charge-transfer emitting Ru(II) complexes indicate an E-type emission, apparently verifying the effective D_3 symmetry of these complexes and the delocalization of the excited state. Polarization spectra can, for the Zn(II) species, be interpreted as indicating single-ring C_{2v} symmetry with hopping consistent with vibronic $\pi\pi^*$ absorption spectra and published ESR triplet and ESR photoselection data. The excitation depolarization measured in the $\pi\pi^*$ singlet and overlap region for the Ir(III) and Rh(III) complexes leads to an ambiguous interpretation. The best present interpretation may be that the emitting chromophore is a multiring D_3 species but that small perturbations (structural or temperature) may result in the single-ring circumstance (C_{2v} with hopping).

Registry No. [Zn(bpy)$_3$](NO$_3$)$_2$, 29881-78-5; [Ir(bpy)$_3$](NO$_3$)$_2$, 71818-71-8; [Ru(bpy)$_3$](ClO$_4$)$_2$, 15635-95-7; [Ru(phen)$_3$](ClO$_4$)$_2$, 14767-24-9; [Rh(bpy)$_3$]Cl$_3$, 32680-72-1; [Rh(phen)$_3$]Br$_3$, 15378-54-8.

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Low-Temperature Matrix Photochemistry of (1,3-Diene)tricarbonyliron Complexes

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UV photolysis of (η^4-2,3-dimethylbutadiene)Fe(CO)$_3$ and (η^4-butadiene)Fe(CO)$_3$ in inert matrices at 10 K was monitored by IR and UV spectroscopy. Elimination of CO is the predominant photoreaction. In the latter case we also observed the decomplexation of the butadiene ligand and hence the formation of (η^2-butadiene)Fe(CO)$_3$. This product is also obtained during the photolysis of (η^2-butadiene)Fe(CO)$_4$ which is subsequently transformed to (η^4-butadiene)Fe(CO)$_3$. For comparison, (η^2-ethylene)Fe(CO)$_4$ and (η^2-1,3-cyclohexadiene)Fe(CO)$_4$ were photolyzed under analogous conditions. Photolysis of (η^4-1,3-diene)Fe(CO)$_3$ complexes in *nitrogen* matrices gives (η^4-1,3-diene)Fe(CO)$_2$N$_2$; formation of (η^2-butadiene)Fe(CO)$_3$N$_2$ from (η^2-butadiene)Fe(CO)$_4$ requires annealing of the nitrogen matrix subsequent to irradiation.

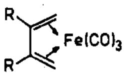
Introduction

Photolysis of binary carbonylmetal complexes in low-temperature matrices and the structures of the resulting carbonyl–metal fragments have been thoroughly invesitgated.[1] Recent studies on a series of carbonylnitrosylmetal[2] and organotricarbonylmetal[3] complexes under analogous conditions revealed a clear-cut discrimination between the different ligands in favor of photoelimination of carbon monoxide. With the provision of such detailed knowledge about primary photoproducts and reactive intermediates, the matrix isolation technique is widely considered as a useful tool with regard to mechanistic problems despite certain limitations and occasional disagreements[4] with reactions in solution.

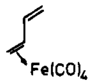
Our interest in optimizing and controlling the photoreactions of (1,3-diene)tricarbonyliron complexes with, e.g., excess 1,3-diene to produce bis(1,3-diene)carbonyliron[5] or with olefins to form C–C coupling products,[6,7] led us to investigate the mechanisms of such processes, in particular the primary photoreactions of (η^4-1,3-diene)tricarbonyliron complexes.

The primary photochemical reactions of (η^4-cyclobutadiene)tricarbonyliron have been thoroughly discussed. From flash photolysis experiments in the gas phase C_4H_4 detachment was concluded to be the major primary photolytic step;[8] however, irradiation in frozen gas matrices[3,9] clearly demonstrates the loss of carbon monoxide, in agreement with the photoreactions in solution.[10,11] Carbonyliron complexes of open chain 1,3-dienes, on the other hand, undergo photosubstitution of both the diene and CO when irradiated in solution in the presence of, e.g., phosphorus ligands.[12]

In this paper we report the IR and UV spectroscopic characterization of various species formed upon irradiation of (η^4-2,3-dimethylbutadiene)tricarbonyliron (**1**) and (η^4-butadiene)tricarbonyliron (**2**) in argon and nitrogen matrices at 10 K.[13] For comparison, the tetracarbonyliron complexes of η^2-coordinated butadiene (**3**, in argon and nitrogen), 1,3-cyclohexadiene (**4**, in argon), and ethylene (**5**, in argon) were similarly photolyzed.



