

## Reactions of Carbon Monoxide with Fe(II) Diethyldithiocarbamate and Fe(II) Ethylxanthate

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Reactions of carbon monoxide with iron(II) diethyldithiocarbamate and iron(II) ethylxanthate were followed using solution IR spectroscopy. In DMF and  $\text{CH}_3\text{CN}$  solutions, the only Fe–dithiocarbamate–carbon monoxide complex observed was  $\text{cis-}[\text{Fe}(\text{CO})_2(\text{dedtc})_2]$ . This complex formed rapidly and appeared to be very stable, resisting displacement of the coordinated CO molecules by other ligands.  $\text{Fe}(\text{exa})_2$  showed very little coordination of CO in DMF solution, but in  $\text{CH}_3\text{CN}$  solution formed the complex  $\text{cis-}[\text{Fe}(\text{CO})_2(\text{exa})_2]$  rapidly via the monocarbonyl intermediate  $[\text{Fe}(\text{CO})(\text{exa})_2\text{CH}_3\text{CN}]$ . In  $\text{CHCl}_3$  solution, in the presence of CO and added bases, a series of complexes,  $[\text{Fe}(\text{CO})(\text{exa})_2L]$ , where  $L = \text{pyridine, pyrrolidine, diethylamine and triphenylphosphine}$ , was formed. However, with the exception of  $[\text{Fe}(\text{CO})(\text{exa})_2(\phi_3P)]$ , these monocarbonyl complexes were unstable with respect to disproportionation to  $\text{cis-}[\text{Fe}(\text{CO})_2(\text{exa})_2]$  and  $[\text{Fe}(\text{exa})_2L_2]$ . No mixed-ligand monocarbonyl complexes were observed with  $\text{Fe}(\text{dedtc})_2$ .

### Introduction

A vast array of Fe(II) complexes with carbon monoxide have been reported in the literature [1]. Complexes incorporating ligands with H [2–4], C [5–7], N [8–10], O [11, 12], halide [13–15], P [16–18], S [19–21], As [15, 22, 23] and Sb [15] donor atoms have been prepared by a variety of synthetic routes. Perhaps the two most common preparative methods have involved oxidative displacement reactions of Fe(0) carbonyl complexes [7, 13, 24] and ligand substitution reactions of Fe(II) carbonyl halides [15].

Of particular interest are those reactions involving direct uptake of CO, either by simple addition to a coordinatively unsaturated Fe(II) complex [8, 9, 16] or by displacement of a coordinated ligand by CO [2, 22, 25].

The differences in behaviour towards the uptake of carbon monoxide by ferrous dithiocarbamate and ferrous xanthate, are the subject of this paper.

### Experimental

All reactions were performed under an inert atmosphere. Solvent peaks in the IR spectra were cancelled by use of a balanced reference cell. Spectra were calibrated with a polystyrene film. Solution cells had a path length of 1 mm. Solutions were sampled and monitored in the infrared region by a previously described method [26].

Iron(II) diethyldithiocarbamate solutions were prepared by adding a solution of  $\text{Fe}(\text{ClO}_4)_2$  in DMF to a solution of Nadedtc in DMF such that the resulting solution contained Fe(II) and dedtc in the ratio of 1:2 at an Fe(II) concentration of  $0.05 \text{ mol dm}^{-3}$ .

Iron(II) ethylxanthate solutions were prepared either by the method above using Kexa, or, more commonly, by dissolving an appropriate amount of  $\text{Fe}(\text{exa})_2(\text{DMF})_2$  [27] in  $\text{CHCl}_3$  or  $\text{CH}_3\text{CN}$ .

Carbon monoxide was bubbled through the solutions and the reactions followed by monitoring diagnostic regions in the infrared spectra of the solutions. The method generally followed was to bubble carbon monoxide through the reaction solution for a short time – 30–60 s (subsequently referred to in the text as ‘limited’ exposure to CO). An aliquot of the solution was then removed, placed in an IR solution cell, and changes in the IR spectrum recorded as a function of time. Carbon monoxide was then re-introduced into the reaction solution and aliquots were successively removed until no further

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changes occurred in the IR spectra as a result of prolonged exposure of the reaction solution CO.

Reactions in the presence of the bases pyridine, aniline, pyrrolidine, diethylamine and triphenylphosphine were performed similarly, with the base being added prior to exposure of the reaction solution to CO.

One or more of the following regions of the infrared were monitored:

- the carbon monoxide stretching frequency region ( $2200\text{--}1800\text{ cm}^{-1}$ ), for the presence of coordinated CO.

