Photochemistry of Tricarbonyl(α-di-imine)iron Complexes. New Mechanistic Aspects for CO Photosubstitution in Solution and Evidence for π,π-Co-ordination of 1,4-Diaza-1,3-butadiene Ligands in Matrices at 10 K †

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The metal-to-ligand charge-transfer photochemistry of [Fe(CO)$_3$(α-di-imine)] has been studied in detail. For [Fe(CO)$_3$L] (L = 1,4-diaza-1,3-butadiene, RN=CH–CH=NR) CO photosubstitution takes place with high quantum yield (Φ ≃ 0.2) in solution *via* a partial dissociation of L. In matrices at 10 K, a changeover from σ,σ-*N,N′*- to π,π-co-ordination is found as primary step in the photolysis of [Fe(CO)$_3$L] complexes. The resulting [Fe(CO)$_3$(π,π-L)] decomposes thermally to a [Fe(CO)$_2$(σ,σ-*N,N′*-L)] fragment with simultaneous release of CO. For [Fe(CO)$_3$(dpipy)] [dpipy = 2-(2′,6′-di-isopropylphenylimino)pyridine] no π,π-co-ordination is observed. A ^{13}CO-labelling force-field calculation has been performed for a [Fe(CO)$_3$L] complex and its photolysis product [Fe(CO)$_2$(σ,σ,-*N,N′*-L)], showing two structurally different conformers of the latter product. The different photochemical behaviour in solution and in a matrix is discussed and a mechanism is proposed for the photosubstitutional reactions in solution.

α-Di-imine complexes of transition metals in a low valence state normally possess metal to α-di-imine charge-transfer (c.t.) transitions in the visible region. The spectroscopic properties of a series of these complexes of the type [M(CO)$_4$(α-di-imine)] (M = Cr, Mo, or W) and [M(CO)$_3$(α-di-imine)] (M = Ru or Fe) have been studied by us in detail.[1-5] Special attention was paid to the resonance Raman (r.R.) spectra of these complexes, from which information could be derived concerning the character of the c.t. transitions, the properties of the c.t. excited states, and the mechanism of the photochemistry. For the complexes [M(CO)$_4$(α-di-imine)] (M = Cr, Mo, or W) a strong r.R. effect was observed for $\nu_{sym}(CO)_{cis}$ upon excitation into the low-lying metal to ligand charge-transfer (m.l.c.t.) band. This effect was explained by a delocalization of the m.l.c.t. excited state over the *cis* carbonyls. As a result of this delocalization the metal to *cis* carbonyl π back-bonding will be weakened and this explains the easy photosubstitution of such a *cis* carbonyl ligand by PR$_3$ (R = alkyl or aryl).[3] Even a qualitative relationship appeared to exist between the photosubstitution quantum yield and the r.R. intensity of $\nu_{sym}(CO)_{cis}$.

However, such a mechanism cannot explain the photochemistry of [Fe(CO)$_3$L] complexes (L = 1,4-diaza-1,3-butadienes, RN=CR′–CR″=NR). The r.R. spectra of two of these complexes have been studied by us.[4,5] They only show very weak r.R. bands upon excitation into the lowest m.l.c.t. band, which means that no bonds of these complexes are severely affected in the m.l.c.t. state. On the other hand, rather high quantum yields for photosubstitution of CO by PR$_3$ (Φ ≃ 0.2) have been reported by Johnson and Trogler [6] for the 1,4-diaza-1,3-butadiene complex [Fe(CO)$_3${PhN=C(Me)–C(Me)=NPh}] and for the corresponding tetra-azadiene complex [Fe(CO)$_3$(MeN=N–N=NMe)]. On the basis of the r.R. results and the molecular orbital (m.o.) calculations performed by us for these complexes [5] and by Trogler *et al.* [7] for the corresponding tetra-azadiene ones, a photoactive excited state model does not appear to be appropriate for rationalising these photoreactivities. Instead, Trogler *et al.* have proposed a strong coupling model for these complexes, in which excited state energy is converted into vibrational motions within the molecule. This vibrational excitation then leads to dissociative loss of a carbonyl ligand followed by reaction with a PR$_3$ ligand.[6] This explanation, however, is not consistent with our observation that the [Fe(CO)$_3$L] complexes are photochemically stable if they are irradiated in the absence of a substituting ligand (see below). In this article we describe the photochemistry of several [Fe(CO)$_3$L] complexes in solution as well as in Ar, N$_2$, and CO matrices. For comparison, the photochemistry of [Fe(CO)$_3$(dpipy)] [dpipy = 2-(2′,6′-di-isopropylphenylimino)pyridine] and of [Fe(CO)$_3$(bipy)] (bipy = 2,2′-bipyridine) has also been studied. It will be shown that an intermediate is formed upon photolysis of the complexes of L in a matrix at 10 K in which the ligand L is π,π-co-ordinated to the metal.[8] On the basis of these observations a mechanism is proposed for this photochemistry.

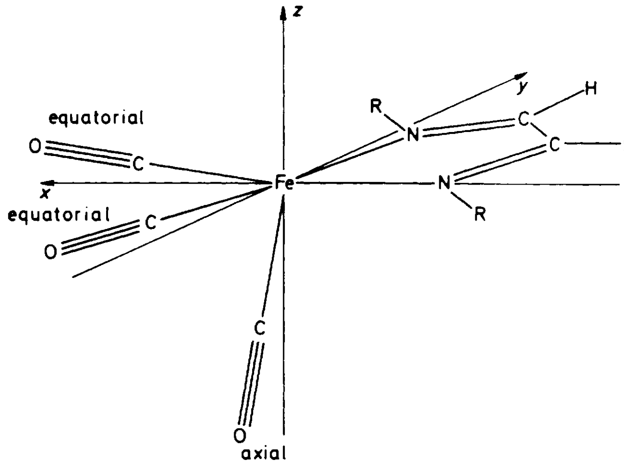

Figure 1. Structure of [Fe(CO)$_3$L] (L = RN=CH–CH=NR)

The structure of a [Fe(CO)$_3$L] type complex is shown in Figure 1. Aromatic ligands used were 1,2-bis(2′,6′-di-isopropylphenylimino)ethane (bdpie) and 1,2-bis(*p*-tolylimino)ethane (bptie) and aliphatic ligands were 1,2-bis(cyclohexylimino)ethane (bchie), 1,2-bis(t-butylimino)ethane (btbie),

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† *Non-S.I. unit employed:* 1 Torr = (101 325/760) Pa.

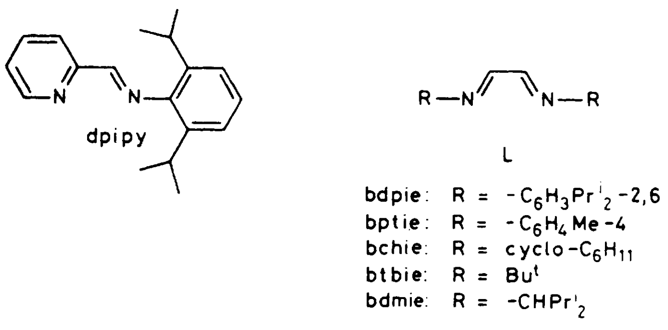

Figure 2. Structures of the complexed α-di-imine ligands

and 1,2-bis(di-isopropylmethylimino)ethane (bdmie). All α-di-imine ligands used are presented in Figure 2.

Experimental

The ligands L and dpipy and their complexes were synthesized according to published methods.[9-12] $[Fe(CO)_3(bipy)]$ was prepared by a ligand-exchange reaction between $[Fe(CO)_3\{PhCH{=}CHC(O)Me\}]$ and an excess of bipy, as has been described as an alternative synthesis for $[Fe(CO)_3L]$.[13] This exchange occurred readily at room temperature {Found: C, 67.45; H, 7.05; N, 5.35. Calc. for $[Fe(CO)_3(bdpie)]$: C, 67.45; H, 7.00; N, 5.45%. Found: C, 56.55; H, 7.00; N, 7.60; O, 13.20. Calc. for $[Fe(CO)_3(bchie)]$: C, 56.70; H, 6.70; N, 7.80; O, 13.30%. Found C, 58.10; H, 8.70. Calc. for $[Fe(CO)_3(bdmie)]$: C, 58.15; H, 8.20%. Found: C, 63.80; H, 5.95; N, 7.40; O, 10.30. Calc. for $[Fe(CO)_3(dpipy)]$: C, 62.10; H, 5.45; N, 6.90; O, 11.80%}.

All spectroscopic samples were dissolved in freshly distilled and deoxygenated solvents and prepared with standard inert-gas techniques in a glove-box. Electronic absorption spectra were measured on a Cary 14 spectrophotometer, ^{31}P n.m.r. spectra on a Varian XL-100 spectrometer, and i.r. spectra on a Nicolet 7199B FT-IR interferometer with a liquid-nitrogen cooled Hg,Cd,Te-detector (32 scans, resolution = 0.5 cm^{-1}). The matrix isolation equipment, a modified Air Products Displex model CSW-202 B closed-cycle helium refrigerator, has been described in detail before.[14] The sample window of LiF or CaF_2 had a temperature of 10 K during deposition and the vacuum was better than 10^{-6} Torr.

$[Fe(CO)_3(btbie)]$ was sublimed at 25 °C, $[Fe(CO)_3(bdmie)]$ at 60 °C, $[Fe(CO)_3(bchie)]$ at 70 °C, $[Fe(CO)_3(bptie)]$ at 85 °C, $[Fe(CO)_3(dpipy)]$ at 100 °C, and $[Fe(CO)_3(bdpie)]$ at 115 °C and gas mixtures were made by adding Ar, N_2, or CO (purity 99.999%) to the vapour of the sample.[15]

Photosubstitution quantum yields were obtained from the electronic absorption spectral changes upon irradiation of a stirred benzene solution (2.5 cm^3, *ca.* 10^{-4} mol dm^{-3}) in a quartz cell (40 × 10 × 10 mm) with a 20—50-mW laser beam as monochromatic light source. The photon flux was calculated from the laser power, which was measured by a Coherent model 201 power meter. Before calculation of the quantum yields, corrections were applied for reflections of the light within the cell, for transmission of the laser beam, and for absorption of the photoproduct. The equipment was tested with ferrioxalate actinometry.[16] As light sources an SP model 171 Ar^+ ion laser and a CR 490 tunable dye laser with Rhodamine 110 in ethylene glycol as dye were used. All samples were characterized by i.r. spectroscopy using an NaCl cell and pentane or methylene chloride as solvent.

^{13}CO *Labelling of* $[Fe(CO)_3(btbie)]$.—The complex was dissolved in freshly distilled and deoxygenated pentane (20 cm^3) and irradiated during 3 h with a medium-pressure mercury lamp ($\lambda > 320$ nm) in an atmosphere of ^{13}CO (90% enriched, *ca.* 2.5 mmol). The reaction was followed by i.r. spectroscopy. After sufficient substitution of ^{12}CO by ^{13}CO the solution was evaporated to 6 cm^3 and the product crystallized at −80 °C (yield, 70%).

