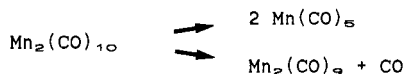


Intermediates in organometallic photochemistry— dinuclear complexes

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Abstract: The photochemistry of dinuclear compounds such as $Mn_2(CO)_{10}$ and $[CpFe(CO)_2]_2$ is now generally agreed to proceed via two pathways, eg:



The evidence for such pathways derives partly from the study of overall photochemical behaviour as a function of wavelength, solvent and reacting ligand, and partly from flash photolysis studies with UV/vis detection. However, the definitive identification of the intermediates, and the unravelling of the reaction mechanism, have relied on more unusual techniques, such as Matrix Isolation and Fast Time-Resolved Infrared spectroscopy. This article shows how these various techniques contribute to an understanding of the photochemistry of a range of dinuclear species, using as examples: $[CpPt(CO)]_2$, $[CpFe(CO)_2]_2$ and $MnRe(CO)_{10}$. We show how the behaviour of these compounds leads to more general conclusions about the photochemistry of dinuclear organometallic compounds.

INTRODUCTION

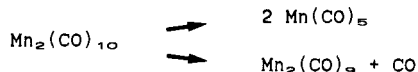
Organometallic photochemistry is important in both synthesis and catalysis as well as being fascinating in its own right [1]. Understanding the mechanisms of these reactions is crucial to improving yields and devising new routes in preparative chemistry. Recently, there has been particular interest in the photochemical behaviour of dinuclear transition metal species containing CO and, often, cyclopentadienyl groups. There has been an excellent review of this area by Meyer and Caspar [2]. We have no intention of repeating their article here but instead we concentrate on the application of novel techniques for answering particular mechanistic problems.

There are relatively few compounds which contain only two transition metal atoms (the same or different) and CO groups (bridged or unbridged) [3]. However, there is a much larger number of dinuclear compounds which contain both CO and the cyclopentadienyl group (C_5H_5 or Cp) - or a substituted cyclopentadienyl group such as the pentamethyl species (C_5Me_5 or Cp') - acting as a η^5 ligand [4]. The vast majority of these complexes are 34 electron systems. There is a wide variety of structures since there is no difference in total electron count between terminal and bridging CO groups and the energy difference between bridged and unbridged isomers is usually small [3]. Only a few of these compounds have been the subject of photochemical studies and in Table 1 we list the more important ones, omitting charged species such as $[Cr_2(CO)_{10}]^-$.

TABLE 1 - Some Dinuclear Carbonyl and Cyclopentadienyl compounds, which have been the subject of detailed photochemical studies

Carbonyl Compounds			
$M_2(CO)_{10}$ (Mn, Re)	$Fe_2(CO)_9$	$Co_2(CO)_8$	
Cyclopentadienyl Compounds			
$[CpM(CO)_3]_2$ (Cr, Mo, W)	$[CpM(CO)_2]_2$ (Cr, Mo, W)	$Cp_2M_2(CO)_3$ (Co, Rh)	$[CpM(CO)]_2$ (Ni, Pt)
	$[CpM(CO)_2]_2$ (M=Fe, Ru)		
Heteronuclear Compounds			
$MnRe(CO)_{10}$ $MnCo(CO)_9$	$CpMo(CO)_3Mn(CO)_5$	$Mn(CO)_5FeCp(CO)_2$	$CpFe(CO)_2Co(CO)_4$

It was long thought that, even in apparently complex reactions, the primary step in the photochemistry of these compounds involved the breaking of the metal-metal bond to give 17-electron radicals [1]. More recently, principally following the pioneering work of Meyer and colleagues [2], it has been realised that there is usually another important path involving loss of CO and the formation of an intermediate which retains the dinuclear structure. Thus, for example, the two paths for $Mn_2(CO)_{10}$ are:



Therefore, to understand the photochemistry of a dinuclear species, it is necessary to know: (i) what are the primary photoproducts and their structure (ii) how the generation of these photoproducts depends on photolysis wavelength and (iii) how the various photoproducts react with themselves, with each other and with other species present in solution. We now describe some of the techniques available for unravelling these problems.