1 (R = CH$_3$)
2 (R= H)



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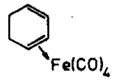

4

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Experimental Section

Low temperatures were achieved by means of a Displex CSW-202 closed-cycle helium cryostat (Air Products) equipped with an APD-IC-1 temperature controller. The target window (NaCl or CaF$_2$) was attached to the cold end by a copper sample holder and indium gaskets. The brass vacuum mantle (ca. 10^{-6} mbar) allows matrix deposition and simultaneous monitoring of the deposition rate by means of a He–Ne laser,[14] as well as irradiation normal to the direction of deposition. Infrared spectra were recorded by using a Grubb-Parson

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(1) J. K. Burdett and J. J. Turner in "Cryochemistry", M. Moskovits and G. A. Ozin, Eds., Wiley-Interscience, New York, 1976, p 493 ff, and references cited therein.

(2) O. Crichton and A. J. Rest, *J. Chem. Soc., Dalton Trans.*, 536, 656 (1977); 202 (1978).

(3) A. J. Rest, J. R. Sodeau, and D. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 651 (1978).

(4) J. D. Black, M. J. Boylan, P. S. Braterman, and W. J. Wallace, *J. Organomet. Chem.*, **63**, C21 (1973).

(5) E. Koerner von Gustorf, J. Buchkremer, Z. Pfajfer, and F.-W. Grevels, *Angew. Chem.*, **83**, 249 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 260 (1971).

(6) R. C. Kerber and E. A. Koerner von Gustorf, *J. Organomet. Chem.*, **110**, 345 (1976).

(7) F.-W. Grevels, U. Feldhoff, J. Leitich, and C. Krüger, *J. Organomet. Chem.*, **118**, 79 (1976).

(8) W. J. R. Tyerman, M. Kato, P. Kebarle, S. Masamune, O. P. Strausz, and H. E. Gunning, *Chem. Commun.*, 497 (1967).

(9) O. L. Chapman, J. Pacansky, and P. W. Wojtkowski, *J. Chem. Soc., Chem. Commun.*, 681 (1973).

(10) P. Reeves, J. Henery, and R. Pettit, *J. Am. Chem. Soc.*, **91**, 5888 (1969).

(11) I. Fischler, K. Hildenbrand, and E. Koerner von Gustorf, *Angew. Chem.*, **87**, 35 (1975); *Angew. Chem., Int. Ed. Engl.*, **14**, 54 (1975).

(12) O. Jaenicke, R. C. Kerber, P. Kirsch, E. A. Koerner von Gustorf, and R. Rumin, to be submitted for publication.

(13) Due to the temperature gradient from the cold end of the cryostat (T_c = 10 K) to the sample, the actual temperature of the sample (T_s) is estimated to be 13–14 K.

(14) P. Groner, I. Stolkin, and Hs. H. Günthard, *J. Phys. E*, **6**, 122 (1973).

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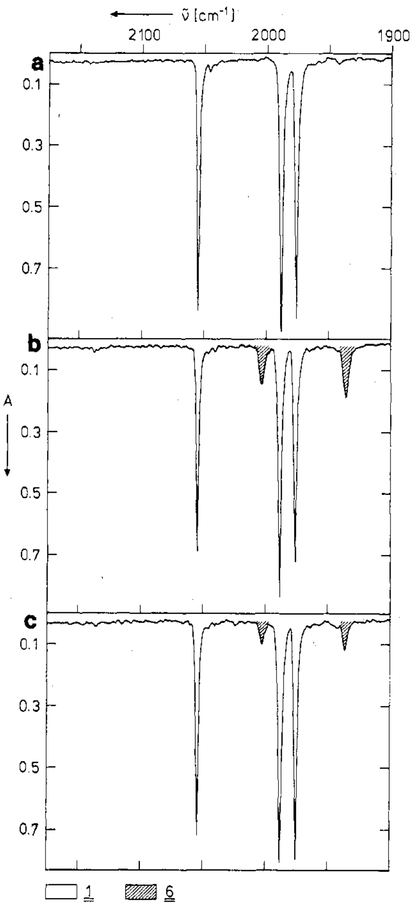

Figure 1. Infrared spectra from experiments with (η^4-2,3-dimethylbutadiene)Fe(CO)$_3$ (**1**) in an argon matrix at 10 K: (a) after 140 min continuous deposition with thickness growth rate at 14.7 μm/h and sample at −35 °C, (b) after 60 min irradiation at 254 nm, (c) after 60 min long-wavelength irradiation (λ >495 nm).