Photochemical Preparation of $[Fe(CO)_2(PPh_3)(bdpie)]$.—$[Fe(CO)_3(bdpie)]$ (0.50 mmol) and PPh_3 (0.75 mmol) were dissolved in freshly distilled and deoxygenated pentane (20 cm^3) and irradiated for *ca.* 4 h with the green line ($\lambda = 514.5$ nm, $P = 400$ mW) of an Ar^+ laser in a nitrogen atmosphere. The reaction was followed by i.r. spectroscopy. After the substitution of CO by PPh_3 was completed, the solution was evaporated to 10 cm^3, during which process the released carbon monoxide was removed. The product crystallized at −30 °C, giving dark brown slightly air-stable crystals (yield, 60%) {Found: C, 73.15; H, 6.80; N, 3.60; O, 4.35; P, 4.25. Calc. for $[Fe(CO)_2(PPh_3)(bdpie)]$: C, 73.60; H, 6.80; N, 3.75; O, 4.00; P, 4.15%}.

Results and Discussion

Photostability of $[Fe(CO)_3$(α-di-imine)$]$.—No photodecomposition was observed when an iso-octane solution of any $[Fe(CO)_3L]$ complexes was irradiated in the absence of a substituting ligand by the green line ($\lambda = 514.5$ nm, $P = 400$ mW) of an Ar^+ laser into the lowest-energy absorption band. However, the complexes $[Fe(CO)_3(dpipy)]$ and $[Fe(CO)_3(bipy)]$ decomposed under the same circumstances. This photostability of the $[Fe(CO)_3L]$ complexes does not agree with the explanation given by Johnson and Trogler[6] for the photosubstitution reactions of the corresponding tetra-azadiene complex $[Fe(CO)_3(MeN{=}N{-}N{=}NMe)]$. According to Trogler, irradiation of this latter complex causes dissociation of a carbonyl group due to fast conversion of electronic excited state energy into vibrational energy. Such a release of CO is, however, not observed for the complexes of L under study. In order to elucidate the mechanism of these reactions we studied the photochemistry both in solution and in Ar, CO, and N_2 matrices at 10 K. In such matrices intermediates in the photochemical process may be stabilized and structurally characterized by i.r. spectroscopy.

Photolysis in Matrices at 10 K.— Figure 3 shows the i.r. spectral changes in the CO-stretching region upon irradiation with $\lambda = 514.5$ nm of $[Fe(CO)_3(bchie)]$ in an Ar matrix at 10 K. Spectrum (*a*) represents the i.r. spectrum of the parent compound before irradiation. CO-Stretching frequencies of several $[Fe(CO)_3L]$ complexes in pentane at room temperature and in matrices at 10 K are collected in Table 1.

Upon photolysis of $[Fe(CO)_3(bchie)]$ in an Ar matrix, six new bands appear at 2 077, 2 069, 2 012, 2 001, 1 984, and 1 972 cm^{-1} [Figure 3(*b*) and (*c*)]. The bands of the parent compound decrease in intensity and no free carbon monoxide is detected. Photolysis in a CO matrix gives only three new bands at 2 068, 1 999, and 1 969 cm^{-1}, respectively. The six bands observed in the Ar matrix are therefore assigned to two isomers, A and B. Support for this assignment can be derived from the annealing experiment of the CO matrix at 30 K. The three bands mentioned above are then replaced by three new bands at 2 074, 2 010, and 1 982 cm^{-1} respectively. These frequency shifts most probably result from isomerization of photoproduct A to B. Finally, the bands in the Ar matrix at 2 077, 2 012, and 1 984 cm^{-1} disappear more rapidly upon further photolysis than the other three bands. This behaviour agrees with an assignment of these bands to different isomers.

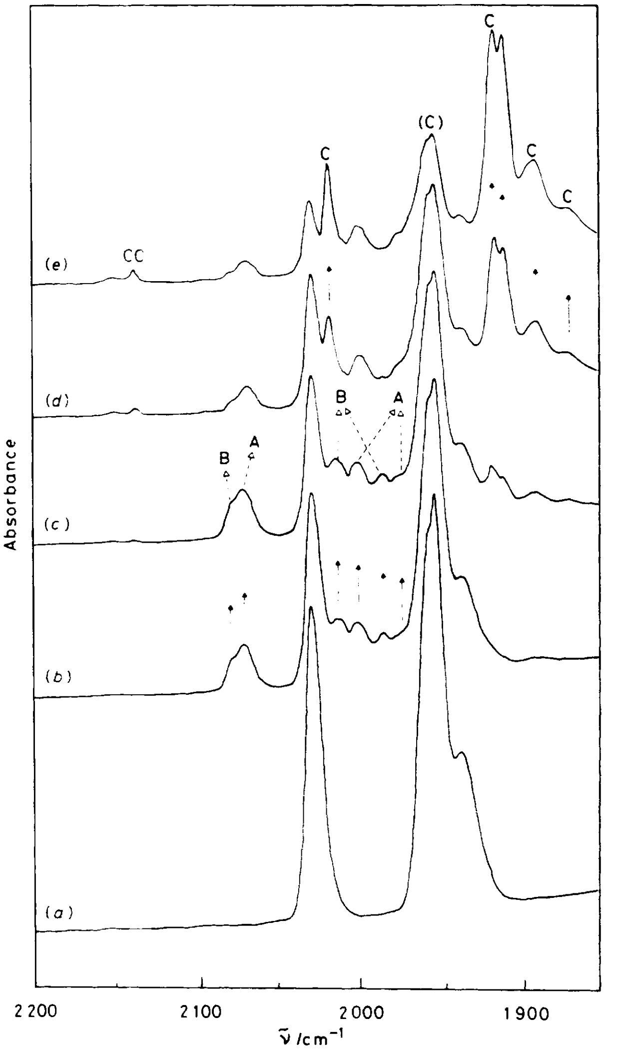

Figure 3. I.r. spectral changes of the carbonyl stretching modes of [Fe(CO)$_3$(bchie)] in an Ar matrix at 10 K after irradiation with λ = 514.5 nm (P = 100 mW). Irradiation times: (*a*) 0, (*b*) 15 min, (*c*) 50 min, (*d*) 2 h, (*e*) 6 h. All spectra are on the same absorbance scale

Table 1. I.r. CO-stretching frequencies (cm^{-1}) of [Fe(CO)$_3$(α-di-imine)] in pentane and in matrices at 10 K *

		Matrix		
Compound	Pentane	Ar	CO	N$_2$
[Fe(CO)$_3$(bchie)]	2 024.8	2 029.1	2 025.3	2 026.8
	1 950.3	1 953.1	1 948.7	1 951.1
		1 937.6		1 931 (sh)
[Fe(CO)$_3$(btbie)]	2 018.0	2 020.5		
	1 940.9	1 943.3		
		1 918 (sh)		
[Fe(CO)$_3$(bdmie)]	2 026.6			2 029
	1 956.0			1 959
	1 948.3			1 949
[Fe(CO)$_3$(bdpie)]	2 040.7	2 042.4		
	1 973.5	1 973.0		
	1 967.3	1 964 (sh)		
[Fe(CO)$_3$(bptie)]	2 038	2 043.4	2 040.1	
	1 976	1 978.0	1 972.3	
	1 965	1 968.4	1 964.1	
[Fe(CO)$_3$(dpipy)]	2 018	2 023.4		
	1 959	1 960.0		
	1 944	1 949.8		
		1 927 (sh)		
[Fe(CO)$_3$(bipy)]	1 979			
	1 896			

* sh = Shoulder.

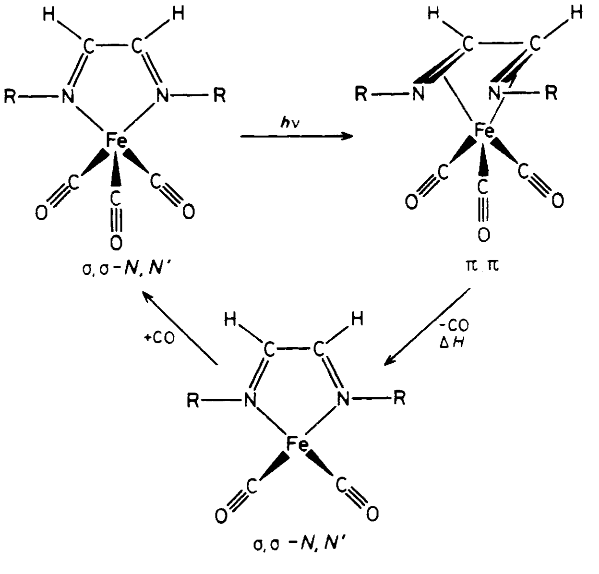

Figure 4. Proposed mechanism for the photolysis of [Fe(CO)$_3$L] in a matrix at 10 K

Because a band for the stretching mode of free carbon monoxide is not present in the i.r. spectra, the first photoproduct will still contain the Fe(CO)$_3$ moiety. Because of the low concentration and low temperature, dimerization may be excluded. The shift of the CO-stretching modes to higher frequency implies a decrease of the metal to carbonyl π back-bonding with respect to the parent compound. This effect will in turn be caused by an increase of π back-bonding from the metal to the ligand L. Such an increase of π back-bonding will take place when L changes its co-ordination from σ,σ-*N,N'* to π,π *via* both CN bonds (see Figure 4). In fact, the CO-stretching frequencies of A and B do agree well with those of the complexes [Fe(CO)$_3$(η^4-1,3-butadiene)] and [Fe(CO)$_3$(η^4-2,3-dimethyl-1,3-butadiene)] in which the butadiene ligands are π,π-co-ordinated to the metal.[17] For [Fe(CO)$_3$(η^4-1,3-butadiene)] the CO vibrations are found at 2 060, 1 995, and 1 983 cm^{-1} in an Ar matrix at 10 K, for [Fe(CO)$_3$(η^4-2,3-dimethyl-1,3-butadiene)] at 2 056, 1 988, and 1 976 cm^{-1} under the same conditions.[17] This result is of great importance, because this is the first time that such a π,π-co-ordination has been found for normal L ligands. Up to now, π,π-co-ordination has only tentatively been proposed for cyclic L ligands,[18,19] but never for normal open-chain ligands. The differences in CO frequencies of the isomers A and B are small (Figure 3) and very much alike for the three vibrations. This means that both isomers have nearly the same structure for the Fe(CO)$_3$ moiety and a slightly different bonding of the π,π-L ligand.

Further support for this π,π-co-ordination is given by the i.r. spectral changes in the region 1 300—1 500 cm^{-1} upon photolysis in a CO matrix (see Figure 5). In this region ν_{sym}(CN) of the parent compound has a band at 1 480 cm^{-1} (assignment based on the r.R. spectra) and ν(CC) at 1 343 cm^{-1}, while the band at 1 453 cm^{-1} is due to a CH bending

Table 2. I.r. CO-stretching frequencies (cm^{-1}) of [Fe(CO)$_3$(π,π-L)] in matrices at 10 K

	Matrix					
Compound	Ar		CO		N_2	
[Fe(CO)$_3$(bchie)]	2 069	2 077	2 068.1	2 074 *	2 067.3	2 076.1 *
	2 001	2 012	1 999.1	2 010 *	1 998.1	2 010.2 *
	1 972	1 984	1 969.2	1 982 *	1 974.7	1 978.6 *
[Fe(CO)$_3$(btbie)]	2 064.5					
	1 993.3					
	1 961.2					
[Fe(CO)$_3$(bdmie)]					2 068	
					1 999	
					1 980	
[Fe(CO)$_3$(bptie)]	2 075.6		2 074.9			
	2 016.1		2 014.3			
	2 000.0		1 994.6			

* Value obtained after annealing to 30 K.

