Abstract

The photochemistry of the clusters \([\text{Os}_3(\text{CO})_{10}(\text{diene})]\) (diene = cis-1,3-butadiene, 1,3-cyclohexadiene) was studied in detail. Upon near-UV irradiation photofragmentation occurs to give mononuclear \([\text{Os}(\text{CO})_2(\text{diene})]\). The second fragmentation product \([\text{Os}_2(\text{CO})_7]\) was trapped by reaction with CO, or with alkenes at low temperatures, to produce the binuclear complexes \([\text{Os}_2(\text{CO})_7(L)_2]\) (\(L = \text{CO}, \text{ethene}, 1\)-octene). The fragmentation was studied further with nanosecond time-resolved UV-vis and IR spectroscopy and was found to proceed via the initial formation of a triosmium photoproduct with a lifetime of about 100 ns in hexane. From the spectroscopic data we infer that this intermediate has a coordinatively unsaturated open-triangular structure with two bridging carbonyl groups, one bridging the split \((\text{CO})_4\text{Os}–\text{Os}(\text{CO})_3(\text{diene})\) bond.
Introduction

Thermal reactions of transition metal carboxyl clusters are frequently performed at elevated temperature and/or pressure, which often induces undesired side reactions. An increasing number of examples demonstrate that the photochemical activation of triruthenium and triosmium clusters may provide an alternative pathway to selective product formation under mild conditions.\textsuperscript{1-9} The photochemical behaviour of the clusters [M\textsubscript{3}(CO)\textsubscript{12}] (M = Ru, Os) has been studied most extensively.\textsuperscript{1,2} These clusters show a rich photochemistry which is strongly dependent on the irradiation wavelength. Irradiation into the two lowest-energy absorption bands has been proposed to give the open-triangular cluster [M\textsubscript{3}(CO)\textsubscript{11}(\mu-CO)] as the primary photoproduct, although this species has never been observed. Recently, it was shown that substitution of two carboxyl ligands in [Os\textsubscript{3}(CO)\textsubscript{12}] by a chelating \(\alpha\)-diimine ligand (e.g. 2,2'-bipyridine) drastically changes the photochemical behaviour.\textsuperscript{3,4,10} Visible irradiation of [Os\textsubscript{3}(CO)\textsubscript{10}(\alpha\text{-diimine})] results in metal–metal bond cleavage yielding reactive biradical or zwitterionic photoproducts, depending on the reaction conditions and the nature of the \(\alpha\)-diimine.

\[ \text{Figure 1. Schematic structure of cluster } [\text{Os}_3(\text{CO})_{10}(\text{1,3-cis-butadiene})], \text{ 1a}. \text\textsuperscript{11} \]

In this chapter the mechanistic investigation of the photochemistry of another class of [Os\textsubscript{3}(CO)\textsubscript{10}(L)] clusters, with L = 1,3-diene coordinated to one of the osmium atoms, is reported. The structure of these clusters with diene =cis-1,3-butadiene (1a)\textsuperscript{11} and 1,3-cyclohexadiene (1b)\textsuperscript{12} is depicted schematically in Figure 1. Substitution of two CO ligands in [Os\textsubscript{3}(CO)\textsubscript{12}] by 1,3-diene is not expected to strongly change the character of the excited states nor the initial photochemical processes. However, it is interesting to learn if the coordinated 1,3-diene undergoes any reaction at the cluster core after photochemical metal–metal bond cleavage or CO-loss. Importantly, the primary photoproducts of 1 could be detected and characterized with nanosecond time-resolved IR (TRIR) and UV-vis absorption (TA) spectroscopy. The results are compared with the photochemical behaviour of the clusters [M\textsubscript{3}(CO)\textsubscript{12}] (M = Ru, Os).
Results and Discussion

**UV-Vis Spectra**

The UV-vis spectra of 1a, 1b and [Os₃(CO)₁₂] are presented in Figure 2 and summarized in Table 1. [Os₃(CO)₁₂] possesses a lowest-energy absorption band at 384 nm, visible as a shoulder of the more intense second band at 325 nm. Similar absorption bands are also present in the UV-vis spectra of 1a and 1b, being slightly shifted to longer wavelengths.

