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Low-Temperature Photochemistry of Matrix-Isolated $Fe(CO)_4$ Complexes of α,β-Unsaturated Esters: C=C vs. Ester Group Coordination

Wolfgang Gerhartz, Friedrich-Wilhelm Grevels,* and Werner E. Klotzbücher*

Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim a.d. Ruhr, Federal Republic of Germany

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Photolysis of various (η^2-olefin)$Fe(CO)_4$ complexes of α,β-unsaturated esters in low-temperature matrices shows that in all cases detachment of CO is the predominant photoreaction. However, instead of the expected (η^2-olefin)$Fe(CO)_3$ species three other $Fe(CO)_3$ complexes are observed, in which the ester group is involved in bonding to the metal. Spectroscopic data indicate bonding of the organic ligand to the $Fe(CO)_3$ moiety (a) in a η^4-1-oxadiene type fashion, (b) via C=C double bond and the ester O—R group, and (c) solely via the ester carbonyl group. Under selective irradiation conditions haptotropic rearrangements involving these three complexes take place. For comparison the photolytic behavior of a (η^4-vinyl ketone)$Fe(CO)_3$ complex was investigated. Furthermore, studies in nitrogen-containing matrices aid in the assignments. In carbon monoxide containing matrices the photolytic detachment of the olefinic moiety, in addition to CO photodissociation, is indicated by the formation of $Fe(CO)_5$.

Introduction

The photochemical behavior of (η^2-olefin)$Fe(CO)_4$ complexes is of general interest with respect to, for example, the formation of (η^2-olefin)$_2Fe(CO)_3$[1,2] and (η^2-olefin)(η^4-diene)$Fe(CO)_2$[3,4] compounds. Complexes of this type are involved in the metal-assisted C–C bond formation[1,3-8] and, e.g., carbonyliron-catalyzed olefin isomerization.[2,9] In the past studies on the initial photoproducts of (η^2-olefin)$Fe(CO)_4$ complexes covered ethene and linear alkenes.[10,11] Our continued interest in carbonyliron-mediated, photoinitiated reactions of olefinic substrates carrying functional groups[3,8,12] led us to investigate more closely a prime example, (η^2-methyl acrylate)$Fe(CO)_4$, by matrix-isolation spectroscopic techniques. For comparison purposes a variety of related complexes were included in this study.

Experimental Section

Details of the experimental equipment used in our photochemical and spectroscopic low-temperature studies have been described previously.[13,14] The setup consists of an Air Products Model CS 202 Displex closed-cycle helium refrigerator, which cools a NaCl spectroscopic window to 10–12 K; the window temperature is monitored separately by a thermocouple embedded in a cavity close to the window center.

The flow of the matrix gases (>99.99%, L'Air Liquide), 1.5–2 mmol h^{-1}, is controlled by a calibrated micrometer needle valve and a vacuummeter assembly; the pressure in the gas inlet line is continuously checked by a separate thermotron gauge.

The samples, purified and transferred under argon, are deposited from a glass capillary with a Teflon valve, held at constant temperature by a Peltier element assembly. When not depositing, samples are kept well below −10 °C. Evaporation rates for each sample are controlled in each experiment by first depositing onto a quartz crystal microbalance (TQ-5/100/5 MHz/30 pF, Telequarz GmbH., Tauberbischofsheim), mounted in good thermal contact to the side of the target window holder.[14] In general the guest:host ratio is better than 1:1000.

Evaporation temperatures for the particular complexes, prepared according to literature procedures, were as follows: tetracarbonyl(η^2-methyl acrylate)iron[15] (**1A**), −18 °C; tetracarbonyl(η^2-methyl (*E*)-2,3-dideuterioacrylate)iron[12] (**1′A**), −18 °C; tetracarbonyl(η^2-methyl (*E*)-3-deuterioacrylate)iron[12] (**1″A**), −18 °C; tetracarbonyl(η^2-dimethyl fumarate)iron[15] (**2A**), 28 °C; tetracarbonyl(η^2-dimethyl maleate)iron[15] (**3A**), −11 °C; tetracarbonyl(η^2-ethyl acrylate)iron[15] (**4A**), −15 °C; tetracarbonyl(η^2-methyl crotonate)iron[19] (**5A**), −10 °C; (η^4-1-buten-3-one)tricarbonyliron[18] (**6B**); −24 °C; tetracarbonyl(η^2-α-methylene-γ-butyrolactone)iron[17] (**7A**), +30 °C; tetracarbonyl(η^2-methyl acrylate)ruthenium[21] (**9A**), −22 °C.

Infrared and UV–visible spectra were taken on the same matrix within a few minutes. Spectrometric data were stored on a Perkin-Elmer 3600 data station. Infrared spectra were recorded on a Perkin-Elmer Model 580 spectrometer, with the visible radiation of the Nernst glower being removed[22] by an Oriel germanium filter. UV–visible spectra were taken on a Perkin-Elmer Model 320 instrument with a variable shutter in the reference beam.

Narrow band (ca. 13 nm) UV–visible irradiation was achieved by combining a 900-W Hg–Xe lamp (Hanovia 977-B 0010) with

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(17) The reaction of α-methylene-γ-butyrolactone (1.47 g, 15 mmol) with $Fe_2(CO)_9$ (3.64 g, 10 mmol) in benzene (50 mL) at room temperature yields **6A** (2.52 g, 94%): yellow crystals from toluene; Fp 98–99 °C.