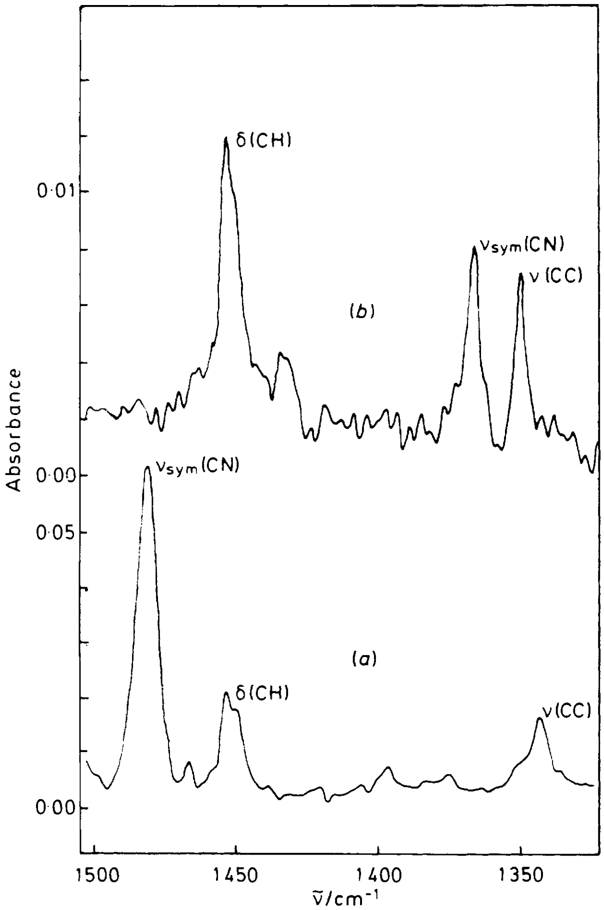

Figure 5. I.r. spectra (1 300—1 500 cm^{-1}) of [Fe(CO)$_3$(bchie)] (*a*) and of its first photoproduct (*b*) in a CO matrix at 10 K. Spectrum (*a*) is obtained by subtraction of (*b*) from a spectrum taken after 15 min of irradiation with λ = 514.5 nm (*P* = 40 mW). The spectra were taken on the same matrix as the CO-stretching frequencies (Tables 1—3)

mode. Upon irradiation, these bands of ν_{sym}(CN) and ν(CC) disappear, whereas the band at 1 453 cm^{-1} only shows a minor shift. Two new bands appear at 1 365 and 1 349 cm^{-1} [see Figure 5(*b*)], which are assigned to ν_{sym}(CN) and ν(CC) of the π,π-co-ordinated ligand L. This assignment agrees with our expectation of a large shift of ν_{sym}(CN) to lower frequency and a shift of ν(CC) to higher frequency on going from σ,σ-*N*,*N*′- to π,π-co-ordination, since the lowest π* level of L is antibonding between C and N and bonding between the C atoms of the diazabutadiene group. For comparison, a shift of 100 cm^{-1} is observed going from [Mn$_2$(CO)$_8$(σ,σ-L)] to [Mn$_2$(CO)$_6$(σ,σ,π,π-L)].[20]

In order to obtain more information about the stability of the π,π-co-ordinated photoproduct, the photolysis experiments were extended to other [Fe(CO)$_3$L] complexes. Complexes with more bulky ligands such as [Fe(CO)$_3$(btbie)] and [Fe(CO)$_3$(bdpie)] only showed weak bands of the π,π-co-ordinated complex. Apparently, π,π-co-ordination is only favourable for L with not too bulky substituents on the nitrogen atoms. This conclusion is confirmed by the difference in behaviour between [Fe(CO)$_3$(bdpie)] and [Fe(CO)$_3$(bptie)]. Both ligands have similar electronic properties, but that in the former complex has much bulkier substituents on the nitrogen atoms than the corresponding ligand in the latter complex. [Fe(CO)$_3$(bdpie)] only gives the second photoproduct, the π,π-co-ordinated product apparently not being sufficiently stable. In contrast with this, [Fe(CO)$_3$(bptie)] reacts photochemically to give the π,π-co-ordinated complex which only very slowly photodecomposes into the second photoproduct. The i.r. frequencies of the CO-stretching modes of several [Fe(CO)$_3$(π,π-L)] complexes are collected in Table 2.

Such a π,π-co-ordination is very unlikely for α-di-imines possessing an aromatic group, such as $C_5H_4N{-}CH{=}NR$. Indeed no such photoproduct is found for [Fe(CO)$_3$(dpipy)]. This complex does not show any photochemical reaction at all upon irradiation with λ = 514.5 nm in an Ar matrix at 10 K. This demonstrates that π,π-co-ordination is a primary step for the formation of the second photoproduct, which is discussed below.

The second photoproduct is formed with simultaneous release of carbon monoxide after prolonged irradiation [ν (CO) = 2 138 cm^{-1}, see for example Figure 3(*d*) and (*e*)]. The π,π-co-ordinated complex then photodecomposes. Figure 3 clearly shows that the CO-stretching frequencies of the second photoproduct of [Fe(CO)$_3$(bchie)] in an Ar or CO matrix are shifted to lower frequencies with respect to the parent compound (bands C in Figure 3). We assign these bands to a [Fe(CO)$_2$(bchie)] fragment in which the L ligand is σ,σ-*N*,*N*′-co-ordinated just as in the parent compound. Annealing of the CO matrix at 30 K caused bands C of this photoproduct to disappear with formation of the parent compound. Co-ordinative unsaturation of [Fe(CO)$_2$(bchie)] is furthermore demonstrated by its reaction with dinitrogen in a N_2 matrix. After the photolysis to the second photoproduct has taken

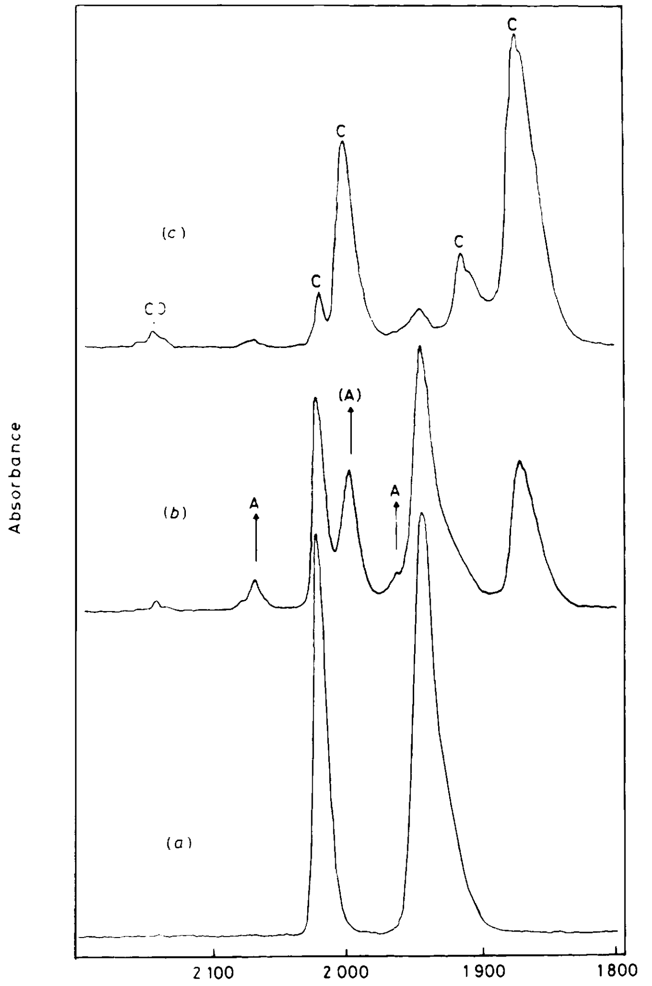

Figure 6. I.r. spectral changes of the carbonyl stretching modes of [Fe(CO)$_3$(btbie)] in an Ar matrix at 10 K after irradiation with λ = 514.5 nm (*P* = 60 mW). Irradiation times: (*a*) 0, (*b*) 3 min, (*c*) 50 min. All spectra are on the same absorbance scale; A = [Fe(CO)$_3$(π,π-L)], C = [Fe(CO)$_2$(σ,σ-L)]

place, a new band appeared at 2 203 cm^{-1}, which is in the range for stretching vibrations of N≡N co-ordinated to iron.[21] Therefore this product is identified as the dinitrogen complex [Fe(CO)$_2$(N$_2$)(bchie)]. For a [Fe(CO)$_2$(bchie)] fragment, only two bands are expected in the CO-stretching region. The observation of more bands points to the presence of different isomers and to matrix splitting. The number of C bands strongly depends on the L ligand (compare, for example, Figures 3 and 6). The formation of this photoproduct can best be studied from the photolysis of [Fe(CO)$_3$(btbie)] in an Ar matrix at 10 K. The i.r. spectral changes in the CO-stretching region are shown in Figure 6.

The spectrum in Figure 6(*c*) shows the almost complete photodecomposition of the parent compound into [Fe(CO)$_2$(btbie)]. The most intense bands of this fragment at 1 998 and 1 871 cm^{-1} are assigned to one of the isomers. The average value of these frequencies (1 934.5 cm^{-1}) is shifted to higher frequency with respect to that of the complex [Fe(CO)$_3$(PPh$_3$)(btbie)] (1 916 cm^{-1}) in agreement with the electron-donating properties of the PPh$_3$ ligand. The CO-stretching frequencies of several [Fe(CO)$_2$(σ,σ-*N*,*N*′-L)] complexes are presented in Table 3. {See also Table 5 for the results of the ^{13}CO-labelling study of [Fe(CO)$_2$(btbie)].}

Table 3. I.r. CO-stretching frequencies (cm^{-1}) of [Fe(CO)$_2$(σ,σ-*N*,*N*′-L)] in matrices at 10 K [a]

	Matrix		
Compound	Ar	CO	N$_2$
[Fe(CO)$_2$(bchie)]	2 018m	2 013m	2 016m
	1 940m	1 940m	~1 945m
	1 915s	1 910s	1 910s
	1 910s	1 902s	1 905s
	1 890m	1 879m	1 870m
	1 873w		
[Fe(CO)$_2$(btbie)]	2 017m		
	1 998s		
	1 908m		
	1 871s		
	1 866 (sh)		
[Fe(CO)$_2$(bdmie)]			2 018w
			1 975s
			1 915 (sh)
			1 907s
			1 885m
[Fe(CO)$_2$(bdpie)]	2 012w		
	1 990s		
	1 923s		
	1 912m		
	1 890w		
[Fe(CO)$_2$(bptie)]	*b*	~2 020m [b]	
		~1 886s [b]	

[a] Relative intensities: s = strong, m = medium, w = weak, sh = shoulder. [b] Bands are too weak and obscured by starting material for certain assignment.

