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Mechanistic study of the photofragmentation of the clusters $[Os_3(CO)_{10}(diene)]$ (diene = *cis*-1,3-butadiene, 1,3-cyclohexadiene): direct observation of the open-triangle primary photoproduct with nanosecond time-resolved infrared and UV–Vis spectroscopy

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Abstract

The photochemistry of the clusters $[Os_3(CO)_{10}(diene)]$ (diene = *cis*-1,3-butadiene, 1,3-cyclohexadiene) was studied in detail. Upon near-UV irradiation photofragmentation occurs to give mononuclear $[Os(CO)_3(diene)]$. The second fragmentation product $[Os_2(CO)_7]$ was trapped by reaction with CO, or with alkenes at low temperatures, to produce the dinuclear complexes $[Os_2(CO)_7(L)_2]$ (L = CO, 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-triangle structure with two bridging carbonyl groups, one bridging the split $(CO)_4Os-Os(CO)_2(diene)$ bond. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Photochemistry; Osmium complexes; Diene complexes; Triosmium complexes

1. Introduction

Thermal reactions of transition metal carbonyl 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 [1–9]. The photochemical behaviour of the clusters [M₃(CO)₁₂] (M = Ru, Os) has been studied most extensively [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 opentriangle cluster $[M_3(CO)_{11}(\mu$ -CO)] as the primary photoproduct; although, to date this species has never been directly observed. Recently, we showed that substitution of two carbonyl ligands in $[Os_3(CO)_{12}]$ by a chelating α -diimine ligand (e.g. 2,2'-bipyridine) drastically changed the photochemical behaviour [3,4,10]. Visible irradiation of $[Os_3(CO)_{10}(\alpha$ -diimine)] results in metalmetal bond cleavage yielding reactive biradical or zwitterionic photoproducts, depending on the reaction conditions and the nature of the α -diimine.

In this paper we report on the mechanistic investigation of the photochemistry of another class of $[Os_3(CO)_{10}(L)]$ clusters, with L = 1,3-diene coordinated to one of the osmium atoms. The structure of these clusters with diene = *cis*-1,3-butadiene (1a) [11] and 1,3cyclohexadiene (1b) [12] is depicted schematically in Fig. 1. We were able to detect and characterize the primary photoproducts of 1 with nanosecond time-resolved IR (TRIR) and UV-Vis absorption (TA) spec-

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Fig. 1. Schematic structure of $[Os_3(CO)_{10}(1,3-cis-butadiene)]$ (1a).

troscopy. The results are compared with the photoreactivity of the clusters $[M_3(CO)_{12}]$ (M = Ru, Os).

2. Experimental

2.1. 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, Me₃NO·2H₂O (Alfa), was dehydrated before use by vacuum sublimation. 1-Octene (Sigma) was passed over alumina and saturated with N₂ before use. Solvents of analytical (Acros: nhexane, dichloromethane, THF, 2-methyltetrahydrofuran (2-MeTHF); Sigma–Aldrich: n-heptane) and spectroscopic (Merck: CCl₄) grade quality were dried over sodium wire (n-hexane, THF, 2-MeTHF) or CaH₂ (n-heptane, dichloromethane, CCl₄) and freshly distilled under nitrogen. CDCl₃ and CD₂Cl₂ (CIL) for NMR experiments were used as purchased.

2.1.1. 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. [11]. We have followed a similar synthetic procedure as employed by Braga et al. for the synthesis of **1b** [12], using $[Os_3(CO)_{10}(MeCN)_2]$ [13]. All syntheses were performed under an inert atmosphere of dry nitrogen, using standard Schlenk techniques.

2.1.1.1. Synthesis of $[Os_3(CO)_{10}(1,3\text{-butadiene})]$ (1a). 1,3-Butadiene was bubbled for 1 min through a solution of $[Os_3(CO)_{10}(MeCN)_2]$ (400 mg) in THF (100 ml). The reaction mixture was stirred for 30 min, 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) v(CO): 2113 (m), 2064 (s), 2033 (s), 2029 (s), 2025 (s), 2011 (s), 1999 (vw), 1992 (w,sh), 1985 (m), 1982 (sh), 1945 (w), 1935 (w) cm⁻¹. ¹H NMR (CDCl₃) δ : 5.39 (2H, t), 2.41 (2H, d), 0.56 (2H, d) ppm. UV–Vis (hexane) λ (ε in M⁻¹ cm⁻¹): 246 (sh), 331 (6.7 × 10³), ca. 400 (sh) nm.

