Photo- and redox activation of homo-and heteronuclear transition metal clusters: experiment and theory
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Chapter 3

First Direct Observation and Characterization of the Lowest Excited State and Primary Photoproducts of [Ru₃(CO)₁₂] and [Os₃(CO)₁₀(1,3-cyclohexadiene)] by Picosecond Time-Resolved UV-vis and IR Spectroscopies

Part of this chapter has been published in:
3.1 Abstract

Combined picosecond transient absorption and time-resolved infrared studies have been performed in order to characterize the excited state and monitor the formation of the primary photoproducts of the clusters [Ru3(CO)12] (1) and [Os3(CO)10(1,3-cyclohexadiene)] (2). The TA spectra of (1), obtained by irradiation into its lowest-energy absorption band, reveal the formation ($\tau = 5.6$ picoseconds) of a coordinatively unsaturated photoproduct, possessing a transient absorption around 505 nm. The latter photoproduct completely regenerates the parent cluster with a lifetime of $46 \pm 5$ picoseconds. Time-resolved IR spectra of 1 on the picosecond time scale show the appearance of a single ν(CO) band in the bridging carbonyl region, decaying with a lifetime of ca. 50 picoseconds. Both results support the assignment of the primary photoproduct of 1 as the coordinatively unsaturated open-triangle isomer [Ru3(CO)11(µ-CO)], consistent with the proposal in the literature. Theoretical (TD-DFT) calculations revealed that the low-lying electronic transitions of cluster 2 possess predominantly σ(core)-to-π*(CO) character. From the lowest $^3\sigma\pi^*$ excited state cluster 2 undergoes fast metal-metal(diene) bond cleavage ($\tau = 3.3$ picoseconds), resulting in the formation of a similar single-bridged primary photoproduct (2a), as observed for 1. Due to the donor ability of the diene ligand and the unequal distribution of electron density in 2a, the subsequent formation of a second CO bridge is observed, producing the secondary photoproduct [Os3(CO)8(µ-CO)2(1,3-diene)] (2b), previously observed on the nanosecond time scale. The latter photoproduct, which is characterized by a pronounced transient absorption band around 630 nm, is known to mainly regenerate the parent cluster with a lifetime of about 100 ns in hexane.

3.2 Introduction

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,\(^1\)\(^2\) 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.\(^3\)\(^6\) In supramolecular systems, where clusters may connect donor and acceptor sites, the photoinduced changes in the electronic and structural properties of a cluster upon excitation may be utilized, for example, in controlled electron/energy transport from the donor to the acceptor (see Chapter 4, Part C).

Time-resolved infrared spectroscopy (TRIR), where UV-visible flash photolysis is combined with (ultra)fast infrared 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 or NO 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 (TA) or TRIR, faster spectroscopic techniques are required to characterize the excited state and to monitor the formation of the primary photoproducts. Although several picosecond (ps) TRIR studies of simple, mononuclear transition metal complexes with \( e.g. M(0) (M = Cr, W) \), \( M(II) (M = Ru, Os) \) and \( Co(I) \) centres have been reported, those of di- and polynuclear transition metal complexes are scarce. In order to explore whether this technique could contribute to the unravelling of complex mechanistic problems in transition metal cluster photochemistry, we performed a TRIR study on the model cluster \([Ru_3(CO)_{12}] (1) \) and the substituted cluster \([Os_3(CO)_{10}(s\text{-}cis\text{-}1,3\text{-cyclohexadiene})] (2) \).

The photoreactivity of the triangular clusters \([M_3(CO)_{12}] (M = Ru, Os) \) has been studied in detail over the last three decades. In brief, irradiation into the two lowest-energy absorption bands of these clusters has been assumed to result in the formation of a reactive isomer of \([M_3(CO)_{12}] (M = Ru, Os) \), the key intermediate for the follow-up thermal reactions that, however, has never been observed directly. This reactive isomer has been proposed 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 (Figure 1a). In contrast to this, two different bridging carbonyl ligands have recently been identified in a photoproduct of the substituted cluster \([Os_3(CO)_{10}(s\text{-}cis\text{-}1,3\text{-cyclohexadiene})] \) with ns TRIR spectroscopy. Similar to the reactive photoisomer of \([Ru_3(CO)_{12}] \), the non-radical photoproduct of \([Os_3(CO)_{10}(s\text{-}cis\text{-}1,3\text{-cyclohexadiene})] \) has been proposed to have one Os-Os(diene) bond split and the two remote osmium centres connected by a bridging carbonyl group. In addition, the resulting electron deficiency at Os1 is partly compensated by donation from a carbonyl group bridging over the Os1-Os2 bond (Figure 1b). Apart from the challenging mechanistic aspects of their photoreactions, the interest in diene-substituted osmium clusters also originates from their application as activated precursors in the synthesis of specific high-nuclearity clusters or derivatives bearing photo- and/or redox active ligands.

![Proposed structure of the open-core photoproducts](image-url)

**Figure 1.** Proposed structure of the open-core photoproducts of: (a) \([M_3(CO)_{12}] (M = Ru, Os) \) and (b) \([Os_3(CO)_{10}(1,3\text{-diene})] \).
In this chapter we present the results of a combined ps TA and TRIR study of the primary photoproducts of \([\text{Ru}_3(\text{CO})_{12}] (1)\) and \([\text{Os}_3(\text{CO})_{10}(s\text{-cis-1,3-cyclohexadiene})] (2)\). For both clusters ps TA spectra were recorded in order to determine the decay kinetics of the excited state and its absorption features. In order to get more information about the clusters in their excited state and the primary photoproducts, a ps TRIR study was performed, which represents the first application of this technique in the field of transition metal clusters. First, photoexcitation followed by IR probing was used to prove whether a bridging carbonyl ligand is indeed present in the reactive photoisomer of \([\text{Ru}_3(\text{CO})_{12}]\). In the second part, ps TRIR spectra in the bridging carbonyl region were recorded in order to reveal at what stage the two different CO bridges in the photoproduct \([\text{Os}_3(\text{CO})_{8}(\mu\text{-CO})_2(1,3\text{-cyclohexadiene})]\) are formed. Density functional theoretical (DFT) calculations were performed in order to support the experimental results.

