Manganese carbonyl compounds reveal ultra-fast metal-solvent interactions

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ABSTRACT Herein we exemplify that time-resolved multiple-probe spectroscopy (TRMPS) with infra-red detection can be used to observe and quantify the dynamic processes occurring during the solvation of a catalytically competent manganese(I) carbonyl compound. TRMPS has been used to demonstrate that a manganese(I) 2-phenylpyridyl (ppy) complex, [Mn(ppy)(CO)4], undergoes photochemically induced loss of a carbonyl ligand on a sub-picosecond timescale to give solvent (S) complexes of the type, *fac*-[Mn(ppy)(S)(CO)3] (S = *n*-C7H16, CH2Cl2, NCMe, C6H5CH3, THF, 1,4-dioxane, *n*-Bu2O and DMSO). An excited state, assigned as 3[Mn(ppy)(CO)4], with a lifetime, , of *ca*. 5 ps. is also formed as a minor photoproduct. The vibrational modes of the carbonyl ligands in *fac*-[Mn(ppy)(S)(CO)3] are diagnostic of the nature of the coordinated solvent and allow for the dynamics of solvation within the coordination of the metal to be observed. For example, in the case of THF, initial interactions with the metal occur through a C-H -interaction, assigned based on the similarity to the bands observed for the related heptane metal complex. Isomerization to the thermodynamically preferred *O*-binding mode was observed,  *ca*. 18 ps, with similar behavior evident in 1,4-dioxane and nBu2O. The lifetime for the isomerization shows a correlation with the number of C-H bonds in the solvent. In 1,4-dioxane, there is no evidence for the initial formation of an *O*-bound complex which indicates that the solvent binding is not stochastic in nature and is likely determined by the topology of the first solvation shell of the metal complex. The insight into these ultra-fast metal-solvent interactions is enabled by the dominant photoprocess, CO-dissociation, being rapid (< 1ps). Which, taken together with prompt vibrational cooling, enables the subtle interplay between metal and solvent during the solvation event to be characterized and quantified.

Introduction

One of the principal advantages of homogenous transition metal catalysts is the ability to modify activity and selectivity through the development of well-defined structure/activity relationships.1 Such relationships allow for judicious choice of catalyst system with enhanced activity (*e.g.* increased turn-over number and turnover frequency, selectivity). This rationale has led to the development of a wide range of parameters which may be used to quantify the steric and electronic effects imparted by a given ligand and their interplay with the intrinsic properties of the metal (oxidation state, period and group number).2-13 This parameterization-led approach has successfully been employed to identify the optimum metal/ligand combination for a given catalytic reaction.14 However, one additional facet of a homogenous reaction is the solvent, which is frequently the greatest component (in term of both weight and molar equivalence) present in the mixture. There are many methods used to parameterize solvents which focus on factors such as bulk polarity and ability to engage in hydrogen bonding.15 Such methods are highly informative, providing insight into solvent/solute interactions from a macroscopic perspective and have been used to rationalize several metal-catalyzed reactions. In contrast, less attention has been paid to understanding the direct interactions between metals and solvents.15

Species containing such interactions, frequently referred to as *solvent complexes*, play a key role in a host of transition metal-catalyzed reactions. To permit substrate coordination, saturated pre-catalysts are required to undergo ligand loss and it is statistically unlikely that an unsaturated metal complex will coordinate directly to the substrate without intermediary solvent complexes being formed. In addition, any dissociative steps (*e.g.* product liberation) within a given mechanistic cycle will also necessitate coordination of the solvent to any formal vacant coordination sites. It is generally perceived that the solvent molecules within such species are weakly bound and have been referred to as “token” ligands.16 However, even alkanes may form well-defined metal complexes in which coordination to the metal through a C-H bond to form a sigma-complex17 may be observed by time-resolved infra-red18-20 and/or NMR spectroscopy.21-24 Furthermore, in the solid-state Weller has demonstrated that C-C -complexes can also be formed by the hydrogenation of a coordinated norbornadiene ligand.25 Therefore, the choice of solvent in transition metal-catalyzed reactions is critical. Reactions may be inhibited if solvent binding is thermodynamically competitive with the substrate and alternatively, if the binding is too weak, the intermediate solvent complexes may be prone to decomposition. For example, Laperle26 has demonstrated that the photochemically induced isomerization of allyl alcohols by iron pentacarbonyl is highly effective in hydrocarbon solvents, but less efficient in amine or alcohol media. This can be linked to the donor ability of the solvent competing with the substrates for the vacant coordination site at the metal.

