Low-Temperature Study of the Iron-Mediated [4 + 1] Cyclization of Allenyl Ketones with Carbon Monoxide

Matthew S. Sigman and Bruce E. Eaton*

Department of Chemistry, Washington State University, Pullman, Washington 99164-4630

Jerald D. Heise and Clifford P. Kubiak*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

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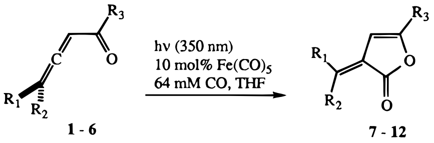
Low-temperature FTIR studies were conducted to probe the mechanism of the $Fe(CO)_5$-catalyzed [4 + 1] cyclization of allenyl ketones and CO to form α-alkylidenebutenolides. Photolysis of $Fe(CO)_5$ in 2-methyltetrahydrofuran (2MeTHF) at 190−230 K produced an iron carbonyl solvento species, $Fe(CO)_4(2MeTHF)$. When the matrix was warmed, $Fe(CO)_5$ was regenerated quantitatively. Photolysis of $Fe(CO)_5$ (in 2MeTHF) at 230 K in the presence of 5-methyl-3,4-hexadien-2-one under similar conditions gave $Fe(CO)_4(2MeTHF)$ initially. Warming the samples regenerates a portion of the $Fe(CO)_5$ while a new band appears at 1767 cm^{-1} corresponding to the α-alkylidenebutenolide **11**. Kinetic experiments at 243 K show no dependence upon CO or allenyl ketone. Reactions in pyridine gave significantly slower rates than THF. This is consistent with rate-determining dissociation of the coordinated solvent to form an unsaturated iron center.

Introduction

Recently, catalytic photochemical [4 + 1] iron-mediated cycloaddition was reported for the synthesis of α-alkylidenebutenolides.[1] Allenyl ketones and allenyl aldehydes (**1**−**6**) react in the presence of CO and a catalytic amount of $Fe(CO)_5$ to form α-alkylidenebutenolides giving high yields and good stereoselectivity (eq 1). The synthetic utility of this reaction motivated us to probe its mechanism in more detail.[2] Herein we report a series of low-temperature FTIR and kinetic experiments undertaken to answer some mechanistic questions involving this catalytic reaction. Despite an extensive amount of photochemistry involving $Fe(CO)_5$ (including matrix isolation studies),[3−5] [4 + 1] cyclization reactions have not been investigated previously.



(1)

		% Yield	*E/Z*
1, 7	$R_1 = C(CH_3)_3$, $R_2 = CH_3$, $R_3 = CH_3$	89	83/17
2, 8	$R_1 = C(CH_3)_3$, $R_2 = CH_3$, $R_3 = H$	62	84/16
3, 9	$R_1 = C(CH_3)_3$, $R_2 = CH_3$, $R_3 = C_6H_5$	76	86/14
4, 10	$R_1, R_2 = CH_3$, $R_3 = H$	54	
5, 11	$R_1, R_2, R_3 = CH_3$	76	
6, 12	$R_1, R_2 = CH_3$, $R_3 = C_6H_5$	64	

Typically, reactions involving $Fe(CO)_5$ require elevated temperatures or UV irradiation. In contrast the reactions depicted by eq 1 occur in the presence of fluorescent light. The apparent high quantum yield (>1) in benzene superficially explains how $Fe(CO)_5$ catalyzed cycloaddition could occur under such mild conditions. The clusters $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$, which have significant absorbance at 350 nm, were shown *not* to catalyze [4 + 1] cycloaddition of **1** with CO.[1] From the previous kinetic analysis and solvent dependence the mechanism shown as Scheme 1 was proposed.

The first step is photochemical activation of $Fe(CO)_5$ generating M**L**. This is consistent with numerous matrix isolation studies[3,4] involving $Fe(CO)_5$. In the presence of the allene substrate **1**, **L** is displaced to give the η^2-complex **A** that is in equilibrium with the metallocycle **B**. These proposed intermediates have precedent in the closely related vinyl ketone,[6] vinyl amide,[7] and allenyl ester[8] iron carbonyl complexes. Step **B** to **C** would require 1 equiv of CO. Reductive elimination could be facilitated by solvent to regenerate M**L** or by CO to give $Fe(CO)_5$. In benzene, the quantum yield at 350 nm is >1 consistent with the resting state of the catalyst being M**L**.