### 3.3 Experimental section

**Materials and preparations.** Solvents of analytical grade (Acros) were freshly distilled from sodium wire (hexane) or CaH₂ (acetonitrile (MeCN), dichloromethane) under an atmosphere of dry N₂. \([\text{Ru}_3(\text{CO})_{12}] (1)\), \([\text{Os}_3(\text{CO})_{12}]\) (Strem Chemicals), 1,3-cyclohexadiene (Acros) and solvents of spectroscopic grade (Aldrich: dichloromethane, heptane) were used as received. Trimethylamine-N-oxide, Me₃NO-2H₂O (Alfa), was dehydrated before use by vacuum sublimation. Silica 60 (70-230 mesh, Merck) for column chromatography was activated by heating in vacuo at 450 K overnight and stored under N₂.

**Synthetic procedures.** All syntheses were performed under an inert atmosphere of dry N₂, using standard Schlenk techniques. For the preparation of \([\text{Os}_3(\text{CO})_{10}(s\text{-cis-1,3-cyclohexadiene})]\) (2) we followed a similar synthetic procedure as employed by Braga et al.,²³ using \([\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]\).²⁴

**Synthesis of \([\text{Os}_3(\text{CO})_{10}(s\text{-cis-1,3-cyclohexadiene})]\) (2).** 1,3-Cyclohexadiene (2.5 ml; 26 mmol) was added to a solution of \([\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]\) (500 mg; 0.54 mmol) in CH₂Cl₂ (70 ml). The reaction mixture was stirred for 2.5 h. After this period the solvent was evaporated in vacuo. Purification of the crude product by column chromatography over silica, using 10:1 hexane/CH₂Cl₂ as eluent, yielded cluster 2 as a yellow powder in 65% yield. IR ν(CO) (hexane): 2111 (m), 2062 (s), 2032 (s), 2023 (vs), 2009 (s), 1991 (w), 1982 (m), 1974 (w), 1938 (w) cm⁻¹. ¹H NMR (CDCl₃): δ 5.58 (dd, 3J = 5.3 Hz, 4J = 3 Hz, 2H, -CH=CH-CH=CH-), 3.76 (d, 3J = 7.2 Hz, 2H, -CH=CH-CH=CH-), 1.87 (bs, 4H, -CH₂-CH₂-). UV-vis (hexane): 244 (sh), 342, 400 (sh) nm.

**Spectroscopic measurements.** Electronic absorption spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer, FT-IR spectra on a Bio-Rad FTS-7 spectrometer and ¹H NMR spectra on a Bruker AMX 300 (300.13 MHz for ¹H) spectrometer.
Photochemistry. Picosecond transient absorption (ps TA) spectra and single-wavelength kinetic traces were recorded using the set-up installed at the University of Amsterdam. Part of the 800 nm output of a Ti-sapphire regenerative amplifier (1 kHz, 130 fs, 1 mJ) was focused into a H₂O flow-through cell (10 mm; Hellma) to generate white light. The residual part of the 800 nm fundamental was used to provide 430 nm (fourth harmonic of the 1500 OPA signal beam) excitation pulses with a general output of 5 µJ pulse. The picosecond time-resolved infrared (ps TRIR) spectra were recorded using the PIRATE set-up at the Central Laser Facility of the Rutherford Appleton Laboratory. Second harmonic generation 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. Further experimental details of the time-resolved absorption and IR set-ups are described in Chapter 2.

Computational details. All density functional calculations were carried out with the Amsterdam Density Functional (ADF2000) programme. The computational details are described in Chapter 2. Full geometry optimizations were performed without any symmetry constraints on models based on the available crystal structures.

3.4 Results and Discussion

Picosecond time-resolved spectroscopy of [Ru₃(CO)₁₂] (1)

The ps TA spectra of cluster 1 in hexane were obtained by excitation at 430 nm and spectral changes were detected in the wavelength region 450-650 nm. Kinetic profiles were probed at 500 nm in 250 fs intervals up to 15 ps and in 20 ps intervals up to 160 ps. The ps TA spectra of 1 in hexane, measured 1-13 ps after the 130 fs laser pulse, are depicted in Figure 2.

The TA spectrum of 1, obtained at t₄ = 1 ps (Figure 2) shows a broad transient absorption with a maximum at 515 nm and shoulders around 550 and 610 nm. Within 15 ps, the absorption maximum at 515 nm decays with a lifetime of 5.6 ± 1.0 ps to ca. 50% of its initial intensity and becomes slightly shifted to higher energy (505 nm). Besides, the shoulders at 550 and 610 nm become less pronounced. In accordance with the time-resolved IR experiments (vide infra) these spectral changes are attributed to the formation of a photoproduct from the excited state. On longer time scales (up to 150 ps), the shape of the TA spectrum does not change anymore and the transient almost completely regenerates the parent cluster with a lifetime of 46 ± 5 ps.
Figure 2. Transient difference absorption spectra of cluster 1 in hexane measured at time delays of -1 (baseline), 1, 2, 4, 5, 7 and 13 ps, respectively, after 430 nm, 130 fs FWHM excitation.

Importantly, the nearly complete back reaction to the starting cluster within ca. 50 ps identifies the primary photoproduct of 1 as a triruthenium cluster, as such behaviour is very unlikely for products of a photofragmentation process. The presence of the long-wavelength absorption in the TA spectra indicates that the primary photoproduct is coordinatively unsaturated. For, similar shifts of absorption bands to considerably longer wavelengths compared to the saturated precursor complexes are encountered for related di- or trinuclear metal carbonyls like [Re₂(CO)₉], [Os₂(CO)₈], [Os₃(CO)₁₁] and [H₂Os₃(CO)₁₀]. The lowest-energy absorption band of [Re₂(CO)₉] in an Ar matrix (530 nm) is, for example, clearly red-shifted compared to the corresponding band in the saturated precursor complex [Re₂(CO)₁₀] (308 nm in hexane).

