ionic (see the tin gross atomic charges). The involvement of the Sn 5d functions is comparable with the small one found in $Sn(CH_3)_4$, owing, in this case, too, to the scarce energy matching between the Sn 5d AOs and the suitable $\pi_{N=C}$ MOs.

Acknowledgment. Thanks are due to CNR (ROME) for a financial support to this study.

Registry No. $Sn(CH_3)_4$, 594-27-4; $SnCl_4$, 7646-78-8; $Sn(CH_3)_3Cl$, 1066-45-1; $Sn(CH_3)_2Cl_2$, 753-73-1; $SnCH_3Cl_3$, 993-16-8; $Sn(CH_3)_3NCS$, 15597-43-0; $Sn(CH_3)_2(NCS)_2$, 15768-03-3.

Reaction of a Diiron μ-Methylidyne Complex with 1,2-Disubstituted Alkenes

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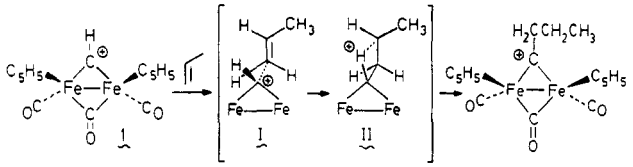
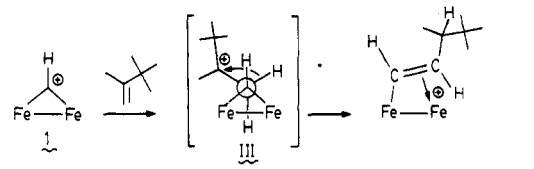
Received February 3, 1986

Reaction of $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (**1**) with *cis*-2-butene produced a 2.3:1.0:1.5 equilibrium mixture of $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH(CH_3)CH_2CH_3)^+PF_6^-$ (**2**) and two isomers of $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}C(CH_3)CH_2CH_3)^+PF_6^-$ (**3**-*E* and **3**-*Z*) in 79% yield. Reaction of this equilibrium mixture with $NaHCO_3$ produced $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_3)CH_2CH_3)$ (**8**) in 80% yield. Reaction of **1** with *trans*-2-butene, cyclohexene, cyclopentene, *trans*-1-propenylbenzene, and *trans*-2-pentene gave similar equilibrium mixtures of μ-alkylidyne and μ-alkenyl complexes which are deprotonated to produce μ-alkylidene complexes. The reaction of **1**-*d* with *cis*-2-butene gave **2**-*d* and **3**-*d* with the deuterium label located on the methylene group of the ethyl group. This result provides conclusive evidence that μ-alkylidyne complexes are the kinetic products in the reaction of **1** with 1,2-disubstituted alkenes. Direct observation of a μ-alkylidyne complex by low-temperature NMR supports this conclusion.

The cationic diiron μ-methylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (**1**) reacts with alkenes to form new carbon–carbon bonds and produces either μ-alkylidyne or μ-alkenyl complexes.[1-5] With terminal alkenes, the methylidyne C–H bond adds regioselectively across the alkene carbon–carbon double bond. Both the relative reactivity of alkenes toward **1** and the observation of an inverse isotope effect on the addition of **1**-*d* to alkenes are consistent with a transition state for μ-alkylidyne formation that involves only carbon–carbon bond formation as shown in I. After the transition state has been reached, a 1,3-hydride shift (possibly from a carbocation intermediate) completes the addition of the C–H unit to the alkene. The transition state for this 1,3-hydride shift is depicted as II.



Some alkenes such as 1-methylcyclohexene, 1,1-diphenylethylene, and 2,3,3-trimethyl-1-butene react with methylidyne complex **1** to produce μ-alkenyl complexes directly. In general, more highly substituted alkenes capable of forming stabilized carbocation intermediates tend to lead directly to μ-alkenyl products. The inverse secondary isotope effect seen in the reaction of 2,3,3-trimethyl-1-butene is consistent with a transition state for μ-alkenyl formation that involves only carbon–carbon bond formation.[5] The resulting carbocation intermediate then undergoes a 1,2-hydrogen or 1,2-carbon shift via transition state III to complete the formation of the μ-alkenyl complex



The transition states for the rate-determining step of μ-alkylidyne and μ-alkenyl formation are very similar and involve only carbon–carbon bond formation. The partitioning of the cationic intermediate between μ-alkylidyne and μ-alkenyl complexes is determined largely by steric effects which affect the relative energies of the product-determining transition states II and III.

When we first observed that *cis*-2-butene and other 1,2-disubstituted alkenes reacted with **1** to produce mixtures of μ-alkylidyne and μ-alkenyl complexes, we proposed that these products were formed directly from **1** by competing pathways.[6] However, we subsequently discovered that μ-alkylidyne complexes with two carbon substituents on the carbon α to the carbyne center undergo rapid and reversible 1,2-hydride shifts to form an equilibrium mixture of μ-alkylidyne and μ-alkenyl complexes.[7] In this paper we present two independent lines of evidence that establish that the reaction of **1** with *cis*-2-butene and other 1,2-disubstituted alkenes occurs via kinetic formation of

(1) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134–1136.
(2) Casey, C. P.; Fagan, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4950–4951.
(3) Casey, C. P.; Fagan, P. J.; Miles, W. H.; Marder, S. R. *J. Mol. Catal.* **1983**, *21*, 173–188.
(4) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Marder, S. R.; Austin, E. A. *J. Am. Chem. Soc.* **1986**, *108*, 4043–4053.
(5) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Colborn, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 4053–4059.
(6) Casey, C. P.; Meszaros, M. W.; Marder, S. R.; Fagan, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 3680–3681.
(7) (a) Casey, C. P.; Marder, S. R.; Fagan, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 7197–7198. (b) Casey, C. P.; Marder, S. R.; Adams, B. R. *J. Am. Chem. Soc.* **1985**, *107*, 7700–7705 and references therein.

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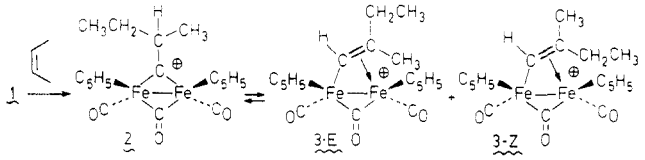
a μ-alkylidyne complex that then equilibrates with a μ-alkenyl complex.

Results

Reaction of μ-Methylidyne Complex 1 with 1,2-Disubstituted Alkenes. When *cis*-2-butene was added to a red suspension of methylidyne complex 1 in CH_2Cl_2 and warmed from −78 °C to ambient temperature, a muddy brown solution was produced. Evaporation of solvent and recrystallization of the residue from acetone–ether led to the isolation of a brown solid which was shown by NMR to be a 2.3:1.0:1.5 mixture of the μ-2-methylbutylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH(CH_3)CH_2CH_3)^+PF_6^-$ (**2**) and of the isomeric μ-2-methyl-1-butenyl complexes $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}C(CH_3)CH_2CH_3)^+PF_6^-$ (**3-*E*** and **3-*Z***) in 79% yield.



