

# Mapping Catalysis with Time-resolved Infra-red Spectroscopy

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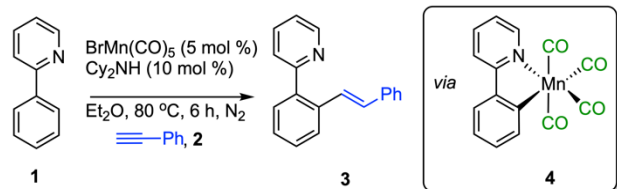
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## Introduction

Catalysis is a central science and critically important to chemical processes, underpinning the synthesis of an eclectic array of modern agrochemicals, pharmaceuticals and materials, including many commonly used products in the home. A single catalyst entity, by definition, speeds up a chemical reaction without being consumed: it offers an alternative, lower energy pathway from the starting materials to the products. Ensuring that the optimum catalyst for a given synthesis is used will improve its efficacy, resulting in lower operating costs as less energy is required to perform the reaction and there are fewer problems with purification, through improve product selectivity.

Understanding the chemical steps which underpin catalysis (the so-called catalytic cycle) enables the key steps which control the rate of the reaction, and the overall selectivity, to be identified. With this information, the structure of the catalyst, *i.e.* the species that first interacts and activates the substrate, can be rationally optimised, resulting in a species with improved activity. However, observing each and every step in a catalytic cycle is fraught with difficulty as the species involved are likely to be present in low concentration and have short lifetimes.

The photochemical activation of a catalyst, which normally operates at high temperatures, offers an opportunity to circumvent these problems. Using light to simulate the chemical process which leads to catalyst activation under thermal conditions will allow time-resolved spectroscopy to monitor its fate as it interacts with the substrates and solvents, thus providing detailed information about its behaviour. To achieve this goal a reaction-catalysed by a manganese(I) carbonyl compounds was selected for study (Scheme 1). This is a potentially powerful synthetic method as it results in the selective functionalisation of a carbon-hydrogen bond in the 2-phenylpyridine substrate, **1**, allowing coupling with unsaturated substrates such as alkynes, **2**, to give **3**.<sup>[1]</sup> The manganese carbonyl complex, **4**, was identified as a key intermediate in this process.<sup>[2]</sup>



Scheme 1. Mn-catalysed C-H functionalisation reaction and structure of key intermediate.

On heating, complex **4** is thought to lose one of the coordinate carbonyl (CO) ligands in order to allow **2** to bind to the metal, a process that previous results have demonstrated could be promoted photochemically.<sup>[3]</sup> It was envisaged that time-resolved infra-red spectroscopy (TRIR) could be used to initiate loss of a CO ligand from **4** and then the changes to the vibrational modes of the remaining three carbonyls would

provide information about the interaction of the metal with substrate **2**. This would result in the highly selective generation and identification of the key catalytic intermediates. Time-resolved multiple probe spectroscopy (TR<sup>MPS</sup>)<sup>[4]</sup> provides the temporal range (ps- $\mu\text{s}$ ) needed to study a wide range of catalytically relevant processes, which can be photochemically initiated.

## Methodology

Carbonyl dissociation from **4** was initiated by photolysis at 355 nm with ultrafast laser pulses. Initial experiments were performed in neat substrate to ensure that this was the only species that the photochemically activated Mn-complex could interact with. Subsequent experiments were performed in a toluene solution of substrate. All spectroscopic data were acquired with the sample flowing through a rastered IR cell to ensure that the sample was refreshed between pump pulses. The subsequent photoproducts were observed through the changes in the metal carbonyl region of the infra-red spectrum (Mn-CO stretching bands at  $1850\text{--}2200\text{ cm}^{-1}$ ) and assignments performed with a combination of control experiments with related substrates, and calculations made using Density Functional Theory.