Apparently, the TA spectra do not provide much structural information about the excited state of cluster 1 and its photoproduct. We therefore monitored the primary events after the photoexcitation with picosecond time-resolved infrared spectroscopy (ps TRIR). The ps TRIR spectra of 1 were recorded in heptane after excitation at 400 nm at several pump-probe delays between 0 and 500 ps. Figure 3 shows representative difference absorption spectra at six selected time delays.

The ground-state IR spectrum of 1 in heptane at room temperature shows four distinct ν(CO) IR bands at 2061, 2031, 2017 and 2012 cm⁻¹. After excitation into the lowest-energy absorption band, previously assigned to an electronic transition having predominant metal-metal bonding-to-antibonding (σ → σ*) character, the initial TRIR spectra display instantaneous bleaching of the parent ν(CO) bands superimposed on a broad, unresolved transient absorption due to the excited state of 1.
Figure 3. TRIR difference spectra of cluster 1 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 pulse⁻¹) excitation. The arrows indicate the shift of the band maxima with increasing time delay following excitation.

Similar broad, featureless transient IR bands have been observed upon excitation into the \( \sigma \rightarrow \sigma^* \) transition of \([M_2(CO)_{10}] \) (M = Mn, Re). They 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 that are highly activated upon light excitation. In the first few picoseconds, this broad transient absorption resolves into distinct product bands (2051, 2021 and 2007 cm⁻¹) as the bands become narrower and shift slightly to higher energy. These spectral changes are attributed to vibrational relaxation of the low-frequency vibrational modes. Upon further decay (≤ 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 the primary photoproduct. On this time scale, there is also a new \( v(CO) \) band growing in at 1850 cm⁻¹. The latter band is assigned to a bridging carbonyl and decays on a similar time scale (20-500 ps) as the bands in the terminal \( v(CO) \) region. Upon decay of the transient IR bands, recovery of the parent bleaches also takes place. On early time scales (≤ 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 such overlap variation does not occur, only shows a minor decrease in signal strength. The excited state is therefore assumed to almost completely convert 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, accordingly, recovery of the parent bleach signals in this time domain is 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; 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 conclusion.
The nearly complete reversibility of the system in the non-coordinating solvent implies that the triruthenium cluster core remains intact. The ps TRIR data also agree with the formation of [Ru$_3$(CO)$_{11}$(μ-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 terminal ν(CO) bands is hampered. However, the appearance of the ν(μ-CO) band at 1850 cm$^{-1}$ is not accompanied by a shift to higher frequency and is therefore presumably not influenced by the vibrational relaxation processes. Gaussian curve fitting was therefore performed on this well-separated ν(μ-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, Figure 4a), which is assumed to correspond with the growth-in of the 1850 cm$^{-1}$ band, and of the lifetime of the primary photoproduct (56.6 ± 6 ps, Figure 4b). The latter lifetime is in good agreement with the values obtained from the terminal ν(CO) bands, viz. τ = 52.5 ± 4 ps at 2051 cm$^{-1}$ (Figure 4c), whose decay after $t_d = 20$ ps is mainly ascribed to the regeneration of the parent cluster. Importantly, the lifetimes obtained from the ps TRIR spectra compare reasonably well with the values obtained from the ps TA experiments. The observed kinetics rules out CO loss as the primary photoprocess since, assuming that photoexpelled CO escapes from the solvent cage, the backreaction in this case would occur under diffusion control and would therefore take place on a much longer time scale.

![Figure 4](image)

**Figure 4.** Kinetic traces of cluster 1 in heptane representing (a) the development 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$^{-1}$.

The minor IR bands of the remaining photoproduct (after 500 ps) are close to those reported for the unsaturated cluster [Ru$_3$(CO)$_{11}$].\textsuperscript{14} According to the literature, [Ru$_3$(CO)$_{11}$] is not likely to be formed from [Ru$_3$(CO)$_{11}$(μ-CO)] and the observation of this species may therefore be due to partial excitation 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)$_{11}$(μ-CO)] photoproduct, no unambiguous conclusions can be drawn. The close correspondence with the
Time-Resolved Study of the Primary Photoprocesses of [Ru$_3$(CO)$_{12}$] and [Os$_3$(CO)$_{10}$(1,3-cyclohexadiene)]

ν(μ-CO) stretching frequency of [Ru$_3$(CO)$_{11}$] (1840-1860 cm$^{-1}$)$^{14}$ suggests cleavage of a Ru-Ru bond and formation of a single CO bridge.

In order to investigate whether a similar CO-bridged primary photoproduct is also formed upon excitation of [Os$_3$(CO)$_{12}$], ps TRIR spectra of the latter cluster were recorded in CH$_2$Cl$_2$ at several pump-probe delays between 0-1000 ps after 400 nm excitation. Although the resulting transient spectra showed similar spectral changes in the terminal ν(CO) region, the presence of a bridging carbonyl ligand could not be established. The absence of any ν(μ-CO) band is, however, in line with the assignment of the lowest-energy absorption band of [Os$_3$(CO)$_{12}$] (see Figure 5) to a transition from the highly delocalized HOMO (mixed Os-CO σ-bonding, Os-Os bonding and Os-CO σ-antibonding contributions) to an empty orbital of largely axial π*(CO) character.$^{17}$ The perturbation of the cluster bonds upon excitation into this transition is expected to be minor. Hence, excitation at 400 nm mainly results in population of an unreactive excited state from which formation of open-triangle photoproducts is very unlikely. Any CO-bridged primary photoproduct resulting from irradiation into the tailing higher-energy band of [Os$_3$(CO)$_{12}$], is probably formed in amounts not detectable by ps TRIR.

