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The photochemistry of dinuclear osmium carbonyl complexes; characterisation of $Os_2(CO)_8$ using matrix isolation

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Abstract

UV photolysis of $Os_2(CO)_9$ or $((\mu\text{-C1,C2})CH_2CH_2)Os_2(CO)_8$ (**1**) isolated in argon matrices causes ejection of a CO or C_2H_4 ligand respectively, and formation of $Os_2(CO)_8$, which has a structure with only terminal CO groups. Long wavelength irradiation of matrix isolated $Os_2(CO)_8$ in the presence of potential 2 electron donor ligands leads to production of $Os_2(CO)_8L$ ($L = CO$, N_2 or C_2H_4), each containing a bridging CO group and a terminally bound ligand L. Photolysis using plane polarised light provides confirmation of the C_{2v} structure of $Os_2(CO)_9$, and gives evidence favouring a D_{2h} structure for $Os_2(CO)_8$. Prolonged UV photolysis of $Os_2(CO)_9$ in CO matrices leads to cleavage of the Os–Os bond and production of $Os(CO)_5$.

Introduction

It seems appropriate that, one hundred years after Ludwig Mond's original publication of the discovery of nickel tetracarbonyl [1], we have been studying the photochemistry of a simple binary metal carbonyl, $Os_2(CO)_9$, the existence of which was uncertain until quite recently. In 1891, a year after his discovery of $Ni(CO)_4$, Mond observed the photochemical decomposition of $Fe(CO)_5$ to give CO and a solid product [2], which was later formulated by Dewar and Jones as $Fe_2(CO)_9$ [3], the iron analogue of $Os_2(CO)_9$. The time of writing is also the 50th anniversary of the first publication of the crystal structure of $Fe_2(CO)_9$ [4], one of the most widely known and well characterised dinuclear metal carbonyls. Indeed, this close relative of $Os_2(CO)_9$ was studied in our laboratory several years ago [5,6], providing evidence for photodissociation of CO and formation of $Fe_2(CO)_8$. A study of

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$Os_2(CO)_9$ provides the opportunity to characterise the unsaturated species $Os_2(CO)_8$, which has been proposed as a reactive intermediate in several studies on polynuclear osmium systems [7–10].

The photochemistry of dinuclear transition metal carbonyls has been the subject of considerable interest in recent times, both in solution and in low temperature matrices [11]. For both homoleptic dinuclear metal carbonyls such as $Mn_2(CO)_{10}$ and cyclopentadienyl complexes such as $[CpFe(CO)_2]_2$ ($Cp = \eta^5\text{-}C_5H_5$), the primary photochemical processes have been found to be (1) dissociative loss of CO to give unsaturated dinuclear complexes (e.g. eq. 1) and (2) homolytic cleavage of the metal–metal bond to give mononuclear, metal centred radicals (e.g. eq. 2) [12,13].

$$Mn_2(CO)_{10} \rightarrow Mn_2(CO)_9 + CO \qquad (1)$$

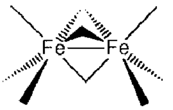
$$Mn_2(CO)_{10} \rightarrow 2Mn(CO)_5 \qquad (2)$$

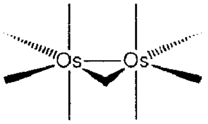
In inert gas matrices, homolysis of the M–M bond is not usually observable, because the bulky radicals produced are held close together in the matrix cage and are forced to recombine. However, ejection of a CO ligand can usually be observed, since the small CO molecule can diffuse away from the complex more easily, thus preventing rapid recombination. The mononuclear fragments formed by metal–metal bond cleavage can often be trapped if a more reactive matrix medium such as CO is employed.

Solution studies have involved both product analysis and the use of flash photolysis to detect the reactive intermediates produced by UV light. It has generally been found that the same dinuclear photoproducts created in low temperature matrices can also be observed in room temperature solutions.

Particularly useful in this respect has been the recent development of time resolved infrared (TRIR) spectroscopy [14], a technique employing UV flash photolysis coupled with fast IR detection. This has allowed the direct comparison of the IR spectra of transient species in room temperature solution with low temperature matrix IR spectra. The ν(C–O) bands of photoproducts observed by TRIR spectroscopy generally give greater structural information than the broad electronic absorptions observed in conventional flash photolysis.

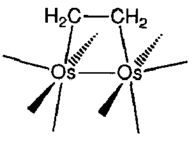
The existence of osmium and ruthenium enneacarbonyls was in doubt for many years after the preparation of their iron analogue, $Fe_2(CO)_9$. The synthesis of $Os_2(CO)_9$ was first reported in 1970 by Moss and Graham [15], who later presented evidence for the formation of $Ru_2(CO)_9$ by a similar route [7]. The infrared and mass spectra of $Os_2(CO)_9$ were consistent with the complex having the structure of C_{2v} symmetry shown below, with four terminal CO groups on each osmium atom, and one CO group bridging the osmium–osmium bond. $Ru_2(CO)_9$ is believed to have a similar structure, whereas $Fe_2(CO)_9$ is known to possess a structure of D_{3h} symmetry with 3 bridging CO groups as illustrated [4,16]. The difference in structure between these molecules is probably due to the longer metal–metal bonds in the osmium and ruthenium species, which make it less energetically favourable for carbonyl groups to occupy a bridging position.





When the matrix photochemistry of $Fe_2(CO)_9$ was studied in our laboratory [5,6], it was found that the photoproduct, $Fe_2(CO)_8$, formed upon loss of a CO ligand, could exist as two structural isomers, either with two bridging CO groups or an unbridged structure. It was possible, using the techniques of ^{13}CO isotopic enrichment and photochemistry with polarised light, to characterise in detail the structures of these two isomers. $Co_2(CO)_8$ is also known to exist in bridged or unbridged forms [17]. It is of interest whether $Os_2(CO)_8$ would show similar structural isomerism, in view of the effect that the metal–metal bond length has on structures of the precursor molecules, $Fe_2(CO)_9$ and $Os_2(CO)_9$.

A carbonyl ligand in $Os_2(CO)_9$ and the olefin unit in $((\mu\text{-C1,C2})CH_2CH_2)Os_2(CO)_8$ (**1**) and related diosmacyclobutanes can be easily replaced by other olefins and acetylenes under mild, thermal conditions [10]. Kinetic studies on these reactions indicate a dissociative mechanism and implicate $Os_2(CO)_8$ as a common reactive intermediate [18]. The ethylene exchange reaction is highly stereospecific [10a] which suggests a concerted mechanism (rather than a diradical one) for the fragmentation of the diosmacyclobutane, **1**, into C_2H_4 and $Os_2(CO)_8$.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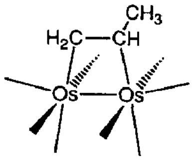

1a

Such a concerted mechanism is more plausible if $Os_2(CO)_8$ has a singlet ground state, although calculations [19] suggest that the HOMO and LUMO of $Os_2(CO)_8$ are very close in energy, and thus make either a singlet or a triplet ground state thinkable. In this paper the technique of matrix isolation photochemistry is used to prepare the reactive species $Os_2(CO)_8$, to determine its geometry and to deduce its electronic structure indirectly.

Experimental

The matrix isolation apparatus, Air Products Displex, and UV photolysis equipment, Philips 125 W HPK medium pressure Hg arc lamp have been described previously [20,21]. Filters used for photolysis were a $NiSO_4$ (800 $g dm^{-3}$)/$CoSO_4$ (400 $g dm^{-3}$) aqueous solution (2 cm path length, band pass 230–345 nm), and $\lambda > 375$ nm and $380 < \lambda < 550$ nm glass filters. For irradiation with longer wavelength light a 180 W Kodak Carousel S slide projector was used together with a $\lambda > 525$ nm glass filter. All IR spectra of matrix isolated species were obtained using a Nicolet 7199 FTIR interferometer and model 1280 data station (32k data collect, 256k Fourier transform, i.e. 0.5 cm^{-1} resolution). Matrices were prepared using the "slow spray-on" technique [21] with the sample of $Os_2(CO)_9$ or $((\mu\text{-C1,C2})CH_2CH_2)Os_2(CO)_8$ (**1**) in a pyrex tube attached to the vacuum shroud surrounding the CsBr matrix window. It was found that the room temperature vapour pressures of both $Os_2(CO)_9$ and **1** were sufficient for sublimation of the sample onto the matrix window at the required rate. The rate of deposition of the matrix gas was controlled using a needle valve. The CsBr matrix window was typically 20 K during deposition of the matrix, and cooled to ca. 12 K before photolysis.

The principles and practice of polarised photochemistry have been described in detail elsewhere [6,21,22]. These experiments involve photolysing the matrix isolated sample using plane polarised light. FTIR spectra are recorded through a polariser with its plane of polarisation either parallel or perpendicular to the plane of the photolysing light. The IR polariser was mounted directly in front of the detector on the Nicolet 7199 interferometer bench. The polariser could be rotated such that the plane of polarisation of the electric vector of the IR light entering the detector was either horizontal or vertical. Single beam background spectra were recorded with the polariser in each of these orientations so that subsequent spectra could be ratioed with the background of correct polarisation. Comparison of the two spectra recorded at each stage of an experiment reveals whether absorption bands of matrix isolated species show any linear dichroism.

