Photochemistry of $[Fe(CO)_4L]$ Complexes (L = NMe_3 or pyridine) in Argon and Xenon Matrices. Evidence for the Formation of C_{3v} $[Fe(CO)_3L]$ and the Reversible Infrared-induced Isomerization to C_s $[Fe(CO)_3L]$

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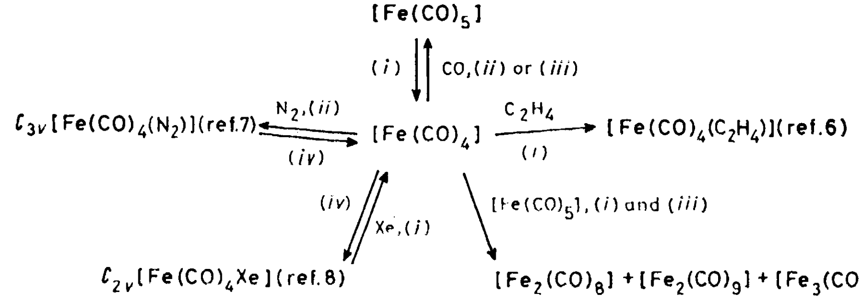
Photolysis of $[Fe(CO)_4L]$ complexes (L = NMe_3 or pyridine) in Ar and Xe matrices at 10 K with the wavelengths 229, 254, 280, 313, 334, 366, 405, 436, and 475 nm resulted in the formation of C_{3v} $[Fe(CO)_3L]$. The reaction is reversed by i.r. light and by annealing the matrix. The C_{3v} $[Fe(CO)_3L]$ complex isomerizes into C_s $[Fe(CO)_3L]$ after i.r. photolysis. The reverse reaction is accomplished by excitation with visible light. Two forms of C_{3v} $[Fe(CO)_3L]$ are detected, which are called ' reversible ' and ' irreversible ' C_{3v} $[Fe(CO)_3L]$. An explanation is given for the observed photochemical reactions based on photoelectron spectroscopy data.

PHOTOCHEMISTRY of iron carbonyl complexes has received increasing attention during the last few years. Poliakoff[1] reported the formation of $[Fe_2(CO)_8]$, after u.v. light photolysis of $[Fe_2(CO)_9]$. The same author reported evidence for the formation of C_{2v} $[Fe(CO)_4]$ after u.v. irradiation of $[Fe(CO)_5]$.[2,3] Prolonged u.v. photolysis resulted in the formation of $[Fe(CO)_3]$ with C_{3v} symmetry,[4] while even Fe atoms could be detected.[5] At the same time it appeared that $[Fe(CO)_4]$ exists in two forms, so-called ' reversible ' $[Fe(CO)_4]$ and ' irreversible ' $[Fe(CO)_4]$, due to diffusion of CO molecules through the matrix. Further reactions of $[Fe(CO)_4]$ are summarized in Scheme 1 from ref. 3.

A combination of matrix isolation and i.r. laser-induced photolysis yielded selective interconversion of ^{13}CO-substituted $[Fe(CO)_4]$ molecules.[3,8,9] This ligand exchange is the first intramolecular ligand-exchange process, that has been characterized by a technique other than dynamic n.m.r.

With the i.r. laser it was also possible to discriminate between molecules trapped in different sites of the matrix.



SCHEME 1 (*i*) U.v. photolysis, (*ii*) Nernst glower λ >320 nm, (*iii*) annealing, and (*iv*) λ >375 nm

Until now the photochemistry in matrices of only a few substituted iron carbonyl complexes had been studied. Chapman *et al.*[10] reported the photolysis of tricarbonyl(cyclobutadiene)iron isolated in argon at 8 K with λ >280 nm; CO and dicarbonyl(cyclobutadiene)-iron were detected. Black and Braterman[11] found $[Fe(CO)_4(NEt_3)]$ and an unidentified unsaturated fragment after photolysis of $[Fe(CO)_5]$ in a hydrocarbon glass doped with triethylamine. Crichton and Rest[12] photolyzed $[Fe(CO)_2(NO)_2]$ and evidence was presented for the formation of $[Fe(CO)(NO)_2]$, $[Fe(CO)(N_2)(NO)_2]$, and $[Fe(N_2)_2(NO)_2]$.

In this paper we describe the photolysis of $[Fe(CO)_4L]$ complexes (L = NMe_3 or pyridine) with various wavelengths in Ar and Xe matrices. Photolysis of $[Fe(CO)_4L]$ with u.v. and visible light resulted in the formation of C_{3v} $[Fe(CO)_3L]$, which rapidly isomerized into C_s $[Fe(CO)_3L]$, after i.r. irradiation.