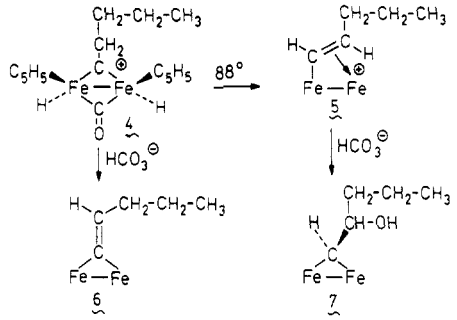
The μ-alkenyl complexes **3-*E*** and **3-*Z*** are readily characterized by their ^1H NMR spectra. The protons on the α-carbon of the bridging alkenyl group of **3-*E*** and **3-*Z*** appear characteristically far downfield at δ 11.90 and 11.81 as singlets in a 1.0:1.5 ratio. The μ-alkylidyne product **2** is characterized by a multiplet in the ^1H NMR spectrum at δ 5.4 and a doublet (J = 6.5 Hz) at δ 1.86 which are assigned to the CH group α to the μ-carbyne center and the methyl group adjacent to the CH unit.

At room temperature, cyclopentadienyl resonances were seen for each of the three complexes. The cyclopentadienyl groups of the μ-alkylidyne complex **2** are diastereotopic due to the presence of an asymmetric carbon in the remote alkylidyne side chain, and two resonances were observed. The cyclopentadienyl groups of each of the isomeric μ-alkenyl complexes **3-*E*** and **3-*Z*** are chemically nonequivalent, and two cyclopentadienyl resonances were seen for each isomer at −60 °C. At room temperature, a rapid fluxional process exchanges the environment of the cyclopentadienyl groups and one coalesced cyclopentadienyl resonance is seen for each isomer, **3-*E*** and **3-*Z***. A combination of decoupling and deuterium-labeling experiments enabled confident assignment of the complex pattern of overlapping resonances due to the ethyl groups of **2**, **3-*E***, and **3-*Z***.

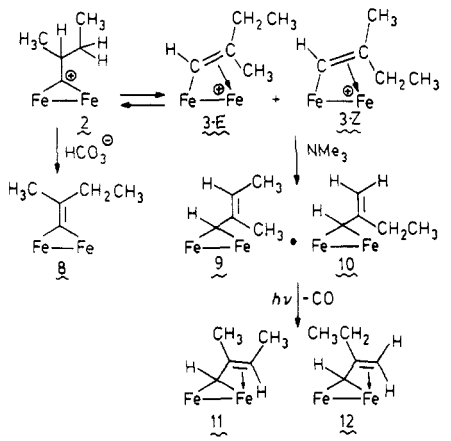
The reaction of *trans*-2-butene with **1** also gave an identical 2.3:1.0:1.5 mixture of **2**:**3-*E***:**3-*Z*** in 82% yield. 2-Butene recovered from the reaction of **1** with *cis*-2-butene (99.80% cis) was analyzed by GC to determine if any *cis*-2-butene was converted to *trans*-2-butene. No isomerization to *trans*-2-butene (<0.5%) was observed by GC. This result excludes the formation of a cationic intermediate that undergoes rotation about the former carbon–carbon double bond and reversal to **1** and isomerized 2-butene. However, the result is compatible with the irreversible formation of a cationic intermediate which undergoes a subsequent rapid 1,3-hydride shift to produce μ-alkylidyne complex **2**.

Since we had discovered earlier that the μ-pentylidyne complex **4** rearranged to μ-pent-1-enyl complex **5** upon heating to 88 °C,[7] we heated the mixture of **2**, **3-*E***, and **3-*Z*** to 88 °C in the hope of converting all the material to μ-alkenyl complexes. However, the ratio of **2**:**3-*E***:**3-*Z*** was not altered by heating at 88 °C for 20 h. This result is now readily understood since we know that equilibration occurs below room temperature.

In an effort to separate the μ-alkenyl complexes **3-*E*** and **3-*Z*** from the μ-alklidyne complex **2**, we attempted to selectively deprotonate **2** and then to isolate the less reactive μ-alkenyl complexes. This seemed feasible since we had demonstrated that the bridging pentylidyne complex **4** was rapidly deprotonated by aqueous bicarbonate treatment to give the bridging pentenylidene complex **6** but that the μ-pentenyl complex **5** reacted only slowly with aqueous bicarbonate over 16 h to give the neutral β-hydroxy-μ-alkylidene complex **7**.[7]



However, when a solution of **2**, **3-*E***, and **3-*Z*** in acetone was reacted with aqueous bicarbonate, the solution immediately turned bright red and the μ-2-methyl-1-butenylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_3)CH_2CH_3)$ (**8**) was isolated in 81% yield after column chromatography. The yield of μ-alkenylidene complex **8** is substantially higher than the amount of μ-alkylidyne complex **2** present (40%). This requires that a major portion of **8** be derived from μ-alkenyl complexes **3-*E*** and **3-*Z***. This result can be explained by rapid equilibration of **2**, **3-*E***, and **3-*Z*** and selective deprotonation of μ-alkylidyne complex **2** which drains off the entire equilibrium mixture to the neutral alkenylidene complex **8**.



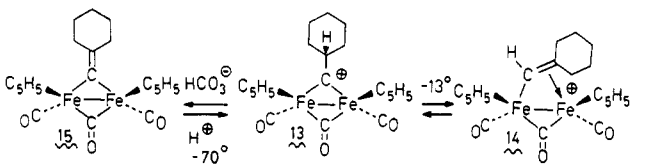
When NMe_3 was used to deprotonate the mixture of **2**, **3-*E***, and **3-*Z***, the vinyl carbene complexes $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHC(CH_3){=}CHCH_3)$ (**9**) and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHC(=CH_2)CH_2CH_3)$ (**10**) arising from deprotonation of the μ-alkenyl complexes **3-*E*** and **3-*Z*** were obtained in addition to **8**. The vinyl carbene complexes **9** and **10** undergo photoinduced loss of carbon monoxide to produce the vinyl carbene complexes **11** and **12** with coordinated vinyl groups.[8] Evidently, deprotonation of **3-*E*** and **3-*Z*** with NMe_3 is fast enough to compete with isomerization to **2**.

Neutral μ-alkylidene complexes such as **8** are easily purified by column chromatography or reverse-phase

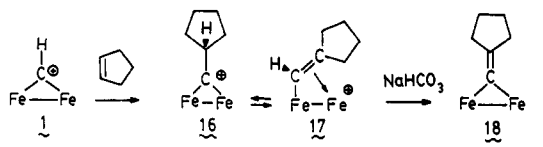
(8) Further characterization of **9** and **11** was achieved by examining pure materials arising from reaction of **1** and 2-butyne. Casey, C. P.; Woo, L. K., submitted for publication in *Organometallics*.

