

# Time-resolved Infra-red Spectroscopy Provides Insight into the Solvation of Unsaturated Transition Metal Complexes

Contact [ian.p.clark@stfc.ac.uk](mailto:ian.p.clark@stfc.ac.uk)

B. J. Aucott, L. A. Hammarback, B. E. Moulton, A. K. Duhme-Klair, I. J. S. Fairlamb and J. M. Lynam

Department of Chemistry  
University of York  
York, YO10 5DD, UK

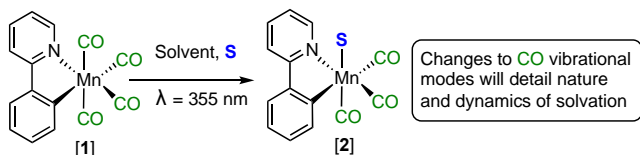
I.P. Clark, I.V. Sazanovich, M. Towrie

Central Laser Facility  
Research Complex at Harwell, STFC Rutherford Appleton  
Laboratory, Harwell Oxford,  
Didcot, OX11 0QX, UK

## Introduction

Homogeneous catalysis plays a vitally important role in chemistry with applications in the synthesis of bulk and fine chemicals. The vast majority of such homogeneous reactions are performed in a liquid solvent in which the catalyst and substrates are dissolved. As such, the solvent is frequently the greatest single component of the reaction. Whereas there has been a significant trend to parameterize the precise steric and electronic influences of different groups surrounding a transition metal catalyst, the solvent is often described in terms of bulk properties, such as dielectric constant and/or ability to engage in hydrogen bonding.<sup>1</sup> Although such an approach may be informative, in homogeneous reactions there will be an intimate interaction between the solvent and the metal as, in order to bind a substrate to the metal, a ligand must be lost from a saturated pre-catalyst. Similarly, liberation of the product from the metal will result in the generation of an unsaturated species. In these instances, it is statistically most likely that the unsaturated metal complex will initially bind to a molecule (or molecules) of solvent prior to coordination to the substrate. Indeed, there is a careful balance to be maintained – if the solvent binds too strongly then the substrate will not be able to subsequently displace it from the metal, whereas if the solvent binds too weakly then the catalyst may undergo undesired reactions resulting in decomposition.

It is therefore important that a quantitative understanding of the interaction between coordinatively unsaturated metal complexes and solvents is obtained. The complex  $[\text{Mn}(\text{ppy})(\text{CO})_4]$ , **[1]** (ppy = 2-phenylpyridine) was selected to directly probe these solvation events.<sup>2</sup> Previous work had demonstrated that CO-loss from **[1]** occurs on irradiation but, when stored under ambient conditions in the dark, it was inert.<sup>3</sup> It was anticipated that **[1]** could be dissolved in a range of solvents which, following photochemical loss of a carbonyl ligand, would coordinate to the metal to give **[2]**. The changes to the frequency and intensity of the vibrational modes of the three remaining carbonyl ligands would then report on the nature and dynamic behaviour of the metal-bound solvent (Scheme 1).



Scheme 1 Structure of compounds **[1]** and **[2]**.

## Methodology

Experiments were performed on the ULTRA A and LIFETIME instruments within the ULTRA facility using the time-resolved multiple probe spectroscopy (TR<sup>M</sup>PS) method. A pump wavelength of 355 nm was employed to irradiate the manganese compounds and the subsequent changes to the stretching modes of the carbonyl modes probes in the region 1800–2100  $\text{cm}^{-1}$ . In order to ensure that photodegradation of the Mn complexes did not affect the experiment, samples were flowed continuously through a Harrick cell which was rastered during the acquisition.

The data are presented as difference spectra with negative peaks corresponding to bands lost on photolysis and positive peaks the light-generated products.

## Results

Photolysis of **[1]** in NCME results in ultra-fast ( $< 1 \text{ ps}$ ) dissociation of a CO ligand and the formation of *fac*- $[\text{Mn}(\text{ppy})(\text{CO})_3(\text{NCMe})]$ , **[2]<sub>NCMe</sub>**. Evidence for this process is shown in the difference spectra in Figure 1. The negative peaks correspond to the ground state bleach for compound **[1]** and two new major features for **[2]<sub>NCMe</sub>** (bands at 2006 and 1898  $\text{cm}^{-1}$ ) are present. Over the course of ca. 30 ps these bands sharpen which may reflect that, at early times, the complex is formed in a vibrationally hot state which then undergoes cooling. The appearance of one broad and one sharp band is consistent with the formation of a complex with facially coordinated CO ligands and pseudo- $C_{3v}$  symmetry, supporting the assignment as *fac*- $[\text{Mn}(\text{ppy})(\text{CO})_3(\text{NCMe})]$ .

In addition to the bands for **[2]** the spectrum also exhibited a number of other peaks for a species with a lifetime,  $\tau$ , of  $(4.1 \pm 0.2) \text{ ps}$ . These peaks were assigned to  $^3\text{[1]}$  which undergoes a change in spin to reform **[1]** in its singlet electronic ground state.

