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Selective loss of CO in the photochemistry of $MnRe(CO)_{10}$: a study using matrix isolation and time-resolved infrared spectroscopy

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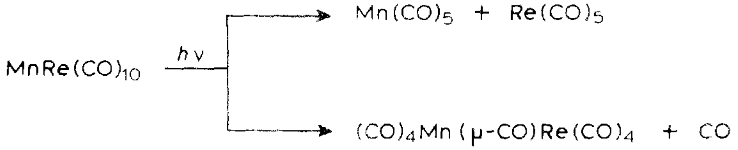
Abstract

Photolysis of $MnRe(CO)_{10}$, in argon matrices or room temperature solution, causes dissociation of CO and the formation of a singly bridged intermediate, $(CO)_4Mn(\mu\text{-}CO)Re(CO)_4$. The reaction has been studied using samples specifically enriched with ^{13}CO on the Re end. Careful monitoring, by infrared spectroscopy, of the intensity ratio of $^{12}CO/^{13}CO$ of free CO (matrix isolation) and of the bridging band of $(CO)_4Mn(\mu CO)Re(CO)_4$ (matrix isolation and time-resolved infrared spectroscopy) show that CO is expelled only from the Mn end of the dimer. There is no evidence for rapid interchange between the bridging CO group and the terminal CO groups on the Mn end of $(CO)_4Mn(\mu\text{-}CO)Re(CO)_4$.

Introduction

Recently there has been considerable interest in the photochemistry of metal–metal bonded systems [1]. The simplest of these are the dinuclear rhenium and manganese decacarbonyls, $M_2(CO)_{10}$ ($M = Mn$, Re), which possess a single metal–metal bond and only terminal CO groups. The photochemistry of these compounds has been studied using a variety of techniques including simple product studies [2], UV flash photolysis [3], matrix isolation [4,5] and most recently time-resolved IR spectroscopy [5–7]. These studies have concluded that there are two primary photochemical pathways; formation of the $M(CO)_5$ radical by homolysis of the metal–metal bond, and generation of $M_2(CO)_9$ by ejection of CO from the parent $M_2(CO)_{10}$.

By contrast, the photochemistry of the mixed metal dimer $MnRe(CO)_{10}$ is less well documented. However a study using matrix isolation and time-resolved IR spectroscopy [5] has confirmed that the same two photochemical processes occur in $MnRe(CO)_{10}$, homolysis of the Mn–Re bond giving $Mn(CO)_5$ and $Re(CO)_5$ radicals and loss of CO forming a product, $MnRe(CO)_9$, with a single bridging CO group, which is probably semibridging as in $Mn_2(CO)_9$ [4].



(1)

In the thermal reactions of $MnRe(CO)_{10}$, substitution by phosphines only occurs on the Re end of the molecule [8]. This is somewhat surprising, because the Mn—CO bond dissociation energy (66.6 kJ mol^{-1}) is much less than that for Re–CO (116.7 kJ mol^{-1}) [9] and, in a dissociative reaction, the Mn–CO bond might be expected to break first. Sonnenberger and Atwood [8] have, therefore, proposed an unusual mechanism in which the initial step is loss of CO from the Mn end of the molecule. A CO-bridged intermediate, $Mn(CO)_4(\mu\text{-}CO)Re(CO)_4$, is then formed and, finally, the phosphine, L, adds to the Re end of the intermediate, eqn. 2.

$$MnRe(CO)_{10} \xrightarrow{-CO} Mn(CO)_4Re(CO)_5 \rightarrow Mn(CO)_4(\mu\text{-}CO)Re(CO)_4 \xrightarrow{+L} Mn(CO)_5Re(CO)_4L \qquad (2)$$

Similar results have since been found for substitution by isonitriles [10].