Further support for the identification of the second photoproduct as an [Fe(CO)$_2$(σ,σ-*N*,*N*′-L)] fragment is given by the i.r. spectral changes during photolysis in the region 1 300—1 550 cm^{-1}. Figure 7 shows this region for the complex [Fe(CO)$_3$(btbie)] and for its second photoproduct. The parent compound has ν_{sym}(CN) at 1 494 cm^{-1} and ν(CC) at 1 330 cm^{-1}. The other bands in this region are mainly due to CH bending modes.

Upon photolysis only minor shifts are observed for the frequencies of the bands. The bands belonging to ν_{sym}(CN) and ν(CC) both decrease in intensity and shift to 1 473 and 1 362 cm^{-1}, respectively. For a π,π-co-ordinated complex a much greater shift is expected as found for [Fe(CO)$_3$(bdpie)] (see above). Most likely formation of the second photoproduct out of the π,π-co-ordinated complex takes place thermally. First of all, the π,π-co-ordinated complex hardly absorbs at the wavelength of irradiation (λ = 514.5 nm) and varying the wavelength of the laser beam to λ = 457.9 nm did not accelerate the decomposition. Besides, the second photoproduct was only formed at high laser beam power. Thus, almost no CO was released after 3 h of irradiation of [Fe(CO)$_3$(bchie)] in an Ar matrix with λ = 514.5 nm of a 20-mW laser beam, whereas 0.5 h of irradiation with 100 mW of the same laser line caused decomposition of 30% of the parent compound into the [Fe(CO)$_2$(bchie)] fragment. It appears that the π,π-co-ordinated complex is heated by the laser beam. Annealing the Ar matrix to 30 K did not confirm the above experiment, presumably because the matrix temperature was still too low.

^{13}*CO-Labelling Force-field Calculations of* [Fe(CO)$_3$(btbie)] *and* [Fe(CO)$_2$(btbie)].—After ^{13}CO was allowed to react photochemically with [Fe(CO)$_3$(btbie)], eight different CO frequencies were observed both in hexane and in an Ar matrix at 10 K. Of these frequencies, the band at 2 018 cm^{-1} of the starting complex [Fe(^{12}CO)$_3$(btbie)] appeared to be weak,

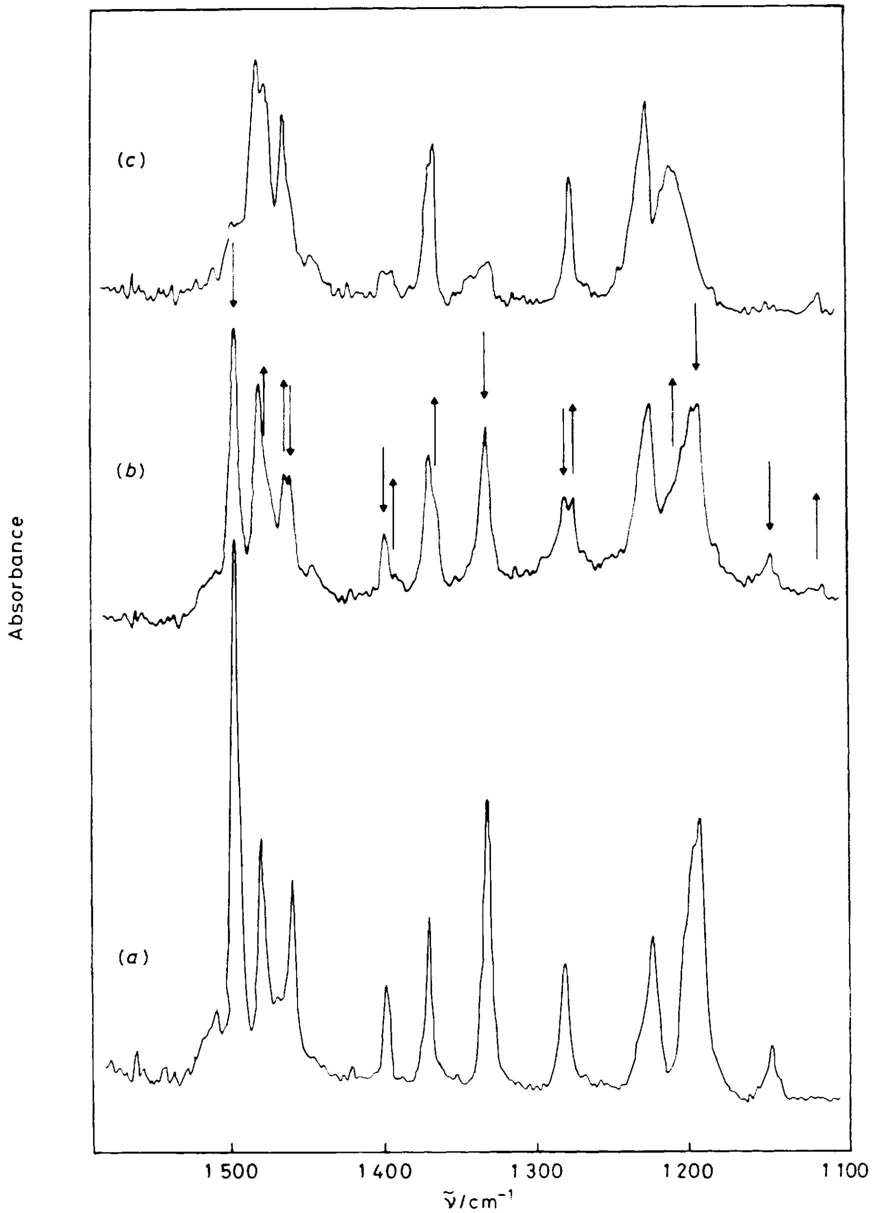

Figure 7. I.r. spectral changes (1 100—1 600 cm^{-1}) of [Fe(CO)$_3$(btbie)] in an Ar matrix at 10 K after irradiation with λ = 514.5 nm (P = 60 mW). Irradiation times: (*a*) 0, (*b*) 3 min, (*c*) 50 min. All spectra are on the same absorbance scale. The spectra were taken on the same matrix as the CO-stretching spectra (Figure 6 and Tables 1—3)

showing that substitution of ^{12}CO by ^{13}CO had occurred to a large extent. I.r. frequencies of the labelled first photoproducts [Fe(CO)$_3$(π,π-btbie)] could not be determined accurately due to a large overlap with the CO bands of the labelled parent compounds.

[Fe(CO)$_3$(btbie)]. Assuming C_s symmetry {see Figure 1, which was derived from the crystal structure of [Fe(CO)$_3$-(bdpie)] [5]}, a mixture of six different isomers is expected: [Fe(^{12}CO)$_3$(btbie)], C_s [Fe(^{12}CO)$_2$(^{13}CO)$_{ax}$(btbie)], C_1 [Fe-(^{12}CO)$_2$(^{13}CO)$_{eq}$(btbie)], C_s [Fe(^{13}CO)$_2$(^{12}CO)$_{ax}$(btbie)], C_1 [Fe(^{13}CO)$_2$(^{12}CO)$_{eq}$(btbie)], and [Fe(^{13}CO)$_3$(btbie)]. These six isomers will produce 18 different CO frequencies. However, some of these CO vibrations will nearly coincide. This is also the case for the unlabelled compound, which has only two i.r. bands in solution and in a matrix (see Table 1). In order to assign the observed CO frequencies of these isomers, force-field calculations had to be performed. All measured frequencies and their relative intensities were used for the assignment. The CO-stretching region of the labelled complex is presented in Figure 8(*a*) and the calculated and observed CO frequencies are presented in Table 4.

The diagonal force constants k_1 and k_2 (both 1 567 N m^{-1}) do not deviate much from k_3 (1 558 N m^{-1}). The same holds for the interaction force constants k_{13}, k_{23}, and k_{12} (40, 40, and 44 N m^{-1} respectively). The Fe(CO)$_3$ moiety has nearly C_{3v} symmetry for [Fe(^{12}CO)$_3$(btbie)] and [Fe(^{13}CO)$_3$(btbie)] and this affects the number of frequencies observed for the ^{12}CO/^{13}CO mixed complexes. Thus, the frequency differences between C_s [Fe(^{12}CO)$_2$(^{13}CO)$_{ax}$(btbie)] and C_1 [Fe(^{12}CO)$_2$-(^{13}CO)$_{eq}$(btbie)] and between C_s [Fe(^{13}CO)$_2$(^{12}CO)$_{ax}$(btbie)] and C_1 [Fe(^{13}CO)$_2$(^{12}CO)$_{eq}$(btbie)] appeared to be too small to be detected in the i.r. spectra.

[Fe(CO)$_2$(btbie)]. As can be seen from Figure 6(*c*), two conformers of [Fe(CO)$_2$(btbie)] are formed after photolysis of

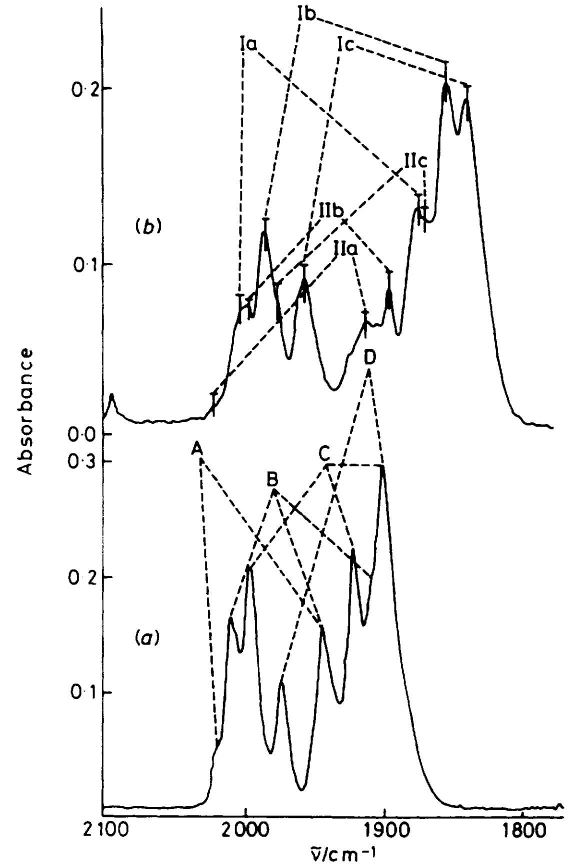

Figure 8. I.r. spectra of the CO-stretching modes of labelled $[Fe(CO)_3(btbie)]$ in an Ar matrix at 10 K (*a*) before and (*b*) after photolysis with $\lambda = 514.5$ nm ($P = 60$ mW). (*a*): bands belonging to the same isomer are connected: A = $[Fe(^{12}CO)_3(btbie)]$, B = $[Fe(^{12}CO)_2(^{13}CO)(btbie)]$, C = $[Fe(^{12}CO)(^{13}CO)_2(btbie)]$, and D = $[Fe(^{13}CO)_3(btbie)]$ (see also Table 4). (*b*): the calculated frequencies are indicated (†) and bands belonging to the same isomer are connected (see Table 5 for assignments)

unlabelled $[Fe(CO)_3(btbie)]$ in an Ar matrix at 10 K, each possessing two CO frequencies. The CO-stretching region of the corresponding photolyzed labelled complex is shown in Figure 8(*b*). The most abundant conformer I gives rise to six CO frequencies, compared with two for the unlabelled one. These are the most intense bands in the i.r. spectrum. Conformer II shows four less intense bands and two partly obscured ones. The calculated and observed CO frequencies and the final set of force constants are presented for conformers I and II in Table 5. The initial force constants were refined with the aid of an iterative computer program, but presumably due to the broadness of the bands no better fit could be obtained.