An understanding of the interactions between solvent molecules and unsaturated metal complexes is therefore vital to rationalizing solvation and its potential relevance to catalysis. Gaining such insight is challenging as the solvation event and resulting dynamics are extremely rapid in many systems. For example, previous studies on complexes M(CO)6 (M = Cr, Mo and W) have demonstrated that the photochemically induced loss of CO to form putative M(CO)5 occurs within 100 fs,27-30 and the subsequent solvation event is occurring between 1-3 ps which depends also on the solvent employed.31 Although there are examples in which CO-dissociation occurs over longer (ps) timescales.32-35 Time-resolved spectroscopy, in which the photochemical activation of a thermally inert substrate acts as a trigger for the spectroscopic probe, provides an excellent tool to investigate this problem. There are a number of possible spectroscopic probes for such interactions, for example, transient absorption spectroscopy (TA) can be used to probe kinetics on a sub-ps timescale, however, it only provides limited structural information. In contrast, time-resolved infra-red spectroscopy (TRIR) provides more detailed information about changes in the coordination sphere of the metal as the stretching frequencies of the metal carbonyl bands (for example) are highly sensitive to the coordination environment of the metal. However, the timescale of solvation dynamics that can be studied is limited by vibrational relaxation. In time-resolved experiments, as the energy of the pump pulse is greater than that required for CO dissociation then new species are formed in a vibrationally excited state.36 A consequence of the formation of these excited or hot states is that the bands in the resulting spectra can be broad and relaxation is required in order to observe the ground state IR spectrum of the photoproducts. This may preclude the observation of solvent dynamics within the coordination sphere of the metal if the rate of vibrational relaxation is, relatively, slow.37

In this paper we demonstrate how [Mn(ppy)(CO)4], [**1a**], can be used as a highly effective probe for the nature of metal-solvent interactions and also the ultrafast dynamics of the solvation event. Such information is of considerable importance due to the role played by [**1a**] (and its structural analogues) as photochemically activated therapeutic CO-releasing molecules38-40 and also as intermediates in manganese-catalyzed C-H bond functionalization reactions.41-45 The loss of a CO ligand from [**1a**] underpins both applications and therefore gaining a detailed understanding of this event, and the subsequent solvation will provide fundamental insight into these applications. We now show that photochemically induced CO dissociation from [**1a**] occurs in under 1 ps and the sensitivity of the changes to the frequency of the CO stretch modes in the resulting spectra allows for the nature of the solvent binding mode and subsequent dynamics to be determined.

Results

Complex [**1a**] was first described by Bruce in 1975 and is readily prepared from the reaction of 2-phenylpyridine with [Mn(CH2Ph)(CO)5].46 In previous studies we have shown that [**1a**], and its derivatives with modified 2-phenylpyridine groups (Figure 1), act as photochemically activated CO-releasing molecules (photoCO-RMs).38-40 Irradiation ( = 400 nm) results in loss of up to three CO-ligands as measured by the conversion of deoxymyoglobin to carboxymyoglobin. Furthermore, time-resolved spectroscopy has demonstrated that photolysis ( = 355 nm) of [**1a**] in the presence of catalytically relevant substrates such as alkynes, alkenes and isocyanates can be used to initiate CO-loss and observe the subsequent states involved in the C-C bond formation event which underpins Mn-catalyzed reactions.47 Prior to this, little was known about the photochemical processes leading to CO dissociation in [**1a**], which is in contrast to the isoelectronic complex [Cr(bpy)(CO)4] (bpy = 2,2’-bipyridyl) which undergoes competitive formation of a CO-dissociative singlet and a non-dissociative 3MLCT states, the latter being the dominant pathway and proportionally increasing on lower energy irradiation.48-54,55



**Figure 1** Left: The [Cr(bpy)(CO)4] complex studied by Vlček and co-workers.48-54 Right: The complexes studied in this work.

**Figure 2**: (a) UV-visible absorption spectrum of [**1a]** in NCMe (30 M). (b) DFT-optimized structure of [**1a**] showing the orientations for the MO diagrams (C grey, H, white, Mn pink, N blue, O red) (c) principal molecule orbitals involved in the transition at *ca*. 355 nm, isosurfaces are shown at 0.5 e A-3.

The lowest-energy band in the UV-visible absorption spectrum (Figure 2a) of [**1a**] is a shoulder from *circa* 425-325 nm. Based on previous results,38-40 irradiation within this wavelength range is known to result in CO loss. DFT was employed to rationalize the observed spectra. The structure of [**1a**] was optimized at the BP86/SV(P) level and the excitation spectra calculated TD-DFT calculations at PBE0/def2-TZVPP level on the resulted structure which had *Cs* symmetry (Figure 2b). This method has previously proven to effectively model other aspects of Mn-carbonyl chemistry.41, 47, 56

The two lowest energy transitions were calculated to appear at 345 nm and 342 nm. Both had two dominant components (Figure 2c) corresponding to orbitals 19a’’→ 20a’’ (HOMO→LUMO largely intraligand -\*) and 62a’ → 63a’ which is from a metal-carbonyl bonding orbital in the same plane as the 2-phenylpyridine ligand into the \*CO orbitals of the two mutually *trans* CO-ligands. The latter of these resembles the lowest-energy MLCT(CO) excited state in [W(en)(CO)4] (en = 1,2-diaminoethane), which is CO dissociative.57 The only significant difference between the two transitions is the weighting of the two orbital components (345 nm 19a’’→20a’’ 76 %, 62a’ → 63a’ 14 %; 342 nm 19a’’→20a’’ 18 %, 62a’ → 63a’ 56 %).

