state **3**. But some issues remain unresolved. The most refined calculations give 1.1 kcal/mol for the process A → **3** → B. This is too large to permit crossing by thermal activation at 4 K. Tunneling through the barrier is a distinct possibility since relatively minor hydrogen motions are required. The magnetic inequivalence of the protons in C_{2v} CH_4^+ is about 100 G. Averaging this inequivalence by tunneling would require a rate of penetration of the barrier of at least 3×10^8 s^{-1}. The calculations on $CH_2D_2^+$ impose an upper limit on this frequency of $ZPE(CH_1H_1D_sD_s^+) - ZPE(CH_1H_sD_1D_s^+) \sim 3 \times 10^{12}$ s^{-1}. These limits do not seem unreasonable in view of the barrier height and the known tunneling frequencies associated with other weakly hindered motions (e.g., ~ 500 MHz for methyl rotors).[16] Variable-temperature studies of the EPR spectra of CH_4^+ and CD_4^+ may reveal changes in the relative intensities of different hyperfine components which could be used to measure the splitting of the ground vibronic level due to tunneling. We also urge similar studies of $CH_2D_2^+$ and other deuterated derivatives to search for other, less stable, isomers and the onset of dynamic behavior.

Acknowledgment. We thank Dr. L. B. Knight, Jr., for stimulating our interest in this problem. We are grateful to the National Science Foundation for financial support of this work through research grants CHE-8402996 and CHE-8213329 and to David C. Spellmeyer and Frank K. Brown for assistance with graphics.

Registry No. CH_4^+, 20741-88-2; $CH_2D_2^+$, 61105-67-7; CD_4^+, 34510-07-1.

(16) Clough, S.; Poldy, F. *J. Phys.* **1973**, *C6*, 1953.

Interconversion of μ-Alkylidyne and μ-Alkenyl Diiron Complexes

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Abstract: The μ-pentylidyne complex $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)_2(\mu\text{-}CCH_2CH_2CH_2CH_3)]^+PF_6^-$ (**3**) rearranged to the μ-pentenyl complex $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHCH_2CH_2CH_3)]^+PF_6^-$ (**4**) upon heating at 88 °C in the solid state or in solution. The rate constant for the rearrangement of **3** to **4** in CD_2Cl_2 solution at 88 °C is $2.9 \pm 0.5 \times 10^{-4}$ s^{-1} ($\Delta G^\ddagger = 27.1 \pm 0.2$ kcal mol^{-1}). Ethylidyne complex $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CCH_3)]^+PF_6^-$ (**10**) gave no detectable isomerization to $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CH_2)]^+PF_6^-$ (**11**) upon heating at 88 °C for 100 h; at this point, 50% decomposition had occurred ($\Delta G^\ddagger \geq 31$ kcal mol^{-1}). The cyclohexyl substituted carbyne complex $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}C\overline{CHCH_2CH_2CH_2CH_2CH_2}\,)]^+PF_6^-$ (**12**) is in rapid equilibrium with the μ-alkenyl complex $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}\overline{CCH_2CH_2CH_2CH_2CH_2}\,)]^+PF_6^-$ (**13**) at ambient temperature ($\Delta G^\ddagger = 19.9 \pm 0.2$ kcal mol^{-1} at −13 °C). The rate of rearrangement of alkylidyne complexes to μ-alkenyl complexes is dramatically accelerated by alkyl substituents on the β carbon of the alkylidyne group. The μ-alkenyl complexes **4** and **13** exhibit a fluxional process which gives rise to a single coalesced cyclopentadienyl resonance at ambient temperature in the ^1H NMR. The barrier for the fluxional process for **4** is 12.9 kcal mol^{-1} and that for **13** is 9.8 kcal mol^{-1} as determined from ^1H NMR coalescence studies. Complex **11** exhibits two resonances for the cyclopentadienyl groups at 27 °C ($\Delta G^\ddagger \geq 14.7$ mol^{-1}). The rates of the fluxional process of the μ-alkenyl complexes and of the rearrangement of μ-alkylidyne complexes are both increased by β-alkyl substitution and indicate increased positive charge at the β-carbon in the transition states for the respective processes.

The diiron methylidyne complex $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CH)]^+PF_6^-$ (**1**) prepared by hydride abstraction from $(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ (**2**)[1] with $(C_6H_5)_3C^+PF_6^-$ is the first compound in which a C–H unit bridges two metal centers.[2] Although **1** can be stored indefinitely (>6 months) in the solid state at −30 °C, it is extremely reactive toward nucleophiles in solution. For example, alcohols, amines, and CO add to the methylidyne carbon of **1** to form isolable 1:1 adducts.[3] Alkenes such as 1-butene react rapidly with **1** at −50 °C in CH_2Cl_2 to produce μ-alkylidyne complexes such as the μ-pentylidyne complex $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}C(CH_2)_3CH_3)]^+PF_6^-$ (**3**); this hydrocarbation reaction proceeds by a regioselective addition of the μ-C—H bond across the C≡C bond.[4] Alkylidyne complex **3** can also be prepared by reaction of $(C_5H_5)_2(CO)_4Fe_2$ with *n*-BuLi followed by acidification with HPF_6.[5] We recently reported that alkylidyne complexes such as **3** rearrange to bridging alkenyl complexes upon heating.[6] The nonequivalent cyclopentadienyl groups of the bridging alkenyl complexes give rise to two separate resonances at low temperature, but a fluxional process interconverts their environment and leads to a single coalesced resonance at ambient temperature. Here we report that the degree of substitution on the β-carbon of the bridging hydrocarbon group has a large effect both on the rate of rearrangement of alkylidyne complexes to bridging alkenyl complexes and on the rate of fluxionality of the bridging alkenyl complexes.

Results

Rearrangement of μ-Alkylidyne to μ-Alkenyl Complexes. When a dilute CD_2Cl_2 solution of pentylidyne complex **3** was heated at 88 °C in a sealed NMR tube for 3.5 h, complete conversion to the bridging alkenyl complex, $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}$

(1) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134.

(2) Subsequently several other μ-methylidyne complexes have been prepared, for example: (a) $\{[(C_5H_5)_2Ru(\mu\text{-dppm})(\mu\text{-}CO)(\mu\text{-}CH)\}^+BF_4^-$ (Davies, D. L.; Gracey, B. P.; Guerchais, V.; Knox, S. A. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1984**, 841); (b) $\{(C_5(CH_3)_5)(CO)FeFe(C_5H_5)(CO)(\mu\text{-}CO)(\mu\text{-}CH)\}^+PF_6^-$ (Miles, W. H. Ph.D. Dissertation, University of Wisconsin—Madison, 1984); and (c) $\{(C_5H_5)_2(NO)_2Fe_2(\mu\text{-}CH)\}^+PF_6^-$ (Casey, C. P.; Roddick, D. M. unpublished results).

(3) Casey, C. P.; Fagan, P. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7360.

(4) Casey, C. P.; Fagan, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4950.