EXPERIMENTAL METHODS

In many cases, synthetic photochemical reactions such as cross-over experiments can reveal probable reaction mechanisms. For instance, the production of the mixed metal dimer $MnRe(CO)_{10}$ on photolysis of a mixture of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ suggests that the five-coordinate mononuclear species, $Mn(CO)_5$ and $Re(CO)_5$, are being generated by homolysis of the metal-metal bonds [5]. In this section, however, we wish to concentrate on more specific techniques aimed at the direct detection of intermediates.

Matrix isolation (MI)

Matrix Isolation has become a firmly established method for the determination of the structure of intermediates in organometallic photochemistry [6]. In this technique an unstable intermediate is generated by photolysis of a stable parent molecule isolated in a low-temperature matrix. These intermediates are usually identified by IR spectroscopy but UV/Vis, MCD, Raman and ESR spectra can often also be recorded. Because the solid matrix encases the photolysed molecule, large fragments cannot separate and therefore recombine. This "cage effect" means that photolysis of a dinuclear metal compound very rarely provides any evidence for homolysis of the metal-metal bond; for instance, photolysis of $Mn_2(CO)_{10}$ in a matrix yields no detectable $Mn(CO)_5$, although $Mn(CO)_5$ is almost certainly being generated transiently.

There have been several variations on the basic matrix isolation technique, each with distinct advantages and disadvantages. When *Frozen Rare Gases* [6a,6c] are used as matrix materials, there are no interfering absorptions from the matrix itself over the whole spectral range. IR bands of trapped species are extremely sharp (although sometimes split into several lines by solid state effects). This sharpness is important since structure determination, particularly establishing the number of bridging CO groups in dinuclear compounds, requires the use of isotopes (eg ^{13}CO) and resolving closely spaced absorption bands. In order to form rigid matrices from gases such as Ar, the apparatus must be capable of reaching very low temperatures. This has the benefit that extremely unstable species, not detectable at higher temperatures, can often be identified. The principal limitation of rare gas matrices is that the molecules under study must be volatile since the matrix is deposited from the gas phase onto a cold spectroscopic window. This limitation is less restrictive than might be imagined since even molecules as involatile as $Fe_2(CO)_9$ [7] and $Fe_3(CO)_{12}$ [8] have been studied in this way. A more serious problem, however, is that the matrix material sublimates at extremely low temperatures (ie 40K for Ar) and hence it is not possible to warm the matrix and follow reactions of intermediates up to room temperature.

The other common variation of matrix isolation involves the use of *Frozen Hydrocarbon Glasses*. This method has been exploited particularly by Wrighton and colleagues [6b]. It has the advantages that the cold matrix is produced by freezing a solution, initially at room temperature, thus avoiding problems of volatility. Similarly, the thermal reactions of trapped intermediates can be followed easily as the glass melts and warms back to room temperature. Another feature is that occasionally a molecule (eg $Ru_3(CO)_{12}$ [9]) can be photolysed to yield detectable intermediates in a glass but not in a frozen gas matrix, presumably because the glasses are rather softer than frozen gases. The main disadvantages of glasses are that the spectral range is limited by absorptions from the glass material and that IR bands are much broader than in rare gas matrices making isotopic work very difficult. Some of the advantages of rare gas and glass matrices have been combined by the use of *Cast Polymer Films* [6c].