- the DMF C=O stretching frequency region ( $1700\text{--}1600\text{ cm}^{-1}$ ), for the presence of coordinated and uncoordinated DMF.

- the 'xanthate region' ( $1300\text{--}1150\text{ cm}^{-1}$ ), which is diagnostic for the C–O vibration of the  $\text{--OCS}_2$  group of the xanthate ligand [28].

- regions diagnostic for coordination of the added base (if appropriate).

## Results and Discussion

### Reactions of Ferrous Diethyldithiocarbamate

When CO was bubbled through a DMF solution of ferrous diethyldithiocarbamate, the resulting brown solution exhibited two strong carbonyl bands of approximately equal intensity at  $2018\text{ cm}^{-1}$  and  $1957\text{ cm}^{-1}$ . These peaks reached maximum intensity in less than 5 min. The CO atmosphere was replaced with  $\text{N}_2$ . No decrease in the intensity of these carbonyl stretches was observed over a period of 1 h. The reaction was repeated in the presence of pyridine, but no change in the carbonyl absorptions was observed.

In  $\text{CH}_3\text{CN}$  solution, identical results were obtained apart from a small shift in the carbonyl stretching frequencies to  $2021\text{ cm}^{-1}$  and  $1961\text{ cm}^{-1}$ .

These carbonyl stretching frequencies agree reasonably well with those reported by Buttner and Feltham [20] for  $\text{Fe}(\text{CO})_2(\text{dedtc})_2$  ( $2010\text{ cm}^{-1}$ ,  $1945\text{ cm}^{-1}$  (nujol)) and  $\text{Fe}(\text{CO})_2(\text{dmdtc})_2$  ( $2020\text{ cm}^{-1}$ ,  $1955\text{ cm}^{-1}$  (nujol)). Thus it is apparent that the only carbonyl complex formed in the above reactions was  $\text{cis-}[\text{Fe}(\text{CO})_2(\text{dedtc})_2]$  [20, 29, 30] and that this complex formed rapidly.

The carbon monoxide molecules in  $\text{Fe}(\text{CO})_2(\text{dedtc})_2$  appear to be bound strongly, resisting displacement by pyridine even in the absence of a carbon monoxide atmosphere.

### Reactions of Ferrous Ethylxanthate

Introduction of CO into a solution of ferrous ethylxanthate in DMF resulted in only very weak carbonyl absorptions in the solution IR spectrum. This contrasted with the very strong carbonyl bands observed under the same conditions using  $\text{dedtc}$ .



Fig. 1. Changes in the IR carbonyl spectrum of an acetonitrile solution of  $\text{Fe}(\text{exa})_2$  versus time, after exposure to CO for 30 s. (a) 2 min, (b) 5 min, (c) 10 min, (d) 30 min.

In  $\text{CH}_3\text{CN}$ , however, three strong carbonyl absorptions were observed at  $2040$ ,  $1990$  and  $1965\text{ cm}^{-1}$ , whose relative intensities varied with time. Figure 1 shows the changes that occurred with time in the IR spectrum of an iron(II) xanthate solution after 'limited' exposure (30 s) to a carbon monoxide atmosphere. Initially, a peak formed at  $1965\text{ cm}^{-1}$  which was gradually replaced by two peaks of approximately equal intensity at  $2040$  and  $1990\text{ cm}^{-1}$ .

By comparison with the reactions for iron(II) diethyldithiocarbamate solutions and the known carbonyl stretching frequencies for  $\text{cis-}[\text{Fe}(\text{CO})_2(\text{dedtc})_2]$ , the peaks at  $2040$  and  $1990\text{ cm}^{-1}$  are assigned to  $\text{cis-}[\text{Fe}(\text{CO})_2(\text{exa})_2]$ . The initial peak at  $1965\text{ cm}^{-1}$  could be due to either the corresponding *trans* dicarbonyl complex, or a monocarbonyl complex, e.g.,  $[\text{Fe}(\text{CO})(\text{exa})_2\text{CH}_3\text{CN}]$ . The position of this band, at a lower frequency than either of the *cis* dicarbonyl stretches, suggests the peak is due to the monocarbonyl complex [15].