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Table I. Infrared ($\tilde{\nu}$, cm^{-1}) and UV-Visible (λ, nm) Data of Complex 1A and Its Photoproducts in Various Matrices at 10–12 K

	argon		Xe		CO		CO:Ar = 1:10		^{13}CO:Ar = 1:2	N_2		N_2:Ar = 1:10		*n*-hexane[1]
	IR	UV	IR	UV	IR	UV	IR	UV	IR	IR	UV	IR	UV	IR
1A (η^2-methyl acrylate)-$Fe(CO)_4$	2106.1	≃270	2102	270	2105	...	2105.5	360	2105.5	2107	≃260	2106.3	260	2100.5
	2041.3	≃350	2036		2038		2039.5	≃340	2037	2041	340	2040.8	340	2035
	2026.7		2021		2027.5		2026		2026.3	2028.5		2026.3		2020.5
	2001.4		1995		1997		1998.7		1995.8	1999.2		1999.7		1997.5
	1721		1716		1717		1718			1721		1720		1720
1B	2070.8	≃320	2065		2069.5		2069.5	≃310	2068	2071		2070	320	2064
	2001.5		1995		≃2000		1999		1996	1999		2000		1994
	1986.1		1982		≃1985		1985		1984	1987		1986		1997
	1452/ 1400/ 1252		...		1457/ 1410/ 1260		1455/ 1400/ 1255		...	...		1452/ 1450/ 1252		
1C	2023	≃380	2020	≃380	2025		2022.5	≃400	2023	2023		2023	≃380	...
	1918	>800	1910		1914		1915		1910	1917.2		1917		...
	1910		1902		1905		1906		1903.7	1909.7		1908		...
	1670		1670		...		1670					1670		
1D							2026			2026		2026		
							1972.5			1974		1972		
							1959			1961		1960		
							1946.7			1948		1949		
							1583/ 1375			...				
1E										2259.5				
										2071				
										1999				
										1992				
$Fe(CO)_5$					2037.9/ 2034.7									
					2026.9 (s)									
					2006.3/ 2002.6									
					1995.6 (s)									

a Kratos-Schoeffel GM 252-1 monochromator, whereas for broad-band irradiation the light of a Philips HPK 125-W mercury lamp was passed through air-cooled cutoff filters (Schott).

Results

The starting materials and products were characterized mainly by the carbonyl stretching vibrational pattern of the $Fe(CO)_n$ moieties and the ester carbonyl stretching mode in the infrared, with the electronic absorptions in the UV–visible spectra assisting in the assignments. Molecules are numbered according to specific olefins, while attached letters refer to starting materials or related intermediates with similar infrared bands.

1. Irradiation of Tetracarbonyl(η^2-methyl acrylate)iron (1A). (a) In Argon. Figure 1a displays the four strong CO stretching bands of **1A** isolated in solid argon at 10–12 K, a pattern characteristic of an equatorially substituted L–$Fe(CO)_4$ complex.[19,23] The four bands appear in argon at 2106, 2041, 2026, and 2001 cm^{-1} and shift only slightly in N_2 and CO matrices (Table I). In the ester carbonyl region a single absorption is observed at 1721 cm^{-1}. Below 1500 cm^{-1} two absorptions at 1178 and 633 cm^{-1} are dominant; minor bands appear at 1471, 1438, 1390, 1204, and 1192 cm^{-1}.

The electronic absorption spectrum exhibits a distinct maximum at 270 nm on the shoulder of a much stronger absorption centered at higher energies (cf. spectrum in hexane solution[24]). A further, weak absorption can be located on the tail end at 350 nm.

Upon narrow band irradiation at 335, 265, and, most effectively, 313 nm the four CO stretching bands, the ester carbonyl band, and the other bands of **1A** diminish, while at least four new features grow in the CO region at 2071, 1986, 1918, and 1910 cm^{-1} together with a band at 2138 cm^{-1} associated with matrix-isolated "free" carbon monoxide (Figure 1b). Furthermore, weak features appear at 1670, 1452, 1400, and 1252 cm^{-1}.

The irradiation of **1A** produces two new species as shown by successive irradiation. One, designated **1B**, appears first, rises quickly in intensity, and reaches a steady state upon prolonged irradiation. This species is characterized by three CO stretching vibrations at 2071, 2001, and 1986 cm^{-1}, with the 2001 cm^{-1} feature coinciding with the 2001 cm^{-1} band of **1A**. The second species, designated **1C**, appears later than **1B** and then rises quickly in intensity, until a steady state is reached. This species is characterized by two strong bands at 1918 and 1910 cm^{-1} and a third, weaker feature, hidden beneath the 2025 cm^{-1} band of **1A** but proven beyond doubt in the computer-assisted subtraction spectra (Figure 1c) and in experiments, where **1A** had been converted nearly quantitatively.

Concomitant with these changes in the infrared spectra the UV–visible absorptions of **1A** at 270 and 350 nm diminish, parallelled by the growth of two broad, weak absorptions centered around 320 and 400 nm (Table I).

Upon subsequent long-wavelength irradiation at 435 nm (or even beyond 610 nm) **1B** and **1C** behave distinctly different: all features associated with **1C** diminish in intensity, whereas the bands associated with **1B** grow slightly and a significant portion of the starting material **1A** is recovered (Figure 1d). Parallel changes in the IR region below 1700 cm^{-1} and in the UV–visible spectra allow us to assign the 1670 cm^{-1} band and the 400 nm absorption to **1C**.