It is sometimes possible to circumvent the limitations of the cage effect in matrix isolation. Thus, if photolysis is carried out in a solid CO matrix, the route involving loss of CO from a carbonyl compound can usually be suppressed. Under these conditions fission of the metal-metal bond may be detectable in the matrix even if the quantum yield for the process is very low. For instance, UV photolysis of $\text{Co}_2(\text{CO})_8$ in Ar matrices generates $\text{Co}_2(\text{CO})_7$ [10] but, in a CO matrix, $\text{Co}(\text{CO})_4$ is detected [11]. Alternatively, important intermediates can be generated by totally different routes which do not involve dinuclear compounds at all. For example, $\text{Mn}(\text{CO})_5$ can be generated from $\text{HMn}(\text{CO})_5$, isolated in a CO matrix, even though it is not formed by direct photolysis of $\text{Mn}_2(\text{CO})_{10}$. Photolysis of $\text{HMn}(\text{CO})_5$ generates both $\text{HMn}(\text{CO})_4$ and $\text{Mn}(\text{CO})_5$ but, in the CO matrix, the $\text{HMn}(\text{CO})_4$ recombines with CO while the H atom reacts with the CO to give HCO, and hence the only species observed is $\text{Mn}(\text{CO})_5$ [12]. A quite different route [13] was used to identify $\text{Re}(\text{CO})_5$ which was first obtained by cocondensation of Re atoms and CO at 10K.

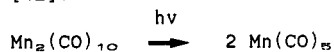
It will become clear from some of the examples given below that one of the most important contributions of matrix isolation involves the use of polarised light. Crucial features of structure and photochemistry are revealed by using plane polarized light both for UV photolysis and also for IR and UV/vis spectroscopy. The experimental details have been described fully elsewhere [14]. Finally, there is the obvious point that matrix isolation is excellent for determining structure but almost useless, except in melted glasses, for providing kinetic information.

Liquid rare gas solvents

In some circumstances photochemistry and IR spectroscopy in low-temperature solvents, particularly liquid rare gases, can be used to identify key intermediates in complex reactions. Most applications of this technique have involved mononuclear species, in particular unstable N_2 and H_2 complexes [15]. Many dinuclear complexes are too insoluble for the technique to be useful but liquid Xe played an important role in unravelling the photochemistry of $\text{Re}_2(\text{CO})_{10}$ [16].

Flash photolysis with UV-visible detection

This technique has been crucial for kinetic measurements on timescales from msec to psec [2]. The limitation, however, is that there is little variation between the spectra of different organometallic intermediates. Most absorptions tend to be broad and featureless yielding little structural information. Matrix isolation often provides UV/vis data for intermediates, the structure of which can be established by IR spectroscopy. These matrix data can then often be used to confirm the identity of species detected by UV/vis spectroscopy in solution. For instance, flash photolysis of $\text{Mn}_2(\text{CO})_{10}$ yields two transient absorption bands [17], one at 800nm, which corresponds to the band at 798nm assigned to matrix-isolated $\text{Mn}(\text{CO})_5$ [12]:



Flash photolysis with IR detection – fast time-resolved IR spectroscopy (TRIR)

Sufficient has already been said about the role of IR spectroscopy to suggest that the IR spectra of short-lived intermediates in room temperature solution would provide valuable information about both structure and kinetics. Thus, whereas UV/vis data from matrix experiments aid the general interpretation of conventional flash photolysis experiments, it is IR matrix data which underpin the relatively new technique of *Fast Time-Resolved IR Spectroscopy* [18]. Several groups have become active in the application of TRIR to organometallic intermediates both in solution and in the gas phase [15,19]. A number of important species have been identified positively in this way. The apparatus used at Nottingham has been fully described elsewhere [20]. Briefly, it consists of a UV excimer laser to initiate reactions and a cw CO IR laser with fast MCT detection to observe the intermediates. One limitation of the technique is that until now only strong IR absorbers (eg $\nu(\text{CO})$, $\nu(\text{NO})$ and $\nu(\text{NN})$) can be detected but fortunately these are the most important chromophores for structure determination. A second limitation is the timescale. Detection techniques in the IR are limited to a time resolution of ca. 100nsec (but see later) and it is clear from experiments with UV/vis detection that important events can occur on much shorter timescales.