$Os_2(CO)_9$ was prepared by olefin/carbonyl exchange (eq. 3):

$$((\mu\text{-C1,C2})CH_2CHCH_3)Os_2(CO)_8 + CO \rightarrow Os_2(CO)_9 + CH_2CHCH_3 \qquad (3)$$

A solution of $((\mu\text{-C1,C2})CH_2CHCH_3)Os_2(CO)_8$ (**1a**) [8,23,24] (96 mg, 0.15 mmol in 20 ml pentane) was added to a 100 ml Fischer & Porter bottle, purged several times with CO and then pressurised to 140 psig CO. The vessel was tightly wrapped in Al foil to exclude light. The stirred solution was allowed to react for 10 h at room temperature, during which time it was vented and recharged periodically to remove propylene. The IR spectrum of the bright yellow solution showed clean conversion to $Os_2(CO)_9$, with traces of $Os_4(CO)_{16}$ [25]. $Os_2(CO)_9$ can be recrystallised directly from the pentane solution at $-20\,^\circ C$ to give orange needles (80 mg, 84% yield collected by filtration). Analytically pure samples can be obtained by sublimation [7,15], but with considerable loss of yield. $Os_2(CO)_9$ is heat and light sensitive but the solid can be stored indefinitely in the dark at $-40\,^\circ C$. Samples were stored under a CO atmosphere for shipping to Nottingham and between matrix experiments without apparent decomposition. It was found that many matrices could be prepared from a single sample of ca. 15 mg $Os_2(CO)_9$ kept in this way.

The diosmacyclobutane $((\mu\text{-C1,C2})CH_2CH_2)Os_2(CO)_8$ (**1**) was prepared by standard literature methods [8,26]. The propylene analogue, $((\mu\text{-C1,C2})CH_2CHCH_3)Os_2(CO)_8$ (**1a**), used in the above synthesis of $Os_2(CO)_9$, was prepared photochemically, using a modified version of literature procedures [8,23,24].

Matrix gases (Ar, N_2 and CH_4, Messer-Griesheim; CO BOC research grade) were all used without further purification.

Results and discussion

UV photolysis of $Os_2(CO)_9$

The IR spectrum of $Os_2(CO)_9$ isolated in an argon matrix at 12 K (Fig. 1a) is essentially identical to the spectrum recorded in n-heptane solution, with 4 strong terminal ν(C–O) bands and 1 bridging ν(C–O) band (see Table 1). The frequencies of these bands show small shifts from the solution spectrum and some of the bands are split into two or more narrow components. These splittings, which vary according to the type of matrix used are assigned to site effects in the crystal lattice of the solid matrix. The weak absorption at 2139 cm^{-1} is due to a small amount of uncoordinated CO trapped in the matrix. This probably originates from a slight decomposition of the $Os_2(CO)_9$ sample under vacuum, during deposition of the

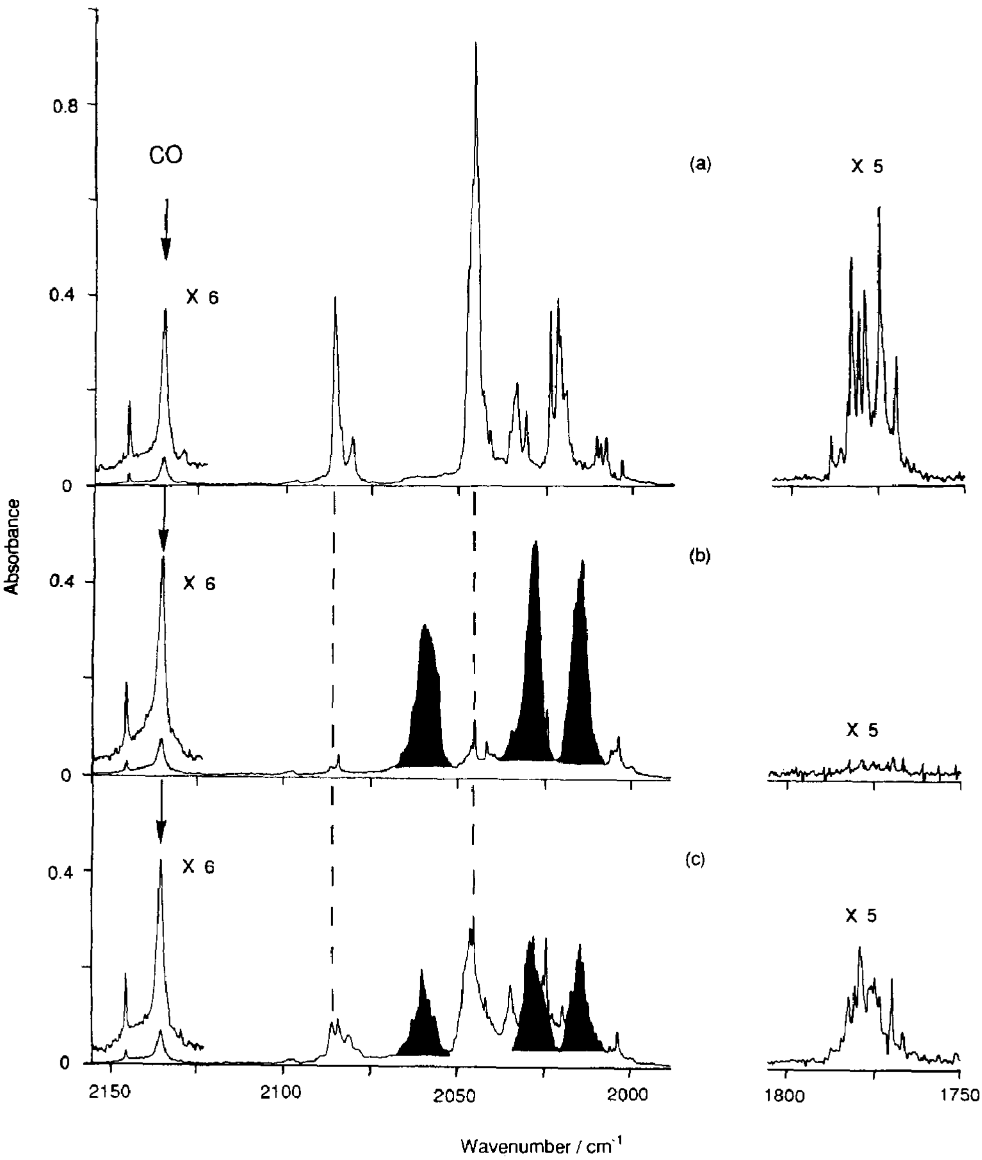


Fig. 1. IR absorption spectra illustrating the photochemistry of $Os_2(CO)_9$ in an argon matrix at 12 K. (a) Before photolysis, (b) After 30 min near UV irradiation (> 375 nm). Bands due to the photoproduct, $Os_2(CO)_8$, are coloured black. (c) After 110 min long wavelength (> 525 nm) photolysis, showing reappearance of bands of $Os_2(CO)_9$ and depletion of $Os_2(CO)_8$ and CO. Note the absorbance scale expansion factors for the bridging ν(C–O) region and for free CO.

matrix. The matrix IR spectrum is thus in agreement with the C_{2v} structure proposed for $Os_2(CO)_9$ [7,15].

Near UV irradiation (> 375 nm) of the matrix leads to a decrease in intensity of all of the ν(C–O) bands assigned to $Os_2(CO)_9$ and the growth of three new intense bands in the terminal ν(C–O) region, coloured black in Fig. 1b. After 30 min UV photolysis the bands of $Os_2(CO)_9$ have virtually disappeared. There is also an increase in the amount of uncoordinated CO in the matrix as shown by the growth of the absorption at 2139 cm^{-1}. The amount of uncoordinated CO produced by

Table 1

Frequencies (cm^{-1}) of ν(C–O) bands of $Os_2(CO)_9$, $Os_2(CO)_8$ and $Os(CO)_5$ in different matrices at 12 K. Weak bands assigned as ^{13}CO satellites are not included.

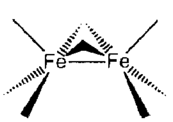
Species	Matrix gas				Solution ^{d}
	Ar	N_2	CO	CH_4	
$Os_2(CO)_9$	2085.2 ^{a}	2087.0 ^{a}	^{c}	2084.3	2080
	2041.9 ^{a}	2046.5 ^{a}	2046.0 ^{a}	2045.1 ^{a}	2038
	2028.8 ^{a}	2026.8	2026.0	2027.5 ^{a}	2024
	2018.4 ^{a}	2013.0 ^{a}	2011.1 ^{a}	2011.3 ^{a}	2013
	1778.5 ^{b}	1771.6 ^{b}	1759.9 ^{b}	1766.3	1778
$Os_2(CO)_8$	2056.8	2059.3 ^{a}	2055.5 ^{a}	2055.7 ^{a}	
	2023.4	2025.0	2022.4	2023.5	
	2007.1	2007.6 ^{a}	2005.3	2004.1	
$Os(CO)_5$			2046.2		
			1995.3		
			1985.6		

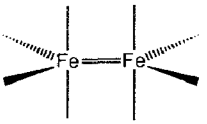
^{a} Strongest component of band split by matrix effects. ^{b} Average frequency of band split into multiplet by matrix effects. ^{c} High frequency band obscured by absorption of CO matrix. ^{d} Recorded in n-heptane solution [7,15].

photolysis is consistent with the ejection of one molecule of CO for each molecule of $Os_2(CO)_9$ destroyed [27]. This suggests that UV photolysis causes dissociation of CO from $Os_2(CO)_9$ to give an unsaturated dinuclear product with the formula $Os_2(CO)_8$ (eq. 4).

$$Os_2(CO)_9 \xrightarrow[\text{Ar/12 K}]{\text{UV}} Os_2(CO)_8 + CO \qquad (4)$$

The IR spectrum of $Os_2(CO)_8$ (Fig. 1b) has three absorptions in the terminal ν(C–O) region but no absorptions in the bridging ν(C–O) region so $Os_2(CO)_8$ must have a structure with only terminal CO ligands. The analogous iron species, $Fe_2(CO)_8$ was found to exist in two isomeric structures, with or without bridging CO groups, as illustrated below [5,6]. The unbridged structure was found to be more thermodynamically stable than the structure with two CO bridges. For $Os_2(CO)_8$, which has a longer metal–metal bond, one would expect a bridged isomer to be even less energetically favourable. This is consistent with our observation of only an unbridged isomer of $Os_2(CO)_8$ in these experiments.





