

New insights into the photochemistry of $[\text{CpFe}(\text{CO})_2]_2$ using picosecond through microsecond time-resolved infrared spectroscopy (TRIR)



Christopher M. Brookes^a, Justin P. Lomont^b, Son C. Nguyen^b, James A. Calladine^a, Xue-Zhong Sun^a, Charles B. Harris^b, Michael W. George^{a,*}

^aSchool of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK

^bDepartment of Chemistry, University of California, Berkeley, CA 94720, USA

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ABSTRACT

Picosecond to microsecond time-resolved infrared spectroscopy (TRIR) has been used to investigate the photochemistry of $[\text{CpFe}(\text{CO})_2]_2$. The early-time TRIR spectra are dominated by vibrationally hot transient species and this leads to spectra with broad featureless bands. The majority (84%) of the well characterized $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_3$, with a band at 1824 cm^{-1} , grows in on a timescale (15–20 ps) similar to the cooling rate of many of the $\nu(\text{CO})$ bands, and this arises from presumably the initially formed species, $[\text{CpFe}(\text{CO})(\mu\text{-CO})_2\text{FeCp}]$ of which we were unable to find clear evidence. However, $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_3$ is formed by two different processes and under CO the remaining slower formation (16%) occurs at the same rate ($46 \pm 2\text{ ns}$) as a transient band at 1908 cm^{-1} decays. The 1908 cm^{-1} had been previously observed in an earlier study but its identity remained unclear. We find that this 1908 cm^{-1} intermediate has no corresponding bridging $\nu(\text{CO})$ band and is formed by a 1-photon process. This band is assigned to a dicarbonyl-loss photoproduct, $[\text{CpFe}(\text{CO})]_2$ and is a rare example of double CO loss occurring following a single-photon excitation in the condensed phase.

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1. Introduction

In solution $[\text{CpFe}(\text{CO})_2]_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) exists as an equilibrium mixture of *cis* and *trans* isomers, with each isomer possessing two terminal and two bridging CO ligands [1–5]. $[\text{CpFe}(\text{CO})_2]_2$ has a rich photochemistry which has been extensively studied both in solution and frozen matrices, with a variety of photoproducts being observed.

Early UV–Vis flash photolysis experiments [6] established the presence of two primary photochemical pathways: (i) CO-loss to yield the triply bridged dinuclear species, $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_3$; and (ii) Fe–Fe bond homolysis to yield a pair of 17-electron $[\text{CpFe}(\text{CO})_2]^\cdot$ radicals. Scheme 1 summarizes the observed photochemical pathways of $[\text{CpFe}(\text{CO})_2]_2$. Photochemical matrix isolation experiments have suggested that only the *trans* parent isomer gives rise to the formation of $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_3$ [7], and the structure of this complex has been confirmed via ^{13}C O substitution experiments as well as characterization of the crystal structure of the permethylated Cp derivative, $\text{Cp}^*\text{Fe}_2(\mu\text{-CO})_3$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) [8].

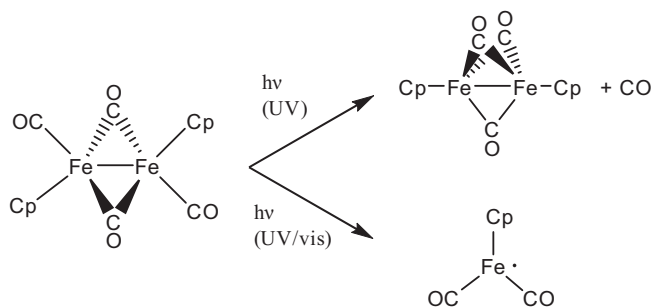
Several time-resolved infrared (TRIR) studies have characterized the reactivity of this complex on timescales ranging from

femtoseconds to microseconds [9–14]. Microsecond TRIR experiments performed following UV (308 nm) photolysis observed the formation of $\text{CpFe}(\text{CO})_2^\cdot$, as well as the triply bridged CO-loss product, $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_3$ [9], whilst visible (510 nm) excitation led only to the formation of the radical [10]. Picosecond experiments [11] showed that the radical species is observable within *ca.* 2 ps after photoexcitation, and femtosecond experiments [12,13] monitored geminate recombination of the radicals to reform the parent complex.

