A MECHANISTIC STUDY OF THE PHOTOCHEMISTRY OF TRICARBONYL(1-AZA-1,3-BUTADIENE)IRON COMPLEXES [Fe(CO)$_3$(R'N=CHCH=CHPh)] IN CH$_4$ MATRICES AT 10 K AND IN SOLUTION AT 293 K

MAARTEN W. KOKKES, PETER C.J. BEENTJES, DERK J. STUFKENS * and AD OSKAM

Anorganisch Chemisch Laboratorium, J.H. van 't Hoff Instituut, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)

Summary

The photochemistry has been studied of the complexes [Fe(CO)$_3$(R^1,Ph-ABD)] (R^1,Ph-ABD represents R^{1}N=CHCH=CHPh; 1R^1,4Ph-1-aza-1,3-butadiene) both in a CH$_4$ matrix at 10 K and in solution at 293 K. Matrix photolysis of [Fe(CO)$_3$(i-Pr,Ph-ABD)] causes breaking of the iron–olefin bond with formation of the 16-electron species [Fe(CO)$_3$(σ-N-i-Pr,Ph-ABD)]. In solution the R^1,Ph-ABD ligand is replaced photochemically by other R^1,Ph-ABD molecules and by R-DAB (R-DAB = 1,4-diaza-1,3-butadiene; RN=CHCH=NR). Photolysis in the presence of PR$_3$ results in the formation of [Fe(CO)$_2$(R^1,Ph-ABD)(PR$_3$)], [Fe(CO)$_3$(PR$_3$)$_2$] and [Fe(CO)$_4$(PR$_3$)]. The relative amounts of these photoproducts depend on the PR$_3$ concentration, on the R^1,Ph-ABD ligand used, and on the polarity of the solvent. A mechanism is proposed in which the product of the matrix photolysis is assumed to be the primary photoproduct of the photosubstitution reactions.

Introduction

The photochemical reactions of [Fe(CO)$_3$(1,3-diene)] complexes in inert gas matrices [1–3] and in solution [4–10] have been studied in detail. Both release of CO and (partial) decomplexation of the diene ligand have been observed, and the reactions were assumed to be primary photoprocesses from different excited states.

Irradiation of the corresponding heterodiene complexes [Fe(CO)$_3$(R-DAB)](R-DAB = 1,4R$_2$-diaza-1,3-butadiene; RN=CHCH=NR) led to different reactions in solution and matrices [11]. In solution a CO ligand was photosubstituted and in an inert gas matrix the R-DAB ligand changed its coordination from σ,σ via the nitrogen lone pairs into η^4 via the CN bonds; this was the first time that such an $\eta^4(\pi,\pi)$ bonded R-DAB ligand had been observed. The change of coordination

---

* To whom correspondence should be addressed.

from σ,σ to π,π was explained in terms of a distortion of the ligand in the lowest metal to ligand charge transfer (MLCT) state as evidenced by resonance Raman (rR) spectroscopy. The photochemical behaviour of the corresponding complexes [Fe(CO)$_3$(R^1,R^2-ABD) (R^1,R^2-ABD = 1R^1,4R^2-1-aza-1,3-butadiene; R^{1}N=CHCH= CHR^2) has not previously been studied. According to the X-ray structure of [Fe(CO)$_3$(Ph,Ph-ABD)] [16], the R^1,R^2-ABD ligand is $\eta^4(\eta^2$-CN,η^2-CC) coordinated to iron. Cardaci et al. [12–15] investigated the thermal reactions of these complexes with PR$_3$ and other Group V ligands, and observed formation of both [Fe(CO)$_3$(PR$_3$)$_2$] and [Fe(CO)$_2$(R^1,R^2-ABD)(PR$_3$)]. For these reactions ring opening of the Fe-ABD metallocycle was proposed, with formation of the intermediate [Fe(CO)$_3$(σ-N-R^1,R^2-ABD)(PR$_3$)] (σ-N denotes monodentate coordination via the nitrogen lone pair). This intermediate reacts by intramolecular chelation to give [Fe(CO)$_2$(R^1,R^2-ABD)(PR$_3$)] and via an associative mechanism with PR$_3$ to give [Fe(CO)$_3$(PR$_3$)$_2$]. This mechanism was supported by the strong dependence of the relative amounts of the products on the PR$_3$ concentration. In the case of the corresponding R-DAB complexes, ring opening was proposed for the thermal reactions only when the substituent R is a bulky group such as t-butyl [17]; [Fe(CO)$_3$(PR$_3$)$_2$] is then formed as the only product. For smaller substituents R [Fe(CO)$_2$(R-DAB)(PR$_3$)] is formed via an associative mechanism. This latter complex is also the main product of the photochemical reaction of these [Fe(CO)$_3$(R-DAB)] complexes [11,18].

Apparently, loss of the heterodiene ligand is more favoured for the R^1,R^2,-ABD than for the R-DAB complexes. In order to find out whether this conclusion also holds for the photochemical reactions of these complexes, we studied the photochemistry of a series of [Fe(CO)$_3$(R^1,R^2-ABD)] complexes. The structure of these complexes, derived from the crystal structure of [Fe(CO)$_3$)(Ph, Ph-ABD)] [16], is shown in Fig. 1.

The complexes under study all contain R^1,R^2-ABD ligands of the type R^1,Ph-ABD (R^1 = i-Pr, n-Bu, t-Bu, Et, Me, chx (cyclohexyl), Ph, p-Tol (para-tolyl)).

Experimental

The ligands R^1,Ph-ABD [19] and R-DAB [20] and the tricarbonyliron complexes [Fe(CO)$_3$(R^1,Ph-ABD)] [21] and [Fe(CO)$_3$(R-DAB)] [22,23] were prepared by published methods.

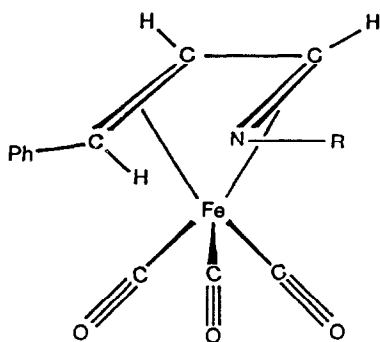Fig. 1. Structure of [Fe(CO)$_3$(R^1,Ph-ABD)].