Repeating the photolysis of $Os_2(CO)_9$ in an argon matrix using light of wavelength 230–345 nm resulted in similar changes in the IR spectrum. $Os_2(CO)_9$ was destroyed and the bands assigned to the photoproducts, $Os_2(CO)_8$ and free CO, grew in. Under these photolysis conditions the rate of the photochemical destruction of $Os_2(CO)_9$ was increased somewhat, indicating either a larger quantum yield for photolysis at these wavelengths, or competition with the reverse reaction, viz.

recombination of $Os_2(CO)_8$ with CO, when longer wavelength irradiation is used (see below).

It was found that similar spectral changes occurred when $Os_2(CO)_9$ was photolysed in CO, N_2 or CH_4 matrices. In each of these experiments, $Os_2(CO)_9$ was destroyed by photolysis and the ν(C–O) absorptions assigned to $Os_2(CO)_8$ grew in. The frequencies of the bands observed in the experiments are shown in Table 1.

Further evidence that the photoproduct observed in these experiments is $Os_2(CO)_8$, was obtained by photolysis of the diosmacyclobutane complex ((μ-C1,C2)CH_2CH_2)$Os_2(CO)_8$ (**1**), in an argon matrix at 12 K. $Os_2(CO)_8$ has been proposed as an intermediate in both thermal and photochemical reactions of diosmacyclobutanes in solution. The olefin fragments in these complexes have been found to exchange with other olefins or acetylenes to yield a range of diosmacycles or with CO to give $Os_2(CO)_9$. Indeed, the preparation of $Os_2(CO)_9$ used here utilises the exchange of CO with propylene in the related complex ((μ-C1,C2)CH_2CHCH_3)$Os_2(CO)_8$ (**1a**) (see Experimental).

Figure 2a shows the IR spectrum of **1** isolated in an argon matrix at 12 K. The terminal ν(C–O) region agrees well with the spectrum recorded in hydrocarbon solution (see Table 2). The changes in the IR spectrum caused by 3 minutes UV photolysis (230–345 nm) can be seen in Fig. 2b. The bands of **1** have virtually disappeared, and three new intense absorptions, coloured black, have grown in. These new absorptions correspond exactly with those observed after photolysis of $Os_2(CO)_9$ in an argon matrix shown in Fig. 1b. (Slight differences in the relative band intensities and widths in the two experiments are probably due to a small variation in the matrix concentration or weak interactions of $Os_2(CO)_8$ with the photoejected CO or C_2H_4 molecules in the matrix cage). A weak absorption at 950.1 cm^{-1}, due to free ethylene in the matrix, is also observed, proving that UV photolysis causes ejection of C_2H_4 from **1** (eq. 5). The fact that the same photo-

Table 2

Frequencies (cm^{-1}) of ν(C–O) bands of $Os_2(CO)_8$-ethylene complexes, **1** and **2**, in an argon matrix at 12 K. Solution data are also given for **1**.

Species	Ar matrix	n-Hexane solution
((μ-C1,C2)CH_2CH_2)$Os_2(CO)_8$	2125.6	2122
(**1**)	2080.5	2077
	2042.2 [a]	2037
	2034.9 [a]	2030
	2025.5	2020
	2014.1	2012
	1997.2	1994
(η^2-C_2H_4)$Os_2(CO)_8$	2121.4	
(**2**)	2072.2	
	2032.7	
	2029.3	
	2019.7	
	2003.4	
	1996.0 [a]	
	1778.9	

[a] Average frequency of band split by matrix effects.

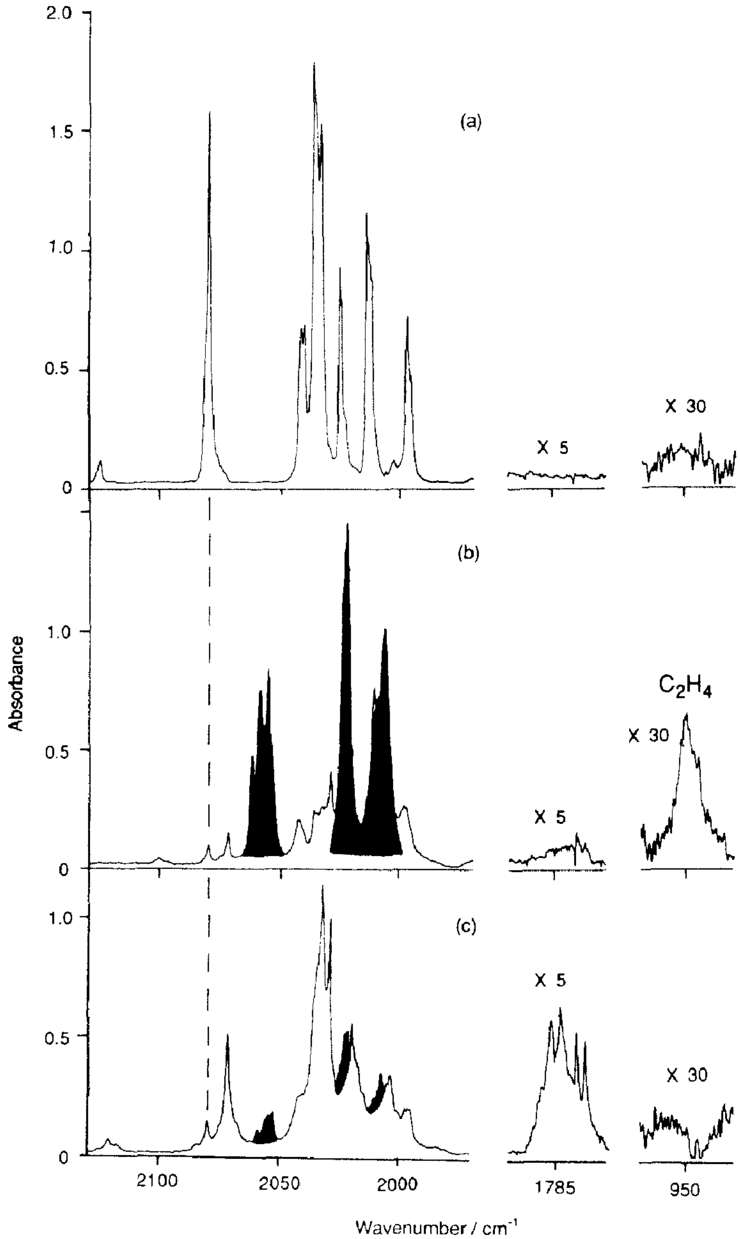


Fig. 2. IR spectra illustrating the photochemistry of $((\mu\text{-C1,C2})CH_2CH_2)Os_2(CO)_8$ (**1**) in an argon matrix at 12 K. (a) Before photolysis. (b) After 3 min UV photolysis (230–345 nm). The bands coloured black are due to $Os_2(CO)_8$. Note the low frequency absorption due to the photoejected C_2H_4. (c) After 15.5 h long wavelength irradiation (> 525 nm).

product is observed, on both dissociation of CO from $Os_2(CO)_9$, and dissociation of C_2H_4 from **1**, gives clear evidence that the photoproduct is, indeed, $Os_2(CO)_8$.

$$\underset{(\mathbf{1})}{((\mu\text{-C1,C2})CH_2CH_2)Os_2(CO)_8} \xrightarrow[\text{Ar/12 K}]{\text{UV}} Os_2(CO)_8 + C_2H_4 \qquad (5)$$

This is the first example of a dinuclear complex where photoejection of a bridging ligand has been shown to occur in matrix isolation studies. As yet we have no evidence to suggest whether a terminal or bridging CO group is ejected from $Os_2(CO)_9$.

Photochemical and thermal reactions of $Os_2(CO)_8$ in matrices

In many previous matrix studies on similar systems, it has been found that unsaturated dinuclear metal carbonyl complexes have electronic absorption bands at longer wavelengths than their saturated precursors [13,28]. By exciting these absorptions with visible light, the unsaturated species can be induced to recombine with the photoejected CO, or with other potential 2 electron donor ligands.

