Journal of Organometallic Chemistry, 383 (1990) 339–356
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20150

Quantitative mechanistic studies of the photoreactions of trinuclear metal carbonyl clusters of iron, ruthenium and osmium

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(Received May 3rd, 1989)

Abstract

Reviewed are quantitative investigations of the solution phase photochemical reaction mechanisms of M_3 carbonyl clusters of the iron triad metals. A unified model is presented for the photoreactions of the unsubstituted clusters $M_3(CO)_{12}$.

Introduction

The possible involvement of multiple metal centers in ligand transformations and catalysis as well as analogies drawn to metal surfaces has fueled considerable interest in the chemistry of metal clusters. With regard to photochemistry, the clusters add dimensions not inherent to mononuclear metal complexes, namely electronic states involving orbitals delocalized over several metal centers as well as reaction pathways potentially leading to the homo- and hetero nuclear cleavage of metal–metal bonds. These features have drawn the attention of this laboratory and others to the quantitative photochemistry of metal carbonyl clusters. In the context of this special issue celebrating the 100th year since Mond's discovery of nickel carbonyl, the present article will review recent developments concerning photoreaction mechanisms of trinuclear clusters of the iron triad.

Photochemistry has long been a synthesis tool of organometallic chemists given that electronic excitation often provides a route to surmounting enthalpy barriers which might otherwise require undesireably high temperatures. One such example is the common synthetic route to tungsten pentacarbonyl derivatives $W(CO)_5L$ indicated by eqs 1 and 2

$$W(CO)_6 + THF \xrightarrow{h\nu} W(CO)_5THF + CO \qquad (1)$$

$$W(CO)_5THF + L \longrightarrow W(CO)_5L + THF \qquad (2)$$

The labilization of CO is by far the most common photoreaction of simple mononuclear metal carbonyls $M(CO)_n$ [1]. In the presence of a trapping ligand,

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quantum yields (defined as moles of product formed per einstein of light absorbed) are generally high, sometimes approaching unity. Furthermore, careful spectroscopic (IR and electronic) examination of the photoreaction intermediates in low temperature matrices [2] as well as by flash photolysis in fluid solutions [3] and in the gas phase [4] have demonstrated that the probable mechanism for most, if not all, simple mononuclear carbonyls is unimolecular dissociation of CO to form a coordinatively unsaturated (or weakly solvated) intermediate.

For dinuclear carbonyls $M_2(CO)_x$, both spectroscopy and photochemistry are strongly affected by the presence of the metal-metal bond [5]. Dissociation of CO (eq. 3) to give unsaturated intermediates remains an important photoreaction pathway [6]; however, homolytic cleavage of the metal–metal bond to give mononuclear fragments, such as 17-electron mononuclear metal radicals, can also be important (eq. 4) [7]. The lowest excited states of such species often involve population of metal–metal antibonding orbitals; thus, efficient homolytic cleavage to mononuclear fragments generally dominates when the two metal centers are linked by a single metal–metal bond unsupported by bridging ligands [8].

$$M_2(CO)_x \xrightarrow{h\nu} M_2(CO)_{x-1} + CO \tag{3}$$

$$M_2(CO)_{2x} \xrightarrow{h\nu} 2\,M(CO)_x \tag{4}$$

For clusters metal–metal bonding becomes more delocalized as the nuclearity increases [9]. This property, combined with the necessity of breaking more than one metal–metal bond in order to effect fragmentation, suggests that photofragmentation should have a diminished efficiency relative to dinuclear complexes. This does appears to be the case, although both metal–metal bond cleavage and ligand labilization certainly play roles in the photochemistry of metal carbonyl clusters. Modest quantum yields of cluster fragmentation (ϕ_f) have been reported for various trinuclear clusters; e.g., in hydrocarbon solutions, photolysis of $Ru_3(CO)_{12}$ under CO leads to $Ru(CO)_5$ formation [10] with a limiting ϕ_f about 0.05 [11] (see below). Tetranuclear clusters appear to be even less inclined to undergo comparable photofragmentations. Fragmentation has been reported [12] for the clusters as $HFeCo_3(CO)_{12}$, $H_2FeRu_3(CO)_{13}$ and $H_2Ru_4(CO)_{13}$ when photolyzed under CO in hydrocarbon solutions but quantum yields are very low ($< 10^{-5}$ for the latter two). This is not to imply that these systems are photoinert. Ligand labilization (e.g. eq. 5) is several orders of magnitude more efficient than fragmentation for these complexes, and other tetranuclear clusters have been observed to be active toward photooxidation in halocarbon solvents [13] or even to be photoluminescent [14]. Furthermore, any generalizations regarding the photoreactivities of the larger clusters should be qualified with the caveat that quantitative studies have been quite limited. The trinuclear metal carbonyl clusters, especially those of the iron triad, have been much more extensively investigated, and the present review will focus its attention on these systems.

$$H_2Ru_4(CO)_{13} + PPh_3 \xrightarrow[\phi_s = 0.016]{h\nu\ (366\ \text{nm})} H_2Ru_4(CO)_{12}PPh_3 + CO \tag{5}$$

Photoreactions of the unsubstituted ruthenium cluster $Ru_3(CO)_{12}$

The most extensively studied of the three unsubstituted clusters is triruthenium dodecacarbonyl. In 1974 Johnson, Lewis and Twigg [10] reported that broad band

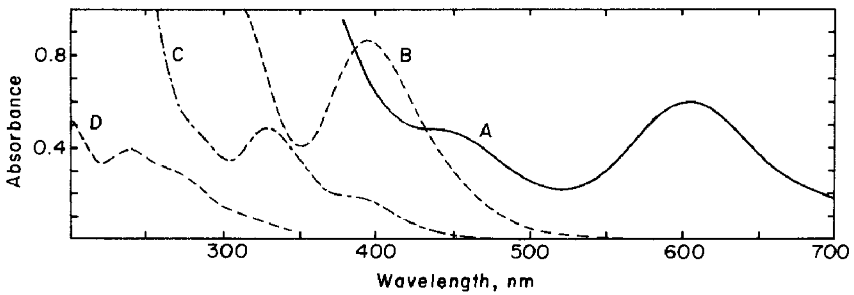


Fig. 1. Optical spectra of $M_3(CO)_{12}$ clusters in 298 K isooctane solution: A: 2.1×10^{-4} *M* $Fe_3(CO)_{12}$, 1 cm cell; B: 1.1×10^{-4} *M* $Ru_3(CO)_{12}$, 1 cm cell; C: 5.3×10^{-5} *M* $Os_3(CO)_{12}$, 1 cm cell; D: solution B, 0.1 cm cell. (Data taken from Fig. 1 in ref. 23).

photolysis of hydrocarbon solutions under CO causes its fragmentation to $Ru(CO)_5$ (eq. 6) while similar photolysis in the presence of ethylene or a phosphine leads to the formation of mono- and/or di-substituted mononuclear complexes (eq. 7) [10,15]. It has also been demonstrated [16,17] that photolysis at wavelengths < 400 nm also leads to substituted clusters when such ligands L are present (eq. 8). Indeed, the disubstituted products of eq. 7 are likely the result of secondary photoreactions, i.e., fragmentation of a cluster already substituted once or more.

$$Ru_3(CO)_{12} + 3\ CO \xrightarrow{h\nu} 3\ Ru(CO)_5 \tag{6}$$

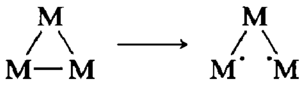
$$Ru_3(CO)_{12} + 3\ L \xrightarrow{h\nu} Ru(CO)_4L + Ru(CO)_3L_2 \tag{7}$$

$$Ru_3(CO)_{12} + L \xrightarrow{h\nu} Ru_3(CO)_{11}L + CO \tag{8}$$

The electronic spectrum of $Ru_3(CO)_{12}$ (Fig. 1) is dominated by an intense absorption bad centered at 392 nm ($\epsilon_{max} = 7.7 \times 10^3\ M^{-1}\ cm^{-1}$ in cyclohexane solution) [11]. Photofragmentation is indicated by a decrease in this band's intensity without a shift in the λ_{max}, while photosubstitution by L shifts this band to longer wavelengths. As illustrated for $L = P(OMe)_3$ in Fig. 2, the photofragmentation quantum yield ϕ_f is relatively insensitive to the irradiation wavelength, decreasing modestly at shorter λ_{irr}, while the photosubstitution quantum yield ϕ_s rises rapidly with decreasing λ_{irr}.