The energy of a UV photon is more than sufficient to break the Re–CO bond, since UV photolysis of $Re_2(CO)_{10}$ is known to produce $Re_2(CO)_9$ [5]. It is, therefore, interesting to ask whether, in the photochemical reactions of $MnRe(CO)_{10}$, CO is still lost preferentially from one end of the molecule. In this paper, we answer this question by using samples of $MnRe(CO)_{10}$, specifically labelled with ^{13}CO at the Re end of the molecule. In photochemical matrix isolation experiments, we show that CO is only lost from the Mn end of the molecule just as in conventional thermal reactions [8,10]. In time-resolved IR experiments, we show that CO is lost in the same way in photochemical reactions at room temperature and that there is no interchange between terminal and bridging CO groups during the lifetime of the intermediate $MnRe(CO)_9$.

In a matrix isolation experiment, one can monitor not only the IR bands of metal carbonyl fragments but also the bands due to photoejected ^{12}CO and ^{13}CO groups. Thus, with a sample of $MnRe(CO)_{10}$, specifically labelled with ^{13}CO, we can use these bands to find out which end of the molecule has lost CO.

Thus, for a sample with 100% ^{13}CO enrichment on the Re end, i.e. $(^{12}CO)_5MnRe(^{13}CO)_5$, purely statistical ejection of CO on photolysis would give rise to bands of equal intensity due to free (i.e. uncoordinated) ^{12}CO and to free ^{13}CO. In addition, the bands due to bridging $\mu\text{-}^{12}CO$ and $\mu\text{-}^{13}CO$ would also be of equal intensity. However, if photoejection of CO occurred predominantly from one end of the molecule, say from the Mn end, one should observe only the peak due to free ^{12}CO but not the peak due to ^{13}CO. In the bridging region, one would only expect a band due to $\mu\text{-}^{13}CO$ since it is probable that, in this case, the bridging μ-CO would originate from the Re. Scrambling of the isotopic label to give

$MnRe(^{12}CO)_5(^{13}CO)_5$ will clearly lead to equal intensities for ^{12}CO and ^{13}CO bands in both free and bridging regions, irrespective of the mode of ejection.

Experimentally, 100% ^{13}CO enrichment at Re is difficult to achieve and we have worked with a less enriched sample which makes the spectra slightly more complicated to interpret. In the following experiments, a sample of $(^{12}CO)_5$-$MnRe(^{12}CO)_{5-x}(^{13}CO)_x$ specifically labelled with ^{13}CO on the Re end (70% enriched on Re) was prepared. This sample was then isotopically scrambled to give statistically enriched $MnRe(^{12}CO)_{10-x}(^{13}CO)_x$ – see below for experimental details. The use of these two samples has enabled us to deduce from which end of the molecule the CO was ejected.

Experimental

Apparatus

The matrix isolation apparatus [11] has been described previously. Matrices were prepared by slow deposition [12]. IR spectra were recorded on a Nicolet MX-3600 FT-IR interferometer and 1280 Data System with a 32K point data collection and transformed with 256K transform points (0.7 cm^{-1} resolution). The photolysis source was a Philips HPK 125W medium pressure Hg arc with Balzers narrow-band interference filters.

The Time-Resolved IR apparatus, based on a Lumonics Hyperex-440 excimer laser (operating on XeCl, 308 nm, 10 ns pulse) and a C.W. CO IR laser has been described previously [13]. The UV laser is flashed repeatedly, the transient IR signal monitored at a series of discrete IR wavelengths and an IR spectrum is constructed "point by point". The solution in the IR cell was changed after each flash of the UV laser.

Isotopic enrichment

In the discussion that follows we use the term *specifically labelled* to describe samples of $MnRe(CO)_{10}$ in which there are ^{13}CO groups on the Re end and no ^{13}CO groups on the Mn end; thus in $(^{12}CO)_5MnRe(^{12}CO)_{5-x}(^{13}CO)_x$ with 70% enrichment, $x =$ ca. 3, and there will be a statistical distribution of molecules with one ^{13}CO, two ^{13}CO etc. appropriate to the value of x. By contrast the term *isotopically scrambled* refers to a sample of $MnRe(CO)_{10}$ in which the ^{13}CO label is statistically distributed throughout the whole molecule.