HPLC and are readily characterized spectroscopically.[4] The nonequivalent cyclopentadienyl groups of **8** give rise to two ^1H NMR resonances at δ 4.96 and 4.95. The methylene protons of the ethyl group are nonequivalent and give rise to two doublets of quartets (J = 13.2, 7.4 Hz) at δ 2.88 and 2.74. The isolated methyl group gives rise to a singlet at δ 2.44, and the methyl group of the CH_2CH_3 unit results in a triplet (J = 7.4 Hz) at δ 1.25. In the ^{13}C NMR of **8**, two resonances at δ 272.1 and 259.1 are assigned to the bridging carbonyl and bridging vinyl carbons, and the nonbridging vinyl carbon appears at δ 144.7. The cis arrangement of the terminal carbonyl groups of **8** is established by the appearance of a strong symmetric stretch at 1993 cm^{-1} and a weaker asymmetric stretch at 1955 cm^{-1}.[9,10]

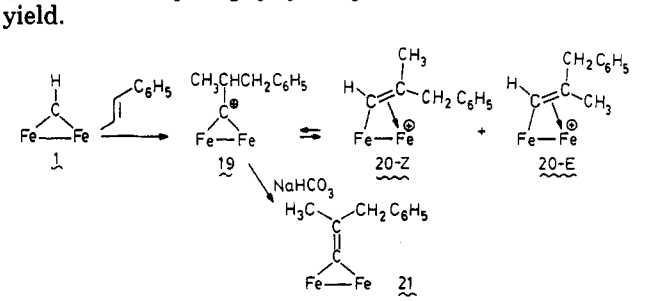
The reaction of μ-methylidyne complex **1** with cyclohexene gave the μ-alkylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCHCH_2CH_2CH_2CH_2CH_2)^+PF_6^-$ (**13**) and μ-alkenyl complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CCH_2CH_2CH_2CH_2CH_2)^+PF_6^-$ (**14**) in 79% yield. The 1.4:1.0 mixture of **13**:**14** was characterized by ^1H NMR and by deprotonation with aqueous bicarbonate to give the μ-alkenylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CCH_2CH_2CH_2CH_2CH_2)$ (**15**) in 70% yield.



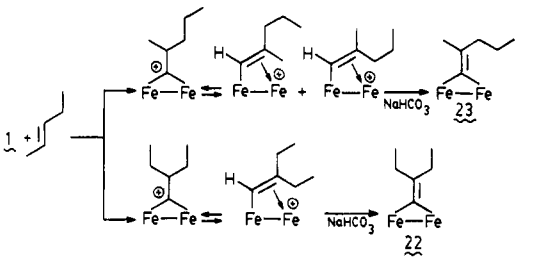
Similarly, cyclopentene reacted with **1** to give a 6:5 ratio of $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCHCH_2CH_2CH_2CH_2)^+PF_6^-$ (**16**) and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CCH_2CH_2CH_2CH_2)^+PF_6^-$ (**17**) in 75% yield. When the mixture of **16** and **17** obtained from reaction of **1** with cyclopentene was directly deprotonated with aqueous bicarbonate, the μ-alkenylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CCH_2CH_2CH_2CH_2)$ (**18**) was isolated in 82% overall yield.



The reaction of *trans*-1-propenylbenzene with **1** gave a 4:3:2 mixture of μ-alkylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH(CH_3)CH_2C_6H_5)^+PF_6^-$ (**19**) and of the two isomeric μ-alkenyl complexes $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}(CH_3)CH_2C_6H_5)^+PF_6^-$ (**20-*E*** and **20-*Z***) in 80% yield.



Virtually no regioselectivity was observed in the reaction of **1** with *trans*-2-pentene. In the ^1H NMR spectrum of the initial mixture of cationic products, three μ-alkenyl resonances were observed at δ 11.93, 11.83, and 11.79. Deprotonation of the mixture of products with aqueous bicarbonate gave a 3:2 mixture of the μ-alkenylidene complexes $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_2CH_3)_2)$ (**22**) and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_3)CH_2CH_2CH_3)$ (**23**) in 81% yield.



Equilibration of μ-Alkylidyne and μ-Alkenyl Complexes. Several observations detailed above suggested that the products of reaction of **1** with 1,2-disubstituted alkenes were equilibrating mixtures of μ-alkylidyne and μ-alkenyl complexes, but these observations did not conclusively establish the equilibration. First, the same mixture of **2**, **3-*Z***, and **3-*E*** was obtained from either *cis*- or *trans*-2-butene; this would be an unlikely coincidence of kinetically determined product ratios. Second, the μ-alkenyl products obtained from 1,2-disubstituted alkenes are invariably the products of a net *hydrogen* migration; in contrast, the kinetically controlled μ-alkenyl products obtained from reaction of **1** with 1-methylcyclohexene and with *trans*-stilbene resulted from preferential *carbon* migration. The net hydrogen migration seen for μ-alkenyl complexes obtained from 1,2-disubstituted alkenes is readily explained by isomerization of an initially formed μ-alkylidyne complex. Third, deprotonation of these mixtures of μ-alkylidyne and μ-alkenyl complexes with aqueous bicarbonate gave only μ-alkenylidene products.

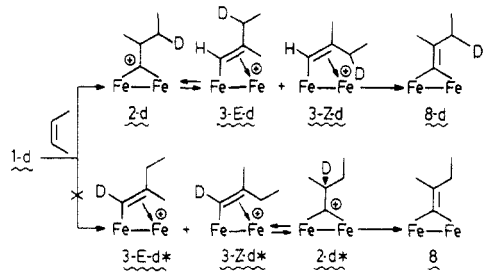
To obtain more direct evidence for the equilibration of these μ-alkylidyne and μ-alkenyl complexes, we independently generated the μ-alkylidyne complexes by protonation of μ-alkenylidene complexes and observed their rearrangement.[7] Both Pettit's[11] group and Stone's[10] group have demonstrated that protonation of μ-alkenylidene complexes generates μ-alkylidyne complexes. When μ-alkenylidene complex **8** was protonated with HBF_4, a 2.3:1.0:1.5 mixture of the BF_4 salt analogues of **2**:**3-*E***:**3-*Z*** was obtained. Apparently, initially formed **2** equilibrates with **3-*E*** and **3-*Z*** below ambient temperature.

When the protonation of the cyclohexyl alkylidene complex **15** with $HBF_4{\cdot}OEt_2$ in acetone-d_6 was monitored by ^1H NMR at −70 °C, only the μ-cyclohexylmethylidyne complex **13** was observed.[7] When the solution was warmed to −13 °C, the slow ($t_{1/2}$ = 0.8 h) formation of an equilibrium mixture of **13** and **14** was seen. The rate of isomerization of **13** to **14** was also determined by NMR saturation transfer experiments; $t_{1/2}$ was found to be 1.1 s at 41 °C ($\Delta G^\ddagger$ = 20 kcal mol^{-1}).[7]

Determination of Kinetically Formed Products by Deuterium-Labeling Studies Using 1-*d*. Since there is rapid ambient-temperature equilibration of the μ-alkylidyne and μ-alkenyl complexes obtained in the reaction of 1,2-disubstituted alkenes with methylidyne complex **1**, the kinetic product could be either the μ-alkylidyne or the

(9) Miles, W. H. Ph.D. Thesis, University of Wisconsin at Madison, 1984.
(10) Dawkins, G. M.; Green, M.; Jeffery, J. C.; Sambak, C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 499–506.
(11) Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911–918.
(12) Bly, R. K., private communication.