The lowest energy allowed transition in [Cr(bpy)(CO)4] corresponds to a HOMO-1 →LUMO MLCT with depopulation of a M-C bonding orbital between the two mutually *trans* CO-ligands.48-54,58 We envisaged that the different electronic structure of [**1a**] compared to [Cr(bpy)(CO)4] may result in markedly different photochemistry and may provide an opportunity to probe the balance of CO-loss versus excited state formation. In particular, if the former were dominant and occurs on an ultra-fast timescale, solvent coordination to the resulting putative “Mn(ppy)(CO)3” complex could be probed by the changes in the vibrational modes of the remaining three carbonyl ligands, allowing for changes in the electron density and symmetry at the metal to be probed. Furthermore, given that [**1a**] is highly soluble in even highly non-polar hydrocarbon solvents (although not in perflouroalkanes), there is the opportunity to study a range of metal-solvent interactions.

TRIR studies were performed with the Time-Resolved Multiple Probe Spectroscopy (TRMPS) method59 which allows for pump-probe delays of between 0.5 ps and 800 s to be recorded permitting the observation of events over a wide temporal range. A pump wavelength of 355 nm [**= (3.05 ± 0.11) × 103 dm3 mol‑1 cm-1 for [**1a**] in NCMe] was employed in order to excite the transitions detailed above. The initial studies focused on exploring the photochemistry of [**1a**] using NCMe as solvent as it was anticipated that the photoproduct from this reaction, [Mn(ppy)(CO)3(NCMe)], would have long-term stability. The infra-red spectrum of [**1a**]in NCMe exhibits four bands in the metal carbonyl region at 2076 (a’), 1989 (a’’), 1976 (a’) and 1933 (a’) cm-1, as expected for a tetracarbonyl complex with *Cs* symmetry. A TRIR study of an NCMe solution of [**1a**] with a pump wavelength of 355 nm resulted in formation of two species within 1 ps (Figure 3 top) which appear as positive bands in the difference spectra, with the concomitant bleaching of ground state [**1a**] shown as negative bands. The dominant photoproduct exhibited a sharp band at 2002 cm‑1 and a broader feature at 1898 cm‑1. This is consistent with loss of one of the two mutually *trans* CO ligands and the formation of a species with *pseudo-C3v* symmetry assigned as *fac*-[Mn(ppy)(NCMe)(CO)3], [**2aNCMe**]**,** (Scheme 1). As noted by Vlcek,53 the *mer*-isomer of complexes [M(L2)(S)(CO)3] (L2 = bidentate ligand), would be expected to show an opposite intensity of the IR-active bands with a smaller peak separation. Our DFT calculations support this assignment and further indicate that the *fac*-isomer of [Mn(ppy)(NCMe)(CO)3] is more thermodynamically stable that the two potential *mer*-isomers (Scheme 1). The calculations support the assignment of the high energy band at 2002 cm-1 to the symmetric stretching mode of the three CO ligands (DFT-predicted value 2038 cm-1, Scheme 1c), whereas the band at 1898 cm-1 is due to a combination of two asymmetric modes (DFT-predicted values 1962 and 1984 cm-1, Scheme 1c).

Complex [**2aNCMe**] was present even at the shortest pump-probe delays employed (1 ps) indicating that prompt photodissocation of CO and solvent coordination had already occurred on this timescale. Over the subsequent 30 ps the bands for [**2aNCMe**] sharpened and showed a small shift to higher energy which is consistent with vibrational cooling. A second photoproduct, which was also formed in the first 1 ps of the experiment, was characterized by a feature at *ca.* 1950 cm-1 and between 2010‑2050 cm‑1 (broad), with a maximum at 2019 cm-1 and a shoulder at 2033 cm-1. This species was assigned as a triplet excited state, 3[**1a**] on the basis of previous studies on the spectra of [Cr(bpy)(CO)4].53 This observed shift of the ground state bands of [**1a**] at 1989, 1976 and 1933 cm-1 to higher energy on formation of 3[**1a**] is mirrored in the DFT-predicted bands of the excited state (see ESI). The bands assigned to 3[**1a**] rapidly decayed, displaying single exponential kinetics with a lifetime of (4.1 ± 0.2) ps. Some recovery (*circa* 20 % in MeCN) of the bleached bands occurred on this timescale which may represent recovery of [**1a**] from 3[**1a**]53 or relaxation from an excited vibrational state.27





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**Figure 3** (Top) TRIR spectra of the 355 nm photolysis of [**1a**] in NCMe. The \* and # (also shown in inset windows) demarcate the 3[**1a**] excited state bands, the band labelled ‡ is unassigned. (Middle) Ground state IR spectrum of [**1a**] in NCMe. (Bottom) Continuous irradiation of an acetonitrile solution of [**1a**], monitored by *in situ* infrared spectroscopy, spectra collected after the irradiation times indicated. The solution was irradiated by a 365 nm LED drawing 6.0 W power and the resolution was 4 cm-1. The results are presented as difference spectra with respect to a reference spectrum recorded immediately before irradiation began.

**Scheme 1**: (a) Photolysis of [**1a**] in NCMe resulting in the formation of solvent complex [**2aNCMe**]. (b) Structures of three possible isomers of [**2aNCMe**] with their Free Energies at 298 K relative to the *fac*-isomer and predicted unscaled harmonic frequencies and normalized intensity of their vibrational modes in the metal carbonyl region at the D3-PBE0/def2-TZVPP//BP86/SV(P) level with COSMO solvent correction in NCMe. (c) predicted normal modes of the CO ligands in *fac*-[**2aNCMe**].