At first sight these results are somewhat surprising. From previous experience one might expect that photodetachment of CO from **1A** would yield the coordinatively

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[23] Darensbourg, D. J.; Nelson III, H. H.; Hyde, C. L. *Inorg. Chem.* **1974**, *13*, 2135.

[24] Grevels, F.-W.; Koerner von Gustorf, E.; *Justus Liebigs Ann. Chem.* **1975**, 547.

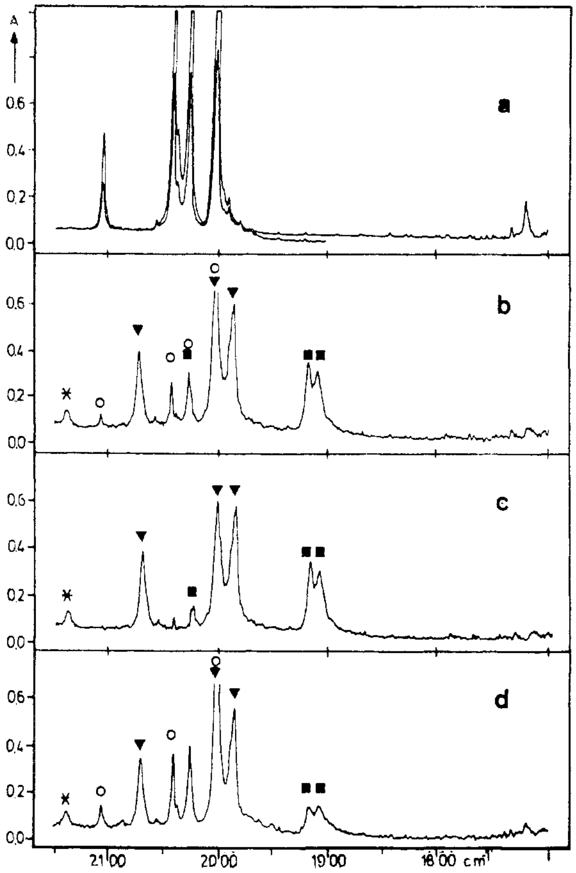
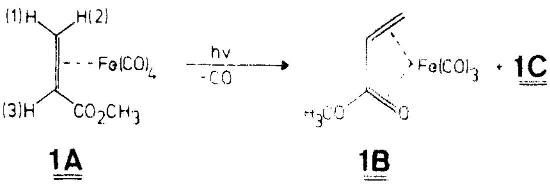


Figure 1. Infrared absorption spectra from experiments with complex 1A in an argon matrix: (a) after 3.5- and 5-h deposition, respectively; (b) after subsequent 100-min irradiation at 265 nm; (c) subtraction plot, spectrum b − 0.12 × spectrum a; (d) after subsequent 90 min irradiation at 435 nm. (Assignments: ○, 1A; ▼, 1B; ■, 1C; *, "free" CO.)

unsaturated species (η^2-methyl acrylate)Fe(CO)$_3$, by analogy with the photoreaction of (η^2-ethene)Fe(CO)$_4$ in low-temperature matrices.[10,11] However, comparison of the respective CO stretching data as well as the fact that neither **1B** nor **1C** exhibit any longer the ester carbonyl vibration in the original region makes it rather unlikely that either of these two species can be the (η^2-olefin)Fe(CO)$_3$ complex. On the other hand, the CO band pattern associated with **1B** resembles strongly, apart from a small shift to higher frequencies, that of (η^4-methyl acrylate)-Fe(CO)$_3$, which has been observed to exist in solution[1] in equilibrium with (η^2-methyl acrylate)$_2$Fe(CO)$_3$ and which has been proven by ^{1}H NMR spectroscopy to contain the acrylate ligand coordinated in the η^4-1-oxadiene fashion.[25,26] Furthermore, the analogous Fe(PF$_3$)$_3$ complexes of methyl methacrylate and related olefins[27] exhibit the ester carbonyl vibration around 1350–1400 cm^{-1}, close to the 1400 cm^{-1} feature of **1B**. These results suggest that photolytic loss of CO from **1A** is accompanied, at least in part, by side-on coordination of the ester carbonyl group.

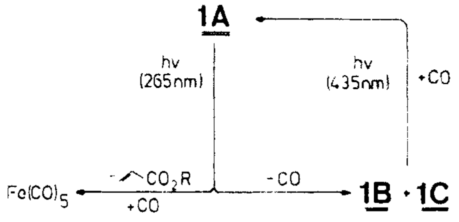
It remains to elucidate the identity of the second species **1C**. One possibility, not to be neglected, is that one of the bands in the region >1900 cm^{-1} might be associated with a M–H rather than a CO stretching mode; metal insertion into vinylic C–H bonds is well documented, e.g. in rhenium carbonyl photochemistry.[28,29] However, photolysis of the



deuterium-labeled complexes **1′A** [H(1), H(3) = D] and **1″A** [H(2) = D] gave the same results as that of **1A**. Consequently, this possibility can be excluded.

(b) In Carbon Monoxide Containing Matrices. Having established that detachment of CO is the primary photoreaction of **1A** in argon the behavior in reactive matrices, particularly in carbon monoxide and dinitrogen, is of great interest.