μ-alkenyl complex or any mixture of the two species. To determine the kinetic product, the reaction of deuterated methylidyne complex 1-*d* with *cis*-2-butene was studied since different locations of the deuterium label would be obtained depending on whether the μ-alkylidyne or μ-alkenyl complex was the kinetic product. If the reaction of 1-*d* with *cis*-2-butene proceeds via hydrocarbation to give the kinetically formed μ-alkylidyne complex 2-*d*, addition of the C–D bond across the alkene would produce μ-alkylidyne complex 2-*d* with the deuterium label on the methylene group of the ethyl group. Subsequent rearrangement of 2-*d* to μ-alkenyl complex 3-*d* by a 1,2-hydride shift would leave the deuterium label on the methylene carbon of the ethyl group. Deprotonation of this equilibrating mixture would give μ-alkenylidene complex 8-*d* with the deuterium label still attached to the methylene carbon of the ethyl group. In contrast, if μ-alkenyl complex 3-*d** is the kinetic product, no cleavage of the C–D bond would occur and the deuterium label would be on the α-bridging carbon as shown in 3-*d**. Rearrangement of 3-*d** would produce μ-alkylidyne complex 2-*d** with deuterium on the carbon α to the bridging carbyne carbon. Deprotonation of the equilibrating mixture of 2-*d** and 3-*d** would lead to undeuterated μ-alkenylidene complex 8.



When *cis*-2-butene was reacted with 1-*d* and the products examined by NMR, the deuterium label was found to be exclusively on the methylene carbon of the ethyl group. In the ^{1}H NMR, three triplets at δ 1.22, 1.34, and 1.14 assigned to the methyl groups of **2**, **3**-*E*, and **3**-*Z* collapsed to broad doublets in **2**-*d* and **3**-*E*-*d*, **3**-*Z*-*d*. In the ^{2}H NMR, resonances were observed only at δ 2.55 (**2**-*d* and **3**-*E*-*d*) and 1.48 (**3**-*Z*-*d*) and no resonances at δ 12 or 5.4 were seen. Thus, ^{2}H NMR provides conclusive evidence that deuterium is located only on the methylene carbons of the ethyl groups of **2**, **3**-*E*-*d*, and **3**-*Z*-*d*.

As further confirmation of the location of the deuterium label, the deuterated mixture of **2** and **3** was deprotonated by using aqueous bicarbonate to give a 79% yield of 8-*d* (>90% d_1 by mass spectral analysis). In the ^{1}H NMR of 8-*d*, the two diastereotopic methylene protons appeared as quartets at δ 2.85 and 2.72 and integrated for 0.5 H each. The adjacent methyl group appeared at δ 1.24 as a doublet (J = 7.6 Hz). In the ^{2}H NMR, the only resonances observed were at δ 2.83 and 2.73 due to the $CHDCH_3$ groups of the two diastereomers of 8-*d*. All of these results require that the reaction of 1-*d* with *cis*-2-butene leads initially to μ-alkylidyne complex 2-*d*.

Similarly, the reaction of 1-*d* with *trans*-2-butene gave a 2.3:1.0:1.5 ratio of **2**-*d*:**3**-*E*-*d*:**3**-*Z*-*d* in which all the deuterium label was located on the methylene carbon of the ethyl groups.

Similar results were seen for the reaction of 1-*d* with cyclohexene and with *trans*-1-propenylbenzene. ^{1}H and ^{2}H NMR of the cationic and neutral products showed a μ-alkylidyne complex was the exclusive kinetic product which subsequently equilibrated with its corresponding μ-alkenyl complex.

Direct Low-Temperature NMR Observation of Kinetic μ-Alkylidyne Products. Study of the reaction of 1 with *trans*-2-butene by ^{1}H NMR at low temperature was difficult due to (1) the low solubility of 1 in CD_2Cl_2 at −50 °C, (2) the temperature-dependent broadening of resonances of the fluxional μ-alkenyl products, and (3) the equilibration of μ-alkylidyne and μ-alkenyl complexes at −13 °C. Nevertheless, low-temperature ^{1}H NMR studies of the reaction of 1 with 2-butene confirmed that μ-alkylidyne complexes are the predominant kinetic products. An NMR tube containing a suspension of 1 and *trans*-2-butene in CD_2Cl_2 was agitated with a Vortex Genie at −78 °C and maintained at −60 °C for 3 h. Prompt ^{1}H NMR analysis at −22 °C revealed only unreacted 1 (~50%) and μ-alkylidyne complex **2** (~50%); no μ-alkenyl complex **3** was detected (<1%). When the solution was warmed to −13 °C, resonances due to the vinyl protons of **3**-*E* and **3**-*Z* grew in at δ 11.68 and 11.61. After the solution was warmed to ambient temperature, ^{1}H NMR indicated a 2.3:1.0:1.5 equilibrium mixture of **2**:**3**-*E*:**3**-*Z*. Similar results were obtained from the reaction of *cis*-2-butene and 1 at −60 °C.

Discussion

In the previous two papers,[4,5] we described the reactions of 1 with alkenes that produced either μ-alkylidyne or μ-alkenyl complexes directly. The transition states of the rate-determining step in both of these reactions are very similar and involve only carbon–carbon bond formation. Subsequent rearrangement of a carbocation intermediate takes place either via a 1,3-hydrogen shift that leads to a μ-alkylidyne complex or via a 1,2-carbon or hydrogen shift that leads to a μ-alkenyl complex. The reaction of 1 with 1,2-disubstituted alkenes initially produces a μ-alkylidyne complex which then rapidly equilibrates with a μ-alkenyl complex. There are two key questions concerning this chemistry. First, why are the interconversions of μ-alkylidyne and μ-alkenyl complexes so rapid for the products from 1,2-disubstituted alkenes? Second, why are μ-alkylidyne complexes the kinetically formed product?

Rapid Equilibration of μ-Alkylidyne and μ-Alkenyl Complexes. In an earlier study, we found that the rate of both the rearrangement of μ-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.[7] Thus, the μ-ethylidyne complex (μ-C—CH_3) is indefinitely stable to rearrangement at 88 °C; the μ-pentylidyne complex (μ-C—$CH_2CH_2CH_2CH_3$) with one alkyl group on the β-carbon rearranges to the μ-pentenyl complex (μ-CH=$CHCH_2CH_2CH_3$) at 88 °C with a half-life of 40 min ($\Delta G^\ddagger$ = 27.1 kcal mol^{-1}); the cyclohexyl-substituted μ-alkylidyne complex (μ-C—$\overline{CH(CH_2)_4CH_2}$) with two alkyl groups on the β-carbon rearranges to the μ-alkenyl complex (μ-CH=$\overline{C(CH_2)_4CH_2}$) with a half-life of 1.9 h at −13 °C ($\Delta G^\ddagger$ = 19.9 kcal mol^{-1}). This trend suggests that there is an extensive buildup of positive charge at the β-carbon atom at the transition state for rearrangement and that this positive center can be stabilized by electron-donating alkyl substituents.