In previous work on [Cr(bpy)(CO)4] with photolysis at a wavelength of 400 nm, the assigned 3MLCT bands were reported to exhibit biexponential decay kinetics indicative of two states with respective lifetimes of (8 ± 3) ps and (76 ± 7) ps.53 However, the single exponential decay kinetics exhibited with [Mn(ppy)(CO)4] suggest that one excitedstate with a short lifetime was present. Based on the intensity of the product bands it is clear that in the case of [**1a**] CO-dissociation is the dominant photoprocess, even when a lower energy excitation wavelength was employed (400 nm). A minor band was observed at 1815 cm-1 (labelled ‡ in Figure 3 top) which could not be unambiguously assigned. A number of possible assignments were considered, including [Mn(ppy)(CO)2(NCMe)2] and manganese (I) acyl complexes however the bands for these complexes do not occur in this region.60

The generation of [**2aNCMe**] could also be performed with a traditional photochemical experiment by irradiation of [**1a**] in NCMe. Photolysis with a 365 nm LED was monitored by *in situ* IR spectroscopy using a ReactIRTM instrument to demonstrate that [**2aNCMe**] was formed (on the second timescale), as in the TRIR experiment (Figure 3 bottom). Although not a direct duplication of the experimental conditions used in the TRIR experiments, for example, bands due to the loss of [**1a**] continue to get larger, but those for [**2aNCMe**] remain constant, suggesting that the photoproduct is decaying thermally or photochemically. This experiment does demonstrate that the same product could be generated by conventional means. As [**2aNCMe**] is long-lived at room temperature, we assign it an low-spin 18-electron singlet configuration, consistent with a *fac*-Mn(CO)3 framework.

The TRIR results were replicated when solvents such as heptane, toluene and CH2Cl2 were used. In all cases, ultrafast CO dissociation from [**1a**] occurred, with the formation of the *pseudo-C3v* solvent complex *fac*-[Mn(ppy)(S)(CO)3] (S = *n*-heptane, [**2ahep**], toluene, [**2atol**], and CH2Cl2, [**2aCH2Cl2**]) as the major photoproduct. In all cases, 3[**1a**] was formed within 1 ps and decayed with single exponential kinetics: the lifetimes for the 3[**1a**] states are given in the ESI, Table S2 and are *ca*. 5 ps.

In heptane, the species formed after 1 ps exhibited broad bands at 1893 and 2003 cm-1: within 50 ps these bands had bleached to be replaced by new ones at 1923, 1933 and 2019 cm-1 (Figure 4). The data are once again consistent with the formation of *fac*-[Mn(ppy)(S)(CO)3] and a number of different possibilities were considered to explain the presence of two sets of bands including (1) the initial formation of 3[**2ahep**] prior to relaxation to 1[**2ahep**] (in a similar vein to the recently reported behavior of complexes based on a TpRh(NCR) framework)20 and (2) the generation of the formally unsaturated complex [Mn(ppy)(CO)3] which then underwent heptane binding to give [**2ahep**]. However, these possibilities may be discounted (see ESI for a comprehensive discussion) and the observed behavior may be due to either vibrational cooling or a rapid isomerization between internal (to C4) and terminal (to C1) positions of the heptane ligand. The latter process was modelled by DFT and the results were dependent on the methodology employed. At the PBE0/def2-TZVPP//BP86/SV(P) level with COSMO solvent correction in heptane the terminal form is more stable than internal by 13 kJ mol-1, however, when a dispersion correction is applied the trend is reversed with the internal form being 5 kJ mol-1 lower in energy. With such small differences in energy it is not possible to make an absolute assignment to the binding mode of the solvent.

The TRIR spectra of the solvent complexes [**2a**] demonstrated that the vibrational modes of the carbonyl ligands are diagnostic of the binding mode of the solvent employed: a systematic shift to lower energy was observed on changing from *n*-heptane > CH2Cl2 > toluene > NCMe (Figure 5 and Table 1). In order assist with the interpretation of these data, all the complexes were modelled with DFT and the resulting trends in vibrational frequencies correlated with those determined experimentally (Table 1). This approach allowed for the binding mode of each solvent to be assigned. For example, in [**2atol**], two potential binding modes for toluene were envisaged, either as -C-H, [**2atol()**], or an 2C=C  complex, [**2atol()**]. The calculated bands for [**2atol()**] closely match those of heptane, whereas those for [**2atol()**] were predicted to have a shift of *ca*. 10 cm-1 to lower energy. This latter case is observed experimentally, hence the 2C=C -binding mode was assigned.