Photofragmentation. The 392 nm absorption band for $Ru_3(CO)_{12}$ has been attributed [9,18] to a transition from a delocalized metal–metal bonding orbital to one antibonding in this regard. Thus, it is not surprising that cluster fragmentation results from photolysis into this band. In alkanes, 405 nm irradiation of $Ru_3(CO)_{12}$ under CO gives $Ru(CO)_5$ with ϕ_f markedly dependent on *P*(CO) [11]. At high *P*(CO), the limiting ϕ_f is about 0.05 mol/einstein, but, in donor solvents such as tetrahydrofuran, diglyme or cyclohexene, ϕ_f values are dramatically smaller. Small quantities of these donors added to octane photolysis solutions act as Stern–Volmer quenchers of ϕ_f. In contrast, 2,5-dimethyltetrahydrofuran does not show such an effect.

Given the well documented role of homolytic metal–metal bond cleavage in the photoreactions of dinuclear carbonyls, a logical hypothesis for the photofragmentations of trinuclear complexes would be to follow a similar path, e.g.:



One diagnostic test for homolytic photofragmentation has been to trap the metal radicals by CCl_4 to give the respective chlorides MCl [8]. When this was attempted with $Ru_3(CO)_{12}$ (405 nm irradiation in a 1.0 *M* CCl_4 octane solution under CO), chlorocarbonyl products $Ru_2(CO)_6Cl_4$ were indeed seen [19]. However, the ϕ_f values were little affected by the presence of CCl_4 yet remained markedly sensitive to [CO], even though CO is not required in the stoichiometry for the formation of these products. The explanation for the failure of CCl_4 to influence fragmentation yields became obvious when it was found that $Ru(CO)_5$ is the initially formed photoproduct even in 1 *M* CCl_4; the chlorocarbonyl ruthenium products proved to be the result of a secondary, dark reaction between the $Ru(CO)_5$ and CCl_4 [19].

Thus, a trappable diradical species is not a key intermediate along the photoreaction coordinate. Furthermore, the presence of two-electron donors ligands which are also π-acids (i.e., CO, ethylene or phosphines PR_3) is required for effective photofragmentation. Little photofragmentation occurs for longer λ_{irr} when L is a harder donor such as THF; indeed, ligands of the latter type inhibit photofragmentation even when CO or PR_3 are present. These observations led to the independent proposals by Desrosiers and Ford [19] and by Malito, Markiewicz and Poë [20] that a key intermediate in the fragmentation mechanism is an isomer (I) of $Ru_3(CO)_{12}$, capable of first order return to the initial cluster in competition with capture by a two electron donor (Scheme 1).

$$Ru_3(CO)_{12} \underset{}{\overset{h\nu}{\rightleftharpoons}} [Ru_3(CO)_{12}^{*}] \longrightarrow I \tag{9}$$

$$I \xrightarrow{k_1} Ru_3(CO)_{12} \tag{10}$$

$$I + L \underset{k_3}{\overset{k_2}{\rightleftharpoons}} \underset{(I')}{Ru_3(CO)_{12}L} \tag{11}$$

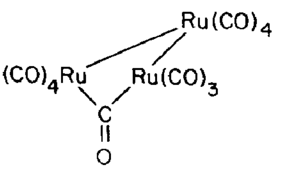
$$I' \xrightarrow{k_4} Ru(CO)_4L + Ru_2(CO)_8 \xrightarrow{+2L,\ fast} 3\ Ru(CO)_4L \tag{12}$$

$$I' \xrightarrow{k_5} Ru_3(CO)_{12} + L \tag{13}$$

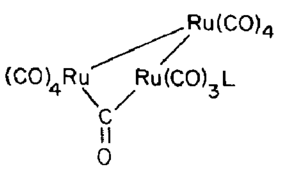
Scheme 1

A possible formulation for I is illustrated below. This could be formed by the heterolytic cleavage of a Ru–Ru bond and corresponding movement of a carbonyl from a terminal to a bridging site to maintain the charge neutrality of both Ru atoms. This would leave one ruthenium electron deficient (a 16 electron species) and capable of capturing a two electron donor to give I′.

The presence of such intermediates was indicated by flash photolysis ($\lambda_{irr} > 395$ nm) of $Ru_3(CO)_{12}$ in cyclohexane solution [11]. No transients with lifetimes > 30



I



I'

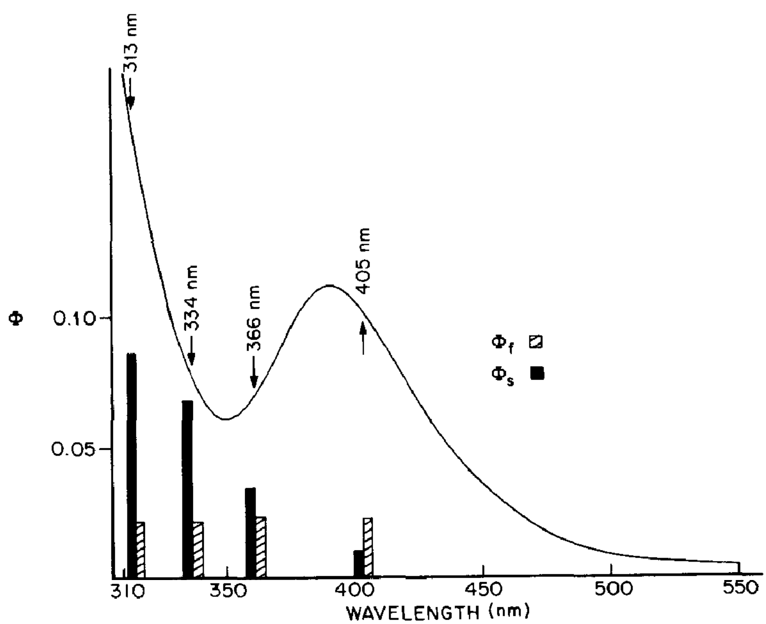


Fig. 2. Wavelength dependence of photofragmentation and photosubstitution quantum yields for a solution of $Ru_3(CO)_{12}$ in octane solution containing 0.012 M $P(OCH_3)_3$.