Reaction of $Os_2(CO)_8$ with CO

When an argon matrix containing $Os_2(CO)_8$ was irradiated with visible light of wavelength > 525 nm, the IR absorptions of $Os_2(CO)_8$ and free CO decreased in intensity and those of $Os_2(CO)_9$ increased (Fig. 1c), indicating that recombination of $Os_2(CO)_8$ with CO is indeed promoted under these photolysis conditions (eq. 6).

$$Os_2(CO)_8 + CO \xrightarrow[Ar/12\ K]{\lambda > 525\ nm} Os_2(CO)_9 \tag{6}$$

Similarly, long wavelength photolysis of $Os_2(CO)_8$ in a pure CO matrix resulted in regeneration of $Os_2(CO)_9$, the reaction proceeding more rapidly than in an argon matrix, as might be expected. The recombination of $Os_2(CO)_8$ with CO in a CO matrix could also be promoted by annealing the matrix to 30 K. These results do not show whether the incoming CO ligand enters a terminal or bridging position. However, preliminary results from ^{13}CO isotopic labelling experiments on $Os_2(CO)_9$ in solution indicate that the ^{13}CO ligand enters a terminal position [29].

To summarize, we have now shown how the unsaturated dinuclear complex $Os_2(CO)_8$ can be created in low temperature matrices, and under what conditions its recombination with CO can be achieved. Before explaining how we were able to elucidate the structure of this species, we will describe the reactivity of $Os_2(CO)_8$ towards other small molecules, such as N_2, C_2H_4 and CH_4.

Photochemistry of $Os_2(CO)_9$ in N_2 matrices

Figure 3a shows the spectrum of $Os_2(CO)_8$ produced by UV photolysis of $Os_2(CO)_9$ in a N_2 matrix at 12 K. Photolysis with light of wavelength > 525 nm leads to a decrease in the bands of $Os_2(CO)_8$ but unlike in argon matrices, no regrowth of the bands of $Os_2(CO)_9$ was observed. Instead, in this experiment, several other new bands appeared after long wavelength irradiation of the matrix (Fig. 3b). The most significant of these bands, arrowed near 2250 cm^{-1}, is in the region normally associated with the ν(N–N) mode of a terminal N_2 ligand coordinated to a metal centre. This shows that photochemical excitation of $Os_2(CO)_8$ in a N_2 matrix can lead to the coordination of a dinitrogen ligand, in preference to the photoejected CO, presumably to give a complex with the formula $Os_2(CO)_8(N_2)$ (N) (eq. 7). (Reaction of unsaturated dinuclear metal carbonyls with N_2 in matrices has previously been observed for both $Fe_2(CO)_8$ and $Re_2(CO)_9$, from which, respectively, $Fe_2(CO)_8(N_2)$ and $Re_2(CO)_9(N_2)$ can be produced [5,6,21,30]).

$$Os_2(CO)_8 \xrightarrow[N_2/12\ K]{\lambda > 525\ nm} Os_2(CO)_8(N_2) \tag{7}$$

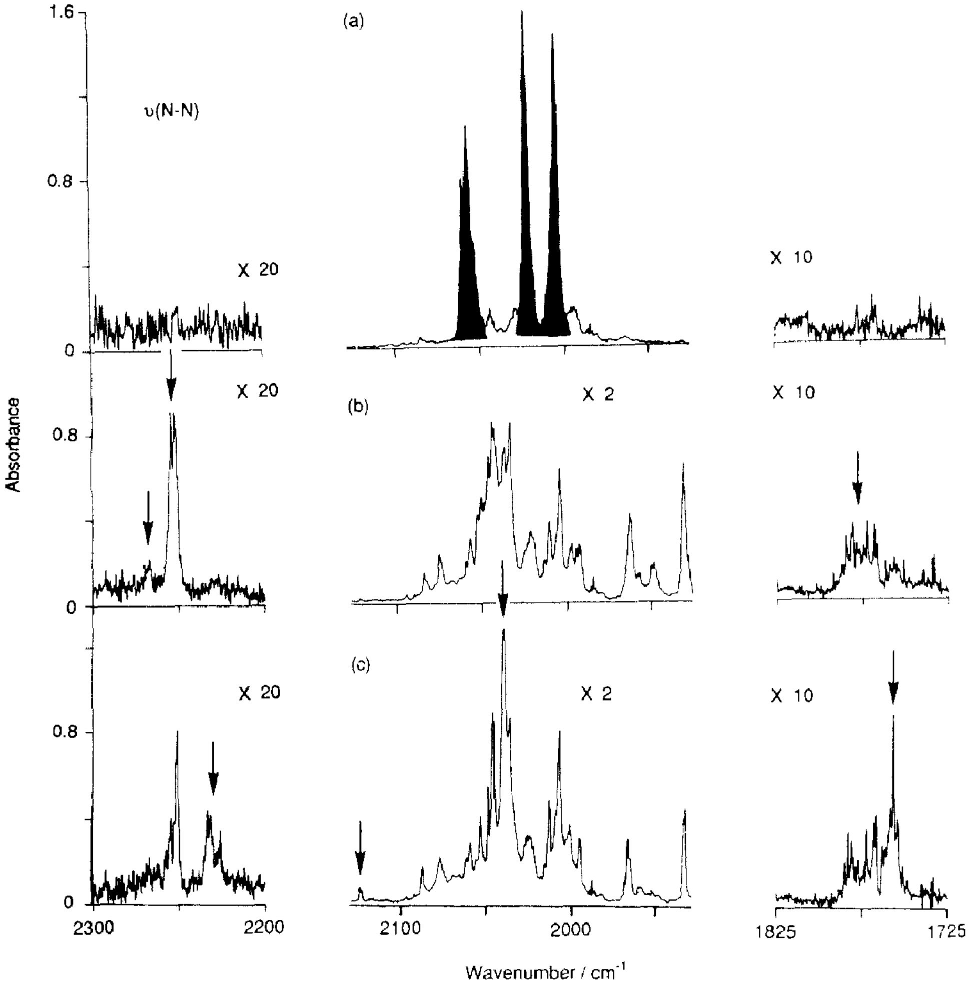


Fig. 3. IR absorption spectra illustrating the reactivity of $Os_2(CO)_8$ towards N_2. (a) Bands of $Os_2(CO)_8$ (coloured black) generated by 6 min UV photolysis of $Os_2(CO)_9$ in a N_2 matrix at 12 K. (b) After 50 min long wavelength irradiation (> 525 nm). New bands in the ν(N–N) and bridging ν(C–O) regions, assigned to N and N′ are arrowed (see text). (c) After annealing the matrix to 30 K for 10 min. New bands assigned to N″ are arrowed.

This behaviour is entirely analogous to the recombination of $Os_2(CO)_8$ with CO under the same photolysis conditions. Several terminal ν(C–O) bands of N can be seen in Fig. 3b and these are listed in Table 3. There is also a weak new absorption marked with an arrow in the bridging ν(C–O) region at higher frequency than the bridging ν(C–O) band of $Os_2(CO)_9$. This can be assigned to a bridging carbonyl group in N. As well as the principal ν(N–N) band produced after long wavelength photolysis, we observed a second, much weaker band near 2270 cm^{-1} (arrowed in Fig. 3b), which is also attributable to the stretch of a terminal N_2 ligand. This may be assigned to N′, a structural isomer of N where the N_2 ligand is bound in a different coordination site (see below).

Figure 3c shows the IR spectrum obtained after annealing the matrix containing N to 30 K. Annealing causes considerable modification to the IR spectrum and several new absorptions, indicated by arrows, have appeared. The terminal ν(C–O)

Table 3

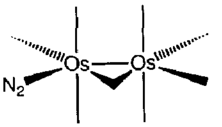
Frequencies (cm^{-1}) of IR bands observed for dinitrogen containing complexes. Bands bracketed together are assigned to a single absorption split by matrix effects.

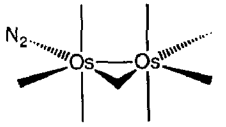
Species	N	N′	N″
ν(N–N)	2254.4 }	2269.2	2233.3
	2252.3 }		
ν(C–O) (terminal) [a]	2077.5		2124.2
	2059.5		2039.5
	2053.1		
	2048.9		
	2045.3		
	2036.1		
	2024.5		
	2013.9		
	2007.2		
	1966.3		
	1951.8		
	1934.2		
ν(C–O) (bridging)	1780.5		1756.6

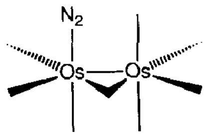
[a] It is difficult to assign bands in the terminal ν(C–O) region to particular species due to the crowded nature of the spectrum. All the bands observed in this region before annealing the matrix are therefore assigned to N. Without doubt, some of these are due to matrix splittings.

region is very complicated and it is difficult to make definite assignments. However the changes in the ν(N–N) region are much simpler. The ν(N–N) band of N has diminished and a previously unobserved band near 2230 cm^{-1} has appeared after annealing the matrix. This is assigned to the ν(N–N) mode of a new species N″, containing a terminal N_2 ligand. Bands assigned to N″ are listed in Table 3, including a new bridging ν(C–O) band at 1756.6 cm^{-1}. The weak new absorption at 2124.2 cm^{-1} could be assigned to either a high frequency terminal ν(C–O) mode or a low frequency ν(N–N) mode. Since several dinuclear osmium carbonyl complexes possess a band near 2130 cm^{-1} (e.g. $ROs_2(CO)_8R'$ (R,R′ = H, CH_3) [31a]), we favour the assignment of this absorption to a ν(CO) mode.