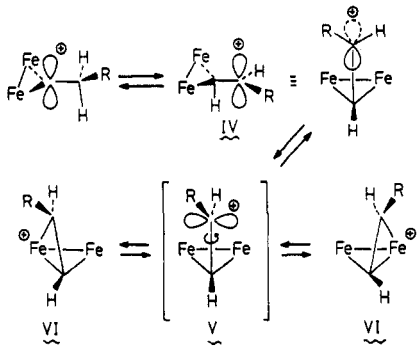
In the hydrogen migration step of the rearrangement of μ-alkylidyne to μ-alkenyl complexes, the C–H bond on the β-carbon of the μ-alkylidyne complex must be parallel to the empty p orbital at the carbyne carbon for maximum overlap during hydrogen migration. As the hydrogen migration proceeds, an empty p orbital develops at the β-carbon in IV. In this nascent geometry, the empty p orbital at the β-carbon has little interaction with the iron

Table I. Relative Reactivities and Isotope Effects for the Reaction of Alkenes with 1.[4]

	rel rate[a]	k_H/k_D[b]
$CH_2{=}CH_2$	1	0.81 ± 0.02[c]
$CH_2{=}CHCH_3$	56	0.74 ± 0.03
$CH_2{=}CH_2Et$	32	
trans-$CH_3CH{=}CHCH_3$	25	0.77 ± 0.03
cis-$CH_3CH{=}CHCH_3$	470	1.45 ± 0.06
$CH_2{=}CMe_2$	6900	0.80 ± 0.03

[a] Competition techniques were used to measure relative reactivity of 1 toward alkenes at −50 °C. [b] Kinetic isotope effect measured at −50 °C. [c] Determined at −25 °C.

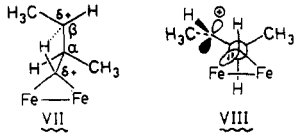
centers and no interaction with the Fe–C_α σ bonds. A 90° rotation about the C_α–C_β bond of IV produces the lower energy geometry V in which the positive center is stabilized both by weak interaction with the two iron centers and by interaction with the Fe–C_α σ bonds. V is also the transition state for the μ-alkenyl fluxional process and provides a smooth pathway to the μ-alkenyl complex VI.



Kinetic Formation of μ-Alkylidyne Complexes. The reaction of 1 with *cis*- and *trans*-2-butenes proceeds by initial formation of a μ-alkylidyne complex as demonstrated by deuterium-labeling studies and by low-temperature ^1H NMR observation of the kinetically formed products. No direct formation of a μ-alkenyl complex was seen.

The transition state for the reaction of *trans*-2-butene with 1 involves only carbon–carbon bond formation. At the transition state, the methylidyne C–H bond is undergoing a change in hybridization from sp^2 to sp^3 that tightens the bending vibrations and is responsible for the observed inverse kinetic isotope effect, k_H/k_D (−50 °C) = 0.77.[4] The rate of reaction of *trans*-2-butene (25) with 1 is similar to that of propene (56) and 1-butene (32) but is much slower than the reaction of isobutylene (6900) with 1 (Table I). This is consistent with buildup of positive charge at one carbon of the alkene at the transition state. The relatively small accelerations caused by alkyl substituents suggest that most of the positive charge is still associated with the diiron methylidyne unit.

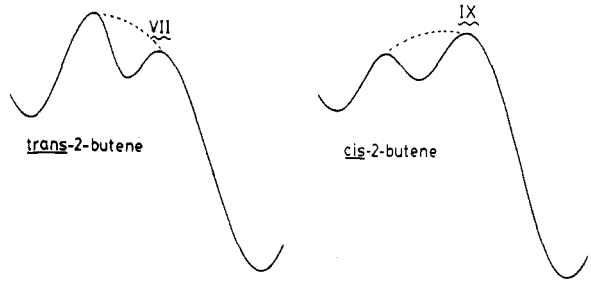
The formation of μ-alkylidyne product from *trans*-2-butene is the result of a lower energy for the product-forming transition state VII leading from an intermediate carbocation to μ-alkylidyne complex than for the product-forming transition state VIII leading to μ-alkenyl product. In the absence of large steric effects, the transition state leading to μ-alkylidyne products is normally of lower energy. Apparently, the steric effect of a single α-Me group in VII is not large enough to overcome this normal preference for μ-alkylidyne complex formation.



The reaction of *cis*-2-butene with 1 is unusual in two respects. First, a small *normal* kinetic isotope effect was seen in the reaction of 1-*d* with *cis*-2-butene, k_H/k_D (−50 °C) = 1.45 ± 0.06. For all other alkenes studied, substantial *inverse* kinetic isotope effects (0.72–0.81) were observed. This indicates some C–H bond breaking in the transition state for reaction of *cis*-2-butene with 1. Second, the relative reactivity of 1 toward *cis*-2-butene (470) is substantially greater than that of mono-substituted alkenes such as propene (56) and 1-butene (32) but not as large as isobutylene (6900). *cis*-2-Butene is 19 times more reactive than *trans*-2-butene.

These facts suggest that the transition state for the rate-determining step in the reaction of 1 with *cis*-2-butene is somewhat different than that for other alkenes. In particular, the normal isotope effect implies that the transition state involves some C–H bond breaking in addition to carbon–carbon bond formation. The transition state therefore occurs somewhat later along the reaction coordinate. While carbon–carbon bond formation is probably much more advanced than carbon–hydrogen bond breaking, both are occurring to some extent at the transition state. These two processes can be considered to be occurring at the same time (concerted) but to different extents (nonsynchronous).

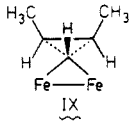
The 19-fold faster rate for *cis*- compared with *trans*-2-butene cannot be explained by relief of strain. Since *cis*-2-butene is only slightly less stable than *trans*-2-butene, this can account for a rate difference of only 5.2 at −50 °C. However, the faster rate for *cis*-2-butene compared with mono-substituted alkenes and *trans*-2-butene can be explained by a later transition state in which more extensive carbon–carbon bond formation has occurred and more positive charge is transferred from the diiron methylidyne unit to the alkene. Electron-donating alkyl substituents should have a greater stabilizing influence on the more electropositive carbon in this later transition state.



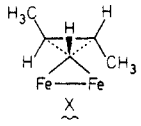
The proposed reaction coordinate diagrams for *cis*- and *trans*-2-butenes are shown above. For *trans*-2-butene, carbon–carbon bond formation dominates the highest energy transition state; for *cis*-2-butene, some carbon–hydrogen bond breaking is occurring at the highest energy point. The reaction coordinates for *cis*- and *trans*-2-butenes are actually quite similar; they differ only in the relative energies of the transition states for carbon–carbon bond formation and for carbon–hydrogen bond breaking. It should be emphasized that we cannot say whether the carbocation is an energy minimum along either reaction coordinate.

Why should the carbon–carbon bond-forming step for *cis*-2-butene be so much lower in energy than that for *trans*-2-butene such that hydrogen transfer becomes somewhat rate limiting for *cis*-2-butene? Perhaps, *cis*-2-butene initially interacts with 1 via the corner-protonated cyclopropane geometry IX. Such a geometry should be more favorable for a symmetrically 1,2-disubstituted alkene than for a monosubstituted alkene or isobutylene. For *trans*-2-butene a similar geometry (X) would be destabi-

lized by a methyl interaction.



