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First direct observation of a CO-bridged primary photoproduct of $[Ru_3(CO)_{12}]$ by picosecond time-resolved IR spectroscopy

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For the first time, a CO-bridged primary photoproduct was observed for $[Ru_3(CO)_{12}]$ by using picosecond time-resolved IR spectroscopy (ps-TRIR).

Photochemical and photophysical studies of transition metal carbonyl clusters are of considerable interest, not only because of the potential of these compounds to act as versatile catalysts or catalyst precursors,[1] for example in fine chemistry, but also in view of their challenging application as key components of more complex supramolecular systems. The photoactivation of (thermally stable) cluster compounds may lead to novel reaction types with high selectivity.[2] In supramolecular systems, where clusters may function as a bridge between a donor and an acceptor site, the changes in the electronic and structural properties of a cluster upon excitation may be utilized, for example, in photoinduced vectorial electron/energy transport from the donor to the acceptor.

Time-resolved IR spectroscopy (TRIR), where UV-visible flash photolysis is combined with (ultra)fast IR detection, is a powerful tool for probing the primary events after photoexcitation. This applies in particular to complexes containing strongly IR-active ligands like CO, that can act as direct IR probes of the electron density at the metal centre. As the excited states of transition metal clusters are usually too short-lived to be studied with nanosecond (ns) transient absorption or TRIR, faster spectroscopic techniques are required to characterize the excited state and to study the formation of the primary photoproducts. Although several picosecond (ps) TRIR studies on simple, mononuclear transition metal complexes with *e.g.* M(0) (M = Cr, W),[3] M(II) (M = Ru, Os)[4] and Co(I)[5] centres have been reported, ps-TRIR studies of polynuclear transition metal complexes are scarce. In order to investigate whether this technique could contribute to the unraveling of complex mechanistic problems in transition metal cluster photochemistry, we performed a ps-TRIR study on the model cluster $[Ru_3(CO)_{12}]$.

The photoreactivity of the triangular clusters $[M_3(CO)_{12}]$ (M = Ru, Os) has been studied in great detail over the last few decades.[6–8] In brief, photoexcitation into the two lowest-energy absorption bands of these clusters has been assumed to result in formation of a reactive isomer of $[M_3(CO)_{12}]$ (M = Ru, Os), which is supposed to be the key intermediate for subsequent reactions but has never been observed directly. This reactive isomer was proposed[7] to consist of an open cluster core in which one M–M bond is heterolytically split and one carbonyl has moved to a bridging position to maintain the charge neutrality at both M atoms (see Fig. 1).

In contrast to this, two different bridging carbonyl ligands were recently revealed for a photoproduct of the substituted clusters $[Os_3(CO)_{10}L]$ (L = 1,3-diene)[9] with ns-TRIR spectroscopy. In this work we present the results of a ps-TRIR study of the reactive photoisomer of $[Ru_3(CO)_{12}]$, which represents the first application of this technique on a transition metal cluster. Excitation at 400 nm followed by IR probing, was used to investigate if a bridging carbonyl is indeed present in this product.

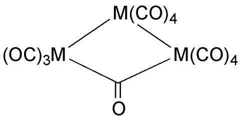

Fig. 1 Proposed structure of the open-core primary photoproduct of $[M_3(CO)_{12}]$ (M = Ru, Os).

The ground state IR spectrum of $[Ru_3(CO)_{12}]$† in heptane at room temperature shows four distinct ν(CO) IR bands at 2061, 2031, 2017 and 2012 cm^{-1}. Picosecond TRIR spectra‡ were recorded in this solvent at several pump-probe delays between 0 and 500 ps after excitation into the lowest-energy absorption band, having predominantly metal–metal bonding to metal–metal antibonding ($\sigma \rightarrow \sigma^*$) character. Fig. 2 shows representative spectra at six selected time delays.

