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THE PHOTOCHEMISTRY OF MATRIX-ISOLATED $(\eta^5\text{-}C_5H_5)Fe(CO)_2Co(CO)_4$: EVIDENCE FOR TWO PHOTOCHEMICAL PATHWAYS

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Summary

Unusual observations of the photochemistry of $CpFe(CO)_2Co(CO)_4$ (Cp = η^5-C_5H_5) are presented. In low temperature matrices (i.e. Ar at 10 K) there are two photochemical pathways (i) reversible CO loss to form $CpFeCo(CO)_5$ and (ii) heterophotolysis leading, in the presence of excess CO, to in situ formation of $[CpFe(CO)_3]^+$ and $[Co(CO)_4]^-$ ions. In N_2-doped matrices, a dinitrogen substitution product, $CpFeCo(CO)_3(N_2)(\mu\text{-}CO)_2$ is formed. All products are identified from their IR spectra.

Introduction

There is considerable current interest in the photochemistry of binuclear transition metal carbonyls and related species [1]. Low-temperature techniques combined with spectroscopic examination (mostly IR) are playing an increasingly important role in unravelling the mechanisms of these reactions. For instance, early work [2] showed that photolysis of $Fe_2(CO)_9$ in a low-temperature matrix produced both bridged and unbridged forms of $Fe_2(CO)_8$. Since then, Wrighton has provided the first positive evidence [3] that formation of $(CO)_4Mn(\mu\text{-}CO)Mn(CO)_4$ from $Mn_2(CO)_{10}$ plays a significant role besides the generation of two $Mn(CO)_5$ radicals. Recent flash photolysis experiments confirm this conclusion [4].

There is evidence for the generation of $Co_2(CO)_7$ by photolysis of matrix isolated $Co_2(CO)_8$ [5]. Flash photolysis of $[CpFe(CO)_2]_2$ suggests alternative photochemical pathways, involving either rupture of the metal–metal bond or CO loss [6]. A singly-bridged intermediate without Fe–Fe bond, $CpFe(CO)(\mu\text{-}CO)CpFe(CO)_2$, has apparently been trapped by phosphite in the photochemical reactions of $[CpFe(CO)_2]_2$ [7]. While a triply-bridged species $CpFe(\mu\text{-}CO)_3CpFe$ has been generated by photolysis of $[CpFe(CO)_2]_2$ isolated in CH_4 or PVC matrices [8].

Kemp et al. were the first to demonstrate heterophotolysis of dinuclear metal carbonyl compounds to give ionic species. For instance [9], in "solvents of high

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donicity", $Mn_2(CO)_{10}$ will give, in a primary step, $[Mn(CO)_5]^+$(solv) and $[Mn(CO)_5]^-$(solv). More recently, this work has been extended by Tyler et al. who concluded that the heterophotolysis depends on the nature of incoming ligand (rather than solvent) in, for example [10]:

$$[CpMo(CO)_3]_2 \xrightarrow[2L]{h\nu} [CpMo(CO)_3]^- + [CpMo(CO)_2L_2]^+ + CO$$

They conclude that the mechanism of this overall reaction involves several steps, including, for instance, the generation of the 19-electron species, $[Cp_2Mo_2(CO)_6]^-$, which then disproportionates to $[CpMo(CO)_3]^-$ and $CpMo(CO)_3$.

As far as we are aware, our own experiments are the only ones where IR spectroscopy has been used to detect ionic metal carbonyl species in matrices. We have generated matrix isolated carbonyl anions by three methods: (i) vacuum UV photolysis of a neutral carbonyl, (ii) co-condensation of a neutral carbonyl with an alkali metal, followed by UV photolysis and (iii) electron bombardment of trapped carbonyls [11]. Species identified include $[V(CO)_6]^-$, $[Cr(CO)_5]^-$, $[Ni(CO)_3]^-$ and $[Fe(CO)_4]^-$. More recently, we have identified $[Fe(CO)_5]^+$ as the counter ion produced by vacuum UV photolysis of $Fe(CO)_5$ [12]. A general problem in identifying ions in matrices, (both in our experiments and those of others) is the lack of any direct method for showing that the species are charged. Identification, therefore, relies heavily on spectral band positions and analogy with spectra of known ionic species in the gas phase or solution.