## Results

The TRIR spectra obtained on photolysis of **4** in neat **2** at a number of pump-probe delays are shown in Figure 1. The data are presented as difference spectra, with the negative bands corresponding to the ground state spectrum of **4**, indicating its consumption, and the positive bands the photoproducts which have been generated. These data provide the evidence for the formation of three new photoproducts, **5**, **6** and **7**. Species **5** is present at even the shortest pump-probe delays (1 ps) and as demonstrated by the presence three bands in its spectrum, corresponds to a species which has undergone ultrafast CO-dissociation. By comparison with a spectrum recorded in toluene solution alone, **2** was assigned as being bound to the manganese though the arene group of the  $\text{PhC}\equiv\text{CH}$ .<sup>[5]</sup>

Over the course of 1 ns, **5** converted to **6**. The carbonyl bands in the IR spectrum in **6** were blue-shifted in comparison to **5** (and also **7**) which indicates a better acceptor ligand is present on the Mn. This is consistent with a change in binding mode of the alkyne to a  $\pi$ -alkyne form. The formation of **7** corresponds to the formal insertion of the alkyne into the Mn-C bond which represents the direct observation of the carbon-carbon bond formation step that underpins the catalytic cycle. Analysis of the kinetics demonstrated that the rate of formation of **7**,  $k = (1.35 \pm 0.09) \times 10^5\text{ s}^{-1}$ , corresponded to the loss of **6**.

Repeating the experiment, but using a 0.5 % *v/v* toluene solution of  $\text{PhC}\equiv\text{CH}$ , resulted in similar observations being made. At short pump-probe delays, the toluene complex **8** was observed which over the course of 500 ns converted to **6**,  $k_{\text{obs}} = (3.85 \pm 0.63) \times 10^6\text{ s}^{-1}$ .

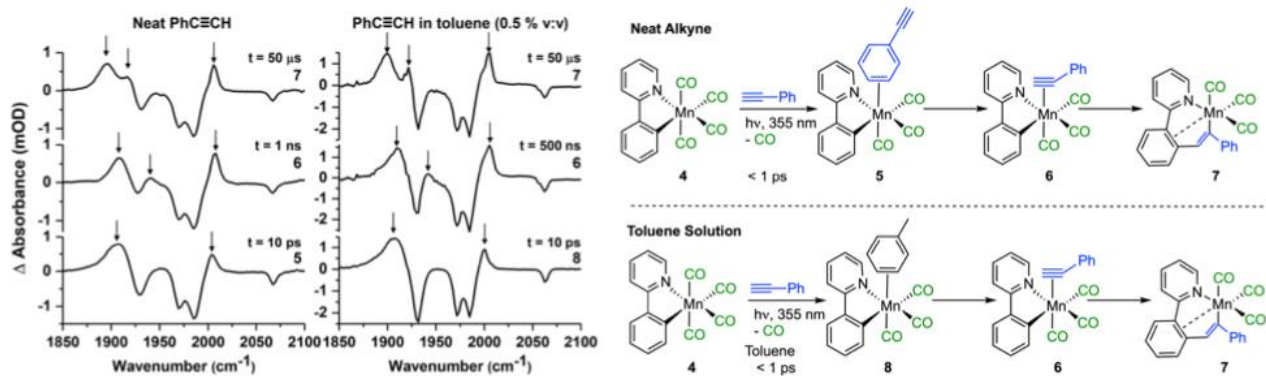


Figure 1. Left TRIR spectra obtained from the photolysis of **4** in neat PhC≡CH and in toluene solution. Right Reaction scheme showing the structures of the complexes formed.

This process demonstrates that the initial coordination event to the manganese(I) centre is statistical in nature – there is more toluene present than **2** – however PhC≡CH is a better ligand for manganese(I), and therefore it substituted the weakly bound solvent. Complex **6** then converted to **7** at a statistically identical rate to that observed in neat **2**,  $k = (1.73 \pm 0.33) \times 10^5 \text{ s}^{-1}$ , consistent with this being an intramolecular coupling. Further evidence for this picture of behaviour comes from an experiment performed with a more concentrated (6% v/v) solution of **2** in toluene. In this case the rate of conversion of **8** to **6** was more rapid than in the more dilute experiment,  $k_{\text{obs}} = (1.77 \pm 1.07) \times 10^7 \text{ s}^{-1}$ , consistent with a bimolecular substitution. The formation of **7** from **6** was again occurring at a statistically identical rate,  $k_{\text{obs}} = (1.63 \pm 0.18) \times 10^5 \text{ s}^{-1}$ .