Specifically labelled $(^{12}CO)_5MnRe(^{12}CO)_{5-x}(^{13}CO)_x$ was prepared by the procedure of Schmidt et al. [14] and the resulting material was ca. 70% specifically enriched on the Re end (i.e. $x =$ ca. 3). Isotopically scrambled $MnRe(^{12}CO)_{10-x}(^{13}CO)_x$ was obtained by heating the specifically labelled compound in n-heptane, in a sealed ampoule under vacuum, to 70 °C for 48 h (12 halflives for scrambling) and the reaction was monitored by IR spectroscopy; consistent ^{13}C NMR (toluene-d^8, −70 °C) were obtained (both samples: δ 179.7 Re–C_{ax}; δ 190.4 Re–C_{eq}; isotopically scrambled sample only: δ 215.2 Mn–C_{ax}; δ 220.1 Mn–C_{eq} [14]). Matrix gases (Messer Griesheim) were used without further purification; n-heptane (Aldrich HPLC Grade) was freshly distilled from CaH_2 under nitrogen before use.

Results and discussion

Matrix isolation

Photolysis of MnRe(CO)$_{10}$ in low temperature matrices leads to the ejection of free CO and the formation of MnRe(CO)$_9$ [5]. Figure 1 shows the free CO and the bridging CO regions of the IR spectra obtained after UV photolysis of (a) unenriched MnRe(CO)$_{10}$ (b) specifically labelled (^{12}CO)$_5$MnRe(^{12}CO)$_2$(^{13}CO)$_3$ and (c) isotopically scrambled MnRe(^{12}CO)$_7$(^{13}CO)$_3$ in argon matrices at 20 K. The wavenumbers of the principal bands are given in Table 1 and their relative intensities are shown in Table 2. These spectra illustrate several points:

(i) For the isotopically scrambled compound, Fig. 1c, the ^{12}CO/^{13}CO ratio both in the free CO and and in the bridging CO regions is the same, ca. 2, thus confirming the degree of ^{13}CO enrichment in the starting material [i.e., x = ca. 3, in (^{12}CO)$_5$-MnRe(^{12}CO)$_{5-x}$(^{13}CO)$_x$].

(ii) The appearance of only two bridging bands (^{12}CO and ^{13}CO) confirms the original experiments [5] which showed that there is only a single bridging CO group, since more complex isotopic patterns are expected for a bridging unit with two or more CO groups.