The absence of carbon monoxide uptake by the iron(II) xanthate solution in DMF indicates that this complex does not bind carbon monoxide as

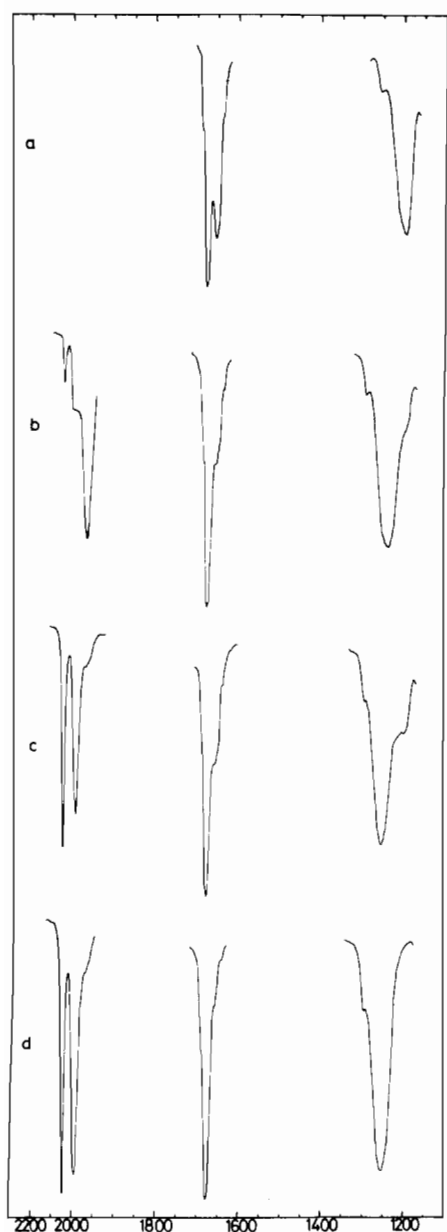
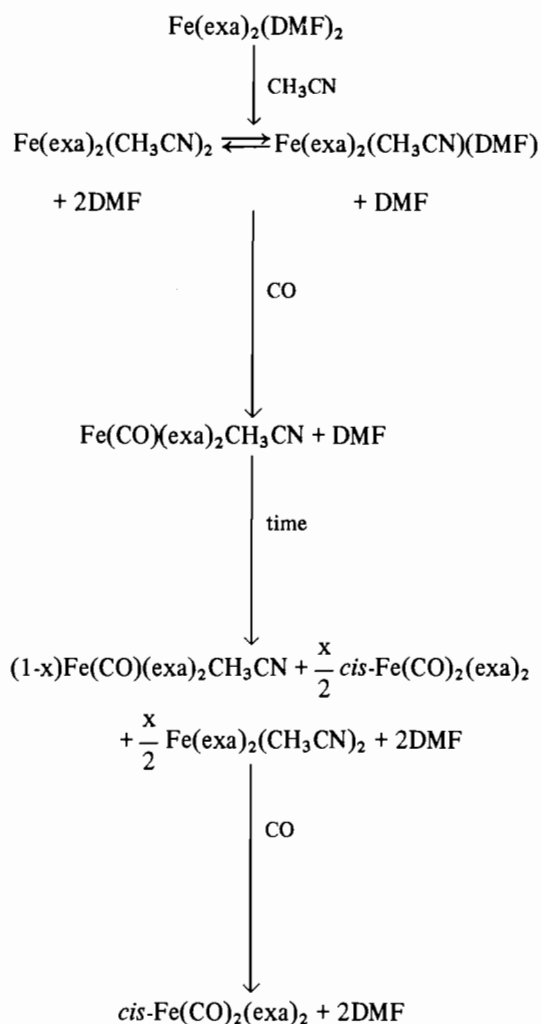


Fig. 2. Reaction of an acetonitrile solution of  $\text{Fe}(\text{exa})_2(\text{DMF})_2$  with CO.

strongly as the corresponding dithiocarbamate complex. This is confirmed by the frequencies observed for the carbonyl stretches of  $\text{cis-}[\text{Fe}(\text{CO})_2(\text{exa})_2]$  in  $\text{CH}_3\text{CN}$ , which are approximately  $25\text{ cm}^{-1}$  higher than those observed for  $\text{cis-}[\text{Fe}(\text{CO})_2(\text{dedtc})_2]$ . The rate of absorption of CO by the xanthate complex in  $\text{CH}_3\text{CN}$  is quite remarkable, with all the Fe apparently coordinating at least one carbon monoxide molecule in less than 30 s at  $20^\circ\text{C}$ .

#### Reactions of $\text{Fe}(\text{exa})_2(\text{DMF})_2$ in $\text{CH}_3\text{CN}$

Using the complex  $\text{Fe}(\text{exa})_2(\text{DMF})_2$  [27] as a source of iron(II) xanthate, it was possible to follow



and interpret the reactions leading to the formation of carbonyl complexes in  $\text{CH}_3\text{CN}$  in more detail.