IX



X

Experimental Section

General Data. See previous paper in this series.[4]

Reaction of *cis*-2-Butene with 1 and 1-*d*. *cis*-2-Butene (0.13 atm, 270 mL, 1.45 mmol) was condensed into a stirred suspension of **1** (160 mg, 0.33 mmol) in CH_2Cl_2 (20 mL) at −78 °C. The reaction mixture was warmed to ambient temperature. Solvent was evaporated, and the residue was dried under high vacuum. The resulting solid was dissolved in acetone (3 mL). Diethyl ether (25 mL) was added, and the resulting brown precipitate was filtered, washed with diethyl ether (3 × 5 mL), and dried under vacuum to give a 2.3:1.0:1.5 ratio of **2**, **3**-*E*, **3**-*Z* (140 mg, 79%). ^1H NMR (acetone-d_6): **2**, δ 5.72, 5.71 (s, C_5H_5), 5.4 (m, CH), 2.51 (m, CH_2), 1.86 (d, J = 6.5 Hz, CH_3), 1.22 (t, J = 7.4 Hz, CH_3); **3**-*E*, δ 11.90 (s, μ-CH=), 5.67 (s, C_5H_5), 2.62 (q, J = 7.3 Hz, CH_2), 1.43 (s, CH_3), 1.34 (t, J = 7.3 Hz, CH_3); **3**-*Z*, δ 11.81 (s, μ-CH=), 5.65 (s, C_5H_5), 2.41 (s, CH_3), 1.45 (q, J = 7.3 Hz, CH_2), 1.14 (t, J = 7.3 Hz, CH_3); IR (CH_2Cl_2) 2039 (s), 2018 (s), 2008 (w), 1853 (m) cm^{-1}.

Similarly, reaction of *cis*-2-butene (0.44 mmol) with **1**-*d* (0.22 mmol) gave a 2.3:1.0:1.5 mixture of **2**-*d*:**3**-*E*-*d*:**3**-*Z*-*d* (74%). ^1H NMR (acetone-d_6): **2**-*d*, δ 5.4 (m, μ-CCH), 2.5 (m, CHD), 1.86 (d, J = 6.5 Hz, $CHCH_3$), 1.22 (b d, J = 7 Hz, $CHDCH_3$); **3**-*E*-*d*, δ 11.90 (s, μ-CH), 2.6 (m, =CCHD), 1.43 (s, CH_3), 1.34 (b d, J = 7 Hz, $CHDCH_3$); **3**-*Z*-*d*, δ 11.81 (s, μ-CH), 2.42 (s, CH_3), 1.46 (m, CHD), 1.14 (b d, J = 7 Hz, $CHDCH_3$). $^2H\{^1H\}$ NMR (acetone): δ 2.6 (CHD of **2**-*d* and **3**-*E*-*d*), 1.5 (CHD of **3**-*Z*-*d*).

Reaction of *trans*-2-Butene with 1 and 1-*d*. Reaction of *trans*-2-butene (5.1 mmol) with **1** (0.25 mmol) gave a 2.3:1.0:1.5 mixture of **2**, **3**-*E*, and **3**-*Z* (82%). Reaction of *trans*-2-butene (5.1 mmol) with **1**-*d* (0.25 mmol) gave a 2.3:1.0:1.5 mixture of **2**-*d*, **3**-*E*-*d*, and **3**-*Z*-*d* (82%).

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_3)CH_2CH_3)$ (8). A saturated aqueous solution of $NaHCO_3$ (10 mL) was added to a suspension of **2**, **3**-*E*, and **3**-*Z*, (120 mg, 0.22 mmol) in diethyl ether (25 mL). The reaction mixture was stirred for 55 min. The organic phase was separated, dried ($MgSO_4$), and filtered. Solvent was evaporated, and the resulting red solid was purified by column chromatography (activity III alumina, 2:1 hexane/ether), to give red crystalline **8** (69 mg, 80%). ^1H NMR (acetone-d_6): δ 4.96, 4.95 (C_5H_5), 2.88 (dq, J = 13.2, 7.4 Hz, $CHHCH_3$), 2.74 (dq, J = 13.2, 7.4 Hz, $CHHCH_3$), 2.44 (s, CH_3), 1.25 (t, J = 7.4 Hz, CH_3). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 272.1, 259.5 (μ-C and μ-CO), 213.4 (CO), 144.7 (=CR_2), 88.1 (C_5H_5), 36.3 (CH_2), 24.6 (CH_3), 14.7 (CH_2CH_3). IR (CH_2Cl_2): 1993 (s), 1955 (w), 1785 (m) cm^{-1}. HRMS for $C_{18}H_{20}Fe_2O_3$: calcd, 393.9949; found, 393.9955. Anal. Calcd C, 54.87; H, 4.60. Found: C, 54.60; H, 4.64.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_3)CHDCH_3)$ (8-*d*). The products from the reaction of *cis*-2-butene (2.15 mmol) with **1**-*d* (140 mg, 0.289 mmol) were dissolved in acetone (7 mL), and a saturated aqueous solution of $NaHCO_3$ (1 mL) was added. Solvent was evaporated under vacuum, and the residue was extracted with diethyl ether (10 mL) and filtered. Evaporation of ether gave red crystalline **8**-*d* (90 mg, 80%). ^1H NMR (acetone-d_6): δ 4.96, 4.95 (C_5H_5), 2.85 (q, J = 7.6 Hz, 0.5 H, CHD), 2.72 (q, J = 7.6 Hz, 0.5 H, CDH), 2.43 (s, 3 H), 1.24 (d, J = 7.6 Hz, CH_3). $^2H\{^1H\}$ NMR (acetone): δ 2.83, 2.73. HRMS for $C_{18}H_{17}O_3DFe_2$: calcd, 395.0012; found, 395.0018.

Reaction of 2 and 3 with NMe_3. *cis*-2-Butene (0.50 atm, 27.5 mL, 0.57 mmol) was stirred with a suspension of **1** (100 mg, 0.21 mmol) in CH_2Cl_2 for 1 h at −50 °C. Excess alkene was evaporated from the solution at ambient temperature. The flask was wrapped in aluminum foil, and trimethylamine (0.40 atm, 250 mL, 4.1 mmol) was added at −78 °C. The solution was evaporated to dryness at ambient temperature. The resulting solid was dissolved in ether, and the filtered red solution was evaporated to give a mixture of **8**, **9**, and **10**. Exposure of an NMR tube containing a CD_2Cl_2 solution of **9** and **10** to fluorescent light resulted in loss of carbon monoxide and coordination of the vinyl group to give a solution of **11** and **12**. ^1H NMR (acetone-d_6): **9**, δ 12.20 (s, μ-CH), 5.86 (q, J = 7 Hz, =CHMe), 4.85 (s, C_5H_5) 2.01 (s, CH_3), 1.67 (d, J = 7 Hz, CH_3); **10**, δ 12.08 (s, μ-CH), 5.02 (s, =C*H*H), 4.90 (s, C_5H_5), 4.71 (s, =CH*H*), 2.64 (q, J = 7.3 Hz, CH_2), 1.28 (t, J = 7.3 Hz, CH_3). ^1H NMR (CD_2Cl_2): **11**, δ 11.73 (s, μ-CH), 4.73 (s, C_5H_5), 4.31 (s, C_5H_5), 2.05 (s, CH_3), 1.18 (d, J = 6.6 Hz, CH_3), −1.07 (q, J = 6.6 Hz, =CHMe); **12**, δ 11.75 (s, μ-CH), 4.76 (s, C_5H_5), 4.39 (s, C_5H_5), 1.73 (m, CH_2), 1.27 (m, CH_3), −1.46, −1.47 (=C*HH*).