UV photolysis experiments in *n*-heptane containing CH_3CN or THF yield a substitution product in which one CO ligand from $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_3$ has been substituted to give the corresponding $\text{Cp}(\text{CO})\text{Fe}(\mu\text{-CO})_2\text{Fe}(\text{L})\text{Cp}$ complex ($\text{L} = \text{CH}_3\text{CN}$ or THF) [10]. In a related study, $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_3$ has been demonstrated to be the reactive intermediate involved in the reaction of $[\text{CpFe}(\text{CO})_2]_2$ with alkenes [16]. Interestingly, microsecond TRIR experiments showed that, while $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_3$ reacts with CH_3CN to yield the substitution product (as expected), neither $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_3$ nor $[\text{CpFe}(\text{CO})_2]^\cdot$ appear to react with THF. Nonetheless, $\text{Cp}(\text{CO})\text{Fe}(\mu\text{-CO})_2\text{Fe}(\text{THF})\text{Cp}$ was observed in sub-microsecond TRIR experiments [8]. Visible photolysis showed reduced intensity for the bands of both $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_3$ and $\text{Cp}(\text{CO})\text{Fe}(\mu\text{-CO})_2\text{Fe}(\text{THF})\text{Cp}$, implying that the formation of these two species is linked in some manner. Concentration dependent UV photolysis experiments showed that as the

* Corresponding author. Tel.: +44 (0)115 9513512.

E-mail address: Mike.George@nottingham.ac.uk (M.W. George).



Scheme 1. Photochemical reaction pathways of *trans*-[CpFe(CO)₂]₂ leading to the formation of the triply bridged species or the radical.

concentration of THF was increased, the yield of Cp(CO)Fe(μ-CO)₂Fe(THF)Cp also increased accompanied by a decrease in the yield of Cp₂Fe₂(μ-CO)₃. However, no effect on the lifetime of Cp₂Fe₂(μ-CO)₃ in solution was observed. These facts point to a precursor species, **X**, that results in subsequent formation of both Cp₂Fe₂(μ-CO)₃ and Cp(CO)Fe(μ-CO)₂Fe(THF)Cp [10]. A proposed candidate for the intermediate **X** has been the di-bridged species Cp(CO)Fe(μ-CO)₂FeCp, though this has never been directly characterized. An ultrafast time-resolved UV/visible absorption study also observed the formation of a precursor to the triply bridged product, which was suggested to be Cp(CO)Fe(μ-CO)₂FeCp [17].

Another transient intermediate, **Y**, observed *via* a band at 1908 cm⁻¹ on the picosecond timescale [14], was proposed to be the singly bridged species Cp(CO)Fe(μ-CO)Fe(CO)Cp. In that study, experimental limitations prevented the collection of data below 1780 cm⁻¹, and thus the presence or absence of a bridging band for **Y** could not be ascertained. **Y** cannot be the aforementioned precursor **X**, since picosecond experiments show that Cp₂Fe₂(μ-CO)₃ is fully formed prior to the decay of **Y**.

Other proposed intermediates in the photochemistry of [CpFe(CO)₂]₂ include CpFe(μ-CO)₂(μ-η¹,η²-CO)FeCp [17], which contains one semi-bridging CO ligand, and Cp(CO)₂Fe(μ-CO)Fe(CO)Cp, a rearrangement isomer of the parent molecule [18]. Extended photolysis in a low-temperature matrix has also been used to observe the dicarbonyl-loss product, [CpFe(CO)]₂, characterized by absorptions at 1958 and 1904 cm⁻¹ [19]. Clearly the photochemistry of this complex has attracted substantial interest in the organometallic chemistry and spectroscopy communities and there are several questions which remain unanswered regarding the structure and reactivity of the intermediates that are formed.

The goal of the present paper is to shed light on the structure of the species **Y** corresponding to the IR band previously observed at 1908 cm⁻¹ in solution and to investigate the formation of the triply bridged CO loss product, Cp₂Fe₂(μ-CO)₃.