To further support the structural assignments, a series of reactions were calculated using the *n*-heptane complex *fac*-[Mn(ppy)(*n*-heptane)(CO)3] [**2ahep**], as a reference state (Table 1). Using [**2atol**], again as an example, the experimentally assigned 2C=C -complex [**2atol()**] is predicted to be thermodynamically more stable than [**2atol()**] supporting the assignment.



|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **Complex** | **Predicted Bands / cm-1** | | | **Observed Bands / cm-1** | | | E / kJ mol-1 | G298 / kJ mol-1 |
|  | [**2aDMSO()**] | 1960 | 1978 | 2039 | 1900 |  | 2007 | 3 | 3 |
|  | [**2ahept**] C1 | 1961 | 1977 | 2039 | 1923 | 1933 | 2019 | 0 | 0 |
|  | [**2aTHF()**] C3 | 1957 | 1976 | 2038 |  |  |  | -1 | -3 |
|  | [**2atol()**] | 1958 | 1977 | 2039 |  |  |  | -5 | -4 |
|  | [**2ahept**] C4 | 1954 | 1975 | 2037 |  |  |  | -11 | -5 |
|  | [**2aDioxane()**] | 1956 | 1976 | 2036 | 1919 |  | 2011 | -12 | -12 |
|  | [**2aTHF()**] C3 | 1954 | 1972 | 2034 | 1912 |  | 2011 | -13 | -14 |
|  | [**2anBu2O()**] C5 | 1960 | 1977 | 2039 | 1916 |  | 2016 | -9 | -15 |
|  | [**2atol()**] | 1949 | 1969 | 2030 | 1906 |  | 2007 | -23 | -15 |
|  | [**2aCH2Cl2**] | 1952 | 1976 | 2037 | 1911 |  | 2012 | -19 | -16 |
|  | [**2anBu2O()**] C2 | 1952 | 1973 | 2035 | 1916 |  | 2016 | -24 | -18 |
|  | [**2aH2O**] | 1958 | 1973 | 2036 | 1904 | 1919 | 2006 | -26 | -32 |
|  | [**2aDioxane(O)**] | 1945 | 1967 | 2032 | 1899 | 1911 | 1999 | -43 | -37 |
|  | [**2aTHF(O)**] | 1943 | 1966 | 2030 | 1889 | 1899 | 1999 | -44 | -37 |
|  | [**2aDMSO(O)**] | 1929 | 1965 | 2026 |  |  | 1994 | -46 | -43 |
|  | [**2anBu2O(O)**] | 1939 | 1968 | 2039 | 1891 | 1909 | 2004 | -59 | -49 |
|  | [**2aNCMe**] | 1962 | 1984 | 2038 | 1898 |  | 2006 | -60 | -61 |
|  | [**2aDMSO(S)**] | 1946 | 1978 | 2039 |  |  | 2007 | -89 | -81 |
|  | [**1a**][a] | 1984 | 2011 | 2017 | 1928 | 1972 | 1986 | -112 | -114 |

**Table 1** Calculated and observed IR bands for the metal carbonyl vibrations in solvent complexes. The DFT-calculated harmonic frequencies have not been scaled. Relative changes to electronic energies (corrected for zero-point energy), E and Gibbs energies at 298 K, G298, for the substitution of a heptane ligand in [**2ahept**] are given at the D3-PBE0/def2-TZVPP//BP86/SV(P) level with COSMO solvent correction in *n*-heptane.[a] Complex [**1a**] exhibits an additional band at 2071 cm-1 (DFT-predicted frequency 2087 cm-1). [Mn] = *fac*-[Mn(ppy)(CO)3].







**Figure 4** (Top) TRIR spectra of the 355 nm photolysis of [**1a**] in *n*-heptane at short pump-probe delays showing the [**1ahep()**] photoproduct. The asterisks demarcate the 3[**1a**] excited state bands. (Middle) Spectra from the same experiment with longer pump-probe delays to show the formation of [**2aH2O**]. (Bottom) Ground state spectrum of [**1a**] in heptane.



**Figure 5**. Stack of normalized absorbance spectra of the solvent complexes formed upon photolysis of [**1a**] in NCMe, toluene, CH2Cl2 and *n*-heptane, all at a pump-probe delay of 100 ps.

**Figure 6** Continuous irradiation of a *n*-heptane solution of [**1a**], monitored by *in situ* infrared spectroscopy, with spectra collected after the irradiation times indicated. The solution was irradiated by a 365 nm LED drawing 6.0 W power and the resolution was 4 cm-1. The results are presented as difference spectra with respect to a reference spectrum recorded immediately before irradiation began.

The solvent complexes [**2ahep**], [**2atol()**], and [**2aCH2Cl2**] were much shorter-lived than [**2aNCMe**]. In the TRIR experiment all *fac*-[Mn(ppy)(S)(CO)3] complexes underwent a further reaction on the μs timescale to form a complex with all three IR stretching bands shifted to lower wavenumbers, assigned to the aqua complex *fac*-[Mn(ppy)(OH2)(CO)3], [**2aH2O**]. A similar observation was made on photolysis of [W(CO)6] in heptane with the initial formation of a C-H solvent complex followed by displacement by trace amounts of water.59 On the basis of the calculated free energy changes on ligand substitution (Table 1) [**2aH2O**] is predicted to be more thermodynamically stable than [**2ahep**], [**2atol**], and [**2aCH2Cl2**] but less stable than [**2aNCMe**], [**2aTHF**] and [**2aDMSO**] (q.v.) which is consistent with the fact that this behavior is not observed in the latter cases.