Spectromajor instrument, modified for grating change at 1800 cm^{-1}. Visible radiation from the Nernst glower of the instrument was absorbed by a CdTe filter (Oriel). DCl was used for calibration; wavenumber accuracy is better than 0.6 cm^{-1}. The UV–vis spectra were taken with a Perkin-Elmer Model 356 two-wavelength spectrometer, calibrated with the D$_2$ emission line. Matrix gases were ≥99.999% pure (l'Air Liquide).

The matrices were prepared by cocondensing the matrix gas and the sample compound onto the cold window. The flow of matrix gas was regulated by means of a controlled leak valve; the concentration of the sample should be in the range of $\lesssim$1:1000 and was controlled by evaporation from a tube, held at constant temperature. Alternatively the pulsing technique[15,16] was employed for matrix preparation.

A Philips HPK 125 W medium-pressure mercury arc in combination with a 5-cm water filter served as the light source for photolysis. For the "254-nm irradiation" we used an interference reflection filter (Schott UV-R-250). In cases where the irradiation wavelength is given as λ >M nm the corresponding cutoff filter WG M (Schott) was used. Handling and preparation of the carbonyl complexes were performed under argon. The (η^4-1,3-diene)Fe(CO)$_3$ complexes **1** and **2**,[17] the (η^2-1,3-diene)Fe(CO)$_4$ complexes **3**[18] and **4**, and (ethylene)Fe(CO)$_4$ (**5**)[19] were prepared according to the literature or by analogous procedures.

Table I. IR (cm^{-1})[20] and UV-vis (nm) Data from Photochemical Experiments with (η^4-2,3-Dimethylbutadiene)tricarbonyliron (1) in Various Matrices

	matrix					
	argon		3-methyl-pentane		nitrogen	
compd	IR	UV	IR	UV	IR	UV
(DMB)Fe(CO)$_3$ (1)	2056	280	2048	275	2053	273
	1988		1979		1985	
	1976		1966		1973	
(DMB)Fe(CO)$_2$ (6)	2003	570	1992	530	1966	
	1936		1926	310 sh	1929	
				295 sh		
(DMB)Fe(CO)$_2$N$_2$ (7)					2201	310 sh
					2012	
					1964	

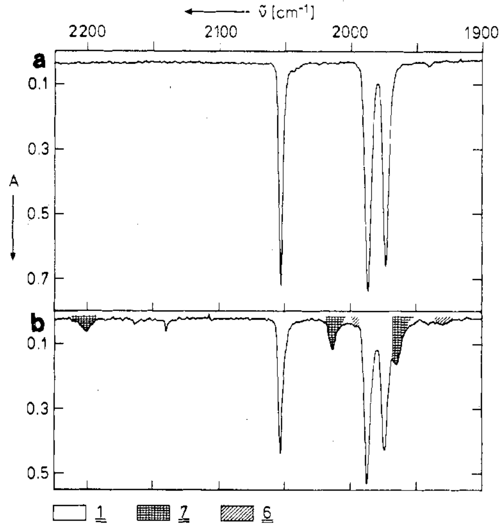

Figure 2. Infrared spectra from experiments with (η^4-2,3-dimethylbutadiene)Fe(CO)$_3$ (**1**) in a nitrogen matrix at 10 K: (a) after 15 min continuous deposition at 4.3 mmol of N$_2$/h and sample at −40 °C, (b) after 60 min irradiation at 254 nm.

Results and Discussion

Photolysis of (η^4-2,3-Dimethylbutadiene)tricarbonyliron, (η^4-DMB)Fe(CO)$_3$ (1). Figure 1a shows the characteristic Fe(CO)$_3$ pattern in the IR spectrum of **1**, isolated in argon (see also Table I[20]), with three strong absorptions in the terminal CO stretching region at 2056 [A′(1)], 1988 [A′(2)], and 1976 [A″][21] cm^{-1}. Upon 254-nm photolysis two new IR bands at 2003 and 1936 cm^{-1} (Figure 1b) and the band of free carbon monoxide at 2138 cm^{-1}[22] gradually appear; simultaneously, a weak absorption in the UV–vis spectrum centered at 570 nm shows up. Since the intensity ratio of the two IR bands at 2003 and 1936 cm^{-1} remains constant throughout the experiment, they are attributed to the same species. The same results were obtained at higher complex concentration, and, therefore, the formation of any polynuclear carbonylmetal complexes can be ruled out. The two new bands are thus clearly assigned to a dicarbonyliron species, (η^4-2,3-dimethylbutadiene)Fe(CO)$_2$ (**6**). The photochemical generation of **6** can also be observed in 3-methylpentane at 77 K (Table I). Compound **6** is characterized as a coordinatively unsaturated species by the fact that the elimination of carbon monoxide from the parent Fe(CO)$_3$ complex **1** can be reversed

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(15) M. M. Rochkind, *Spectrochim. Acta, Part A*, **27**, 547 (1971).