All spectroscopic samples were dissolved in freshly distilled and deoxygenated solvents and handled with standard inert gas techniques. Electronic absorption spectra were measured on a Cary-14 spectrophotometer and IR 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-202B closed cycle helium refrigerator has been described in detail previously [24]. The sample window of CaF_2 had a temperature of 10 K during deposition and the vacuum was better than 10^{-6} Torr. [Fe(CO)$_3$(i-Pr,Ph-ABD)] was sublimed at 20°C and [Fe(CO)$_3$(p-Tol,Ph-ABD)] at 60°C and gas mixtures were made by adding CH_4, N_2 or CO (purity 99.999%) to the vapour of the sample [25].

A Coherent CR 8 Ar ion laser was used as the light source for the photolysis experiments. The laser power was 30 to 50 mW and the laser beam was defocused before entering the sample.

Results and discussion

According to the X-ray structural results the R^1,R^2-ABD ligands are $\eta^4(\eta^2$-CN,η^2-CC) coordinated to the metal [16]. The structure is therefore closely analogous to that of the [Fe(CO)$_3$(η^4-1,3-diene)] complexes. MO calculations and ultraviolet photoelectron (UP) spectra [26] have shown that the HOMO of these complexes has mixed metal(d)-R^1,R^2-ABD (π^*) character just as in the case of [Fe(CO)$_3$(1,3-butadiene)] [27–29] and [Fe(CO)$_3$(R-DAB)] [30]. The electrons in this HOMO have an IP of 7.4 eV, compared with that of 8.3 eV for the electrons in the other three coinciding metal(d) orbitals. There is a decrease of the metal to ligand π-backbonding going from the 1,3-butadiene to the R^1,R^2-ABD complexes. This may be due to either the asymmetry of the R^1,R^2-ABD ligand induced by the nitrogen atom or to the bonding interaction between the nitrogen lone pair and the central metal atom.

The electronic absorption spectra of these complexes (see Fig. 2 and Table 1) show a weak band ($\epsilon_{max} \cong 800$ dm^3 mol^{-1} cm^{-1}) between 400 and 500 nm and a much stronger one ($\epsilon_{max} \cong 6000$ dm^3 mol^{-1} cm^{-1}) at about 300 nm. Introduction of an electron-withdrawing substituent in the R^1,R^2-ABD ligand causes the low-energy band to shift to lower energy; this effect is typical for a metal to (R^1,R^2-ABD) ligand charge transfer (MLCT) transition and the band is assigned accordingly. This assignment agrees with that for the low-energy band ($\lambda_{max} \cong 500$ nm) of the corresponding [Fe(CO)$_3$(R-DAB)] complexes. The MCD spectra of the latter complexes have shown that the first ligand field transition occurs at 300 nm [31]. The low intensity of the MLCT band may be due to the relative weak π-backbonding deduced from the UP spectra. The intense broad band at about 300 nm is assigned to (nearly) coinciding ligand field and metal(d) $\rightarrow$ CO(π^*) transitions, and the band at 255 nm to a phenyl $\pi \rightarrow \pi^*$ transition.

In agreement with the C_s symmetry of the complexes three IR bands are observed in the CO stretching region. For several of the complexes the frequencies of these bands are listed in Table 3.

The resonance Raman (rR) spectra, obtained by excitation into the low-energy MLCT band are very weak, just as for the corresponding [Fe(CO)$_3$(R-DAB)] complexes. No CO frequencies are observed which means that the lowest excited

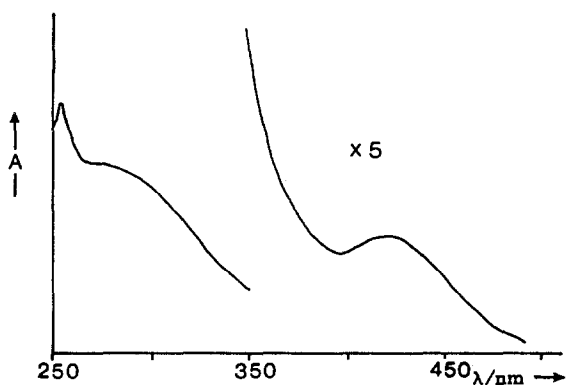Fig. 2. Electronic absorption spectrum of [Fe(CO)₃(i-Pr, Ph-ABD)] taken from a CH_4 matrix at 10 K. The visible spectrum is multiplied by a factor 5 with respect to the UV spectrum.

state is completely localized at the $Fe(R^1,Ph\text{-}ABD)$ moiety of the complexes. The weakness of these spectra indicate that no bound of the complex is severely affected going from the HOMO to the LUMO.

Photolysis of [Fe(CO)₃(i-Pr,Ph-ABD)] in a CH₄ matrix at 10 K

Figure 3 shows the IR spectral changes in the CO stretching region upon irradiation of [Fe(CO)₃(i-Pr,Ph-ABD)] with the λ 488.0 nm line of an argon ion laser in a CH_4 matrix at 10 K. Upon photolysis new bands appear at 2048, 2011, 1986, 1980, 1906, 1900 and 1884 cm⁻¹, as shown in Fig. 3(a). At the same time the bands of the parent compound disappear. No free carbon monoxide (ν(CO) 2138 cm⁻¹) is observed. A difference spectrum, obtained by subtraction of the spectrum of the parent compound from a spectrum taken after 10 h of photolysis, is presented in Fig. 3(b).

The three most intense bands at 2011, 1906 and 1900 cm⁻¹ as well as the shoulder at 1884 cm⁻¹, are assigned to [Fe(CO)₃(σ-N-i-Pr,Ph-ABD)], a coordinatively unsaturated species in which the (i-Pr,Ph-ABD) ligand is σ-monodentately coordinated via its N lone pair to the metal. (Support for this assignment comes from the close correspondence between these frequencies and those observed for (C_{3v})-[Fe(CO)₃(NMe₃)] [32]. This latter species, which is formed by photolysis of [Fe(CO)₄)(NMe₃)] in an Ar matrix, has CO frequencies at 2012, 1906 and 1889

TABLE 1

DATA FOR LOW-ENERGY ABSORPTION BANDS OF SEVERAL [Fe(CO)₃(R¹,Ph-ABD)] COMPLEXES MEASURED IN n-PENTANE

Complex	$\lambda_{max}{}^a$ (nm)	$\delta^{\,b}$
[Fe(CO)₃(t-Bu,Ph-ABD)]	433 (744)	−5
[Fe(CO)₃(p-Tol,Ph-ABD)]	447 (817)	+6
[Fe(CO)₃(p-ClPh, Ph-ABD)]	448	+8
[Fe(CO)₃(i-Pr,Ph-ABD)]	411 (849)	+5