The photolysis of [**1a**] in heptane solutions was also monitored by *in situ* ReactIR spectroscopy. After 30 mins bands were observed from *circa* 1890-1920 cm-1 (br) and 2006 cm-1 (Figure 6) which are similar to those observed for [**2aH2O**] in heptane solution (1904, 1919 and 2006 cm-1). At later times, other bands were observed to grow in intensity most notably at 2024 cm-1. These were tentatively assigned to the formation of high-nuclearity MnI carbonyl complexes with bridging hydroxide ligands such as [Mn(CO)3(μ3-OH)3]4 which has bands at 1891, 1932 and 2027 cm-1.61 The formation of this species may be rationalized by the protonation of the ppy ligand by water to form uncoordinated 2-phenylpyrindine with concomitant generation of “Mn(CO)3(OH)” which then undergoes a tetramerization. The formation of these species is thought to be a major catalyst deactivation pathway in Mn-catalyzed C-H functionalization reactions.56

TRIR experiments performed in ether solvents (1,4-dioxane, THF and *n*-Bu2O) exhibited a significant difference in behavior when compared to NCMe, heptane, CH2Cl2 and toluene. Using THF as an example (Figure 7), the initial photoproduct was characterized by a broad feature with bands at 1912 cm-1 (br) and 2009 cm‑1, the relative intensity and frequency again supporting the formation of a *fac*-[Mn(ppy)(S)(CO)3] complex. All the bands for this photoproduct sharpened and shifted (by *ca.* 5 cm ‑1) to higher wavenumber within the first ~10 ps after photolysis, consistent with vibrational cooling.36 The photoproduct then exhibited exponential decay ( = 15.1 ± 2.2 ps) and concomitant with its disappearance a new, long-lived, species with bands at 1893, 1902 and 1995 cm-1 grew in intensity over the same timescale (18.9 ± 1.6) ps. Performing the same experiment under air, 1 atm dry N2, and 1 atm CO all resulted in the same behavior and lifetimes within error, as did a reaction in THF-d8: the lack of kinetic isotope effect indicating that no C-H bond cleavage occurred in rate-controlling states. The results are summarized in Table 2.







**Figure 7** (Top) TRIR spectra of the 355 nm photolysis of [**1a**] in tetrahydrofuran. The asterisks and insets demarcate the 3[**1a**] excited state bands. (Middle) Ground state spectrum of [**1a**] in THF. (Bottom) kinetic plots showing the decay of the 1912 cm-1band of [**2aTHF()**] and the rise of the band at 1999 cm-1 corresponding to [**2aTHF(O**)]. The dashed lines represent fits to single exponential kinetics. Fitting started from 5 ps due to the initial growth and vibrational cooling of [**2aTHF(**] at short delays.

Based on the similarity of the spectra to [**2ahep**], the initial photoproduct was assigned to a species in which the C-H bond of the ether solvent was bound to the metal as a C-H -complex, [**2aTHF()**]. It is not possible from the available spectroscopic data to determine which C-H bond(s) within THF is bound to the metal. However, this species is then proposed to isomerize to an oxygen-bound THF complex, [**2aTHF(O)**], consistent with the shift in CO stretching vibrational frequency to lower energy. The significant shift in frequency is inconsistent with vibrational cooling (where a sharpening of the CO bands and shift to higher wavenumber would be expected)37 but are in good agreement with those predicted by DFT on the basis of -C-H/O-bound isomerization (Table 1). Derivatives [**1b-d**] (Table 2 and ESI) featuring substituted 2-phenylpyrdine ligands showed analogous behavior in THF solution reinforcing the notion that initial formation of [**1THF()**] followed by isomerization to [**1THF(O)**] is a general phenomenon.

Essentially identical behavior was observed when 1,4-dioxane was used as the solvent, although the conversion of the initial photoproduct, [**2aDioxane()**] into the longer-lived species, [**2aDioxane(O)**] was faster ( = 10.8 ± 1.2 ps for the decay of the former and  = -12.8 ± 0.8 ps for the growth of the latter). An analogous process also took place in *n*-Bu2O and in this case the decay of the initially observed photoproduct ( = 103 ± 26 ps) and growth of the long-lived species ( = -88 ± 29 ps) were markedly slower than in the cyclic ether solvents. Therefore, the rate of the proposed -C-H/O-bound isomerization broadly matches the number of hydrogens present, suggesting a kinetic preference for C-H binding before isomerization to the thermodynamically preferred coordination mode (Scheme 2).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Solvent | Atmosphere | [**2S()**]/ ps | [**2S(O)**] / ps |
| [**1a**] | THF | Air | 15.1 ± 2.2 | -18.9 ± 1.6 |
| [**1a**] | 1,4-dioxane | Air | 10.8 ± 1.2 | -12.8 ± 0.8 |
| [**1a**] | *n*-Bu2O | Air | 103 ± 26 | -88 ± 29 |
| [**1a**] | THF | N2 | 17.6 ± 1.3 | -18.7 ± 0.8 |
| [**1a**] | THF | CO | 15.9 ± 0.7 | -18.2 ± 0.7 |
| [**1a**] | THF-*d*8 | Air | 17.7 ± 3.7 | -17.0 ± 1.8 |
| [**1b**] | THF | Air | 19.0 ± 1.6 | -19.8 ± 1.0 |
| [**1c**] | THF | Air | 17.9 ± 0.9 | -22.2 ± 4.3 |
| [**1d**] | THF | Air | 25.1 ± 2.6 | -21.0 ± 1.1 |

**Table 2**: Summary of the isomerization of ether solvent sigma complexes to the O-bound isomer. All lifetimes are based on single exponential fits with the 95 % confidence intervals shown. S = solvent.