In the next section, we give three examples, all involving the photochemistry of dinuclear compounds, concentrating on intermediates which are formed by loss of CO. These examples illustrate the power of matrix isolation and time-resolved IR to answer specific mechanistic questions about the reactions of such compounds. We follow the examples with some brief comments about the photolysis of some of the other compounds listed in Table 1 and conclude with some general remarks on the mechanism of such reactions.

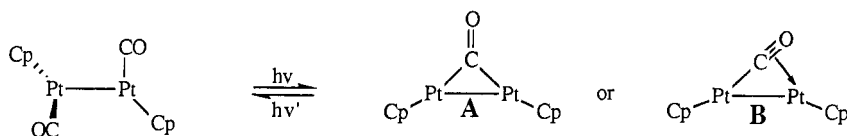
THREE EXAMPLES

I. An application of matrix isolation

What is the structure of the reaction intermediate $Cp_2Pt_2(CO)$?

Since the first synthesis of the complexes $[CpM(CO)]_2$ ($M = Ni, Pt$) twenty five years ago [21], their photochemistry has been relatively neglected. The two compounds have different structures [22,23]; the Ni complex has two bridging CO's whereas both $[CpPt(CO)]_2$, and the recently synthesised $[Cp'Pt(CO)]_2$, have only terminal CO groups, with the relative orientation of the two Pt-CO bonds reminiscent of the two O-H bonds in H_2O_2 . Photolysis of the Ni complex in cast PVC films [24] suggests dissociative loss of one of the bridging CO groups to form $CpNi(u-CO)NiCp$. The analogous Pt species, $CpPt(u-CO)PtCp$, has been proposed as an intermediate in the thermal reactions of $[Cp'Pt(CO)]_2$ with acetylenes [23].

The complex $[Cp'Pt(CO)]_2$ has no bands in the $\nu(CO)$ bridging region. On photolysis in an Ar matrix, free CO is generated, a strong band appears in the bridging $\nu(CO)$ region and the matrix turns bright red [25]. Irradiation of this coloured matrix with visible light causes the photoproduct to recombine with the photo-ejected CO and $[Cp'Pt(CO)]_2$ is regenerated. Repeating the experiment with $[Cp'Pt(CO)]_2$ 35% enriched with ^{13}CO leads to only two bridging $\nu(CO)$ bands. This isotopic experiment proves that there is only one CO group in the photoproduct, which is, therefore, confidently assigned as $Cp'Pt(u-CO)PtCp'$. However one cannot, at this stage, distinguish between structures A and B.



The nature of the bridging CO group can be determined by photochemistry and spectroscopy with plane polarised light. These experiments prove that the CO bond is perpendicular to the Pt-Pt axis (ie. A). Thus, the structure of $CpPt(u-CO)PtCp$ is in contrast to that of $Mn_2(CO)_9$ where similar experiments with polarised photolysis suggest that the bridging CO group is "non-classical" lying at 45° to the Mn-Mn bond [26a].



$CpPt(u-CO)PtCp$ has also been detected by TRIR and it is remarkably unreactive with a lifetime >20 msec in solution at room temperature [25].

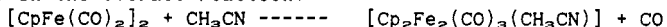
It is also important to realise what these experiments have not shown. The primary photochemical act is presumably the ejection of a terminal CO from $[Cp'Pt(CO)]_2$. What is not clear is whether the transformation of the remaining terminal CO to the bridging position is concerted with the CO loss, or whether there is a primary species $[Cp(CO)PtPtCp]$, which is too unstable to be trapped even at 15K and which is too short-lived for the timescale of the TRIR experiment. This problem might be resolved by performing matrix experiments at very low temperatures, $< 4K$, or by improvements in time-resolution of TRIR. It should be noted that such problems are often a feature of attempts to detect very unstable fragments.