It is probable that N″ is another structural isomer of $Os_2(CO)_8(N_2)$ with a bridging CO group formed by a thermal rearrangement of N, in which the N_2 ligand shifts to occupy a different coordination site. Thus we have evidence for three structural isomers of $Os_2(CO)_8(N_2)$. Previous studies have shown that $Re_2(CO)_9(N_2)$ exists as axially or equatorially substituted isomers [30]. Three possible structures for $Os_2(CO)_8(N_2)$ are shown below. These are based on the replacement of terminal CO groups of $Os_2(CO)_9$ with an N_2 ligand. Our evidence does not indicate which of the three possible positions is occupied by the N_2 ligand in each of the observed species.







None of these dinitrogen complexes could be formed by merely annealing a N_2 matrix containing $Os_2(CO)_8$ to 35 K, indicating that $Os_2(CO)_8$ has less thermal reactivity towards N_2 than towards CO. (The unbridged isomer of $Fe_2(CO)_8$ was also found to be unreactive when annealed in a N_2 matrix [6]).

UV irradiation of a matrix containing these dinitrogen complexes leads to the disappearance of all their absorptions and the reappearance of the bands of $Os_2(CO)_8$, indicating that UV photolysis can cause dissociation of N_2 from these species (eq. 8).

$$Os_2(CO)_8(N_2) \xrightarrow[N_2/12\ K]{UV} Os_2(CO)_8 + N_2 \tag{8}$$

Reaction of $Os_2(CO)_8$ with ethylene

We have already shown how $Os_2(CO)_8$ can be generated by photodissociation of ethylene from the diosmacyclobutane, **1**, in an argon matrix. When the matrix containing $Os_2(CO)_8$ and free ethylene is photolysed with light of wavelength > 525 nm, the IR absorptions of both $Os_2(CO)_8$ and free C_2H_4 are destroyed (Fig. 2c). However, none of the starting complex, **1**, is regenerated. Instead, several new ν(C–O) absorptions are observed, including a low frequency band assigned to a bridging CO group (see Table 2). (These absorptions are already present with low intensity after UV photolysis, Fig. 2b).

These observations lead to the conclusion that long wavelength photolysis induces the recombination of $Os_2(CO)_8$ with C_2H_4 to give a product in which the C_2H_4 ligand is coordinated to the $Os_2(CO)_8$ fragment in a different manner than in the starting complex, **1**. In view of our observation of an IR absorption of a bridging CO group, it would seem likely that the product has the formulation $(OC)_4Os(\mu\text{-}CO)Os(CO)_3(C_2H_4)$ (**2**) containing ethylene bound to one of the osmium atoms as an η^2-ligand. (The mononuclear species, $Os(CO)_4(C_2H_4)$ is known to include an ethylene ligand bound in this fashion [31]).

$$Os_2(CO)_8 + C_2H_4 \xrightarrow[Ar/12\ K]{\lambda > 525\ nm} \underset{(\mathbf{2})}{(OC)_4Os(\mu\text{-}CO)Os(CO)_3(\eta^2\text{-}C_2H_4)} \tag{9}$$

This reaction (eq. 9) is entirely analogous with that of $Os_2(CO)_8$ with CO or N_2 under the same photolysis conditions. In each case, our results indicate that the incoming ligand binds to one end of the dinuclear complex, with one of the terminal CO groups of $Os_2(CO)_8$ migrating to a bridging position in the product. UV irradiation of **2** leads to the regeneration of the IR bands of $Os_2(CO)_8$ and C_2H_4, indicating that ethylene can be photoejected from 2 (eq. 10). This is a process similar to that observed for the N_2 complexes (see above).

$$\underset{(\mathbf{2})}{(OC)_4Os(\mu\text{-}CO)Os(CO)_3(\eta^2\text{-}C_2H_4)} \xrightarrow[Ar/12\ K]{UV} Os_2(CO)_8 + C_2H_4 \tag{10}$$

Note added in proof. Recent results obtained independently by Grevels and co-workers show that $Os_2(CO)_8$ can be generated by flash photolysis of **1** in cyclohexane at room temperature [32a]. The ν(CO) bands monitored by time-resolved IR spectroscopy show gratifying agreement with those we have recorded in low temperature matrices. $Os_2(CO)_8$ was observed to decay with a lifetime of ca. 40 μs at room temperature. A longer lived species, generated by recombination of $Os_2(CO)_8$ with ethylene, has a very similar IR spectrum to complex **2**, above, Grevels et al. propose the doubly CO-bridged $(OC)_3Os(\mu\text{-}CO)_2((\mu\text{-}C1,C2)C_2H_4)$-

$Os(CO)_3$ as an alternative isomeric structure for this product. However, we favour the isomer with terminal η^2-C_2H_4 ligand for two reasons: (1) The intensity of the bridging $\nu(CO)$ band relative to the terminal $\nu(CO)$ bands is similar to that in $Os_2(CO)_9$, which has a single CO bridging group. (2) Our observation of a weak high frequency $\nu(CO)$ band at 2121.4 cm^{-1} is consistent with the structure of lower symmetry. In a separate study, Weitz has used time-resolved IR spectroscopy to monitor the products of flash photolysis of gas phase $Os(CO)_5$ [32b]. The $\nu(CO)$ bands assigned to $Os_2(CO)_8$ again match well with our matrix data.

Photochemistry of $Os_2(CO)_9$ in methane matrices

A similar experiment was performed where $Os_2(CO)_8$ was created by photolysing $Os_2(CO)_9$ in a methane matrix. On subsequent irradiation with light of wavelength > 525 nm, the recombination of $Os_2(CO)_8$ with CO to give $Os_2(CO)_9$ was again promoted. However, we also observed some weak features in the terminal $\nu(C-O)$ region of the IR spectrum, at 2117, 2068 and 1929 cm^{-1}, which grew in upon long wavelength photolysis. These absorptions did not occur in other matrices and may be due to a species in which CH_4 interacts in some way with the unsaturated $Os_2(CO)_8$ complex. At present we have insufficient evidence to suggest what this interaction might be. Previously it has been suggested that the unsaturated mononuclear species, $Fe(CO)_4$ and $Os(CO)_4$ can interact with methane in low temperature matrices [33].

Photolysis using plane polarised light

Photochemistry and spectroscopy with polarised light has proved extremely valuable in the structural characterisation of dinuclear metal carbonyls trapped in low temperature matrices [6,21,28,34]. The technique relies on the fact that photolysis using plane polarised light will preferentially destroy those molecules which are oriented in the matrix with their photoactive transition moment vector parallel with the oscillating electric dipole of the photolysing light. It is assumed that molecules as bulky as dinuclear metal carbonyls have insufficient thermal energy to rotate within the matrix cage. Thus, this technique leads to the generation of partially oriented, dichroic samples of both parent and photoproduct in the matrix, and observation of the dichroism of individual absorption bands is helpful in assigning these absorptions.

Figure 4b shows the dichroism in the $\nu(C-O)$ bands of $Os_2(CO)_9$ and $Os_2(CO)_8$ produced by 7 min polarised photolysis (380–550 nm) of $Os_2(CO)_9$ isolated in a N_2 matrix. The polarisation of each band relative to the plane of photolysis is also given in Table 4. We will first consider the bands of those molecules of $Os_2(CO)_9$ remaining intact after photolysis. The $\nu(C-O)$ modes of $Os_2(CO)_9$, assuming the C_{2v} structure proposed by Moss and Graham [7,15], are illustrated in Fig. 5. As long as the bridging carbonyl group does not cause any large departure from D_{2h} symmetry for the terminal CO groups, the $a_1(1)$, $a_1(2)$ and $b_2(3)$ vibrations, although formally IR active for C_{2v} symmetry, are likely to be very weak.

The low frequency band due to the bridging carbonyl in $Os_2(CO)_9$ exhibits dichroism parallel to the plane of the photolysing light. The change in dipole moment for the a_1 stretch of a symmetrically bridging carbonyl group must be perpendicular to the metal–metal bond. Therefore this observation shows that the remaining molecules of $Os_2(CO)_9$ have a preferred orientation with their Os–Os

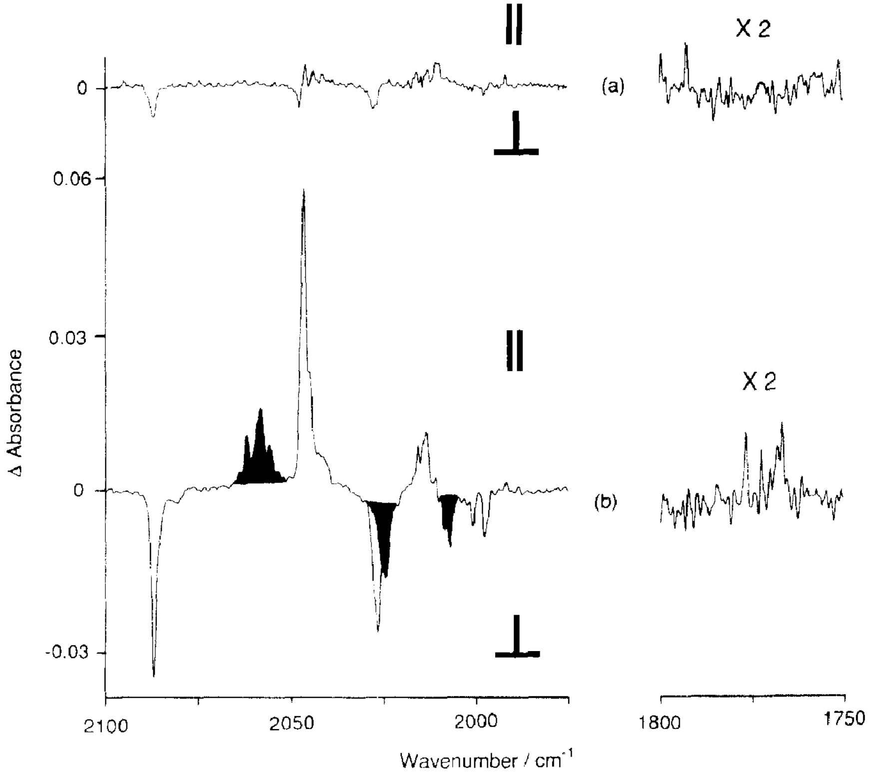


Fig. 4. IR spectra illustrating the dichroism generated by near-UV photolysis of Os$_2$(CO)$_9$ in an N$_2$ matrix with plane polarised light. These are subtraction spectra showing the difference in absorbance between spectra measured through a polariser either parallel or perpendicular to the plane of photolysis. (Δ absorbance) = $A_{\parallel} - A_{\perp}$). (a) Before photolysis; essentially a non-dichroic spectrum indicating a randomly oriented sample. (b) After 7 min plane polarised photolysis (380–550 nm). Bands due to Os$_2$(CO)$_8$ are coloured black.