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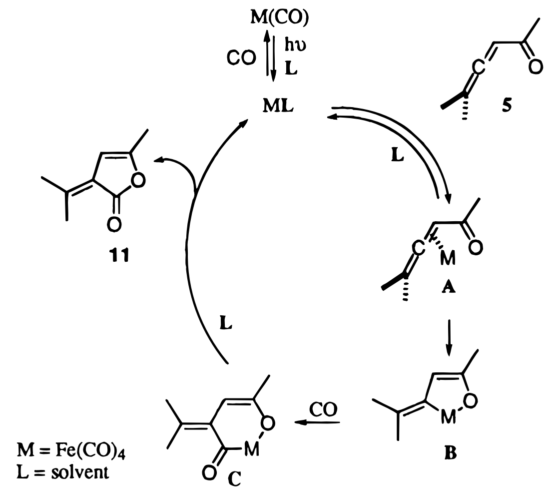
Scheme 1



There remain many unanswered questions about how this iron-catalyzed reaction occurs. The lack of CO dependence at ambient temperature for the reaction in benzene suggests that formation of coordinatively unsaturated intermediates, as in step **B** to **C**, is not rate determining. However at lower temperature (−78 °C) the reaction is slowed significantly. This implies a thermal rate-limiting step is involved. At ambient temperature the coordinating solvent CH_3CN is proposed to stabilize M**L** reducing its catalytic efficiency, perhaps requiring photochemical activation to allow substitution by the allene substrate.[4d] The low-temperature experiments described herein were designed to probe whether any intermediates in the [4 + 1] cycloaddition could be observed directly in 2MeTHF glass. Low-temperature kinetic experiments were performed to determine the dependence of CO, allenyl ketone, and coordinating solvents on the rate of reaction.

Experimental Section

All reactions and manipulations were conducted under a dry argon atmosphere either using an inert atmosphere glovebox or standard Schlenk techniques. All NMR data were recorded on a Bruker AMX (300 MHz ^{1}H). 2-Methyltetrahydofuran, 99%, was purchased from Aldrich and was used without further purification. Iron pentacarbonyl was purchased from Aldrich and was bulb to bulb distilled prior to use. THF-d_8 was purchased from Aldrich and distilled form K/benzophenone prior to use. Pyridine-d_5 was purchased form Aldrich and distilled from CaH_2 prior to use. Samples of the allenyl ketone were prepared as previously reported.[9]

IR Sample Preparation. IR solutions were prepared in a glovebox from freshly degassed 2MeTHF and placed in a cell with CaF_2 windows with a path length of 0.05 mm. Typical concentrations of the reaction components were 50 mM in $Fe(CO)_5$ and 150 mM in **5**.

Experimental Design and Apparatus. The experiments were conducted by irradiating reaction mixtures at temperatures ranging from 77 to 230 K in 2MeTHF followed by a series of annealing sequences that terminated near ambient temperatures. All of the room-temperature and cryogenic FTIR data were obtained on an PE1710 FTIR equipped with a 1700/PC instrument control and IRDM software. Radiation at 355 nm (36−38 mJ/pulse at 10 Hz) was obtained using a Quanta Ray DCR Nd:Yag laser system. Cryogenic temperatures were maintained through the use of an Air Products displex CS-202 cold end and shroud and an Air Products Model 1RO2A compressor module. The shroud was fitted with two quartz windows to allow UV photolysis and two CaF_2 windows along a perpendicular axis to allow IR observation. Temperatures were controlled through an Air Products Model 3700APD-E digital temperature indicator/controller.