Three regions of the IR spectrum were monitored – the carbonyl stretching frequency region, – the DMF C=O stretching frequency region ( $1700\text{--}1600\text{ cm}^{-1}$ ). DMF coordinated to iron(II) xanthate absorbed at  $1650\text{ cm}^{-1}$  in  $\text{CH}_3\text{CN}$ , while uncoordinated DMF absorbed at  $1670\text{ cm}^{-1}$ , – the 'xanthate region' ( $1300\text{--}1150\text{ cm}^{-1}$ ). This region was obscured by perchlorate peaks in reaction solutions prepared using  $\text{Fe}(\text{ClO}_4)_2$  and Kexa.

The sequence of IR spectra which accompany CO uptake by a  $\text{CH}_3\text{CN}$  solution of  $\text{Fe}(\text{exa})_2(\text{DMF})_2$  is

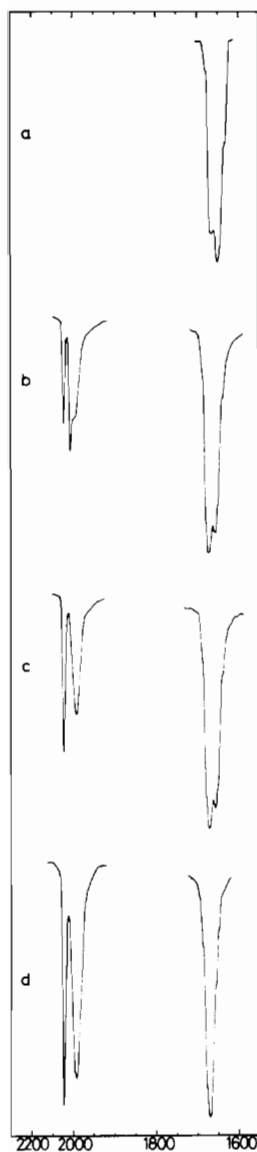
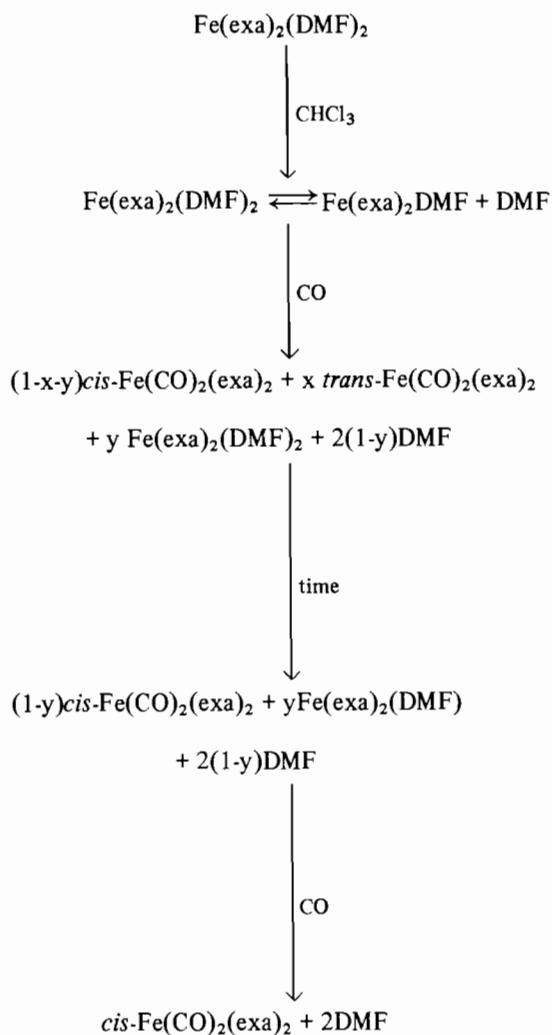


Fig. 3. Reaction of a chloroform solution of  $\text{Fe}(\text{exa})_2(\text{DMF})_2$  with CO.

reproduced in Fig. 2. Figure 2(a) shows the IR spectrum of a solution of  $\text{Fe}(\text{exa})_2(\text{DMF})_2$  in  $\text{CH}_3\text{CN}$  before the introduction of CO. A major portion of the DMF appears to be uncoordinated (peak at  $1670\text{ cm}^{-1}$ ), presumably displaced from the coordination sphere of Fe(II) by  $\text{CH}_3\text{CN}$ . The xanthate ( $-\text{O}-\text{CS}_2$ ) vibration is seen at  $1194\text{ cm}^{-1}$ .