(5) Nitay, M.; Priester, W.; Rosenblum, M. *J. Am. Chem. Soc.* **1978**, *100*, 3620.

(6) Casey, C. P.; Marder, S. R.; Fagan, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 7197.

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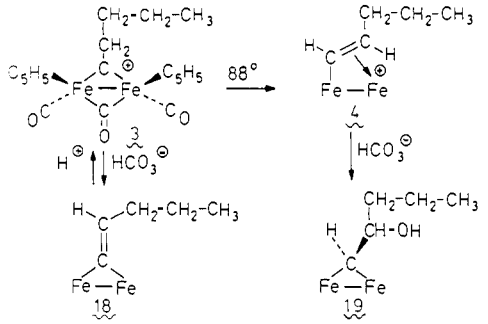
η^1,η^2-(*E*)-CH=CHCH$_2$CH$_2$CH$_3$)]$^+$PF$_6^-$ (**4**), was observed. The rearrangement of **3** to **4** was more conveniently carried out by heating solid **3** at 88 °C for 29 h under N_2, which led to the isolation of **4** in 89% yield (≥98% conversion) after recrystallization.

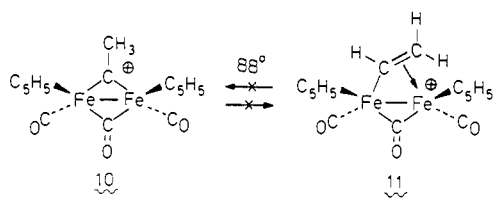
The structure of complex **4** was spectroscopically deduced. In the low-temperature ^{1}H NMR spectrum of **4**, singlets at δ 5.83 and 5.62 are assigned to nonequivalent cyclopentadienyl groups, a doublet (J = 11.8 Hz) at δ 12.06 is assigned to the proton on the α-vinyl carbon, a multiplet at δ 3.62 is assigned to the proton of the β-vinyl carbon, and multiplets at δ 2.27, 1.63, and 1.00 are assigned to the $-CH_2CH_2CH_3$ group. In the low-temperature $^{13}C\{^1H\}$ NMR of **4**, two cyclopentadienyl resonances are seen at δ 92.6 and 89.8 and resonances due to the α- and β-vinyl carbons are observed at δ 175.4 and 96.7. In the ambient-temperature ^{1}H NMR spectrum of **4**, the cyclopentadienyl resonances appear as a coalesced singlet at δ 5.67. Similar ^{1}H and ^{13}C chemical shifts for the μ-vinyl group of [(C_5H_5(CO)Fe)$_2$(μ-CO)(μ-η^1,η^2-CH=CH_2)]$^+$BF$_4^-$ (**5**) were reported by Pettit and Dyke.[7,8]

The conversion of μ-alkylidyne complexes with one alkyl substituent on C_β to μ-alkenyl complexes is rather general. Thus, [(C_5H_5)$_2$(CO)$_2$Fe$_2$(μ-CO)(μ-CCH_2CH_3)]$^+$PF$_6^-$ (**6**) is cleanly converted to [(C_5H_5)$_2$(CO)$_2$Fe$_2$(μ-CO)(μ-η^1,η^2-(*E*)-CH=$CHCH_3$)]$^+$PF$_6^-$ (**7**) upon heating at 88 °C for 30 h and [(C_5H_5)$_2$(CO)$_2$Fe$_2$(μ-CO)(μ-C(CH_2)$_4CH_3$)]$^+$PF$_6^-$ (**8**) rearranges to [(C_5H_5)$_2$(CO)$_2$Fe$_2$(μ-CO)(μ-η^1,η^2-(*E*)-CH=CH-(CH_2)$_3CH_3$)]$^+$PF$_6^-$ (**9**) under similar conditions.

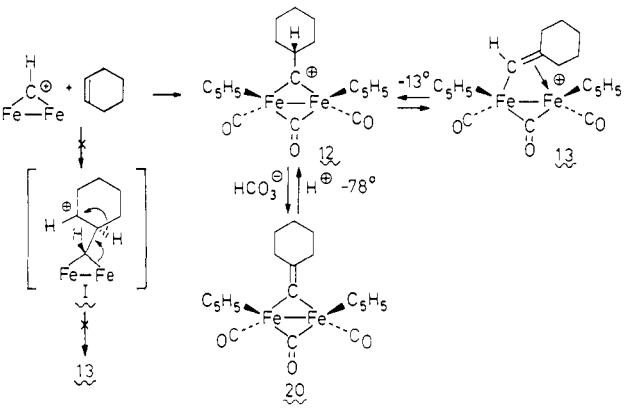


In dilute CD_2Cl_2 solution, the rearrangement of **3** to **4** at 88.0 ± 0.1 °C proceeds with a first-order rate constant of 2.9 ± 0.5 × 10^{-4} s^{-1} which corresponds to $\Delta G^{\ddagger}_{361K}$ = 27.1 ± 0.2 kcal mol^{-1}.

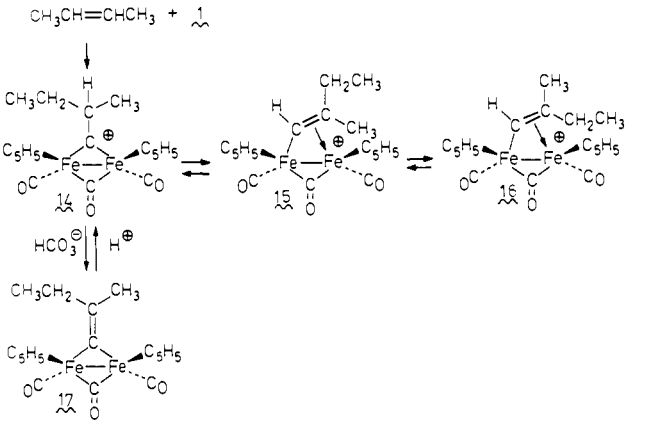
To further define the scope of this unprecedented rearrangement reaction, the ethylidyne complex [(C_5H_5)$_2$(CO)$_2$Fe$_2$(μ-CO)(μ-CCH_3)]$^+$PF$_6^-$ (**10**)[5,7] was heated in CD_2Cl_2 solution at 88 °C. After 100 h, no detectable isomerization to [(C_5H_5)$_2$(CO)$_2$Fe$_2$-(μ-CO)(μ-η^1,η^2-CH=CH_2)]$^+$PF$_6^-$ (**11**)[7,8] was observed (≤5%); however, 50% decomposition had occurred. The potential rearrangement product **11** was independently synthesized and heated at 88 °C in CD_2Cl_2. After 20 h, no ethylidyne complex **10** was observed but 80% decomposition of **9** had occurred. Thus the rate of interconversion of **10** and **11** must be very slow at 88 °C. Apparently, an alkyl group on the β-carbon of the alkylidyne complex can greatly accelerate the rate of rearrangement to the corresponding μ-alkenyl complex. From the observation that only 50% of **10** was destroyed after 100 h, a lower limit for $\Delta G^{\ddagger}$ for the conversion of **10** to **11** was calculated to be ≥31.0 kcal mol^{-1}.