In what follows, we first show that photolysis of $CpFe(CO)_2Co(CO)_4$ in Ar matrices leads to CO loss, while photolysis in a CO-doped generates quite different products. We then use N_2 matrices to show that only one CO group is lost during the primary photochemical step. Then, the spectra of the photoproducts in CO doped matrices are shown to be consistent with the known spectra of $[CpFe(CO)_3]^+$ and $[Co(CO)_4]^-$. Finally we discuss possible mechanisms for these photochemical processes.

Experimental

The low temperature apparatus (Air Products Displex CS202-A) and associated equipment have been described elsewhere [13]. IR spectra were recorded on a Nicolet MX-3600 FT-IR interferometer with 32k data collection and three degrees of zero-filling (0.7 cm^{-1} resolution) [13]. UV/visible spectra were recorded on a Perkin–Elmer Lambda 5 spectrophotometer.

Matrices were prepared by simultaneous slow deposition of the matrix gas and sublimation of $CpFe(CO)_2Co(CO)_4$. Ar and N_2 (Messer Griesheim) and CO (BOC Research Grade) were used without further purification. The sample of $CpFe(CO)_2Co(CO)_4$ was slightly contaminated with $[CpFe(CO)_2]_2$, which, being significantly less volatile [14], did not interfere with the matrix experiments. The photolysis source was a Philips HPK 125 W medium pressure Hg arc with Balzers narrow band interference filters when appropriate.

Results

Two photochemical pathways

$CpFe(CO)_2Co(CO)_4$, (**1**) can be sublimed into the matrix with only slight decomposition, indicated by formation of free CO. Figure 1(a) shows the ν(CO) region of the IR spectrum of **1**, co-condensed with Ar at 10 K. Apart from the absorption due to free CO, all other bands can be assigned to well isolated molecules of **1**, because the spectrum does not change with increasing dilution of the matrix. Manning and co-workers have studied the IR spectrum of **1** and related compounds in a variety of solvents and have assigned the bands to different isomers [15]. The spectrum of matrix isolated **1** is consistent with the doubly bridged isomer, $CpFe(CO)(\mu\text{-}CO)_2Co(CO)_3$. Figure 1(b) shows the spectrum obtained after this matrix was irradiated with UV light (λ 367 nm) a wavelength corresponding to the near-UV absorption band of **1**. It is immediately clear that the amount of free CO in the matrix has increased. There are also several new bands. A careful study of the growth and decay of these bands show that they are due to a single metal carbonyl species, **2**. This photo-product, **2**, must contain fewer CO groups than **1**, because free CO is also produced. **2** must there have the formula $CpFeCo(CO)_{6-x}$. Subsequent irradiation of the matrix with broadband visible light, $\lambda > 375$ nm, causes a decrease in the IR bands of both **2** and free CO, and a simultaneous regeneration of **1**, (spectra not illustrated) *. Thus we have one photochemical pathway, the reversible loss of CO (eq. 1).

$$CpFe(CO)_2Co(CO)_4 \underset{\lambda > 375\text{ nm}}{\overset{367\text{ nm, Ar, 10 K}}{\rightleftarrows}} CpFeCo(CO)_{6-x} + xCO \qquad (1)$$

When **1** is isolated in an Ar matrix doped with 10% CO, the same wavelength UV radiation (367 nm) produces an effect quite different from that in a pure Ar matrix. Figure 1(c) shows the IR spectrum obtained after irradiation of the CO doped matrix. The bands due to photoproduct **2** are absent and there are strong absorptions between 1950 and 1850 cm^{-1}, a region where the spectrum in pure Ar has none, cf. Fig. 1(b) and 1(c). Even without detailed analysis, it is clear that the photoproduct (or photoproducts), **3**, in the doped matrix must be different. Thus we have a second photochemical pathway (eq. 2).

$$\mathbf{1} + CO \xrightarrow{\text{Ar/CO 10 K, 367 nm}} \mathbf{3} \qquad (2)$$

The formation of **3** only occurs in the presence of CO and we believe that the IR spectra can only be explained in terms of ionic species. However, before discussing these spectra in more detail, we return to the nature of the photoproduct, **2**, generated by loss of CO from **1**. The wavenumbers of all products are summarized in Table 1.