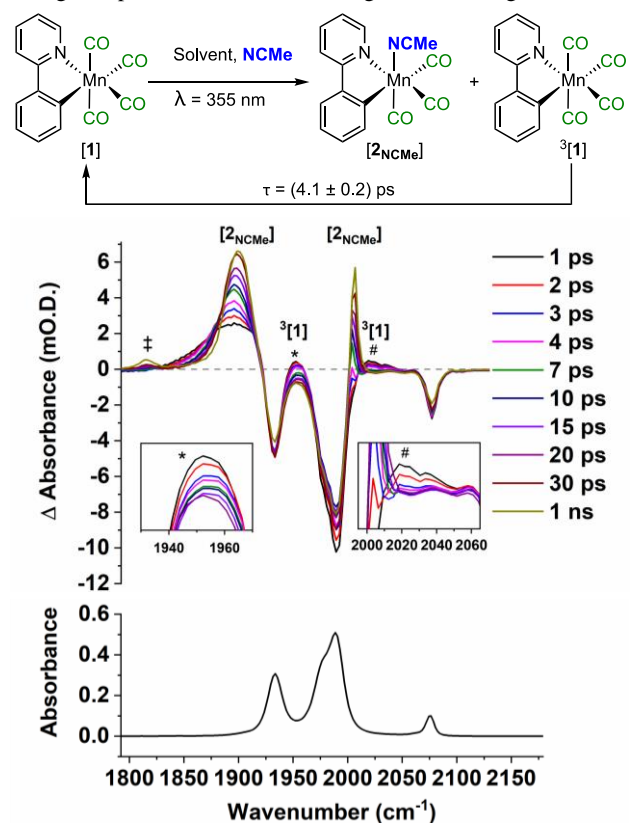
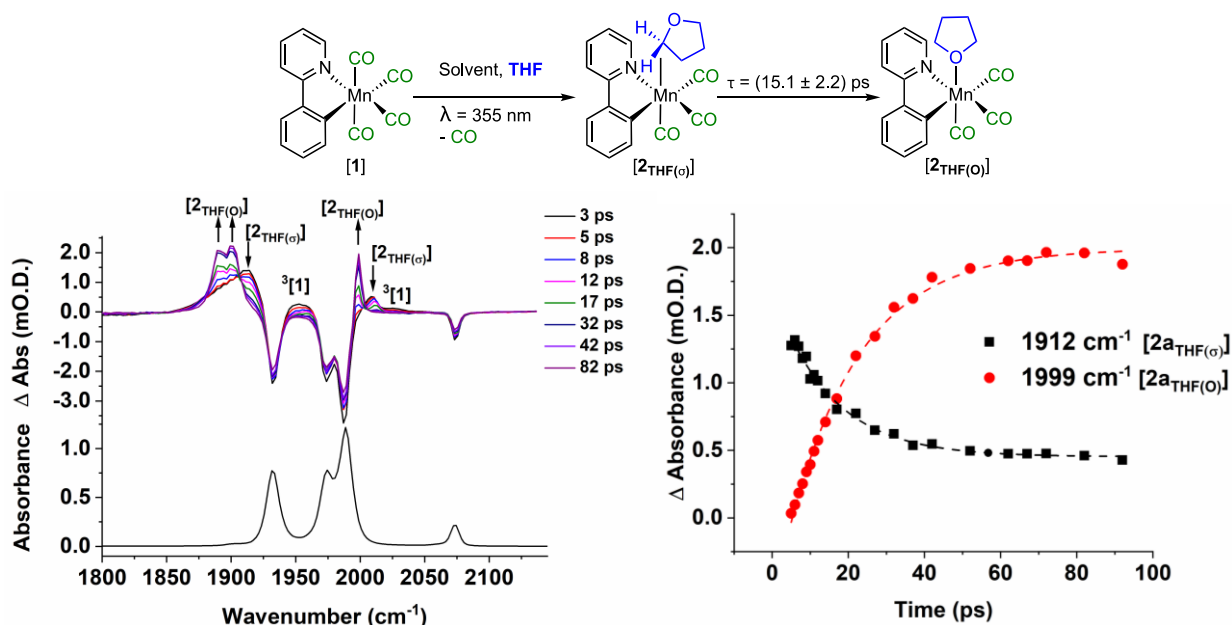


Figure 1 Top Scheme showing the reaction pathway. Middle TRIR spectra showing the formation of **[2]<sub>NCMe</sub>** and  $^3\text{[1]}$ . Bottom Ground state spectrum of **[1]** in NCMe.



**Figure 2** Top Reaction profile for the irradiation of [1] in THF solution. *Left* TRIR spectra showing the formation of [2<sub>THF(σ)</sub>] and [2<sub>THF(O)</sub>]. *Right* kinetic plot showing the loss of [2<sub>THF(σ)</sub>] and formation of [2<sub>THF(O)</sub>].