![UV-Vis Spectra of Clusters](image)

**Figure 2.** UV-vis spectra of the clusters [Os₃(CO)₁₂] (---), 1a (—) and 1b (- - -) in hexane at 293 K.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>λₓₓₓ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Os₃(CO)₁₂]</td>
<td>243, 325, 384 (sh)</td>
</tr>
<tr>
<td>1a</td>
<td>246 (sh), 331 (6.7 x 10³), ca. 400 (sh, br)</td>
</tr>
<tr>
<td>1b</td>
<td>244 (sh), 342 (10.1 x 10³), ca. 400 (sh, br)</td>
</tr>
</tbody>
</table>

**Continuous-Wave Photochemistry**

In order to initiate photoreactions from the low-lying excited states, solutions of 1a and 1b were irradiated with a high-pressure mercury lamp using cut-off filters transparent at λₒ > 420, 375 or 335 nm. For comparison, the unsubstituted cluster [Os₃(CO)₁₂] has been found to be photoreactive only in the presence of Lewis base ligands (e.g. alkenes, phosphines) upon irradiation into its two lowest absorption bands in hydrocarbon solvents.¹,² In contrast to
[Os3(CO)12], irradiation of 1a and 1b in pure hexane resulted already at room temperature in fragmentation of the clusters according to eq 1. The products were characterized by IR and 1H NMR spectroscopy.

\[
\text{[Os3(CO)10(diene)] } \xrightarrow{\text{hv}} \text{[Os(CO)3(diene)] + [Os3(CO)12] + \text{other carbonyl products}} (1)
\]

Table 2. IR ν(CO) wavenumbers of the photoproducts of the clusters 1a and 1b

<table>
<thead>
<tr>
<th>cluster</th>
<th>T (K)</th>
<th>solvent</th>
<th>photoproduct</th>
<th>ν(CO) (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a⁶</td>
<td>298</td>
<td>pentane</td>
<td>3a'</td>
<td>2068, 1995, 1985</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[Os3(CO)12]</td>
<td>2068, 2036, 2015, 2004</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>not assigned</td>
<td>2118, 2086, 2055, 2047, 2021</td>
</tr>
<tr>
<td>1b⁵</td>
<td>298</td>
<td>hexane</td>
<td>3b'</td>
<td>2063, 1987, 1981</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[Os3(CO)12]</td>
<td>2068, 2036, 2015, 2004</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>not assigned</td>
<td>2082, 2057, 2043, 2024, 1997</td>
</tr>
<tr>
<td>1a⁴</td>
<td>298</td>
<td>hexane/CO</td>
<td>3a'</td>
<td>2069, 1994, 1984</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[Os2(CO)3]²</td>
<td>2079, 2037, 2023, 2011, 1776</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>not assigned</td>
<td>2085, 2045</td>
</tr>
<tr>
<td>1a⁴</td>
<td>213</td>
<td>hexane/CO</td>
<td>3a'</td>
<td>2070, 1994, 1983</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[Os2(CO)3]²</td>
<td>2081, 2038, 2024, 2011, 1773</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[Os(CO)4]³</td>
<td>2037, 1994</td>
</tr>
<tr>
<td>1a⁴</td>
<td>213</td>
<td>hexane/ethene</td>
<td>3a'</td>
<td>2070, 1994, 1983</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[Os(CO)4]³</td>
<td>2081, 2038, 2024, 2011, 1773</td>
</tr>
<tr>
<td>1a⁴</td>
<td>213</td>
<td>hexane/1-octene</td>
<td>3a'</td>
<td>2069, 1993, 1983</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[Os2(CO)3]²</td>
<td>2081, 2038, 2024, 2011, 1773</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[Os(CO)4]³</td>
<td>2037, 1994</td>
</tr>
</tbody>
</table>