μsec were detectable in the absence of added ligands or when the only additives were CO or ethylene. However, a CO equilibrated cyclohexane solution of $Ru_3(CO)_{12}$ containing THF (1.0 M) displayed transient bleaching in the spectral region 380–460 nm which decayed exponentially ($k_d = 20 \pm 5\ s^{-1}$) to give a final absorbance consistent with a small amount of net photoreaction. Similar transient bleaching at 390 nm followed by exponential decay was seen in argon equilibrated cyclohexane solutions containing cyclohexene, PPh_3, or $P(OMe)_3$. Decay rates for these transients were found to be independent of [L] but dependent on the ligand's identity. The measured k_d values follow the order THF < cyclohexene < PPh_3 < $P(OMe)_3 \ll$ CO.

According to Scheme 1, ϕ_f is determined by three pairs of processes. The first is the formation of I from $Ru_3(CO)_{12}^*$ in competition with decay to $Ru_3(CO)_{12}$ with an efficiency ϕ_I. The second is the competition between decay of I back to $Ru_3(CO)_{12}$ (rate constant k_1) and capture of I by L to give I′ (k_2). The third is the competitive decay of I′ to $Ru_3(CO)_{12}$ (k_5) or to fragmentation products (k_4). Analysis of the various quantum yield and flash photolysis experiments in terms of Scheme I have led to the following conclusions: (1) The limiting ϕ_f (λ_{irr} 405 nm) in hydrocarbon solutions would be ϕ_I, about 0.05 moles/einstein. (2) Trapping of I to give I′ is relatively insensitive to the nature of L, relative values of k_2 being 1.6, 1.1 and 1.0 for CO, $P(OCH_3)_3$ and PPh_3, respectively, consistent with I being coordinatively unsaturated species, relatively unselective between available ligands. (3) For various ligands, relative rates for the fragmentation of I′ to products fall into the sequence: CO, $CH_2{=}CH_2 \gg P(OCH_3)_3 > PPh_3 \gg$ cyclohexene > THF, an order which qualitatively parallels the π-acidity of L. A possible explanation is that the activation barrier for initial fragmentation (to give $Ru(CO)_4L$ plus possibly $Ru_2(CO)_8$, see below) which would involve the bridging CO → terminal CO transformation may be lower for a π-acid L owing to the more electron-withdrawing nature of the bridging CO of I′.

Strong evidence for the existence of an intermediate such as I′ comes from FTIR studies of low temperature (195 K) isooctane solutions of $Ru_3(CO)_{12}$ plus PPh_3 [21]. Long wavelength (> 420 nm) photoexcitation of these solutions leads to the initial formation of an intermediate displaying an bridging CO $\nu(CO)$ band at 1792 cm^{-1}. This intermediate decays back to $Ru_3(CO)_{12}$ in competition with formation of the substitution product $Ru_3(CO)_{11}(PPh_3)$ and fragmentation products. Similar photolysis of isooctane solution of $Ru_3(CO)_{12}$ at this temperature under CO or C_2H_4 leads to photofragmentation to give mono- and di-nuclear products, e.g.,

$$Ru_3(CO)_{12} \xrightarrow[195\text{ K, isooctane}]{h\nu\ (>420\text{ nm})} Ru(CO)_5 + Ru_2(CO)_9 \tag{14}$$

Related photolysis studies at 90 K indicate an associative pathway for CO exchange between $Ru_3(CO)_{12}$ and free CO in methylcyclohexane glasses resulting from long wavelength excitation, the behavior being markedly different from that seen for irradiation at 313 nm where CO dissociation is the predominant photoreaction (see below). From these studies, one can conclude that, although at room temperature the intermediate I′ (L = CO, C_2H_4, PPh_3, etc.) must primarily undergo fragmentation or reformation of $Ru_3(CO)_{12}$ (eq. 13), competitive loss of CO to give a substitution product via this associative mechanism must have greater prominence at lower temperatures (eq. 15).

$$I' \xrightarrow{\text{low } T} CO + Ru_3(CO)_{11}L \tag{15}$$

Photosubstitution resulting from short wavelength excitation. At room temperature, continuous photolysis of $Ru_3(CO)_{12}$ in hydrocarbon solutions with added PPh_3 or $(P(OCH_3)_3$ and at wavelengths shorter than 405 nm leads to spectral changes indicating formation of substituted clusters [11,17]. The marked wavelength dependence of the photosubstitution quantum yields (Fig. 1) is consistent with the direct reaction from an upper level excited state prior to internal conversion to the state(s) responsible for fragmentation. Unlike the fragmentation pathway, the photosubstitution quantum yields ϕ_s are little affected by solvent; therefore, ϕ_s/ϕ_f ratios are much higher in THF than hydrocarbon solutions.

Initial flash photolysis studies using a conventional xenon flash lamp system ($\lambda_{irr} > 315$ nm) were carried out in THF under excess CO [11]. Transient absorbance was seen in the range 480 to 550 nm, which decayed exponentially to the starting spectrum with a [CO] dependent k_{obs}. Similar flash photolysis of $Ru_3(CO)_{12}$ in argon flushed THF solution with excess PPh_3 or $P(OCH_3)_3$ also gave initial transient absorptions at these monitoring wavelengths similar to those noted under CO. However, in these cases, the system underwent further absorbance increases exponentially to a product spectrum consistent with formation of the substituted clusters $Ru_3(CO)_{11}L$.

These data are interpretable in terms of Scheme 2 where the primary photoreaction is the dissociation of CO to $Ru_3(CO)_{11}$ (II) which is trapped by THF to give the solvated species $Ru_3(CO)_{11}S$ (II′). The relative solvent independence of ϕ_s supports the view that the first step is CO dissociation rather than an associative displacement by solvent or another ligand. Analysis of these flash data allows calculation of the relative k_L values 8, 1.5 and 1.0 for CO, $P(OCH_3)_3$ and PPh_3, respectively.

$$Ru_3(CO)_{12} \xrightarrow{h\nu} \underset{(II)}{Ru_3(CO)_{11}} + CO \tag{16}$$

$$II + THF \underset{k_{-s}}{\overset{k_s}{\rightleftharpoons}} \underset{(II')}{Ru_3(CO)_{11}THF} \tag{17}$$

$$II + CO \xrightarrow{k(CO)} Ru_3(CO)_{12} \tag{18}$$

$$II + L \xrightarrow{k(L)} Ru_3(CO)_{11}L \tag{19}$$

Low temperature photochemical studies using FTIR to characterize intermediates and products [21], confirm the dissociative nature of the photosubstitution mechanisms concluded for Scheme 2. Short wavelength excitation (313 nm) of $Ru_3(CO)_{12}$ in 90 K alkane glass was shown to give first a $Ru_3(CO)_{11}$ species with only terminal CO's which then rearranged to an isomeric form of $Ru_3(CO)_{11}$ having a bridging CO. Stoichiometric formation of free CO was also demonstrated. In the presence of various L, these intermediates reacted to form the $Ru_3(CO)_{11}L$ photosubstitution product.

A recent reexamination of the photosubstitution pathways using a XeCl excimer laser as the excitation source (308 nm) and a tunable diode IR laser as the probe source (deadtime of detection electronics about 40 ns) has allowed direct observation of the intermediate II in ambient temperature isooctane solutions [22]. The IR spectrum of this species 200 ns subsequent to photoexcitation is consistent with that of the $Ru_3(CO)_{11}$ isomer with a bridging carbonyl described in the low temperature photolysis experiment above. Trapping of this species by reaction with CO or THF occurs with the surprisingly high rate constants 2.4×10^9 M^{-1} s^{-1} and 6.1×10^9 M^{-1} s^{-1}. The equilibrium constant for eq. 17 was calculated to be 1.2×10^3 M^{-1}.