Low-Temperature Kinetic Experiments. Experiments were performed in silanized Wilmad 522-PP 5 mm high-pressure or 5 mm J. Young valve NMR tubes. In a typical experiment, 100 μL of a 500 mM THF-d_8 solution of **5**, 100 μL of a 100 mM THF-d_8 solution of $Fe(CO)_5$, and 300 μL of THF-d_8 were added to a tube. The tubes were freeze−pumped−thawed three cycles and pressurized to the desired CO pressure. An initial ^{1}H NMR was taken using the residual THF peaks an internal standard. The tubes were then placed into a Pyrex Dewer flask attached to a circulating constant temperature bath at 243 K and irradiated in a Rayonet photochemical reactor using 350 nm bulbs (10 × 10 W). The reaction was monitored by ^{1}H NMR and pressurized again after collecting each data point.

Results and Discussion

Low-temperature FTIR. Complexes related to M**L** of the type $Fe(CO)_{5-X}(2MeTHF)_X$ ($X = 1, 2$)[4a] and $Fe(CO)_4(L)$ (L = hydrocarbon, N_2, or Xe)[3,4b−d] have been characterized previously by low-temperature FTIR. The carbonyl region of $Fe(CO)_5$ in 2MeTHF shows two bands in the FTIR spectrum, one at 2020 cm^{-1} (A_2) and a more intense band at 1997 cm^{-1} (E). The allenyl ketone **5** has two absorbances, one at 1685 cm^{-1} corresponding to the stretching frequency of the carbonyl and a less intense band at 1953 cm^{-1} due to the asymmetric stretch of the allenyl group.[10] The most intense peak corresponding to the alkylidenebutenolide is the carbonyl stretching frequency at 1768 cm^{-1}. The appearance of this band was used to determine if cyclization had occurred.

Experiments were conducted where $Fe(CO)_5$ (50 mM in 2MeTHF) was cooled to 220 K and irradiated for 1 min at 355 nm. The two bands corresponding to $Fe(CO)_5$ decreased by ∼50% relative intensity, and two new bands appeared at 2052 cm^{-1} (w, sharp), and 1939 cm $^{-1}$ (s, broad). The reaction mixture was annealed, and an IR spectrum was obtained at each of the following temperatures: 240, 262, and 289 K (Figure 1). Over this temperature gradient the intensity of the two bands increased until there was essentially a quantitative reconversion to $Fe(CO)_5$. The complex responsible for the bands at 2052 and 1939 cm^{-1} was assigned to $Fe(CO)_4(2MeTHF)$. This is similar to the findings of Black and Braterman.[4a]

Reaction mixtures containing $Fe(CO)_5$ and **5** in 2MeTHF photolyzed at 77 K resulted in the formation of the solvento species $Fe(CO)_4(2MeTHF)$. Spectra taken before photolysis showed all the bands corresponding to the individual starting materials are clearly present and do not appear to undergo any type of complex formation. Extended irradiation (5−10 min) shows a new band appearing at 1892 cm^{-1} assigned to $Fe(CO)_3(2MeTHF)_2$.[4a] The formation of these species in inert gasses and hydrocarbons at low temperatures has also been demonstrated by the work of Poliakoff,[3a,b] Turner,[4b] Stolz,[4c] and Newlands.[4d] Formation of **11** was not observed. Continued irradiation during warming from 77 to 140 K did not produce **11**.

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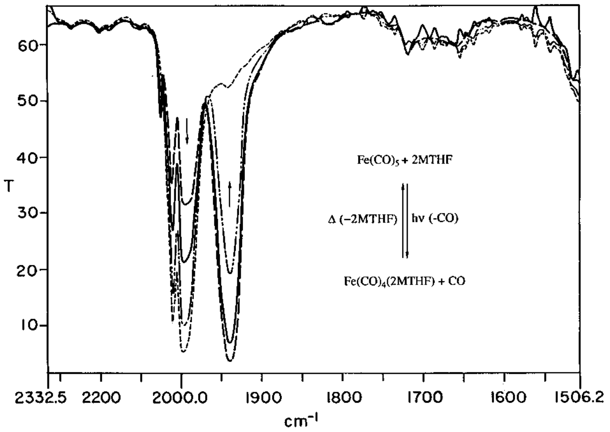

Figure 1. IR spectra for Fe(CO)5 (0.050M) in 2MTHF: — — = photolyzed at 355 nm for 1 min at 220 K; — = probed warmed to 240 K; — ••— = probe warmed to 262 K; - - - = probe warmed to 289 K.

