(2), Me(3)) is seen to occur before complete averaging of these resonances with the Me(1) resonance. This is to be contrasted with the simultaneous collapse of all three resonances computed for a nondissociative process (eq 5 or 6), which closely matches the observed temperature dependence of these resonances.

A stepwise mechanism, similar to that depicted in eq 6, has previously been proposed to account for mutarotation in optically active 1,2-cyclononadieneplatinum complexes (**15**), where Am represents a chiral secondary amine.[26] Of the intermediates considered (**16** and **17**), the first is analogous to the cation postulated in the stepwise mechanism of eq 6, but such a structure appears to be little precendented in the chemistry of either platinum or the closely related palladium allene complexes.[7] On the other hand, the change **15** → **17**, involving ligand transfer of halogen, is better precedented,[7] but for Fp(allene) complexes no ligand is available for analogous transfer from the metal to the allene ligand.



The activation energy data for the 1,2-shift (Table II) do not provide grounds for favoring either the stepwise or concerted mechanism, since the observed decrease in the fluxional barrier on increasing methyl substitution is compatible with either pathway. Increasing methyl substitution of the allene ligand might clearly be expected to promote stepwise rearrangement through stabilization of the allyl cation intermediate. Furthermore such substitution might be expected to progressively lower the activation energy for the concerted process if the ground state for the complexes is sterically distabilized more effectively than is the transition state.

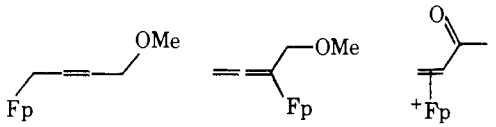
A clear choice between these two mechanisms may, however, be made by use of a chiral allene complex. As with the platinum complexes, and antarafacial change in a chiral 1,3-disubstituted alleneiron complex, which takes place through a series of concerted 1,2-shifts, results in interconversion of diastereomers, but not in racemization (eq 7). By contrast, the stepwise mechanism (eq 8) passes through a planar, achiral intermediate and hence must result in racemization as well as diastereomer exchange.



As a test of these mechanisms, optically active cyclononadiene complex (**11**), $[\alpha]^{27}D$ 26°, was prepared from optically active allene,[27] $[\alpha]^{28}D$ 22°, by exchange with **2**. After heating in nitromethane at 80 °C for 30 min, the complex was recovered by precipitation with ether and had $[\alpha]^{27}D$ 22°. A second sample of **11**, heated in 1,2-dichloroethane for 40 min, was recovered and decomposed with NaFp. The free allene had $[\alpha]D$ 20°. The fact that a rapid 1,2-shift of the Fp group is occurring under these conditions is clearly evidenced by the

reversible broadening of vinyl proton resonances at τ 3.53 and 5.40 in **11** at these temperatures. The stepwise 1,2-shift mechanism, depicted in eq 6, is thereby eliminated.

Cumulene Complexes. Although a number of uncharged iron complexes of cumulated systems are known,[28] cumulated analogues of Fp(olefin) cations are not well characterized.[29] In an attempt to prepare such a species by acid-catalyzed elimination from a (2-butynyl)Fp complex, 4-methoxy-2-butynyl-1-benzenesulfonate was metalated with Fp anion. The spectral properties of the product, obtained in good yield, were, however, not those anticipated for the butynyl complex (**18**), but were instead in accord with the isomeric allenyl complex (**19**). Treatment of this substance with 48% aqueous fluoroboric acid, followed by precipitation of the product with ether gave a cation which proved to be the Fp complex of methyl vinyl ketone (**20**).[30] Although cationic cumulene or acetylene complexes can be depicted as intermediates in this reaction, the present evidence does not provide grounds for distinguishing between these or excluding other reaction paths.



18 **19** **20**

Experimental Section

All operations were carried out in a nitrogen atmosphere. Solvents were dried, degassed, and stored under nitrogen, over molecular sieves. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer. ^{1}H NMR spectra were determined on a Varian A-60 spectrometer (N1H GM-13183) and on a Perkin-Elmer R-32 spectrometer (NSF GP-31214 X2). Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Preparation of Fp(allene) Complexes—General Procedure. The isobutylene complex (**2**) as the tetrafluoroborate (1.6 g, 5 mmol) was taken up in 50 mL of 1,2-dichloroethane in a 125-mL Erlenmeyer flask fitted with a rubber septum, thermometer, nitrogen inlet, and a syringe needle for gases to escape. The solution was heated to 65 °C and stirred vigorously while the allene (10 mmol) was injected by syringe. In the case of the parent allene, the gas was bubbled in for 10 min. The solution was kept at 65 °C for 15 min, and then cooled to room temperature and diluted with anhydrous ether (100 mL). The precipitated complex was filtered and recrystallized from methylene chloride-ether. Individual yields, spectral, and analytical data are given for each complex.