In the course of the irradiation, the IR spectra showed the disappearance of the ν(CO) bands of the starting compounds with simultaneous appearance of ν(CO) bands of the mononuclear complexes [Os(CO)3(diene)] (dien e = cis-1,3-butadiene (3a)¹³, 1,3-cyclohexadiene (3b)¹⁴). Additional new ν(CO) bands showed up due to the formation of [Os3(CO)12] and one or more unassigned carbonyl compounds (see Table 2). 1H NMR spectra were recorded before and after irradiation of 1a in CD2Cl2 in the NMR tube. New signals of 3a were observed at 0.28 (2H, m), 1.89 (2H, m) and 5.39 (2H, m) ppm, in good agreement with the literature values.¹³ In the ‘aromatic’ region two multiplets were observed at 6.93 and
8.63 ppm, with an overall intensity lower than 5% compared to that of the 3a signals. The corresponding minor product(s) were not characterized further.

During the photofragmentation of 1a and 1b, mono- and/or binuclear intermediates are presumably formed, that are coordinatively unsaturated and therefore highly reactive. In order to trap and characterize such transient species, the photoreactions of 1a were also performed in the presence of suitable donor molecules. During near-UV irradiation of 1a in CO-saturated hexane (λ_{irr} > 335 nm) at room temperature a neat conversion of the cluster into [Os(CO)3(cis-1,3-butadiene)] (3a) and [Os2(CO)9] (ref. 15) was monitored by IR spectroscopy. Prolonged irradiation led to decomposition of [Os2(CO)9] and formation of [Os3(CO)12]. When the experiment was repeated at 213 K, initially produced [Os2(CO)9] photodecomposed into [Os(CO)3], in agreement with the observations of Turner et al.\textsuperscript{16}

\[ (L)(CO)_3 Os - Os(CO)_3(L) \]

\textit{Figure 3. Proposed structure for [Os2(CO)6(μ-CO)(L)2] with L = ethene (4), 1-octene (5).}

Another revealing result was obtained upon irradiation of 1a (λ_{irr} > 335 nm) dissolved in (a) ethene-saturated, and (b) 0.1 M 1-octene-containing hexane at 213 K. Besides formation of [Os(CO)3(cis-1,3-butadiene)] (3a), a new product was observed, possessing an IR ν(CO) band at 1768 cm\textsuperscript{-1} (ethene) or 1764 cm\textsuperscript{-1} (1-octene) which is characteristic for the presence of a bridging CO ligand. In analogy with [Os2(CO)9] (ν(CO) at 1776 cm\textsuperscript{-1}) and [Os2(CO)8(ethylene)] (ν(CO) at 1780 cm\textsuperscript{-1}),\textsuperscript{16} the latter product is proposed to be the hitherto unobserved [Os2(CO)7(L)2] (L = ethene, 4, 1-octene, 5) with one carbonyl group occupying a bridging position, as illustrated in Figure 3. The lower ν(CO) frequencies of the CO bridge in 4 are consistent with the substitution of two and one terminal CO ligands in [Os2(CO)9] and [Os2(CO)8(ethylene)], respectively. In accordance with the more electron-donating character of 1-octene, the complex [Os2(CO)7(1-octene)2], 5, has all its ν(CO) bands slightly shifted to lower frequency compared with the ethene-containing derivative 4. It is noteworthy that neither [Os(CO)4(alkene)] nor [Os2(CO)8(μ-alkene)], that are formed upon irradiation of [Os3(CO)12] in the presence of alkene,\textsuperscript{17-19} were observed as the photoproducts of 1a and 1b.

\textbf{Nanosecond Time-Resolved Measurements}

Summarizing the results described above, the diene cluster 1 undergoes photofragmentation into the mononuclear complex [Os(CO)3(diene)] and a diosmium complex. Assuming that a (CO)₄Os–Os(CO)₂(diene) bond in 1 becomes significantly weakened in the excited state, the initial step on the reaction path is metal–metal bond
cleavage and formation of a biradical or \([\text{Os}_3(\text{CO})_6(\mu-\text{CO})(\text{diene})]\), the structural analogue of the proposed primary photoproduct formed upon near-UV irradiation of \([\text{Os}_3(\text{CO})_{12}]^{1,2}\) In order to detect and assign such transient species, nanosecond time-resolved absorption (TA) spectra were recorded under different conditions.