After excitation, the first spectra display instantaneous bleaching of the parent ν(CO) bands superimposed on a broad, unresolved transient absorption due to the excited state of $[Ru_3(CO)_{12}]$. Similar broad, featureless transient absorption bands were observed upon excitation into the $\sigma \rightarrow \sigma^*$ transition of $[M_2(CO)_{10}]$ (M = Mn, Re)[10] and have been reported to result from the appearance of red-shifted CO stretching frequencies due to the anharmonic coupling with low-frequency (M–C stretching and M–C–O bending) vibrational modes, which are highly activated upon light excitation.

In the first few picoseconds, this broad transient absorption resolves into distinct product absorption bands (2051, 2021 and 2007 cm^{-1}) as the bands become narrower and slightly shift to higher frequency. These spectral changes are attributed to vibrational relaxation of the low-frequency vibrational modes.[3,5,10] Upon further decay ($\leq$20 ps) another positive shift of *ca.* 5 cm^{-1} is observed for the 2021 and 2051 cm^{-1} product bands, which is attributed to the formation of a primary photoproduct. On this time scale also a new ν(CO) band grows in at 1850 cm^{-1}. The latter band is assigned to a bridging

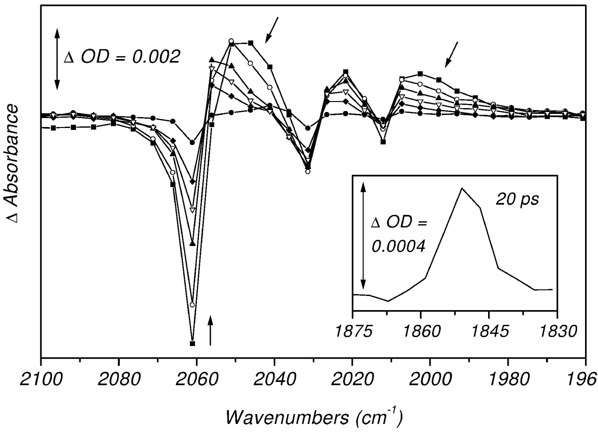

Fig. 2 TRIR spectra of $[Ru_3(CO)_{12}]$ in heptane at (■) 0 ps, (○) 3 ps, (▲) 20 ps, (∇) 40 ps, (◆) 80 ps and (●) 500 ps after 400 nm (*ca.* 150 fs FWHM, 5 μJ per pulse) excitation. The arrows indicate the shift of the band maxima with increasing time delay following excitation.

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carbonyl and decays on a similar time scale (20–500 ps) as the bands in the terminal ν(CO) region. Upon decay of the transient absorption bands parent bleach recovery also takes place. On early time scales ($\leq$20 ps), the partial recovery of the parent bleach at 2061 cm^{-1} is mainly due to increased overlap with the product absorption band. This is inferred from the observation that the parent bleach at 2031 cm^{-1}, for which no such change in overlap takes place, only shows a minor decrease in signal strength. The excited state is therefore assumed to be almost completely converted into the primary photoproduct. On longer time scales (up to 500 ps), the shape and position of the transient absorption bands do not change and recovery of the parent bleach signals on these time scales is accordingly ascribed to the regeneration of the parent cluster. At 500 ps after the laser pulse the initially formed transient absorption bands have almost completely disappeared and two small remaining bands at 2040 and 2007 cm^{-1} indicate the formation of a minor amount ($<$10%) of a second, longer-lived photoproduct. The incomplete bleach recovery supports this latter conclusion.

The nearly complete reversibility of the system under the experimental conditions implies that the cluster core remains intact and agrees with the formation of $[Ru_3(CO)_{11}(\mu\text{-}CO)]$ as the primary photoproduct. As both vibrational relaxation processes and decay of the excited state take place within a few picoseconds, the determination of the excited state lifetime from the decay of the terminal ν(CO) bands is hampered. However, the grow in of the bridging ν(CO) band at 1850 cm^{-1} is not accompanied by a shift to higher frequency and is therefore assumed not to be influenced by vibrational relaxation processes. Gaussian curve fitting was therefore performed on this well separated bridging ν(CO) band. Plotting the peak area of the 1850 cm^{-1} band for each time delay against time allows the determination of both the excited state lifetime (3.9 ± 0.9 ps, Fig. 3(a)), which is assumed to correspond with the grow in of the 1850 cm^{-1} band, and the lifetime of the primary photoproduct (56.6 ± 6 ps, Fig. 3(b)). The latter lifetime is in good agreement with the values obtained from the terminal ν(CO) bands (*e.g.* τ = 52.5 ± 4 ps at 2051 cm^{-1}, Fig. 3(c)), whose decay after t_d = 20 ps can be mainly ascribed to regeneration of the parent cluster. The observed kinetics rule out CO loss as the primary photoprocess since, assuming that photoexpelled CO escapes from the solvent cage, the back-reaction in this case would occur under diffusion control and would therefore take place on a much longer time scale.

