Mechanism of Carbon-Carbon Bond Formation in the Reaction of 1,2-Disubstituted Alkenes with a Cationic Bridging Methylidyne Iron Complex

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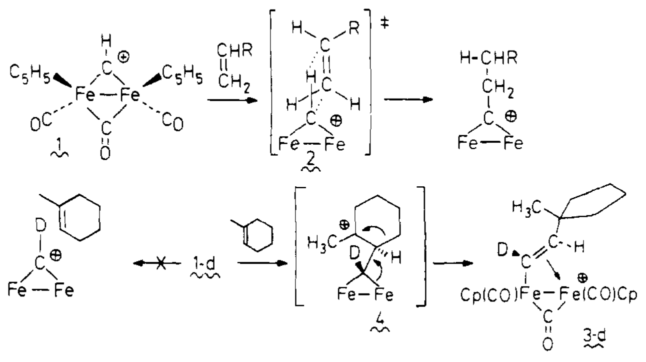
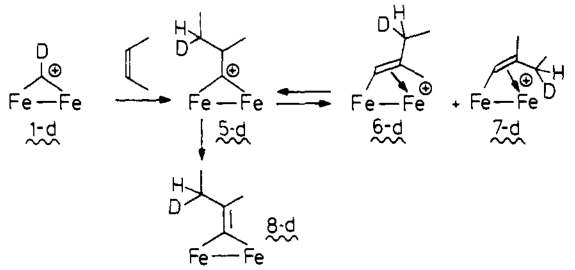
The diiron μ-methylidyne complex $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CH)]^+PF_6^-$ (**1**) reacts with ethylene and with terminal alkenes by adding the methylidyne C–H bond across the carbon–carbon double bond.[1,2] This unprecedented hydrocarbation reaction was proposed to occur via a concerted process involving a transition state **2** in which the C–H bond and C=C bonds are parallel. The reaction of **1** with 1-methylcyclohexene proceeds by an essentially different pathway to produce the μ-vinyl complex $[cis\text{-}(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(trans\text{-}\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHC(CH_3)CH_2CH_2CH_2CH_2)]^+PF_6^-$ (**3**). Formation of **3** was proposed to involve initial generation of a carbocation intermediate **4** that undergoes carbon migration to give ring contracted product **3**. The failure of 1-methylcyclohexene to undergo hydrocarbation may be due to a combination of steric inhibition of formation of the hydrocarbation transition state and of acceleration of a carbocation process by formation of an intermediate tertiary cation.



The reaction of μ-methylidyne complex **1** with *cis*- or *trans*-2-butene, cyclohexene, or other 1,2-disubstituted alkenes led to the formation of mixtures of μ-alkylidyne and μ-alkenyl complexes.[3,4] Unlike *carbon migration* product **3** seen in the reaction of **1** with 1-methylcyclohexene, the μ-alkenyl complexes derived from 1,2-disubstituted alkenes resulted from a net *hydrogen migration.*[3] Initially we proposed that these products were formed by competing hydrocarbation and carbocation pathways. However, we recently discovered that μ-alkylidyne complexes with two carbon substituents on the carbon α to the carbyne center undergo rapid and reversible hydride shifts to form an equilibrium mixture of μ-alkylidyne and μ-alkenyl complexes.[4] The rapid equilibration of the μ-alkylidyne and μ-alkenyl products of the reaction of **1** with 1,2-disubstituted alkenes is consistent with either the hydrocarbation or carbocation mechanism for the key carbon–carbon bond-forming step. Here we present two independent lines of evidence that establish that reactions of **1** with 1,2-disubstituted alkenes occurs via hydrocarbation followed by equilibration.

The reaction of deuterated **1**-*d* with *cis*-2-butene was studied to determine the kinetic product of the reaction. Initial hydrocarbation would place the deuterium label in the methylene unit of the ethyl group of **5** and rearrangement would leave the label in the methylene units of the ethyl groups of **6** and **7**. In contrast,



a carbocation process would lead to deuterium in the α-vinyl position of **6** and **7** and rearrangement to alkylidyne complex **5** would place the deuterium label at the α-methine center of **5**. The reaction of **1**-*d* with excess *cis*-2-butene in CH_2Cl_2 at 0 °C gave a 2.3:1.0:1.5 mixture of $\{cis\text{-}(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CCH(CH_3)CHDCH_3)\}^+PF_6^-$ (**5**-*d*), $\{cis\text{-}(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)((E)\text{-}\mu\text{-}\eta^1,\eta^2\text{-}CH{=}C(CH_3)CHDCH_3)\}^+PF_6^-$ (**6**-*d*), and $\{cis\text{-}(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)((Z)\text{-}\mu\text{-}\eta^1,\eta^2\text{-}CH{=}C(CH_3)CHDCH_3)\}^+PF_6^-$ (**7**-*d*) in 75% isolated yield. Comparison of the NMR spectra of labeled and unlabeled material revealed that the deuterium label was located exclusively on the methylene carbons of the ethyl groups.[5] In the $^2H\{^1H\}$ NMR, resonances were seen only at δ 2.55 and 1.48 for the $CHDCH_3$ groups.