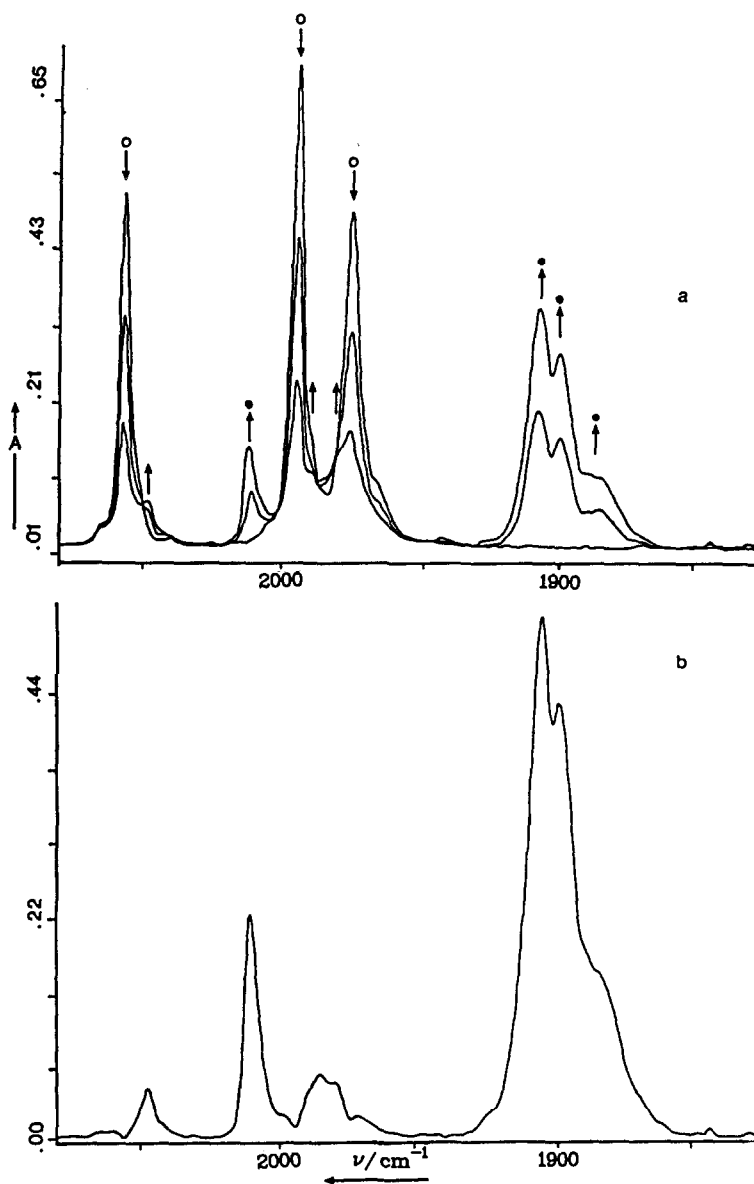^{a} ϵ_{max}(dm³ mol⁻¹ cm⁻¹) given in parentheses. ^{b} $\delta = \lambda_{max}(CH_2Cl_2) - \lambda_{max}(C_5H_{12})$.

Fig. 3. (a) IR spectral changes in the CO stretching region upon photolysis of [Fe(CO)$_3$(i-Pr, Ph-ABD)] with λ 488.0 nm (p 70 mW) in a CH$_4$ matrix at 10 K. The irradiation times are 0, 40 and 220 min, respectively. O, [Fe(CO)$_3$(i-Pr, Ph-ABD); ●, [Fe(CO)$_3$(σ-N-i-Pr,Ph-ABD)]. (b) The IR spectrum of the photoproducts obtained by subtracting the spectrum of the parent compound from a spectrum taken after 10 h of photolysis.

cm^{-1}.) The shoulder at about 1884 cm^{-1} is assigned to a matrix splitting of the 1906 and 1900 cm^{-1} bands. This change of coordination of the (i-Pr,Ph-ABD) ligand from π,π-bidentate into σ-N-monodentate agrees with the observed shift of the CO stretching modes to lower frequencies. The π-backbonding to the (i-Pr,Ph-

82

TABLE 2

IR CO STRETCHING FREQUENCIES (cm^{-1}) for [Fe(CO)$_3$(R^1,Ph-ABD)] AND THEIR PHOTOLY-
SIS PRODUCTS, RECORDED IN MATRICES AT 10 K

Compound	Matrix	ν(CO) [a]			
[Fe(CO)$_3$(i-Pr,Ph-ABD)]	CH$_4$	2056(m)	1994(s)	1974(m)	
[Fe(CO)$_3$(i-Pr,Ph-ABD)]	CO	2056(m)	1993(s)	1973(m)	
[Fe(CO)$_3$(p-Tol,Ph-ABD)]	N$_2$	2064(m)	2004(s)	1991(m)	
[Fe(CO)$_3$(σ-N-i-Pr,Ph-ABD)]	CH$_4$	2011(m)	1906(s)	1900(m)	1884(sh)
[Fe(CO)$_3$(σ-N-i-Pr,Ph-ABD)]	CO	2008(m)	1902(vs)	1894(sh)	
[Fe(CO)$_3$(σ-N-p-Tol,Ph-ABD)]	N$_2$	2015(m)	1915(s)	1905(m)	
[Fe(CO)$_3$(i-Pr,Ph-ABD)], isomer	CH$_4$	2048(w)	1986(w)	1980(w)	
[Fe(CO)$_3$(i-Pr,Ph-ABD)], isomer	CO	2049(m)	1988(m)		
[Fe(CO)$_3$(p-Tol,Ph-ABD)], isomer	N$_2$	2051(w)	1984(w)	1979(w)	
[Fe(CO)$_4$(σ-N-i-Pr,Ph-ABD)] [b]	CO	2045(m)	1963(m)	1941(vs)	1934(sh)
[Fe(CO)$_2$(di-i-Pr,Me-DAB)] [c]	N$_2$	2018(w)	1975(s)	1915(sh)	1907(s)	1885(m)
[Fe(CO)$_3$(NMe$_3$)] [d]	CH$_4$	2012(m)	1906(s)	1890(m)	
[Fe(CO)$_3$(η^2-1,3-butadiene)] [e]	Ar	2029	1970	1953	
[Fe(CO)$_3$] [f]	CH$_4$	2040	1930		

[a] Relative intensities: vs, very strong; s, strong; m, medium; w, weak and sh, shoulder. [b] Values obtained
after annealing. [c] Ref. 11. [d] Ref. 32. [e] Ref. 1. [f] Ref. 33.