2.1.1.2. Synthesis of $[Os_3(CO)_{10}(1,3\text{-cyclohexadiene})]$ (1b). 1,3-Cyclohexadiene (1.8 ml) was added to a solution of $[Os_3(CO)_{10}(MeCN)_2]$ (330 mg) in CH₂Cl₂ (100 ml). The reaction mixture was stirred for 1 h. After this period the solvent was evaporated in vacuo. Purification of the crude product by column chromatography over silica using 1:5 dichloromethane/hexane as eluent yielded **1b** as a yellow powder in 70% yield. IR (hexane) ν (CO): 2111 (m), 2062 (s), 2032 (s), 2023 (vs), 2009 (s), 1991 (w), 1982 (m), 1972 (w), 1938 (w) cm⁻¹. ¹H NMR (CDCl₃) δ : 5.59 (2H, dd), 3.79 (2H, d), 1.88 (4H, s) ppm. UV–Vis (hexane) λ (ε in M⁻¹ cm⁻¹): 244 (sh), 342 (10.1 × 10³), ca. 400 (sh) nm.

2.2. Spectroscopic measurements

UV–Vis absorption spectra were recorded on a Varian Cary 4E and a Hewlett–Packard 84533 spectrophotometer, and FT IR 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 CaF₂ and quartz windows. ¹H NMR spectra were recorded with a Bruker AMX 300 spectrometer.

2.3. 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.

TA spectra were obtained by irradiating the samples with 7 ns pulses (fwhm) of a 355 nm line (5 mJ pulse $^{-1}$), 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 or 600 g mm⁻¹ grating and a tunable slit (1-500 µm), 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



Fig. 2. UV–Vis spectra of the clusters $[Os_3(CO)_{12}]$ (· · ·), **1a** (—) and **1b** (- - -) in hexane at 293 K.

Table 1

UV–Vis absorption maxima of $[Os_3(CO)_{12}]$ and the diene clusters 1a and 1b in hexane

Cluster	λ_{\max} (nm)
[Os ₃ (CO) ₁₂]	243, 325, 384 (sh)
1a	246 (sh), 331 (6.7 10 ³), ca. 400 (sh, br)
1b	244 (sh), 342 (10.1 10 ³), ca. 400 (sh, br)

OMA-4 setup, I and I_0 are measured simultaneously using a double 8 kernel 200 µm optical fiber. This setup is programmed and accessed using WINSPEC (v 1.6.1, Princeton Instruments) under Windows.

Time-resolved IR (TRIR) experiments were performed using the set-up at the University of Nottingham [14]. 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 Monitoring S-100) with a rise-time 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 rise-time of approximately 7 ns.

3. Results and discussion

3.1. UV–Vis spectra

The UV–Vis spectra of **1a**, **1b** and $[Os_3(CO)_{12}]$ are presented in Fig. 2 and summarized in Table 1. $[Os_3(CO)_{12}]$ 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.

3.2. 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 $\lambda_{irr} > 420$, 375 or 335 nm. For comparison, the unsubstituted cluster $[Os_3(CO)_{12}]$ 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 $[Os_3(CO)_{12}]$, irradiation of **1a** and **1b** in pure hexane at room temperature already resulted in fragmentation of the clusters according to Scheme 1. The products were characterized by IR and ¹H NMR spectroscopy.



Scheme 1. Reaction mechanism for the photofragmentation of the triosmium diene clusters 1a and 1b.