The site of deuterium incorporation was confirmed by conversion of the mixture of **5**-*d*, **6**-*d*, and **7**-*d* to the neutral vinylidene complex $cis\text{-}(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_3)CHDCH_3)$ (**8**-*d*) (80% yield >90% d_1 by mass spectrometry[5]) by treatment with aqueous bicarbonate. Previously, we have shown that this reaction proceeds by deprotonation of the alkylidyne component in the rapidly equilibrating mixture of **5**, **6**, and **7**.[3] If the reaction of **1**-*d* with *cis*-2-butene had proceeded by a carbocation intermediate, no deuterium would have been incorporated into vinylidene complex **8**.

Similarly, the reaction of **1**-*d* with *trans*-2-butene gave a 2.3:1.0:1.5 ratio of **5**-*d*/**6**-*d*/**7**-*d* in which all of the deuterium label was located in the methylene units of the ethyl groups.[6]

The reaction of **1**-*d* with cyclohexene in CH_2Cl_2 at 0 °C gave a 1.4:1 mixture of $\{cis\text{-}(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CCHCHDCH_2CH_2CH_2CH_2)\}^+PF_6^-$ (**9**-*d*) and $\{cis\text{-}(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CCHDCH_2CH_2CH_2CH_2)\}^+PF_6^-$ (**10**-*d*), in 74% yield.[5] Deprotonation of the mixture of **9** and **10** by treatment with aqueous bicarbonate gave vinylidene complex $cis\text{-}(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}C{=}CCHDCH_2CH_2CH_2CH_2)$ (**11**-*d*) (77% yield, >89% d_1[5]). In the $^2H\{^1H\}$ NMR[5] of **11**-*d*, the only resonance observed was at δ 2.90 due to allylic deuterium.

The reaction of **1**-*d* with 1-methylcyclohexene gave the ring-contracted bridging vinyl complex **3**-*d*[5] (80%) with a very different labeling pattern consistent with a carbocation mechanism. The only resonance seen in the $^2H\{^1H\}$ NMR of **3**-*d* is a singlet at δ 11.96 due to the vinyl deuterium.

By studying the reaction of **1** with *trans*-2-butene at −60 °C, we have directly observed μ-alkylidyne complex **5** as the kinetic product of the reaction. A mixture of **1** and *trans*-2-butene (12.4 μmol) in 0.34 mL of CD_2Cl_2 was stirred at −60 °C for 3 h and then analyzed by ^1H NMR at −22 °C.[7] In addition to unreacted **1** (~50%), the ^1H NMR indicated that alkylidyne complex **5** was the major addition product of the reaction (~50%); no **6** or **7** (<1%) were detected. Upon warming the solution to −13 °C, resonances due to the vinyl protons of **6** and **7** grew in at δ 11.68

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(5) See supplementary material for full spectral and analytical characterization.

(6) The mixture of **5**-*d*, **6**-*d*, and **7**-*d* from the reaction of **1**-*d* with *trans*-2-butene was converted to **8**-*d* (45%) by treatment with aqueous bicarbonate.[5]

(7) A mixture of **1** and *cis*-2-butene in CD_2Cl_2 was maintained at −60 °C for 28 h. ^1H NMR analysis at −30 °C indicated less than 5% of **1** remained and a mixture of **5**/**6**/**7** was formed in a 85:6:9 ratio. The small amounts of **6** and **7** are probably due to rearrangement of initially formed **5** during the 28-h time needed to assure complete reaction of **1**.

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and 11.61. After warming to room temperature, ^{1}H NMR indicated a 2.3:1.0:1.5 equilibrium mixture of **5**/**6**/**7**.

We now know that both monosubstituted alkenes and 1,2-disubstituted alkenes react with **1** via a concerted C–H addition pathway. Only when this pathway is blocked by steric hinderance (1-methylcyclohexene and *trans*-stilbene)[8] or when a carbocation can be greatly stabilized (1,1-diphenylethylene)[9] have we seen reactions of **1** with alkenes that involve carbocation intermediates.

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Supplementary Material Available: Spectral and analytical characterizations of compounds **3**-*d* and **5**-*d* to **11**-*d* (2 pages). Ordering information is given on any current masthead page.

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(8) *trans*-Stilbene reacts with **1** to give a μ-alkenyl compound via exclusive phenyl migration.[3]

(9) 1,1-Diphenylethylene reacts with **1**-*d* to give a μ-alkenyl product with the deuterium exclusively at the vinyl position (^{2}H{^{1}H} NMR, δ 12.39). Casey, C. P.; Colborn, R. E.; Meszaros, M. W., unpublished results.

Double-Bond Isomerization Barrier in the 2^1A_g Excited Singlet State of *cis*,*trans*-1,3,5,7-Octatetraene[†]

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The unsubstituted linear polyene 1,3,5,7-octatetraene readily photoisomerizes, even in a crystalline matrix maintained at 4.2 K.[1-3] This photochemical activity opens new opportunities to determine the properties of the potential energy surfaces that control the fate of electronic excitation in the linear polyenes. Activation energies for isomerization on ground- and excited-state potential energy surfaces are of particular interest.