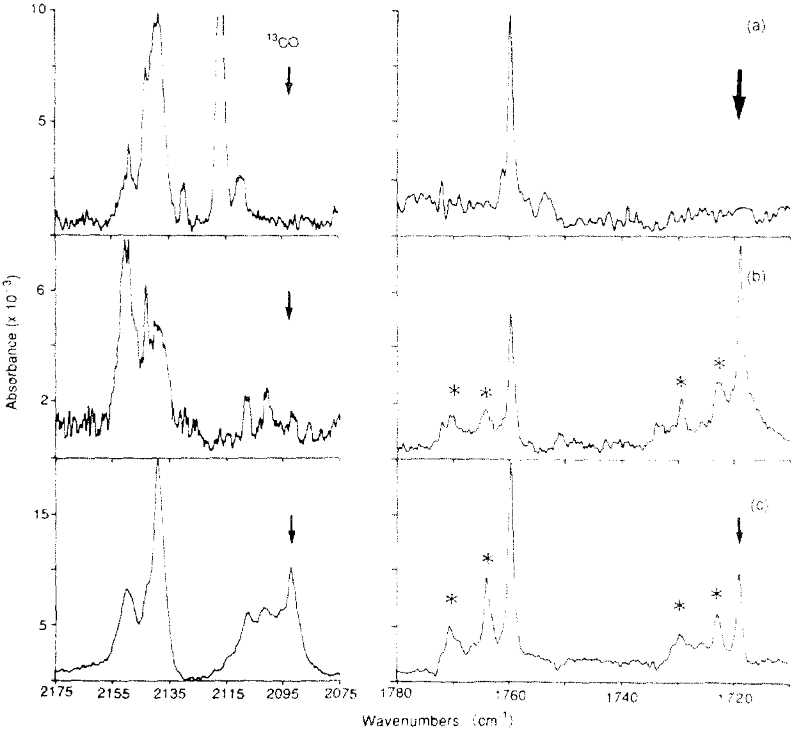


Fig. 1. Infrared spectra in the ν(CO) region, obtained after 290 nm photolysis (60 min) of (a) unenriched MnRe(CO)$_{10}$; the dotted line is due to MnRe(CO)$_{10}$ starting material, (b) specifically labelled (^{12}CO)$_5$MnRe(^{12}CO)$_{5-x}$(^{13}CO)$_x$ and (c) scrambled MnRe(^{12}CO)$_{10-x}$(^{13}CO)$_x$ in argon matrices at 20 K. The arrowed absorptions are due to ^{13}CO species. The askerisks mark matrix splittings. Broad band UV photolysis (several minutes) removes these site splittings [16].

Table 1

Wavenumbers (cm^{-1}) of the ^{12}CO and ^{13}CO ν(C–O) bands due to free CO and the bridging CO band of MnRe(CO)$_8$(μ-CO) in argon matrices at 20 K and in n-heptane solution at room temperature

	Free CO (Matrix, 20 K)	Bridging CO (Matrix, 20 K)	Bridging CO (n-heptane, 25 °C)
^{12}CO	2140.2 [a] 2137.8	1770.0 [a] 1763.9 [a] 1759.8	1765
^{13}CO	2094.3 [a] 2090.1	1729.3 [a] 1722.5 [a] 1718.1	1722

[a] Minor components due to matrix splitting.

(iii) For the specifically labelled sample, Fig. 1b, only free ^{12}CO is observed which implies that the CO is ejected only from the Mn end of the molecule.

(iv) The bridging bands from the specifically labelled sample, Fig. 1b, have relative intensities almost exactly as predicted for the CO bridge originating exclusively from the Re end of the molecule, see Table 2. It should be noted that only total photoejection from the Mn end of the molecule would give such good agreement, even partial ejection from the Re end would introduce substantial differences between the observed and calculated intensity ratios.

Time-resolved infrared spectroscopy

Time-resolved IR experiments have been carried out in n-heptane solution at room temperature; spectroscopic experiments to establish whether the photochemical behaviour of MnRe(CO)$_{10}$ is the same in solution as in low temperature matrices; and kinetic experiments to observe whether, in the short-lived intermediate MnRe(CO)$_9$, there is significant interchange between the bridging CO group and the terminal CO groups on the Mn end of the molecule.

Table 2

Ratio of peak absorbance (^{12}CO/^{13}CO) for the ν(C–O) bands listed in Table 1, obtained from specifically labelled and isotopically scrambled MnRe(CO)$_{10}$ in argon matrices at 20 K and in n-heptane solution at room temperature

	Free CO (Matrix, 20 K)	Bridging CO (Matrix, 20 K)	Bridging CO (n-heptane, 25 °C)	Bridging CO (calc.)
Specifically labelled [c]	[a]	0.65	0.69 [b]	0.66 ± 0.1 [d]
Isotopically scrambled [c]	2.01	1.92	2.22 [b]	–

[a] Very large, only the band due to ^{12}CO is observed. [b] Mean value over the first 200 μs (ca. 3 halflives). [c] See Experimental section for details of labelling. [d] The degree of enrichment, x, can be calculated from the ratio of the intensities of the ^{12}CO and ^{13}CO bridging bands observed for the isotopically scrambled sample. For MnRe(^{12}CO)$_{10-x}$(^{13}CO)$_x$, the ratio for bridged ^{12}CO/^{13}CO will be: ^{12}CO bridge/^{13}CO bridge $= (10-x)/x$. From the observed ratio for the isotopically scrambled complex, $x = 3.0 \pm 0.2$. Hence this value for x can be used to predict the ^{12}CO/^{13}CO bridging ratio for the specifically labelled complex, assuming that all the CO is ejected from the Mn end: ^{12}CO bridge/^{13}CO bridge $= (5-x)/x$.