![Figure 5. UV-vis spectra of clusters 1 (---), 2 (—), [Os$_3$(CO)$_{10}$(s-cis-1,3-butadiene)] (—) and [Os$_3$(CO)$_{12}$] (⋯⋯) in hexane at 298 K.](image)

**Frontier orbital calculations of [Os$_3$(CO)$_{10}$(s-cis-1,3-diene)]**

Prior to experimental studies of the primary events following the photoexcitation of cluster 2, density functional theoretical (DFT) calculations were performed in order to obtain more insight into the bonding properties of the cluster and to assign the lowest electronic transitions. The cluster [Os$_3$(CO)$_{10}$(1,3-butadiene)] served as a model, as the available X-ray structures for this complex$^{27}$ provided a good starting point for the calculations. Two known isomers for which crystal structures have been reported,$^{27}$ are depicted in Figure 6. In cluster
The diene ligand is coordinated to a single osmium centre in a chelating fashion, with one C=C bond equatorial and the other one in an axial position (s-cis). Isomer 2'' possesses approximate C_2 symmetry, with the diene ligand bridging over an Os-Os bond and the C=C bonds at different osmium centres in equatorial positions (s-trans). Geometry optimization with DFT revealed that isomer 2'' with the diene coordinated in the trans fashion is more stable by 10 kJ mol$^{-1}$. Despite the fact that the trans isomer is calculated to be more stable, the cluster [Os$_3$(CO)$_{10}$(s-cis-1,3-butadiene)] is obtained in high yields from both [H$_2$Os$_3$(CO)$_{10}$]$^{28}$ and [Os$_3$(CO)$_{10}$(MeCN)$_2$],$^{20}$ the latter cluster being pre-activated for the s-trans geometry due to the coordination of the MeCN ligands at different osmium centres.$^{34}$

**Figure 6.** Optimized geometries and relative energies (in kJ mol$^{-1}$) of the structural models 2' and 2''.

This implies that formation of the s-cis-butadiene isomer is most likely controlled by kinetics. Obviously, the same holds for the reaction of [Os$_3$(CO)$_{10}$(MeCN)$_2$] with 1,3-cyclohexadiene that yields the s-cis isomer 2. As the latter cluster was used in the ps IR photochemical studies, frontier orbital calculations are exclusively presented for the corresponding s-cis isomer of [Os$_3$(CO)$_{10}$(1,3-butadiene)]. The geometry of model 2' is in good agreement with the experimental structure (Table 1), although the calculated Os-Os bond distances are slightly longer and the C-C bond distances within the diene ligand are slightly shorter than the experimental ones. The overestimation of the metal-metal bond distances appears to be a general result of DFT calculations and was also observed for related clusters [Os$_3$(CO)$_{12}$]$^{35}$ [Os$_3$(CO)$_{10}$($\alpha$-diimine)]$^{36}$ and [Os$_3$(CO)$_{10}$($\beta$-biphasphine)]$^{37}$ The slight twist of the equatorial C=C bond out of the Os$_3$ plane will hardly affect the bonding interactions within the cluster core.
From the ground-state DFT calculations, the composition of the molecular orbitals for 2' has been obtained. The contribution of the relevant atomic wavefunctions to the frontier orbitals are given in Table 2, with the HOMO (H) and LUMO (L) indicated in bold. Three-dimensional representations of the three highest occupied molecular orbitals (HOMO, HOMO-1 and HOMO-2) and of the lowest unoccupied molecular orbital (LUMO) are depicted in Figure 7. The LUMO of 2' has dominant axial π*(CO) character, together with small contributions from the osmium centres. The HOMO of 2' has significant contributions from all three metal centres and from the equatorial carbonyl groups.

Table 1. Comparison of selected calculated bond lengths [Å] and angles [°] in cluster 2' with corresponding experimental crystallographic data.

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a See Figure 6.

Table 2. Characters and one-electron energies of selected frontier orbitals of [Os₃(CO)₁₀(s-cis-1,3-butadiene)], as calculated by the ADF/BP method (L = LUMO, H = HOMO).

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</table>

a See Figure 6.
According to the 3D plot, the HOMO is predominantly σ-bonding with respect to the Os1 and Os3 centres and, therefore, can best be described as a σ(Os1-Os3) bonding orbital. By contrast, the HOMO-1 is mainly localized on Os3 and is best described, in accordance with the 3D plot, as a π(C=C-Os3-C(10)O) bonding orbital. All three metal centres participate in the HOMO-2 that is σ-bonding between Os1 and Os2 and σ-bonding between Os3 and the equatorial C=C bond of the diene. The HOMO-3 has a character similar to the HOMO with significant contributions from all three metal centres and the carbonyl groups. Based on the contributions of the atomic wavefunctions to the frontier orbitals, the HOMO-LUMO transition is best described as having predominant σ(Os1-Os3)-to-π*(CO) character. The excitation energies and the oscillator strengths of the low-lying electronic transitions of 2' were calculated using TD-DFT and are presented in Table 3.

**Figure 7.** Three-dimensional plots of the LUMO (a), HOMO (b), HOMO-1 (c) and HOMO-2 (d) of [Os₇(CO)₁₀(s-cis-1,3-butadiene)].
Electronic absorption spectra of \([\text{Os}_3(\text{CO})_{10}(1,3\text{-diene})]\)

The electronic absorption spectrum of cluster 2 in hexane (Figure 5) shows a non-solvatochromic lowest-energy absorption band around 400 nm close to a more intense band at 331 nm. Similar absorption bands are also present in the spectra of \([\text{Os}_3(\text{CO})_{10}(s\text{-cis-1,3-butadiene})]\), the model complex for the DFT calculations, and \([\text{Os}_3(\text{CO})_{12}]\). The bands of the latter cluster are, however, slightly shifted to higher energy. The position of the maximum of the lowest-energy band of \([\text{Os}_3(\text{CO})_{10}(s\text{-cis-1,3-butadiene})]\) is in good agreement with the TD-DFT calculated values (Table 3).

Table 3. TD-DFT calculated lowest-energy singlet excitation energies \((E)\) and oscillator strengths \((\Omega S.)\) for \([\text{Os}_3(\text{CO})_{10}(s\text{-cis-1,3-butadiene})]\) \((2^\cdot)\).