Short-wavelength (265 nm) or broad-band (HPK lamp) irradiation of **1A**, isolated in neat carbon monoxide, again yields species **1B** and **1C** (Table I), although to a smaller extent. In addition, a new ester carbonyl band appears at 1730 cm^{-1} and the two bands of **1A** at 2027 and 1997 cm^{-1} broaden slightly. Upon subsequent long-wavelength irradiation (435 nm) these two features become more distinctly observable while the bands of **1B** and **1C** gradually vanish. Subtraction of the spectra shows that two new CO stretching absorptions have grown in at approximately 2027 and 2000 cm^{-1}, frequencies characteristic for pentacarbonyliron (Table I). Obviously photolytic detachment of both methyl acrylate or CO is observable in a CO matrix, the latter process being reversible under these conditions.



In a number of spectra from experiments in both argon and neat CO matrices we had noticed a weak band at 2086 cm^{-1} and some other minor features in the 1970 cm^{-1} region. While the behavior of the former could not be safety correlated with other spectral changes, the development of the latter bands could be promoted by selective irradiation in experiments employing argon-diluted carbon monoxide (Ar:CO $\simeq$ 10:1) matrices.

In detail: Figure 2a displays the CO stretching vibrational region after co-condensing **1A** with Ar:CO $\simeq$ 10:1 for 2 h. Figure 2b shows the results of altogether 70-min narrow-band irradiation at 265 nm. One immediately notices the nearly complete conversion of the starting material **1A** (only a trace of the 2039 cm^{-1} absorption remains visible) and the excellent resolution of the formerly hidden bands (cf. Figure 1b) of **1B** and **1C** at 2001 and 2023 cm^{-1}, respectively. These bands are overlapping with those of Fe(CO)$_5$, which is formed in small amounts as indicated by changes in the intensity ratios of all the bands associated with **1B** and **1C**.

Contrary to the results in pure argon, subsequent long-wavelength irradiation (λ > 610 nm) does not lead to recovery of **1A** but instead yields a new product, **1D**, exhibiting four characteristic bands at 2026, 1972, 1959, and 1946 cm^{-1} (Figure 2c) as well as two new absorptions

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[25] Grevels, F.-W.; Habilitationsschrift, Universität Duisburg, 1981.

[26] ^{1}H NMR data of **1B** (toluene-d_8, −5 °C): δ 1.67, 1.37 (CH$_2$=), 4.40 (=CH—), and 3.06 (CH$_3$); J(gem) = 1.5 Hz, *J*(cis) = 6.2 Hz, and *J*(trans) = 8.2 Hz.

[27] Kruck, T.; Knoll, L. *Chem. Ber.* **1973**, *106*, 3578.

[28] Franzreb, K. H.; Kreiter, C. G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 1058.

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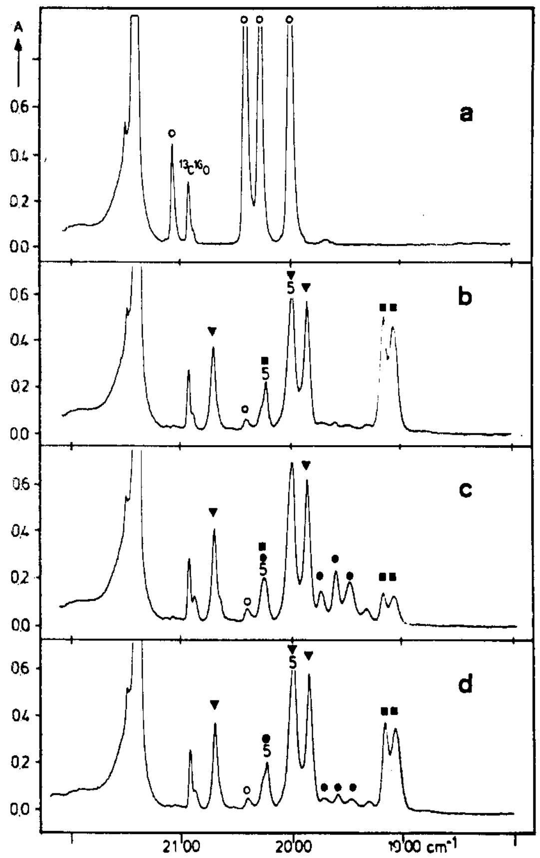
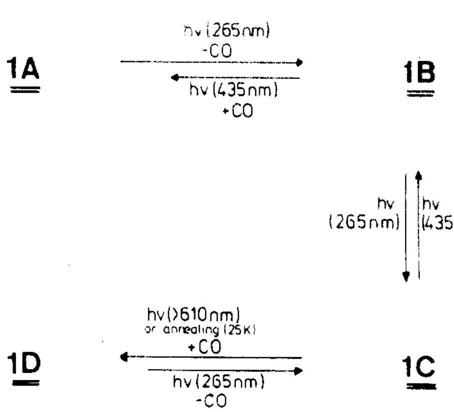


Figure 2. Infrared absorption spectra from experiments with complex 1A in a 10:1 argon-diluted CO matrix: (a) after 2-h deposition; (b) after subsequent 70-min irradiation at 265 nm; (c) after subsequent 2-h irradiation with λ > 610 nm; (d) after subsequent 5-min irradiation at 265 nm. (Assignments: ○, 1A; ▼, 1B; ■, 1C; ●, 1D; 5, Fe(CO)$_5$.)

at 1583 and 1375 cm^{-1}. A further band at 1931 cm^{-1} belongs to a different species, most probably Fe(CO)$_3$ with known absorptions at 2042 and 1935 cm^{-1} in argon.[30] The same results, formation of **1D** and simultaneous disappearance of **1C**, could be obtained by annealing the matrix at 20–25 K. Regardless of the method employed, the new species **1D** vanishes upon short-wavelength irradiation at 265 nm in favor of re-formation of **1C** (Figure 2d), which suggests that **1C** is coordinatively unsaturated.