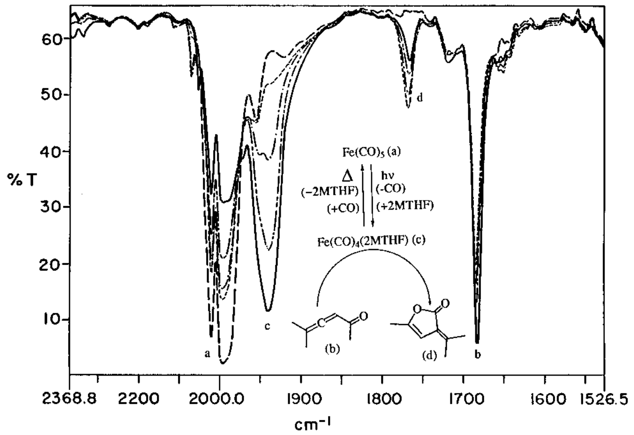

Figure 2. IR spectra for Fe(CO)5 (0.051 M) and 5 (0.15 M) in 2MTHF: — — = no photolysis, 230 K; — = photolysis (355 nm) for 2 min; 230 K, — ••— = probe warmed to 265 K; — •— = probe warmed to 275 K; - - - = probe warmed to 285 K.

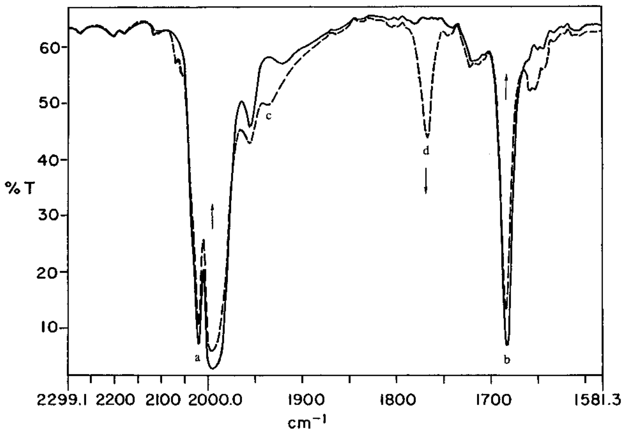

Figure 3. IR spectra: — = Fe(CO)$_5$ + **5** before photolysis; --- = after photolysis and warming sequence; (a) Fe(CO)$_5$, (c) **5**, (d) **11**.

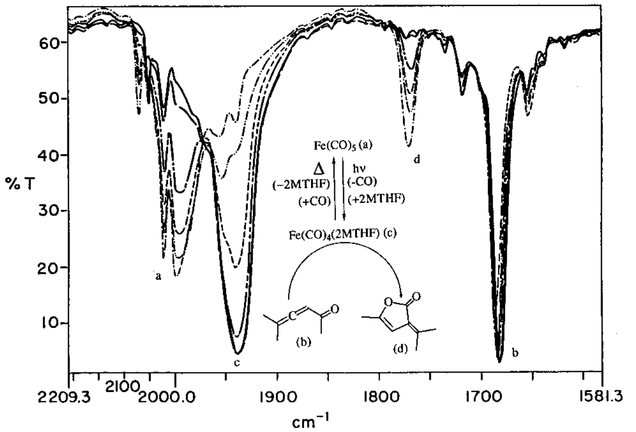

Figure 4. IR spectra for Fe(CO)5 (0.050 M) + 5 (0.15 M) in 2MTHF: s = photolysis (355 nm) for 2 min at 190 K; — — = probe warmed to 231 K; — -- — = probe warmed to 264 K; --- = probe warmed to 275 K; — ••— = probe warmed to 285 K; —•— = probe warmed to 318 K.