For conformer I the diagonal force constants k_1 and k_2 are equal (1 515 N m^{-1}). For conformer II they are different (1 528 and 1 585 N m^{-1}, respectively). Therefore we propose that in conformer I the axial carbonyl has been released and in conformer II, one of the equatorial carbonyls (see Figure 1).

Photosubstitution Reactions in Solution.—We have investigated in detail the photosubstitution reactions of the complex $[Fe(CO)_3(bdpie)]$ in solution at room temperature. This complex readily undergoes photosubstitution of CO when it is irradiated into the lowest-energy absorption band. Mono-, as well as di-substitution was found dependent on the π-accepting properties of the entering nucleophile. The complexes $[Fe(CO)_3(dpipy)]$ and $[Fe(CO)_3(bipy)]$ also showed photosubstitution of CO but no quantum yields could be determined for these reactions due to simultaneous photodecomposition of the parent compounds. Three different types of reactions, (1)—(3), were studied: L′ = PEt_3, $PBu^n{}_3$, $PPr^i{}_3$, $P(C_6H_{11})_3$ (C_6H_{11} = cyclohexyl), PPh_3, pyridine (py), 4-cyanopyridine (4CN-py), 4-acetylpyridine, pyridazine (pydz), 5,6-diazaphenanthrene, or $Ph_2PCH_2CH_2PPh_2$; L″ = $P(OMe)_3$ or C≡NR (R = $C_6H_3Me_2$-2,6, $C_6H_4NO_2$-4, or Bu^t).

$$[Fe(CO)_3(bdpie)] + L' \longrightarrow [Fe(CO)_2L'(bdpie)] + CO \quad (1)$$

$$[Fe(CO)_3(bdpie)] + 2L'' \longrightarrow [Fe(CO)(L'')_2(bdpie)] + 2CO \quad (2)$$

$$[Fe(CO)_3(bdpie)] + bchie \longrightarrow [Fe(CO)(bchie)(bdpie)] + 2CO \quad (3)$$

Table 4. Observed and calculated CO-stretching frequencies (cm^{-1}) of $[Fe(CO)_3(btbie)]$ in an Ar matrix at 10 K [a]

Compound	Point group	Symmetry	ṽ(CO) Observed	ṽ(CO) Calculated
$[Fe(^{12}CO)_3(btbie)]$	C_s	a'	2 018.0 [b]	2 019.0
		a''	1 943.3 [b]	1 941.6
		a'	1 943.3	1 941.0
$[Fe(^{12}CO)_2(^{13}CO)_{ax}(btbie)]$	C_s	a'	2 008.5	2 010.1
		a''	1 942.5	1 941.6
		a'	1 907	1 906.5
$[Fe(^{12}CO)_2(^{13}CO)_{eq}(btbie)]$	C_1	a	2 008.5	2 007.8
		a	1 942.5	1 941.1
		a	1 907	1 909.2
$[Fe(^{13}CO)_2(^{12}CO)_{ax}(btbie)]$	C_s	a'	1 994.8	1 993.4
		a'	1 920.4	1 922.6
		a''	1 899.2	1 898.7
$[Fe(^{13}CO)_2(^{12}CO)_{eq}(btbie)]$	C_1	a	1 994.8	1 996.6
		a	1 920.4	1 920.0
		a	1 899.2	1 898.3
$[Fe(^{13}CO)_3(btbie)]$	C_s	a'	1 972.4	1 974.5
		a''	1 899.2	1 898.7
		a'	1 899.2	1 898.1

[a] The force constants are: $k_1 = k_2 = 1\,567$, $k_3 = 1\,558$, $k_{13} = k_{23} = 40$, and $k_{12} = 44$ N m^{-1}. [b] Value obtained from the photolysis experiment of the unlabelled species (Figure 6 and Table 1).

Figure 9 shows the changes in the electronic absorption spectrum upon irradiation of $[Fe(CO)_3(bdpie)]$ in a benzene solution in the presence of PPh_3 while Figure 10 shows the changes in the CO-stretching region upon irradiation of a pentane solution of $[Fe(CO)_3(bdpie)]$ in the presence of PEt_3. The samples were irradiated with $\lambda = 488.0$ (Figure 9) and 514.5 nm (Figure 10). The spectra possess good isosbestic points, showing that the reaction proceeded without decomposition. Due to substitution of the electron-withdrawing carbonyl ligand by the basic phosphine, the electronic absorption bands shift to longer wavelength and the CO-stretching modes to lower frequency.

The stretching vibrations of the remaining two carbonyls of the photoproduct $[Fe(CO)_2(PEt_3)(bdpie)]$ are doublets (see Figure 10). The relative intensities of the components and their frequency differences are nearly equal for both vibrations. These doublets therefore most likely belong to different isomers and this assumption is supported by the temperature dependence of the i.r. spectrum. Lowering the temperature

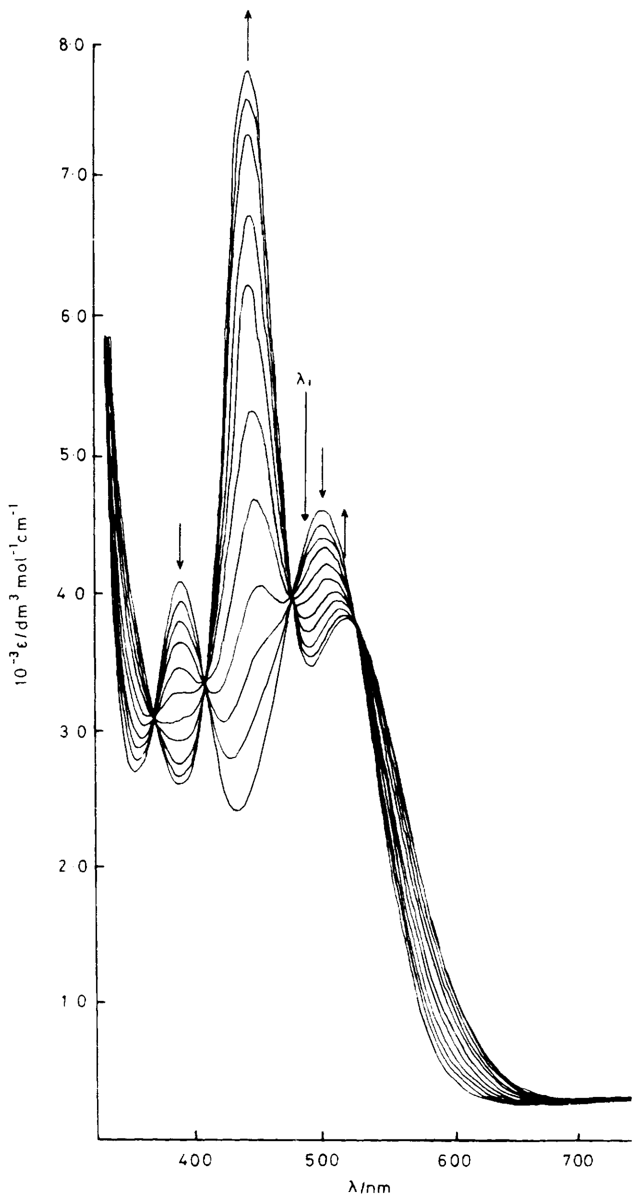

Figure 9. Electronic absorption spectral changes of a benzene solution of [Fe(CO)$_3$(bdpie)], containing a 200-fold excess of PPh$_3$, during photolysis with λ_i = 488.0 nm (P = 30 mW)

causes a change of the relative intensities of the doublet bands. This points to a change of the equilibrium between both isomers. These isomers interconvert rapidly because at −70 °C no splitting could be observed for the ^{31}P n.m.r. signal of the photoproduct in [^{2}H$_8$]toluene.

Reaction (1) was observed for all ligands L′ indicated above, although the photoproducts of the substituted pyridine, pyridazine, and 5,6-diazaphenanthrene ligands appeared to be thermally unstable at room temperature. In this photosubstitution reaction, Ph$_2$PCH$_2$CH$_2$PPh$_2$ clearly acts as a monodentate ligand. The CO-stretching frequencies of several monosubstituted complexes are collected in Table 6. These vibrations clearly shift to higher frequency when the substituting ligand becomes more electron withdrawing.

Photosubstitution of two carbonyl ligands according to reaction (2) was only observed for small ligands with good π-accepting properties such as P(OMe)$_3$ or aromatic isocyanides. For one of these reactions, that of 2,6-dimethylphenyl isocyanide (dmpi) with [Fe(CO)$_3$(bdpie)], the changes in the CO-stretching region during the photochemical reaction are shown in Figure 11. The upper part of this figure represents the formation of the monosubstituted product [Fe(CO)$_2$(dmpi)(bdpie)] [spectrum (*b*)] out of the parent compound [spectrum (*a*)]. The lower part of Figure 11 shows the conversion into the disubstituted complex [Fe(CO)(dmpi)$_2$(bdpie)] [spectrum (*c*)]. By subtraction, the spectrum (*b*) of the not yet isolated monosubstituted product could be deduced from the spectra (see insert of Figure 11 and Table 6). Going from spectrum (*a*) to (*b*) the CO frequencies decrease due to photosubstitution of a CO ligand by the less electron-withdrawing isocyanide. Substitution of a second carbonyl ligand, however, causes a shift to higher frequency (1 995 cm^{-1}). At the same time, the band becomes very broad. Apparently the CO ligand is rather loosely bonded in the disubstituted complex. The bands at 2 038 and 2 010 cm^{-1} (two bands, due to two isomers) in spectrum (*b*) and at 2 081 and 2 028 cm^{-1} in spectrum (*c*) are due to C≡N stretching vibrations of the co-ordinated isocyanide ligands.

The vibration of the remaining CO ligand in the corresponding complex of the less electron-withdrawing t-butyl isocyanide has a much lower frequency and its i.r. band is much narrower. In this complex the CO ligand is apparently more tightly bonded. The CO stretching frequencies of several disubstituted complexes are collected in Table 7.

[Fe(CO)$_3$(bdpie)] also reacted according to reaction (3) with other ligands L. The reaction of [Fe(CO)$_3$(bdpie)] with bchie gave a stable photoproduct [Fe(CO)(bchie)(bdpie)] with one CO-stretching frequency at 1 905 cm^{-1}. Unfortunately, until now this product and comparable ones could not be isolated. Generally, stable products could only be obtained in solution when a more electron-withdrawing aromatic ligand L was used in combination with a more electron-releasing aliphatic L. This so-called push-pull effect has been applied, for example, by Cavell *et al.*[22] to prepare stable [Pt^{0}L(olefin)] complexes. Such complexes could only be prepared when an electron-withdrawing olefin was used in combination with a basic ligand L. Thus, the reaction of [Fe(CO)$_3$(bdpie)] with aromatic L ligands or with bipy gave only photodecomposition. In a forthcoming article we will discuss the spectroscopic and structural properties of these complexes in more detail.