<table>
<thead>
<tr>
<th>Transition</th>
<th>Composition</th>
<th>(E) [eV]</th>
<th>Wavelength [nm]</th>
<th>Exptl. (\lambda_{\text{max}}^{a}) [nm]</th>
<th>O.S. ((\times 10^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>69% (H→L); 15% (H-1→L)</td>
<td>2.82</td>
<td>440</td>
<td>380</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
<td>84% (H-1→L); 11% (H→L)</td>
<td>2.88</td>
<td>431</td>
<td>331</td>
<td>4.3</td>
</tr>
<tr>
<td>3</td>
<td>89% (H→L+1)</td>
<td>3.07</td>
<td>404</td>
<td>351</td>
<td>7.6</td>
</tr>
<tr>
<td>4</td>
<td>63% (H-2→L); 18% (H-3→L)</td>
<td>3.14</td>
<td>395</td>
<td>366</td>
<td>400(^b) 29</td>
</tr>
<tr>
<td>5</td>
<td>97% (H-1→L+1)</td>
<td>3.27</td>
<td>379</td>
<td>379</td>
<td>58</td>
</tr>
<tr>
<td>6</td>
<td>62% (H→L+2); 21% (H-3→L)</td>
<td>3.31</td>
<td>375</td>
<td>331</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>42% (H-3→L); 25% (H→L+2)</td>
<td>3.39</td>
<td>366</td>
<td>361</td>
<td>16</td>
</tr>
<tr>
<td>8</td>
<td>12% (H-2→L+1);</td>
<td>3.44</td>
<td>361</td>
<td>361</td>
<td>1.2</td>
</tr>
<tr>
<td>9</td>
<td>68% (H-2→L+1); 21% (H→L+3)</td>
<td>3.53</td>
<td>351</td>
<td>351</td>
<td>34</td>
</tr>
<tr>
<td>10</td>
<td>98% (H-1→L+2)</td>
<td>3.59</td>
<td>346</td>
<td>351</td>
<td>34</td>
</tr>
<tr>
<td>11</td>
<td>46% (H→L+3); 31% (H-3→L+1)</td>
<td>3.59</td>
<td>346</td>
<td>346</td>
<td>12</td>
</tr>
<tr>
<td>12</td>
<td>6% (H-2→L+1)</td>
<td>3.59</td>
<td>346</td>
<td>346</td>
<td>12</td>
</tr>
</tbody>
</table>

\(^a\) Observed absorption maxima for \([\text{Os}_3(\text{CO})_{10}(s\text{-cis-1,3-butadiene})]\) in hexane at 298 K. \(^b\) Asymmetric band with shallow resolved maximum (ca. 380 nm) and shoulder around 410 nm. \(^c\) Non-resolved. \(^d\) Presumably falling within an intense absorption band below 300 nm.

As the absorption features in the visible region are generally broad and poorly resolved, the first four transitions (440-395 nm, Table 3) may all contribute to this lowest-energy band. This band therefore most likely consists of several allowed transitions directed to the LUMO and LUMO+1, possessing predominant cluster core-to-\(\pi^*(\text{CO})\) characters. At a higher energy, a second group of fairly intense transitions is found (close-lying transitions 6 and 7, Table 3). Similar to the first group, these transitions are directed to orbitals having predominant \(\pi^*(\text{CO})\)
character, while the parent occupied orbitals, viz. HOMO, HOMO-2 and HOMO-3, are bonding with respect to specific metal-metal bonds within the cluster core. Therefore, the more intense 331 nm band in the UV-vis spectrum of \([\text{Os}_3(\text{CO})_{10}(\text{cis}-1,3\text{-butadiene})]\) has also \(\sigma(\text{core})-\pi^*(\text{CO})\) character. The higher intensity of the latter band compared to the lowest-energy one presumably results from overlap with the high-energy band below ca. 300 nm. Taking into account the calculated energy difference between transitions 7 and 10 (Table 3), the latter, fairly intense, transition presumably contributes to this high-energy UV band.

The TD-DFT results thus document that the electronic transitions of \([\text{Os}_3(\text{CO})_{10}(s\text{-cis}-1,3\text{-butadiene})]\) in the visible region have predominant \(\sigma(\text{core})-\pi^*(\text{CO})\) character. The calculated excitation energies and oscillator strengths compare reasonably well with the experimental data recorded in hexane. Similar to the lowest-energy transition of \([\text{Os}_3(\text{CO})_{12}]\) (vide supra), excitation into the \(\sigma(\text{core})-\pi^*(\text{CO})\) transitions is not expected to result in large perturbations of the cluster bonds. However, in contrast to \([\text{Os}_3(\text{CO})_{12}]\),\(^{13}\) for which indeed no significant photoreactivity is observed upon selective irradiation into the lowest-energy absorption band, visible irradiation of \([\text{Os}_3(\text{CO})_{10}(s\text{-cis}-1,3\text{-cyclohexadiene})]\) partly results in fragmentation into mono- and dinuclear complexes, most likely via the intermediate formation of the proposed open-structure photoproduction \([\text{Os}_3(\text{CO})_4(\mu\text{-CO})_2(1,3\text{-cyclohexadiene})]\).\(^{20}\) The observed difference in the photoreactivity compared to \([\text{Os}_3(\text{CO})_{12}]\) may be due to a weakening of the Os-Os bonds by the donor diene ligand, facilitating the cleavage of a metal-metal(diene) bond on excitation. It remains, however, to be decided whether the initial bond cleavage reaction takes place straightforwardly from the \(3\sigma\pi^*\) state, for example, as reported for the mononuclear complexes \([\text{Re}(\text{R})(\text{CO})_3(\alpha\text{-diimine})]\) (\(\text{R} = \text{ethyl}, \text{benzyl}\)),\(^{38-40}\) or more likely via its interaction with a rapidly decaying dissociative state of \(\sigma\sigma^*\) character. A similar avoided crossing along the reaction coordinate (potential surface) that transforms the \(3\sigma\pi^*\) into a dissociative state, is known to occur for the clusters \([\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})]\) (Chapter 4, Part A).