2. Experimental

Some of the findings in this paper were made independently in both laboratories and we have published these findings together. The data shown is from the Nottingham ps/ns-TRIR apparatus, the details of which have been described elsewhere. [20] Briefly, the 1 kHz output (800 nm, 100 fs) of a Ti:Sapphire oscillator/regenerative amplifier system (Spectra Physics) pumps a TOPAS-C OPA (Light Conversion) with a difference frequency generator to produce tunable mid-IR pulses with a spectral bandwidth of ca. 180 cm⁻¹. A portion of the IR pulse is reflected onto a single-element MCT detector (Kolmar Technology) which serves to reference the pulse-to-pulse intensity fluctuations. The remainder of the IR probe beam is focused and overlaps with the pump beam at the sample cell. For ps-TRIR experiments, the 266 nm pump is obtained with a harmonic generator (Minioptic Technology, Inc.)

and the timing controlled using an optical delay line. In the experiments on longer time scales (ns to μs), the excitation pulse is produced by a Q-switched Nd:YVO₄ laser (Advanced Optical Technology) synchronized to the Spitfire Pro amplifier. The delay between the pump and probe pulses is controlled with a pulse generator (Stanford Research Systems) from 0.5 ns to 100 μs. The broadband transmitted probe pulse is dispersed with a 250 mm spectrograph (Spectral Products) and detected with a 128-element MCT array detector (Infrared Associates). A 144-channel amplifier and 16-bit analogue-to-digital converter (Infrared Systems Development Corp.) were employed. The pump energy is altered using neutral density filters. An IR flow cell with CaF₂ windows is mounted on a rapid XY raster to eliminate laser-induced heating and photochemical degradation of the sample and windows.

3. Results and discussion

3.1. A precursor to Cp₂Fe₂(μ-CO)₃; the identity of intermediate **X**

Following up on previous studies indicating the existence of a precursor to the formation of the triply bridged species, Cp₂Fe₂(μ-CO)₃ [10,16], picosecond TRIR experiments were carried out on [CpFe(CO)₂]₂ in *n*-heptane under 1.5 atm of CO. Fig. 1 shows the TRIR difference spectra at several time delays after 266 nm photolysis. A precursor species to Cp₂Fe₂(μ-CO)₃, **X**, has previously been suggested to exist based on evidence surrounding the linked formation of Cp₂Fe₂(μ-CO)₃ and Cp(CO)Fe(μ-CO)₂Fe(THF)Cp [10]. A short-lived transient precursor has also been observed in time-resolved UV-Vis experiments [16]. In both cases the precursor has been posited to be Cp(CO)Fe(μ-CO)₂FeCp, but direct evidence for its structure has not been previously observed.

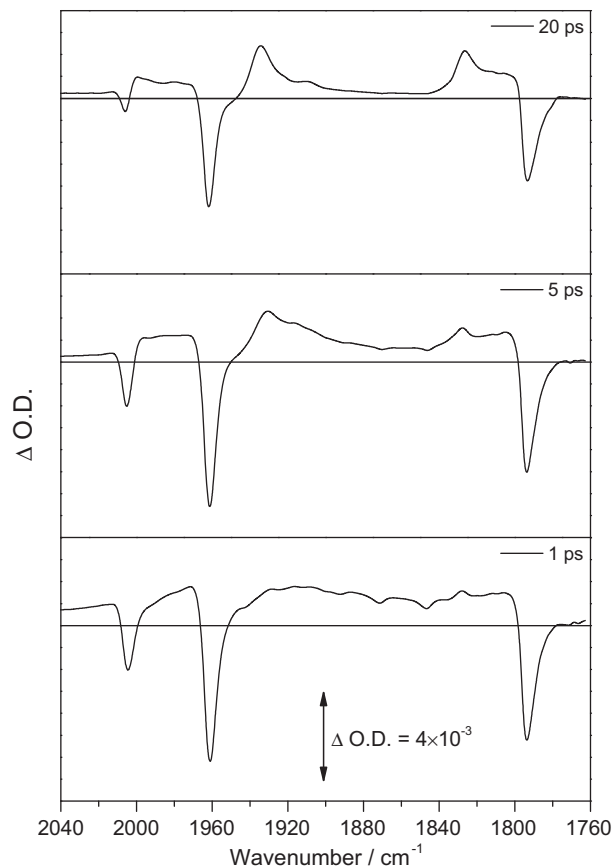


Fig. 1. Picosecond TRIR difference spectra of [CpFe(CO)₂]₂ following 266 nm photolysis in *n*-heptane under 1.5 atm CO.

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