![Figure 4. Nanosecond time-resolved transient absorption spectra recorded during the partial back reaction of the primary photoproduct of \(1\text{b}\) in hexane; the time delay between the spectra equals 45 ns. The dotted line represents the UV-vis spectrum of the parent cluster \(1\text{b}\).](image)

Transient absorption spectra were recorded at various time delays after excitation with the laser pulse. Directly after excitation of \(1\text{a}\) in hexane, bleaching was observed below 445 nm due to depletion of the ground state, while a broad and intense transient absorption arose between 445 and 750 nm with a maximum at 632 nm. This transient disappeared completely and the bleaching of the absorption of \(1\text{a}\) recovered (ca. 70%) at the same rate (lifetime \(\tau = 105\) ns). The partial recovery of \(1\text{a}\) agrees with the fragmentation of the transient to the final photoproducts. Similar results were obtained for the cluster \(1\text{b}\) (see Figure 4). In this case, the long-wavelength transient species (\(\lambda_{\text{max}} = 636\) nm) lived 94 ns.

For both clusters \(1\) the experiments were repeated in CCl\(_4\), that has been proven to be an efficient scavenger for triosmium (bi)radicals.\(^3\) Importantly, in this case the use of CCl\(_4\) hardly affected the TA spectra. For \(1\text{a}\) the lifetime of the transient slightly decreased to 85 ns, for \(1\text{b}\) it slightly increased to 127 ns. These results exclude the possible generation of a biradical as the primary photoproduct. In the case of biradical formation, the reaction with CCl\(_4\) should considerably shorten the transient lifetime as determined in hexane.
The TA spectra of 1a and 1b in a hexane solution containing the donor ligand 1-octene again revealed the same absorption changes. In this case, however, the lifetime of the transient species was reduced to 48 ns and 32 ns for 1a and 1b, respectively. In addition, no recovery of the bleach was observed. This result indicates that the primary photoproducts, 2a and 2b, are coordinatively unsaturated and readily undergo complexation with 1-octene. The latter adduct is very labile and undergoes fast fragmentation preventing the back reaction to the parent clusters 1a and 1b.

The presence of the long-wavelength absorption in the TA spectra supports the hypothesis that the primary photoproducts 2a and 2b are coordinatively unsaturated. Related bi- or trinuclear metal carbonyls possessing an absorption band at considerably longer wavelength than the saturated precursor complexes, are frequently encountered. As examples may serve [Re₂(CO)₉] (ref. 20), [Pt₂(CO)Cp₂] (ref. 21), [Os₂(CO)₈] (ref. 22), [Os₃(CO)₁₁] (ref. 18) and [H₂Os₃(CO)₁₀] (ref. 23).

<table>
<thead>
<tr>
<th>cluster</th>
<th>solvent</th>
<th>τ(ns)</th>
<th>λₘₐₓ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>hexane</td>
<td>105</td>
<td>632</td>
</tr>
<tr>
<td>1a</td>
<td>1.0 M 1-octene in hexane</td>
<td>48</td>
<td>630</td>
</tr>
<tr>
<td>1a</td>
<td>CCl₄</td>
<td>85</td>
<td>632</td>
</tr>
<tr>
<td>1b</td>
<td>hexane</td>
<td>94</td>
<td>636</td>
</tr>
<tr>
<td>1b</td>
<td>1.0 M 1-octene in hexane</td>
<td>32</td>
<td>632</td>
</tr>
<tr>
<td>1b</td>
<td>CCl₄</td>
<td>127</td>
<td>635</td>
</tr>
</tbody>
</table>