Nature of the products of CO loss and N_2 addition

Figure 2(a) shows the IR spectrum of product **2** in an Ar matrix, obtained by computer subtraction of IR bands due to the unphotolysed starting material, **1**. Although some of the bands of **2** are slightly split by matrix effects, it is clear that there are at least three "terminal" C–O stretching bands and one "bridging" C–O

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* **1** has a near-UV absorption maximum at 355 nm and it is presumably this transition which is excited by the 367 nm photolysis lamp. The photoproduct, **2**, does not show any strong absorption maxima $\lambda > 300$ nm, although it must clearly absorb light $\lambda > 375$ nm or else the light would have no effect in reversing the formation of **2**.

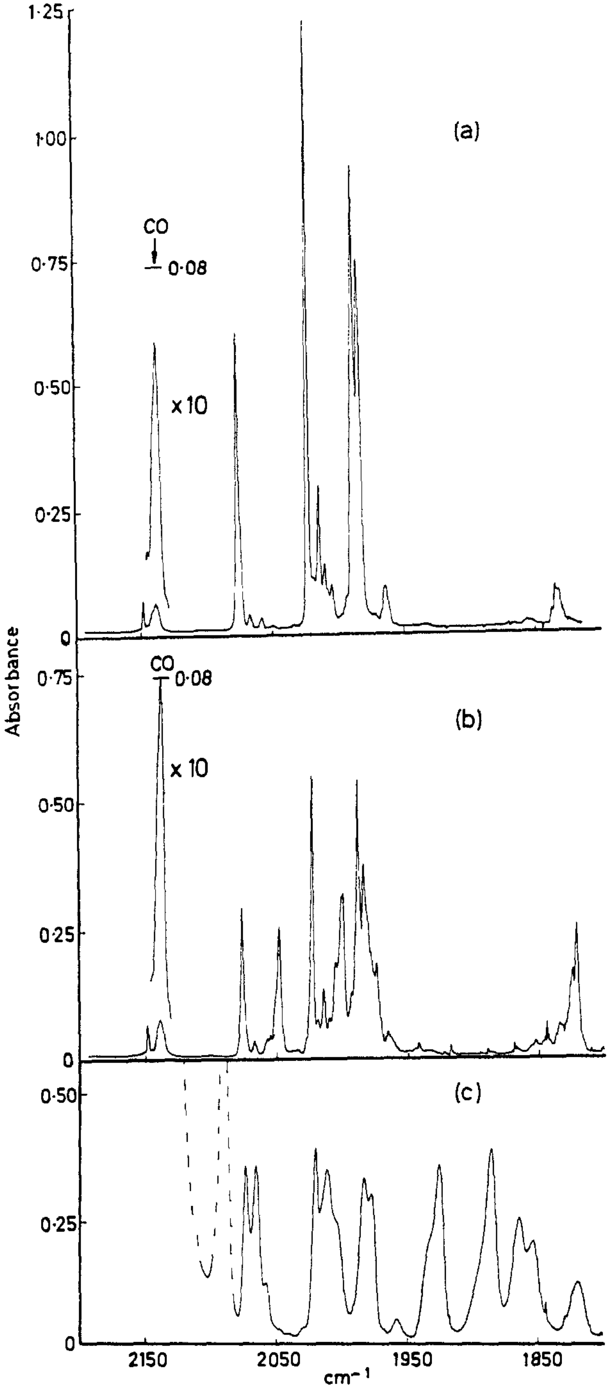

Fig. 1. IR absorption spectra of $CpFe(CO)_2Co(CO)_4$ (**1**) (a) after deposition in an Ar matrix at 10 K, (b) after 450 min irradiation, 367 nm, of this matrix. Note the growth of the band due to free CO in the matrix, (c) after 400 min irradiation, 367 nm, of **1** isolated in an Ar matrix doped with 10% CO. Note the strong absorptions in the region 1950–1850 cm^{-1}, (Bands drawn in broken lines are due to the CO dopant in the matrix).

TABLE 1

WAVENUMBERS (cm^{-1}) OF IR ABSORPTIONS OF $CpFe(CO)_2Co(CO)_4$ AND ITS PHOTOPRODUCTS IN N_2, Ar AND Ar+10% CO MATRICES AT 10 K

$CpFe(CO)_2Co(CO)_4$		
N_2	Ar[a]	Ar+10% CO
2076.2	2076.6	2073.7
2023.6	2023.1	2020.3
2014.6	2014.5	2010.6
1987.2	1988.2	1981.8
1985.4		
1979.8	1984.3	1978.2
1958.1	1963.5	1957.8
1827.2	1833.2	1819.6
Photoproducts		
N_2[b]	Ar[a,b]	Ar+10% CO[a,c]
2245		2106.8
2046.6	2047.5	(2066.1)
2006.5	1999.8	2058.9
1992.6	1977.9	(2014.2)
1843.1	1974.1	2005.4
1818.6	1820.6	1933.0
		(1924.3)
		1889.5
		(1865.1)
		1861.5
		(1854.3)

[a] See Fig. 1. [b] See Fig. 2. [c] See Fig. 3. Bands in parentheses are those which are relatively stronger in Fig. 3(a) and decrease in intensity after irradiation with the unfiltered Hg arc.