The IR bands of the remaining photoproduct (after 500 ps) are close to those reported for the unsaturated cluster $[Ru_3(CO)_{11}]$.[8] According to the literature, $[Ru_3(CO)_{11}]$ is not likely to be formed from $[Ru_3(CO)_{11}(\mu\text{-}CO)]$ and the observation of this species may therefore be due to irradiation into the tailing higher-energy transition of $[Ru_3(CO)_{12}]$, which is known to result in CO loss. Concerning the structure of the $[Ru_3(CO)_{11}(\mu\text{-}CO)]$ photoproduct, no unambiguous conclusions can be drawn. The close correspondence with the ν(μ-CO) stretching frequency of $[Ru_3(CO)_{11}]$ (1840–1860 cm^{-1})[8] suggests cleavage of a M–M bond and formation of a single CO bridge. Quantum chemical calculations including geometry optimizations to support these assignments, are in progress.

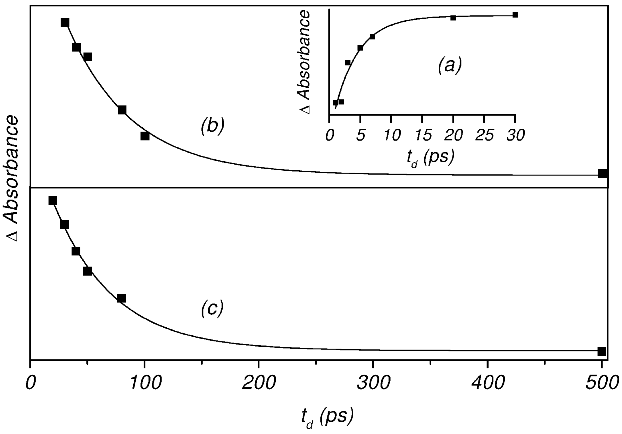

Fig. 3 Kinetic traces of $[Ru_3(CO)_{12}]$ in heptane representing (a) the grow in of the ν(CO) band at 1850 cm^{-1} (b) the decay of the 1850 cm^{-1} band and (c) the decay at 2051 cm^{-1}.

In conclusion, picosecond TRIR spectroscopy proves to be a powerful tool in the field of photochemistry of transition metal carbonyl clusters. For the first time we were able to observe and characterize the primary photoproduct of $[Ru_3(CO)_{12}]$. The appearance of a single ν(CO) band in the bridging carbonyl region supports the formation of a reactive isomer of $[Ru_3(CO)_{12}]$, as proposed in the literature.

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Notes and references

† $[Ru_3(CO)_{12}]$ (Strem Chemicals) and heptane (spectroscopic grade, Aldrich) were used as received.

‡ The ps-TRIR spectra were recorded using the PIRATE set-up at the Central Laser Facility of the Rutherford Appleton Laboratory. Second harmonic generation of a part of the 800 nm output of a Ti-sapphire regenerative amplifier (1 kHz, 150 fs, 2 mJ) produced 400 nm pulses for excitation of the sample. The other part of the 800 nm light was used to pump an optical parametric amplifier generating tuneable mid IR outputs (150–200 cm^{-1} FWHM, 200 fs) by frequency down conversion of the signal and idler outputs in an $AgGaS_2$ crystal. Changes in the IR absorption were recorded by normalising the outputs from a pair of HgCdTe linear array detectors on a shot-by-shot basis.

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