(16) In order to define the concentration of (η^4-butadiene)Fe(CO)$_3$ (**2**) in the gas mixtures used for the pulsing experiments, we measured the vapor pressure of **2** in the range from −2 to +17 °C by the static method by using a quartz spiral pressure gauge (Texas Instruments): log (p/p^+) = $-2636.4/T + 9.1443$ (p^+ = 1 mbar).

(17) E. Koerner von Gustorf, Z. Pfajfer, and F.-W. Grevels, *Z. Naturforsch., B*, **26**, 66 (1971).

(18) H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, **45**, 1156 (1962).

(19) H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, **46**, 1588 (1963).

(20) Splitting of IR bands due to matrix effects is occasionally observed. In these cases the wavenumbers listed in the tables refer to the strongest band of a given absorption.

(21) Symmetry notations refer to assumed C_s structure; for assignments cf. J. D. Warren and R. J. Clark, *Inorg. Chem.*, **9**, 373 (1970).

(22) H. Dubost and L. Abouaf-Marguin, *Chem. Phys. Lett.*, **17**, 269 (1972).

Table II. IR (cm^{-1})[20] and UV–vis (nm) Data from Photochemical Experiments with (η^4-Butadiene)tricarbonyliron (**2**) in Various Matrices

	matrix				
	argon		xenon	nitrogen	
compd	IR	UV	IR	IR	UV
(η^4-B)$Fe(CO)_3$ (**2**)	2060	278	2054	2058	274
	1995		1985	1992	
	1983		1976	1981	
(η^4-B)$Fe(CO)_2$ (**8**)	2009	578 br	1999		
	1944		1934		
(η^2-B)$Fe(CO)_3$ (**9**)	2029	~400 sh	2023	2027	
	1970		1963	1967 sh	
	1953		1944	1946	
(η^4-B)$Fe(CO)_2N_2$ (**10**)				2209	
				2018	310 sh
				1971	
(η^2-B)$Fe(CO)_3N_2$ (**11**)				1936	

by annealing the matrix to temperatures which allow diffusion of CO (34 K in argon,[23] 100 K in 3-methylpentane) or by long-wavelength irradiation[1] (λ >495 nm, Figure 1c).

Coordinative unsaturation of (η^4-DMB)$Fe(CO)_2$ (**6**) is furthermore demonstrated by its reaction with dinitrogen as shown by the photolysis of (η^4-DMB)$Fe(CO)_3$ (**1**) in a nitrogen matrix (Figure 2 and Table I). In nitrogen the IR bands of **1** are shifted by -3 cm^{-1} relative to argon. A similar red shift (-7 cm^{-1}) is observed for the IR bands of **6** (1996 and 1929 cm^{-1}) which can vaguely be detected after photolysis of **1** in nitrogen (Figure 2b). The major new photoproduct, however, exhibits higher terminal CO stretching frequencies (2012 and 1964 cm^{-1}). These absorptions along with a band at 2201 cm^{-1}, which is in the range for terminal stretching vibrations of N≡N coordinated to iron,[3] identify the new product as the dinitrogen complex (η^4-DMB)$Fe(CO)_2N_2$ (**7**). Contrary to **6**, the dinitrogen complex is stable toward annealing to 34 K. Its formation during the irradiation of (η^4-DMB)$Fe(CO)_3$ in the N_2 matrix is remarkable insofar as other complexes such as (η^2-butadiene)$Fe(CO)_4$ (**3**, see below) and (η^4-diene)$Cr(CO)_4$[24] react with dinitrogen only upon annealing subsequent to photolysis.[25]