band. Thus, **2** must contain at least four CO groups. Unfortunately, one cannot be more precise about the number of CO groups on the basis of this spectrum, because **1**, which has four terminal CO groups has only three distinct terminal C–O bands, Fig. 1(a) *. Photolysis of **1** in an N_2 matrix, however, provides more evidence.

When **1** is photolysed in pure N_2 matrices, free CO is generated but no bands due to **2** are observed. Instead, six new IR bands can be assigned to the primary photoproduct, **4**, see Fig. 2(b). Of these bands, one occurs in the N–N stretching region, three in the terminal C–O stretching region and two in the bridging C–O

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* We attempted to characterize the structure of **2** by photolysing a sample of **1**, 30% enriched with ^{13}CO. The enrichment was achieved by exposing a solution of **1** in cyclohexane to 1 atm. pressure of ^{13}CO (BOC Prochem) for ~ 4 h at room temperature. The use of ^{13}CO to characterize mononuclear carbonyls has been reviewed previously [16]. Here, our primary objective was to determine the number of bridging CO groups in **2**. If **2** had one bridging group, one strong ^{13}CO satellite band would be predicted but, if it had two bridging groups, two strong ^{13}CO satellites would be expected, provided that the vibrational coupling between the two bridging CO groups were significant. Although only one ^{13}CO satellite band was observed in the spectrum of **2**, 1785.2 cm^{-1}, no definite conclusion can be drawn about the number of bridging CO groups in **2** because **1**, which is known to have two groups, only shows one ^{13}CO satellite band, presumably because of weak vibrational coupling. This is in contrast to the case of $CpFe(\mu\text{-}CO)_3FeCp$ where the coupling was strong enough to establish the number of bridging CO groups [8].