The reaction of 1,2-disubstituted alkenes with methylidyne complex **1** gave mixtures of hydrocarbation products and μ-alkenyl rearrangement products. For example, reaction of **1** with cyclohexene gives alkylidyne product **12** and μ-alkenyl product **13**. Initially we considered the possibility that these products might have arisen from two competing pathways. The alkylidyne complex **12** could have arisen from hydrocarbation. The μ-alkenyl complex **13** could have arisen from initial electrophilic addition of **1** to cyclohexene to produce the intermediate carbocation I, which subsequently underwent a 1,2-hydrogen migration to give **13**.[9]



A related phenomenon was seen in the reaction of **1** with either *cis*- or *trans*-2-butene which led to mixtures of hydrocarbation product **14** and two isomeric μ-alkenyl products **15** and **16** which are the result of hydrogen migrations.[9] These results can also be explained in terms of two competing reactions. However, the observation that both *cis*- and *trans*-2-butene gave the same 2.3:1.0:1.5 ratio of products **14**:**15**:**16** was not readily understood in terms of this mechanism. We have now discovered that alkylidyne complex **14** and μ-alkenyl rearrangement products **15** and **16** rapidly equilibrate at room temperature. Consequently, the observed products could be the result of initial hydrocarbation or electrophilic addition followed by equilibration. In light of the rearrangement of pentylidyne complex **3** to bridging alkenyl complex **4**, we heated the mixture of alkylidyne **14** and μ-alkenyl complexes **15** and **16**, obtained from the reaction of **1** with *cis*-2-butene, at 88 °C in the hope of converting all the material to μ-alkenyl complexes. However, the ratio of complexes **14**:**15**:**16** was not altered upon heating at 88 °C for 20 h. Similarly, the ratio of products from the reaction of **1** with cyclohexene remained unchanged after heating at 88 °C for 27 h. These results are readily explained by the rapid room-temperature equilibration of the alkylidyne and bridging alkenyl complexes which was established as outlined below.



(7) Kao, S. C.; Lu, P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911.
(8) Dyke, A. F.; Knox, S. A. R.; Morris, M. J.; Naish, P. J. *J. Chem. Soc, Dalton. Trans* **1983**, 1417.

(9) Products arising from electrophilic addition of **1** to alkenes followed by carbocation rearrangement have been observed in several cases. For example, the reaction of **1** with *trans*-stilbene leads to the μ-alkenyl complex [(C_5H_5)$_2$(CO)$_2$Fe$_2$(μ-CO)(μ-η^1,η^2-(*E*)-CH=CHCH(C_6H_5)$_2$)]$^+$PF$_6^-$ which is formed by initial electrophilic addition following by a 1–2 phenyl migration. Casey, C. P.; Fagan, P. J.; Miles, W. H.; Marder, S. R. *J. Mol. Catal.* **1983**, *21*, 173.

We next attempted to remove the cationic μ-carbyne complex **14** from the reaction mixture by conversion to the neutral bridging alkenylidene complex **17** from which the cationic μ-alkenyl complexes **15** and **16** would be more easily separable. This appeared feasible since we had shown that the bridging pentylidyne complex **3** was rapidly deprotonated by aqueous bicarbonate treatment to give the bridging pent-1-enylidene complex **18** in 87% yield.[10] In contrast, the μ-pentenyl complex **4** reacts only slowly with aqueous bicarbonate over 16 h to give the neutral bridging β-hydroxy alkylidene complex **19** in 47% yield.

However, when a 2.3:1.0:1.5 mixture of **14**:**15**:**16** was treated with aqueous bicarbonate, a rapid reaction occurred to convert *all* three compounds into the same bridging alkenylidene complex **17**. This result can be explained by rapid equilibration of the carbyne and bridging alkenyl complexes and deprotonation of the carbyne complex **14** to bridging alkenylidene complex **17**. When the mixture of products from reaction of cyclohexene with μ-methylidyne complex **1** was treated with aqueous bicarbonate, the entire reaction mixture was converted to alkenylidene complex **20**. Similarly a mixture of $[(C_5H_5)_2(CO)_2Fe(\mu\text{-}CCHCH_2CH_2CH_2CH_2)]^+PF_6^-$ (**21**) and $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CCH_2CH_2CH_2CH_2)]^+PF_6^-$ (**22**), obtained from the reaction of **1** with cyclopentene, can be converted to the alkenylidene complex $(C_5H_5)_2Fe_2(\mu\text{-}CO)(\mu\text{-}C{=}CCH_2CH_2CH_2CH_2)$ (**23**) by treatment with aqueous HCO_3^-.

Since Pettit[7] and Stone[11] have shown that protonation of bridging alkenylidene complexes leads to the formation of bridging alkylidyne complexes, we studied the protonation of the bridging alkenylidene complexes obtained above. Reprotonation of **17** gave the same mixture of **14**:**15**:**16** as obtained from reaction of **1** with *cis*- or *trans*-2-butene in 47% yield. This result provides further evidence for the rapid equilibration of these complexes.

When a sample of the bridging alkenylidene complex in the cyclohexyl series, **20**, was protonated with $H{-}O(CH_2CH_3)_2^+BF_4^-$ at −78 °C, only the bridging alkylidyne complex **12** was observed by ^1H NMR at 203 K. Upon warming to 260 K, slow formation of an equilibrium mixture of **12** and the bridging alkenyl complex **13** was observed. By monitoring the resonances for the cyclopentadienyl peaks of **12** and **13** over time at 260 K a first-order rate constant for the conversion of **12** to **13** was determined to be $1.0 \pm 0.4 \times 10^{-4}$ s^{-1}, which corresponds to a $\Delta G^{\ddagger}_{260K} = 19.9 \pm 0.3$ kcal mol^{-1}.

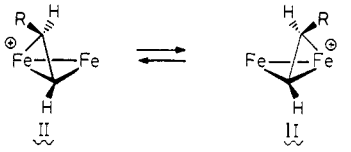
Further evidence for a rapid equilibrium between **12** and **13** was obtained from a saturation transfer experiment.[12] The isomerization of **12** to **13** interconverts H_β of **12** (δ 5.22) with H_α of **13** (δ 11.96). Saturation of the δ 5.22 resonance for 20 s at 315 K followed by an observation pulse resulted in a 60% decrease in the integrated intensity of the δ 11.96 resonance. By varying the length of the saturation pulse prior to the observation pulse, the rate of saturation transfer was determined. The first-order rate constant for the conversion of **12** to **13** was found to be 0.61 ± 0.1 s^{-1}; this corresponds to $\Delta G^{\ddagger}_{315K} = 18.8 \pm 0.1$ kcal mol^{-1}. Having established that alkylidyne complexes and μ-alkenyl complexes resulting from the reaction of **1** with 1,2-disubstituted alkenes were equilibrating at ambient temperature, we next sought to determine the kinetic product of the reaction. Both deuterium-labeling studies and direct low-temperature observation indicate that the kinetic products of the reaction of **1** with 1,2-disubstituted alkenes are alkylidyne complexes.[13]

Mechanism of Rearrangement of Alkylidyne Complexes to μ-Alkenyl Complexes. To determine exactly which hydrogen atoms actually migrate in the net 1,2-hydrogen migration that accompanies the conversion of μ-alkylidyne complexes to μ-alkenyl complexes, the rearrangement of $\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCD_2CH_2CH_2CH_3)\}^+CF_3SO_3^-$ (**3-*d*$_2$**) was studied. Complex **3-*d*$_2$** was prepared by deuterium exchange of pentenylidene complex **18** with CF_3CO_2D–D_2O (which gave **18-*d*$_1$**), followed by reaction with CF_3SO_3D.