The close correspondence between the electronic absorption spectra of clusters 2 and \([\text{Os}_3(\text{CO})_{12}]\) (Figure 5) implies that also the second absorption band of the latter cluster belongs to transitions possessing predominant \(\sigma(\text{core})-\pi^*(\text{CO})\) character. This assignment, however, deviates from previous studies\(^{13, 17}\) where the second absorption band of \([\text{Os}_3(\text{CO})_{12}]\) was ascribed, in accordance with the observed photoreactivity, to a transition having predominant \(\sigma\sigma^*\) character. Without higher level (TD-DFT or \textit{ab initio}) calculations on \([\text{Os}_3(\text{CO})_{12}]\), it remains therefore unanswered whether the observed photofragmentation upon irradiation into the 329 nm band of \([\text{Os}_3(\text{CO})_{12}]\) indeed results from direct optical population of a \(\sigma\sigma^*\) excited state or involves a \(\sigma\pi^*\) state, as argued above for the corresponding diene-substituted clusters.
Picosecond time-resolved spectroscopy of \([\text{Os}_3(\text{CO})_{10}(s\text{-}c\text{-}i\text{s}-1,3\text{-cyclohexadiene})]\) (2)

In order to investigate the primary events following the photoexcitation of cluster 2, picosecond transient absorption (ps TA) spectra were recorded in hexane and CH\(_2\)Cl\(_2\). The ps TA spectra were obtained by excitation at 430 nm and spectral changes were monitored in the wavelength region 450-650 nm. Kinetic profiles were probed at 500 nm in 250 fs intervals up to 15 ps. The ps TA spectra of 2 in CH\(_2\)Cl\(_2\), measured 1-10 ps after the 130 fs laser pulse, are depicted in Figure 8. The kinetic profile of 2 in CH\(_2\)Cl\(_2\) is shown in Figure 9.

![Figure 8. Transient difference absorption spectra of cluster 2 in CH\(_2\)Cl\(_2\), measured at time delays of -1 (baseline), 1, 2, 3, 5, 8 and 10 ps, respectively, after 430 nm, 130 fs FWHM excitation.](image)

The ps TA spectrum of 2 in CH\(_2\)Cl\(_2\) recorded at \(t_d = 1\) ps (Figure 8) is very similar to that obtained for cluster 1. It shows two broad, overlapping transient absorption bands with maxima around 505 nm and 595 nm. Within 10 ps, the lowest-energy band becomes considerably red-shifted and turns into a broad, well-resolved absorption band with a distinct maximum at 630 nm. On the same time scale, the band at 505 nm initially shows a small blue shift, viz. to 480 nm at \(t_d = 4\) ps. After this time delay no distinct maximum can any longer be observed between 450 and 550 nm and only a broad unresolved absorption remains. The kinetic profile of 2 probed at 500 nm is clearly mono-exponential in both hexane and CH\(_2\)Cl\(_2\) and provides an excited-state lifetime of 2.5 ± 0.1 ps (Figure 9). The transient absorption at \(t_d = 10\) ps is very similar to that observed in the ns TA spectra of this cluster, which has previously been assigned to the photoproduc \([\text{Os}_3(\text{CO})_8(\mu-\text{CO})_2(L)]\) (L = 1,3-butadiene, 1,3-cyclohexadiene).\(^2\) In order to verify that the absorptions in the ps and ns time domains refer to the same species, we also measured the TA spectra at 300, 600 and 900 ps after the laser pulse. These spectra do not differ from those measured at 10 ps as well as at 10 ns. From this observation we conclude that the CO-bridged photoproduc observed previously on the ns time scale is already present in the ps time domain. Similar to cluster 1, the presence of the
long-wavelength absorption in the TA spectrum at $t_d = 10$ ps indicates the formation of a coordinatively unsaturated photoproduct. The results of the previous ns TA study,\textsuperscript{20} where the lifetime of the photoproduct in the presence of 1.0 M 1-octene was reduced from 94 ns to 32 ns, support this conclusion.

![Figure 9](image-url)

**Figure 9.** Kinetic profile of the difference absorption of cluster 2 in CH$_2$Cl$_2$, probed at 500 nm after 430 nm, 130 fs FWHM excitation.

Another important aim of this work was to find out whether the different bridging carbonyl ligands in the photoproduct [Os$_3$(CO)$_6$($\mu$-CO)$_2$(1,3-cyclohexadiene)] are formed in a stepwise fashion or in a concerted process directly from the excited state. For this purpose, ps TRIR spectra of cluster 2 were recorded in heptane after 400 nm excitation at several pump-probe delays between 0 and 500 ps. Representative difference IR spectra in the regions 2130-2070 cm$^{-1}$ and 1900-1750 cm$^{-1}$ are shown in Figures 10 and 11, respectively. Due to the lower symmetry of 2, its ground-state IR spectrum displays a considerably larger number of $\nu$(CO) bands than that of cluster 1. The extensive overlap between the bleached $\nu$(CO) bands of the complex in the ground state and the excited-state absorptions therefore largely precludes the assignment of the excited-state CO-stretching modes. In fact, only the clearly separated highest-frequency band at 2111 cm$^{-1}$ could be used to monitor the population of the excited state and the subsequent formation of photoproducts. After irradiation into the lowest-energy absorption band of 2 in heptane, the ps TRIR spectra at early time delays ($< 3$ ps) display instantaneous bleaching of the parent $\nu$(CO) bands, together with broad transient absorption bands due to the excited state of 2. The highest-frequency ground state band at 2111 cm$^{-1}$ becomes shifted to smaller wavenumbers in the excited state (2090 cm$^{-1}$, Figure 10). This behaviour is in line with an excited state possessing predominant $\sigma\pi^*$ character and results from a decrease in the C-O bond order due to the population of anti-bonding $\pi^*$(CO) orbitals. In case the lowest excited state would be localized at the metal core having mainly $\sigma\sigma^*$ character, a decrease in $\pi$-backbonding to the carbonyl ligands would be expected, resulting in
a shift of the corresponding v(CO) bands in opposite direction. At $t_d = 1$ ps the transient v(CO) band at 2090 cm$^{-1}$ possesses a high-frequency shoulder around 2100 cm$^{-1}$ that develops into a distinct band at the expense of the band at 2090 cm$^{-1}$, reaching its maximum intensity at about 2.5 ps. On longer time scales (up to 10 ps) the latter band also decays and a new v(CO) band appears at 2106 cm$^{-1}$, which further shifts to 2111 cm$^{-1}$ at $t_d = 500$ ps. The remaining difference spectrum at $t_d = 500$ ps closely resembles the reported difference IR spectrum of cluster 2 on the ns time scale.$^{20}$