Photolysis of [1] in a range of other solvent media was explored. In all cases ultra-fast CO-dissociation occurred to give complexes *fac*-[Mn(ppy)(CO)<sub>3</sub>(S)] (S = heptane, toluene, CH<sub>2</sub>Cl<sub>2</sub>, THF, 1,4-dioxane, <sup>n</sup>Bu<sub>2</sub>O, DMSO) as the dominant pathway with a small amount of <sup>3</sup>[1] being observed which relaxed to its ground state. The band positions for the complexes [2] were highly sensitive to the nature of the solvent,<sup>2</sup> hence these species act as probes for metal-solvent interactions.

This is demonstrated when examining the data obtained when the ethers THF, 1,4-dioxane and <sup>n</sup>Bu<sub>2</sub>O were used as solvents. In THF, the spectra indicated that initial coordination of the solvent occurs through a C-H bond to give [2<sub>THF(σ)</sub>] (Figure 2) which then converted to the thermodynamically more stable oxygen-bound form, [2<sub>THF(O)</sub>]. Complex [2<sub>THF(σ)</sub>] exhibits bands which are essentially identical to those observed when heptane is used as a solvent, supporting the notion that the THF solvent is binding to the metal through C-H bonds in a σ-type interaction. Over the course of *ca.* 20 ps ( $\tau = 15.1 \pm 2.2$  ps) the bands for [2<sub>THF(σ)</sub>] decrease in intensity to be replaced by two modes at lower energy, consistent with oxygen, a better donor atom, being present in the coordination sphere of the metal.

Corresponding experiments with 1,4-dioxane and <sup>n</sup>Bu<sub>2</sub>O resulted in essentially identical behaviour with initial binding to the metal occurring through a C-H bond of the solvent, prior to isomerisation to the O-bound form. These experiments provided important information about the mechanism of this process. Firstly, the spectra recorded at short pump-probe delays in 1,4-dioxane showed no evidence of the oxygen-bound form. This is important as if the initial binding to the solvent was random then there are four lone pairs (two on each oxygen) and eight C-H bonds, therefore stochastic coordination would have resulted in a 1:2 ratio of O- and C-H-bound complexes.

Secondly the lifetime of the C-H-bound complex correlates with the number of C-H bonds in the substrate. For example, in <sup>n</sup>Bu<sub>2</sub>O the lifetime of the σ-complex was (103 ± 26) ps, substantially longer than in THF. This may represent the time required for the manganese complex to chain walk along the solvent molecule until the thermodynamically most favourable binding mode is obtained.

Such a phenomenon appears to be general - in DMSO solution C-H binding occurs rapidly prior to isomerization to both O- and S-bound forms of the solvent.<sup>2</sup> When exploring reactions of relevant to manganese-catalysed C-H functionalisation using

substrates such as PhC≡CH, evidence for initial binding of the arene group of the alkyne to the metal was obtained, prior to conversion to π-bonding through the triple bond.<sup>4</sup>

## Conclusions

Photolysis of [1] in organic solvents results in two divergent pathways. The dominant route is loss of a CO ligand and solvent coordination and the minor pathway formation of <sup>3</sup>[1] which then relaxes to the ground state. This behaviour is reminiscent of the photochemistry of the isoelectronic complex [Cr(bpy)(CO)<sub>4</sub>] (bpy = 2,2'-bipyridyl),<sup>5</sup> but the relative population of the two pathways is reversed.

These data indicate that the initial solvation of unsaturated metal complexes is a kinetically controlled event. Photochemical loss of a CO ligand results in the formation of a vacant coordination site, and [ML<sub>5</sub>] complexes with a low-spin d<sup>6</sup> electronic configuration and π-acceptor ligands are highly Lewis-acidic. Metal binding to the closest area of electron density occurs and so the initial solvation event is controlled by the topology of the local solvent shell. For the ether solvents this results in binding to a C-H bond prior to chain walking to generate the thermodynamically most favourable binding mode of the solvent being obtained.

## Acknowledgements

We are grateful to the EPSRC (PhD studentship to B. J. A., B. E. M.) and CASE award with Syngenta (L. A. H) for funding.

## References

1. P. J. Dyson and P. G. Jessop, *Catal. Sci. Technol.*, 2016, **6**, 3302–3316.
2. B. J. Aucott, A.-K. Duhme-Klair, B. E. Moulton, I. P. Clark, I. V. Sazanovich, M. Towrie, L. A. Hammarback, I. J. S. Fairlamb and J. M. Lynam, *Organometallics*, 2019, **38**, 2391–2401.
3. J. S. Ward, J. M. Lynam, J. W. B. Moir, D. E. Sanin, A. P. Mountford and I. J. S. Fairlamb, *Dalton Trans.*, 2012, **41**, 10514–10517.
4. L. A. Hammarback, I. P. Clark, I. V. Sazanovich, M. Towrie, A. Robinson, F.; Clarke, S. Meyer, I. J. S. Fairlamb and J. M. Lynam, *Nat. Catal.*, 2018, **1**, 830–840.
5. I. R. Farrell, P. Matousek, M. Towrie, A. W. Parker, D. C. Grills, M. W. George and A. Vlček, *Inorg. Chem.*, 2002, **41**, 4318–4323.