II. An application of time-resolved IR

What is the role of $Cp_2Fe_2(CO)_3$ in the solution reactions of $[CpFe(CO)]_2$?

In hydrocarbon solution, $[CpFe(CO)]_2$ exists as an equilibrium mixture of two isomeric forms, $Cp(CO)Fe(u-CO)_2Fe(CO)Cp$, with the two Cp groups arranged either trans or cis to each other. There is a negligible concentration of the unbridged isomer. Extensive kinetic flash photolysis studies on $[CpFe(CO)]_2$ employing UV/vis detection showed that two species were formed - $CpFe(CO)_2$ and a CO-loss product with a visible absorption band centred at 510 nm. However, as is usual in such experiments, the UV/vis data could not supply any structural information [2]. Matrix isolation experiments, similar to those described above and including the use of ^{13}CO enrichment [27, 28], showed that photolysis of $[CpFe(CO)]_2$ leads to the formation of $CpFe(u-CO)_3FeCp$ with three equivalent bridging CO groups. Moreover, the product has a visible band at 510 nm, coincident with the absorption observed by flash photolysis. The analogous compound $Cp'Fe(u-CO)_3FeCp'$, which is sufficiently stable to be isolated, has a paramagnetic ground state and its structure has been confirmed by X-ray crystallography [29].

TRIR of $[\text{CpFe}(\text{CO})_2]_2$ in cyclohexane solution produces clear IR evidence for the formation of both $\text{CpFe}(\text{CO})_2$ ($\nu(\text{CO})$ 2004 and 1938 cm^{-1}) and $\text{CpFe}(\text{u-CO})_3\text{FeCp}$ with an IR band at 1823 cm^{-1} , shifted only 10 cm^{-1} from the matrix band [30]. Once the spectra had been determined and the kinetic behaviour of the two photoproducts established, it was possible to monitor the behaviour of these species in the presence of potential reactants other than CO. For instance, in the overall reaction:



TRIR shows [31] that it is $\text{CpFe}(\text{u-CO})_3\text{FeCp}$ which reacts with CH_3CN . $\text{CpFe}(\text{CO})_2$ which is also generated by the UV flash, takes no part in the reaction (see Fig. 1). A similar mechanism applies to the reaction of $[\text{CpFe}(\text{CO})_2]_2$ with phosphines and detailed kinetic studies using TRIR [31] allow the activation parameters for the reactions of $\text{CpFe}(\text{u-CO})_3\text{FeCp}$ to be measured - see Table 2.

Fig. 1. Time-resolved IR spectra obtained after photolysis with a UV flash lamp of $[\text{CpFe}(\text{CO})_2]_2$ (6×10^{-4} M) and MeCN (6×10^{-3} M) in cyclohexane solution at 25°C. The first three spectra correspond to the duration of the firing of the flash lamp and subsequent spectra are shown at intervals of 10 μ s.

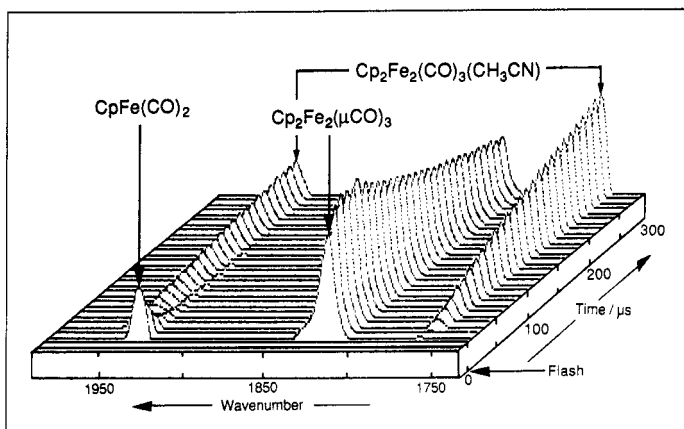


Table 2 - Rate constants and activation parameters for the reaction of $\text{CpFe}(\text{u-CO})_3\text{FeCp}$ with MeCN, PBU^n_3 and PPh_3 in cyclohexane solution