We will compare these results with the photochemistry of $[Cr(CO)_5(NMe_3)]$ in Ar and Xe matrices.[13]

EXPERIMENTAL

Syntheses.—The compound $[Fe(CO)_4(NMe_3)]$ was prepared according to the reaction described by Elzinga and Hogeveen.[14] Treatment of $[Fe(CO)_5]$ with $NOMe_3$ in tetrahydrofuran (thf) at −30 °C resulted in the formation of $[Fe(CO)_4(NMe_3)]$ as an orange-red solid, with the evolution of CO_2.

The complex $[Fe(CO)_4(py)]$ (py = pyridine) was prepared from $[Fe_2(CO)_9]$ by adding an excess of pyridine to the complex in thf under a CO atmosphere, according to the method of Cotton and Troup.[15] Stirring and evaporation to dryness yielded a brownish orange solid. Recrystallization and sublimation yielded orange crystals of $[Fe(CO)_4(py)]$. Products were identified by i.r. spectroscopy.

Equipment.—Details of the cryostat, matrix gases, and of the i.r. and u.v.–visible spectrometers, have been given in earlier papers.[13,16] The photoelectron spectra were recorded on a Perkin-Elmer PS-18 spectrometer modified with an Helectros He(I)–He(II) source and calibration was performed before and after the measurement.

Deposition of gas mixtures was achieved using the method developed for [Cr(CO)$_5$(NMe$_3$)].[13] For [Fe(CO)$_4$(py)] which has a low vapour pressure it was necessary to raise the temperature of the oven to 45 °C. This resulted in partial decomposition of [Fe(CO)$_4$(py)] into [Fe(CO)$_5$]. Reverse reactions were accomplished by i.r. irradiation with a silicon-filtered Xe lamp (450 W) supplied by Bausch and Lomb.

TABLE 1

Infrared frequencies (cm^{-1}) of [Fe(CO)$_4$L] complexes with C_{3v} symmetry (L = PMe$_3$, NMe$_3$, or pyridine)

Assignments		L = PMe$_3$	L = NMe$_3$					L = pyridine				
		octane [a]	KBr	Nujol mull	n-hexane	Ar, 10 K	Xe, 10 K	KBr	Nujol mull	n-hexane	Ar, 10 K	Xe, 10 K
ν(C–O)	A_1	2 051	2 045	2 049.8	2 050.6	2 052.7	2 049.3	2 050	2 053.2	2 054.8	2 059.5	2 052.5
	A_1	1 977	1 949	1 961.2	1 964.0	1 966.8	1 963.5	1 960	1 965.7	1 970.4	1 972.7	1 968.2
	E	1 936	1 920	1 929.7	1 933.5	1 939.3	1 929.7	1 935	1 941.1	1 945.2	1 950.7	1 942.6
						1 924.9	1 919.5				1 947.9	1 935.3
ν(^{13}C–O)				1 896.0	1 898.6	1 905.9	1 895.3		1 905.4	1 908.6	1 919.3	
δ(M–C–O)	A_1	630		641	647				634	638	b	b
	E	622	621	623	628	627	630	628	626	624	b	b
	E	523	527		554	b	533			512	b	b
	E	423	437	435	439	b	436	460 [c]	445	449	b	b
ν(M–C)	A_1	440	468	464	465	b	470	460 [c]	464		b	b
	A_1	497	500		490	b	497	460 [c]	488	482	b	b
	E	497	500		490	b	497	460 [c]	488	482	b	b
ν(N–C) of NMe$_3$ bonded ligand			830	834	b	832 834 (sh)	830					
Free ligand [d]			827		b	823						

[a] Data from ref. 17. [b] Not measured. [c] Broad band. [d] Data from ref. 18.

RESULTS

Infrared Spectra.—The i.r. spectra of [Fe(CO)$_4$(NMe$_3$)] and [Fe(CO)$_4$(py)] as solids in KBr and in n-hexane solutions show three absorptions in the CO stretching region, which are assigned to the $2A_1$ and E modes of a structure with local C_{3v} symmetry.