Photolysis of (η^4-butadiene)$Fe(CO)_3$, (η^4-B)$Fe(CO)_3$ (2). The IR spectrum of (η^4-B)$Fe(CO)_3$ in argon (Figure 3a and Table II) is very similar to that of (η^4-DMB)$Fe(CO)_3$. The bands are shifted to slightly higher wavenumbers, which reflect the smaller electron-donating capability of butadiene vs. dimethylbutadiene. Contrary to the previous experiment with (η^4-DMB)$Fe(CO)_3$, the 254-nm photolysis of (η^4-B)$Fe(CO)_3$ in an argon matrix produces CO and five weak new bands in the CO stretching region of the IR spectrum (Figure 3b). Under our irradiation conditions a stationary state is reached after about 3 min. With thicker matrices we could demonstrate that the bands belong to two sets, the intensities of which vary slightly relative to each other under different photolysis conditions, and are thus assigned to two compounds **8** (2009 and 1944 cm^{-1}) and **9** (2029, 1970, and 1953 cm^{-1}) (Table II). In the UV–vis spectrum of the photolyzed matrices two weak absorptions can be detected at 578 and ca. 400 nm.

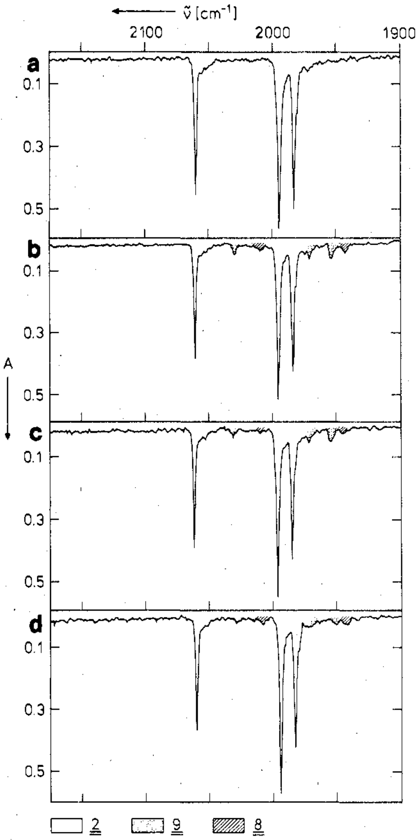

Figure 3. Infrared spectra from experiments with (η^4-butadiene)tricarbonyliron (**2**) in an argon matrix at 10 K: (a) after deposition of 12 pulses[15] of a 1:1000 **2**/argon mixture[16]) (1 pulse = 6 mL at 690 mbar), (b) after 15 min irradiation at 254 nm, (c) after 90 min irradiation at λ >495 nm, (d) after 15 min irradiation at λ >320 nm.

Comparison with the spectral data of (η^4-DMB)$Fe(CO)_2$ indicates that **8** should be identified as (η^4-B)$Fe(CO)_2$. Indeed, the bands attributed to **8** and CO decrease in intensity upon annealing to 34 K or long-wavelength irradiation (λ >495 nm; Figure 3c). At the same time the bands of **9** are not significantly affected. Their intensity decreases, however, upon irradiation through a λ >320 nm cutoff filter (Figure 3d). This photochemical behavior led us to assign the absorptions at 578 nm and ca. 400 nm to (η^4-B)$Fe(CO)_2$ (**8**) and compound **9**, respectively. In a xenon matrix (η^4-B)$Fe(CO)_3$ displays the same photolytic behavior as in argon (Table II).

In a nitrogen matrix, again in analogy to the (η^4-DMB)$Fe(CO)_3$ experiment, the IR bands of the coordinatively unsaturated dicarbonyl complex **8** can hardly be observed after irradiation (Table II). Instead, new absorptions at 2209, 2018, and 1971 cm^{-1} due to (η^4-B)$Fe(CO)_2N_2$ (**10**) arise which are stable toward annealing to 34 K. As in argon the second photoproduct **9** gives rise to weak IR bands at 2027, 1967 (sh), and 1946 cm^{-1}; however, the bands of **9** decrease in intensity upon annealing the dinitrogen matrix. A rather weak band at 1936 cm^{-1} shows up simultaneously; i.e., a new product (**11**, see below) is formed by reaction of **9** with dinitrogen. Already at this point the tentative assignment of **9** to the 16-electron species (η^2-B)$Fe(CO)_3$ appears reasonable, and the following experiments are intended to confirm this assumption.

Photolysis of (ethylene)$Fe(CO)_4$ (5), (η^2-butadiene)$Fe(CO)_4$ (3), and (η^2-1,3-cyclohexadiene)$Fe(CO)_4$ (4). In order to approach the intermediate (η^2-B)$Fe(CO)_3$ independently and thus unequivocally identify the bands of **9** obtained in the experiments described above, we investigated the photolytic behavior of (η^2-butadiene)$Fe(CO)_4$ (**3**) and, for comparison, of (ethylene)$Fe(CO)_4$ (**5**) and (η^2-1,3-cyclohexadiene)$Fe(CO)_4$ (**4**) in low-temperature matrices.