Table 2 IR v(CO) wavenumbers of the photoproducts of the clusters **1a** and **1b**

Cluster	<i>T</i> (K)	Solvent	Photoproduct	$v(CO) (cm^{-1})$
1a ^a	298	pentane	3a (Ref. [15]) $[Os_3(CO)_{12}]$ not assigned	2068, 1995, 1985 2068, 2036, 2015, 2004 2118, 2086, 2055, 2047, 2021
1b ^b	298	hexane	3b (Ref. [16]) $[Os_3(CO)_{12}]$ not assigned	2063, 1987,1981 2068, 2036, 2015, 2004 2082, 2057, 2043, 2024, 1997
1a ^c	298	hexane/CO	3a (Ref. [15]) $[Os_2(CO)_9]$ (Ref. [17]) $[Os_3(CO)_{12}]^d$ not assigned	2069, 1994, 1984 2079, 2037, 2023, 2011, 1776 2069, 2036, 2015, 2003 2085, 2045
1a °	213	hexane/CO	3a (Ref. [15]) $[Os_2(CO)_9]$ (Ref. [17]) $[Os(CO)_5]^d$	2070, 1994, 1983 2081, 2038, 2024, 2011, 1773 2037, 1994
1a °	213	hexane/ethene	3a (Ref. [15]) 4	2070, 1994, 1983 2060, 2037, 2020, 2012, 1768
1a °	213	hexane/1-octene	3a (Ref. [15]) 5	2069, 1993, 1983 2054, 2036, 2015, 2008, 1764

^a $\lambda_{\rm irr} > 375$ nm.

^b $\lambda_{\rm irr}$ > 420 nm.

 $^{\rm c}\lambda_{\rm irr}\!>\!335$ nm.

^d Secondary photoproducts formed upon prolonged irradiation. Ref. [18].

In the course of the irradiation, the IR spectra showed the disappearance of the v(CO) bands of the starting compounds with simultaneous appearance of v(CO)bands of the mononuclear complexes $[Os(CO)_3(diene)]$ (diene = cis-1,3-butadiene (3a) [15], 1,3-cyclohexadiene (3b) [16]). Additional new v(CO)bands showed up due to the formation of $[Os_3(CO)_{12}]$ 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 [15]. 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**, monoand/or dinuclear 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 ($\lambda_{irr} > 335$ nm) at room temperature a neat conversion of the cluster into $[Os(CO)_3(cis-1,3-butadiene)]$ (**3a**) and $[Os_2(CO)_9]$ [17] was monitored by IR spectroscopy. Prolonged irradiation led to decomposition of $[Os_2(CO)_9]$ and formation of $[Os_3(CO)_{12}]$. When the experiment was repeated at 213 K, initially produced $[Os_2(CO)_9]$ photodecomposed into $[Os(CO)_5]$, in agreement with the observations of Turner and co-workers [18].

Another revealing result was obtained upon irradiation of **1a** ($\lambda_{irr} > 335$ 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 v(CO) band at 1768 cm⁻¹ (ethene) or 1764 cm⁻¹ (1-octene), which is characteristic for the presence of a bridging CO ligand. In analogy with $[Os_2(CO)_9]$ (v(CO) at 1776 cm⁻¹) and $[Os_2(CO)_8(ethene)]$ (v(CO) at 1780 cm^{-1}) [18], the latter product is proposed to be the hitherto unobserved $[Os_2(CO)_7(L)_2]$, (L = ethene, 4, 1octene, 5) with one carbonyl group occupying a bridging position, as illustrated in Fig. 3. The lower v(CO)frequencies of the CO bridge in 4 and 5 are consistent with the substitution of two and one terminal CO ligands in $[Os_2(CO)_9]$ and $[Os_2(CO)_8(ethene)]$, respectively. In accordance with the more electron-donating character of 1-octene, the complex [Os₂(CO)₇(1octene)₂] (5) has all its v(CO) bands slightly shifted to lower frequency compared with the ethene-containing



Fig. 3. Proposed structure for $[Os_2(CO)_6(\mu-CO)(L)_2]$ with L = ethene (4), 1-octene (5).

derivative **4**. It is noteworthy that neither $[Os(CO)_4(alkene)]$ nor $[Os_2(CO)_8(\mu-alkene)]$, that are formed upon irradiation of $[Os_3(CO)_{12}]$ in the presence of alkene [19–21], were observed as the photoproducts of **1a** and **1b**.