Table 4

Linear dichroism observed in ν(C–O) bands of Os$_2$(CO)$_9$ and Os$_2$(CO)$_8$ after plane polarised photolysis of Os$_2$(CO)$_9$ in a N$_2$ matrix at 12 K. Assignments are based on C_{2v} symmetry for Os$_2$(CO)$_9$ and D_{2h} symmetry for Os$_2$(CO)$_8$. The ν(C–O) vibrations for these species are illustrated in Fig. 5. The Os–Os bonds of Os$_2$(CO)$_9$ molecules have a preferred orientation perpendicular to the plane of photolysis, and those of Os$_2$(CO)$_9$ parallel to the plane of photolysis (see text).

	ν(C–O) (cm^{-1})	Polarisation relative to plane of photolysis	Polarisation relative to Os–Os bond	Assignment
Os$_2$(CO)$_9$	2087.0	$\perp$	$\parallel$	b_2 (1)
	2046.5	$\parallel$	$\perp$	b_1
	2026.8	$\perp$	$\parallel$	b_2 (2)
	2013.0	$\parallel$	$\perp$	a_1 (3)
	1771.6	$\parallel$	$\perp$	a_1 (bridge)
Os$_2$(CO)$_8$	2059.3	$\parallel$	$\parallel$	b_{2u} (1)
	2025.0	$\perp$	$\perp$	b_{3u} + b_{2u} (2)
	2007.6	$\perp$	$\perp$	b_{1u}

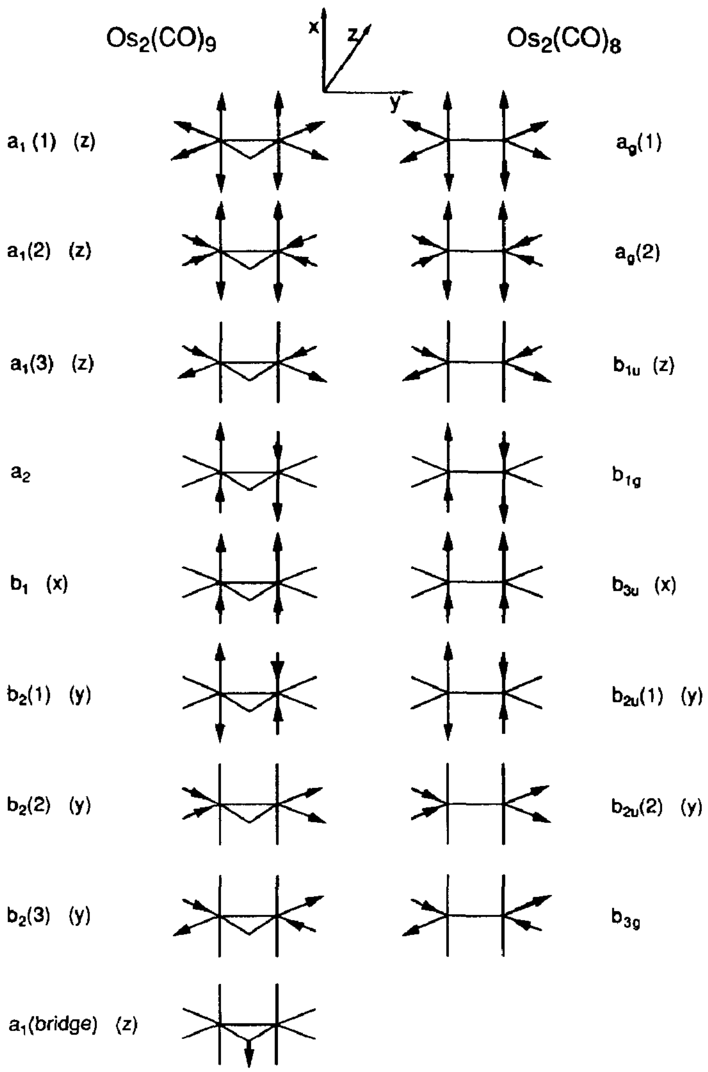


Fig. 5. Normal ν(C–O) vibrational modes for C_{2v} $Os_2(CO)_9$ and D_{2h} $Os_2(CO)_8$. The directions of the transition moment vectors for IR active modes are given in brackets. The same reference axes have been used in each case to illustrate the correlation between the symmetry modes of the two species.

bonds perpendicular to the plane of photolysis. In other words, molecules of $Os_2(CO)_9$ with Os–Os bonds parallel to the plane of photolysis have been preferentially destroyed by photolysis. This implies that the photoactive transition moment responsible for the ejection of CO from $Os_2(CO)_9$ is parallel to the Os–Os bond.

The highest frequency band of $Os_2(CO)_9$ is polarised in the opposite direction to the bridging band. This is consistent with the assignment of this band to a ν(C–O) mode for which the change in dipole moment is parallel to the Os–Os bond. By analogy with studies on the infrared spectrum of $Os_3(CO)_{12}$ [35,36] we assign this high frequency band to the $b_2(1)$ vibration of the axial CO ligands.

The strongest ν(C–O) band of $Os_2(CO)_9$ is polarised in the same direction as the bridging carbonyl band, so the dipole moment change for this vibration would be expected to be perpendicular to the Os–Os bond. It is assigned to a b_1 vibration of the axial CO ligands, again in agreement with the studies on $Os_3(CO)_{12}$ [35,36].

The two lower frequency terminal ν(C–O) bands are due to vibrations predominantly of the equatorial CO groups. The higher of these bands is polarised perpendicular to the plane of photolysis, and is assigned to the $b_2(2)$ vibration with a dipole moment change along the Os–Os bond. The lower frequency band is polarised in the opposite direction (i.e. perpendicular to the Os–Os bond) and is assigned to the $a_1(3)$ vibration of the equatorial CO groups. Thus the polarised IR spectrum of $Os_2(CO)_9$ is consistent with the C_{2v} structure proposed for this molecule. This is an example of how polarised photochemistry can give evidence for the structure of a molecule for which no crystallographic data are available.

We will now show how polarised photochemistry has helped us to determine the structure of $Os_2(CO)_8$. There are several possible structures for an unbridged

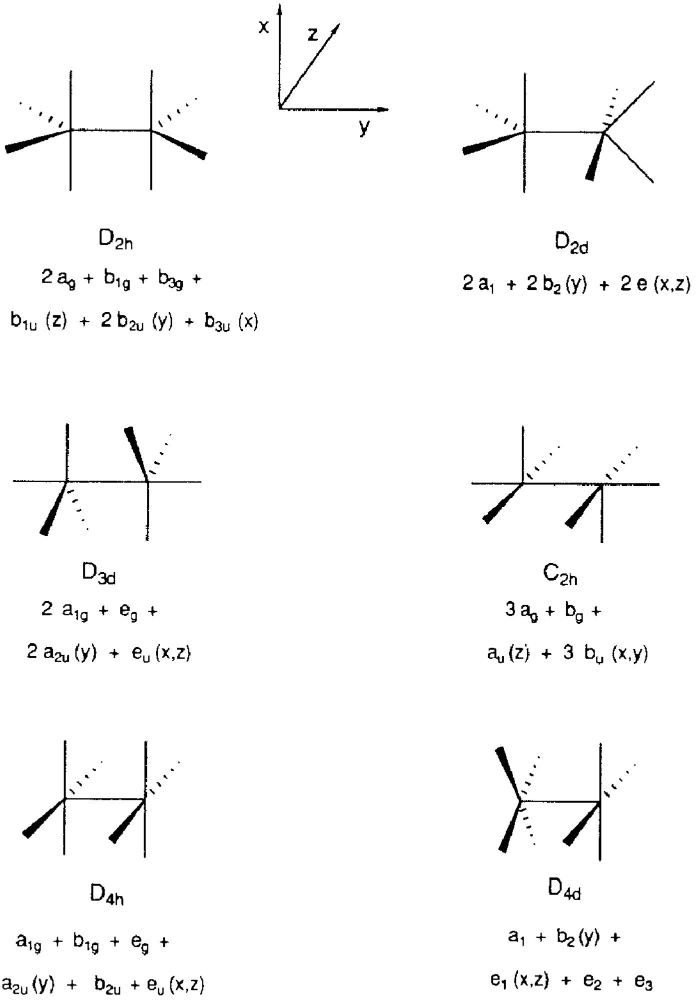


Fig. 6. Six possible structures for an unbridged $M_2(CO)_8$ molecule. The point group and predicted normal ν(C–O) vibrational modes are given for each structure, using the same set of cartesian axes in each case (as illustrated). The directions of the transition moment vectors for IR active modes are given in brackets.