The problems experienced in achieving intermolecular reactions at these temperatures are inherent to the matrix, where the slow rates of diffusion inhibit the union of the reacting species. At these temperatures, the cage effect[5d,g] of the glass matrix enhances recombination of CO with its respective iron carbonyl fragment. At 77 K, warming the sample to allow for diffusion and complexation of the substrate resulted only in re-forming Fe(CO)$_5$.

When solutions containing **5** (150 mM) and Fe(CO)$_5$ (50 mM) in 2MeTHF were irradiated at 230 K, initially Fe(CO)$_4$(2MeTHF) was generated along with **11**. Some of the Fe(CO)$_5$ was regenerated, and the peak corresponding to the cycloadduct **11** increased in intensity as the reaction mixture was annealed (Figure 2). Figure 3 shows a spectrum of the reaction mixture before photolysis and a spectrum at the end of the annealing process. There is a net loss of the allenyl ketone and Fe(CO)$_5$, but most importantly there is a new band at 1768 cm^{-1} which corresponds to cycloadduct **11**. It should be noted, that unlike previous studies of this reaction, there were no additions of CO to the reaction mixtures requiring 1 equiv of CO to be scavenged from Fe(CO)$_5$. It is reasonable to assume that the remaining Fe(CO)$_4$ fragment exists as a 2MeTHF solvento species. This notion is supported by the shoulder (labeled c) seen in the dashed IR spectrum in Figure 3 which is in the area where Fe(CO)$_4$(2MeTHF) has been observed. Also note that there is a small shoulder at 2068 cm^{-1} indicating that at these high concentrations of iron that some of the dinuclear iron cluster ($C_{16}H_{16}Fe_2O_7$), whose X-ray structure has been determined,[1] was formed.

In an attempt to observe other intermediates along the [4 + 1] cycloaddition path, another set of experimental conditions were employed in treating Fe(CO)$_5$ with **5**. The initial temperature during irradiation was changed to 190 K. The FTIR spectrum, shown by a solid line (Figure 4) after 2 min of photolysis at 190 K, showed a trace of cycloaddition product **11**. Annealing the matrix to 231 K does not allow **11** to form at an appreciable rate. As the probe was warmed to 264 K, a peak corresponding to the alkylidenebutenolide starts to increase in intensity. As the probe was warmed further, the concentration of **11** increases. Likewise the bands corresponding to Fe(CO)$_5$ increase due to the recombination of CO with Fe(CO)$_4$(2MeTHF).

Low-Temperatures Kinetics. The matrix FTIR data clearly established the formation of Fe(CO)$_4$(2MeTHF). It was unclear whether the allenyl ketone entered the iron coordination sphere by a dissociative or associative mechanism. It was therefore of interest to determine if there was a allenyl ketone concentration dependence on the rate of [4 + 1] cycloaddition at low

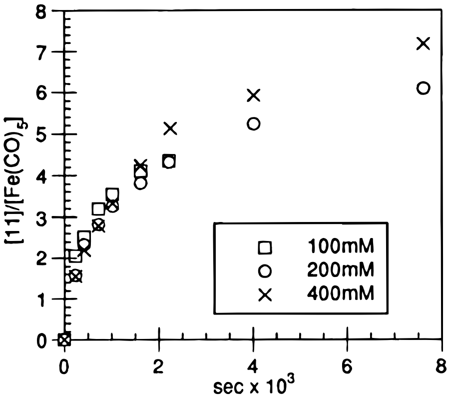

Figure 5. Dependence of [**5**] on the rate of [4 + 1] cycloaddition at 243 K under continuous irradiation at 350 nm.

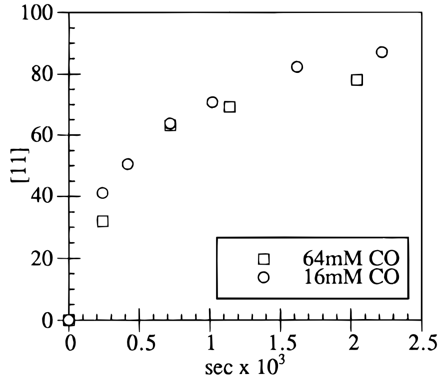

Figure 6. Dependence of CO concentration on the rate of [4 + 1] cycloaddition at 243 K under continuous irradiation at 350 nm.

temperature. Experiments were performed in low-pressure NMR tubes irradiated at 350 nm and cooled to 243 K. No rate dependence was observed for 5 turnovers of **5** based on Fe(CO)$_5$ concentration in THF[11] (Figure 5). This rules out rate-determining associative coordination of **5** in the thermal step after photochemical activation.