In the simplest case, (ethylene)$Fe(CO)_4$ (**5**) in an argon matrix (2094, 2020, 2009, and 1991 cm^{-1}), photolysis clearly

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(23) J. B. Davies and H. E. Hallam, *J. Chem. Soc., Faraday Trans. 2*, **68**, 509 (1972).

(24) I. Fischler, W. Gerhartz, E. A. Koerner von Gustorf, and R. N. Perutz, to be submitted for publication.

(25) In order to reveal the reason for these contrasting photochemical reactivities, one must conduct a thorough study on the structures and rearrangements of the particular carbonylmetal fragments, which goes beyond the scope of this paper.

Table III. IR (cm^{-1})[20] and UV–vis (nm) Data from Photochemical Experiments with (η^2-Butadiene)tetracarbonyliron (**3**) in Various Matrices

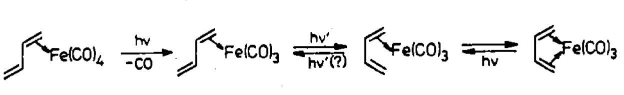
	matrix				
	argon		xenon	nitrogen	
compd	IR	UV	IR	IR	UV
(η^2-B)Fe(CO)$_4$ (**3**)	2088	241	2084	2088	
	2018	285	2012		360 sh
	2008	367 sh	2005	2009	
	1988		1983	1981	
(η^2-B)Fe(CO)$_3$ (**9**)	2028		2023	2024	
	1969	450 sh, br	1962	1963	440 sh, br
	1950		1942	1943	
(η^4-B)Fe(CO)$_3$ (**2**)	2060		2054	2056	
	1994		1985	1988	
	1983		1976	1977	
(η^4-B)Fe(CO)$_2$ (**8**)	2009	572 br	1999		
	1943		1936		
(η^2-B)Fe(CO)$_3$N$_2$ (**11**)				2209	
				1936[a]	
(η^4-B)Fe(CO)$_2$N$_2$ (**10**)				2209	
				2017	
				1970 sh	

[a] Other bands supposedly belonging to **11** are missing and probably hidden.

causes elimination of carbon monoxide to take place. The new IR bands of the coordinatively unsaturated (ethylene)Fe(CO)$_3$ (**12**) appear at 2039, 1976, and 1950 cm^{-1}.

The IR spectrum of (η^2-B)Fe(CO)$_4$ (**3**) in an argon matrix at 10 K is shown in Figure 4a. The wavenumbers (Table III) and the relative intensities of the IR bands are similar to those of (ethylene)Fe(CO)$_4$. (η^4-B)Fe(CO)$_3$ (**2**) is present as an impurity as shown by its absorptions in the IR spectrum. Short-wavelength irradiation of this matrix causes three new bands at 2028, 1969, and 1950 cm^{-1} (Figure 4b and Table III) to arise along with the absorption of free CO. The obvious analogy to the elimination of CO from (ethylene)Fe(CO)$_4$ leads us to assign the new bands to the coordinatively unsaturated (η^2-B)Fe(CO)$_3$. The good agreement of these wavenumbers with those of species **9** obtained upon photolysis of (η^4-B)Fe(CO)$_3$ in argon shows that **9** is indeed (η^2-butadiene)Fe(CO)$_3$. Comparison of the corresponding experiments in xenon matrices (Tables II and III) provides further evidence.

The photolysis (254 nm) of (η^2-B)Fe(CO)$_4$ (**3**) in argon leads to a stationary concentration of (η^2-B)Fe(CO)$_3$ (**9**) which is reached after a few minutes. Upon prolonged irradiation (Figure 4c) the starting material disappears almost completely whereas the bands of the "impurity", (η^4-B)Fe(CO)$_3$ (**2**), increase considerably in intensity. This shows that **9** is a steady-state intermediate in the photochemical formation of (η^4-B)Fe(CO)$_3$ from (η^2-B)Fe(CO)$_4$. The conversion **9** → **2** under argon matrix conditions is a photoreaction rather than a thermal process, since annealing of a matrix containing **9** to 36 K does not cause any change in the IR spectrum. On account of this finding we assume that the actual structure of the observed (η^2-B)Fe(CO)$_3$ species is represented by **9a** with a s-trans configurated η^2-butadiene ligand. Conversion of the s-cis configurated butadiene from η^2 to η^4 coordination should occur in the dark even in the low-temperature range from 10 to 34 K, provided that a free coordination site at the metal is available, as it is the case in **9b**.