Ligand	$10^{-5} k/\text{s}^{-1}\text{dm}^3\text{mol}^{-1}$	$\Delta H^\ddagger/\text{kJmol}^{-1}$	$\Delta S^\ddagger/\text{Jmol}^{-1}\text{K}^{-1}$
CH_3CN	7.6 (24.0°C)	24.4	-50.0
PBU^n_3	1.25(24.6)	28.1	-52.3
PPh_3	2.1 (24.7)	23.3	-64.8

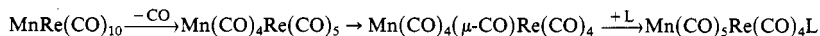
(The rate constant for PPh_3 agrees well with the value obtained by UV/flash photolysis-see ref. 2)

The differences between these ligands can be rationalised on steric grounds by taking account of the cone angles of the phosphines. However, the fact that there is any activation barrier at all reflects almost certainly the change in spin between the triplet ground state of $\text{CpFe}(\text{u-CO})_3\text{FeCp}$ and the singlet ground state of the products. There are still two unanswered questions about $\text{CpFe}(\text{u-CO})_3\text{FeCp}$; is it really a primary photoproduct and what precisely is the mechanism of the reaction with phosphines and CH_3CN ?

III.A combined application of matrix isolation and time-resolved IR

Heteronuclear compounds; where does the CO come from?

Both Matrix Isolation and TRIR show that $\text{Mn}_2(\text{CO})_{10}$ has a CO bridge [26,19a,32] but that $\text{Re}_2(\text{CO})_{10}$ is unbridged [16,33] (see below). The same techniques show that $\text{MnRe}(\text{CO})_{10}$ is bridged [34], as in the rather unusual reaction mechanism postulated by Sonnenberger and Atwood to explain the thermal reactions of $\text{MnRe}(\text{CO})_{10}$ [35].



The key feature of this mechanism is that CO is lost specifically from the Mn end of the molecule. Wrighton has pointed out in several places that one cannot usually use ^{13}C labelling methods to determine from which end of a molecule CO is lost, because fluxional processes scramble the isotopic label long before the experiment can begin. However the isotopic labels in $(^{12}\text{CO})_5\text{MnRe}(^{13}\text{CO})_5$ do not scramble at room temperature [36] and so this molecule provided an excellent means of testing the postulated mechanism.

Matrix photolysis of the specifically ^{13}C enriched species $(^{12}\text{CO})_5\text{MnRe}(^{12}\text{CO})_5\text{-x}(^{13}\text{CO})_x$ with 70% enrichment (ie $x = \text{ca.}3$) produces only ^{12}C in the matrix, showing that the CO is only ejected from the Mn end of the molecule. Moreover the $\nu(\text{CO})$ bands arising from the (u- ^{12}C O)