Rearrangement of **3-*d*$_2$** gave $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CD{=}CDCH_2CH_2CH_3)]^+CF_3SO_3^-$ (**4-*d*$_2$**), in which >95% of the deuterium was located in the vinylic sites as established by ^2H NMR. This indicates that the net 1,2-hydride shift involves only the protons of the β-carbon of **3**.

In an attempt to determine whether the rearrangement of μ-alkylidyne complexes to μ-alkenyl complexes was intra- or intermolecular, a crossover experiment was performed in which a mixture of $\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}^{13}C\text{-}CD_2(CH_2)_3CH_3]\}^+PF_6^-$ (**8-^{13}*C*-*d*$_2$**) and unlabeled μ-hexylidyne complex **8** was heated in solution. The resulting μ-hexenyl complex **9** was shown by ^1H NMR to contain a 1:1 ratio of μ-^{13}CH=C (δ 12.05, d, $J_{^{13}CH}$ = 162 Hz) and μ-^{12}CH=C (δ 12.06, br s) groups. However, we now know that μ-alkylidyne complexes are quite acidic,[14] and we believe that the starting materials **8-^{13}*C*-*d*$_2$** and **8** scrambled deuterium label prior to thermolysis.

Fluxionality of μ-Alkenyl Complexes. In the low-temperature ^1H NMR spectra of $\{[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHR)\}^+$ complexes, the nonequivalent cyclopentadienyl groups give rise to two resonances. Upon warming, the two peaks coalesce to a single averaged cyclopentadienyl resonance as first shown by Knox.[8] The fluxional process that exchanges the environment of the cyclopentadienyl groups involves movement of the β-carbon from one iron center to the other. During this process, C_α is always bonded to both iron centers while C_β is bonded to only a single iron center. A convenient way of describing the μ-alkenyl system is in terms of the 1,2-diiron bicyclobutane structure II.



This formulation helps to explain the similarity of ^{13}C NMR chemical shifts for C_α (δ 175.4) in the bridging alkenyl complex **4** and for C_α (δ 172) in the bridging alkylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (**24**). This formulation also explains the similar μ-C–Fe distances (both 1.980 (8) Å) seen for μ-alkenyl complex **5** and the μ-C–Fe distances (both 1.986 (3) Å) seen for μ-alkylidene, **24**.[15] We decided to see if alkyl substituents on the β-carbon of the μ-alkenyl group would accelerate the rate of the fluxional process.

Knox has reported that the unsubstituted vinyl complex **5** has two cyclopentadienyl resonances in the ^1H NMR even at 50 °C.[8] For the monosubstituted μ-alkenyl complexes **4** (μ-CH=$CHCH_2CH_2CH_3$) and **7** (μ-CH=$CHCH_3$) coalescence of the cyclopentadienyl resonances occurred at about −8 °C which corresponds to $\Delta G^{\ddagger}$ of 12.9 ± 0.2 kcal mol^{-1} (see Experimental Section). For the disubstituted complex **13**, coalescence of the cyclopentadienyl resonances occurred at about −63 °C which corresponds to $\Delta G^{\ddagger}$ of 9.8 ± 0.2 kcal mol^{-1}. At −63 °C, interconversion of μ-alkenyl complex **13** and the related μ-alkylidyne complex **12** is very slow and does not greatly interfere with the observation of the fluxional process.

To further probe electronic effects on the fluxional process, $\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CH\text{-}C_6H_4\text{-}p\text{-}CH_3)\}^+PF_6^-$ (**25**) was examined. Conjugate addition of *p*-tolyllithium to the β-carbon of μ-vinyl complex **11** gave $\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_2C_6H_4\text{-}p\text{-}CH_3)\}$ (**26**). β-Hydride abstraction from **26** occurred upon treatment with $(C_6H_5)_3C^+PF_6^-$ to produce **25**. The cyclopentadienyl resonances of **25** coalesce

(10) Similarly, the hexylidyne complex **8** generated in situ from the reaction of **1** with 1-pentene can be deprotonated to give the hex-1-enylidene complex $(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_2CH_2CH_2CH_3)$ in 75% yield (based on **1**). Casey, C. P.; Marder, S. R., unpublished results.

(11) Dawkins, G. M.; Green, M.; Jeffery, J. C.; Sambale, C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 499.

(12) Martin, M. L.; Delpuch, J. J.; Martin, G. J. "Practical NMR Spectroscopy"; Heyden: London, **1980**; pp 315–322.

(13) Casey, C. P.; Meszaros, M. W.; Marder, S. R.; Fagan, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 3680.

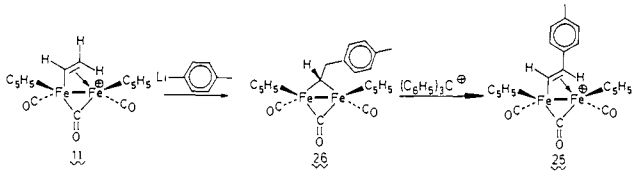
(14) Complex **3**, for example, is approximately as acidic as CF_3COOH: Casey, C. P.; Austin, E. A., unpublished observations.

(15) Orpen, A. G. *J. Chem. Soc., Dalton. Trans.* **1983**, 1427.