Unfortunately, the transient absorption UV-vis spectra do not provide sufficient structural information about the primary photoproducts 2a and 2b. For this reason we studied the course of the photoreaction of 1b with nanosecond time-resolved infrared (TRIR) spectroscopy. The TRIR spectrum of 1b was recorded in heptane by monitoring the changes in absorption between 2130 and 1740 cm⁻¹ directly after excitation with the 355 nm pulse of a Nd:YAG laser. The resulting difference absorption spectrum is shown in Figure 5. Within the detector risetime, strong bleaching of the absorption bands of 1b was observed. Simultaneously, v(CO) bands arose at 2118, 2050, 2031, 2017, 2004, 1995, 1951, 1857, 1801 cm⁻¹, which were attributed to the novel transient product 2b. The most interesting feature of the TRIR spectrum is the presence of the two v(CO) bands at 1857 and 1801 cm⁻¹, which can be attributed to bridging carbonyl ligands. The v(CO) bands of the transient species disappeared completely after 200 ns, while only a partial recovery of the parent cluster was observed, estimated to ca. 70% from comparison of the initial and final band intensities at 2063 and 2024 cm⁻¹. The lifetime of the transient species 2b was determined by monitoring the intensity of the v(CO) bands at 1857 and 1801 cm⁻¹ as a function of time. The calculated value of 68 ns compares reasonably well with the result obtained from the ns TA spectra of 1b in hexane,
considering the quality of the kinetic traces. The quality of the TRIR spectrum was not sufficiently high to trace unambiguously $\nu$(CO) bands due to the fragmentation products.

\[ \begin{array}{c}
\text{Figure 5. TRIR spectrum of 2b, the primary photoproduct of 1b, in heptane measured 45 ns after laser excitation with 355 nm. For comparison, the FTIR spectrum of the parent cluster 1b is shown as a dotted line.} \\
\text{Evaluation of the results of the time-resolved experiments allows to propose a plausible structure of the primary photoproduct 2. First of all, its formation within a few nanoseconds and nearly complete back reaction to the starting cluster within a few hundred nanoseconds identifies it as a triosmium cluster, as such behaviour is very unlikely for products of a photofragmentation process. The inertness of the primary photoproduct towards CCl}_4 \text{ excludes its biradical nature. Another possibility is a structure analogous to that postulated for the open-triangle transients [M}_3(CO)_{11}((\mu\text{-CO})]) (M = Ru, Os) (see Figure 6A). However, in such a case a single IR $\nu$(CO) band is expected in the bridging-CO region, as was observed for the closely related photoproduct [Ru}_3(CO)_{12}(\mu\text{-CO})], see Figure 6B, and for the binuclear species [Os}_2(CO)\text{(ethene)}. The TRIR spectrum of 1b instead exhibits two bands in the $\nu$(CO) bridging region, which points to the doubly CO-bridged structure of the transient [Os}_3(CO)\text{Os}(\mu\text{-CO})_2(L)], 2 as depicted schematically in Figure 6C. In this structure, the (CO)_4Os-Os(CO)_2(diene) bond between Os1 and Os2 is split and the two osmium centres}
\end{array} \]
are connected together by the bridging carbonyl group, which probably moved from a terminal position at Os2 in 1. The resulting electron deficiency at Os2 is partly compensated by donation from the carbonyl ligand bridging the Os2–Os3 bond. It is important to note that semi-bridging carbonyls at a cluster core are hardly detectable by IR spectroscopy.\textsuperscript{25,26} The primary photoproduct 2 is still coordinatively unsaturated, which explains its shorter lifetime in the presence of added 1-octene (see Table 3).

![Diagram](image)

**Figure 6.** Proposed structures of the open-core (primary) photoproducts of (A) \([M_3(CO)_{11}(\mu-CO)] \) (M = Ru, Os), (B) \([Ru_3(CO)_{12}(\mu-CO)] \) under CO atmosphere, and (C) of the diene cluster 1.