We have also investigated the photosubstitution of [Fe(CO)$_2$(PPh$_3$)(bdpie)]. This latter compound was prepared photochemically. Irradiation (λ = 514.5 nm) of a pentane solution of [Fe(CO)$_2$(PPh$_3$)(bdpie)] in the presence of PBu$^n{}_3$ resulted in substitution of PPh$_3$, yielding [Fe(CO)$_2$(PBu$^n{}_3$)(bdpie)].

Mechanism of the Photochemical Reactions.—All complexes of L appeared to be stable photochemically when they were irradiated in solution in the absence of a substituting ligand. This means that dissociative loss of a carbonyl ligand as proposed by Johnson and Trogler[6] for the tetra-azadiene complex [Fe(CO)$_3$(MeN=N–N=NMe)] cannot take place for the [Fe(CO)$_3$L] (L = 1,4-diaza-1,3-butadienes) complexes. Quantum yields for photosubstitution of CO in [Fe(CO)$_3$(bdpie)] are collected in Table 8 for various substituents and at different wavelengths. Variation of the cone angle[23] of the substituting ligand does not influence the quantum yield and this clearly points to a dissociative mechanism. In this respect these photochemical reactions differ from thermal substitution reactions of these complexes for which a cone angle dependence has been found and an associative mechanism accordingly proposed.[13,24] Now, instead of a metal–carbon bond, one of the metal–nitrogen bonds can be broken

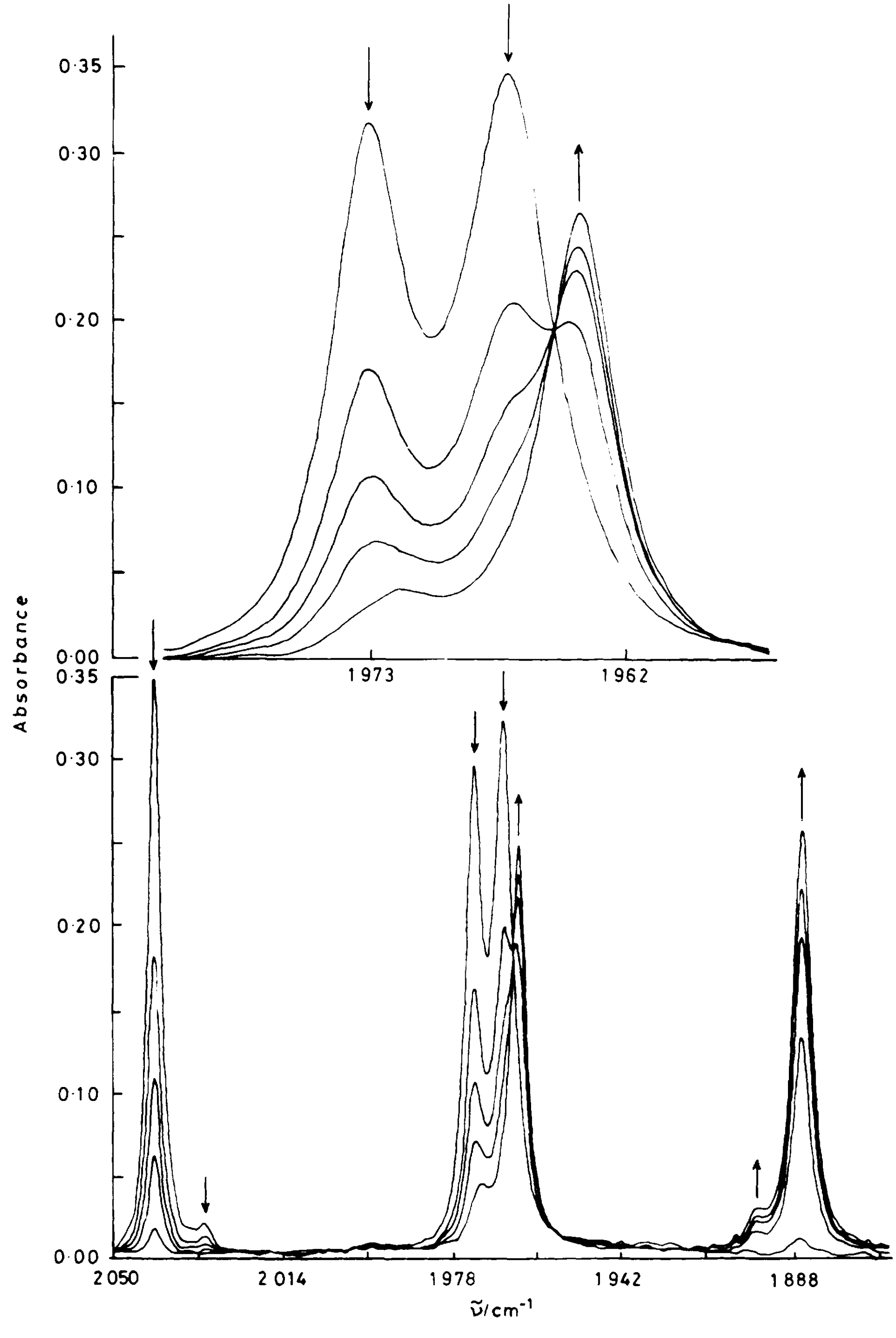

Figure 10. I.r. spectral changes of the carbonyl stretching modes of a pentane solution of $[Fe(CO)_3(bdpie)]$, containing an excess of PEt_3, during photolysis with $\lambda = 514.5$ nm ($P = 60$ mW)

giving rise to σ-*N*-monodentate co-ordination of L: structure (B), Figure 12.

σ-*N*-Co-ordination of L has been reported, *e.g.* for $[Cr(CO)_5L]$,[25] $[M(CO)_5(4,4'\text{-dialkyl-}2,2'\text{-bipyridine})]$ (M = Cr, Mo, or W),[26] and for $[MCl_2(PPh_3)(btbie)]$ (M = Pd or Pt).[27] Such a co-ordinatively unsaturated compound (B) will rearrange rapidly to the parent compound (A) in the absence of a substituting ligand, and this explains the photochemical stability of the complexes of L in solution. In the presence of a substituting ligand, complex (B) will react further to give complexes (C) and (D), respectively. The quantum yield of this reaction will not depend on the cone-angle of the nucleophile. This reaction scheme also agrees with our observation that the quantum yield decreases upon lowering the concentration of PPh_3 for the photosubstitution reaction of this ligand with $[Fe(CO)_3(bipie)]$ (see Table 9). At lower concentrations the back-reaction from (B) to (A) becomes important. According to this mechanism the photosubstitution reaction involves the breaking and closing of a metal–nitrogen bond. The same mechanism has been proposed for the thermal olefin exchange in $[PtCl_2(\eta^2\text{-olefin})(L\text{-}L)]$ (L–L = *N*,*N*′-disubstituted-1,2-diaminoethane)[28] and $[PtCl_2(\eta^2\text{-olefin})L]$,[28] and extensive evidence has been put forward for the occurrence of reversible σ,σ-*N*,*N*′ chelate to σ-*N* monodentate

Table 5. Observed and calculated CO-stretching frequencies (cm^{-1}) of [Fe(CO)$_2$(btbie)] in an Ar matrix at 10 K [a]

Compound	Point group	Symmetry	$\tilde{\nu}$(CO)	
			Observed	Calculated
[Fe(^{12}CO)$_2$(btbie)] (Ia)	C_{2v}/C_s	a_1/a'	1 998.0 [b]	1 997.0
		b_2/a''	1 871.4 [b]	1 873.3
[Fe(^{12}CO)(^{13}CO)(btbie)] (Ib)	C_1	a	1 980.4	1 978.6
		a	1 849.3	1 849.0
[Fe(^{13}CO)$_2$(btbie)] (Ic)	C_{2v}/C_s	a_1/a'	1 952.3	1 952.9
		b_2/a''	1 835.0	1 832.0
[Fe(^{12}CO)$_2$(btbie)] (IIa)	C_1	a	2 016.8 [b]	2 016.7
		a	1 907.9 [b]	1 907.6
[Fe(^{12}CO)(^{13}CO)(btbie)] (IIb)	C_1	a	1 993.5	1 991.4
		a	1 891.5	1 889.3
[Fe(^{13}CO)$_2$(btbie)] (IIc)	C_1	a	~1 970 [c]	1 972.2
		a	~1 863 [c]	1 865.6

[a] The force constants are $k_1 = k_2 = 1\ 515$ and $k_{12} = 97$ N m^{-1} for conformer I; $k_1 = 1\ 528$, $k_2 = 1\ 585$, and $k_{12} = 82$ N m^{-1} for conformer II. [b] Value obtained from the photolysis experiment of the unlabelled species (Figure 6 and Table 3). [c] Partly obscured.

Table 6. I.r. CO-stretching frequencies (cm^{-1}) of some [Fe(CO)$_2$L'(α-di-imine)] and [Fe(CO)$_2$L''(α-di-imine)] [a] complexes, measured in pentane

Compound	$\tilde{\nu}$(CO)	
[Fe(CO)$_2$(PPh$_3$)(bdpie)]	1 984	1 925 (sh)
[Fe(CO)$_2$(PEt$_3$)(bdpie)]	1 972/1 969	1 912/1 904
[Fe(CO)$_2${P(C$_6$H$_{11}$)$_3$}(bdpie)]	1 966/1 959	1 905/1 900
[Fe(CO)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)(bdpie)]	1 967	1 910
[Fe(CO)$_2${P(OMe)$_3$}(bdpie)] [a]	1 987.2/1 977.4	1 929.6/1 920.2
[Fe(CO)$_2$(py)(bdpie)]	1 974/1 972	1 911/1 903
[Fe(CO)$_2$(dmpi)(bdpie)] [a]	1 984	1 942/1 922
[Fe(CO)$_2$(C$\equiv$NC$_6$H$_4$NO$_2$-4)(bdpie)] [a,b]	1 977	1 940
[Fe(CO)$_2$(C$\equiv$NBu^t)(bdpie)] [a]	1 985	1 933
[Fe(CO)$_2$(PPh$_3$)(bchie)]	1 955	1 896
[Fe(CO)$_2$(PBu$^n{}_3$)(bchie)]	1 951	1 890
[Fe(CO)$_2${P(OMe)$_3$}(bchie)] [a]	1 969	1 911
[Fe(CO)$_2$(PPh$_3$)(btbie)]	1 947	1 886
[Fe(CO)$_2$(PPh$_3$)(bdmie)]	1 959	1 901
[Fe(CO)$_2$(PPh$_3$)(dpipy)]	1 964	1 907/1 888
[Fe(CO)$_2$(PEt$_3$)(dpipy)]	1 967	1 900/1 877
[Fe(CO)$_2${P(OMe)$_3$}(dpipy)] [c]	1 985/1 975	1 927/1 918
[Fe(CO)$_2$(PPh$_3$)(bipy)]	1 924	1 865

[a] Values obtained by subtracting the [Fe(CO)$_3$L] and [Fe(CO)(L'')$_2$L] frequencies from a spectrum in which all three complexes were present. [b] Measured in CH$_2$Cl$_2$. [c] This compound was isolated by a thermal CO-substitution (ref. 20).