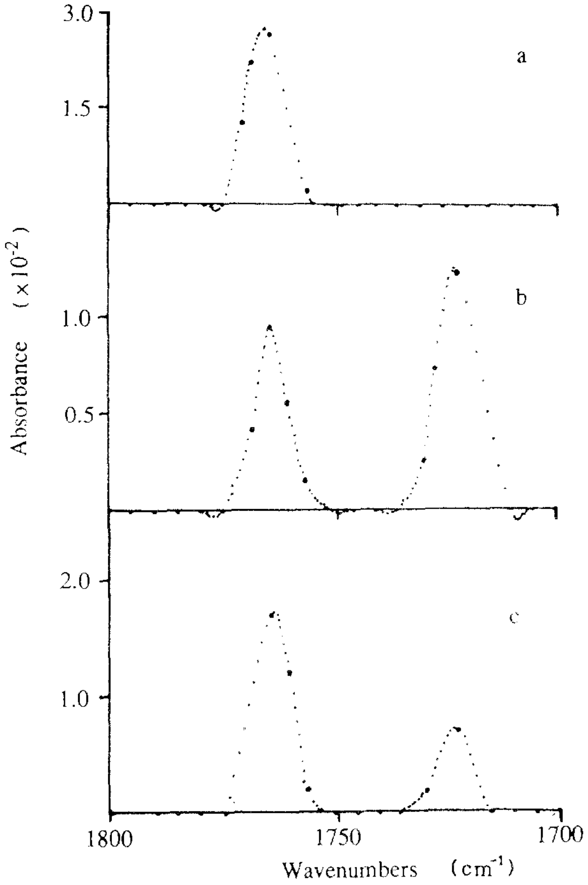


Fig. 2. Time-resolved IR spectra in the ν(CO) bridging region (1800–1700 cm^{-1}) obtained 10 μs after UV flash photolysis of (a) unenriched $MnRe(CO)_{10}$ (b) specifically labelled $(^{12}CO)_5MnRe(^{12}CO)_{5-x}(^{13}CO)_x$ and (c) scrambled $MnRe(^{12}CO)_{10-x}(^{13}CO)_x$ (ca. 5×10^{-4} *M*) in n-heptane solution at 25°C.

Figure 2 shows time-resolved IR spectra similar to the bridging CO region of the spectra in Fig. 1. (It was not possible to monitor the free CO in these time-resolved IR experiments.) The spectra correspond to a time, 10 μs after the UV laser flash photolysis, of (a) unenriched $MnRe(CO)_{10}$, (b) a specifically ^{13}CO labelled sample, identical to that used for the matrix experiments and (c) an isotopically scrambled sample with the same degree of ^{13}CO enrichment. The ratio of the intensities of the μ-^{12}CO and μ-^{13}CO bridging bands are given in Table 2. There is excellent agreement between the data for matrix and time-resolved experiments, confirming the photochemical mechanism is the same.