$M_2(CO)_8$ system, as illustrated in Fig. 6 together with their predicted ν(C–O) vibrational modes.

Hoffmann's isolobal analogy [37] predicts that the most likely structure is the one with D_{2h} symmetry, consisting of two trigonal bipyramidal metal centres joined through an equatorial coordination site. This is expected to have a singlet electronic ground state and is the structure proposed for unbridged $Fe_2(CO)_8$ in earlier studies [6]. It can be produced, formally at least, by simply removing the bridging CO group from $Os_2(CO)_9$. A closely related structure is the one of D_{2d} symmetry where one of the equatorially linked $M(CO)_4$ units is twisted through 90° with respect to the other.

The terminal ν(C–O) region of the IR spectrum of $Os_2(CO)_8$, with either a D_{2h} or D_{2d} structure, would be expected to be very similar to that of the parent compound, given the close resemblance of the structures However, $Os_2(CO)_8$ shows only three strong absorptions in the terminal ν(C–O) region, whereas four bands are predicted for D_{2h} or D_{2d} symmetry. However, a structure with D_{3d} symmetry, where two trigonal bipyramidal metal centres are joined through an axial position, would be expected to give rise to three strong terminal ν(C–O) bands. If $Os_2(CO)_8$ had D_{3d} symmetry it would be required to possess a triplet ground state. The HOMO and LUMO of $Os_2(CO)_8$, which are calculated to be close in energy if a D_{2h} structure is assumed, become degenerate in D_{3d} symmetry and a triplet ground state is the inevitable result [19]. For similar reasons the 32e$^-$ dimer (η^5-C_5Me_5)$Fe_2(\mu$-$CO)_3$, the core of which has D_{3h} symmetry, has a triplet ground state [38]. Polarised photochemistry has been used to help us rule out the D_{3d} structure for $Os_2(CO)_8$.

The polarisations of the bands of $Os_2(CO)_8$ produced in the early stages of plane polarised photolysis of $Os_2(CO)_9$ in a N_2 matrix can be seen in Fig. 4b are listed in Table 4. Earlier we showed that the photoactive transition moment responsible for CO loss from $Os_2(CO)_9$ has a direction parallel to the Os–Os bond. If we assume that $Os_2(CO)_8$ is produced from $Os_2(CO)_9$ without rotation of the Os–Os bond, then the molecules of $Os_2(CO)_8$ produced should exhibit a preferred orientation with their Os–Os bonds parallel to the plane of photolysis.

The high frequency band of $Os_2(CO)_8$ is polarised parallel to the plane of photolysis, so the dipole moment change for this vibration must be parallel to the Os–Os bond if the above assumption is correct. The two lower frequency absorptions are polarised in the opposite direction i.e. with dipole moment changes perpendicular to the Os–Os bond.

By analogy with complexes of known D_{3d} symmetry, such as $Hg(Co(CO)_4)_2$ [39], D_{3d} $Os_2(CO)_8$ is expected to have two higher frequency bands of a_{2u} symmetry polarised parallel to the Os–Os bond, with the lower frequency e_u band polarised in a perpendicular direction. Clearly, our observations are not in agreement with the assignment of a D_{3d} structure to $Os_2(CO)_8$, and we can definitely rule out this structure.

As already stated, the IR spectrum of $Os_2(CO)_8$ with a D_{2h} structure should have four bands in the terminal ν(C–O) region. The vibrational modes responsible for these bands and their correlations with those of $Os_2(CO)_9$ are shown in Fig. 5. If the molecules of $Os_2(CO)_8$ are preferentially aligned with their Os–Os bonds pointing in one direction, the two vibrations of b_{2u} symmetry should be polarised in the opposite direction to the b_{1u} and b_{3u} vibrations. By analogy with the previous

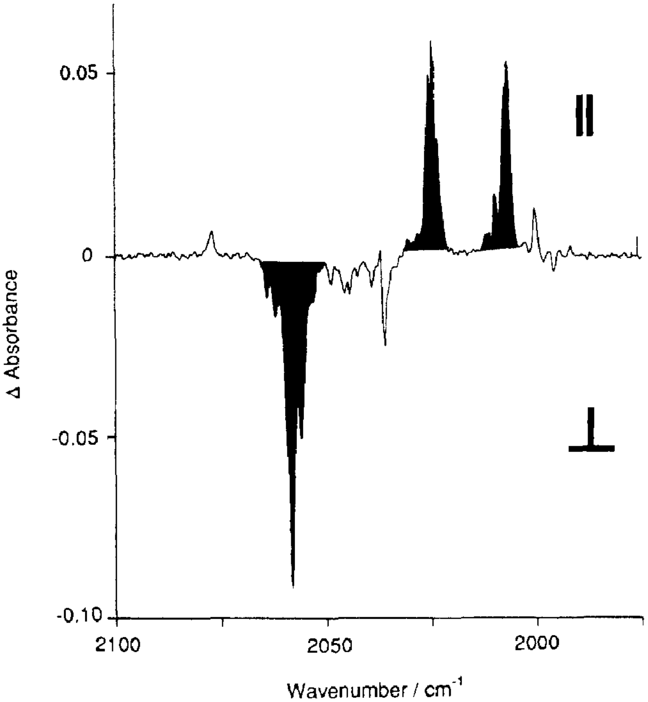


Fig. 7. IR difference spectrum (Δ absorbance = $A_{\parallel} - A_{\perp}$) showing the dichroism generated by 10 min irradiation of a randomly oriented sample of $Os_2(CO)_8$ in a N_2 matrix with plane polarised light (> 525 nm). The polarisations of the bands of the remaining $Os_2(CO)_8$ are the opposite to those observed in Fig. 4b (see text for discussion).

assignments for $Os_2(CO)_9$, the high frequency band of $Os_2(CO)_8$ can be assigned as the b_{2u} vibration of the axial CO groups, polarised along the Os–Os bond. Similarly the low frequency band is the radial b_{1u} mode, polarised in a perpendicular direction. If the axial b_{3u} (perpendicular) and radial b_{2u} (parallel) absorptions were coincident at an intermediate frequency, this would lead to our observation of a 1/2 ($\parallel/\perp$) ratio of band polarisations. (The polarisation of the intense b_{3u} band would outweigh that of the weak b_{2u} absorption).

Hence our observations are consistent with a D_{2h} structure for $Os_2(CO)_8$. It is impossible to rule out the closely related D_{2d} structure which would have similar IR polarisation properties. However we favour the former structure due to its very close relationship with the structure of the parent molecule, $Os_2(CO)_9$.

Figure 7 shows the polarised IR spectrum obtained after plane polarised photolysis (> 525 nm) of a randomly oriented sample of $Os_2(CO)_8$ in a N_2 matrix. It shows that the polarisations produced in each of the ν(C–O) bands of $Os_2(CO)_8$ are the opposite to those observed on the production of $Os_2(CO)_8$ from $Os_2(CO)_9$ (see Fig. 3). This implies that molecules of $Os_2(CO)_8$ with their Os–Os bonds aligned parallel to the plane of photolysis have been preferentially destroyed. This shows that the electronic transition of $Os_2(CO)_8$ excited by light of wavelength > 525 nm (promoting combination with CO, N_2 or C_2H_4) has a transition moment vector along the Os–Os bond.

Evidence for photochemical cleavage of the Os–Os bond

Filtered UV irradiation (230–345 or 380–550 nm) of $Os_2(CO)_9$ in a pure CO matrix produced results similar to those in other matrices, with $Os_2(CO)_9$ being