In a review of Scheme 1, three explanations remained for the rate-determining step in the low-temperature [4 + 1] cycloaddition of **5** with CO: First, the dissociation of the THF in Fe(CO)$_4$THF; second, CO insertion to generate metallocycle **C**; third, reductive elimination to give the product and re-form M**L**. To rule out that the CO insertion step was rate limiting at 243 K, the kinetics were measured at [CO] = 16 and 64 mM in THF-d_8 to 80% conversion (Figure 6). Within experimental error there is no CO dependence on the rate of reaction over this range of CO concentrations.

Thus far the data suggested that the velocity of the reaction was dictated by dissociation of solvent from the photochemically activated species Fe(CO)$_4$S (S = solvent). Supporting this notion was the observation that at ambient temperature in benzene these reactions are autocatalytic while in CH$_3$CN the quantum yield is <1. However, at low-temperature it was still uncertain whether there was a slow thermal step, which could be either dissociation of solvent from Fe(CO)$_4$S or association of solvent to drive reductive elimination. To rule out one of these possibilities **5** was treated at −30 °C with Fe(CO)$_5$ in pyridine-d_5 and irradiated at 350 nm. In pyridine (Figure 7), rates were considerably slower (~90 times) ruling out solvent-driven reductive elimination and consistent with rate-determining loss of solvent from Fe(CO)$_4$S.

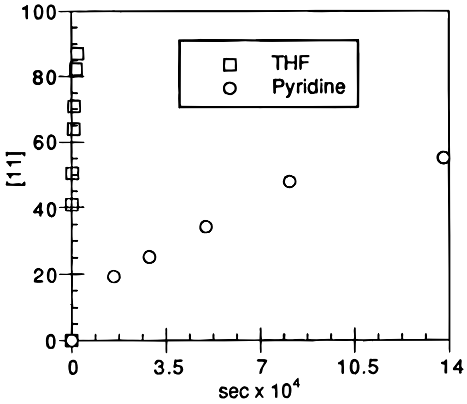

Figure 7. Effect of coordinating solvents on the rate of [4 +1] cycloaddition at 243 K under continuous irradiation at 350 nm.

In summary, under our experimental conditions one intermediate in this catalytic cycle was observable. Photolysis of Fe(CO)$_5$ (<2 min) in 2MeTHF at temperatures in the range of 190−230 K produces Fe(CO)$_4$(2MeTHF). Under appropriate conditions and in the presence of **5**, formation of **11** can be observed. After Fe(CO)$_4$(2MeTHF) has been generated photochemically, a thermal [4 + 1] cycloaddition can occur that in 2MeTHF requires the matrix to be warmed before **11** is formed.[12] In addition, the reaction rate is independent of the concentrations of **5** and CO, ruling out substrate association or CO insertion as the rate-determining steps. The more strongly coordinating solvent pyridine gave a significantly slower rate which is consistent with rate-determining thermal loss of solvent from Fe(CO)$_4$S to form the 16 e$^-$ Fe(CO)$_4$ complex. This solvent dissociation is most likely due to the thermally initiated singlet/triplet interconversion between Fe(CO)$_4$(2MeTHF) and Fe(CO)$_4$.

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[11] THF was used as a solvent to be consistent with the FTIR data.

[12] Poliakoff and Turner[3a] have shown that the dissociation of N$_2$ from Fe(CO)$_4$(N$_2$) can be achieved by IR irradiation of a Nernst glower. Although our experiments showed that Fe(CO)$_4$((2MeTHF) was stable in the IR beam for hours, warming of our samples gave enough thermal energy for the dissociation of solvent.