### Conclusions

The experimental results document that substitution of two carbonyls in \([Os_3(CO)_{12}] \) by a 1,3-diene ligand strongly affects the photochemistry of the cluster. The reaction course is summarized in Scheme 1. Excitation of 1 leads to the short-lived primary photoproduct 2, for which a structure has been proposed on basis of the combined spectroscopic data. In the absence of the donor ligands alkene or CO, 2 mainly reacts back, but for \textit{ca.} 30\% fragmentation occurs, producing \([Os(CO)_{3}(\text{diene})] \) and \([Os_2(CO)_{7}] \). The latter intermediate could not be directly detected, as it rapidly decomposes into \([Os_3(CO)_{12}] \) and other, unassigned osmium carbonyl products. In contrast to 1, for the clusters \([M_3(CO)_{12}] \) (M = Ru, Os) in hexane, the open-core primary photoproduct \([M_3(CO)_{11}(\mu-CO)] \) has not been detected so far, being probably much shorter-lived and prone to rapid fragmentation in the presence of Lewis base ligands. Apparently, the presence of the diene ligand stabilizes the primary photoproduct 2 with regard to the regeneration of the parent cluster. At the same time, the photofragmentation of the cluster becomes competitive. In the presence of alkene the formation of 2 is completely irreversible. At low temperatures, the fragmentation products \([Os_2(CO)_{7}(L)_2] \) (L = CO, alkene) could be observed besides \([Os(CO)_{3}(\text{diene})] \). No evidence was obtained for a reaction of the 1,3-diene ligand at the cluster core upon irradiation of 1 and 2.
Scheme 1. Reaction mechanism for the photofragmentation of the triosmium diene clusters 1a and 1b

```
[Os_3(CO)_12] + other carbonyl products

[Os_2(CO)_7] + \[\text{other carbonyl products}\]

\[\text{[Os(CO)}_3(\text{diene})] + 2 \text{L}\]

a: cis-1,3-butadiene
b: 1,3-cyclohexadiene
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Experimental Section

Materials and Preparations

[Os_3(CO)]_{12} (ABCR), 1,3-butadiene (UCAR), 1,3-cyclohexadiene (Acros), ethene (Hoek Loos) and CO (99.5%, Hoek Loos) were used as purchased. Trimethylamine-N-oxide dihydrate, Me_3NO_2H_2O (Alfa), was dehydrated before use by vacuum sublimation. 1-Octene (Sigma) was passed over alumina and saturated with N_2 before use. Solvents of analytical (Acros: n-hexane, dichloromethane, THF, 2-methyltetrahydrofuran (2-MeTHF); Sigma-Aldrich: n-heptane) and spectroscopic (Merck: CCL_4) grade quality were dried over sodium wire (n-hexane, THF, 2-MeTHF) or CaH_2 (n-heptane, dichloromethane, CCL_4) and freshly distilled under nitrogen. CDCl_3 and CD_2Cl_2 (CIL) for NMR experiments were used as purchased.

Synthetic Procedures

The syntheses of the clusters 1a and 1b using [H_2Os_3(CO)]_{10} as a starting material have been reported by Tachikawa et al.\textsuperscript{11} We have followed a similar synthetic procedure as employed by Braga and co-workers for the synthesis of 1b,\textsuperscript{12} using [Os_3(CO)]_{10}(MeCN)_2.\textsuperscript{27} All syntheses were performed under an inert atmosphere of dry nitrogen, using standard Schlenk techniques.

Synthesis of [Os_3(CO)]_{10}(1,3-butadiene), 1a

1,3-butadiene was bubbled for 1 minute through a solution of [Os_3(CO)]_{10}(MeCN)_2 (400 mg) in THF (100 ml). The reaction mixture was stirred for 30 minutes, followed by solvent evaporation in vacuo. The crude product was purified by column chromatography over silica using dichloromethane/hexane 1:4 as eluent. The product was obtained as a yellow powder in 65 % yield. IR (hexane) ν(CO): 2113 (m), 2064 (s), 2033 (s), 2029 (s), 2025 (s), 2011 (s), 1999 (vw), 1992 (w,sh), 999
Photofragmentation of the Clusters \([\text{Os}_3(\text{CO})_{10}(\text{diene})]\\)