In Ar and Xe matrices only the E mode was split, which means that the distortion from C_{3v} symmetry is small. At *ca.* 1 900 cm^{-1} a weak absorption was detected, which was assigned to the most intense vibration of [Fe(CO)$_3$(^{13}CO)L]. In going from Ar to Xe only small intensity changes were detected. For [Fe(CO)$_4$L], which has a C_{3v} structure, four δ(M–C–O) (*i.e.* $A_1 + 3E$) and three ν(M–C) (*i.e.* $2A_1 + E$) vibrations were expected and were found. The assignments were made according to Bigorgne.[17] Ligand vibrations of NMe$_3$ in matrices could only be detected under signal-expansion conditions: the ν(N–C) band was detected at 832 cm^{-1} in an Ar matrix, which is in agreement with the assignment of Goldfarb and Khare[18] for free NMe$_3$ and ν(N–C) found for [Cr(CO)$_5$(NMe$_3$)].[13] Ligand vibrations of pyridine were not measured. The influence of the various media (KBr, Nujol mull, n-hexane, Ar matrix, and Xe matrix) is shown in Table 1.

TABLE 2

Vertical ionization potentials (eV) of [Fe(CO)$_5$], [Fe(CO)$_4$L], [Cr(CO)$_5$L], and L

Assignments	$d_{xy},d_{x^2-y^2}$	d_{xz},d_{yz}	M–N bonding	Lone pair
[Fe(CO)$_5$] [a]	8.6	9.9		
[Fe(CO)$_4$(NMe$_3$)]	7.66	8.70	11.10	
[Fe(CO)$_4$(py)] [b]	7.3 7.58	8.53	11.70	
[Cr(CO)$_5$(NMe$_3$)]			10.6	
[Cr(CO)$_5$(py)] [b]			11.46	
NMe$_3$				8.45
Pyridine [b]				9.67

[a] Data from ref. 19. [b] Data from ref. 20.

Photoelectron Spectra.—In going from [Fe(CO)$_5$] to [Fe(CO)$_4$L] (L = NMe$_3$ or pyridine) changes are expected for the relative positions of the d orbitals. Replacement of one axial CO ligand by a ligand with no (or less) π-back-bonding capability results in an increase of electron density on the metal, which is reflected in the shift of the metal d ionization potentials (see Table 2). Figure 1 shows the He(II) photoelectron spectrum of [Fe(CO)$_4$(NMe$_3$)] and Figure 2 the one-electron d-orbital energy diagram of [Fe(CO)$_5$] and [Fe(CO)$_4$L] (L = NMe$_3$ or pyridine). The energy difference between e' and e'' in [Fe(CO)$_5$] appeared to be 1.26 eV and

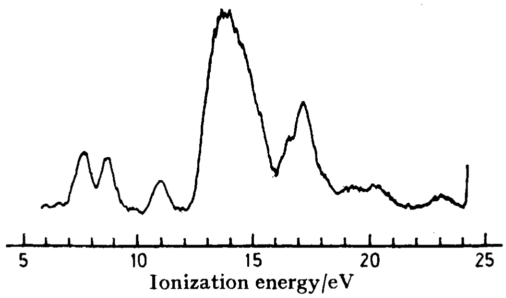


FIGURE 1 The He(II) photoelectron spectrum of [Fe(CO)$_4$(NMe$_3$)]

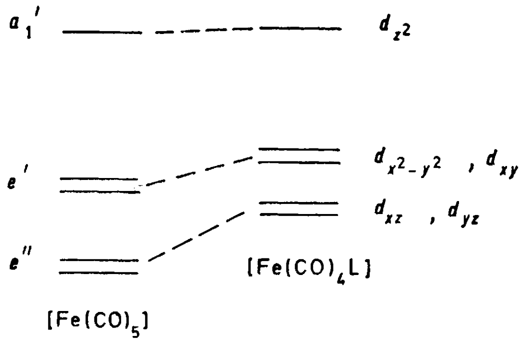


FIGURE 2 d-Orbital energy diagram of [Fe(CO)$_5$] and [Fe(CO)$_4$L] (L = NMe$_3$ or pyridine) decreased to 1.04 eV for the corresponding orbitals in [Fe(CO)$_4$(NMe$_3$)] and [Fe(CO)$_4$(py)].[20,21] If an axial CO ligand is replaced by a *N*-donor ligand no significant changes, apart from the above mentioned charge effects, occur in the *xy* plane. However, replacement of CO results in a decrease of π back-bonding for d_{xz} and d_{yz}, causing an extra destabilization of these orbitals. At the same time the d_{z^2} orbital is destabilized by the increase of σ interaction along the *z* axis.