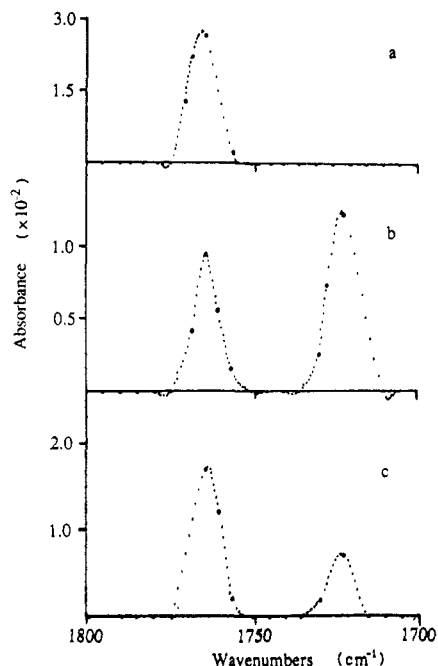


Fig. 2. Time-resolved IR spectra in the $\nu(\text{CO})$ bridging region obtained 10 μs after UV flash photolysis with an excimer laser of (a) unenriched $\text{MnRe}(\text{CO})_{10}$, (b) specifically labelled $(^{12}\text{CO})_9\text{MnRe}(^{12}\text{CO})_{5-x}(^{13}\text{CO})_x$ and (c) scrambled $\text{MnRe}(^{12}\text{CO})_{10-x}(^{13}\text{CO})_x$ (ca. 5×10^{-4} M) in *n*-heptane solution at 25°C. (From ref. [37] with permission)

and ($u\text{-}^{13}\text{CO}$) bridging groups in the photoproduct have relative intensities almost exactly as predicted for the CO bridge originating exclusively from the Re end of the molecule [37]. Experiments with deliberately scrambled isotopic labels produce molecular CO and ($u\text{-CO}$) IR bands with intensity ratios consistent with this mechanism.

TRIR experiments at room temperature on $\text{MnRe}(\text{CO})_{10}$, with both specific and random ^{13}C enrichment, give results identical to those observed in matrices. These results show that the reaction intermediate, $\text{MnRe}(\text{CO})_9$, is not fluxional on the timescale of the TRIR measurements (see Fig. 2). This is particularly surprising as intermediates are intuitively expected to be highly fluxional at room temperature. These photochemical experiments are, therefore, a striking confirmation of the Sonnenberger/Atwood reaction mechanism.

DISCUSSION

The overall conclusion from all three of our examples is that these spectroscopic techniques can and do provide answers to real questions posed by solution photochemists. Similar questions have been answered by the studies on most of the compounds listed in Table 1. Together, the results of these experiments allow generalizations to be made about the photochemistry of dinuclear compounds while at the same time raising some interesting points as to the nature of primary photoproducts. Perhaps the most interesting point relates to bridging CO groups.

Bridging CO groups

It should be clear from our examples that IR spectroscopy is a reliable and simple way of detecting the presence of bridging CO groups in reaction intermediates either in matrices or in solution. In nearly all of the dinuclear systems examined so far, loss of CO results in a change in the number of bridging CO groups, always involving an odd number of groups, usually plus or minus one. This effect can be rationalized quite simply. In most cases, there is either explicit or implicit evidence that photolysis leads to ejection of a terminal CO group. Loss of such a group will lead to a 32 electron system, where the two metal centres have, formally at least, different electron counts. Subsequent conversion of a bridging CO group to a terminal position (or vice versa) can result in an intermediate with the same electron count on both centres.

A recent review [38], based on X-ray crystal structures, summarizes the variety of known bridging CO groups in stable compounds, ranging from the almost terminal to bent non-symmetric semi-bridging and from symmetric bridging to linear semi-bridging. Given this range of possible structures, it is clear that IR spectroscopy, even with polarisation studies, is unlikely to be very precise about the nature of the bridging groups in a particular intermediate, except in very favourable cases such as $\text{Mn}_2(\text{CO})_9$ or $\text{CpPt}(u\text{-CO})\text{PtCp}$ (see above). Furthermore, the energy difference between bridged and unbridged structures of these unstable species can sometimes be extremely small. In the case of matrix isolated $\text{Fe}_2(\text{CO})_8$ both bridged and unbridged isomers were observed and the bridged could be converted to the unbridged merely by warming the matrix from 15K to 30K [7].