In the dark, a hexane solution of *cis,trans*-octatetraene is stable at room temperature. However, when excited to its lowest energy singlet state, *cis,trans*-octatetraene in *n*-hexane reverts to the trans,trans isomer at a rate of approximately 10^7 s^{-1} at 55 K. This establishes that the isomerization of *cis,trans*-octatetraene to trans,trans-octatetraene can take place on the 2^1A_g excited-state potential energy surface over a barrier of order 1.1 kcal mol^{-1}.

A solution containing roughly equal amounts of *cis,trans*-octatetraene and *trans,trans*-octatetraene in *n*-hexane was prepared from a solution of the *trans,trans* isomer by photolysis and HPLC purification as has been described previously.[1] A 2-μL quartz capillary cell filled with this solution was mounted in a closed-cycle helium refrigerator that has been modified so as to maintain an atmosphere of cold helium gas over the sample and the final cold stage. Fluorescence in the region of the origin of the 2^1Ag to 1^1A_g (S_1 to S_0) transition was excited at 313 nm by a 100-W Hg lamp dispersed through a JY-DH20 double monochromator equipped with 1-mm slits giving a bandwidth of approximately 2 nm. After recording the fluorescence at 8 K, the sample was shielded from the exciting light, heated to an elevated temperature, and then exposed to the photolyzing light source (same as the fluorescence source except that the light flux was quadrupled by doubling the slit width) for 10 min. The intensity of the photolysis source was such that in 10 min the number of photons absorbed was comparable to the number of octatetraene molecules in the sample. After photolysis the sample was recooled to 8 K and the fluorescence was rescanned. Below 10 K the fluorescence spectra of these molecules are well resolved and distinct providing an unambiguous assay for the relative amounts of the cis,trans and trans,trans isomers.[1]

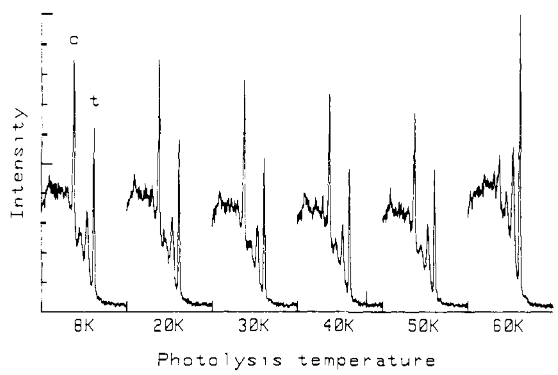

Figure 1. Repeated scans of the fluorescence at 8 K from a hexane solution containing *cis,trans*- and *trans,trans*-octatetraene. In the first scan the fluorescence origin for the cis,trans isomer at 28 646 cm^{-1} is labeled c and that of the trans,trans isomer at 28 737 cm^{-1} is labeled t. Prior to taking each scan the sample temperature was raised to the value that labels that scan and irradiated at 313 nm until roughly one photon had been absorbed for each octatetraene molecule.

The initial fluorescence spectrum and the spectra at 8 K following photolyses at 20, 30, 40, 50, and 60 K are shown in Figure 1. The fluorescence origins for the cis,trans (28646 cm^{-1}) and trans,trans (28737 cm^{-1}) isomers are labeled in the intial scan. The decrease in intensity of both of these features in subsquent spectra is due in part to a slow drift in excitation lamp intensity. For the photolyses at temperatures up to 50 K, the relative intensities of the fluorescence origins of the cis,trans and trans,trans isomers remains nearly constant. After photolysis at 60 K, the cis,trans origin vanishes while the intensity of the fluorescence origin of the trans,trans isomer increases significantly. Clearly, the rate of cis to trans photoisomerization has increased dramatically with increasing temperature. Similar behavior has been observed for octatetraene in *n*-octane.

This dramatic increase in the efficiency of cis to trans photoisomerization with increasing temperature must come from a thermally activated isomerization process on the excited state potential energy surface. We have shown that within 10 ps excitation to vibrationally excited levels of the 1^1Bu state (S_2) is relaxed to a thermal distribution in the vibrational levels of the 2^1A_g state (S_1).[4] Thus, this thermally assisted photoisomerization takes place on the 2^1A_g potential energy surface. The data in Figure 1 show that the rate for this isomerization channel begins to compete effectively with the decay of the excited state at temperatures between 50 and 60 K. At 10 K the lifetime of the 2^1A_g state of *cis,trans*-octatetraene in *n*-hexane is 70 ns and does not strongly depend on temperature between 10 and 30 K.[5] Thus, to good approximation we may set the isomerization rate equal to (70 ns)$^{-1}$ at 55 K. Assuming an Arrhenius preexpontential factor of 10^{10}–10^{13}, the activation energy for this excited state isomerization channel is 1.1 ± 0.4 kcal mol^{-1}. This is approximately a factor of 50 smaller than estimates of the isomerization barrier on the ground-state potential energy surface.[6-8]

From the observed spectra it is clear that, with respect to torsional coordinates, minima on the excited-state potential energy surface are not displaced from the ground-state equilibrium

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