$$[\mathrm{Fe(CO)_4L}] \underset{\text{i.r.}, \Delta T}{\overset{\lambda = 229-475\text{ nm}}{\rightleftharpoons}} C_{3v}[\mathrm{Fe(CO)_3L}] + \mathrm{CO} \underset{\substack{\lambda = 475,\ 591\text{ nm} \\ \text{daylight}}}{\overset{\text{i.r.}, \lambda > 1050\text{ nm}}{\rightleftharpoons}} C_s[\mathrm{Fe(CO)_3L}]$$

SCHEME 2

Although the energy difference, Δ, between the occupied *d* orbitals is in general a measure for the π-back-bonding capabilities of the ligand, this is not the case for NMe$_3$ and pyridine. Here, Δ is measured to be the same for both complexes, 1.04 eV.[19,20]

Ultraviolet–visible Spectra.—The u.v.-visible absorption spectra of [Fe(CO)$_4$L] complexes consist mostly of broad bands. Two charge-transfer bands were detected in n-hexane at 220 and at *ca*. 280 nm which have both been assigned to π^*(CO)$\leftarrow$Fe(3*d*) transitions, while only one *d–d* transition is observed at 475 nm. A red shift of this transition going from [Fe(CO)$_5$] to C_{3v} [Fe(CO)$_4$L] is also observed in [Cr(CO)$_{6-x}$L$_x$] complexes.[13,16]

In [Fe(CO)$_4$(py)] the same bands were detected together with the π^*(py)$\leftarrow$Fe(3*d*) charge-transfer transition at 360 nm (see Table 3). In Ar and Xe matrices only one charge-transfer transition was detected for [Fe(CO)$_4$(NMe$_3$)] and [Fe(CO)$_4$(py)]. All the spectra contained very broad bands.

Photochemistry.—Photolysis of [Fe(CO)$_4$L] (L = NMe$_3$ or pyridine) in Ar and Xe matrices at 10 K with the wavelengths 229, 254, 280, 313, 334, 366, 405, 436, and 475 nm resulted in the formation of C_{3v} [Fe(CO)$_3$L]. This was concluded from the detection of free CO at 2 138.8 cm^{-1} in argon † and from the new bands which appeared in the i.r. spectra. In the CO stretching region two new bands were detected at 2 017.9 (A_1) and 1 907.9 cm^{-1} (E) for L = NMe$_3$ and 2 020.1 and 1 912.8 cm^{-1} for L = pyridine. This latter band was split in almost the same way as the *E* mode of [Fe(CO)$_4$L]. In the absorption spectrum, however, no new absorptions were detected and attempts to detect new *d–d* transitions in the near-infrared region failed.

TABLE 4

Infrared frequencies (cm^{-1}) of the photoproducts of [Fe(CO)$_4$L]

Assignments		A_1	E		A'		A''	
C_{3v} [Fe(CO)$_3$(NMe$_3$)] [a]	Ar matrix, 10 K	2 017.9	1 907.9 [b]	1 893.9				
	Xe matrix, 10 K	2 013.7	1 899.2 [b]	1 887.8				
C_s [Fe(CO)$_3$(NMe$_3$)]	Ar matrix, 10 K				1 991.6	1 923.5	1 874.3	
	Xe matrix, 10 K				1 986.4	1 888.5	1 865.9 [b]	1 856.7
C_{3v} [Fe(CO)$_3$(py)]	Ar matrix, 10 K	2 020.1	1 912.8 [b]	1 895.5				
	Xe matrix, 10 K	2 014.5	1 904.0 [b]	1 883.6				
C_s [Fe(CO)$_3$(py)]	Ar matrix, 10 K				1 991.5	1 930.0	1 881.4	
	Xe matrix, 10 K				1 985.3	1 887.5	1 869.4	

[a] C_{3v} [Fe(CO)$_3$(NMe$_3$)] Ar matrix, 10 K irreversible: 2 011.6 (A_1), 1 906.4 and 1 889.3 (E) and reversible: 2 017.9 (A_1), 1 907.9 and 1 893.9 (E). [b] Strongest band.