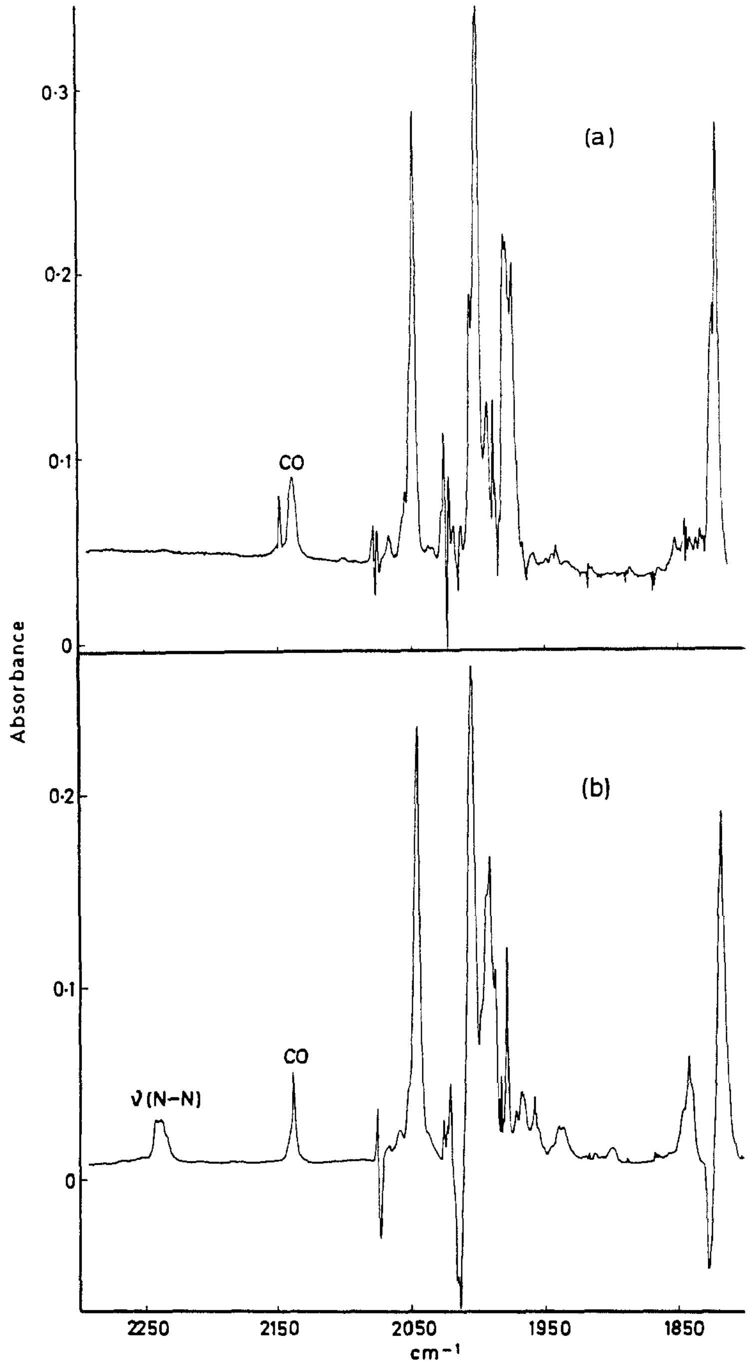

Fig. 2. (a) IR absorption spectrum of the photoproduct, **2**, generated by photolysis of **1** in an Ar matrix. The spectrum was obtained by a scaled computer subtraction, Fig. 1(b) minus Fig. 1(a) to remove the bands of **1**. (b) IR absorption spectrum of the photoproduct, **4**, generated by 5 min photolysis (unfiltered Hg arc) of **1**, isolated in an N_2 matrix at 10 K. Spectrum obtained by computer subtraction of the residual bands of **1**.