Dicarbonyl η^5-Cyclopentadienyl(allene)iron Tetrafluoroborate (4). Yield 1.14 g (75%), mp 170–175 °C (dec without melting); IR (KBr) 2080 and 2030 cm^{-1}; NMR (CD_3NO_2) τ 3.41 (m, 1, CH=), 3.75 (m, 1, CH=), 4.24 (s, 5 Cp), 6.7 (t, 2, J = 4 Hz, $=CH_2(M^+)$). Anal. Calcd for $C_{10}H_9BF_4FeO_2$: C, 39.47; H, 2.96. Found: C, 39.59; H, 2.97.

Protonation of 1-Fp-2-butyne. Preparation of 5. The butyne complex (**12a**) (460 mg, 2 mmol) was taken up in 200 mL of degassed ether. The solution was cooled to −30 °C and 48% aqueous fluoroboric acid (3 mL) was added dropwise with rapid swirling. The precipitated yellow solid was filtered off rapidly and washed with cold anhydrous ether. Recrystallization from precooled (~ −30 °C) acetone-ether gave 550 mg of product (86%); IR (KBr) 2000 and 2040 cm^{-1}; NMR (CD_3NO_2) τ 3.08 (m, 1, =CH), 4.20 (s, 5, Cp), 6.8 (m, 2, $=CH_2(M)^+$), 7.70 (dt, 3, J = 6 and 3 Hz, $=CCH_3$). Anal. Calcd for $C_{11}H_{11}BF_4FeO_2$: C, 41.51; H, 3.46. Found: C, 41.55; H, 3.59.

Dicarbonyl η^5-Cyclopentadienyl(1,2-η^2-3-methylallene)iron Tetrafluoroborate. Complexes 5 and 6. From 2.4 g of isobutylene complex (**2**) and 4 g of methylallene, 2.2 g of product as a mixture of **5** and **6** was obtained (92%): NMR (CD_3NO_2) τ 3.08 (m, =CH), 3.65 (m, =CH), 4.21, 4.27 (2s, 5, Cp), 6.8 (m, 2, $=CH_2(M)^+$), 7.80 (m, 3 CCH_3). The ratio of **5**/**6** isomers determined from the relative integrated intensities of the Cp proton resonances was 1:2.1. The same ratio of isomers was obtained on heating CD_3NO_2 solutions of **5** (see above) on a steam bath for 30 min.

Dicarbonyl η^5-Cyclopentadienyl(η^2-1,3-dimethylallene)iron. Complexes 7 and 8. Yield 1.41 g (85%), mp 157–160 °C dec; IR (KBr) 2080 and 2040 cm^{-1}; NMR (CD_3NO_2) τ 3.25 and 3.8 (m, 1), 4.25 and 4.33 (2s, 5, Cp), 7.6–8.5 (m, 7). Anal. Calcd for $C_{12}H_{13}BF_4O_2$: C, 43.38; H, 3.92. Found: C, 43.61; H, 3.91. The ratio of the two isomers was 1:2.4 (**7**/**8**).

Dicarbonyl η^5-Cyclopentadienyl(1,2-η^2-3,3-dimethylallene)iron Complex 9. Yield 1.66 g (100%), mp 142–145 °C dec; IR (KBr) 2060 and 2010 cm^{-1}; NMR (CD_3NO_2) τ 4.21 (s, 5, Cp), 6.98 (m, 2, J = 2 Hz, $=CH_2(M^+)$), 7.7 (t, 3, J = 2 Hz, Me(4)), 7.74 (t, 3, J = 2 Hz, Me(3). Anal. Calcd for $C_{12}H_{13}BF_4FeO_2$: C, 43.38; H, 3.92. Found: C, 43.21; H, 3.96.

Dicarbonyl η^5-Cyclopentadienyl(η^2-tetramethylallene)iron. Complex 10. Yield 1.6 g (88%), mp 165–169 °C dec; IR (KBr) 2060 and 2010 cm^{-1}; NMR (CD_3NO_2, 10 °C) τ 4.25 (s, 5, Cp), 7.65 (s, 3, Me(4)), 7.85 (s, 3, Me(3)), 8.15 (s, 6, Me(1), Me(2)). Anal. Calcd for $C_{14}H_{17}BF_4FeO_2$: C, 46.66; H, 4.72. Found: C, 46.46; H, 4.83.