Decay kinetics of ^{13}CO labelled $MnRe(CO)_9$

Information about possible fluxional behaviour comes from the decay rates of the $MnRe(CO)_9$ transients in solution. The bridging μ-CO group always originates from the Re end of the molecule to give, in the case of the specifically labelled sample, a greater than statistical number of molecules with μ-^{13}CO groups. The fact that we observed different time-resolved IR spectra from the specifically labelled and the isotopically scrambled samples means that there cannot be very rapid interchange between the bridging CO group and the terminal CO groups on the Mn end of the molecule. However one could imagine that interchange might be occurring on a somewhat slower timescale which was still faster than the overall rate of decay of the $MnRe(CO)_9$, ca. 200 μs. In this case the interchange would affect the overall decay kinetics in the experiments with the specifically labelled sample. The decay of $MnRe(CO)_9$ in solution occurs via recombination with the photo-ejected CO [5], eqn. 3:

$$MnRe(CO)_9 + CO \rightarrow MnRe(CO)_{10} \qquad (3)$$

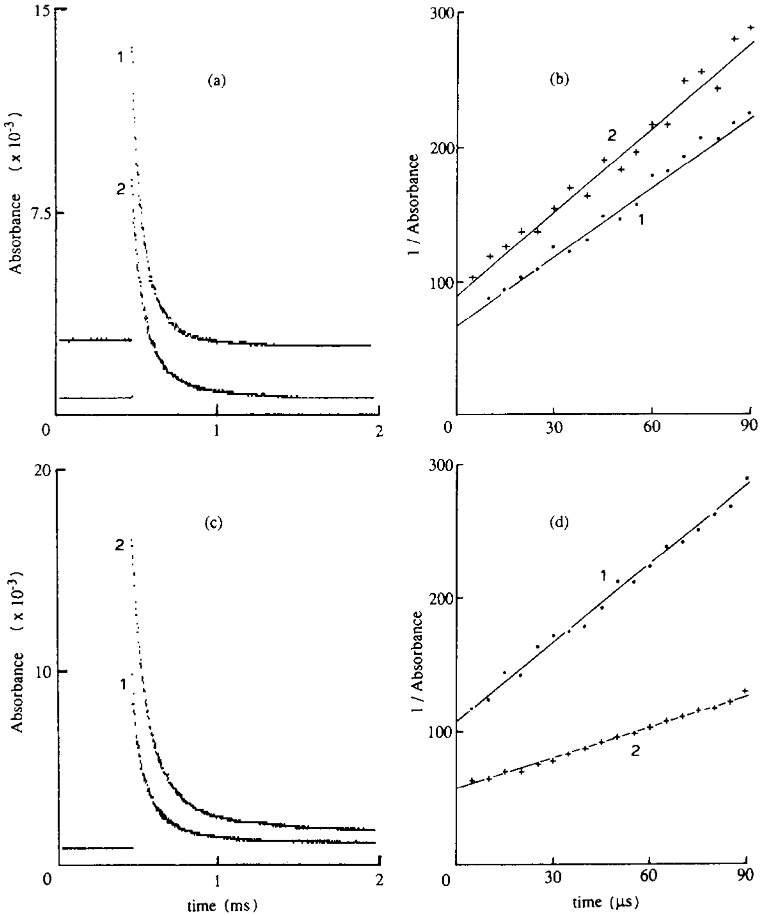


Fig. 3. Kinetic traces showing the decay of the ^{13}CO bridged species (1) and the ^{12}CO bridged species (2) generated by UV flash photolysis of (a) specifically labelled $(^{12}CO)_5MnRe(^{12}CO)_{5-x}(^{13}CO)_x$ and (c) scrambled $MnRe(^{12}CO)_{10-x}(^{12}CO)_x$. These traces were averaged over 8 laser shots, changing the solution in the cell between shots. (Note that the baselines in (a) are offset to enhance the clarity of the diagram.) Graphs of 1/absorbance vs. t for the ^{13}CO bridged species (1) and the ^{12}CO bridged species (2) for (b) specifically labelled $(^{12}CO)_5MnRe(^{12}CO)_{5-x}(^{13}CO)_x$ and (d) scrambled $MnRe(^{12}CO)_{10-x}(^{12}CO)_x$.