Table I. $\Delta G^{\ddagger}$ for Rearrangement of Alkylidyne Complexes to μ-Alkenyl Complexes and for the Fluxional Process of μ-Alkenyl Complexes

alkylidyne	μ-Alkenyl	$\Delta G^{\ddagger}$ rearrangement (kcal mol^{-1})	$\Delta G^{\ddagger}$ fluxionality (kcal mol^{-1})
10	**11** (μ-CH=CH_2)	>31.0	>14.7
3	**4** (μ-CH=$CHCH_2CH_2CH_3$)	27.1	12.9
12	**13** (μ-CH=$CCH_2CH_2CH_2CH_2CH_2$)	19.9	9.8
	25 (μ-CH=CHC_6H_4-*p*-CH_3)		10.1

at −55 °C which corresponds to $\Delta G^{\ddagger}$ of 10.1 ± 0.2 kcal mol^{-1}. Thus, a *p*-tolyl group lowers the barrier of the fluxional process more than a single β-alkyl substituent but less than two β-alkyl substituents.[16]



Both *E* and *Z* isomers of the μ-CH=$C(CH_3)CH_2CH_3$ complex **15** and **16**, are obtained in the reaction of methylidyne complex **1** with 2-butene. At room temperature, the cyclopentadienyl resonances of **15** and **16** are coalesced and give rise to resonances at δ 5.59 and 5.61 for the two isomers. While the fluxional process is fast, the interconversion of **15** and **16** is slow on the NMR time scale as evidenced by sharp resonances for each complex. A barrier of at least 17 kcal mol^{-1} for *E* to *Z* isomerization around the carbon–carbon double bond is required by these observations.

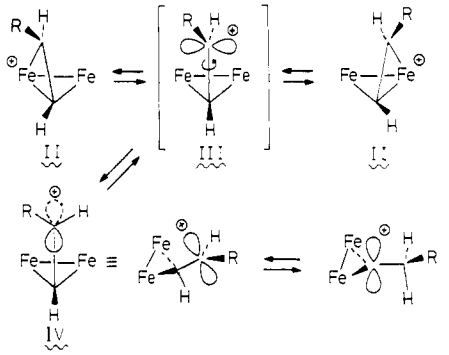
Discussion

The results presented here indicate that the rate of both the rearrangement of alkylidyne complexes to μ-alkenyl complexes and the fluxionality of μ-alkenyl complexes is strongly dependent on the degree of alkyl substitution at the β-carbon of the bridging group (see Table I). These trends suggest a buildup of positive charge on the β-carbon in the transition state for both processes. Each added alkyl group lowers the barrier for μ-alkylidyne to μ-alkenyl rearrangement by about 7 kcal per β-alkyl substituent. The overall barrier for μ-alkenyl fluxionality is smaller than for the rearrangement reaction and the sensitivity to β-alkyl substitution is also reduced to about 3 kcal per alkyl group. The lower sensitivity to β-alkyl substitution indicates that there is less buildup of positive change in the transition state for the fluxional process than in the rearrangement process.

The β-alkyl rate dependencies will be discussed in terms of the structures depicted in Scheme I. In the static structure of a bridging alkenyl complex, the β-carbon interacts with a single iron atom. During the fluxional process, C_β moves away from one iron until symmetric transition state III is reached in which C_β interacts weakly with both iron atoms. In this transition state which has a p orbital at C_β parallel to the iron–iron bond, positive charge is somewhat localized at C_β due to its weakened interactions with the iron centers. Transition-state III appears to be quite similar to the most stable conformation of the cyclopropylcarbinyl cation and thus may be further stabilized by interaction of the empty p orbital on C_β with the two Fe–C_α bonds. Overall, the β-carbon in transition-state III is more electron deficient than in the μ-alkenyl complex and its formation can be assisted by electron-donating carbon substituents on the β-carbon.

The hydrogen migration step in the rearrangement of μ-alkylidyne to μ-alkenyl complexes has very different geometrical requirements. The C–H bond on the β-carbon of the μ-alkylidyne complex must be parallel to the empty p orbital at the alkylidyne carbon for maximum overlap during hydrogen migration. As the hydrogen migration proceeds, an empty p orbital develops at the

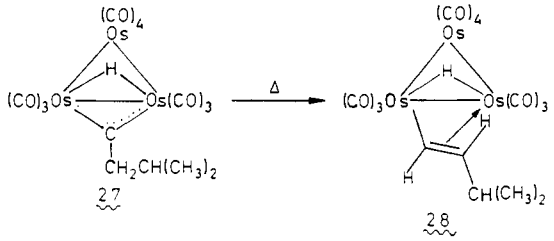
Scheme I



β-carbon in IV. In this nascent geometry, the empty p orbital at the β-carbon has little interaction with the iron centers and no interaction with the FeC_α σ bonds. IV and III are conformers of the same cation and are related by a 90° rotation. However, the electron-deficient β-carbon of III is substantially stabilized relative to IV both by weak interaction with the two iron centers and by interaction with the Fe–C_α σ bonds. Since IV is a less stable structure than III, it should be more difficult to form. This is largely responsible for the greater activation energy seen for rearrangement of μ-alkylidyne complexes than for the fluxional behavior of μ-alkenyl complexes. Since the β-carbon in IV is more electron deficient than in III, electron-donating β-alkyl groups stabilize it to a greater extent than in III. This explains the greater sensitivity to β-alkyl substitution seen in the rearrangement of μ-alkylidyne complexes. Larger substituent effects are normally seen for reactions involving less stable cationic centers which make greater demands on electron-donating substituents.[17]

Silvestre and Hoffmann have carried out extended Hückel molecular orbital (EHMO) calculations on the rearrangement of alkylidyne complexes to μ-alkenyl complexes.[18] These calculations suggest that the transition state for rearrangement involves a bridging hydrogen and that as one continues along the reaction coordinate to IV substantial positive charge becomes localized on C_β.

While our discovery of the rearrangement of μ-alkylidyne to μ-alkenyl complexes was unprecedented, we believe that this process is facile and that many additional examples will be found. Green recently reported that the neutral μ_2-alkylidyne complex **27** is converted to the μ-η^1,η^2-alkenyl complex **28** upon heating.[19]



Somerjai has shown that the stable surface species formed from the chemisorption of ethylene on the Pt(111) surface is a triply bridged ethylidyne. The mechanism which was proposed involves conversion of a vinyl to a vinylidene which could then react with chemisorbed hydrogen to give a surface ethylidyne.[20] The work described here raises the possibility of a direct vinyl to ethylidyne interconversion. In fact, Knox has observed the isomerization of the μ-η^1,η^2-vinyl complex **29** to the μ_3-ethylidyne complex **30**.[21]

Mononuclear and dinuclear organometallic compounds display related chemistry in many cases. Here the μ-alkylidyne to μ-alkenyl diiron rearrangements are analogous to the conversion

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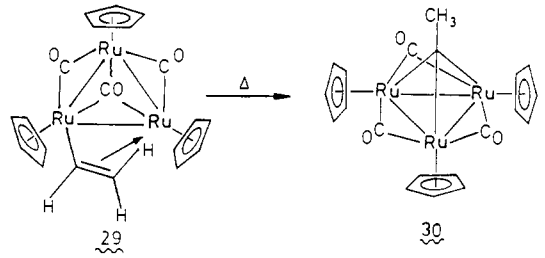