ABD) ligand then decreases, and this in turn causes an increase in the π-backbond-
ing to the carbonyls and a lowering of the CO frequencies. The coordinative
unsaturation of the photoproduct becomes apparent from the annealing experiment
in a CO matrix; the CO bands of the photoproduct disappear and there is a slight
increase in the bands of the parent compound, and, in addition, new bands appear
at 2049, 1963, 1941 and 1934 cm^{-1}, which can be assigned to [Fe(CO)$_4$(σ-N-i-
Pr,Ph-ABD)] [19], which is a known, complex, stable at room temperature. Forma-
tion of a photoproduct in which the ligand is η^2-coordinated to the metal via its CC
or CN bonds might also be expected; such photoproducts have been observed upon
photolysis of [Fe(CO)$_3$(η^4-1,3-butadiene)] [1]. However, the CO vibrations for
[Fe(CO)$_3$(η^2-1,3-butadiene)] are found at 2029, 1970 and 1954 cm^{-1}, which means
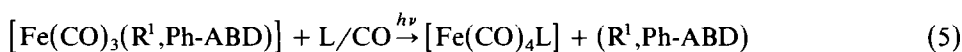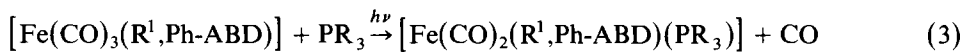there is a large shift to higher frequencies compared with those of our main
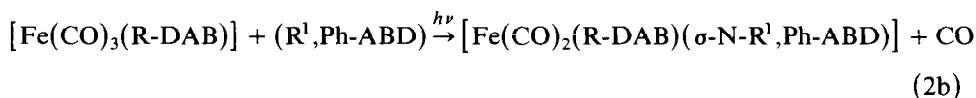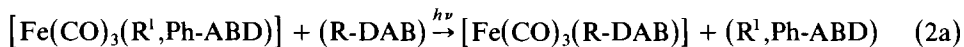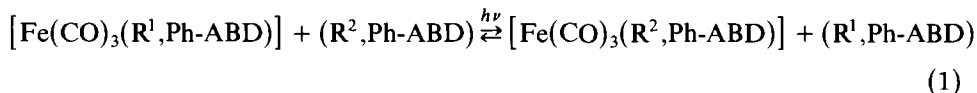photoproduct.

In addition to these rather strong bands, three weaker ones are observed after
photolysis, at 2051, 1984 and 1979 cm^{-1}. These bands are close in frequency to
those of the parent compound and like the bands of the parent compound they
increase in intensity upon annealing the CO matrix. This means that they belong to
a coordinatively saturated species closely resembling the parent compound. These
bands are therefore assigned to an isomer of the parent compound. Such isomers
have also been observed for the analogous complex [Fe(CO)$_3$(η^4-R-DAB)], the
photoproduct of [Fe(CO)$_3$(σ,σ-R-DAB)] in matrices [11].

The CO stretching frequencies of all photoproducts are presented in Table 2,
together with those of isostructural species from other photolysis experiments.

Photosubstitution reactions in solution

In the absence of a substituting ligand the complexes are photostable. Only after
prolonged irradiation is a light photodecomposition observed, involving formation
of [Fe(CO)$_5$] and [Fe(CO)$_4$(σ-N-R^1,Ph-ABD)].

Upon irradiation in the presence of a nucleophilic ligand different reactions are observed depending on the ligand, the $(R^1,Ph\text{-}ABD)$ molecule and the polarity of the solvent. The following reactions have been observed, and will be discussed in some detail:

$$[Fe(CO)_3(R^1,Ph\text{-}ABD)] + (R^2,Ph\text{-}ABD) \overset{h\nu}{\rightleftarrows} [Fe(CO)_3(R^2,Ph\text{-}ABD)] + (R^1,Ph\text{-}ABD)$$

$$(1)$$

$$[Fe(CO)_3(R^1,Ph\text{-}ABD)] + (R\text{-}DAB) \overset{h\nu}{\rightarrow} [Fe(CO)_3(R\text{-}DAB)] + (R^1,Ph\text{-}ABD) \quad (2a)$$

$$[Fe(CO)_3(R\text{-}DAB)] + (R^1,Ph\text{-}ABD) \overset{h\nu}{\rightarrow} [Fe(CO)_2(R\text{-}DAB)(\sigma\text{-}N\text{-}R^1,Ph\text{-}ABD)] + CO$$

$$(2b)$$

$$[Fe(CO)_3(R^1,Ph\text{-}ABD)] + PR_3 \overset{h\nu}{\rightarrow} [Fe(CO)_2(R^1,Ph\text{-}ABD)(PR_3)] + CO \quad (3)$$

$$[Fe(CO)_3(R^1,Ph\text{-}ABD)] + 2PR_3 \overset{h\nu}{\rightarrow} [Fe(CO)_3(PR_3)_2] + (R^1,Ph\text{-}ABD) \quad (4)$$

$$[Fe(CO)_3(R^1,Ph\text{-}ABD)] + L/CO \overset{h\nu}{\rightarrow} [Fe(CO)_4L] + (R^1,Ph\text{-}ABD) \quad (5)$$

Unfortunately, reliable quantum yields could not be determined due to the small changes in the absorption spectrum.

Reactions with $(R^2,Ph\text{-}ABD)$ (1)

Photolysis of $[Fe(CO)_3(R^1,Ph\text{-}ABD)]$ in the presence of $(R^2,Ph\text{-}ABD)$ causes substitution of the ABD ligand. Thus, irradiation with λ 488 nm of a n-hexane solution of $[Fe(CO)_3(i\text{-}Pr,Ph\text{-}ABD)]$ and (p-Tol,Ph-ABD) (five-fold excess) results in the formation of a mixture of $[Fe(CO)_3(i\text{-}Pr,Ph\text{-}ABD)]$ and $[Fe(CO)_3(p\text{-}Tol,Ph\text{-}ABD)]$. The yield of the former complex is, however, much the larger, eventhough an excess of (p-Tol,Ph-ABD) was present. This result is in line with the fact that (i-Pr,Ph-ABD) is a more basic ligand than (p-Tol,Ph-ABD).