(c) In Dinitrogen-Containing Matrices. Incorporation of N$_2$ from the matrix environment is commonly used to substantiate the existence of a vacant coordination site at a metal center. Short-wavelength (265 nm) irradiation of **1A** in neat dinitrogen again yields first **1B** and then considerable amounts of **1C**, **1D**, and further, unidentified products with weak bands at 1932 and 1877 cm^{-1}. Even after ca. 90% of **1A** has been converted, absorptions in the N$_2$ stretching region are barely above noise level. Subsequent irradiation at 435 nm again leads back to the starting material, but this time the process is accompanied by the emergence of a new species with three CO (2071, 1999, 1992 cm^{-1}) and one N$_2$ (2259.5 cm^{-1}) stretching bands. This product **1E** is probably (η^2-methyl acrylate)Fe(CO)$_3$(N$_2$) as the ester carbonyl absorption of η^2-coordinated methyl acrylate at 1723 cm^{-1} shows an increase in intensity larger than the CO stretching bands of the starting material **1A**. A number of less significant absorptions point to the existence of a second N$_2$-containing species [ν(N$_2$) = 2246 cm^{-1}]; however, the bands in the CO stretching region are not unequivocally assigned.

Table II. Infrared ($\tilde{\nu}$, cm^{-1}) and UV-Visible (λ, nm) Data of Complexes 2A and 3A and Their Photoproducts in Various Matrices at 10–12 K

	argon		N$_2$		CO	
	IR	UV	IR	UV	IR	UV
2A	2116.5	≃275	2118		2117	
	2054.5		2056		2055	
	2047		2047		2046	
	2011.5		2012		2010.5	
	1718.5		1717		1717	
2B	2081	≃320	2082		2080.5	
	2018		2019		2016	
	2003		2004.5		2003	
	1370		1370		1372	
2C	2025	≃440	2020		...	
	1922		1919		≃1915	
	1912		1912		≃1908	
2D	...					
	1978		1978			
	1963		1961			
	1947		1949			
3A	2117	≃260	2117		2115.5	≃260
	2058		2056		2054.5	
	2031		2036.5		2035	
	2012.5		2011		2008.5	
	1720		1717		1714	
3B	2080	≃320	2078		2077	
	2015		2011		2009	
	1996		1998		1996	
3C	2020	430	2020		...	
	1916		1913.5		1911.5	
	1905		1904		1902	

The analogous experiment in argon-diluted dinitrogen (Ar:N$_2$ = 10:1) does not yield a N$_2$-containing complex. Short-wavelength irradiation of **1A** follows the pattern outlined for argon and neat dinitrogen matrices up to the stage of complete conversion to **1B** and **1C**. Again **1D** is formed upon subsequent long-wavelength irradiation or annealing to an extent comparable to the traces observed in argon. However, neither this treatment nor irradiation at 435 nm produces **1E** or any other N$_2$-containing species. Obviously, although CO is present only in the small amount generated by photodissociation from **1A**, with respect to coordination it is strongly preferred over N$_2$ which is present in a large excess.

As stated above, it is evident at this stage that **1C** is a coordinatively unsaturated complex containing the Fe(CO)$_3$ moiety attached in some way to methyl acrylate. Clearly, more information is needed to substantiate any structural assignment. Therefore, various other (η^2-olefin)Fe(CO)$_4$ complexes were investigated.

2. Irradiation of Tetracarbonyl(η^2-dimethyl fumarate)iron (2A) and Tetracarbonyl(η^2-dimethyl ma-

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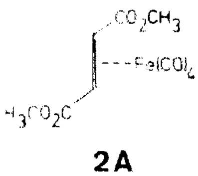
(30) Poliakoff, M. *J. Chem. Soc., Dalton Trans.* 1974, 210.

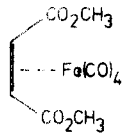
Table III. Infrared ($\tilde{\nu}$, cm^{-1}) and UV-Visible (λ, nm) Data of Complexes 4A–9A and Their Photoproducts in Argon Matrices at 10–12 K

	4		5		6		7		8		9	
	IR	UV	IR	UV	IR	UV	IR	UV	IR	UV	IR	UV
A	2105.2 2040.2 2025 2000 1716	≃260 ≃340	2102.2 2036.7 2018.4 1996.5	270			2107 2044 2020.5 2000.5	265			2127.5 2056 2040.5 2014.5	
B	2069.3 2000 1985.4	320	2064.2 1997 1981.2		2079.2 2013.2 1993.7	310 (420)	2074.5 2010.5 1986				2081 2014 1995.5	
C	2024 1917.3 1909.5	≃380 >800	2022.5 1916.8 1906.6	≃370	2022.5 1921.0 1911.5	... ...	2021 1910 1906	370	... 1914 1905.5			
D	... 1972 1960 1950								... ... 1956.5 1942			
F			2081 2014 1996				2081 2014 2000					
G					1993 1951							

leate)iron (3A). The infrared spectrum of complex **2A** resembles that of **1A** apart from a general blue shift on the order of 10–20 cm^{-1} in the carbonyl stretching bands (Table II, cf. ref 19) and a slight red shift of the ester carbonyl frequency to 1718.5 cm^{-1}. In the electronic spectrum a band at 275 nm dominates on the shoulder of an absorption at higher energy.