processes in square-planar [{PtX$_{2-n}$(PR$_3$)$_{1+n}$(L–L)}X$_n$] and [{PtX$_{2-n}$(PR$_3$)$_{1+n}$L}X$_n$] (n = 0 or 1; X = Cl or Br) complexes.[26] Furthermore, Bellachioma and Cardaci [29,30] have shown by kinetic studies that the thermal substitution of CO in the complexes [Fe(CO)$_3$(RHC=CH–CH=NR')] also occurred *via* partial dissociation of the ligand, yielding an intermediate in which the ligand is σ-*N*-co-ordinated. Unfortunately, we could not detect such a σ-*N*-monodentate intermediate even at low temperature. For the photochemical reaction of [Fe(CO)$_3$(bdpie)] with 2-methyltetrahydrofuran (mthf) at 140 K (λ = 514.5 nm, P = 40 mW) only (D) was found as a photoproduct. Contrary to the [Fe(CO)$_3$L] complexes, those of dpipy and bipy show photodecomposition in solution upon irradiation into the m.l.c.t. band in the absence of a substituting ligand. This behaviour may be due to a lower stability of the σ-*N*-monodentate intermediate or to the fact that formation of a σ-*N*-monodentate intermediate has a high activation barrier. Such different behaviour between ligands L and that of dpipy and bipy has also been observed for the thermal displacement reactions of L–L in [PtCl$_2$(η^2-olefin)(L–L)] and L in [PtCl$_2$(η^2-olefin)L].[28]

The photochemistry of these complexes in matrices at 10 K differs from that in solution. The [Fe(CO)$_3$L] complexes all photodecompose in a matrix with release of CO and formation of a [Fe(CO)$_2$(σ,σ-*N*,*N'*-L)] fragment. For L with not too bulky substituents on the nitrogen atoms, an intermediate is formed in which L is π,π-co-ordinated to the metal. Such a difference in photochemical behaviour between complexes in matrices and those in normal solutions at room temperature is not uncommon. For example, [Cr(CO)$_5$(pydz)] undergoes in solution photosubstitution of pyridazine by other nucleophiles upon irradiation into the lowest-energy m.l.c.t. transition. On the other hand, CO is released in a matrix at 10 K with formation of a [Cr(CO)$_4$(pydz)] fragment.[31] In matrices at 10 K the photochemical reactions after irradiation into the m.l.c.t. band will take place from the long-lived m.l.c.t. state. The formation of a π,π-co-ordinated intermediate from this state agrees with our r.R. results. These spectra show a weak r.R. effect for deformation modes of the L ligand which means that L becomes distorted in the m.l.c.t. excited state. As a result of this distortion the complex may relax to a π,π-co-ordinated intermediate, which can then decompose to the [Fe(CO)$_2$(σ,σ-*N*,*N'*-L)] fragment. As shown above, this latter decomposition is thermal.

In solution at room temperature other processes can compete with the reaction from the m.l.c.t. state. First of all, fast

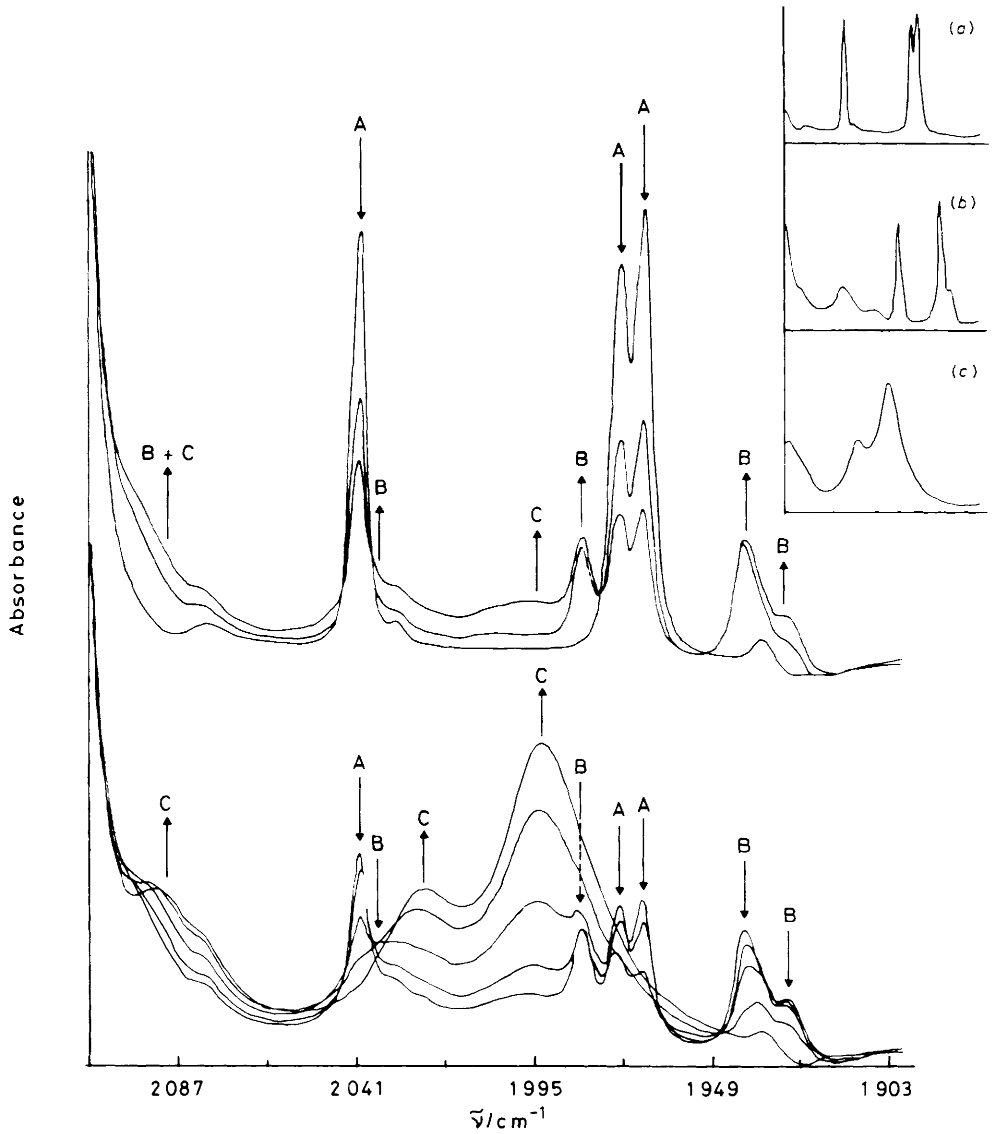

Figure 11. I.r. spectral changes of CO-stretching modes of a pentane solution of [Fe(CO)$_3$(bdpie)], containing an excess of dmpi, during photolysis with λ = 514.5 nm (*P* = 60 mW). All spectra are on the same absorbance scale. Insert: (*a*) [Fe(CO)$_3$(bdpie)] (A), (*b*) [Fe(CO)$_2$-(dmpi)(bdpie)] (B), (*c*) [Fe(CO)(dmpi)$_2$(bdpie)] (C); spectrum (*b*) was obtained by subtraction of (*a*) and (*c*) from a spectrum in which all three complexes were present

Table 7. I.r. CO-stretching frequencies (cm^{-1}) of some [Fe(CO)-(L'')$_2$L] complexes and [Fe(CO)(bchie)(bdpie)] measured in pentane

Compound	$\tilde{\nu}$(CO)
[Fe(CO){P(OMe)$_3$}$_2$(bdpie)]	1 918/1 911
[Fe(CO)(dmpi)$_2$(bdpie)]	1 995 (br)
[Fe(CO)(C≡NC$_6$H$_4$NO$_2$-4)$_2$(bdpie)] *	1 996/1 978
[Fe(CO)(C≡NBu^t)$_2$(bdpie)]	1 918
[Fe(CO)(bchie)(bdpie)]	1 905
[Fe(CO){P(OMe)$_3$}$_2$(bchie)]	1 911/1 903

* Measured in CH$_2$Cl$_2$.

conversion of excited state energy into vibrational motions within the molecule can lead to the breaking of a metal–nitrogen bond (see above). This mechanism most probably accounts for the photosubstitution reactivity of the [Fe(CO)$_3$L] complexes under study. It differs from the mechanism proposed by Johnson and Trogler [6] for the photochemistry of [Fe(CO)$_3$(MeN=N–N=NMe)] in that a metal–nitrogen bond is broken instead of a metal–carbonyl one. For this process only a relatively constant fraction of the excitation energy is required and therefore a higher quantum yield at higher energy is expected. This is indeed found for the photosubstitution of CO in [Fe(CO)$_3$(bdpie)] by PPh$_3$ and PBu$^n_3$ (see Table 8). An alternative explanation is a two-state scheme in which chemical reactions occur from a ligand field (l.f.) state lying above the m.l.c.t. state and in steady-state equilibrium with it. Such a mechanism has been proposed by Lees and Adamson [32] for [W(CO)$_5$L'] (L' = 4-substituted pyridine) which undergoes photodissociation of the ligand L' upon irradiation into the lowest m.l.c.t. transition. This mechanism is, however, less probable here. First of all, the energy difference between the l.f. and m.l.c.t. states is expected to be much larger for the [Fe(CO)$_3$L] (L = RN=CH–CH=NR) complexes than for *e.g.* [W(CO)$_5$(4CN-py)]. In this latter complex the l.f. and m.l.c.t. transitions are close in energy

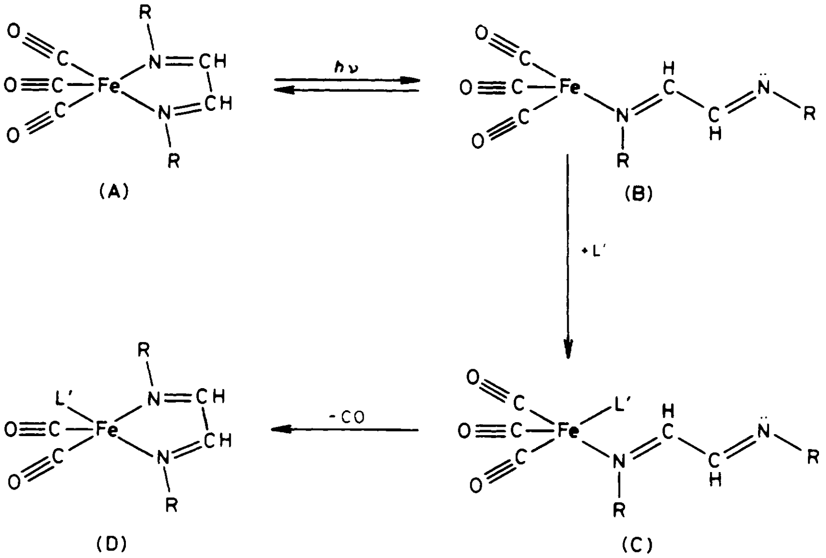

Figure 12. Proposed mechanism for solution CO photosubstitution in [Fe(CO)$_3$L]