After limited exposure of the solution to CO, its IR spectrum (Fig. 2(b)) shows a coordinated carbonyl peak at  $1965\text{ cm}^{-1}$ . Nearly all the DMF has now been displaced from the Fe(II) coordination sphere and the xanthate vibration has shifted to  $1233\text{ cm}^{-1}$ . On standing, the IR spectrum of this solution transformed to that of the *cis* dicarbonyl complex, with a shoulder at  $\sim 1194\text{ cm}^{-1}$  reappearing on the xanthate peak, now centred at  $1250\text{ cm}^{-1}$  (Fig. 2(c)).



This supports the assignment of the  $1965\text{ cm}^{-1}$  carbonyl peak to the complex  $[\text{Fe}(\text{CO})(\text{exa})_2\text{CH}_3\text{CN}]$ , which apparently disproportionates to *cis*- $[\text{Fe}(\text{CO})_2(\text{exa})_2]$  and  $[\text{Fe}(\text{exa})_2(\text{CH}_3\text{CN})_2]$ .

Figure 2(d) shows the IR spectrum after prolonged reaction with CO. Now only the *cis* dicarbonyl stretches at  $2040$  and  $1990\text{ cm}^{-1}$  remain, no coordinated DMF is present and the xanthate peak has sharpened at  $1250\text{ cm}^{-1}$ . The shoulder at  $1193\text{ cm}^{-1}$  has disappeared.

#### Reactions of $\text{Fe}(\text{exa})_2(\text{DMF})_2$ in $\text{CHCl}_3$

Due to interference from solvent absorption [31], the xanthate region ( $1300\text{--}1150\text{ cm}^{-1}$ ) could not be monitored in  $\text{CHCl}_3$ .

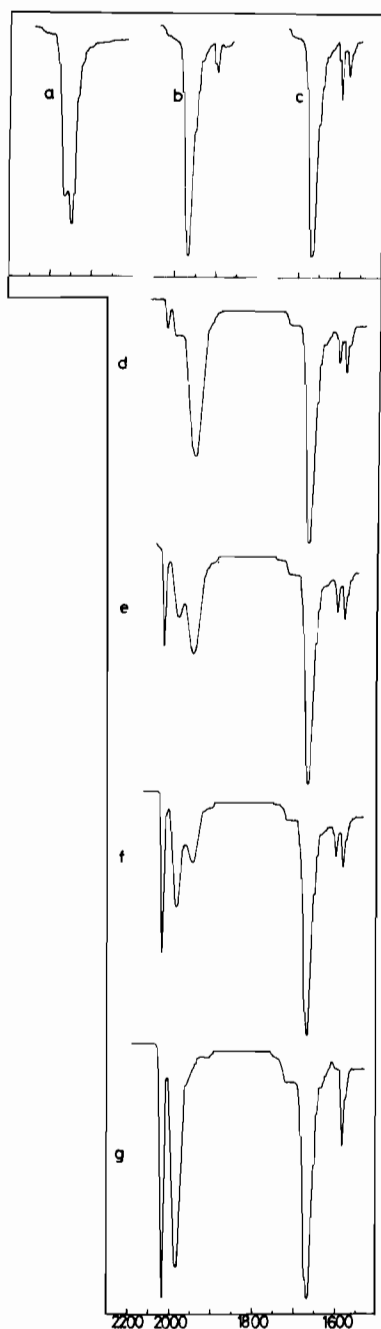
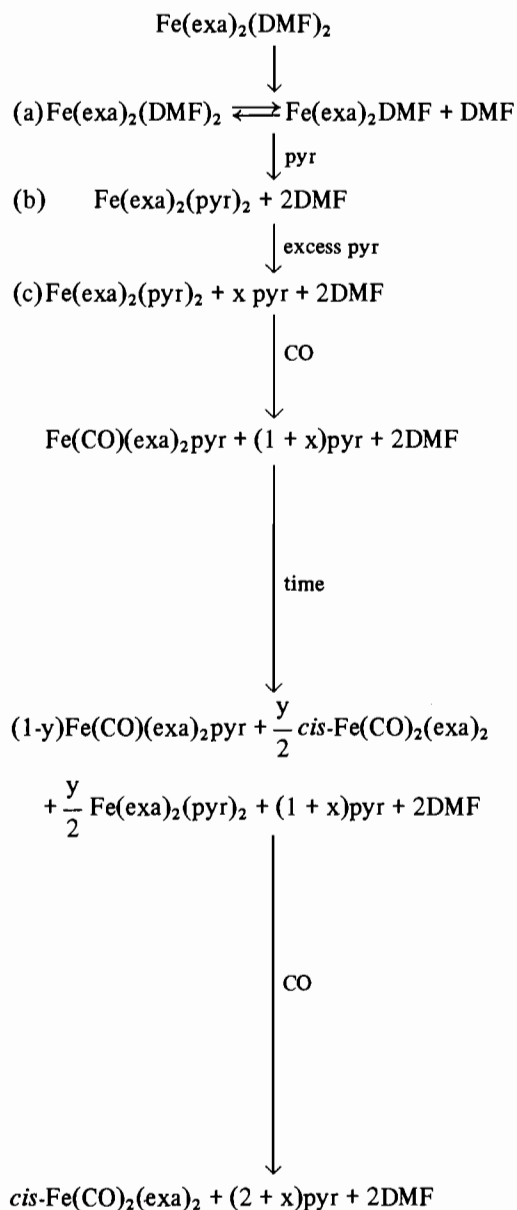