Photoreactions of $Fe_3(CO)_{12}$ and $Os_3(CO)_{12}$

Although triiron dodecacarbonyl has been used as a visible light absorbing precursor for photocatalytic processes [23], its quantitative photochemistry has received less attention than the heavier metal analogs. The visible absorption spectrum in 298 K hydrocarbon solutions shows a band centered at 603 nm ($\epsilon = 2.9 \times 10^3$ M^{-1} cm^{-1}) and a second band about 440 nm (shoulder) of comparable intensity (Fig. 1). Visible range photolysis in the presence of CO, an alkene or a phosphine has been reported [23,24] to lead to cluster fragmentation with a ϕ_f value about 10^{-2} (eq. 20).

$$Fe_3(CO)_{12} + 3L \xrightarrow{h\nu} 3\ Fe(CO)_4L \tag{20}$$

The intermediates generated by photolysis of this cluster have been studied in depth in low temperature solutions by FTIR techniques [21]. When photolyses were carried out in 90 K methylcyclohexane, no photochemistry was observed for irradiation of the long wavelength absorption feature, and little reaction was seen for 436 nm photolysis. However, when λ_{irr} was 366 nm or 313 nm, the IR spectral changes show formation of free CO in amounts equal to the $Fe_3(CO)_{12}$ consumed while the electronic spectrum is consistent with formation of a Fe_3 cluster product.

Thus, CO photodissociation (eq. 21) was concluded to be the primary photoreaction of $Fe_3(CO)_{12}$ at shorter wavelengths in analogy to the reactions noted above for $Ru_3(CO)_{12}$.

$$Fe_3(CO)_{12} \xrightarrow{h\nu\ (313\ \text{nm})} Fe_3(CO)_{11} + CO \qquad (21)$$

Warming the above solution to 293 K led to quantitative reformation of $Fe_3(CO)_{12}$. However, when the 90 K photolysis was carried out with 10 mM PPh_3 present, warming to 195 K led to formation of the substituted cluster $Fe_3(CO)_{11}PPh_3$, which underwent fragmentation to mononuclear products when the solution was warmed further to room temperature. In a 2-methyltetrahydrofuran glass at 90 K similar near-UV irradiation leads to the formation of the $Fe_3(CO)_{11}$(2-MeTHF) complex.

Longer wavelength (436 nm) photoexcitation at 90 K leads to detectable photointermediates only when a π-acid ligand such as 1-pentene is present [21]. At higher temperatures both substitution and fragmentation appear to be competing consequences of long wavelength photoexcitation. Thus, it can be concluded that, as was seen for $Ru_3(CO)_{12}$, the shorter wavelength photochemistry is dominated by CO dissociation but the longer wavelength photochemistry involves an associative pathway for reaction with ligands, possibly via an intermediate which is a $Fe_3(CO)_{12}$ isomer in analogy to I suggested above.

As one might expect, the products and intermediates formed in the photochemical reactions of $Os_3(CO)_{12}$ appear to be considerably more robust than for the analogous iron and ruthenium clusters. Early studies [23,25] demonstrated that photofragmentation is at most extremely small under CO (λ_{irr} 313 nm). However, in the presence of alkenes, photofragmentation does occur with a modest quantum yield (0.03) [23], and in chlorocarbon solvents, small quantum yields (0.002 for λ_{irr} 313 nm in CCl_4) were found for photofragmentation to the chlorocarbonyl product $Os(CO)_4Cl_2$ [25]. The latter result was taken as evidence that a metal radical intermediate, perhaps a diradical, is formed as the result of photoexcitation. (However, one should note that radical reactions are not the only pathways for forming such a product.) Photolysis (λ_{irr} 366 nm) of $Os_3(CO)_{12}$ plus PPh_3 in toluene solution was shown to give $Os_3(CO)_{11}PPh_3$ plus multiple substitution products believed to be the result of secondary photoreactions. Values of ϕ_s were not determined. A related process may be the photoreaction with H_2 which gives the hydride cluster $H_2Os_3(CO)_{10}$ [23].

Subsequently, Burke et al. [26] demonstrated that products of the photoreaction ($\lambda_{irr} > 370$ nm) between $Os_3(CO)_{12}$ and a large excess of the olefinic ester methyl acrylate in benzene leads to fragmentation to give the expected mononuclear $Os(CO)_4(\eta^2\text{-olefin})$ product plus the dinuclear 1,2-diosmacyclobutane derivative $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}CH_2{=}CHCO_2CH_3)$. This result would be consistent with the formation of the dinuclear intermediate $Os_2(CO)_8$ along the photofragmentation pathway. Similar reactions were noted with other alkenes and with several alkynes [27].

A more extensive mechanistic investigation of $Os_3(CO)_{12}$ photochemistry by Poë and Sekhar [28] demonstrates that this cluster may in fact be nearly as photoactive as its ruthenium analog. Photoexcitation (436 nm) in benzene leads to photofragmentation to mono- and dinuclear products when 1-octene is present (eq. 22). Quantum yields increase with increasing 1-octene concentration with a limiting value of 0.03. The donor solvent diglyme was found to retard this reaction with Stern-Volmer quenching kinetics being obeyed. The presence of CO was also demonstrated to retard the photofragmentation but did not change ϕ_f (limiting).

$$\mathrm{Os_3(CO)_{12}} \xrightarrow[\text{1-octene}]{h\nu\ (436\ \text{nm})} \mathrm{Os(CO)_4}(\eta^2\text{-1-octene}) + \mathrm{Os_2(CO)_8}(\mu\text{-}\eta^1,\eta^1\text{-1-octene}) \qquad (22)$$

Photolysis in the presence of $P(OEt)_3$ under otherwise similar conditions was found to lead only to photosubstitution (eq. 23) [28]. Again the quantum yield increases with increasing [L] but is retarded by carrying out the photolysis under CO rather than Ar. However, CO does not affect the value of the limiting quantum yield, which at high $[P(OEt)_3]$ is about 0.045, distinguishably different from the ϕ_f seen with 1-octene present.

$$\mathrm{Os_3(CO)_{12} + P(OEt)_3} \xrightarrow{h\nu\ (436\ \text{nm})} \mathrm{Os_3(CO)_{11}P(OEt)_3 + CO} \qquad (23)$$

Although there are some distinct differences, which are discussed in the next section, these data are supportive of a mechanism for both the photoreactions (eq. 22 and 23) which result from 436 nm excitation proceeding through a common intermediate. This common intermediate III would be a $Os_3(CO)_{12}$ isomer with an open coordination site similar to species I first proposed as key intermediate in the photofragmentation of $Ru_3(CO)_{12}$ [20,21]. Once formed such a species could be trapped (eq. 24) by a two electron donor such as 1-octene or $P(OEt)_3$ to give a second intermediate $Os_3(CO)_{12}L$ (analogous to I′ above). The competitive reactions of this second intermediate (eq. 25), i.e. loss of L, loss of CO or fragmentation, would thus determine the respective products and their limiting quantum yields.

$$\begin{tikzcd} \mathrm{Os_3(CO)_{12}} \arrow[r, "h\nu"] & {[\mathrm{Os_3(CO)_{12}}]'} \arrow[r] \arrow[dr, "+L"'] & \mathrm{Os_3(CO)_{12}} \\ & \text{(III)} & {[\mathrm{Os_3(CO)_{12}L}]} \\ & & \text{(III}'\text{)} \end{tikzcd} \qquad (24)$$

$$\begin{tikzcd} & \mathrm{Os_3(CO)_{12} + L} \\ \text{III}' \arrow[ur, "(a)"] \arrow[r, "(b)"] \arrow[dr, "(c)"'] & \mathrm{Os_3(CO)_{11}L + CO} \\ & \text{fragmentation products} \end{tikzcd} \qquad (25)$$

The above mechanism may also explain the somewhat contradictory observation [29] that $Os_3(CO)_{12}$ in 298 K isooctane containing PPh_3 shows no apparent photochemistry when irradiated at 436 nm [29]. In this case, the decay of the proposed $[Os_3(CO)_{12}L]$ intermediate would have to be primarily to starting material (eq. 25a) rather than to substitution products (eq. 25b); however, it seems rather remarkable that such differences in the partitioning of III′ would be the consequence of using PPh_3 rather than $P(OEt)_3$.