This methodology has been extended to study related carbon-carbon bond formation reactions catalysed by manganese(I).<sup>[5]</sup> For example, photolysis of **4** in neat *n*-butylacrylate, **9**, results in a complex series of events (Figure 2).

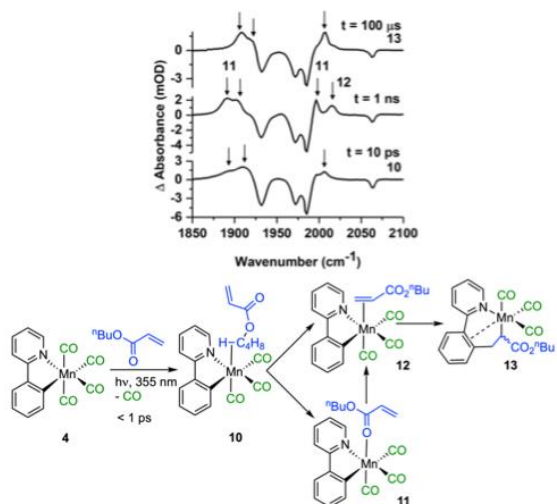


Figure 2 Top TRIR spectra obtained from the photolysis of **4** in neat <sup>n</sup>BuCO<sub>2</sub>CH=CH<sub>2</sub>. Bottom Reaction scheme showing the structures of the complexes formed.

At short times a manganese(I) complex, in which the <sup>n</sup>BuCO<sub>2</sub>CH=CH<sub>2</sub> is bound to the metal through the two electrons of a C-H bond, **10** is formed. Over the course of 1 ns, **10** converts to two new species, **11** ( $k = (2.89 \pm 0.55) \times 10^{10} \text{ s}^{-1}$ ) and **12** ( $k = (2.72 \pm 0.79) \times 10^{10} \text{ s}^{-1}$ ). In complex **11** the acrylate is bound to the manganese(I) through the oxygen atom of the ester (likely C=O) group, whereas in **12** it is bound in an η<sup>2</sup>-alkene fashion. The isomerisation from **10** to **11** and **12** was investigated with the aid of the ethylacrylate EtCO<sub>2</sub>CH=CH<sub>2</sub>, in this case the isomerisations were more rapid  $k = (5.95 \pm 0.51) \times 10^{10} \text{ s}^{-1}$  and  $k = (4.96 \pm 0.71) \times 10^{10} \text{ s}^{-1}$ , which is consistent with a picture in which the manganese(I) complex is “chain walking”

along the alkyl chain to either the oxygen atom or the carbon-carbon double bond. This process of chain walking is simply quicker with the shorter ethyl chain.

Complex **13** was observed to be formed over 100 μs and corresponding to C-C bond formation between the cyclometalated ligand and the acrylate. In order to determine which species was involved in the C-C bond formation the kinetics of the formation of **11**, **12** and **13** were modelled against a series of potential reaction mechanisms. The best fit to the experimental data was the scenario **11** → **12** → **13** with rate constants of  $k = (3.21 \pm 0.01) \times 10^4 \text{ s}^{-1}$  and  $k = (3.62 \pm 0.01) \times 10^4 \text{ s}^{-1}$  respectively. The mechanistic picture is supported by calculations using Density Functional Theory, which demonstrated that there is a low energy transition state connecting **12** and **13**, but the formation of **13** from **11** would proceed through a far too high energy state.

## Conclusions

The photochemical activation of thermally inert manganese(I) carbonyl compounds to simulate the activation of the catalyst under more forcing conditions. The temporal flexibility provided by TR<sup>M</sup>PS has allowed for a range of catalytically relevant events to be observed. At short pump-probe delays, kinetically controlled binding occurs and, in toluene the solvation event is observed. The substitution of the bound solvent occurs over a period of ns, before the direct observation of carbon-carbon bond formation. This demonstrates the power of TR<sup>M</sup>PS to observe the events underpinning catalysis by manganese(I) carbonyl species, where the method can be exploited in the study of other systems that can be suitably activated by light.

## Acknowledgements

We are grateful to Syngenta and the EPSRC (CASE studentship to L.A.H. (EP/N509413/)) for funding as well as the Science and Technology Facilities Council for access to the ULTRA facilities at the Rutherford Appleton Laboratory.

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