**Figure 10.** TRIR difference spectra of cluster 2 in heptane between 2130-2070 cm$^{-1}$: (■) 1 ps, (○) 2 ps, (▲) 3 ps, (□) 5 ps, (●) 10 ps, (●) 40 and (×) 500 ps after 400 nm (ca. 150 fs FWHM, 5 μJ pulse$^{-1}$) excitation. Inset: Kinetic trace representing the decay of the 2090 cm$^{-1}$ band.

In order to monitor also the CO bridge formation, we focused in the next step on the IR spectral changes in the wavenumber region 1900-1750 cm$^{-1}$. After excitation of cluster 2 at 400 nm, the ps TRIR spectra at early time delays (< 5 ps) show the appearance of a broad $\nu(\mu$-CO) band around 1815 cm$^{-1}$ that reaches its maximum intensity after ca. 3 ps (Figure 11). Having reached this point, a shoulder at 1801 cm$^{-1}$ and a new band at 1857 cm$^{-1}$ further develop at the expense of the 1815 cm$^{-1}$ band. At $t_d = 20$ ps, the initial $\nu(\mu$-CO) band completely disappeared and only the two new $\nu(\mu$-CO) bands at 1801 and 1857 cm$^{-1}$ are present, whose intensity does not change up to 500 ps. Importantly, the latter $\nu(\mu$-CO) bands closely resemble those observed on the ns time scale.$^{20}$
Figure 11. TRIR difference spectra of cluster 2 in heptane between 1900-1750 cm\(^{-1}\): (a) 1.5 ps, (b) 2.5 ps, (c) 3 ps, (d) 5 ps, (e) 7 ps and (f) 20 ps after 400 nm (ca. 150 fs FWHM, 5 μJ pulse\(^{-1}\)) excitation.

The ps TRIR spectra of 2 in the region 1900-1750 cm\(^{-1}\) reveal that formation of the two different CO bridges in [Os\(_3\)(CO)\(_{10}\)(μ-CO)\(_2\)(1,3-cyclohexadiene)] proceeds stepwise. Initially, the formation of a primary photoproduct 2\(a\) is observed, possessing only a single ν(μ-CO) band at 1815 cm\(^{-1}\). The bridging carbonyl in 2\(a\) is expected to connect the two osmium centres in a similar way as proposed for the primary photoproduct of cluster 1 (Scheme 1). In accordance with the proposed open-core structure of transient 2\(a\) and the IR spectral changes in the terminal ν(CO) region, the observation of the 1815 cm\(^{-1}\) band already at 1.5 ps after the laser pulse implies that population of the σπ* excited state and concomitant depopulation of a σ(Os-Os) bonding orbital results in rapid cleavage of an Os-Os(diene) bond on the subpicosecond time scale. The ps TRIR spectra do not unambiguously reveal whether the π*(CO) orbitals are populated from a molecular orbital having predominant σ(Os1-Os3) (HOMO) or σ(Os1-Os2) (HOMO-2) character. However, based on the nature of the fragmentation products formed upon continuous wave irradiation of [Os\(_3\)(CO)\(_{10}\)(s-cis-1,3-cyclohexadiene)],\(^{20}\) the Os1-Os2 bond is concluded to remain intact and connect the two Os centres in the dinuclear photoproducts [Os\(_2\)(CO)-(L)\(_2\)] (L = CO, ethene). As this reasoning does not agree with the depopulation of the HOMO-2 (Figure 7), the reactive σπ* excited state is proposed to have σ(Os1-Os3)π*(CO) (HOMO/LUMO) character. In a second step, primary photoproduct 2\(a\) rapidly transforms within a few picoseconds into a second product 2\(b\), in which two CO bridges are present. In accordance with the proposed structure for [Os\(_3\)(CO)\(_8\)(μ-CO)\(_2\)(1,3-cyclohexadiene)],\(^{20}\) this process involves the movement of a terminal CO to a bridging position in order to partly compensate for the resulting electron deficiency at Os1. In the case of cluster 1 the electron density in the primary photoproduct is equally distributed over the two remote Ru centres connected via the single CO bridge. The
movement of a second carbonyl to a bridging position is therefore redundant in this case. The consecutive formation of the different carbonyl bridges in 2 is also reflected in the IR spectral changes in the terminal ν(CO) region (Figure 10). The transient ν(CO) band at 2100 cm⁻¹ grows in on the same time scale as the ν(μ-CO) band at 1815 cm⁻¹ and can therefore be ascribed to transient 2a. As this band develops at the expense of the 2090 cm⁻¹ band, the latter band is assigned to the σπ* excited state of 2. Finally, the ν(CO) band at 2106 cm⁻¹, which in turn arises at the expense of the 2100 cm⁻¹ band, reaches its maximum intensity at the same time delay as the ν(μ-CO) bands at 1857 and 1801 cm⁻¹ and is therefore ascribed to 2b. As the ν(μ-CO) bands at 1801 and 1857 cm⁻¹ do not change in intensity or position after t_d = 20 ps, the shift of the 2106 cm⁻¹ band to 2111 cm⁻¹ at longer time delays (t_d > 50 ps) is not ascribed to the formation of a tertiary photoproduc but most likely reflects a structural rearrangement within 2b. In general, the shift of the highest-frequency ν(CO) band of cluster 2 in the excited state to larger wavenumbers upon formation of 2a and 2b, reflects the decreased π-backbonding towards the terminal CO ligands owing to the consecutive formation of the two strongly π-accepting CO bridges.