Dicarbonyl η^5-Cyclopentadienyl(η^2-1,2-cyclononadiene)iron. Complex 11. Yield 1.4 g (73%), mp 159–160 °C; IR (KBr) 2080 and 2040 cm^{-1}; NMR (CD_3NO_2) τ 3.6 (m, 1, =CH), 4.33 (s, 5, Cp), 5.65 (m, 1, =CH), 7.3–8.8 (br d, m, 13, $=CH(M^+)$, CH_2). Anal. Calcd for $C_{16}H_{19}BF_4FeO_2$: C, 49.73; H, 4.92. Found: C, 49.77; H, 4.95.

Dicarbonyl η^5-Cyclopentadienyl(η^1-1-methoxymethylallenyl)iron. Complex 18. A solution of sodium dicarbonyl-η^5-cyclopentadienylferrate was prepared from 10.62 g (60 mmol) of $[C_5H_5Fe(CO)_2]_2$ and excess 2% sodium amalgam in 200 mL of tetrahydrofuran. The anion solution was cooled to 0 °C and 4-methoxy-2-butynyl 1-benzenesulfonate (12 g, 50 mmol) was added. The solution was further stirred for 1 h and solvent was removed under reduced pressure. The residue was extracted seven times with petroleum ether (bp 30–60 °C) and these extracts were filtered through 50 g of sand under nitrogen. Solvent was removed from the filtrate and the residue was chromatographed on basic alumina. Elution with ether-hexane (3:7) gave the product as an amber oil: yield 10 g (77%); IR (neat film); 2020 and 1960 cm^{-1}; NMR (CS_2) τ 5.21 (s, 5, Cp), 6.05 (t, 2, J = 2.5 Hz, CH_2), 6.26 (t, 2, J = 2.5 Hz, CH_2), 6.8 (s, 3, OCH_3). Anal. Calcd for TCNE adduct $C_{18}H_{12}N_4FeO_3$: C, 55.68; H, 3.09. Found: C, 55.42; H, 2.97.

Protonation of 18. Preparation of Complex 20. The complex (**18**) (1.04 g, 4 mmol) was taken up in ether (100 mL) and cooled to 0 °C. With a rapid stream of nitrogen bubbling in, tetrafluoboric acid (48% solution, 1 mL) was added. The precipitated solid was filtered and recrystallized from acetone-ether; yield 0.8 g (57%); IR 2080, 2040, and 1700 cm^{-1}; NMR (CD_3NO_2, −10 °C) τ 4.15 (s, 5, Cp), 5.05 (dd, 1, J = 8 and 14 Hz, =CH), 5.54 (d, 1, J = 8 Hz, *cis*-CH_2=), 5.91 (d, 1, J = 14 Hz, *trans*-CH_2=), 7.45 (s, 3, CH_3). Anal. Calcd for $C_{11}H_{11}BF_4FeO_3$: C, 39.53; H, 3.29. Found: C, 39.22; H, 3.41.

Preparation of Optically Active Complex 11. 1,2-Cyclononadiene was prepared from cyclooctene, following the procedure of Skattebøl.[31] Reduction of 5.0 g (41 mmol) of 1,2-cyclononadiene with pinanyldiborane, prepared from (−)-α-pinene (5.45 g, 40 mmol, $[\alpha]^{26}$D −44.6° (*c* 0.26 g/mL heptane)) and sodium borohydride (0.84 g, 22 mmol) in triglyme following the procedure of Moore, Anderson, and Clark,[27b] gave 1.64 g (67%) of 1,2-cyclononadiene, $[\alpha]^{28}$D 22.1° (*c* 0.17 g/mL heptane).

A solution of 1.6 g (13 mmol) of 1,2-cyclononadiene, $[\alpha]^{28}$D 22.1°, in 70 mL of 1,2-dichloroethane, containing 3.2 g (10 mmol) of **2**, was heated to 70 °C for 40 min. The reaction mixture was then added to 300 mL of ether and the resulting yellow solid was collected to give 3.60 g (93%) of **11**, $[\alpha]^{27}$D 26 ± 0.7° (*c* 0.35 g/mL acetone).

This material was heated at 80 °C for 30 min in nitromethane, then recovered by precipitation with ether, $[\alpha]^{27}$D 22 ± 2.0° (*c* 0.27 g/mL acetone).