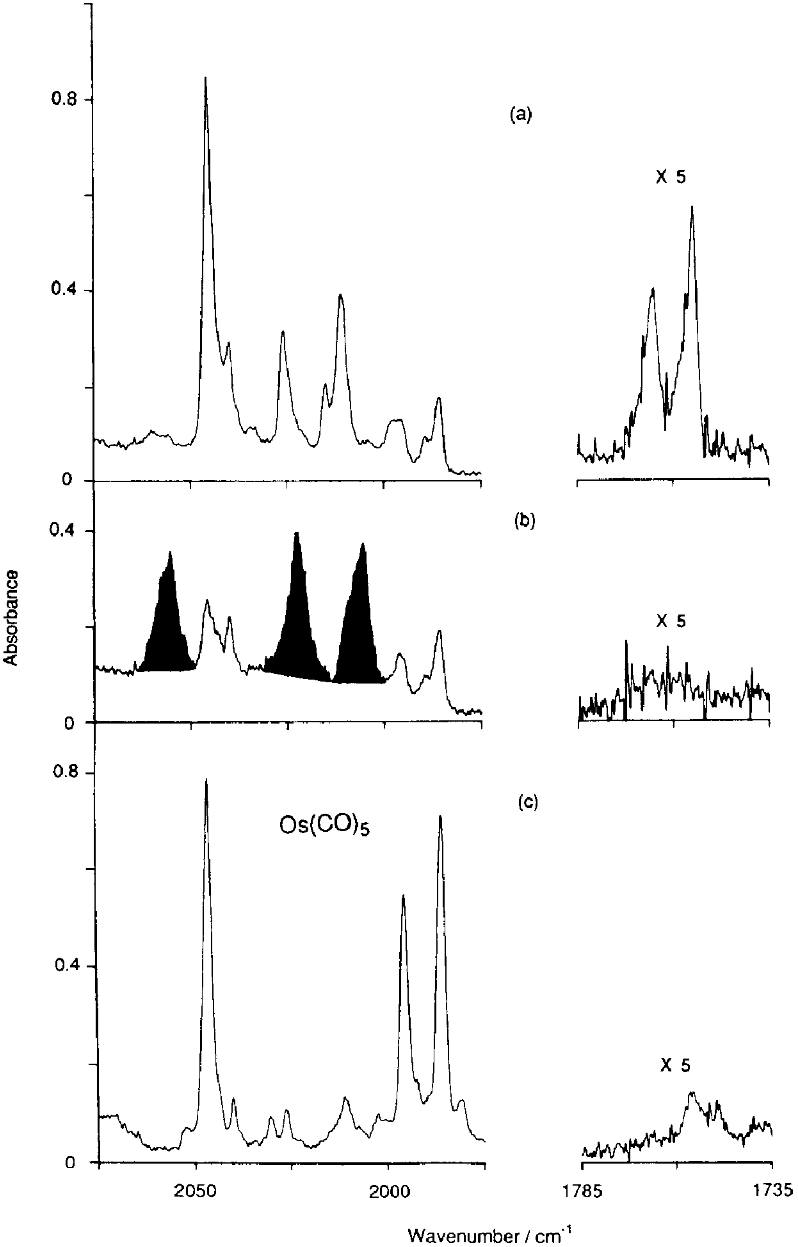


Fig. 8. IR spectra illustrating cleavage of the Os–Os bond of $Os_2(CO)_9$. (a) After deposition of $Os_2(CO)_9$ in a CO matrix at 12 K. The high frequency ν(C–O) band of $Os_2(CO)_9$ was masked by the absorption of the CO matrix, so the region of the spectrum above 2075 cm^{-1} is not shown. (b) After 21.5 min near UV photolysis (380–550 nm). Bands due to $Os_2(CO)_8$ are coloured black. (c) After 15 h unfiltered UV/visible photolysis giving almost total conversion to $Os(CO)_5$. Note that a small amount of $Os(CO)_5$ is observed even before unfiltered photolysis in spectra (a) and (b). This is likely to originate from a small amount of decomposition of $Os_2(CO)_9$ during deposition of the matrix.

destroyed and the bands of $Os_2(CO)_8$ growing in (see Fig. 8a and 8b). Further photolysis was carried out with an unfiltered medium pressure Hg arc lamp. Therefore all wavelengths of light emitted by the lamp were allowed to impinge on the matrix at once, in order to promote all possible photochemical processes. After prolonged unfiltered photolysis, most of the $Os_2(CO)_9$ and $Os_2(CO)_8$ had been destroyed and the spectrum shown in Fig. 8c was obtained, with three intense absorptions in the terminal ν(C–O) region. These absorptions, which are listed in Table 1, correspond exactly with those observed when $Os(CO)_5$ was isolated in a pure CO matrix [40]. Two infrared active ν(C–O) modes ($a_2'' + e'$) are predicted for $Os(CO)_5$ on the basis of D_{3h} symmetry but the low frequency (e') mode is split into a doublet by matrix effects. The formation of this mononuclear product proves that photolysis can lead to cleavage of the metal–metal bond in this system. The same process was observed to occur when $Fe_2(CO)_9$ was subjected to prolonged unfiltered photolysis in a CO matrix, giving $Fe(CO)_5$ as the photoproduct [6].

It is not clear whether the Os–Os bond of an $Os_2(CO)_9$ or $Os_2(CO)_8$ molecule is broken initially (i.e. eq. 11 or 12).

$$Os_2(CO)_9 \overset{h\nu}{\rightleftharpoons} Os(CO)_5 + Os(CO)_4 \xrightarrow{CO} 2Os(CO)_5 \qquad (11)$$

$$Os_2(CO)_8 \overset{h\nu}{\rightleftharpoons} 2Os(CO)_4 \xrightarrow{2CO} 2Os(CO)_5 \qquad (12)$$

This result illustrates how the use of a pure CO matrix and unfiltered UV/VIS photolysis can make CO loss easily reversible and an alternative photochemical pathway, such as metal–metal bond cleavage, irreversible. The unsaturated mononuclear species $Os(CO)_4$ implied in eq. 11 and 12 is trapped by a CO molecule in the surrounding matrix to give the stable product, $Os(CO)_5$, preventing regeneration of a dinuclear complex.

Conclusions

The results presented here have shown that photolysis of $Os_2(CO)_9$ in a variety of frozen gas matrices leads to dissociation of CO and the formation of the unsaturated dinuclear photoproduct, $Os_2(CO)_8$ which contains no bridging CO groups. The same product, which has been implicated as a reactive intermediate in several previous studies, can also be generated by photoejection of the bridging ethylene ligand from $((\mu\text{-}C1,C2)CH_2CH_2)Os_2(CO)_8$ (1). It is of interest that $Os_2(CO)_9$ and $Os_2(CO)_8$ each contain two less bridging CO groups than their iron analogues, $Fe_2(CO)_9$ and its primary photoproduct, bridged $Fe_2(CO)_8$ [5,6]. This is attributable to the fact that the third row transition metal complex has a longer metal–metal bond which makes it more difficult for a CO group to occupy a bridging position.

Polarised photochemistry has given further evidence for the C_{2v} structure of $Os_2(CO)_9$ and enabled us to rule out a D_{3d} structure for $Os_2(CO)_8$ which would have required a triplet electronic ground state. A D_{2h} structure is favoured for $Os_2(CO)_8$ with an expected singlet electronic ground state. The recombination of $Os_2(CO)_8$ with CO, to regenerate the parent compound, has been shown to occur both thermally and photochemically in matrices. Irradiation with long wavelength light can also induce $Os_2(CO)_8$ to react with N_2 or C_2H_4. In each case the incoming ligand coordinates in a terminal site, with a CO group migrating to a bridging position. $Os_2(CO)_8(N_2)$ is thought to undergo thermal isomerisation at ca. 30 K.

The alternative photochemical process normally found for dinuclear metal carbonyls, namely metal–metal bond cleavage, is also observed in this system. Strong photolysis of $Os_2(CO)_9$ in a pure CO matrix leads to production of the mononuclear species, $Os(CO)_5$.

The conversion of the singly CO bridged $Os_2(CO)_9$ to the unbridged $Os_2(CO)_8$ obviously involves a change in the number of bridging carbonyl groups of -1. Our results do not show whether a terminal or a bridging carbonyl group is ejected from a molecule of $Os_2(CO)_9$ excited by UV light. However, previous studies on $Fe_2(CO)_9$ indicated that a terminal CO group was ejected. The primary photoproduct would thus have an unsymmetrical structure with the metal atoms having electron counts of 15 and 17 (ignoring any metal–metal bond). Subsequent rapid migration of a CO group from a bridging to a terminal position would give the observed symmetrical structure. If the bridging CO group was ejected from $Os_2(CO)_9$, then no rearrangement would be necessary to give a symmetrical structure. A symmetrical electronic structure may confer enhanced stability on an unsaturated dinuclear complex. For example, $Os_2(CO)_8$ was found to be thermally unreactive towards N_2 in matrices, whereas coordination of N_2 to the unsymmetrical $Re_2(CO)_9$ is known to occur even at 15–20 K [30].

As a general rule, when a CO ligand is ejected from a dinuclear metal carbonyl complex, the number of bridging carbonyls changes by ± 1. It seems that this change in the number of bridging CO groups results from the desire of the unsaturated $32e^-$ intermediate to have equal electron density on each metal atom. The complex is more stable with $16e^-$ counts for each metal atom than with one $17e^-$ and one $15e^-$ metal centre. Clearly, the conversion of $Os_2(CO)_9$ to the $Os_2(CO)_8$ concurs with this rule. There are, however, two examples known where this rule is not obeyed. Both $Re_2(CO)_{10}$ and its photoproduct $Re_2(CO)_9$ have no bridging CO groups [30]. Also $Co_2(CO)_7$, which can be produced from the doubly bridged or non bridged isomers of $Co_2(CO)_8$, is thought to have an unbridged structure [41]. In the rhenium case, the lack of bridging CO groups is probably a consequence of the length of the Re–Re bond. The explanation of the unbridged structure of $Co_2(CO)_7$, is less obvious.

The experiments described in this work have ruled out a D_{3d} structure for $Os_2(CO)_8$ (which would have required it to have a triplet ground state) and favour a D_{2h} one (which is expected if it has a singlet ground state). The concerted, thermal reaction of ethylene with singlet $Os_2(CO)_8$ (or the reverse fragmentation) is "forbidden" by orbital symmetry in analogy to the $2\pi + 2\pi$ dimerisation of cyclobutane [9,37]. However we have also shown that matrix isolated $Os_2(CO)_8$ reacts with ethylene (at least photochemically) to give a diosmium species with a terminally bound olefin. The presence and possible role of such species in the thermal elimination and exchange of olefins involving diosmacyclobutanes such as **1** is currently under study.

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