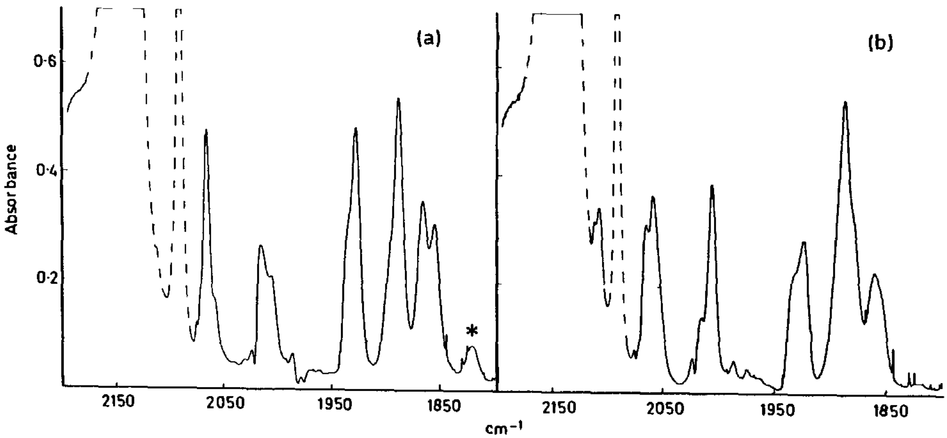

Fig. 3. (a) IR absorption spectra of photoproducts, **3**, generated by 130 min irradiation ($\lambda > 375$ nm) of **1** isolated in Ar doped with 10% CO (cf. Fig. 1(c)). (b) Spectrum after a further 140 min irradiation with an unfiltered Hg arc. In both spectra bands shown in broken lines are those of the CO matrix and bands due to residual **1** have been removed by computer subtraction (NB the band marked with an asterisk in (a) has not been fully removed by the computer subtraction).

stretching region. Thus, the overall reaction must be as shown in eq. 3.

$$\underset{(1)}{\mathrm{CpFeCo(CO)_4(\mu\text{-}CO)_2}} + \mathrm{N_2} \xrightarrow{h\nu} \underset{(4)}{\mathrm{CpFeCo(CO)_3(N_2)(\mu\text{-}CO)_2}} + \mathrm{CO} \qquad (3)$$

Since formation of **4** involves loss of only one CO group from **1**, it seems reasonable to suppose that the formation of **2** also involves the loss of one CO group. Thus **2** is $\mathrm{CpFeCo(CO)_5}$.

Identification of ionic photoproducts in CO-doped matrices

The photolysis of **1**, in Ar matrices doped with CO, appears to take place in two distinguishable stages. After irradiation of the matrix with 367 nm light, the spectrum illustrated in Fig. 3(a) is obtained (note that the residual bands of **1** have been removed by computer subtraction). Subsequent irradiation with an unfiltered Hg arc, initially produces a slight regeneration of starting material, **1**, and a final spectrum (Fig. 3(b)) which is similar to Fig. 3(a) but with changes in the relative intensities and splittings of the bands. In view of the broadness of the bands, experiments with ^{13}CO are unlikely to be helpful in the identification of these products, and were not attempted.

In Fig. 4 we compare schematically the observed IR frequencies of the photoproducts with those of some known CpFe and Co carbonyl species *. There were no absorptions observed in the region 1840–1700 cm^{-1} where bridging CO groups might absorb (Fig. 4(a)). Thus it is unlikely that the photoproducts are either a $(\mu\text{-CO})_3$ species, analogous to Rest's $\mathrm{CpFe(\mu\text{-}CO)_3FeCp}$ [8] (Fig. 4(f)) or a bridged

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* It seems unlikely that the product, **3**, could be the "triple-decker-sandwich" isomer of **1**, $\mathrm{(CO)_3Fe(\mu\text{-}Cp)Co(CO)_3}$, similar to compounds analysed theoretically by Hoffman and co-workers and concluded to be improbable as stable entities [24].