2A



3A

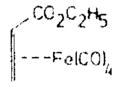
Similar to the studies on **1A**, irradiation into the 275 nm band results in effective liberation of carbon monoxide from **2A** and appearance of two new species with spectral features analogous to those of the major products of **1A**. Consequently, one of these, characterized by absorptions at 2081, 2018, 2003, and 1370 cm^{-1}, is designated as **2B** and the other, with bands at 2025, 1922, and 1912 cm^{-1}, as **2C**. Furthermore, weak absorptions at 1978, 1963, and 1947 cm^{-1} can, by analogy, be assigned to **2D**; the expected fourth band of **2D** at ca. 2020–2030 cm^{-1} is too weak to be distinguishable from other overlapping bands. Subsequent long-wavelength irradiation at 435 nm again leads to partial recovery of the starting material, mainly at the expense of **2C**.

By contrast to the acrylate complex **1A** no trace of any N_2-containing product of **2A** could be detected upon photolysis, even in neat dinitrogen only **2B**, minor amounts of **2C**, and traces of **2D** were observed (Table II).

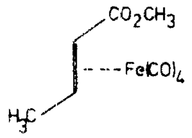
Likewise, **2B** and a small amount of **2C** were formed upon 290-nm irradiation of **2A** in a carbon monoxide matrix, and further photolysis (λ = 435 nm) followed the pattern outlined for **1A**.

No significantly new information could be obtained from the irradiations of the dimethyl maleate complex **3A** in argon, dinitrogen, and carbon monoxide matrices; the data for the photoproducts **3B** and **3C** are summarized in Table II.

3. Irradiation of Tetracarbonyl(η^2-ethyl acrylate)iron (4A) and Tetracarbonyl(η^2-methyl crotonate)iron (5A). Introduction of a further methyl group at the ester moiety (**4A**) or at the olefinic double bond (**5A**) did not significantly alter the photochemical behavior of the complexes.



4A



5A

The results obtained with (η^2-ethyl acrylate)Fe(CO)$_4$ (**4A**) in argon are nearly identical with those of **1A**; the data are summarized in Table III.

Methyl substitution at the C=C double bond causes a red shift of about 4 cm^{-1} in the CO stretching vibrations of **5A** and **5B** in which the C=C unit is coordinated to the metal (Table III, Figure 3a). Interestingly, this effect is much less pronounced in the case of **5C**, giving a first hint that in this type of species the olefinic double bond is not coordinated. Due to this fortunate difference in spectral shifts the previously overlapping bands of type A and C complexes around 2020 cm^{-1} are now clearly resolved (Figure 3b).

Furthermore, the previously unidentified weak feature around 2086 cm^{-1}, observed in the experiments with **1A** and **4A**, appears at 2081 cm^{-1} in the case of **5A** and is greatly enhanced upon long-wavelength irradiation (λ = 435 nm; Figure 3c) following 313-nm photolysis of the starting material. For this reason, and due to the nearly complete disappearance of the overlapping absorptions of **5A**, it is now possible to identify two further bands (2014 and 1996 cm^{-1}), the growth characteristics of which parallel that of the 2081 cm^{-1} feature. This species, designated **5F**, is formed almost exclusively at the expense of **5C**, which is quantitatively recovered upon subsequent 313-nm irradiation (Figure 3d).

The relatively high frequencies of the three CO stretching bands lead us to consider **5F** as a coordinatively saturated tricarbonyliron complex (cf. (η^2-ethene)Fe(CO)$_4$ vs. (η^2-ethene)Fe(CO)$_3$[10,11]). Bearing in mind, furthermore, the stated 5 cm^{-1} red shift of the highest band due to the methyl substituent, we conclude that the C=C double bond is metal-coordinated. However, as **5F** differs from

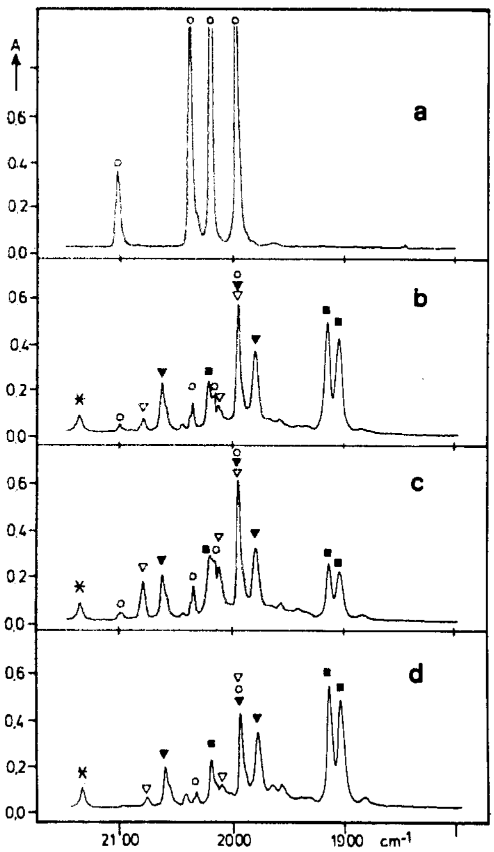
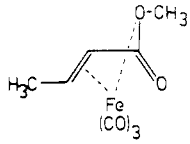
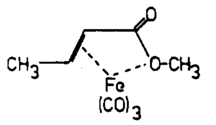


Figure 3. Infrared absorption spectra from experiments with complex **5A** in an argon matrix: (a) after 65-min deposition; (b) after subsequent 7-min irradiation at 313 nm; (c) after subsequent 20-min irradiation at 435 nm; (d) after subsequent 5-min irradiation at 313 nm. (Assignments: ○, **5A**; ▼, **5B**; ■, **5C**; ▽, **5F**; *, "free" CO.)