Fig. 4. Reaction of a chloroform solution of  $\text{Fe}(\text{exa})_2(\text{DMF})_2$  plus pyridine, with CO.

The IR spectrum in the DMF region ( $1700\text{--}1600\text{ cm}^{-1}$ ) of a solution of  $\text{Fe}(\text{exa})_2(\text{DMF})_2$  in  $\text{CHCl}_3$  is reproduced in Fig. 3(a). Most of the DMF remains coordinated (peak at  $1650\text{ cm}^{-1}$ ) in this non-coordinating solvent, in contrast to the behaviour in  $\text{CH}_3\text{-CN}$ .

After limited exposure of this  $\text{CHCl}_3$  solution to CO, three carbonyl absorptions appeared at 2040,



2004 and  $1990\text{ cm}^{-1}$  (sh), and the DMF was displaced from the Fe(II) coordination sphere (peak at  $1670\text{ cm}^{-1}$ , Fig. 3(b)). On standing, the IR spectrum of this solution transformed to that shown in Fig. 3(c), where only the two *cis* dicarbonyl peaks at 2040 and  $1990\text{ cm}^{-1}$  remain. The ratio of coordinated to uncoordinated DMF did not change during this transformation.

TABLE I. Carbon Monoxide Stretching Frequencies ( $\text{cm}^{-1}$ ) observed in IR Spectra of  $\text{CHCl}_3$  Solutions of  $\text{Fe}(\text{exa})_2(\text{DMF})_2$  Containing Various Ligands.

Ligand	After limited exposure to CO	Limited exposure to CO + time	After prolonged exposure to CO
Aniline	2040(w) 2004(s) 1990(w)	2040(s) 2004(w) 1990(s)	2040(s) 1990(s)
Pyrrolidine	1948(s)	2040(s) 1990(s) 1948(w)	2040(s) 1990(s)
Diethylamine	2040(s) 2004(s) 1990(s) 1948(w,br)	2040(s) 1990(s)	2040(s) 1990(s)
Triphenylphosphine	1955(s)	1955(s)	2040(s) 1990(s) 1955(s)

Introduction of further carbon monoxide into the solution produced the IR spectrum shown in Fig. 3(d), indicating complete conversion to  $\text{cis}[\text{Fe}(\text{CO})_2(\text{exa})_2]$ .

The origin of the peak at  $2004 \text{ cm}^{-1}$ , tentatively assigned to  $\text{trans}[\text{Fe}(\text{CO})_2(\text{exa})_2]$ , is discussed later in this paper.

#### Reactions of $\text{Fe}(\text{exa})_2(\text{DMF})_2$ in $\text{CHCl}_3$ in the Presence of Bases

Figure 4 shows the changes that occur in the IR spectrum of a  $\text{CHCl}_3$  solution of  $\text{Fe}(\text{exa})_2(\text{DMF})_2$  on addition of pyridine, followed by exposure to CO.

Figure 4(a) shows the C=O stretches of coordinated and uncoordinated DMF initially present in the IR spectrum of the above solution.

Figures 4(b) and (c) show the changes that occur on addition of pyridine. Pyridine was added dropwise until all the coordinated DMF was displaced. This was evidenced by the disappearance of the peak at  $1650 \text{ cm}^{-1}$  due to coordinated DMF, and a corresponding increase in the intensity of the uncoordinated DMF peak at  $1670 \text{ cm}^{-1}$  (Fig. 4(b)). A single pyridine peak was evident at  $1600 \text{ cm}^{-1}$ . On addition of more (excess) pyridine (Fig. 4(c)), a further peak appeared at  $1583 \text{ cm}^{-1}$  due to uncoordinated pyridine. It is interesting to note that although all the DMF was uncoordinated in the solution giving rise to the spectrum shown in Fig. 4(b), further addition of pyridine increased the intensity of the coordinated pyridine peak as well as giving rise to an uncoordinated pyridine absorption (Fig. 4(c)).