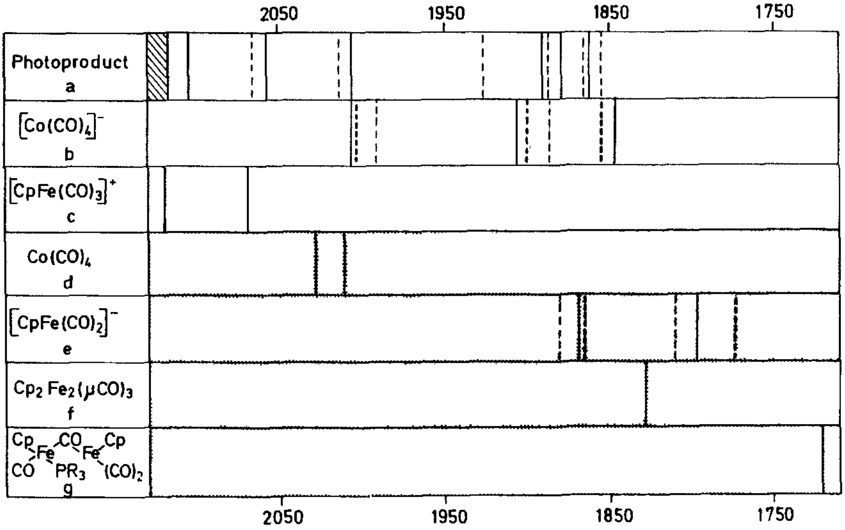

Fig. 4. Schematic representation of IR spectra comparing the absorptions obtained after UV irradiation of $CpFe(CO)_2Co(CO)_4$ in Ar + 10% CO matrices, with those of possible photoproducts. (a) Spectrum after irradiation, see Fig. 3. Bands shown in broken lines are those which are stronger in Fig. 3(a). They are listed in parentheses in Table 1. The hatched area is obscured by the CO in the matrix. (b) $Na^+ [Co(CO)_4]^-$ in THF solution; the different lines correspond to different ion pairs. (c) $[CpFe(CO)_3]^+ BPh_4^-$ in Nujol mull [19]. (d) $Co(CO)_4$ in CO matrix 20 K [17]. (e) $Ph_4As^+ [CpFe(CO)_2]^-$, THF/CH_3CN solution [20]. (f) $Cp_2Fe_2(\mu\text{-}CO)_3$, PVC film, 10 K [8]. (g) Bridging CO band (THF solution) of proposed intermediate $CpFe(CO)(P(O\text{-}i\text{-}Pr)_3)(\mu\text{-}CO)CpFe(CO)_2$ which is believed to have a bridging CO group but no Fe–Fe bond [7].

species without a metal–metal bond (cf. Tyler's intermediate [7] Fig. 4(g)). Similarly the observed bands (Fig. 4(a)) do not correspond to the known spectrum of matrix isolated $Co(CO)_4$ (Fig. 4(d)), [17] eliminating the possibility of homolytic cleavage *.

$$\underset{(1)}{CpFe(CO)_2Co(CO)_4} + CO \xrightarrow{UV} CpFe(CO)^{\bullet}_{2(\text{or } 3)} + Co(CO)^{\bullet}_4 \qquad (4)$$

Perhaps the most striking feature of the observed spectra is the group of intense absorptions in the region 1950–1850 cm^{-1} (see above), where neutral unsubstituted dinuclear carbonyls do not normally absorb. These bands are, however, close to those of the $[Co(CO)_4]^-$ anion in solution (Fig. 4(c)) where extensive studies by Edgell and co-workers have shown that the exact band positions and intensities are very sensitive to ion-pairing and environment [18]. Similarly the higher frequency bands of the photoproducts are close to those of the cation $[CpFe(CO)_3]^+$ [19], (Fig. 4(b)). The observed spectra are therefore consistent with heterophotolysis to form ions (eq. 5).

$$\underset{(1)}{CpFe(CO)_2Co(CO)_4} + CO \xrightarrow{h\nu} [CpFe(CO)_3]^+ + [Co(CO)_4]^- \qquad (5)$$