5B, we suspect that in this case the ester OR moiety is attached to the metal, either as **5F′** or as **5F″**.



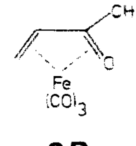
5F'



5F"

4. Irradiation of Tricarbonyl(η^2-buten-3-one)iron (6B) and Tetracarbonyl(η^2-α-methylene-γ-butyrolactone)iron (7A). Further support for the above proposal can be found in the experiments with the α,β-unsaturated ketone complex **6B** where, due to the lack of an ester OR group, formation of type F products is not possible.

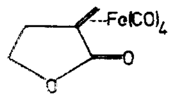
Thus, when **6B** is irradiated at 313 nm in an argon matrix, one does observe a steady growth of three bands assignable to the type **C** species (Table III) and, in subtraction spectra, of two additional bands at 1993 and 1951 cm^{-1}. Assignment of the latter features to a (η^4-oxadiene)$Fe(CO)_2$-type species (**6G**) is aided by comparison with the respective data of (η^4-diene)$Fe(CO_3)$ and (η^4-diene)-$Fe(CO)_2$ compounds.[10] Subsequent long wavelength irradiation (above 435 nm) results in partial recovery of the starting material at the expense of both **6C** and **6G**.



6B

However, at no stage of the experiment could we observe any absorption in the spectral region above ca. 2080 cm^{-1} where the highest frequency band of a type **F** species would be expected to occur (cf. the respective data of **5B** and **5F**, Table III).

When (η^2-α-methylene-γ-butyrolactone)$Fe(CO)_4$ (**7A**) is extensively irradiated in an argon matrix at 313 nm, it is completely converted into the tricarbonyl photoproducts **7B** and **7C** (Table III), with **7C** becoming dominant in the course of the experiment at the expense of **7B**. Two weaker features at 1924 and 1917 cm^{-1} could not be assigned to a particular species. Subsequent annealing up to 25 K does not cause any significant change in the spectrum, whereas longer wavelength irradiation (435 nm) yields a small amount of **7F**. As in this case the alkoxy group is fixed in the s-trans orientation, the analogous species **5F** probably also adopts the structure **5F′** rather than **5F″**.



7A

5. Irradiation of Pentacarbonyliron in the Presence of Methyl Propionate. There remains to ascertain the identity of the type **C** species (Tables I–III). The extremely low CO stretching frequencies and the ready access of **6C** from **6B** point toward a coordinatively unsaturated $Fe(CO)_3$ product. As $Fe(CO)_3$[30] itself or (η^2-olefin)$Fe(CO)_3$[10] can easily be ruled out, the most plausible type of structure left is sole coordination of an ester carbonyl group to the $Fe(CO)_3$ moiety. Involvement of the ester OR group has already been excluded by the appearance of a type **C** species in the case of the butenone complex **6B**.

To substantiate this idea pentacarbonyliron was photolyzed at 313 nm in an argon matrix doped with a saturated ester, methyl propionate ($Fe(CO)_5$:ester:Ar $\simeq$ 1:30:1000). In addition to several features assignable to $Fe(CO)_4$[31] (1973 cm^{-1}) and $Fe(CO)_3$[30] (1936 cm^{-1}) two strong bands grow in at 1914 and 1905.5 cm^{-1}, in good agreement with the data of **1–7C** (Tables I–III); the third, high-frequency band expected for such a species (**8C**) at around 2022 cm^{-1} is hidden by the 2025 cm^{-1} absorption of $Fe(CO)_5$. Whereas **1–7C** were transformed to the (η^4-1-oxadiene)$Fe(CO)_3$-type species **1–7B** upon long-wavelength irradiation, such a process is not possible in this case and is, indeed, not observed. We merely notice the growth of two minor absorptions at 1956.5 and 1942 cm^{-1}, partly resembling the pattern of **1D**, **2D**, and **4D** (Tables I–III) and, therefore, assigned to **8D**.

Parallel to the appearance of the two strong metal carbonyl bands at 1914 and 1905.5 cm^{-1} a weaker feature grows in at ca. 1660 cm^{-1}. This indicates an end-on coordinated ester carbonyl group.[6] Concomitant appearance of two UV–vis absorptions around 360 and 800 nm is analogous to the spectral changes observed for **1C** (Table I).

Discussion

Taking all the experimental evidence into account, we are now in a position to establish a general reaction scheme