1985 (m), 1982 (sh), 1945 (w), 1935 (w) cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 5.39 (2H, t), 2.41 (2H, d), 0.56 (2H, d) ppm. UV-vis (hexane) \(\lambda (\epsilon \text{ in M}^{-1}\text{cm}^{-1})\): 246 (sh), 331(6.7 - 10\(^3\)), ca. 400 (sh) nm.

**Synthesis of \([\text{Os}_3(\text{CO})_{10}(1,3\text{-cyclohexadiene})]\\), 1b**

1,3-cyclohexadiene (1.8 ml) was added to a solution of \([\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2\] (330 mg) in CH\(_2\text{Cl}_2\) (100 ml). The reaction mixture was stirred for 1h. After this period the solvent was evaporated in vacuo. Purification of the crude product by column chromatography over silica using dichloromethane/hexane 1:5 as eluent yielded 1b as a yellow powder in 70 % yield. IR (hexane) \(\nu(\text{CO})\): 2111 (m), 2062 (s), 2032 (s), 2023 (vs), 2009 (s), 1991 (w), 1982 (m), 1972 (w), 1938 (w) cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 5.59 (2H, dd), 3.79 (2H, d), 1.88 (4H, s) ppm. UV-vis (hexane) \(\lambda (\epsilon \text{ in M}^{-1}\text{cm}^{-1})\): 244 (sh), 342 (10.1 - 10\(^3\)), ca. 400 (sh) nm.

**Spectroscopic Measurements**

UV-vis absorption spectra were recorded on a Varian Cary 4E and a Hewlett Packard 84533 spectrophotometer, and FTIR spectra on a Bio-Rad FTS-7 or a Bio-Rad FTS-60A spectrometer (16 scans at 2 cm\(^{-1}\) resolution). Low temperature IR measurements were performed using an Oxford Instruments DN 1704/54 liquid nitrogen cryostat with CaF\(_2\) and quartz windows. \(^1\)H NMR spectra were recorded with a Bruker AMX 300 spectrometer.

**Photochemistry**

All photochemical samples were prepared under a nitrogen atmosphere using standard inert gas techniques. Typical concentrations used were \(10^{-3} - 10^{-4}\) M cluster and 0.1 - 1.0 M alkene . The solution for the TRIR experiment was pump-degassed and overpressured with argon.

For continuous-wave photochemistry a Philips HPK 125 W high pressure mercury lamp served as a light source, equipped with the appropriate cut-off filters.

Nanosecond time-resolved absorption (TA) spectra were obtained by irradiating the samples with 7 ns pulses (fwhm) of a 355 nm line (5 mJ/pulse), obtained by frequency doubling of the 1064 nm fundamental of a Spectra Physics GCR-3 Nd:YAG laser. As the compounds under study were not photostable, a home-made flow cell was used. The probe light from a low-pressure, high power EG&G FX-504 Xe lamp was passed through the sample cell and dispersed by an Acton SpectraPro-150 spectrograph equipped with 150 g/mm or 600 g/mm grating and a tunable slit (1-500 \(\mu\)m), resulting in a 6 or 1.2 nm maximal resolution, respectively. The data collection system consisted of a gated intensified CCD detector (Princeton Instruments ICCD-576EMG/ RB), a programmable pulse generator (PG-200), and an EG&G Princeton Applied Research Model 9650 digital delay generator. With this OMA-4 setup, \(I_1\) and \(I_0\) are measured simultaneously using a double 8 kernel 200 \(\mu\)m optical fiber. This setup is programmed and accessed using WinSpec (v1.6.1, Princeton Instruments) under Windows.

Time-resolved IR (TRIR) experiments were performed using the set-up at the University of Nottingham.\(^{28}\) A Nd:YAG laser (Quanta-Ray GCR-12; 355 nm) was used to initiate reactions and the change in infrared absorption was determined using an infrared diode laser (Mütek MSD 1100). The changes in IR absorption at a selected wavenumber were monitored with a photovoltaic 77 K MCT.
detector (Laser Monitorings S-100) with a risetime of approximately 100 ns. The kinetic traces obtained at different wavenumbers were used to construct the transient IR spectra point by point. The solution in the TRIR cell was replaced after each laser shot. An accurate time profile for the kinetic traces were recorded using a faster photovoltaic 77 K MCT detector (Kolmar Technologies) with a risetime of ca. 40 ns.

References