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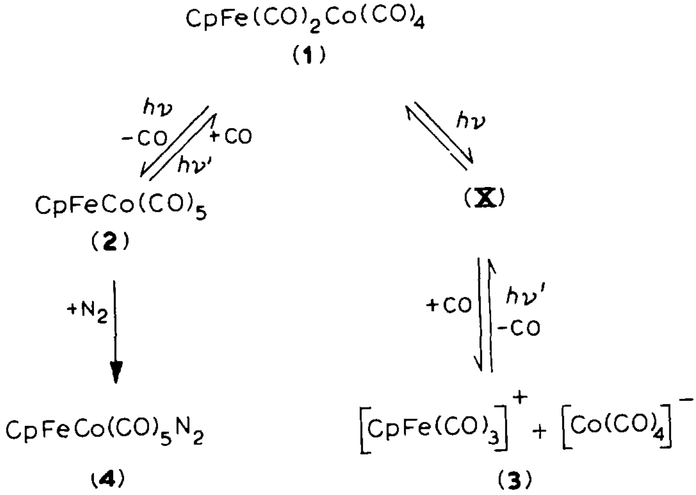
* In pure CO matrices, prolonged photolysis of **1** gives rise to two IR bands, 2029 and 2011 cm^{-1}, assignable to $Co(CO)_4$ [17]. This radical is probably generated from $[Co(CO)_4]^-$ rather than by homolysis of **1** because photolysis of $[CpFe(CO)_2]_2$ under similar conditions [23] produces bands at ~ 1970 cm^{-1}, (possibly due to $CpFe(CO)_x$ species) which were not observed in these experiments.

We can discount the alternative heterophotolysis to form $[Co(CO)_5]^+$ and $[CpFe(CO)_2]^-$, because the spectrum of the anion is known to have strong absorptions at ~ 1800 cm^{-1} (Fig. 4(e)) [20], where there are no observed bands.

The starting material, **1**, was trapped in a more or less rigid matrix cage, which would necessarily prevent the separation of the ions, trapping them in a particularly tight ion pair. The differences in bands between the spectra in Figs. 3(a) and 3(b) could, therefore, be ascribed to photochemically induced reorientation of the ions, similar to that observed for neutral species [21] *.

Discussion

Our experiments do not provide detailed evidence for the structures of the species generated by photolysis of **1**. We cannot tell, for example, whether the dinitrogen group in **4** is bound to the Fe or Co atoms. Nevertheless, the results do provide the broad framework necessary to outline the photochemical pathways occurring, (Scheme 1). On excitation, **1** undergoes one of two processes: (i) loss of CO or (ii) formation of some transient intermediate, **X**, which apparently immediately reverts to **1** in the absence of excess CO. **X** may well be an isomer of **1** perhaps without a metal–metal bond. Unfortunately it is not clear whether the charge separation occurs during the initial photoexcitation, or only during the subsequent reaction of **X**.



SCHEME 1

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* The changes in the IR spectrum between Figs. 3(a) and 3(b) were accompanied by a striking change in the visible spectrum of the matrix, which turned from colourless to bright blue, with an intense absorption maximum at 650 nm. This absorption appears to be associated with the ions although its origin is not entirely clear. It is unlikely to be a charge transfer band analogous to that proposed for $V(CO)_6$ [22] because both ions are already 18-electron species. A somewhat speculative suggestion is that a CO group of $[Co(CO)_4]^-$ could be interacting with the π electrons of the C_5H_5 ring of the $[CpFe(CO)_3]^+$ ion to form a charge-transfer complex. This could also explain the unexpectedly high intensity of the band at 2005 cm^{-1}, which is IR inactive in the isolated $[Co(CO)_4]^-$ ion [18].

The heterophotolysis of **1** differs from the recently reported disproportionation of $[CpMo(CO)_3]_2$ (see [10]) in that it can only involve a single molecule of **1**, because the matrix dilution prevents bimolecular processes. Our experiments add weight to previous reports of binuclear carbonyls undergoing competitive photochemical pathways (bond fission or CO loss) and perhaps the presence of two pathways will transpire to be a general property of such compounds. Further, the fact that ionic species can apparently be formed in matrices suggests that ions should also be considered when proposing reaction schemes for similar compounds in non-polar solutions.

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