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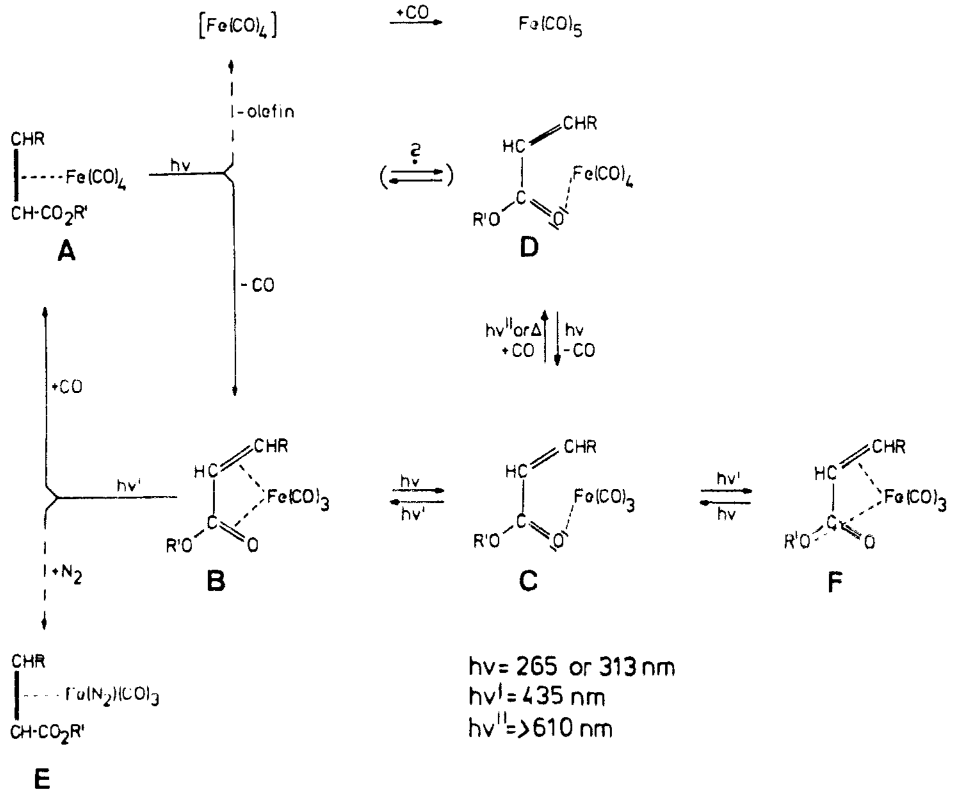
(31) Poliakoff, M.; and Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1974**, 2276.

Scheme I



(Scheme I) for the processes occurring upon irradiation of tetracarbonyliron complexes of α,β-unsaturated esters.

As discussed in detail, essentially all processes are photoreversible. However, there is a pronounced wavelength effect attributed to the specific UV–vis absorptions of the particular species; this results in discrete, wavelength-dependent photostationary states of the system.

The characteristic feature in the UV–vis spectra of $(\eta^2\text{-olefin})Fe(CO)_4$ complexes around 270 nm has been tentatively attributed to a MLCT transition.[24] However, on the basis of the observed photoreactivity, this absorption may also be interpreted in terms of ligand field excitation: e.g., in solution $(\eta^2\text{-methyl acrylate})Fe(CO)_4$ (**1A**) undergoes photosubstitution of both the olefin and a CO ligand.[25] Bearing this in mind one might expect that in low-temperature matrices not only CO-loss products but also the species $Fe(CO)_4$ should be formed. However, in argon matrices photodetachment of the olefin could not be observed; this is most probably due to fast recombination in the matrix cage. Nevertheless, $Fe(CO)_4$ must be an intermediate in the formation of $Fe(CO)_5$ when **1A** is photolyzed in neat carbon monoxide.

To our surprise the expected primary product of CO photodetachment, $(\eta^2\text{-olefin})Fe(CO)_3$,[10,11] was not observed in any of the α,β-unsaturated ester complexes investigated. The first observable product is of type **B**, thus indicating that the ester carbonyl group immediately takes up the free coordination site. Unexpectedly, dechelation of the α,β-unsaturated ester upon further photolysis of **B** occurs in such a way that the C=C moiety is detached from the metal whereas the ester carbonyl group remains coordinated. Although it was demonstrated that, under selective irradiation conditions, the haptotropic rearrangements **A** → **D** and **B** → **F** proceed via the intermediate C, direct conversion pathways cannot entirely be excluded. Short-wavelength irradiation of **A** and **B** may lead to **D** and **F**, respectively; however, as these products are not stable under such conditions, they would not accumulate.

It will be of interest to see to which extent these results can be transferred to the analogous complexes of the other iron triad metals.[32,33] Preliminary experiments with $(\eta^2\text{-methyl acrylate})Ru(CO)_4$ (**9A**) proved the formation of **9B**, whereas photoproducts of type **C**, **D**, and **F** have not been observed.

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Registry No. **1A**, 12287-67-1; **1B**, 51922-76-0; **1C**, 109468-42-0; **1D**, 93169-62-1; **1E**, 109468-40-8; **1'A**, 109468-32-8; **1''A**, 56846-48-1; **2A**, 12287-98-8; **2B**, 109582-12-9; **2C**, 109468-43-1; **2D**, 109468-38-4; **3A**, 12287-97-7; **3B**, 109468-39-5; **3C**, 109582-13-0; **4A**, 12287-82-0; **4B**, 109468-37-3; **4C**, 109468-44-2; **4D**, 109468-35-1; **5A**, 52613-73-7; **5B**, 109468-36-2; **5C**, 109468-45-3; **5F**, 109468-49-7; **6B**, 53535-98-1; **6C**, 109468-46-4; **6G**, 109494-89-5; **7A**, 109468-41-9; **7B**, 109468-50-0; **7C**, 109468-47-5; **7F**, 109494-88-4; **8C**, 109468-48-6; **8D**, 109468-34-0; **9A**, 78319-35-4; **9B**, 109468-33-9; $Fe(CO)_5$, 13463-40-6.

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(32) Grevels, F.-W.; Reuvers, J. G. A.; Takats, J. *J. Am. Chem. Soc.* 1981, *103*, 4069.

(33) Burke, M. R.; Takats, J.; Grevels, F.-W.; Reuvers, J. G. A. *J. Am. Chem. Soc.* 1983, *105*, 4092.