**Scheme 2**: Photochemical reaction of [**1a**] in tetrahydrofuran (THF). Solvent coordination can occur *via* theO atom or a C-H bond before isomerization to the more stable O-bound complex [**2aTHF(O)**].

In all three ether solvents, the weak features of the short-lived 3[**1a**] state were detected as a minor photoproduct. The lifetimes for this state were (5.7 ± 0.9) and (5.1 ± 0.7) ps in THF and 1,4-dioxane respectively. In *n*-Bu2O, 3[**1a**] was observed and decayed on a similar timescale, but its features were too weak for the lifetime to be quantified.

Photolysis of [**1a**] in DMSO resulted in even more complex behaviour than the ether solvents, Figure 8. An initial product with bands at 1902 (br) and 2010 cm-1 was observed, which was assigned as a -C-H complex [**2aDMSO()**] on the basis of its similarity to the corresponding species observed in heptane and THF. This species then converted to two new complexes with overlapping bands between 1865 and 1892 cm‑1: two sharper features were observed at 1994 and 2007 cm-1. This is consistent with the formation of two *fac-*[Mn(ppy)(DMSO)(CO)3] complexes and two possible binding modes (S- [**2aDMSO(S)**] or O-bound, [**2aDMSO(O)**]) were considered for the DMSO in these long-lived species. On the basis of the DFT calculations, [**2aDMSO(S)**] is thermodynamically more favourable than [**2aDMSO(O)**] and predicted to have higher energy vibrational modes, as such it was assigned to the species at 2007 cm-1. The bands at 1994 cm-1 was therefore assigned to [**2aDMSO(O)**].

Complex [**2aDMSO()**] had a lifetime of (11.9 ± 1.5) ps, whereas the bands assigned to [**2aDMSO(S)**] and [**2aDMSO(O)**] grew in with lifetimes of (23.0 ± 7.9) ps and (19.6 ± 1.5) ps, respectively. This is consistent with a mechanism in which the -C-H bond is undergoing an unselective transformation to the S- and O-bound species each process having the same lifetime. However, over the timescale of the experiment (ca 800 s) no evidence for the conversion of [**2aDMSO(O)**] to the thermodynamically more favorable [**2aDMSO(S)**] was obtained.



**Figure 8**: (Top) TRIR spectra of the 355 nm photolysis of [**1a**] in dimethyl sulfoxide. The asterisks demarcate the 3[**1a**] excited state bands. (Bottom) Ground state spectrum of [**1a**] in DMSO.



**Scheme 3**. Photochemical reaction of [**1a**] in dimethyl sulfoxide (DMSO). Solvent coordination can occur *via* theS or O atoms, or *via* a C-H bond before isomerization to the S- and O- bound complexes.

Discussion

Irradiation of [**1a**]at 355 nm results in two competing manifolds, the dominating major pathway being ultra-fast dissociation of a carbonyl ligand from the manganese resulting in the formation of *fac*-[Mn(ppy)(CO)3(S)] (S = solvent). The minor pathway involves the formation of a short-lived ( ≈ 5 ps) complex which was assigned as 3[**1a**]. Qualitatively, these observations are related to those reported by Vlcek for [Cr(bpy)(CO)4], although the population of the different two manifolds is reversed.53

The fact that CO-dissociation is the dominant light-induced process in [**1a**], coupled with the complexes high-solubility and thermal stability in a range of media, has allowed for the characterization of a range of species *fac*-[Mn(ppy)(CO)3(S)]. An important observation is that the vibrational modes of the remaining carbonyl ligands are highly sensitive to the nature of the solvent ligand. For example, the changes observed in the frequencies between the [**2ahept**] and [**2atol()**] support different binding modes (2-C-H and 2-C-C respectively) for these two solvents. The rapid rates of vibrational cooling and high spectral dispersion resulting from coordination of different solvents has allowed new dynamic process occurring on the ultra-fast time scale to be elucidated. Comparison of the vibrational spectra observed for the initial product formed on coordination of ethers to the manganese with [**2ahept**] allowed for an 2-C-H binding mode to be assigned. Subsequent isomerization to the thermodynamically preferred O-bound form then occurred. Although such a 2-C-H/O rearrangement process has previously been proposed on the basis of transient absorption spectroscopy,31 the use of, the more structurally informative, TRIR has allowed for the precise nature of the metal-solvent interactions to be probed and discerned.