The following other possible reactions could be rejected. (*a*) Formation of [Fe(CO)$_4$] since no band at 823 cm^{-1} of free NMe$_3$ in argon and no frequencies due to [Fe(CO)$_4$] were detected. (*b*) Formation of C_s [Fe(CO)$_3$L]. Should this complex be formed after photolysis of [Fe(CO)$_4$L] three bands in the CO stretching region would be expected, while only two main bands were observed directly after photolysis. (*c*) Formation of dimers such as [Fe$_2$(CO)$_8$]. The frequencies found after photolysis did not agree with the frequencies expected for dimers such as [Fe$_2$(CO)$_8$].[1]

TABLE 3

U.v.-visible absorption bands (nm) of [Fe(CO)$_5$] and [Fe(CO)$_4$L]

Assignments	$d\rightarrow\pi^*$(CO)		$d\rightarrow\pi^*$(L)	$d\rightarrow d$
[Fe(CO)$_5$] [a] Isopentane–methylcyclohexane	200	240		282
[Fe(CO)$_4$(NMe$_3$)] n-Hexane	220	275		475
[Fe(CO)$_4$(py)] n-Hexane	220	280	360	[b]

[a] Data from ref. 21. [b] Not detected.

The photochemical reaction was reversed by irradiation with i.r. light from the Nernst glower or by filtering a 450 W Xe lamp (λ >1 050 nm). The same holds for annealing the matrix to 30 K, resulting in diffusion of CO through the matrix.

Infrared photolysis not only reversed the reaction, but also resulted in three new absorptions at 1 991, 1 924, and 1 874 cm^{-1} in Ar and 1 986, 1 889, and 1 866 cm^{-1} in Xe for L = NMe$_3$. The latter band was split in the same way as the *E* modes of [Fe(CO)$_4$L] and C_{3v} [Fe(CO)$_3$L], especially in Xe. At the same time no free NMe$_3$ was detected and splitting off of a CO molecule could be excluded since the energy of i.r. irradiation is too low to break an Fe–C bond (ΔH = 118 kJ mol^{-1}).[25] From the CO stretching vibrations it is deduced, that i.r. photolysis resulted in isomerization of C_{3v} [Fe(CO)$_3$L] into C_s [Fe(CO)$_3$L] giving rise to three CO stretching modes (2 A' and A''). This i.r. induced isomeriz-

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† After deposition normally two CO frequencies were detected at 2 138.8 cm^{-1} and 2 150.6 cm^{-1}. Photolysis of [Fe(CO)$_4$L] complexes increased the 2 138.8 cm^{-1} band while the reverse reaction resulted in a decrease of this band. In ' free ' CO, the band at 2 150.6 cm^{-1} has been assigned to the vibration of monomeric CO and the 2 138.8 cm^{-1} band to aggregates (see refs. 22 and 23). From the behaviour of the latter band after photolysis, we conclude that this band is not due to polymers but to interaction of CO with the produced fragment C_{3v} [Fe(CO)$_3$L], which is in agreement with Burdett *et al.* (ref. 24).

ation to C_s [Fe(CO)$_3$L] is reversed by irradiation with λ = 475, 591 nm or by standing in daylight for 3—4 h.

Scheme 2 summarizes the photochemical reactions found for [Fe(CO)$_4$(NMe$_3$)] and [Fe(CO)$_4$(py)]. The i.r. frequencies of the photoproducts are recorded in Table 4.

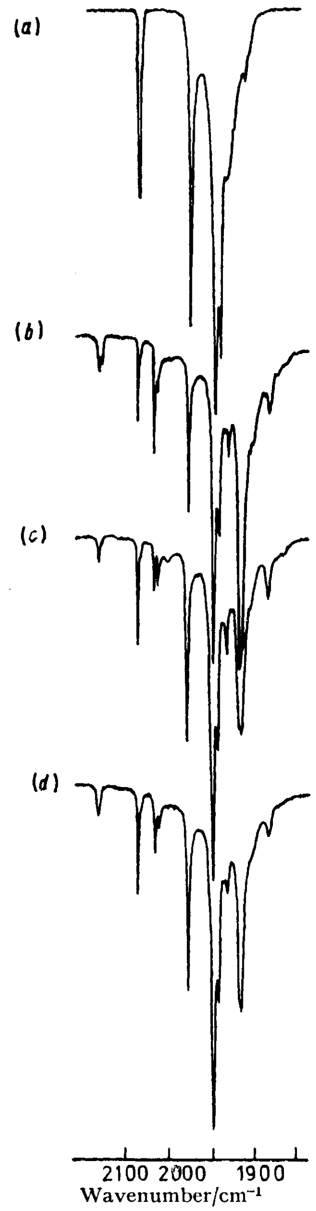

FIGURE 3 Infrared spectrum of [Fe(CO)$_4$(NMe$_3$)] in an Ar matrix at 10 K. (*a*) After deposition, (*b*) after 45 min photolysis with λ = 229 nm, (*c*) after further photolysis with i.r. light for 1 125 min, and (*d*) after 155 min standing in the daylight of the same sample

Figures 3 and 4 show the i.r. spectra after photolysis of [Fe(CO)$_4$(NMe$_3$)] with the various wavelengths in Ar and Xe matrices.