After limited exposure of this solution to carbon monoxide, the carbonyl stretching frequency region of the IR was dominated by a band at  $1950 \text{ cm}^{-1}$  (Fig. 4(d)). All the DMF remained uncoordinated (peak at  $1670 \text{ cm}^{-1}$ ), while the absorption at  $1583 \text{ cm}^{-1}$ , due to uncoordinated pyridine, grew in intensity at the expense of the coordinated pyridine peak. On standing, the IR spectrum of this solution slowly transformed to give the carbonyl stretching frequencies of  $\text{cis}[\text{Fe}(\text{CO})_2(\text{exa})_2]$  at the expense of the  $1950 \text{ cm}^{-1}$  carbonyl stretching band (Fig. 4(e) and (f)). The relative amounts of coordinated and uncoordinated pyridine did not change during this transformation.

Further exposure of the reaction solution to CO resulted in an IR spectrum showing only the carbonyl stretching frequencies due to  $\text{cis}[\text{Fe}(\text{CO})_2(\text{exa})_2]$ , with all the pyridine being displaced to give a single absorption at  $1583 \text{ cm}^{-1}$  (Fig. 4(g)).

These spectra, in conjunction with the results observed for the analogous reaction in the absence of pyridine, indicate that the initial CO absorption at  $1950 \text{ cm}^{-1}$  is attributable to  $[\text{Fe}(\text{CO})(\text{exa})_2(\text{pyr})]$  and that this complex slowly disproportionates to  $\text{cis}[\text{Fe}(\text{CO})_2(\text{exa})_2]$  and  $[\text{Fe}(\text{exa})_2(\text{pyr})_2]$ .

Similar reactions were performed in the presence of aniline ( $\phi\text{NH}_2$ ), pyrrolidine ( $(\text{CH}_2)_4\text{NH}$ ), diethylamine ( $(\text{C}_2\text{H}_5)_2\text{NH}$ ) and triphenylphosphine ( $\phi_3\text{P}$ ). In each case, neat ligand (or a saturated  $\text{CHCl}_3$  solution in the case of  $\phi_3\text{P}$ ) was added dropwise to a solution of  $\text{Fe}(\text{exa})_2(\text{DMF})_2$  in  $\text{CHCl}_3$  until no coordinated DMF peak ( $1650 \text{ cm}^{-1}$ ) remained in the solution IR spectrum. Carbon monoxide was then introduced into the reaction solution for a short

TABLE II. Carbon Monoxide Stretching Frequencies of Iron(II) Diethyldithiocarbonate and Iron(II) Ethylxanthate Carbonyl Complexes.

Complex	Solvent	Carbonyl stretching frequencies (cm <sup>-1</sup> )
<i>cis</i> -Fe(CO) <sub>2</sub> (dedtc) <sub>2</sub>	DMF	2018, 1957
	CH <sub>3</sub> CN	2021, 1961
<i>cis</i> -Fe(CO) <sub>2</sub> (exa) <sub>2</sub>	CH <sub>3</sub> CN	2040, 1990
	CHCl <sub>3</sub>	2040, 1990
<i>trans</i> -Fe(CO) <sub>2</sub> (exa) <sub>2</sub>	CHCl <sub>3</sub>	2004
Fe(CO)(exa) <sub>2</sub> CH <sub>3</sub> CN	CH <sub>3</sub> CN	1965
Fe(CO)(exa) <sub>2</sub> pyr	CHCl <sub>3</sub>	1950
Fe(CO)(exa) <sub>2</sub> ((CH <sub>2</sub> ) <sub>4</sub> NH)	CHCl <sub>3</sub>	1948
Fe(CO)(exa) <sub>2</sub> ((C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH)	CHCl <sub>3</sub>	1948 (w,br)
Fe(CO)(exa) <sub>2</sub> (φ <sub>3</sub> P)	CHCl <sub>3</sub>	1955

time. The solution was then sampled, and its IR spectrum monitored as a function of time. More CO was then bubbled through the reaction solution and the sampling and monitoring procedure repeated. The results are summarized in Table I.

#### Aniline

The three carbonyl bands observed in the IR spectrum of the reaction solution containing aniline, after a limited exposure to CO, were identical to those observed in the absence of any added ligand (see Fig. 3(b)), *i.e.*, there was no evidence to suggest that aniline formed a carbon monoxide complex with iron(II) xanthate under the conditions used. However, the fact that all the DMF was displaced by aniline before the introduction of CO, suggests that the peak at 2004 cm<sup>-1</sup> was not due to a DMF complex (the origin of this peak is discussed later).