We propose a mechanistic picture in which initial CO-loss and solvent coordination occurs within 1 ps. There are two potential models for this solvation event. Firstly, solvent binding could be random with the putative Lewis acidic complex [Mn(ppy)(CO)3] simply binding in a stochastic fashion to the solvent prior to any subsequent isomerization, such as that observed in ether solvents and DMSO. Alternatively, the coordination mode of the solvent could reflect the topology of the first solvation sphere of the metal which would result in the binding mode being dictated by the orientation of the solvent with respect to the newly formed vacant coordination site. It is somewhat difficult to differentiate between these pathways as in all ether solvents employed there are more C-H bonds than oxygen lone pairs hence in the stochastic model the former would always dominate. In dioxane, however, the ratio of C-H bonds to oxygen lone pairs is 2:1 which in a stochastic model would be the kinetic distribution of products. However, no evidence for [**2aDioxane(O)**] was obtained in the TRIR spectra obtained as short-pump probe delays (Figure S12) which favors the directed, non-stochastic solvation model, at least in this case. There is also an apparent correlation between the lifetime of the C-H sigma complexes and the C-H/O ratio in the ether. Considering an intramolecular rearrangement, in the case of dioxane, one of the two available 1,2 migration pathways from [**2aDioxane()**] will always lead to [**2aDioxane(O)**], whereas in THF there are two possible C-H sigma complexes (2- and 3-position) and 1,2-migration from the later will still lead to a C-H sigma complex. Of course, in the case of *n*-Bu2O only 1,2 migration from the C-H bond next to the oxygen atom will lead to the thermodynamically most favored binding mode. However, it is also possible that an intermolecular substitution is occurring and, as noted by Harris in the related rearrangement of alcohol ligands in complexes [Cr(CO)5(ROH)],37 the discrimination between the intra- and intermolecular pathways is extremely challenging.

An interesting corollary to this discussion is that no evidence for interconversion between complexes [**2aDMSO(O)**] to the thermodynamically more favorable [**2aDMSO(S)**] was obtained over the course of the experiment. A transition state, [**TS2aDMSO**], for the conversion of [**2aDMSO(O)**] to [**2aDMSO(S)**] was located which lies 48 kJ mol-1 higher in energy than[**2aDMSO(O)**]. As the Mn-S and Mn-O bonds in [**TS2aDMSO**] are considerably elongated compared to the ground state structures (Figure 9) indicating that the DMSO is weakly bound. It is therefore proposed that the putative conversion of [**2aDMSO(O)**] to [**2aDMSO(S)**] is essentially dissociative in nature.

**Figure 9** Structure of [**2aDMSO(O)**], [**2aDMSO(S)**] and [**TS2aDMSO**] showing Mn-O and Mn-S bond lengths. Carbon grey, hydrogen, white, manganese pink, nitrogen blue and oxygen red. Energies are Gibbs energies at 298 K at the D3-PBE0/def2-TZVPP//BP86/SV(P) level with COSMO solvent correction in DMSO.

All spectra obtained were consistent with the formation of the *fac-*isomer of the complex on solvation resulting from the formal loss of one of the two mutually *trans* carbonyl ligands. The *fac*-isomer of these complexes is thermodynamically more stable that the two potential *meridional* arrangements of CO ligands, therefore, our results do not allow us to discriminate between scenarios in which (1) an axial CO is photo-ejected from the metal resulting in direct formation of the *fac*-isomer (2) one of the two chemically distinct *meridional*-CO ligands is lost and isomerization to the *fac*-isomer occurs on a sub-ps timescale or (3) CO loss is random prior to the formation of the *fac*-isomer. Indeed, an examination of the orbitals involved in the electronic transition pumped at 355 nm reveal that a M-C bonding orbital between the two mutually *cis* CO-ligands is depopulated and an M-C antibonding orbital between the two mutually *trans* CO-ligands is populated.

Conclusion

We have demonstrated that [**1a**] is a highly versatile and viable probe for the nature of metal-solvent interactions. The high spectral dispersion of the vibrational bands in complexes [**2a**] has allowed for the ready differentiation between solvent binding modes. Furthermore, as the vibrational cooling in most instances of complexes [**2a**] is extremely rapid, it has been possible to observe ultra-fast formal rearrangements of the coordinated solvents, which allowed for the conclusion that, following CO loss from [**1a**], initial solvent coordination is kinetically controlled. These data are complementary to related rearrangements of alcohols in the coordination sphere of Cr(CO)5 which occurs with a lifetime of typically several 100 ps.37 Here we were able to observe -C-H to O-bound conversions with a lifetime of 10-20 ps, whereas in the chromium case, this is the same timescale as vibrational cooling. Hence, we have been able to employ TRIR spectroscopy to garner structural information about this interconversion that cannot be obtained by TA. Given the role of complexes related to [**1a**] as versatile CO-RMs38-40 and in Mn-catalyzed C-H functionalization reactions,41, 43 56, 62we anticipate that further TRIR studies will provide vital insight into their behavior. Importantly, when [**1a**] is photolyzed in neat alkynes, alkenes and isocyanates kinetically controlled coordination (as shown for ethers and DMSO) also occurs. For example, PhC2H shows initial binding through the aryl ring, whereas nBuCO2CH=CH2 coordinated through the alkyl chain – both species then undergo a rearrangement on the ps timescale to give thermodynamically more stable - and O-bound complexes.47 Taken with the results reported herein, this appears to be a general phenomenon.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Further TRIR spectra, kinetic analysis and details of the DFT calculations.

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The manuscript was written through contributions of all authors and the work within contributes to the PhD thesis of BJA.

Notes  
The authors declare no competing financial interest.

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