29 30

of mononuclear carbene complexes such as $[C_5H_5(CO)_2Fe{=}C(CH_3)_2]^+$ to alkene complexes.[22] For mononuclear systems, the alkene complex is usually the thermodynamically favored material. In the dinuclear cases reported here, the μ-alkylidyne and μ-alkenyl complexes are of such similar thermodynamic stability that the position of equilibrium can be shifted by β-alkyl substituents. For example, the μ-alkylidyne complex **12** is favored over μ-alkenyl complex **13** by a 1.4:1 ratio at equilibrium. For mononuclear systems, the first case of the conversion of an alkene complex to a carbene complex was recently reported by Cooper: $[W(\eta\text{-}C_5H_5)_2(C_2H_4)H]^+$ in the presence of I_2 forms $[W(\eta\text{-}C_5H_5)_2(CHCH_3)I]^+$.[23]

Experimental Section

General. ^1H NMR spectra were recorded on a Bruker WP200, WP270, or WH270 spectrometer. ^{13}C NMR were recorded on a JEOL FX 200 spectrometer operating at 50.10 MHz; all samples were prepared with 0.07 M $Cr(acac)_3$. CD_2Cl_2 was dried over P_2O_5; acetone-d_6 was dried over molecular sieves or B_2O_3; CD_3NO_2 was dried over P_2O_5; benzene-d_6 was distilled from purple solutions of sodium and benzophenone. NMR samples were prepared and sealed on a vacuum line and centrifuged prior to analysis. IR spectra were recorded on a Beckman 4230 infrared spectrometer calibrated with polystyrene film. Mass spectra were obtained on an AEI-MS-902 or a KRATOS MS-80 mass spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Labs. Air-sensitive compounds were handled with use of standard Schlenk procedures and glovebox manipulations. Diethyl ether, THF, and hexane were distilled from purple solutions of sodium and benzophenone. CH_2Cl_2 was distilled from CaH_2.

$[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHCH_2CH_2CH_3)]^+PF_6^-$ (4). **3**[24] (5.07 g, 9.39 mmol) was heated at 88 °C for 29 h in a clamped ball and socket vial. The resulting brown crystalline material was dissolved in acetone, filtered, and precipitated by addition of diethyl ether to give brown microcrystalline **4** (4.56 g, 90%). ^1H NMR (270 MHz, acetone-d_6 231 K) δ 12.06 (d, J = 11.8 Hz, FeHC=C), 5.83, 5.71 (C_5H_5), 3.62 (m, CC*H*CH_2), 2.27 (m, CH*C*H_2CH_2), 1.63 (m, CH_2CH_3), 1.00 (t, J = 7.4 Hz, CH_3); $^{13}C\{^1H\}$ NMR (acetone-d_6, 233 K) δ 243.4 (μ-CO), 214.6, 208.4 (CO), 175.4 (*C*H=CHCH$_2$), 96.7 (CH=*C*HCH$_2$), 92.6, 89.8 (C_5H_5), 43.4 (CH*C*H$_2$CH$_2$), 24.4 (*C*H$_2$CH$_3$), 13.9 (CH_3); IR (Nujol mull) 2014 (s), 1996 (s), 1875 (s) cm^{-1}.

Anal. Calcd for $C_{18}H_{19}F_6Fe_2O_3P$: C, 40.04, H, 3.55. Found: C, 39.78; H, 3.63.

$[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CH\text{-}CH_3)]^+PF_6^-$ (7). Solid $[(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_3)]^+PF_6^-$[24] (**6**) (0.63 g 1.2 mmol) was heated at 88 °C for 30 h. Recrystallization from acetone–ether gave **7** (0.53 g, 84%, >96% conversion). ^1H NMR (270 MHz acetone-d_6, 231 K) δ 11.99 (d, J = 11.0 Hz, FeC*H*=CHCH$_3$), 5.81, 5.61 (C_5H_5), 3.85 (m, CH=C*H*CH$_3$), 1.73 (d, J = 8.1 Hz, CH_3); $^{13}C\{^1H\}$ NMR (acetone-d_6, 229 K) δ 243.7 (μ-CO), 214.6, 208.4 (CO), 177.0 (*C*H=CHCH$_3$), 93.2 (CH=*C*HCH$_3$), 92.5, 89.9 (C_5H_5), 26.9 (CH_3); IR (Nujol mull) 2040 (s), 2005 (s), 1845 (s) cm^{-1}.

Anal. Calcd for $C_{16}H_{15}F_6Fe_2O_3P$: C, 37.54; H, 2.95. Found: C, 37.39, H, 2.75.

$[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CH(CH_2)_3CH_3)]^+PF_6^-$ (9). Solid **8**[24] (100 mg, 0.18 mmol) was heated at 88 °C for 32 h to directly give analytically pure **9** (95 mg, 95%, ≥95% conversion). ^1H NMR (270 MHz acetone-d_6) δ 12.07 (d, J = 9.3 Hz, FeC*H*=C), 5.67 (s, C_5H_5), 3.65 (m, FeCH=C*H*), 2.34 (m, CHC*H*$_2$), 1.66–1.50 (m, C*H*$_2$CH$_2$CH$_3$), 0.96 (t, J = 7.1 Hz, CH_3); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 212 (CO), 175.8 (FeCH), 99.3 (CH=C*H*CH$_2$), 91.4 (C_5H_5), 41.2 (=CH*C*H$_2$), 31.1 (CH$_2$*C*H$_2$CH$_2$), 23.3 (*C*H$_2$CH$_3$), 14.2 (CH_3), μ-CO not observed; IR (CH_2Cl_2) 2027 (s), 2001 (m), 1864 (m) cm^{-1}.

Anal. Calcd for $C_{19}H_{21}F_6Fe_2O_3P$: C, 41.19; H, 3.82. Found: C, 40.92; H, 3.89.

Solution Rate for the Conversion of 3 to 4. A dilute CD_2Cl_2 solution of **3** was heated at 88 ± 0.1 °C in a sealed NMR tube. The reaction was periodically monitored by cooling the tube to −78 °C and then obtaining a ^1H NMR at −50 °C.

The extent of reaction was determined by following the disappearance of the Cp resonance of **3** and the appearance of the Cp resonances arising from **4**. The first-order rate constant for conversion of **3** to **4** was calculated to be 2.9 ± 0.5 × 10^{-4} s^{-1} which corresponds to $\Delta G^{\ddagger}_{361K}$ = 27.1 ± 0.2 kcal mol^{-1}.