Reaction of Cyclohexene with 1 and 1-*d*. Cyclohexene (0.11 atm, 278 mL, 1.2 mmol) was condensed into a stirred suspension of **1** (130 mg, 0.269 mmol) in CH_2Cl_2 (20 mL) at −78 °C. The reaction mixture was warmed to ambient temperature, and solvent was evaporated under high vacuum. The residue was dissolved in acetone (3 mL). Diethyl ether (10 mL) was added, and the resulting precipitate was filtered, washed with ether (3 × 5 mL), and dried under vacuum to give a 1.4:1.0 mixture of **13** and **14** (120 mg, 80%). ^1H NMR (acetone-d_6): **13**, δ 5.72 (C_5H_5), 5.24 (m, μ-CCH), 2.79 (m, CH_2), 2–1.5 (m, CH_2); **14**, δ 11.96 (μ-CH), 5.67 (C_5H_5), 2.66 (t, J = 6 Hz, CH_2), 2.0–1.5 (m, CH_2). IR (Nujol): 2051 (s), 2012 (s), 1995 (w), 1870 (m), 1840 (m) cm^{-1}.

Similarly, reaction of cyclohexene (0.73 mmol) with **1**-*d* (0.423 mmol) gave a 1.4:1.0 mixture of **13**-*d*:**14**-*d* (73%). $^2H\{^1H\}$ NMR (acetone): δ 2.7, 1.9.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}\overline{CCH_2CH_2CH_2CH_2CH_2})$ (15). A saturated aqueous solution of $NaHCO_3$ (5 mL) was added to a stirred solution of **13** and **14** (250 mg, 0.44 mmol) in acetone (10 mL) and ether (20 mL). After 30 min, water (20 mL) was added to facilitate phase separation. The red ether phase was separated, and the aqueous phase was extracted with ether. The combined ether solutions were dried ($MgSO_4$), filtered, and concentrated. Column chromatography (activity III alumina, 2.5:1 hexane/ether) gave bright red **15** (129 mg, 70%). ^1H NMR (acetone-d_6: δ 4.94 (s, C_5H_5), 2.92 (m, 4 H, =CCH_2), 1.82–1.56 (m, 6 H). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 270.5, 256.0 (μ-C, μ-CO), 212.1 (CO), 147.2 (=C), 86.9 (C_5H_5), 39.9 (=CCH_2), 29.0 (=CCH_2CH_2), 27.6 (=$CCH_2CH_2CH_2$). IR (CH_2Cl_2): 1990 (s), 1951 (w), 1782 (m) cm^{-1}. HRMS for $C_{20}H_{20}Fe_2O_3$: calcd, 420.0105; found, 420.0112. Anal. Calcd: C, 57.19; H, 4.80. Found: C, 57.18; H, 4.82.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}\overline{CCHDCH_2CH_2CH_2CH_2})$ (15-*d*). A saturated aqueous solution of $NaHCO_3$ (0.5 mL) was added to a stirred solution of **13**-*d* and **14**-*d*, (130 mg, 0.23 mmol) in acetone (20 mL). Solvent was evaporated under vacuum, and the residue was extracted with ether (20 mL) and filtered. Evaporation of ether gave red crystalline **15**-*d* (70 mg, 73%). ^1H NMR (acetone-d_6): δ 4.94 (s, C_5H_5), 2.91 (m, 3 H, CH_2, CHD), 1.9–1.5 (m, 6 H). $^2H\{^1H\}$ NMR (acetone): δ 2.90 (=CCHD). HRMS for $C_{20}H_{19}DFe_2O_3$: calcd, 421.0168; found, 421.0180.

Reaction of Cyclopentene with 1. Cyclopentene (70 μL, 0.80 mmol) was added to **1** (134 mg, 0.277 mmol) in CH_2Cl_2 (5 mL) at −78 °C. Recrystallization from acetone–ether gave a 1.2:1 mixture of **16** and **17** (115 mg, 75%) as a red-brown solid. ^1H NMR (acetone-d_6: **16**, δ 5.68 (C_5H_5), 5.5 (m, μ-CCH), 2.97 (m, $CH(CHH)_2$), 2.2 (m, $CH(CHH)_2$), 1.95–1.8 (m, 4 H); **17**, δ 12.12 (μ-CH), 5.66 (C_5H_5), 2.73 (t, J = 7 Hz, =CCH_2), 1.95–1.8 (m, 4 H), 1.69 (t, J = 6.5 Hz, =CCH_2).

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}\overline{CCH_2CH_2CH_2CH_2})$ (18). The products from the reaction of cyclopentene (8.81 mmol) with **1** (0.83 mmol) were dissolved in acetone (20 mL), and a saturated aqueous solution of $NaHCO_3$ (1.0 mL) was added. Solvent was evaporated, and the resulting solid was extracted with 20 mL of ether and filtered. The solution was concentrated to 2 mL, and hexane (10 mL) was added to give **18** (275 mg, 81%) as a red precipitate. ^1H NMR (acetone-d_6): δ 4.93 (s, C_5H_5), 3.25 (m, 2 H, =CC*H*H), 2.92 (m, 2 H =CCH*H*), 1.84 (m, 4 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 270.2, 253.0 (μ-C and μ-CO), 211.7 (CO), 149.4 (μ-C=C), 86.7 (C_5H_5), 38.3 (=C*C*), 28.7 (=CC*C*). IR (CH_2Cl_2): 1985 (s), 1947 (w), 1780 (m) cm^{-1}. HRMS for $C_{19}H_{18}Fe_2O_3$: calcd, 405.9954; found, 405.9989.

Reaction of trans-1-Propenylbenzene with 1 and 1-*d*. *trans*-1-Propenylbenzene (70 μL, 0.53 mmol) was added to a stirred suspension of **1** (210 mg, 0.43 mmol) in CH_2Cl_2 (35 mL) at −78 °C. The reaction mixture was warmed to room temperature, and the solution was concentrated to 8 mL by evaporation

of CH_2Cl_2 under high vacuum. Diethyl ether (15 mL) was added, and the resulting precipitate was filtered, washed with diethyl ether (2 × 5 mL), and dried under vacuum to give a 4:3:2 ratio of **19**, **20**-*E* and **20**-*Z* (215 mg, 82%) as a dark reddish brown solid. ^1H NMR (acetone-d_6): **19**, δ 7.65–7.3 (m, C_6H_5), 5.78 (s, C_5H_5), 5.6 (m, μ-CCH), 3.9 (d, J = 13 Hz, C*H*H), 3.2 (d, J = 13 Hz, CH*H*), 1.68 (d, J = 6.7 Hz, CH_3); **20**-*E*, δ 12.27 (s, μ-CH), 7.65–7.3 (m, C_6H_5), 5.81 (s, C_5H_5), 3.91 (s, CH_2), 1.27 (s, CH_3); **20**-*Z*, δ 12.01 (s, μ-CH), 7.65–7.3 (m, C_6H_5), 5.75 (s, C_5H_5), 2.83 (s, CH_2), 2.26 (s, CH_3). IR (CH_2Cl_2): 2037 (s), 2016 (s), 2005 (w), 1851 (m) cm^{-1}.