In contrast, measurable, wavelength dependent, quantum yields for photosubstitution were found for $L = PPh_3$ or $P(OCH_3)_3$ at lower λ_{irr}. In THF under Ar, 313 nm photoexcitation of $Os_3(CO)_{12}$ in the presence of various concentrations of $P(OCH_3)_3$ gives a limiting ϕ_s of 0.08 for $Os_3(CO)_{11}P(OCH_3)_3$ formation [11b]. Notably, these ϕ_s were not affected by adding radical traps such as CCl_4 or t-butyl-*p*-cresol [11b]. Studies of this reaction in low temperature media (90 K methylcyclohexane) using the FTIR technique [29] indicate the slow formation upon photolysis ($\lambda_{irr} < 300$ nm) of free CO and a new cluster species with spectral and reactivity properties consistent with the formulation $Os_3(CO)_{11}$. Thus the higher energy dissociative mode for photosubstitution (eq. 26) appears to be functioning for the osmium cluster as well.

$$Os_3(CO)_{12} \xrightarrow[-CO]{h\nu\ (<300\ nm)} Os_3(CO)_{11} \xrightarrow[+L]{} Os_3(CO)_{11}L \tag{26}$$

FTIR studies in 90 K methylcyclohexane glasses show that longer wavelength excitation does not lead to the formation of $Os_3(CO)_{11}$ in the absence of other ligands and only to small amounts of $Os_3(CO)_{11}L$ when L is a simple Lewis base such as 2-MeTHF; however, when $L = C_2H_4$ or 1-pentene, substantially greater concentrations of the substituted adduct plus free CO are found [29]. Since there is little or no effect on yields of $Os_3(CO)_{11}L$ formation resulting from changing the nature of L when $\lambda_{irr} < 300$ nm, the results from longer wavelength excitation can be taken as indicating that two different mechanisms are responsible for photosubstitution under these conditions, a CO dissociation mechanism (i.e., eq. 26) operating for photoexcitation at short wavelengths and an associative pathway (e.g. eqs. 24 and 25) operating at longer λ_{irr} [29]. In this context, it is also notable that, while no cluster fragmentation was observed to result from longer λ_{irr} photolyses at 90 K, similar photolysis at 195 K of solutions containing C_2H_4 leads to the slow formation of $Os(CO)_4(\eta^2\text{-}C_2H_4)$ as the principal photoproduct.

A unified view of the photoreactions of the unsubstituted clusters $M_3(CO)_{12}$

Although various photoreaction pathways and mechanisms have been suggested or claimed over the past decade, the more recent quantitative investigations [11,21,22,28,29] of the continuous and flash photolysis chemistry of the unsub-

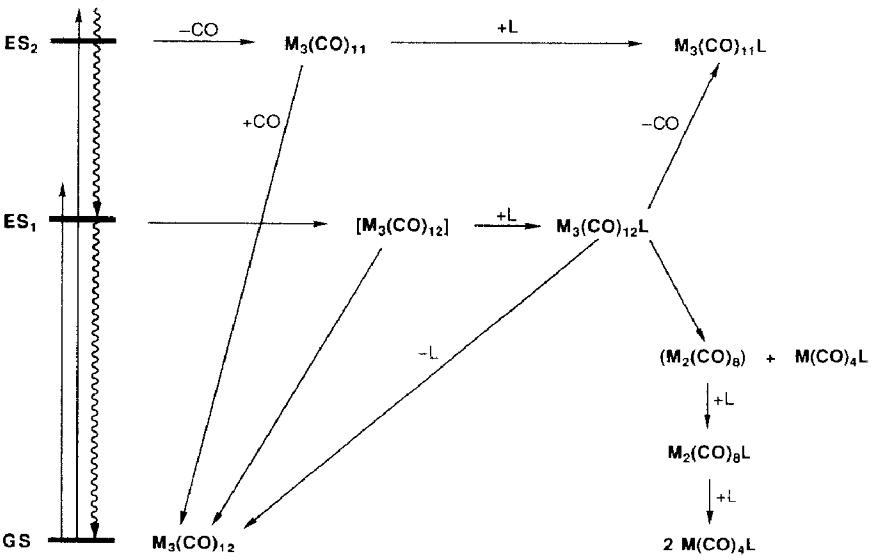


Fig. 3. Unified scheme for the photoreactions of the unsubstituted clusters $M_3(CO)_{12}$ (M = Fe, Ru or Os) in the presence of an added ligand L.

stituted clusters point to two common themes for all three metals. For shorter wavelength photolysis (the λ_{irr} ranges being functions of M and the medium) photodissociation of CO occurs to give a highly reactive, unsaturated cluster $M_3(CO)_{11}$ which is easily trapped by other ligands to give the substituted clusters. For M = Ru, this reactive intermediate reacts with CO or THF in ambient temperature isooctane solutions at rates only an order of magnitude less than diffusion control [22] and with N_2 in low temperature (110 K) methylcyclohexane solution to give $Ru_3(CO)_{11}(N_2)$ [21]. For longer wavelength excitation, the primary photoreaction appears in each case to give an isomer of $M_3(CO)_{12}$ which can undergo rapid associative reaction with two electron donor ligands L to give a second intermediate $M_3(CO)_{12}L$. The eventual fate of this species is proposed to be determined by competition between three (presumably first order) processes, fragmentation to mono- and dinuclear complexes, loss of CO to give $M_3(CO)_{11}L$ or loss of L to regenerate the starting cluster. This photoreaction model is illustrated in Fig. 3.

In support of this model are the several spectroscopic and kinetics studies described above which have identified or implicated the presence of various intermediates. For the dissociative pathway, both free CO and the unsaturated cluster intermediate $M_3(CO)_{11}$ have been identified in low temperature media for all three metals using FTIR [21,29]. Flash photolysis studies using IR detection have identified the same cluster intermediate for M = Ru in ambient temperature solutions and characterized the dynamics of reaction with CO and THF [22]. For the associative pathway, the evidence is largely indirect and based on the dependence of product formation on the nature and concentrations of various ligands. However, an intermediate with an FTIR spectrum and reactivity consistent with those expected for $Ru_3(CO)_{12}L$ has been identified in low temperature studies [21]; the analogous intermediate has been observed for various L by room temperature flash photolysis studies using optical detection [11]. Clearly, observation and characterization of the first intermediate in the suggested sequence, i.e., $[M_3(CO)_{12}]$ (I for M = Ru), would contribute significantly to confidence in the mechanism proposed for the associative pathway to fragmentation and substitution.