$(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CHCH_2C_6H_4\text{-}p\text{-}CH_3)$ (26). p-$CH_3C_6H_4Li$ (2.00 mL, 0.98 M in ether, 1.96 mmol) was added to a mixture of **11**[7] (650 mg, 1.3 mmol) and $CuIP(C_4H_9)_3$ (50 mg, 0.12 mmol) in 140 mL of CH_2Cl_2 at −78 °C. The mixture was stirred for 1.5 h at −78 °C and 2 h at ambient temperature. Solvent was evaporated under vacuum, and the residue was extracted with 30 mL of ether. The ether extract was passed through a short plug of activity I alumina (45 × 45 mm). The plug was washed with an additional 50 mL of ether. The combined ether fractions were concentrated to 15 mL and 100 mL hexane was added. The solution was concentrated to 40 mL and cooled to −78 °C to give red-orange crystalline **26** (270 mg, 47%). ^1H NMR (270 MHz, acetone-d_6) δ 11.76 (t, J = 8.3 Hz, CH), 7.42 (d, J = 8 Hz, 2 H), 7.23 (d, J = 8 Hz, 2 H), 4.69 (s, C_5H_5), 4.28 (d, J = 8.7 Hz, CH_2), 2.35 (s, CH_3); $^{13}C\{^1H\}$ NMR (acetone-d_6), δ 272.6 (μ-CO), 214.6 (CO), 179.3 (μ-CH), 145.0, 135.4 (ipso, para), 129.7, 129.2 (ortho, meta), 88.4 (C_5H_5), 61.9 (CH_2), 21.2 (CH_3); IR (CH_2Cl_2) 1975 (s), 1935 (m), 1776 (m) cm^{-1}. HRMS calcd for $C_{22}H_{20}Fe_2O_3$ 444.0105, found 444.0111.

$[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHC_6H_4\text{-}p\text{-}CH_3)]^+PF_6^-$ (25). **26** (0.089 g, 0.20 mmol) and $(C_6H_5)_3C^+PF_6^-$ (0.073 g, 0.19 mmol) were stirred in CH_2Cl_2 (3 mL) at 0 °C for 1.5 h. Addition of hexane (8 mL) produced a brown oil which was difficult to crystallize. Solvent was decanted and the oil triturated with hexane. The oil was dissolved in CH_2Cl_2 (2 mL); addition of hexane (8 mL) again yielded an oil. Trituration of this oil with hexane finally gave a solid. After five repetitions of this CH_2Cl_2 solution–hexane precipitation–hexane trituration procedure, **25** (45 mg, 41%) was obtained as a brown solid. ^1H NMR (270 MHz, acetone-d_6) δ 12.90 (d, J = 11.7 Hz, FeCH), 7.80 (d, J = 7.8 Hz, 2 H), 7.30 (d, J = 7.7 Hz, 2 H), 5.55 (s, C_5H_5), 4.81 (d, J = 11.4 Hz, FeCH=C*H*), 2.34 (s, CH_3); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 210.5 (CO), 167.2 (FeCH), 139.5, 135.1 (ipso, para), 129.5, 127.1 (ortho, meta), 93.5 (FeCH=*C*H), 90.5 (C_5H_5), 20.2 (CH_3), μ-CO not observed; IR (CH_2Cl_2) 2025 (s), 2000 (m), 1865 (m) cm^{-1}.

Anal. Calcd for $C_{22}H_{19}F_6Fe_2O_3P$: C, 44.94; H, 3.26. Found: C, 45.21; H, 3.53.

Attempted Rearrangement of $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CCH_3)]^+PF_6^-$ (10). The procedure reported by Pettit for the corresponding BF_4^- salt was used for the synthesis of **10**.[7] Reaction of $(C_5H_5)_2(CO)_4Fe_2$ (28.2 mmol) with CH_3Li (39 mmol) followed by acidification with 60% aqueous HPF_6 gave **10** (9.57 g, 67%). ^1H NMR (270 MHz, CD_2Cl_2) δ 5.35 (C_5H_5), 5.12 (CH_3); $^{13}C\{^1H\}$ NMR (acetone-d_6, 231 K) δ 497.9 (μ-C), 253.0 (μ-CO), 93.3 (C_5H_5), 65.4 (CH_3), terminal CO obscured by solvent; IR (Nujol) 2040 (s), 2002 (s), 1845 (s) cm^{-1}.

10 was heated in CD_2Cl_2 at 88 ± 0.1 °C in an NMR tube. After 20 h, very little decomposition (≤10%) was noted; after 97 h about 50% decomposition had occurred. No peaks at δ 12.52 (FeC*H*=CH$_2$) or at δ 5.46 or 5.22 (C_5H_5) attributable to the potential rearrangement product **11** were observed at any time throughout the experiment; however, after 97 h at least 13 new resonances between δ 4 and 6 were observed.

Attempted Rearrangement of $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CH_2)]^+PF_6^-$ (11). **11** (0.875 g, 89%) was prepared by the reaction of $(C_6H_5)_3C^+PF_6^-$ (0.760 g, 9.96 mmol) and $(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$[7] (0.730 g, 2.03 mmol) in CH_2Cl_2 using Pettit's procedure for the synthesis of the corresponding BF_4^- salt.[7] ^1H NMR (270 MHz, acetone-d_6) δ 12.68 (m, 1 H), 5.79 (br s, C_5H_5), 5.58 (s, C_5H_5), 5.17 (d, J = 7.4 Hz, FeCH=CH*H*), 3.00 (d, J = 13.2 Hz, FeCH=CH*H*); $^{13}C\{^1H\}$ NMR (acetone-d_6, 223 K) δ 242.7 (μ-CO), 213.7, 208.2 (CO), 185.3 (*C*H=CH$_2$), 92.8, 89.5 (C_5H_5), 64.4 (CH=*C*H$_2$). A CD_2Cl_2 solution of **11** was heated at 88 ± 0.1 °C in a sealed NMR tube. After 20 h, 80% decomposition had occurred; but no peaks at δ 5.35 or 5.12 due to the potential rearrangement product, **10**, were observed.

$(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CHCH(OH)CH_2CH_2CH_3)$ (19). **4** (0.500 g, 0.98 mmol) was stirred with $NaHCO_3$ (0.10 g, 1.19 mmol) in acetone (20 mL) and H_2O (2 mL) for 26 h. Solvent was evaporated under vacuum and the residue was extracted with 10 mL of toluene. Addition of hexane (5 mL) to the filtered toluene extract gave **19** (180 mg, 47%) as a red-orange solid. ^1H NMR (270 MHz, acetone-d_6) δ 11.40 (d, J = 11.0 Hz, μ-C*H*), 4.93 (s, C_5H_5), 4.88 (s, C_5H_5), 4.02 (m, C*H*(OH)C), 3.25 (dd, J = 3.7, 1.4 Hz, O*H*), 2.18–1.47 (m, *CH*$_2$*CH*$_2$CH$_3$), 0.95 (t, J = 7.4 Hz, CH_3); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 271.7 (μ-CO), 214.4,

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214.0 (CO), 180.2 (μ-C), 88.5 (C_5H_5), 57.5 (COH), 44.4 (CH_2CH_2C-H_3), 20.6 (CH_2CH_3), 14.5 (CH_3); IR (ether) 3600–3200 (br), 1983 (s), 1946 (w), 1797 (m) cm^{-1}; MS, *m/e* (int) 412 (0.1, M^+), 394 (2.9, $M^+ - H_2O$), 384 (0.3, $M^+ - CO$), 366 (3.3, $M^+ - CO - H_2O$), 338 (20.3, $M^+ - 2CO - H_2O$), 186 (100, $Fe(C_5H_5)_2^+$).