DISCUSSION

Photolysis of [Cr(CO)$_5$L] (L = NMe$_3$, pyridine, or pyrazine) in Ar and Xe matrices at 10 K showed a wavelength dependence. High-energy photolysis (λ ⩽313 nm) resulted in formation of C_s [Cr(CO)$_4$L] and photolysis with λ ⩾366 nm yielded free ligand L and [Cr(CO)$_5$].[16] However, photolysis of [Fe(CO)$_4$L] (L = NMe$_3$ or pyridine) resulted only in loss of axial CO and was independent of the wavelengths of excitation.

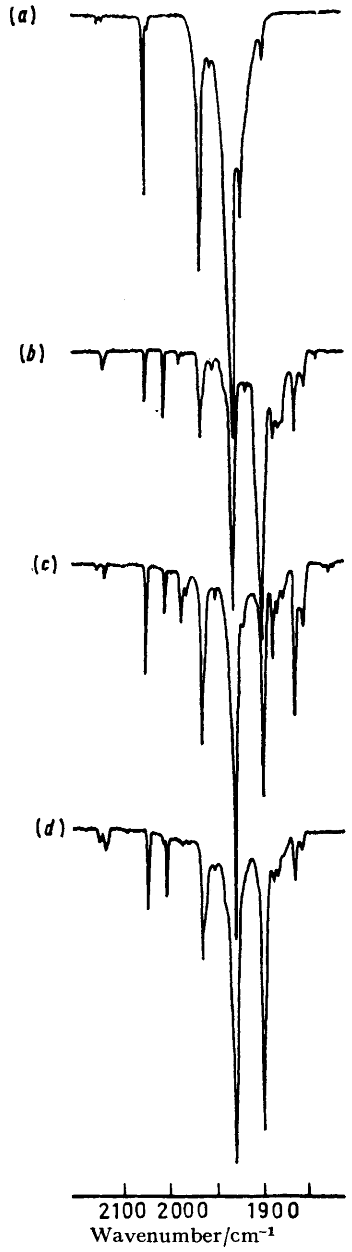

FIGURE 4 Infrared spectrum of [Fe(CO)$_4$(NMe$_3$)] in a Xe matrix at 40 K. (*a*) After deposition, (*b*) after 260 min photolysis with λ = 436 nm, (*c*) after further photolysis with i.r. light for 1 000 min, (*d*) after further photolysis with λ = 591 nm for 65 min

The reason for this different photochemical behaviour is due primarily to their difference in orbital splittings. The complexes [Cr(CO)$_5$L] have two different σ antibonding *d* orbitals (d_{z^2} and $d_{x^2-y^2}$) and [Fe(CO)$_4$L] complexes possess only one σ antibonding orbital, the d_{z^2} orbital. Labilization along the *z* axes or along the *x* and *y* axes produces the observed [Cr(CO)$_5$] and C_s [Cr(CO)$_4$L] complexes.[16] Figure 2 shows the *d*-orbital energy diagram of [Fe(CO)$_4$L] complexes. Both long- and short-wavelength photolysis will occupy the d_{z^2} orbital with a concomitant labilization of both axial ligand bonds. However, photolysis of [Fe(CO)$_4$L] always leads to the formation of C_{3v} [Fe(CO)$_3$L], while occupation of the d_{z^2} orbital in [Cr(CO)$_5$L] complexes results in the formation of [Cr(CO)$_5$].

The following effects could be responsible for the observed difference in photochemical behaviour: in going from iron to chromium carbonyl complexes, the frequency of the *trans* CO vibration decreases, indicating that in the iron complexes the *trans* CO group is more weakly bonded to the metal than in the chromium complexes.[16] Furthermore, comparing the ionization potentials of the lone pair of electrons on the nitrogen atom in NMe$_3$ and pyridine to those found for the M–N bonding orbitals in the complexes [Fe(CO)$_4$L] and [Cr(CO)$_5$L], the stabilization of this lone pair on complexation is different for the iron and chromium complexes (see Table 2). This difference (0.5 eV for the NMe$_3$ complexes and 0.24 eV for the pyridine complexes) points to the conclusion that in the iron complexes the ligand is more strongly bonded to the metal than in the corresponding chromium complexes. Besides this, the d_{z^2} orbital probably has low σ antibonding character in the [Fe(CO)$_4$L] complexes.[21] These facts may explain why labilization of the *z* axis in the iron complexes results in rupture of axial CO and not in the formation of [Fe(CO)$_4$].