Reactions with R-DAB (2a and 2b)

As in the above case, photolysis in the presence of R-DAB causes substitution of the $(R^1,Ph\text{-}ABD)$ ligand. Figure 4 shows the changes in the CO stretching region upon irradiation of a n-hexane solution of $[Fe(CO)_3(i\text{-}Pr,Ph\text{-}ABD)]$ and t-Bu-DAB. The spectra show good isosbestic points, indicating a clean reaction. New bands show up at 2018 and 1941 cm^{-1} which belong to $[Fe(CO)_3(t\text{-}Bu\text{-}DAB)]$ [11,31].

Prolonged irradiation of $[Fe(CO)_3(p\text{-}Tol,Ph\text{-}ABD)]$ in the presence of chx-DAB causes a second reaction to occur. After replacement of the ABD ligand by chx-DAB, a CO ligand is photosubstituted by the released (p-Tol,Ph-ABD) molecule. The other possible reaction, photosubstitution of two CO groups of $[Fe(CO)_3(chx\text{-}DAB)]$ by chx-DAB [11], is not observed. The CO stretching frequencies of $[Fe(CO)_2(chx\text{-}DAB)(\sigma\text{-}N\text{-}p\text{-}Tol,Ph\text{-}ABD)]$ are presented in Table 3 together with those for other photosubstitution products of $[Fe(CO)_3(R^1,Ph\text{-}ABD)]$.

It is important to note that apart from the strong bands at 1947 and 1882 cm^{-1} two weaker bands are observed for this photoreaction, at 1975 and 1926 cm^{-1}, respectively. It is very unlikely that these bands belong to an isomer of $[Fe(CO)_2(chx\text{-}DAB)(\sigma\text{-}N\text{-}p\text{-}Tol,Ph\text{-}ABD)]$. Although such isomers have been ob-
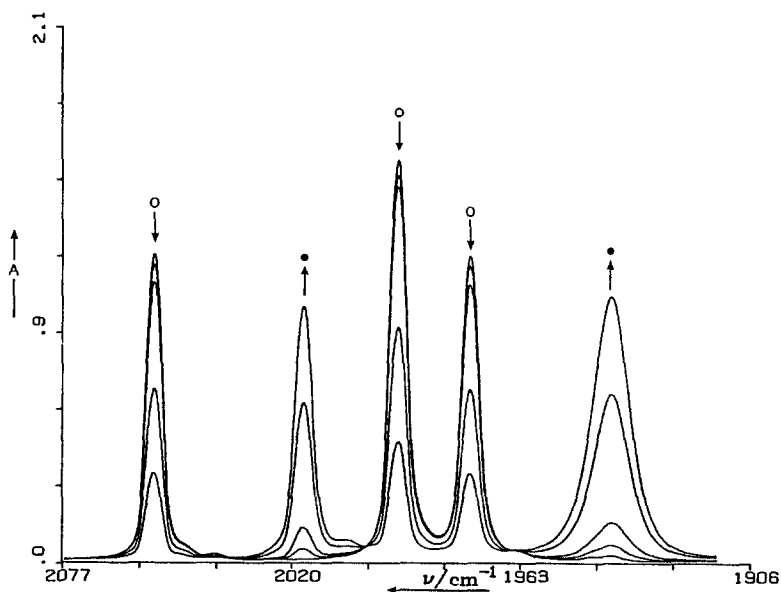
Fig. 4. IR spectral changes of the carbonyl stretching modes of a n-hexane solution of [Fe(CO)$_3$(i-Pr,Ph-ABD)], containing an excess of t-Bu-DAB, during photolysis with λ 488.0 nm (p 60 mW). O, [Fe(CO)$_3$(i-Pr,Ph-ABD); ●, [Fe(CO)$_3$(t-Bu-DAB)].

served for [Fe(CO)$_2$(2,6-di-i-Pr,Ph-DAB)(PR$_3$)] [11], the frequency differences between them vary from 3 to 10 cm^{-1}, which is much less than the shifts observed here (25 and 44 cm^{-1}, respectively). We therefore suggest that these weaker bands belong to [Fe(CO)$_2$(chx-DAB)(η^2-p-Tol,Ph-ABD)], a complex in which the ABD ligand has changed its coordination. The shift of the CO vibrations to higher frequencies with respect to the (σ-N-p-Tol,Ph-ABD) complex is due to the stronger π-backbonding to the η^2-coordinated ligand. The shift is analogous to that observed on going from [Fe(CO)$_3$(σ-N-p-Tol,Ph-ABD)] to [Fe(CO)$_3$(η^2-1,3-butadiene)] (see Table 2 and ref. 1).

TABLE 3

IR CO STRETCHING FREQUENCIES (cm^{-1}) OF SOME [Fe(CO)$_3$(R^1,Ph-ABD)] COMPLEXES AND THEIR PHOTOPRODUCTS, IN n-HEXANE

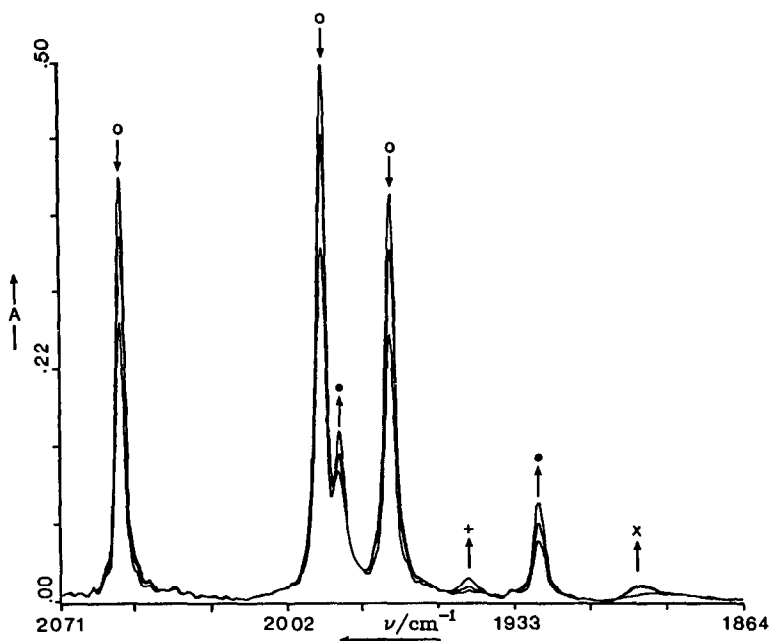| Compound	ν(CO)		
[Fe(CO)$_3$(i-Pr,Ph-ABD)]	2055	1994	1976
[Fe(CO)$_3$(t-Bu,Ph-ABD)]	2052	1962	1971
[Fe(CO)$_3$(p-Tol,Ph-ABD)]	2059	2000	1987
[Fe(CO)$_3$(p-ClPh,Ph-ABD)]	2061	2003	1991
[Fe(CO)$_2$(i-Pr,Ph-ABD)(PPh$_3$)]		1988	1930
[Fe(CO)$_2$(t-Bu,Ph-ABD)(PPh$_3$)]		1986	1926
[Fe(CO)$_2$(p-Tol,Ph-ABD)(PPh$_3$)]		1990	1932
[Fe(CO)$_2$(σ-N-p-Tol,Ph-ABD)(chx-DAB)]		1947	1882
[Fe(CO)$_2$(η^2-p-Tol,Ph-ABD)(chx-DAB)]		1975	1926