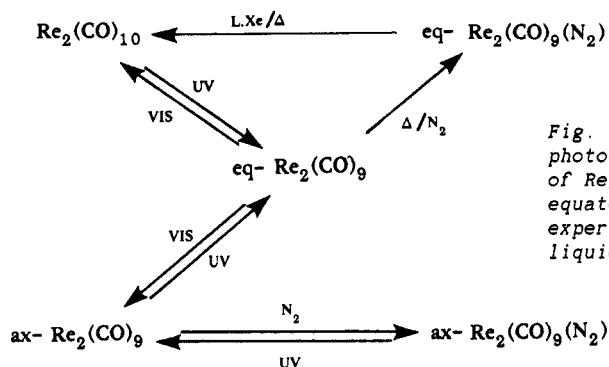


Fig. 3. Schematic representation of the photochemistry of $\text{Re}_2(\text{CO})_{10}$ involving two forms of $\text{Re}_2(\text{CO})_9$ with vacant sites in the axial and equatorial positions. The scheme is based on experiments in low-temperature matrices and liquid Xe [16].

The major exception is $\text{Re}_2(\text{CO})_{10}$ [16,33,34,39]. Both $\text{Re}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_9$ are unbridged, presumably because the Re-Re bond is too long to support a CO bridge. The overall reaction scheme for $\text{Re}_2(\text{CO})_{10}$ is, in fact, surprisingly complicated, see Fig. 3, with two interconvertible isomers of $\text{Re}_2(\text{CO})_9$. The existence of these isomers has been rationalized [16] on the basis of an isolobal analogy with the isomers of $\text{CH}_3\text{Re}(\text{CO})_4$.

It is probable that many dinuclear intermediates can occur in isomeric forms and it is likely that detailed studies of the wavelength dependence of photolysis of matrix isolated dinuclear compounds will reveal further structural possibilities for intermediates.

Primary photoproducts

As stated earlier the fact that one sees an unstable species in a matrix does not prove that this is a primary photoproduct. If an intermediate is detected in solution, the certainty with which it can be identified as a primary photoproduct depends on the timescale of the measurement. In the photolysis of $\text{Mn}_2(\text{CO})_{10}$, it is highly probable that $\text{Mn}_2(\text{CO})_9$ is a primary product since its UV/vis absorption appears within picoseconds of the UV flash [17]. Of course this UV/vis band is rather broad and it is not possible to say whether the CO bridge in $\text{Mn}_2(\text{CO})_9$ is formed on this timescale. Such information would be provided by picosecond TRIR. In an elegant experiment, Hochstrasser and colleagues [40] have photolysed carboxymyoglobin and monitored the $\nu(\text{CO})$ IR band on ca. 50 psec timescale. Unfortunately, the experiment requires extremely sophisticated optical mixing techniques to shift the IR absorptions into the visible region and the timescale is still slightly too long for the definitive identification of primary photoproducts. Nevertheless, the prospect of performing similar picosecond TRIR experiments on organometallics is most exciting. Such experiments might answer mechanistic questions which are currently too complex to tackle. For example, in a dinuclear intermediate, does the initial attack by an incoming ligand occur at a bridging or terminal position?

CONCLUSIONS

The study of organometallic intermediates is at an exciting stage. New spectroscopic techniques, particularly time-resolved IR spectroscopy, are unravelling mechanistic questions which have remained unanswered for many years. Of course, as these experiments probe the mechanism of reactions in greater detail, a whole set of new questions is being raised. Fortunately techniques continue to improve and it is clear that over the next few years there will be a substantial increase in our understanding of mechanistic organometallic chemistry.

Acknowledgements

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For details about other compounds in Table 1 see the following references:

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- 43 For details of $\text{CpFe}(\text{CO})_2\text{Co}(\text{CO})_4$, see S. C. Fletcher, M. Poliakoff and J. J. Turner, J. Organomet. Chem., **268**, 259 (1984). Note that for this compound there is evidence that photolysis in a CO matrix generates the ionic species $[\text{CpFe}(\text{CO})_3]^+$ and $[\text{Co}(\text{CO})_4]^-$. If this is true it is extraordinary since heterophotolysis involves the primary production of neutral species followed by reaction with ligands to produce the ions [44].
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