' Reversible ' and ' Irreversible ' C_{3v} [Fe(CO)$_3$(NMe$_3$)].—Figure 3 shows that after photolysis of [Fe(CO)$_4$(NMe$_3$)] with $\lambda = 229$ nm two bands are found for the A_1 mode of C_{3v} [Fe(CO)$_3$(NMe$_3$)]: 2 017.9 and 2 011.6 cm^{-1}. The 2 017.9 cm^{-1} band decreased after irradiation with the Nernst glower, but the 2 011.6 cm^{-1} band remained constant. At the same time the *E* mode of C_{3v} [Fe(CO)$_3$(NMe$_3$)] changed. After photolysis with $\lambda = 229$ nm the absorption maximum lay at 1 907.9 cm^{-1} with a shoulder at 1 906 cm^{-1}; photolysis with the Nernst glower resulted in a decrease of the 1 907.9 cm^{-1} band and the maximum appeared at 1 906.4 cm^{-1}. From this we concluded that in Ar two different C_{3v} [Fe(CO)$_3$(NMe$_3$)] molecules exist, one conformer (' reversible ') with bands at 2 017.9 and 1 907.9 cm^{-1} for which the reaction to form [Fe(CO)$_4$(NMe$_3$)] can be reversed and a second (' irreversible ') with bands at 2 011.6 and 1 906.4 cm^{-1} for which the reverse reaction is not possible because of diffusion of CO from the cage.

Reversible Isomerization of C_{3v} [Fe(CO)$_3$L] *to* C_s [Fe(CO)$_3$L].—From a ^{13}C n.m.r. study of Spiess *et al.*[26] it was concluded that solid [Fe(CO)$_5$] is fluxional down to at least 100 K. In matrices at 20 K this fluxionality is frozen out [26,27] and rigid [Fe(CO)$_5$] and [Fe(CO)$_4$] are detected. Davies *et al.*[3] found, after laser-induced isomerization of [Fe(CO)$_{4-x}$(^{13}C^{18}O)$_x$], a non-statistical distribution. This distribution was raised very efficiently by i.r. light from the Nernst glower due to absorption of light associated with a *d–d* transition lying in the near-i.r. region.[3]

Comparing these results with the reversible isomerization of C_{3v} into C_s [Fe(CO)$_3$L] (L = NMe$_3$ or pyridine) we found that this isomerization is also i.r. induced and involves an electronic excitation. Isomerization, *via* excitation of CO stretching vibrations, is probably not possible, because in contrast to the laser-induced isomerization (1.5—3 W) the intensity of the i.r. radiation both of the glower and of the Xe source is too low. The *d–d* transition of C_{3v} [Fe(CO)$_3$L] probably lies in the i.r. region, which is expected when one CO of [Fe(CO)$_4$] is replaced by a *N*-donor ligand, as discussed below. Attempts to measure this transition failed, however.

The reverse reaction of C_s [Fe(CO)$_3$L], the structure of which closely corresponds to C_{2v} [Fe(CO)$_4$], is accomplished by irradiation with $\lambda = 475$, 591 nm and daylight and from this we concluded that C_s [Fe(CO)$_3$L] is electronically different from C_{3v} [Fe(CO)$_3$L] and has a *d–d* transition in the visible region of the absorption spectrum. Removal of the axial CO ligand from [Fe(CO)$_4$L] increases the electron density on the metal, resulting in a destabilization of the occupied *d* orbitals. The d_{z^2} orbital will become less antibonding, which explains the red shift found for the *d–d* transition of C_{3v} [Fe(CO)$_3$L].

The same destabilization effect is expected when an equatorial CO is replaced. However, the position of the d_{z^2} orbital will be almost unchanged and a *d–d* transition of C_s [Fe(CO)$_3$L] is expected in the visible region leading to the observed photochemical behaviour of C_s [Fe(CO)$_3$L] and C_{3v} [Fe(CO)$_3$L].