Protonation of $(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_3)CH_2CH_3)$ (17). $HBF_4{\cdot}OEt_2$ (19 μL, 0.15 mmol) was added to a solution of **17**[24] (37 mg, 0.090 mmol) in 3 mL of ether at −78 °C. The resulting precipitate was washed with ether and recrystallized from acetone–ether to give a 2.3:1.0:1.5 mixture of **14**:**15**:**16** (24 mg, 48%) as determined by ^1H NMR.[13]

Low-Temperature Protonation of $(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}C{=}CCH_2CH_2CH_2CH_2CH_2)$ (20). A solution of $HBF_4{\cdot}Et_2O$ (2 μL, 15 μmol) in 0.2 mL of acetone-d_6 was added to a solution of **20**[24] (2 mg, 5 μmol) in 0.2 mL of acetone-d_6 in an NMR tube cooled to −78 °C. The tube was sealed under vacuum and centrifuged at −78 °C. In the ^1H NMR spectrum at 203 K, the only observed cyclopentadienyl resonance was the peak at δ 5.76 due to **12**. When the sample was warmed to 260 K, a new resonance at δ 5.68 due to **13** slowly grew in. The vinylic proton of **13** and the proton on the carbon α to the carbyne-carbon of **12** were not observed by ^1H NMR presumably due to prior deuterium exchange of $HBF_2{\cdot}Et_2O$ with $(CD_3)_2CO$.

The first-order rate constant for the conversion of **12** to a 1.4:1 equilibrium mixture of **12**:**13** was measured by monitoring the cyclopentadienyl resonances at δ 5.76 and 5.68 and was found to be $k_e = 2.4 \pm 1.0 \times 10^{-4}$ s^{-1}. The rate constant for the conversion of **12** to **13** is given by $k = k_e(1 + K_{eq}^{-1})^{-1} = 1.0 \pm 0.4 \times 10^{-4}$ s^{-1} which corresponds to $\Delta G^{\ddagger}_{260K} = 19.9 \pm 0.3$ kcal mol^{-1}.

Saturation Transfer Measurement of Rate of Conversion[12] of 13 to 12. The experiment was performed at 315 ± 0.5 K by quickly saturating the magnetization of the δ 5.22 μ-CC*H* resonance of **12** and monitoring the decay of magnetization of the δ 11.96 μ-C*H*=C resonance of **13**. The δ 5.22 resonance was saturated with a 50-ms pulse at 200 mW followed by a variable length pulse at 0.02 mW to maintain saturation. The decoupler was then gated off and data were accumulated for 2.28 s. A 30-s relaxation delay was included between each scan. Representative magnetizations in arbitrary units (length of saturating pulse in s): 170.3 (0.051), 137.2 (0.300), 121.0 (0.600), 99.6 (0.900), 92.7 (1.200), 72.6 (20.0).

The data were analyzed in terms of eq 1 where $M(t)$ is the magnetization at time t, M_0 is the magnetization in the absence of a saturation pulse, $M_\infty = M_0\tau_1/T_1$ is the steady state magnetization in the presence of a saturation pulse. τ is the average lifetime of a spin at the observation site, T_1 is the spin lattice relaxation time of the observed magnetization and $1/\tau_1 = 1/\tau + 1/T_1$.

$$M(t) = M_\infty + M_0(\tau_1/\tau)\exp(-t/\tau_1) \quad (1)$$

The value of τ was obtained by an iterative linear least-squares fitting of eq 2 where M_∞ was varied to obtain the best fit. The final estimates

$$\ln(M(t) - M_\infty) = \ln(M_0(\tau_1/\tau)) - t/T_1 \quad (2)$$

were $1/\tau_1 = 0.70$ s^{-1}, $M_\infty = 72.55$, $1/\tau = 0.85$ s^{-1}. The rate constant for **13** → **12** is $1/\tau = 0.85$ s^{-1}. The equilibrium constant K_{eq} = [**12**]/[**13**] = 1.4. The calculated rate constant for **12** → **13** is therefore 0.61 s^{-1}.

Table II. Coalescence Temperature of μ-Alkenyl Complexes

	$\Delta\nu^a$ (Hz)	T_c (K)[b]	k_c (s^{-1})[c]	$\Delta G^{\ddagger}$ (kcal mol^{-1})[d]
5[8]	57	≤300	≤127	≥14.7
7	52	264	116	12.9 ± 0.2
4	54	265	121	12.9 ± 0.2
25	173	218	383	10.1 ± 0.2
13	117	210	259	9.8 ± 0.2

[a] $\Delta\nu$ = peak separation of cyclopentadienyl resonances at low-temperature limit (185–235 K). [b] Temperature of coalescence of cyclopentadienyl resonances. [c] Exchange rate at coalescence temperature. [d] $\Delta G^{\ddagger}$ at coalescence temperature calculated from $\Delta G^{\ddagger} = RT_c \ln(k$ Boltzman $T_c/hk_c)$.

$[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CCD_2CH_2CH_2CH_3)]^+CF_3SO_3^-$ (3-d_2). **18**[24] (0.50 g, 1.27 mmol) was stirred with CF_3COOD (1 mL 25.7 mmol) for 5 min at 0 °C. Degassed D_2O (3 mL) was added dropwise over 20 min, and an oily precipitate formed. The reaction vessel was centrifuged and the supernatent decanted. The oil which remained was dried under vacuum, and the above deuteration procedure was repeated. The resulting red oil was dissolved in 5 mL of ether. Addition of CF_3SO_3D (0.8 mL, 9.0 mmol) at −78 °C gave a pink precipitate. Recrystallization from acetone–ether gave **3-d_2** (0.390 g, 47.1% based on **18**). Integration of the ^1H NMR (270 MHz, acetone-d_6) of **3-d_2** indicated that the site α to the carbyne–carbon was 79% deuterated [δ 5.67 (10 H, C_5H_5), 5.55 (0.42 H, CCH_2)].

Rearrangement of 3-d_2. Solid **3-d_2** was heated in a NMR tube at 88 °C for 9.5 h. $^2H\{^1H\}$ NMR (30.60 MHz acetone) had resonances at δ 12.19 and 3.62 for the vinyl protons of the deuterated **4-d_2** as well as a peak at δ 5.54 for **3-d_2**. The ratio of **4-d_2**:**3-d_2** was 93:7.

Barriers for Fluxionality of μ-Alkenyl Complexes. In the ^1H NMR spectra of **5**, **7**, **4**, **25**, and **13** at about −90 to −40 °C two sharp cyclopentadienyl resonances are seen with the peak separations listed in Table II. The peak separations varied less than 10% for **7** between 231 and 261 K and were assumed to be invariant with temperature in all calculations. Several spectra for each compound were measured near the coalescence limit, and the coalescence temperature was measured to a precision of ±2 °C. The rate constant for the fluxional process at the coalescence temperature was calculated by using the equation $k = 2.22(\Delta\nu)$, where $\Delta\nu$ is the peak separation at the low-temperature limit.

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