The fragmentation pathway depicted in Fig. 3 as leading from the $M_3(CO)_{12}L$ intermediate to dinuclear and mononuclear complexes is based on the observation that M_2 species are stable products in the longer λ_{irr} photoreactions of $Os_3(CO)_{12}$ with L = alkenes or alkynes at ambient temperature [26–28]. Furthermore, while dinuclear ruthenium products are not observed under similar conditions, the photofragmentation resulting from $\lambda_{irr} > 420$ nm photolysis of $Ru_3(CO)_{12}$ in 195 K isooctane under CO gives $Ru(CO)_5$ plus $Ru_2(CO)_9$ as products [21].

Another consistent observation from the above studies is that fragmentation of the $M_3(CO)_{12}L$ intermediate is favored only for ligands L which are strong π-acceptors [11,29]. This appears to be a necessary but not sufficient condition given that long λ_{irr} excitation of $Os_3(CO)_{12}$ under CO does not lead to photofragmentation [25]. Nonetheless, for M = Ru, flash photolysis studies indicate that the intermediate I′ decays to fragmentation products at rates parallelling the order of L π-acceptor strengths [11]. Overall, while the proposal of intermediates such as I and I′ is consistent with the key observations described above, it is clear that the actual photoproducts and their quantum yields will be determined by a complicated partitioning between competitive processes, the rates and activation parameters of which will each be functions of the individual metals M and ligands L.

Lastly, remarks are in order relating the spectroscopy and photochemistry of these clusters. The spectra for the $M_3(CO)_{12}$ clusters (Fig. 1) each display at least three bands. Theoretical analysis of these [9,30] has concluded that the strong lowest energy band for $Ru_3(CO)_{12}$ corresponds to a transition between an orbital which is bonding with regard to the metal cluster framework to one which is antibonding in this regard (the $\sigma^b \rightarrow \sigma^\star$ band). Thus, it is not surprising that excitation of this band would lead to cluster fragmentation, although, according to the above model, the primary photoreaction is not fragmentation but is isomerization to give a cluster intermediate, i.e. I, capable of associative reaction with various donor ligands. The observed cluster fragmentation is proposed to be the result of secondary thermal reactions of the resulting intermediate $M_3(CO)_{12}L$.

The spectroscopic analyses also argue that the transitions with the corresponding $\sigma \rightarrow \sigma^\star$ assignment in the $Os_3(CO)_{12}$ and $Fe_3(CO)_{12}$ are not the lowest energy bands evident in the absorption spectra of these clusters (Fig. 1) but are those at 329 nm and 440 nm, respectively. This is consistent with the observations in low temperature experiments (where the absorption bands sharpen to decrease overlap) that it is irradiation of the second band of these clusters which gives the intermediate susceptible to associative reaction. These two compounds show no significant photoreaction as the result of low temperature excitation into the longest wavelength absorption band [21,29], which has been assigned to a $\sigma^\star \rightarrow \sigma^\star$ transition for which the perturbation of the cluster bonds are minor [9]. (Thus, for these complexes a model more complete than Fig. 3 might show an unreactive excited state at an energy below those designated as ES_1 and ES_2.)

The dissociative route to CO substitution results from excitation into the overlapping second and third bands of $Ru_3(CO)_{12}$ or the third band of $Os_3(CO)_{12}$ or $Fe_3(CO)_{12}$. The third band has also been assigned as having $\sigma^\star \rightarrow \sigma^\star$ character; however, the $\sigma^\star$ orbital populated in this case is significantly antibonding with respect to the metal–equatorial carbon bonds [9]. Thus, the key differences between the $M_3(CO)_{12}$ are the orbital parentages of the lowest energy absorption bands. However, since λ_{irr} dependent photochemistry is seen, the coupling between upper and lower energy excited states must be sufficiently slow that chemical reactions from the upper states are competitive with decay to the lower energy, less reactive states of the Fe_3 and Os_3 carbonyl complexes.

Photoreactions of derivatives of the M_3 clusters

The several studies of the substituted clusters $M_3(CO)_{12-n}L_n$ have mostly reported products although a few quantum yields have been reported under limited sets of conditions. Any mechanistic arguments must thus be based largely on analogy to the unsubstituted clusters. Some examples are summarized in Table 1 [11,25,31–33]. Among triruthenium derivatives the 405 nm photolysis of each member of the series $Ru_3(CO)_{12-n}L_n$ was investigated under CO (1.0 atm) in cyclohexane solution for $n = 1$ to 3 and $L = P(OCH_3)_3$, P(*p*-tolyl)$_3$ and P(O(*o*-tolyl))$_3$ [11]. In each case, photosubstitution of CO for L was apparently negligible and photofragmentation followed the stoichiometry of eq. 27. The quantum yields determined for the mono- and di-substituted clusters were comparable (actually slightly larger) than the ϕ_f for $Ru_3(CO)_{12}$ under analogous conditions but the trisubstituted clusters gave much smaller values.

$$\mathrm{Ru_3(CO)_{12-\mathit{n}}L_{\mathit{n}} + 3CO \xrightarrow{h\nu\ (405\ nm)} (3-\mathit{n})Ru(CO)_5 + \mathit{n}Ru(CO)_4L} \tag{27}$$

The marked difference between ϕ_f value for $n = 2$ and $n = 3$ would be consistent with the model proposed for photofragmentation in Scheme 1 and Fig. 3. For $Ru_3(CO)_9L_3$, the intermediate corresponding to I would be expected to be considerably less reactive with an incoming ligand owing to the steric bulk of the ligands L on each Ru. This argument gains further credence from the observation that for the various L's the effect of trisubstitution is largest for the most bulky ligands, with ϕ_f values of 0.02, 0.005, 0.0008, 0.0004 and 0.0002 for L = CO, $P(OCH_3)_3$, PPh_3, $P(p\text{-tolyl})_3$ and $P(O(o\text{-tolyl}))_3$, respectively [11]. An alternative explanation would be that ligand substitution has led to a reversal in the excited state order so that the $\sigma \rightarrow \sigma^{\star}$ state responsible for photofragmentation of $Ru_3(CO)_{12}$ is no longer the lowest energy state in the trisubstituted complexes [30]. This proposal seems unlikely given the smooth progression in the λ_{max} of the dominant lowest energy absorption band to lower energy as n is varied from 0 to 3 but the sharp discontinuity in ϕ_f on going from $n = 2$ to $n = 3$ is significant in each case [11]. However, it should be noted that, according to the mechanistic model in Fig. 3, the intermediate proposed as the precursor to fragmentation has several competing pathways for decay, thus observed variation in the efficiency of but one of these (fragmentation in this case) without examining other key potential pathways (e.g., CO exchange) does not necessarily reflect variations in the yields for formation of those intermediates.