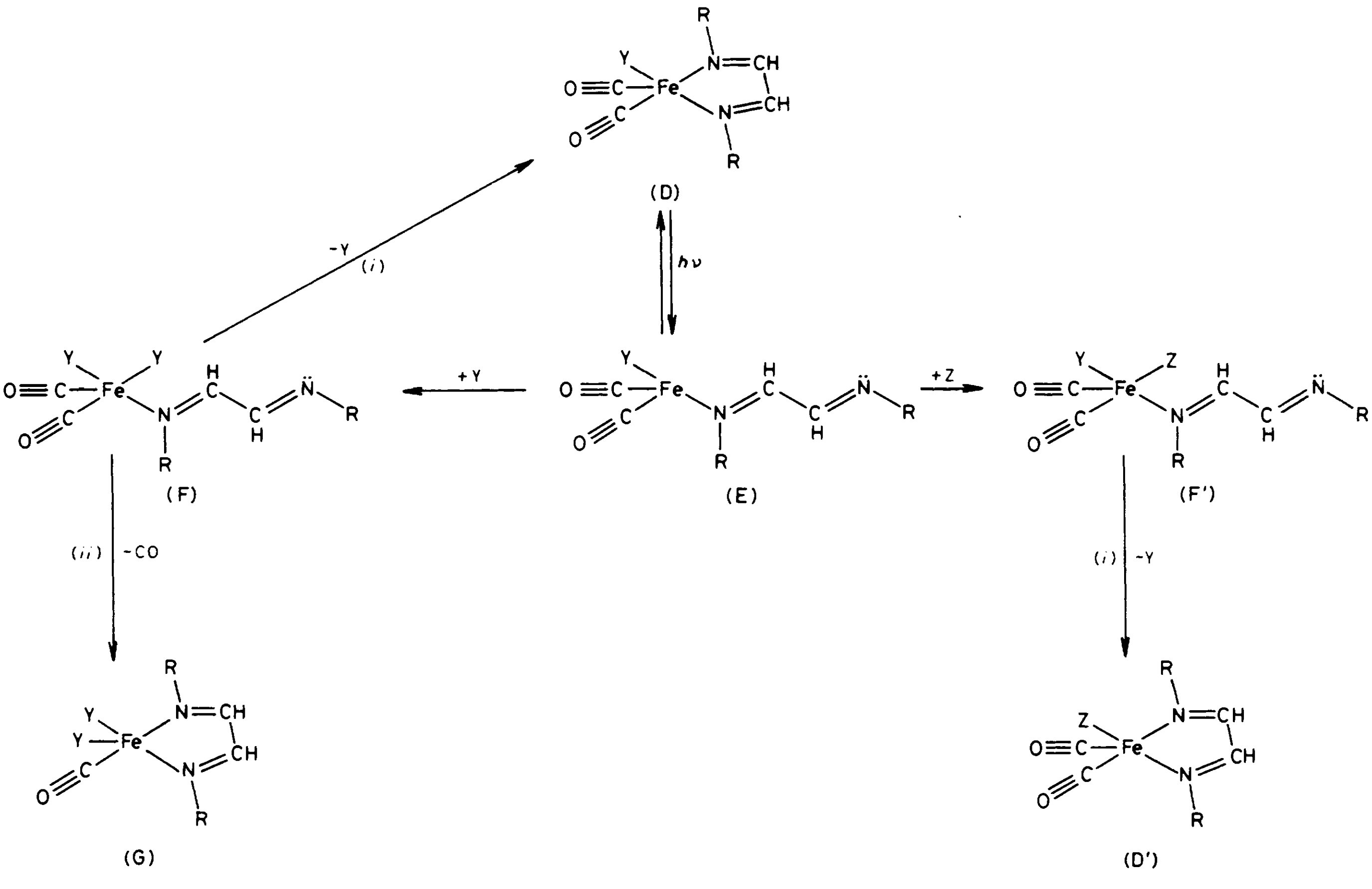

Figure 13. Proposed mechanism for photosubstitution in [Fe(CO)$_2$YL] [Y, Z are substituting ligands L′ or L″ (see text)]

(400 and 435—470 nm, respectively),[32] whereas the l.f. and m.l.c.t. transitions of the [Fe(CO)$_3$L] complexes have a much larger energy separation (*ca.* 300 and 450—540 nm, respectively).[5] This makes a steady-state equilibrium for the [Fe(CO)$_3$L] complexes in solution unlikely. Besides, the observed photosubstitution quantum yields, $\Phi \simeq 0.2$, are too high for such a process and the photosubstitution reaction appeared to take place rather efficiently in mthf at 140 K.

A referee has suggested that the primary photoprocess is the same in solution and in matrices and that the π,π-co-ordinated complex [Fe(CO)$_3$(π,π-L)] is formed in both media as the first photoproduct. The different photochemistry could

Table 8. Quantum yields for the photosubstitution of CO by L′ in $[Fe(CO)_3(bdpie)]$ [a]

L′	Cone angle (°) [b]	Φ_p^{i} [c] 580 nm	514.5 nm	488 nm	457.9 nm	351 nm
PPh_3	145	0.21	0.24	0.25	0.30	0.36
PEt_3	132		0.27			
PBu^n_3	132	0.18	0.25	0.27	0.32	0.34
PPr^i_3	160		0.28			
$P(C_6H_{11})_3$	170		0.23			
py			0.25		0.29	
pydz				0.17		
bchie		0.09	0.09	0.08		

[a] All reactions were carried out in benzene solutions at 20 °C; estimated error for the quantum yields is ±10%. [b] Cone angle according to ref. 23. [c] Φ_p^{i} = initial quantum yield of product formation.

Table 9. Quantum yields for the photosubstitution of CO by PPh_3 at different concentrations of $[Fe(CO)_3(bdpie)]$ [a]

$[PPh_3]/[Fe(CO)_3(bdpie)]$	Φ_p^{i} [b]
$\geqslant 250$	0.25
21	0.20
5	0.13
2	0.08

[a] All reactions were carried out in benzene solutions at 20 °C; estimated error for the quantum yields is ±15%. [b] Φ_p^{i} = initial quantum yield of product formation.

then be the result of different secondary processes. This proposition, however, does not account for the fact that whereas the same photochemistry is observed in solution for L as well as for the dpipy and bipy complexes, only the ligands L are expected to give a π,π-co-ordinated intermediate. This conclusion is supported by our observation that no π,π-co-ordinated complex was formed in the matrix upon photolysis of the complex $[Fe(CO)_3(dpipy)]$. The vapour pressure of the corresponding bipy complex appeared to be too low for matrix studies.

More information about the second photosubstitution reaction, which is only observed for nucleophiles with good π back-bonding capacities, such as $P(OMe)_3$ and aromatic isocyanides, can be obtained from the photochemical behaviour of $[Fe(CO)_2(PPh_3L)(bdpie)]$. For the photosubstitution of Y by Z in $[Fe(CO)_2Y(bdpie)]$ partial dissociation of the L ligand (bdpie) is expected to occur first as in the case of the $[Fe(CO)_3L]$ complexes (Figure 13). This leads to the four-co-ordinated intermediate (E), which will react with Y or Z to compound (F) or (F′) respectively. When the π back-bonding capacity of Y is not large enough to rival that of the carbonyls, dissociative loss of Y will occur [reaction (*i*)]. This is the case for Y = PPh_3. When the π back-bonding of Y is strong enough, reaction (*ii*) will occur leading to release of CO and formation of the disubstituted photoproduct (G). This latter reaction appeared to occur for Y = $P(OMe)_3$ or aromatic isocyanide. Other substituents with less π back-bonding capacity are expected to give the same product (F). In this case, however, reaction (*i*) prevails, leading to equal starting and final products, and no reaction is observed.

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References

1 R. W. Balk, D. J. Stufkens, and A. Oskam, *Inorg. Chim. Acta*, 1978, **28**, 133.
2 R. W. Balk, D. J. Stufkens, and A. Oskam, *Inorg. Chim. Acta*, 1979, **34**, 267.
3 R. W. Balk, T. L. Snoeck, D. J. Stufkens, and A. Oskam, *Inorg. Chem.*, 1980, **19**, 3015.
4 R. W. Balk, D. J. Stufkens, and A. Oskam, *J. Chem. Soc., Dalton Trans.*, 1982, 275.
5 M. W. Kokkes, D. J. Stufkens, and A. Oskam, *J. Chem. Soc., Dalton Trans.*, 1983, 439.
6 C. E. Johnson and W. C. Trogler, *J. Am. Chem. Soc.*, 1981, **103**, 6352.
7 W. C. Trogler, C. E. Johnson, and D. E. Ellis, *Inorg. Chem.*, 1981, **20**, 980.
8 M. W. Kokkes, D. J. Stufkens, and A. Oskam, *J. Chem. Soc., Chem. Commun.*, 1983, 369.
9 H. Bock and H. tom Dieck, *Chem. Ber.*, 1967, **100**, 228.
10 S. Otsuka, T. Yoshida, and A. Nakamura, *Inorg. Chem.*, 1967, **6**, 20.
11 H. tom Dieck and A. Orlops, *Angew. Chem.*, 1975, **87**, 246.
12 L. H. Staal, L. H. Polm, K. Vrieze, F. Ploeger, and C. H. Stam, *Inorg. Chem.*, 1981, **20**, 3550.
13 Q. Z. Shi, T. G. Richmond, W. C. Trogler, and F. Basolo, *Organometallics*, 1982, **1**, 1033.
14 G. Boxhoorn and A. Oskam, *Inorg. Chim. Acta*, 1978, **29**, L207.
15 G. Boxhoorn, A. C. Jesse, J. M. Ernsting, and A. Oskam, *Thermochim. Acta*, 1978, **27**, 261.
16 S. L. Murov, ' Handbook of Photochemistry,' Marcel Dekker, New York, 1973, p. 119.
17 G. Ellerhorst, W. Gerhartz, and F. W. Grevels, *Inorg. Chem.*, 1980, **19**, 67.
18 H. tom Dieck and H. Bock, *Chem. Commun.*, 1968, 1271.
19 H. tom Dieck, I. W. Renk, and H. P. Brehm, *Z. Anorg. Allg. Chem.*, 1970, **369**, 169.
20 M. W. Kokkes, D. J. Stufkens, and A. Oskam, unpublished work.
21 A. J. Rest, J. R. Sodeau, and D. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 1978, 651.
22 K. J. Cavell, D. J. Stufkens, and K. Vrieze, *Inorg. Chim. Acta*, 1980, **47**, 67.
23 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 3, 313.
24 C. Y. Chang, C. E. Johnson, T. G. Richmond, Y. T. Chen, W. C. Trogler, and F. Basolo, *Inorg. Chem.*, 1981, **20**, 3167.
25 L. H. Staal, D. J. Stufkens, and A. Oskam, *Inorg. Chim. Acta*, 1978, **26**, 255.
26 R. J. Kazlauskas and M. S. Wrighton, *J. Am. Chem. Soc.*, 1982, **104**, 5784.
27 H. van der Poel, G. van Koten, and K. Vrieze, *Inorg. Chem.*, 1980, **19**, 1145.
28 H. van der Poel, G. van Koten, and G. C. van Stein, *J. Chem. Soc., Dalton Trans.*, 1981, 2164.
29 G. Bellachioma and G. Cardaci, *J. Chem. Soc., Dalton Trans.*, 1977, 2181.
30 G. Bellachioma, G. Reichenbach, and G. Cardaci, *J. Chem. Soc., Dalton Trans.*, 1980, 634.
31 R. W. Balk, G. Boxhoorn, T. L. Snoeck, G. L. Schoemaker, D. J. Stufkens, and A. Oskam, *J. Chem. Soc., Dalton Trans.*, 1981, 1524.
32 A. J. Lees and A. W. Adamson, *J. Am. Chem. Soc.*, 1982, **104**, 3804.

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