Fig. 5. IR spectral changes of the carbonyl stretching modes of a n-hexane solution of [Fe(CO)$_3$(t-Bu,Ph-ABD)], containing an equivalent amount of PPh$_3$, during photolysis with λ 514.5 nm (p 60 mW). O, [Fe(CO)$_3$(t-Bu,Ph-ABD); ●, [Fe(CO)$_2$(t-Bu,Ph-ABD)(PPh$_3$)]; ×, [Fe(CO)$_3$(PPh$_3$)$_2$]; +, [Fe(CO)$_4$(PPh$_3$)].

Reactions with PR$_3$ (3, 4 and 5)

Photolysis in the presence of PPh$_3$ results in the formation of three photoproducts, [Fe(CO)$_3$(PPh$_3$)$_2$], [Fe(CO)$_2$(R^1,Ph-ABD)(PPh$_3$)] and, in a few cases, [Fe(CO)$_4$(PPh$_3$)]. Figure 5 shows the changes in the CO stretching region upon irradiation of a n-hexane solution of [Fe(CO)$_3$(t-Bu,Ph-ABD)] and PPh$_3$ (1/1) with λ 488 nm. The bands of the parent compound disappear and new bands appear at 1986, 1947, 1926 and 1885 cm^{-1}. Of these bands, those at 1947 and 1885 cm^{-1} belong to [Fe(CO)$_4$(PPh$_3$)] and [Fe(CO)$_3$(PPh$_3$)$_2$], respectively [34].

The bands at 1986 and 1926 cm^{-1} are assigned to [Fe(CO)$_2$(t-Bu,Ph-ABD)(PPh$_3$)]. Substitution of an electron-withdrawing CO group by the basic phosphine causes a shift of the CO stretching modes to lower frequency. Almost the same frequency shift is observed upon photosubstitution of CO by PR$_3$ in [Fe(CO)$_3$(R-DAB)] complexes [11]. Table 3 lists the CO stretching frequencies for several [Fe(CO)$_2$(R^1,Ph-ABD)(PR$_3$)] complexes. The relative quantities of [Fe(CO)$_3$(PR$_3$)$_2$] and [Fe(CO)$_2$(R^1,Ph-ABD)(PR$_3$)] depend on the concentration of the PR$_3$ ligand, on the ABD ligand, and on the polarity of the solvent. For the above reaction of [Fe(CO)$_3$(t-Bu,Ph-ABD)] with PPh$_3$ (1/1) in n-hexane (Fig. 5) the main photoproduct is [Fe(CO)$_2$(t-Bu,Ph-ABD)(PPh$_3$)], but when, a 25-fold excess of PPh$_3$ is used the main photoproduct is [Fe(CO)$_3$(PPh$_3$)$_2$]. Performing this reaction in more polar solvents such as CH$_2$Cl$_2$ or THF, favours the formation of [Fe(CO)$_3$(PPh$_3$)$_2$]. Only when a low concentration of PPh$_3$ is used ([Fe(CO)$_3$(R^1,Ph-ABD)]/[PPh$_3$] = 1/2) can a small amount of [Fe(CO)$_2$(R^1,Ph-
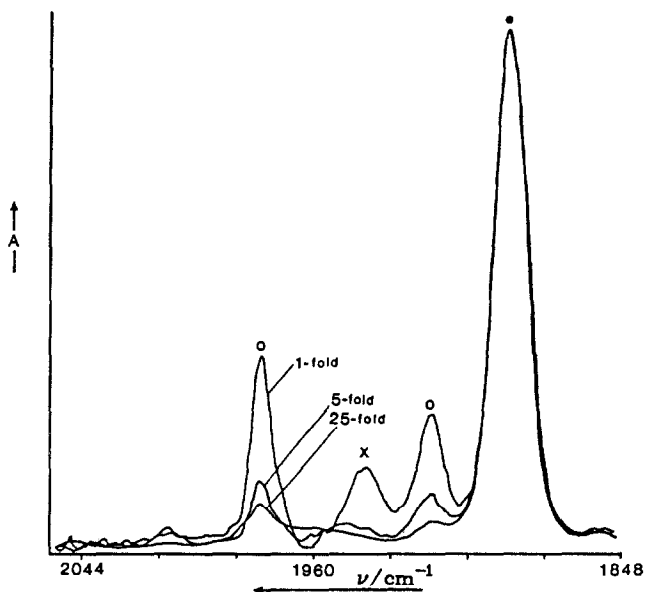
Fig. 6. CO stretching modes of the products formed upon photolysis of [Fe(CO)₃(t-Bu,Ph-ABD)] in THF with λ 514.5 nm in the presence of PPh₃ (1-fold, 5-fold and 25-fold excess). The spectra were obtained by subtracting the spectrum of the parent conpound from a spectrum taken after photolysis. All spectra are scaled to the absorbance of [Fe(CO)₃(PPh₃)₂]. ○, [Fe(CO)₂(t-Bu, Ph-ABD)(PPh₃)]; ●, [Fe(CO)₃(PPh₃)₂]; ×, [Fe(CO)₄(PPh₃)].
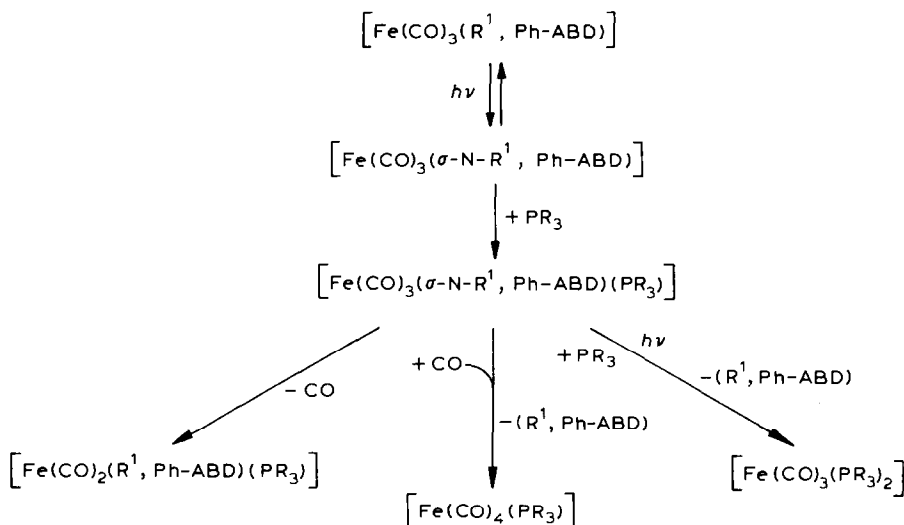
ABD)(PPh$_3$] be observed. Figure 6 shows the CO stretching modes of the products formed upon photolysis of [Fe(CO)$_3$(t-Bu,Ph-ABD)] in THF with λ 514.5 nm at various concentrations of PPh$_3$. The spectra are scaled to the absorbance of [Fe(CO)$_3$(PPh$_3$)$_2$]. From a comparison of Fig. 5 and 6 it is clear that even for a concentration ratio of 1/1 more [Fe(CO)$_3$(PPh$_3$)$_2$] is formed in THF than in n-hexane. [Fe(CO)$_4$(PPh$_3$)] is only formed as a side product and its concentration increases with that of [Fe(CO)$_2$(R^1,Ph-ABD)(PPh$_3$)]. In those cases in which only [Fe(CO)$_3$(PPh$_3$)$_2$] is formed and hardly any [Fe(CO)$_2$(R^1,Ph-ABD)(PPh$_3$)] (e.g. in CH$_2$Cl$_2$ or THF at higher PPh$_3$ concentration), no [Fe(CO)$_4$(PPh$_3$)] is formed either.