The Reverse Reaction: [Fe(CO)$_3$L] + CO $\xrightarrow{\text{i.r.},\Delta T}$ [Fe(CO)$_4$L].—Photolysis of C_{3v} [Fe(CO)$_3$L] with i.r. light reverses the reaction and [Fe(CO)$_4$L] is formed. We could not determine whether C_s [Fe(CO)$_3$L] also reacts with CO after photolysis with visible light resulting in the formation of C_{3v} [Fe(CO)$_4$L] or C_{2v} [Fe(CO)$_4$L]. However, the latter structure is excluded because no new bands were detected. Here, the mechanism of the i.r.-induced reverse reaction is thermal. This is concluded from the fact that annealing promotes the reverse reaction.

For a better understanding of the reactions described and in order to determine the *d–d* transitions in the near-i.r. region a study with an i.r. laser is planned.

Conclusions.—(*i*) As compared with [Cr(CO)$_5$L] (L = NMe$_3$ or pyridine) an unexpected release of axial CO is observed for the corresponding [Fe(CO)$_4$L] complexes, (*ii*) i.r.-induced isomerization is not limited to [Fe(CO)$_4$] alone, and (*iii*) two forms of C_{3v} [Fe(CO)$_3$(NMe$_3$)] exist in a matrix, reversible and irreversible fragments, as a result of diffusion of CO.

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REFERENCES

[1] M. Poliakoff and J. J. Turner, *J. Chem. Soc. (A)*, 1971, 2403.

[2] M. Poliakoff and J. J. Turner, *J.C.S. Dalton*, 1973, 1351.

[3] B. Davies, A. McNeish, M. Poliakoff, and J. J. Turner, *J. Amer. Chem. Soc.*, 1977, **99**, 7573.

[4] M. Poliakoff, *J.C.S. Dalton*, 1974, 210.

[5] M. Poliakoff and J. J. Turner, *J.C.S. Faraday II*, 1974, 93.

[6] M. J. Newlands and J. F. Ogilvie, *Canad. J. Chem.*, 1971, **49**, 343.

[7] B. Davies, A. McNeish, M. Poliakoff, M. Tranquille, and J. J. Turner, *J.C.S. Chem. Comm.*, 1978, 36.

[8] M. Poliakoff and J. J. Turner, *J.C.S. Dalton*, 1974, 2276.

[9] A. McNeish, M. Poliakoff, K. P. Smith, and J. J. Turner, *J.C.S. Chem. Comm.*, 1976, 859.

[10] O. L. Chapman, J. Pacansky, and P. W. Wojtkowski, *J.C.S. Chem. Comm.*, 1973, 681.

[11] J. D. Black and P. S. Braterman, *J. Organometallic Chem.*, 1975, **85**, C7.

[12] O. Crichton and A. J. Rest, *J.C.S. Dalton*, 1977, 656.

[13] G. Boxhoorn, D. J. Stufkens, and A. Oskam, preceding paper.

[14] J. Elzinga and H. Hogeveen, *J.C.S. Chem. Comm.*, 1977, 705.

[15] F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, 1974, **96**, 3438.

[16] G. Boxhoorn, D. J. Stufkens, and A. Oskam, *Inorg. Chim. Acta*, 1979, **33**, 215.

[17] M. Bigorgne, *J. Organometallic Chem.*, 1970, **24**, 211.

[18] T. D. Goldfarb and B. N. Khare, *J. Chem. Phys.*, 1967, **46**, 3379.

[19] E. J. Baerends, Ch. Oudshoorn, and A. Oskam, *J. Electron Spectrosc. Relat. Phenom.*, 1975, **6**, 259.

[20] H. Daamen and A. Oskam, *Inorg. Chem. Acta*, 1978, **26**, 81.

[21] M. Dartiguenave, Y. Dartiguenave, and H. B. Gray, *Bull. Soc. chim. France*, 1969, 4223.

[22] G. E. Leroi, G. E. Ewing, and G. C. Pimentel, *J. Chem. Phys.*, 1964, **40**, 2298.

[23] J. B. Davies and H. E. Hallam, *J.C.S. Faraday II*, 1972, 509.

[24] J. K. Burdett, *Co-ordination Chem. Rev.*, 1978, **27**, 1.

[25] J. A. Connor, H. A. Skinner, and Y. Virmani, *Faraday Symp. Chem. Soc.*, 1973, **8**, 18.

[26] H. W. Spiess, R. Grosescu, and U. Haeberlen, *Chem. Phys.*, 1974, **6**, 226.

[27] J. K. Burdett, J. M. Grzybowski, M. Poliakoff, and J. J. Turner, *J. Amer. Chem. Soc.*, 1976, **98**, 5728.