Similarly, reaction of *trans*-1-propenylbenzene (0.46 mmol) with 1-*d* (0.24 mmol) gave a 4:3:2 mixture of **19**-*d*:**20**-*E*-*d*:**20**-*Z*-*d* (110 mg, 77%) as a red-brown solid. $^2H\{^1H\}$ NMR (acetone): δ 3.9, 3.3, 2.8.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_3)CH_2C_6H_5)$ (21). A saturated aqueous solution of $NaHCO_3$ (2 mL) was added to a stirred solution of **19**, **20**-*E*, and **20**-*Z* (210 mg, 0.35 mmol) in acetone (40 mL). After 20 min, solvent was evaporated and the resulting solid was purified by column chromatography (alumina, 3:1 hexane/CH_2Cl_2) to give **21** (126 mg, 80%) as red crystals. ^1H NMR (acetone-d_6): δ 7.5–7.2 (m, C_6H_5), 5.04, 4.97 (C_5H_5), 4.30 (d, J = 15.1 Hz, C*H*H), 4.12 (d, J = 15.1 Hz, CH*H*), 2.33 (s, CH_3). ^{13}C NMR (CD_3NO_2): δ 274.2, 262.7 (μ-CO, μ-C), 214.1, 213.9 (CO), 143.8, 141.8 (ipso, μ-C=*C*), 129.8, 129.6 (d, J = 160 Hz, C_6H_5), 126.9 (d, J = 163 Hz, C_6H_5), 88.8 (d, J = 178 Hz, C_5H_5), 49.5 (t, J = 123 Hz, CH_2), 25.6 (q, J = 129 Hz, CH_3). IR (CH_2Cl_2): 1990 (s), 1952 (w), 1784 (m) cm^{-1}. HRMS for $C_{23}H_{20}Fe_2O_3$: calcd, 456.0105; found, 456.0110.

Similarly, deprotonation of a mixture of **19**-*d*, **20**-*E*-*d* and **20**-*Z*-*d* (0.12 mmol) gave $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_3)CHDC_6H_5)$ (**21**-*d*) (40 mg, 75%). $^2H\{^1H\}$ NMR (acetone): δ 4.26, 4.10.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_2CH_3)_2)$ (22) and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_3)CH_2CH_2CH_3)$ (23). A solution of *trans*-2-pentene (0.13 atm, 235 mL, 1.28 mmol) and **1** (170 mg, 0.35 mmol) in CH_2Cl_2 (25 mL) was warmed from −78 °C to ambient temperature. Recrystallization from acetone–ether gave a brown-red solid (110 mg, 57%). This solid was dissolved in acetone (25 mL) and stirred with aqueous bicarbonate. Column chromatography (alumina, 3:1 hexane/CH_2Cl_2) gave a 1.5:1 mixture of **22** and **23** (60 mg, 42% from **1**). ^1H NMR (acetone-d_6): **22**, δ 4.95 (C_5H_5), 2.87 (m, CH_2), 1.22 (t, J = 7.5 Hz, CH_3); **23**, δ 4.96, 4.94 (C_5H_5), 2.8 (m, CH_2), 2.43 (s, =CCH_3), 1.7 (m, CH_2Me), 1.05 (t, J = 7.5 Hz, CH_2CH_3).

Low-Temperature Reaction of 1 with *trans*-2-Butene. *trans*-2-Butene (0.033 atm, 9.0 mL, 12.4 μmol) was condensed into an NMR tube containing **1** (3 mg, 6.2 μmol) and CD_2Cl_2 (0.34 mL) at −196 °C. The tube was sealed under vacuum and agitated with a Vortex Genie at −78 °C to dissolve **1**. The tube was maintained at −60 °C for 3 h and then centrifuged at −78 °C. The initial ^1H NMR spectrum at −22 °C indicated the presence of ~50% unreacted **1** (δ 22.8, CH) and ~50% alkylidyne complex **2** [δ 2.35 (m, CH_2), 1.80 (d, J = 6.2 Hz, $CHCH_3$), 1.23 (t, J = 7.1 Hz, CH_2CH_3)]; no resonance (≤1%) due to **3**-*E* (δ 11.68 (FeCH)) or **3**-*Z* (δ 11.61 (FeCH)) was observed. When the solution was warmed to −13 °C for ~30 min, resonances assigned to **3**-*E* and **3**-*Z* began to grow in and resonances due to **1** disappeared. After the solution was warmed to room temperature, a 2.3:1.0:1.5 equilibrium mixture of **2**:**3**-*E*:**3**-*Z* was seen by NMR.

Low-Temperature Reaction of 1 with *cis*-2-Butene. *cis*-2-Butene (0.024 atm, 9.0 mL, 8.9 μmol) was condensed into an NMR tube containing **1** (3 mg, 6.2 μmol). After 28 h at −50 °C, the sample was promptly analyzed by ^1H NMR at −30 °C. Analysis of the spectra indicated that less than 5% of **1** remained and that an 85:6:9 mixture of **2**:**3**-*E*:**3**-*Z* was formed. Upon warming to ambient temperature an equilibrium mixture of **2**:**3**-*E*:**3**-*Z* was seen. The small amounts of **3**-*E* and **3**-*Z* are probably due to rearrangement of **2** either during the extended period of time at −60 °C needed to obtain high conversion of **1** or upon unavoidable sample warming in transferring the tube to the NMR spectrometer.

Acknowledgment. Support from the National Science Foundation is gratefully acknowledged. S.R.M. was supported by a fellowship from W. R. Grace. P.J.F. was a National Science Foundation Postdoctoral Fellow. We thank Phillips Petroleum Co. for the generous gift of high-purity *cis*- and *trans*-2-butene.

Steric and Electronic Factors Influencing the Amounts of μ-Alkylidyne and μ-Alkenyl Products Obtained from Reaction of Diiron Methylidyne Complexes with Alkenes

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Received October 16, 1985

The reaction of $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (**1**) with vinylcyclopropane followed by deprotonation with NMe_3 gave $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH{=}CHCHCH_2CH_2)$ (**13**) in 78% yield. Through deprotonation–reprotonation studies and deuterium labeling using 1-*d*, it was determined that 2-methyl-1-butene, 2-methyl-2-butene, and 1-methylcyclopentene gave both μ-alkylidyne and μ-alkenyl complexes as kinetic products in their reaction with **1**. The reaction of **1** with 9,9-dimethyl-10-methylene-9,10-dihydroanthracene, **19**, gave the μ-alkylidyne complex **20** as the major isomer in 71% yield. The reaction of $[(C_5Me_5)(CO)Fe][(C_5H_5)(CO)Fe](\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (**32**) with 1-pentene produced $[(C_5Me_5)(CO)Fe][(C_5H_5)(CO)Fe](\mu\text{-}CO)(\mu\text{-}CCH_2CH_2CH_2CH_2CH_3)^+PF_6^-$ (**33**) in 65% yield. However, the reaction of **32** with isobutylene gave the μ-alkenyl complex $[(C_5Me_5)(CO)Fe][(C_5H_5)(CO)Fe](\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHCH(CH_3)_2)^+PF_6^-$ (**35**) in 82% yield.

The cationic diiron μ-methylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (**1**) reacts with alkenes to form new carbon–carbon bonds and produces either μ-alkylidyne or μ-alkenyl complexes.[1-5] The formation of

0276-7333/86/2305-1879$01.50/0