As mentioned above the relative amounts of [Fe(CO)$_3$(PPh$_3$)$_2$] and [Fe(CO)$_2$(R^1,Ph-ABD)(PPh$_3$)] also depend on the ABD ligand used. When the substituent R^1 is an aromatic group such as p-tolyl, much more [Fe(CO)$_3$(PPh$_3$)$_2$] is formed than when R^1 is aliphatic (e.g. i-Pr).

Mechanism of the photochemical reactions

The results of the matrix experiments reveal the formation of the coordinatively unsaturated species [Fe(CO)$_3$(σ-N-i-Pr, Ph-ABD)] in which the ABD ligand is bonded to iron via its nitrogen lone pair. This 16-electron species is a stable compound in the matrix but it would be very reactive in solution. The same complex has been proposed as an intermediate in the thermal substitution of CO in [Fe(CO)$_3$(R^1,R^2-ABD)] complexes by PR$_3$ (R = Ph, n-Bu) [13] and SbPh$_3$ [12].

In the absence of a substituting ligand the coordinatively unsaturated complex will revert to the stable parent compound, as in the case of the [Fe(CO)$_3$(R-DAB)]

$$\left[\text{Fe(CO)}_3(\text{R}^1, \text{Ph-ABD}) \right]$$

$$h\nu \updownarrow$$

$$\left[\text{Fe(CO)}_3(\sigma\text{-N-R}^1, \text{Ph-ABD}) \right]$$

$$\downarrow +\text{PR}_3$$

$$\left[\text{Fe(CO)}_3(\sigma\text{-N-R}^1, \text{Ph-ABD})(\text{PR}_3) \right]$$

$$-\text{CO} \qquad +\text{CO} \quad +\text{PR}_3 \quad h\nu \quad -(\text{R}^1, \text{Ph-ABD})$$

$$-(\text{R}^1, \text{Ph-ABD})$$

$$\left[\text{Fe(CO)}_2(\text{R}^1, \text{Ph-ABD})(\text{PR}_3) \right] \qquad \left[\text{Fe(CO)}_4(\text{PR}_3) \right] \qquad \left[\text{Fe(CO)}_3(\text{PR}_3)_2 \right]$$

SCHEME 1

complexes. This back reaction, which is prevented in the matrix by the rigidity of the medium, accounts for the photostability of these complexes in solution.

In the presence of a nucleophile such as PPh_3 the intermediate readily takes up this ligand with formation of $[Fe(CO)_3(\sigma\text{-N-R}^1,\text{Ph-ABD})(PPh_3)]$. The dissociative mechanism proposed for these reactions is supported by the observation that variation of the cone angle of the phosphine does not influence the rate of the photochemical reaction. Irradiation during 10 s (λ 514.5 nm, p 85 mW) of a CH_2Cl_2 solution of $[Fe(CO)_3(\text{p-Tol},\text{Ph-ABD})]$ with a five-fold excess of PR_3 gives about the same conversion to $[Fe(CO)_3(PR_3)_2]$ for R = Et, i-Pr, or chx. Unfortunately quantum yields could not be determined because of the small changes in the absorption spectrum.

The $[Fe(CO)_3(\sigma\text{-N-R}^1,\text{Ph-ABD})(PR_3)]$ complex is not observed as a stable product in solution. It reacts (see Scheme 1) to give $[Fe(CO)_2(R^1,\text{Ph-ABD})(PR_3)]$ by loss of CO and re-formation of the metal-ABD ligand chelate bond. However, in the presence of excess PR_3, in polar solvents, the metal-($\sigma\text{-N-R}^1$,Ph-ABD) bond is apparently destabilized, since $[Fe(CO)_3(PR_3)_2]$ is then formed predominantly. Moreover, in a weakly coordinating solvent such as THF or in the presence of excess PR_3, the formation of the metal-ABD chelate bond may be prevented. This loss of ABD is not observed in the thermal reactions of these complexes. Cardaci and Bellachioma [13] observed only small traces of $[Fe(CO)_3(PR_3)_2]$ during the thermal reactions of $[Fe(CO)_3(R^1,R^2\text{-ABD})]$ with PR_3 in C_6H_6. The corresponding photochemical reaction in C_6H_6 gives mainly $[Fe(CO)_3(PR_3)_2]$, just as in THF or CH_2Cl_2.