In order to describe the observed kinetics in a qualitative way, the formation of photoproduc 2b is represented by two consecutive irreversible first-order reactions (Scheme 1). After excitation of 2, the transient 2a is assumed to be formed quantitatively from the excited state 2* (rate constant k₁). This is inferred from the negligible change in intensity of the highest-frequency bleach of 2 at 2111 cm⁻¹ at t_d between 2 and 3 ps whereas the ν(CO) band at 2090 cm⁻¹ due to the excited state (2*) significantly decreases. In a second step, primary photoproduc 2a can either regenerate the parent cluster (rate constant k₂) or transform into 2b with rate constant k₃. Finally, photoproduc 2b mainly regenerates the parent cluster (ca. 70%, rate constant k₄) while a small part of the molecules fragments into mono- and dinuclear products (ca. 30%, k₅).²⁰ As the latter two processes only take place in the ns time domain (τ₂b = 94 ns in hexane),²⁰ k₄ and k₅ do not influence the kinetics on the early picosecond time scale (i.e., k₁ and k₃). According to the mechanism depicted in Scheme 1, the reactive σπ* excited state 2* decays mono-exponentially with a lifetime 1/k₁. Although both vibrational σπ* excited state 2* decays mono-exponentially with a lifetime 1/k₁. Although both vibrational cooling processes and the decay of the excited state take place on similar time scales, the excited-state lifetime (τ₂* = 3.3 ± 0.1 ps) was estimated by plotting the integrated intensity of the 2090 cm⁻¹ band against time (Figure 10, inset). In accordance with the development of the 1815 cm⁻¹ band, this implies that photoexcitation of 2 results in rapid cleavage of an Os-Os(diene) bond, accompanied by the formation of a single CO bridge in transient 2a (k₁ = 3 x 10¹¹ s⁻¹). In the proposed mechanism the concentration of 2a in time is described by the kinetics of a consecutive process, which unfortunately cannot be solved from the available experimental data. However, as 2a is clearly observable by means of the ν(CO) bands at 1815 and 2100 cm⁻¹, its conversion to 2b together with the decay to the ground state
(\(k_2 + k_3\)) must be slower than its formation from the excited state (\(k_1\)). Moreover, as the absorption molar coefficients of the \(\nu(\mu\text{-CO})\) bands of \(2a\) and \(2b\) are assumed to be similar, the fairly high intensity of the \(\nu(\text{CO})\) bands at 1801 and 1857 cm\(^{-1}\) (\(2b\)) also indicates that regeneration of the parent cluster from transient \(2a\) is either a process of minor importance (\(k_2 < k_3\)) or does not take place at all. Formation of photoproduct \(2b\) is therefore concluded to be the rate-determining step.

**Scheme 1.** Schematic representation of the primary events taking place after photoexcitation of cluster 2.

The excited-state lifetime of 3.3 ps, derived from the ps TRIR experiments, closely resembles the value of 2.5 ps obtained from the TA measurements. Consistent with the TRIR experiments, the UV-vis spectral changes within the first 10 ps following excitation (Figure 8) represent both the formation of \(2a\) from the \(3\sigma^*\) excited state and its conversion into \(2b\). As the 500 nm kinetic profile of cluster 2 in CH\(_2\)Cl\(_2\) (Figure 9) is clearly mono-exponential and the \(\nu(\mu\text{-CO})\) bands attributed to \(2b\) only reach their maximum intensity after ca. 20 ps (Figure 11), the initial 2.5 ps TA process mainly corresponds to the decay of the excited state and concomitant formation of \(2a\). As no kinetic change is observed at 500 nm upon subsequent formation of \(2b\), both photoproducts \(2a\) and \(2b\) are assumed to absorb similarly around this wavelength.

### 3.5 Conclusions

Picosecond TRIR spectroscopy proved to be a powerful tool for obtaining structural information about clusters 1 and 2 in their lowest excited state and for monitoring the formation of their primary photoproducts. For cluster 1, the detection of a single \(\nu(\text{CO})\) band in the bridging carbonyl region confirms the formation of a coordinatively unsaturated, CO-
bridged primary photoproduct, as was proposed in the literature. A similar primary photoproduct is formed upon excitation of cluster 2. However, in contrast to 1, the IR spectral changes of 2 reveal the stepwise formation of a second CO bridge, producing the previously observed photoproduct [Os₃(CO)₆(µ-CO)₂(1,3-cyclohexadiene)]. The demand for a second CO bridge in the latter cluster is ascribed to the unequal distribution of electron density in the primary photoproduct 2a by the presence of the diene ligand.

Both the experimental data and the TD-DFT results support the assignment of the low-lying electronic transitions of 2 as having predominant σ(core)-to-π*(CO) character. Based on the nature of the fragmentation products, the lowest ³σπ* excited state, most likely being populated via rapid intersystem crossing from the higher-lying, optically accessible σ(Os1-Os2)π* state, is ascribed a σ(Os1-Os3)π*(CO) character. It remains to be theoretically investigated whether the latter excited state is reactive by itself or the observed photoreactivity results from an avoided crossing with a dissociative state of, for example, σσ* character.

According to the close correspondence between the electronic absorption spectra of clusters 2 and [Os₃(CO)₁₂], the assignment of the low-lying electronic transitions of 2 as having predominant σπ* character possibly also holds for the unsubstituted cluster. The formation of similar open-structure transients as observed for 2 is then not feasible in the absence of the diene ligand or another Lewis base. Clearly, higher-level theoretical (DFT or \textit{ab initio}) calculations on [Os₃(CO)₁₂] and the corresponding triruthenium cluster are required in order to revise the previous assignments of their electronic transitions, which have mainly been based on the observed photoreactivity, and to describe the optically accessible and reactive excited states with precision.

3.6 References

Time-Resolved Study of the Primary Photoprocesses of [Ru$_3$(CO)$_{12}$] and [Os$_3$(CO)$_{12}$1,3-cyclohexadiene]