Photolysis (436 nm) of the catalytically interesting, surface confined trisub-

Table 1

Photoreaction quantum yields for substituted M_3 Clusters (25° C)

Reaction	Quantum yield	Ref.
$\mathrm{Ru_3(CO)_{12} \xrightarrow[+CO]{405\ nm^{a}} 3Ru(CO)_5}$	0.019	11
$\mathrm{Ru_3(CO)_{11}P(OCH_3)_3 \xrightarrow[+CO]{405\ nm^{a}} 2\ Ru(CO)_5 + Ru(CO)_4P(OCH_3)_3}$	0.044	11
$\mathrm{Ru_3(CO)_{10}(P(OCH_3)_3)_2 \xrightarrow[+CO]{405\ nm^{a}} Ru(CO)_5 + 2\ Ru(CO)_4P(OCH_3)_3}$	0.031	11
$\mathrm{Ru_3(CO)_9(P(OCH_3)_3)_3 \xrightarrow[+CO]{405\ nm^{a}} 3\ Ru(CO)_4P(OCH_3)_3}$	0.005	11
$\mathrm{Ru_3(CO)_{11}Ptol_3 \xrightarrow[+CO]{405\ nm^{a}} 2\ Ru(CO)_5 + Ru(CO)_4Ptol_3}$	0.031	11
$\mathrm{Ru_3(CO)_{10}(Ptol)_3)_2 \xrightarrow[+CO]{405\ nm^{a}} Ru(CO)_5 + 2\ Ru(CO)_4Ptol_3}$	0.021	11
$\mathrm{Ru_3(CO)_9(Ptol_3)_3 \xrightarrow[+CO]{405\ nm^{a}} 3\ Ru(CO)_4Ptol_3}$	0.002	11
$\mathrm{Ru_3(CO)_9(PPh_3)_3 \xrightarrow[+CO]{405\ nm^{a}} 3\ Ru(CO)_4PPh_3}$	0.008	11
$\mathrm{Os_3(CO)_9(PPh_3)_3 \xrightarrow[+CO]{366\ nm^{b}} 3\ Os(CO)_4PPh_3}$	0.005	25
$\mathrm{H(\mu\text{-}H)Os_3(CO)_{10}PPh_3 \xrightarrow[-CO]{366\ nm^{c}} (\mu\text{-}H)_2Os_3(CO)_9PPh_3}$	0.02	31
$\mathrm{HOs_3(CO)_{10}(\mu\text{-}\eta^1\text{-}N_2Ph) \xrightarrow{313\ nm^{d}} HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}N_2Ph)}$	0.06	32
$\mathrm{Fe_3(CO)_{11}{}^{2-} \xrightarrow[+PPh_3,\ -CO]{504\ nm^{e}} Fe(CO)_4{}^{2-} + 2\ Fe(CO)_3(PPh_3)_2}$	0.005	33

[a] P(CO) = 1 atm, cyclohexane solution, $Ptol_3 = P(p\text{-tolyl})_3$. [b] $[PPh_3] = 0.001$ mol l^{-1}, toluene solution. [c] Alkane solution. [d] n-heptane solution. [e] Acetonitrile solution.

stituted cluster $[SiO_2]L_3Ru_3(CO)_9$ (the product of anchoring the cluster $Ru_3(CO)_9(Ph_2PCH_2CH_2Si(OEt)_3)_3$ to high surface area SiO_2) in an isooctane suspension under CO leads to the surface confined mononuclear complexes $[SiO_2]LRu(CO)_4$ [34]. The three mononuclear fragments apparently remain in close proximity since they readily self-assemble to the trinuclear cluster when irradiated at shorter wavelengths under argon. Analogous photofragmentation occurs for the precursor cluster $Ru_3(CO)_9(Ph_2PCH_2CH_2Si(OEt)_3$ when irradiated in solution under otherwise similar conditions; however, there was no apparent photoreaction when the surface confined complex was irradiated in rigid, low temperature hydrocarbon matrices.

That the medium has dramatic effects on a photoreaction's course was demonstrated by an investigation of $Ru_3(CO)_{12}$ absorbed onto porous vycor glass (PVG) [35]. Physisorption of this cluster gives a surface species with a structure little distorted from that in solution. Photolysis (350 nm) of dry samples of the cluster on PVG in vacuo leads to spectrum changes concluded to be the result of oxidative addition of a surface silinol group (eq. 28). The quantum yield was estimated as 0.03. Placing the photoproduct under CO (1 atm) leads to the slow thermal reversion of $HRu_3(CO)_{10}(OSi_{surf})$ to $Ru_3(CO)_{12}(ads)$. Photolysis under CO (1 atm) completely quenches the oxidative addition reaction. Furthermore, mononuclear species were not formed, $\phi_f < 10^{-5}$. With regards to mechanism, it would appear that either intermediate I (of Scheme 1) or II (Scheme 2) would provide the open coordination site available for oxidative addition of the surface silinol. Indeed under 350 nm irradiation it is likely that both intermediates would be formed. The failure of the cluster to undergo fragmentation in the presence of CO could be rationalized in terms of the predominance of the photodissociative pathway under these conditions but is more likely to be the responsibility of the PVG surface rigidity and topology.

$$Ru_3(CO)_{12}(ads) \xrightarrow{h\nu\ (350\ \mathrm{nm})} HRu_3(CO)_{10}(OSi_{surf}) + 2CO \tag{28}$$

The photochemical transformations of ligands in organometallic derivatives of the M_3 clusters and related species have proved to be extremely rich. Several examples are listed Table 2 [36–39]. Mechanistic attention has understandably lagged behind the exploratory discovery of new reactions, although one may often deduce a logical pathway from analogies drawn from studies of the unsubstituted clusters. For example, the photoinduced formation of phosphido bridged clusters such as shown in the first example of Table 2 [36] may be deduced to be the result of producing an unsaturated intermediate by photodissociation of CO followed by

Table 2

Some photoinduced transformations of ligands coordinated to M_3 clusters

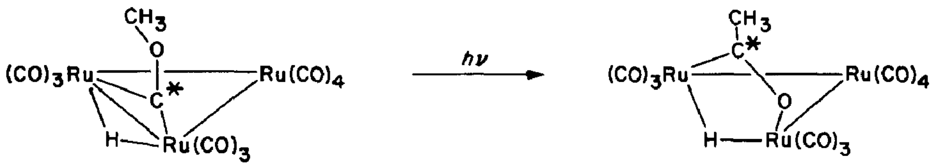
Reaction	Ref.
(1) $Ru_3(CO)_9(PPh_2H)_3 \xrightarrow{>300\ \mathrm{nm}} H_2Ru_3(CO)_7(\mu\text{-}PPh_2)_2(PPh_2H) + HRu_3(CO)_7(\mu\text{-}PPh_2)_3$ + minor products	36
(2) $HOs_3(CO)_{10}(\mu\text{-}SPh) \xrightarrow{h\nu} C_6H_6 + Os_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$	37
(3) $Ru_3(CO)_{10}(NO)^- + 2CO \xrightarrow{h\nu} Ru_3(CO)_{11}(NCO)^-$	38
(4) $Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6) \xrightarrow{h\nu} H_2Os_3(CO)_9(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_6H_4)$	39

intramolecular oxidative addition of a P–H bond to the metal cluster rather than other secondary thermal and/or photo reactions.