The decay should follow second-order kinetics and, assuming that the rate constant for reaction with CO is the same for μ-^{12}CO and μ-^{13}CO, we can derive rate equations for the two isotopic species, eq. 4.

$$-\mathrm{d}[\mu\text{-}12]/\mathrm{d}t = k[\mu\text{-}12][\mathrm{CO}] \text{ and } -\mathrm{d}[\mu\text{-}13] = k[\mu\text{-}13][\mathrm{CO}] \qquad (4)$$

where $[\mu\text{-}12]$ = concentration of $\mathrm{MnRe(CO)_8(\mu\text{-}^{12}CO)}$
$[\mu\text{-}13]$ = concentration of $\mathrm{MnRe(CO)_8(\mu\text{-}^{13}CO)}$
$[\mathrm{CO}]$ = concentration of free CO = $[\mu\text{-}12] + [\mu\text{-}13]$,
since all of the CO comes from photolysis of the starting material.

Figure 3 shows the decay of μ-12 and μ-13 for both scrambled (c) and specifically enriched (a) samples.

For the isotopically scrambled sample, $[\mu\text{-}12]/[\mu\text{-}13] = 2$, see Table 2. Thus, the integrated rate equations become:

$$1/[\mu\text{-}12]_t = 3kt/2 + 1/[\mu\text{-}12]_0 \qquad (5)$$

$$1/[\mu\text{-}13]_t = 3kt + 1/[\mu\text{-}13]_0 \qquad (6)$$

Thus plots of $1/[\mu\text{-}12]_t$ and $1/[\mu\text{-}13]_t$ vs. t should give straight lines with gradients of $3k/2$ and $3k$ and with intercepts $1/[\mu\text{-}12]_0$ and $1/[\mu\text{-}13]_0$ respectively. The observed ratios both of gradients and of intercepts are 2/1 as predicted, see Fig. 3d.

For the specifically labelled species, $[\mu\text{-}12]/[\mu\text{-}13] = 2/3$ and the appropriate equations are:

$$1/[\mu\text{-}12]_t = 5kt/2 + 1/[\mu\text{-}12]_0 \qquad (7)$$

$$1/[\mu\text{-}13]_t = 5kt/3 + 1/[\mu\text{-}13]_0 \qquad (8)$$

Equations 7 and 8 will only apply if there is no interchange between bridging and terminal CO groups. Interchange would scramble the isotopic label and cause a progressive acceleration in the rate of decay of μ-^{13}CO relative to that of μ-^{12}CO. Figure 3b shows plots of $1/[\mu\text{-}12]_t$ and $1/[\mu\text{-}13]_t$ vs. t which give straight lines with gradients and intercepts both in the ratio 2/3, exactly in accordance with the equations, thus confirming that interchange does not occur. It should be noted that the plots are of 1/absorbance vs. t and we have assumed that the extinction coefficient is the same for both bridged species.

Conclusions

These experiments provide the first definite evidence that UV photolysis of a heterobimetallic carbonyl compound can lead to loss of CO from only one end of the molecule. We have shown that photolysis of $\mathrm{MnRe(CO)_{10}}$ both in inert gas matrices at 20 K and in solution at room temperature leads to the formation of $\mathrm{Mn(CO)_4(\mu\text{-}CO)Re(CO)_4}$ where the CO has been ejected from the Mn end of the $\mathrm{MnRe(CO)_{10}}$ molecule and the bridging CO group has come from the Re end of the molecule. Once $\mathrm{Mn(CO)_4(\mu\text{-}CO)Re(CO)_4}$ is formed, there is no interchange of the bridging CO group and the terminal CO groups on the Mn end during the lifetime of the intermediate in solution at 25 °C.

The key to the success of these experiments has been the combination of stereospecific ^{13}CO labelling and IR spectroscopy. Such an approach has previously been applied to matrix isolation experiments [15] but this is the first application to time-resolved IR spectroscopy in solution. The results suggest that similar experiments with suitably labelled compounds will be able to provide valuable information about the mechanisms of more complicated photochemical reactions.

Acknowledgements

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