This assumption is confirmed by the photolysis of (η^2-1,3-cyclohexadiene)tetracarbonyliron (**4**) in argon at 10 K (CO stretching vibrations at 2092, 2018, 2009, and 1989 cm^{-1}). In this case the s-cis configuration of the diene ligand is a priori given, and indeed no intermediate corresponding to **9** is observed after photolysis. Instead, the only detectable product bands are those of (η^4-1,3-cyclohexadiene)Fe(CO)$_3$ (**13**) at 2054, 1985, and 1978 cm^{-1}.

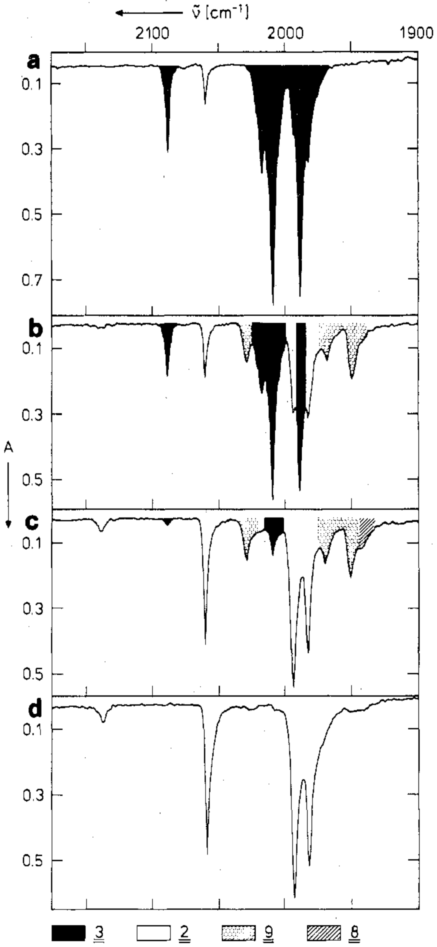


Figure 4. Infrared spectra from experiments with (η^2-butadiene)tetracarbonyliron (**3**) in an argon matrix: (a) after 30 min continuous deposition with thickness growth rate at 10.5 μm/h and sample at −40 °C, (b) after 5 min irradiation at 254 nm; (c) after 15 min irradiation at 254 nm, (d) after 90 min irradiation at λ >320 nm.

The relevant result in this context is clearly that the photolysis of (η^4-B)Fe(CO)$_3$ (**2**) induces not only the elimination of CO but also the dechelation of the diene ligand from η^4 to η^2 coordination along with, at least in part, s-cis to s-trans rearrangement. The observability of (η^2-*s-trans*-butadiene)Fe(CO)$_3$ (**9a**) is due to the restricted rotation about the C(2)–C(3) bond of the diene under low-temperature matrix conditions. Upon electronic excitation, however, this rotation is clearly brought about as demonstrated by the disappearance of **9a** upon irradiation with long-wavelength light (λ >320 nm) (Figures 3d and 4d).[26]

Irradiation of (η^2-B)Fe(CO)$_4$ (**3**) in a nitrogen matrix (Table III) supported the assignment of the IR bands made earlier: (η^2-B)Fe(CO)$_3$ (**9**) and (η^4-B)Fe(CO)$_3$ (**2**) arise as products of short-wavelength (254 nm) irradiation. Only upon annealing to 34 K does a new absorption at 1936 cm^{-1} increase in intensity at the expense of the bands due to **9**. The si-

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(26) The barrier for s-trans → s-cis interconversion of uncoordinated butadiene was reported to be 2504 cm^{-1} (30 kJ mol^{-1}): L. A. Carreira, *J. Chem. Phys.*, **62**, 3851 (1975). The reverse process ($\Delta G^{\ddagger}$ = 20 kJ mol^{-1}) can also not be observed in argon at 36 K: P. Huber-Wälchli, personal communication.

multaneously emerging N≡N stretching vibration at 2209 cm^{-1} and comparison with the analogous experiment with (η^4-B)Fe(CO)$_3$ (**2**, see above) demonstrate that the 1936-cm^{-1} absorption belongs to (η^2-B)Fe(CO)$_3$N$_2$ (**11**). Unfortunately, the IR bands are broad and overlapping under these conditions and the missing two carbonyl absorptions of **11** are hidden by the bands of the other compounds. Again, subsequent long-wavelength irradiation ($\lambda > 320$ nm) of the matrix gives (η^4-B)Fe(CO)$_3$ (**2**) as the major product along with absorptions due to (η^4-B)Fe(CO)$_2$N$_2$ (**10**).