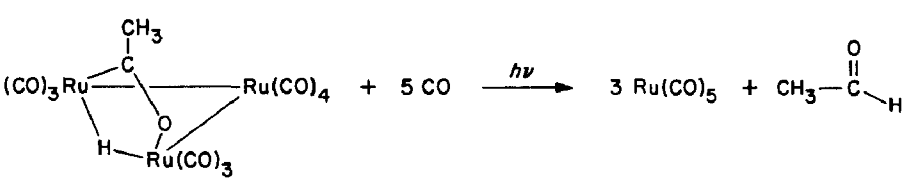
$$\mathrm{Ru_3(CO)_9(PPh_2H)_3} \xrightarrow[-\mathrm{CO}]{h\nu\ (>300\ \mathrm{nm})} \mathrm{Ru_3(CO)_8(PPh_2H)_3} \qquad (29)$$

$$\longrightarrow \mathrm{HRu_3(CO)_8(\mu\text{-}PPh_2)(PPh_2H)_2} \rightarrow \text{etc.}$$

The photochemistry of the triruthenium μ_2-methoxyalkylidyne derivative $\mathrm{HRu_3(CO)_{10}(\mu\text{-}COCH_3)}$ (**A**) was initially surveyed with goal of probing the possibility that linking two of the ruthenium sites with a bridging ligand would perturb the fragmentation patterns. Indeed this proved to be the case, but instead of giving detectable diruthenium intermediates or products as projected, the result was an unprecedented oxygen-to-carbon migration of the CH_3 group of the bridging methoxyalkylidyne ligand [40,41] with quantum yields ϕ_i strongly dependent on λ_{irr} (0.05 at 313 nm, $< 10^{-5}$ at 405 nm) and linear in $P(\mathrm{CO})$ over the range 0 to 1.0 atm (despite the absence of a stoichiometric requirement for CO in eq. 30). Photolysis of the specifically labelled complex $\mathrm{HRu_3(CO)_{10}(\mu\text{-}^{13}COCH_3)}$ demonstrated that the isomerization indeed involves migration of the methyl group from the methoxyalkylidyne oxygen to the adjacent carbon of the same functional group as shown in eq. 30. Long term photolysis of the bridging acyl product $\mathrm{HRu_3(CO)_{10}(\mu,\eta^2\text{-}C(O)CH_3)}$ (**B**) under CO (1 atm) did lead to cluster fragmentation (eq. 31) with a small quantum yield (0.001 at 313 nm).



(30)



(31)

In the presence of added ligands including ^{13}CO, the alkylidine complex was also subject to facile photosubstitution (eq. 32) with a λ_{irr} dependence parallelling that of the ϕ_i. While the λ_{irr} dependence of ϕ_i plus the substitution lability of **A** might suggest a mechanism proceeding through a CO photodissociation as in $\mathrm{Ru_3(CO)_{12}}$, such a mechanism would not show the $P(\mathrm{CO})$ dependence described for ϕ_i above. Furthermore, other evidence, including the role of donor solvents such as THF, which promote eq. 30. in the absence of CO but suppress photosubstitution, point to a common intermediate for the isomerization and substitution pathways, analogous to the intermediate proposed for the photofragmentation of the unsubstituted M_3 clusters. An abbreviated version of the proposed mechanism (with L = CO) with

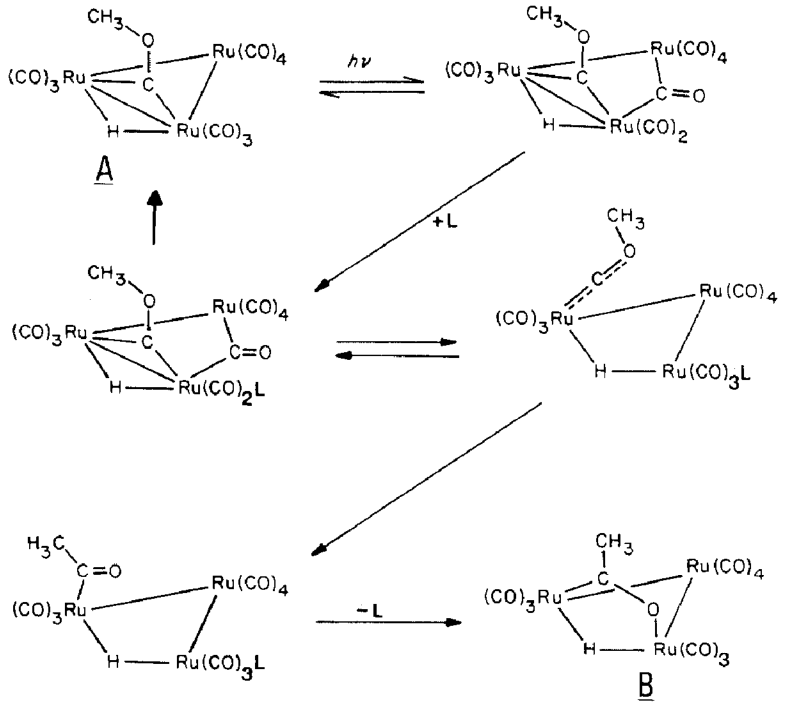


Fig. 4. Proposed mechanism for the photoisomerization of the methoxyalkylidine complex $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ in solution.

some speculation regarding how the bridging methoxy alkylidine group might undergo isomerization to a bridging acetyl is illustrated in Fig. 4.

$$HRu_3(CO)_{10}(\mu\text{-}COCH_3) + L \xrightarrow{h\nu} HRu_3(CO)_9L(\mu\text{-}COCH_3) + CO$$

$$\left(L = {}^{13}CO,\ P(OCH_3)_3,\ PBu_3 \text{ or pyridine}\right) \quad (32)$$

Summary

A consistent theme throughout the above discussion is that two independent photoreaction mechanisms dominate the photochemistry of the unsubstituted clusters $M_3(CO)_{12}$ and probably that of the various substituted and organometallic derivatives. Higher energy excitation leads to CO dissociation to prepare an unsaturated cluster capable of reacting with added ligands to give substitution products, but also capable of intramolecular reactions of coordinated ligands or even bimolecular processes to give higher order clusters [42]. In this context, there certainly is analogy to the CO dissociation noted for higher energy photolysis of dinuclear complexes (see above) or for most wavelengths with mononuclear carbonyls. A second photoreaction mechanism for these trinuclear complexes is the formation of another intermediate which is an isomer of the starting cluster but is capable of rapid associative reaction with a variety of two electron donor ligands. This intermediate is generally formed by lower energy excitation and is the precursor for cluster fragmentation, but is also a potential precursor for substitution reactions as well. This species might be a diradical like that proposed in early speculation regarding cluster photofragmentation mechanisms in analogy to the well documented radical formation in reactions of dinuclear carbonyls. However, while a short lived diradical cannot be excluded, the failure of radical trapping agents to intercepts these certainly argues against radical character of any intermediates with significant lifetimes. Thus, we and others have argued that a formulation meeting the reactivity requirements of the apparent intermediate would be one such as I where metal–metal bond breaking is concomitant with migration of a CO from a terminal to a bridging site. This would result in a species with an even electron count on each metal but having an open coordination site on one metal center, hence providing facile access to associative reaction with an external ligand. Stronger documentation of the latter mechanism is certainly needed.

In general, it is important to keep in mind that the primary photoreactions of the excited states are the formations of the first intermediates. The prolific chemical transformations which have been observed for these trinuclear clusters as the result of electronic excitation represent the various competitive thermal reactions by which these intermediates decay. It is our contention that the number of such primary photoreactions is quite small and the competitive reactions of these can be understood from a fundamental understanding of the thermal reactions of these transient species.

Acknowledgments

Research in these laboratories concerned with the photochemistry of metal carbonyl clusters and with the dynamics of reactive intermediates prepared from such clusters has been supported by the Chemistry Division of the US National Science Foundation and by the US Department of Energy, Office of Basic Energy Sciences. The following individuals contributed to these experimental studies: M.F. Desrosiers, D.A. Wink, R. Trautman, A.E. Friedman, J. DiBenedetto and D. Ryba.

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