The breaking of the metal-($\sigma\text{-N-R}^1$,Ph-ABD) bond is therefore assumed to be promoted by the laser light. The formation of $[Fe(CO)_2(R^1,\text{Ph-ABD})(PR_3)]$ is accompanied by loss of CO, which in turn reacts with $[Fe(CO)_3(\sigma\text{-N-R}^1,\text{Ph-ABD})(PR_3)]$ with formation of $[Fe(CO)_4(PR_3)]$. Proof of this is the observation that the concentration of $[Fe(CO)_4(PR_3)]$ depends wholly on the concentration of

[Fe(CO)$_2$(R^1,Ph-ABD)(PR$_3$)]. The fact that the [Fe(CO)$_3$(R^1,Ph-ABD)] complexes with R^1 = aryl give [Fe(CO)$_3$(PR$_3$)$_2$] whereas for R = alkyl [Fe(CO)$_2$(R^1,Ph-ABD)(PR$_3$)] are mainly formed, arises from the fact that the metal–(σ-N-R^1,Ph-ABD) bond is weaker for R^1 = p-Tol.

A similar intermediate, [Fe(CO)$_3$(σ-N-R-DAB)(PR$_3$)], has been proposed for the photosubstitution reactions of the [Fe(CO)$_3$(R-DAB)] complexes [11]. In that case, however, only [Fe(CO)$_2$(R-DAB)(PR$_3$)] is formed and no [Fe(CO)$_3$(PR$_3$)$_2$] or [Fe(CO)$_4$(PR$_3$)]. Apparently, chelate formation is much more favoured for the R-DAB than for the R^1,R^2-ABD complexes.

References

1 G. Ellerhorst, W. Gerhartz and F.W. Grevels, Inorg. Chem., 19 (1980) 67.
2 A.J. Rest, J.R. Sodeau and D.J. Taylor, J. Chem. Soc. Dalton Trans., (1978) 651.
3 O. Chapman, J. Pacansky and P.W. Wojtkowski, J. Chem. Soc. Chem. Commun., (1973) 681.
4 O. Jaenicke, R.C. Kerber, P. Kirsch, E.A. Koerner von Gustorf and R. Rumin, J. Organomet. Chem., 19 (1980) 67.
5 E.A. Koerner von Gustorf, J. Buchkremer, Z. Pfajfer and F.W. Grevels, Angew. Chem., 83 (1971) 249.
6 R.C. Kerber and E.A. Koerner von Gustorf, J. Organomet. Chem., 110 (1976) 345.
7 F.W. Grevels, U. Feldhof, J. Leitich and C. Krüger, J. Organomet. Chem., 118 (1976) 79.
8 W.J.R. Tyerman, M. Kato, P. Kebarle, S. Masamune, O.P. Strausz and H.E. Gunning, J. Chem. Soc. Chem. Commun., (1967) 497.
9 P. Reeves, J. Henery and R. Pettit, J. Am. Chem. Soc., 91 (1969) 5888.
10 I. Fischler, K. Hildenbrand and E.A. Koerner von Gustorf, Angew. Chem., 87 (1975) 35.
11 M.W. Kokkes, D.J. Stufkens and A. Oskam, J. Chem. Soc. Dalton Trans., (1984) 1005.
12 G. Bellachioma, G. Reichenbach and G. Cardaci, J. Chem. Soc. Dalton Trans., (1980) 634.
13 G. Bellachioma and G. Cardaci, J. Chem. Soc. Dalton Trans., (1977) 2181.
14 G. Bellachioma and G. Cardaci, J. Chem. Soc. Dalton Trans., (1977) 909.
15 G. Cardaci and G. Bellachioma, Inorg. Chem., 16 (1977) 3099.
16 A. de Cian, P.M.L. 'Huiller and R. Weiss, Acta Cryst. B, 28 (1972) 3264.
17 Q.-Z. Shi, T.G. Richmond, W.C. Trogler and F. Basolo, Organometallics, 1 (1982) 1033.
18 C.E. Johnson and W.C. Trogler, J. Am. Chem. Soc., 103 (1981) 6352.
19 G. Cardaci and G. Bellachioma, J. Chem. Soc. Dalton Trans., (1976) 1735.
20 H. Bock and H. tom Dieck, Chem. Ber., 100 (1967) 228.
21 S. Otsuka, T. Yoshida and A. Nakamura, Inorg. Chem., 6 (1967) 20.
22 L.H. Staal, L.H. Polm, K. Vrieze, F. Ploeger and C.H. Stam, Inorg. Chem., 20 (1981) 3550.
23 H. tom Dieck and A. Orlops, Angew. Chem., 87 (1975) 246.
24 G. Boxhoorn and A. Oskam, Inorg. Chim. Acta, 29 (1978) L207.
25 G. Boxhoorn, A.C. Jesse, J.M. Ernsting and A. Oskam, Thermochim. Acta, 27 (1978) 261.
26 R.R. Andréa, P.C.J. Beentjes, D.J. Stufkens and A. Oskam, J. Organomet. Chem., 288 (1984) 79.
27 J.C. Green, Structure and Bonding, 43 (1981) 37.
28 A.H. Cowley, Prog. Inorg. Chem., 26 (1979) 46.
29 H. van Dam and A. Oskam, Trans. Met. Chem., Edited by G.A. Melson and B.N. Figgis, Marcel Dekker Inc., New York, Vol. 9, 1984, p. 125–308.
30 R.R. Andréa, J.N. Louwen, M.W. Kokkes, D.J. Stufkens and A. Oskam, J. Organomet. Chem., 281 (1985) 273.
31 M.W. Kokkes, D.J. Stufkens and A. Oskam, J. Chem. Soc. Dalton Trans., (1983) 439.
32 G. Boxhoorn, M.B. Cerfontain, D.J. Stufkens and A. Oskam, J. Chem. Soc. Dalton Trans., (1980) 1336.
33 M. Poliakoff, J. Chem. Soc. Dalton Trans., (1974) 211.
34 D.M. Adams, Metal-Ligand and Related Vibrations, Edward Arnold Ltd, London, 1967, p. 150.