#### Pyrrolidine

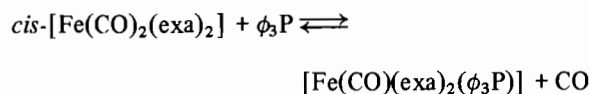
The strong carbon monoxide peak observed at 1948 cm<sup>-1</sup> after limited exposure of this solution to CO, suggests that the complex [Fe(CO)(exa)<sub>2</sub>((CH<sub>2</sub>)<sub>4</sub>NH)] formed initially in solution. On standing, this complex disproportionated to *cis*-[Fe(CO)<sub>2</sub>(exa)<sub>2</sub>] and presumably [Fe(exa)<sub>2</sub>((CH<sub>2</sub>)<sub>4</sub>NH)<sub>2</sub>].

#### Diethylamine

A weak broad carbonyl peak initially present at 1948 cm<sup>-1</sup> suggests minimal formation of the complex [Fe(CO)(exa)<sub>2</sub>((C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH)]. The absorption at 2004 cm<sup>-1</sup>, initially observed in reaction solutions containing no added ligand was also present in this spectrum, together with peaks due to *cis*-[Fe(CO)<sub>2</sub>(exa)<sub>2</sub>]. The spectrum transformed to that of *cis*-[Fe(CO)<sub>2</sub>(exa)<sub>2</sub>] with time.

#### Triphenylphosphine

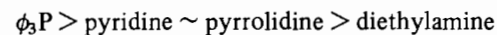
φ<sub>3</sub>P appears to form a stable monocarbonyl complex [Fe(CO)(exa)<sub>2</sub>(φ<sub>3</sub>P)] (CO peak at 1955 cm<sup>-1</sup>) which, unlike the other initially formed monocarbonyl complexes, does not disproportionate to *cis*-[Fe(CO)<sub>2</sub>(exa)<sub>2</sub>]. Indeed, by adding more or less φ<sub>3</sub>P, it was possible to obtain spectra indicating varying proportions of [Fe(CO)(exa)<sub>2</sub>(φ<sub>3</sub>P)] and *cis*-[Fe(CO)<sub>2</sub>(exa)<sub>2</sub>] in solution. All these spectra were stable with respect to time. It therefore appears that a true equilibrium existed in these solutions



#### Conclusions

Under the experimental conditions used in this study, the only iron(II)–dedtc–CO complex observed was *cis*-[Fe(CO)<sub>2</sub>(dedtc)<sub>2</sub>]. This complex appeared to bind CO more strongly than the corresponding exa complex, probably due to the greater π-electron donating properties of dedtc [26].

By contrast, a series of monocarbonyl iron(II) xanthate complexes were observed. Their relative order of stabilities appeared to be



Analogous monocarbonyl complexes containing aniline or DMF were not observed. The experiments performed did not allow the relative stability of [Fe(CO)(exa)<sub>2</sub>(CH<sub>3</sub>CN)] to be estimated with respect to the other monocarbonyl complexes. Of the monocarbonyls, only the φ<sub>3</sub>P complex did not disproportionate to *cis*-[Fe(CO)<sub>2</sub>(exa)<sub>2</sub>] and [Fe(exa)<sub>2</sub>L<sub>2</sub>].

An initial carbon monoxide peak was seen at  $2004\text{ cm}^{-1}$  in  $\text{CHCl}_3$  reaction solutions of  $\text{Fe}(\text{exa})_2$ - $(\text{DMF})_2$  containing aniline, diethylamine or in the absence of any base. Assuming that  $\text{CHCl}_3$  did not coordinate  $\text{Fe}(\text{II})$ , this absorbance could be due to either a five-coordinate complex [8, 9, 16], e.g.,  $[\text{Fe}(\text{CO})(\text{exa})_2]$ , or *trans*- $[\text{Fe}(\text{CO})_2(\text{exa})_2]$ . Attempts to obtain Raman spectra on solutions exhibiting this peak were unsuccessful, hence its origin is still uncertain; however, the position of the peak (between the two *cis* dicarbonyl absorbances) is consistent with its assignment to the *trans* dicarbonyl complex [15]. A corresponding peak did not appear in the coordinating solvent,  $\text{CH}_3\text{CN}$ .

With the exception of the  $\phi_3\text{P}$  monocarbonyl complex, the instability of the  $[\text{Fe}(\text{CO})(\text{exa})_2\text{L}]$  complexes with respect to disproportionation, makes their isolation in pure form unlikely.

A summary of the complexes observed in this study, together with their IR carbonyl stretching frequencies, is given in Table II.

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