3.3. 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 therefore metal-metal bond cleavage and formation of a biradical or $[Os_3(CO)_9(\mu-CO)(diene)]$, the structural analogue of the proposed primary photoproduct formed upon near-UV irradiation of $[Os_3(CO)_{12}]$ [1,2]. In order to detect and assign such transient species, we recorded nanosecond time-resolved absorption (TA) spectra under different conditions.

Transient absorption spectra were recorded at various time delays after excitation with the laser pulse. Directly after excitation of **1a** 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 **1a** recovered (approximately 70%) at the same rate (lifetime $\tau = 105$ ns). The partial recovery of **1a** agrees with the fragmentation of the transient to the final photoproducts. Similar results were obtained for the cluster **1b** (see Fig. 4). In this case, the long-wavelength transient species ($\lambda_{max} = 636$ 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 1a the lifetime of the transient slightly decreased to 85 ns, for 1b 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 backreaction to the parent clusters **1a** and **1b**.

Fig. 4. Nanosecond time-resolved transient absorption spectra recorded during the partial back reaction of the primary photoproduct of **1b** in hexane; the time delay between the spectra equals 45 ns. The dotted line represents the UV–Vis spectrum of the parent cluster **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 di- or trinuclear metal carbonyls possessing an absorption band at considerably longer wavelength than the saturated precursor complexes, are frequently encountered. As examples may serve $[Re_2(CO)_9]$ [22], $[Pt_2(CO)Cp_2]$ [23], $[Os_2(CO)_8]$ [24], $[Os_3(CO)_{11}]$ [20] and $[H_2Os_3(CO)_{10}]$ [25].

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 Fig. 5.

Within the detector rise-time, 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 completely disappeared after 200 ns, while only a partial recovery of the parent cluster was observed, estimated to approximately 70%





Fig. 5. TRIR spectrum of **2b**, the primary photoproduct of **1b**, in heptane measured 45 ns after laser excitation with 355 nm. For comparison, the FT IR spectrum of the parent cluster **1b** is shown as a dotted line.

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 v(CO)bands due to the fragmentation products.

Evaluation of the results of the time-resolved experiments allows one 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 photo-



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

Table 3

Lifetimes and absorption maxima of the primary photoproducts of **1a** and **1b** obtained from the nanosecond time-resolved absorption spectra

Cluster	Solvent	τ (ns)	$\lambda_{\rm max}$ (nm)
1a	hexane	105	632
1a	1.0 M 1-octene in hexane	48	630
1a	CCl_4	85	632
1b	hexane	94	636
1b	1.0 M 1-octene in hexane	32	632
1b	CCl ₄	127	635

product towards CCl₄ excludes its biradical nature. Another possibility is a structure analogous to that postulated for the open-triangle transients $[M_3(CO)_{11}(\mu -$ CO)] (M = Ru, Os) (see Fig. 6(A)). In such a case, however, a single IR v(CO) band is expected in the bridging-CO region, as was observed for the closely related photoproduct $[Ru_3(CO)_{12}(\mu-CO)]$ [26], see Fig. 6(B), and for the dinuclear species $[Os_2(CO)_7(\mu-$ CO)(ethene)] [18]. The TRIR spectrum of 1b instead exhibits two apparent small-wavenumber v(CO) bands, which points to the doubly CO-bridged structure of the transient $[Os_3(CO)_8(\mu-CO)_2(L)]$ (2) as depicted schemat-6(C). In this structure, ically in Fig. the $(CO)_4Os-Os(CO)_2$ (diene) bond between Os1 and Os2 is split and the two osmium centres 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 semibridging carbonyls at a cluster core are hardly detectable by IR spectroscopy [27,28]. The primary photoproduct 2 is still coordinatively unsaturated, which explains its shorter lifetime in the presence of added 1-octene (see Table 3).

4. 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. The excitation of **1** leads to the short-lived primary photoproduct **2**, for which a structure has been proposed on the basis of the combined spectroscopic data. In the absence of the donor ligands alkene or CO, **2** mainly reacts back, but for approximately 30% fragmentation occurs, producing $[Os(CO)_3(diene)]$ 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 opencore 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 $[Os(CO)_3-$ (diene)].

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