Decomposition of Cyclononadiene Complex. A suspension of 1.01 g (2.63 mmol) of cyclononadiene complex, prpeared as described above, in 20 mL of THF, was treated with 2.90 mmol of sodium dicarbonylcyclopentadienylferrate in THF solution. The yellow salt dissolved, yielding a red solution. After 5 min, solvent was removed and the residue was extracted with petroleum ether and filtered through a 7-cm silica gel column. Removal of solvent gave 220 mg (69%) of 1,2-cyclononadiene, which was further purified by bulb to bulb distillation and GLC (10% TCEP, 2 m × ⅜ in., 75 °C, 100 ml/min) to give pure diene, $[\alpha]^{26}$D 19.7° (*c* 0.015 g/mL heptane).

Kinetic Measurements. Rate of Interconversion 5 ⇄ 6. Freshly prepared samples of **5**, made by low temperature protonation of the butyne complex **12a**, were taken up in CD_3NO_2. Integrated intensities

of η^5-Cp proton resonances for **5** and **6** were recorded over at least 2 half-lives at temperatures of 35, 40, and 50 °C, at both 60 and 90 MHz. First-order plots showed good linearity throughout. Rates were computed by a weighted linear least-squares program, and activation parameters by a least-squares fitting of the rate data.

Rotational Barriers in Allene Complexes 4, 5, 9 and 10. Rate constants for rotation at the coalescence point (k_c) were determined using the approximate equation $k_c = \pi\Delta\nu/\sqrt{2}$. This equation is strictly applicable for coalescence of an uncoupled AB set, and would therefore hold only for complex **10.** Nevertheless, coupling between geminal protons in complexes **4, 5,** and **9** is likely to be less than 1 Hz, based on the NMR spectra of monosubstituted Fp(olefin) cations[32] and consequently the effect of incorporating coupling constants into the rate equation is likely to be very small. Coupling between protons C(1) and C(3) in complexes **4** and **5** is not averaged on rotation of the ligand about the metal-olefin bond and should therefore not affect the rate calculations. Rate estimations using the approximate equation above have been shown to compare closely with those obtained by complete line shape analysis,[33] and values of $\Delta G^{\ddagger}$ are known to be relatively insensitive to errors in rates.[34] Hence, although the accuracy in the determination of rates may not be high, the values of $\Delta G^{\ddagger}$ and especially the difference between these for the complexes studied are significant.

Coalescence temperatures for the complexes studied were determined at 90 MHz in CD_3NO_2 for **10** and in CD_3COCD_3 for **4, 5,** and **9.** Data for these complexes were as follows (complex, $\Delta\nu$ (Hz), coalescence temp (°C), k_c): **10,** 16, −25 °C, 36; **4,** 63, <−100 °C, >140); **5,** 59, −50 °C, 131; **9,** 63, −38 °C, 140.

No coalescence point was observed for **4,** down to −100 °C, although considerable broadening of methylene absorption was observed at this temperature. The maximum rotational rate at −100 °C is estimated by taking the value of $\Delta\nu$ as equal to that observed in complex **9.**

Fluxional Barrier. The exchange matrices (K) for nondissociative exchange (eq 5 or 6) and for dissociative exchange (eq 4), which were used in computing line shapes in Figure 3, are given below. Proton numbering follows the convention shown in eq 5.

nondissociative exchange

$$\begin{bmatrix} -1 & 0.5 & 0.5 \\ 1 & -1 & 0 \\ 1 & 0 & -1 \end{bmatrix}$$

dissociative exchange

$$\begin{bmatrix} -0.50 & 0.25 & 0.25 \\ 0.50 & -0.75 & 0.25 \\ 0.50 & 0.25 & -0.75 \end{bmatrix}$$

Relative rates of proton exchange for the dissociative and nondissociative mechanisms (k_i^d and k_i^n), based on mean proton lifetimes (τ) taken as independent of mechanism, with $k_{1\to2}^d = k_{1\to3}^d = 1$ are: $k_1^d = 2$, $k_2^d = k_3^d = 3$ and $k_1^n = k_2^n = k_3^n = 4$.

Experimental spectra for complex **10** were matched with computed line shapes calculated by the EXCHSYS program[25] and plotted by a Calcomp plotter. Points (12) covering a temperature range of ±25 °C about the coalescence temperature were used to calculate activation parameters by a linear least-squares program. These were found to be: $\Delta H^{\ddagger}$ 15.7 kcal mol^{-1}, $\Delta S^{\ddagger}$ −1.9 eu, $\Delta G^{\ddagger}$ 16.3 kcal mol^{-1}.

The activation free energy for 1,2-shift in a mixture of **7** and **8,** obtained from an exchange reaction with **2,** was estimated from the coalescence temperature of 75 °C for the methyl resonances. Since these absorptions are multiplets in **7** and **8,** the energy figure given in Table II is of lower accuracy than the activation energies for **5** or **10.**

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References and Notes

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