Conclusion and Outlook

We have shown that in argon matrices CO elimination as well as partial decomplexation of the diene ligand takes place when (η^4-butadiene)Fe(CO)$_3$ (**2**) is irradiated with UV light. The observability of the (η^2-butadiene)Fe(CO)$_3$ (**9**) intermediate is due to the facts that the s-cis → s-trans conversion of the diene ligand takes place upon photolysis and that the reverse reaction cannot occur thermally in argon at cryogenic temperatures.

The UV spectrum of **2**[27] in hexane solution at ambient temperature displays a broad band around 278 nm (ϵ 2800 L mol^{-1} cm^{-1}) which in 10 K matrices sharpens to a distinct yet structureless maximum. A second, more intense absorption at 218 nm (ϵ 14800 L mol^{-1} cm^{-1}) was thought to be associated with a nondissociative excited state, presumably (M → L) charge transfer in character, since in the vapor phase a well-resolved vibrational fine structure ($\Delta\tilde{\nu} = 1400$ cm^{-1}) was observed.[28] The 278-nm band had been assigned to a ligand field (d–d) transition. It was pointed out, however, that the observed spectrum probably results from several superimposing absorptions. In fact, the CD spectra of optically active tricarbonyliron complexes of substituted 1,3-dienes[29] clearly show several distinct bands in the range from 450 to 220 nm. Furthermore, a recent SCCC–MO study[30] suggests that in this spectral range a variety of ligand field and charge-transfer transitions involving both the diene and the CO ligands should be found. The reactivities of the particular excited states with respect to CO vs. diene detachment from the metal were predicted in terms of calculated changes of bond orders relative to the ground state. These results could explain[30] the wavelength-dependent photolytical behavior of **2** and other (η^4-diene)Fe(CO)$_3$ complexes in solution.[12]

In the matrix photolysis experiments the excitation wavelength was usually selected to be 254 nm. Increasing the irradiation wavelength led to a change, albeit very small, in the photoproduct ratio from **2**, thus enabling us to assign the two sets of bands of **8** and **9**. In view of the above discussion there is little likelihood of the photoproducts to originate in the same excited state under the various conditions of irradiation. Any detailed assignments, however, of particular excited states to be involved in the product formation or to undergo, e.g., internal conversion could only be speculative at the present stage. Moreover, the rigidity of the matrix imposes restrictions other than electronic in nature, and care has to be taken not to extrapolate the results of matrix photoreactions to solution or even gas-phase photochemistry without due criticism.

This is demonstrated by the irradiation of (η^4-2,3-dimethylbutadiene)Fe(CO)$_3$ (**1**) which in argon matrices gives the dicarbonyliron complex **6** as the sole photoproduct. Since the UV bands of **1** in hexane solution (287 nm (ϵ 1600 L mol^{-1} cm^{-1}), 217 nm (sh) (ϵ 18000 L mol^{-1} cm^{-1})) are almost identical with those of **2** and experience a similar sharpening in argon at 10 K, it appears unlikely that the differing photochemistry of the two complexes under matrix conditions is due to different excited states of the starting molecules to be involved. Most probably, the bulkier methyl substituents of the 2,3-dimethylbutadiene ligand hinder the rotation about the C(2)–C(3) bond in solid argon and consequently the observation of (η^2-DMB)Fe(CO)$_3$. Thus, both reactions—CO elimination and partial decomplexation of the diene ligand—have to be faced as the primary photoprocesses in solution. We are therefore currently attempting to supplement these matrix results with flash photolysis studies in solution at ambient temperature using fast IR detection.

In nitrogen matrices we find that substitution of CO by the dinitrogen ligand takes place during irradiation of square-pyramidal (η^4-diene)Fe(CO)$_3$ complexes. In the case of the (η^2-butadiene)Fe(CO)$_4$ complex, however, annealing subsequent to the photolysis is required to achieve the corresponding substitution. We suspect that in the former case this is a consequence of the better accessibility of the central atom toward the entering ligand. Whether some general conclusions can be drawn from this observation will be a subject of further experiments.

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Registry No. **1**, 31741-56-7; **2**, 12078-32-9; **3**, 12317-64-5; **6**, 71435-58-0; **7**, 71435-59-1; **8**, 71435-60-4; **9**, 71435-61-5; **10**, 71435-62-6; **11**, 71435-63-7.

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