Dalton Perspectives

The Generation and Reactivity of Versatile Ruthenium Carbonyl Organometallic Intermediates by Cluster Photochemistry

Nicholas E. Leadbeater
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

The use of inorganic cluster photochemistry in the synthesis of both mononuclear and higher-nuclearity compounds is discussed. Owing to its selectivity, cluster photochemistry offers a high-yield route to both known and novel target compounds by the selective labilisation of ligands and cleavage of metal–metal bonds. Attention is focused on the trinuclear cluster $[Ru_3(CO)_{12}]$, looking mechanistically at both photofragmentation and photosubstitution processes and at the synthetic potential of the reactive intermediates formed. The role of cluster photochemistry in catalysis and in the elucidation of the mechanism for a number of catalytic processes is also discussed.

Transition-metal organometallic chemistry offers a link between organic and inorganic research as it involves the interaction of metal atoms or ions with organic groups. A large number of modern industrial processes rely on organometallic chemistry and it is an area of increasing study. This article focuses on the generation and subsequent reactivity of metal carbonyl compounds, in particular those of ruthenium. Many metal carbonyl complexes were originally synthesised by unplanned routes or as by-products in other reactions, and it is only over recent years that more systematic approaches have been developed. It is the aim of this article to highlight the applications of photochemistry to selective generation of target products and in particular discuss the uses of this technique in the synthesis of mononuclear and cluster organometallic ruthenium compounds.

Photochemistry offers a simple and often highly selective route to organometallic compounds, overcoming large enthalpy barriers which would otherwise involve high temperatures.[1] Perhaps the simplest example of this is the photochemical labilisation of carbonyl groups in mononuclear carbonyl complexes in the presence of a ligand L with the generation of substituted derivatives [equations (1) and (2)]. In addition to

$$M(CO)_n \xrightarrow{h\nu} M(CO)_{n-1} + CO \qquad (1)$$

$$M(CO)_{n-1} \xrightarrow{L} M(CO)_{n-1}L \qquad (2)$$

the labilisation of carbonyl groups there is the possibility of metal–metal bond cleavage yielding lower-nuclearity fragments. It is therefore one of the first objectives of this work to discuss the factors effecting the products formed in the photolysis of clusters. Attention will be focused on triruthenium dodecacarbonyl, $[Ru_3(CO)_{12}]$ **1**, as it is by far the most studied system due both to the synthetic potential of highly reactive ruthenium complexes and to the fact that, together with $[Os_3(CO)_{12}]$ **2**, it is one of the simplest metal carbonyl clusters and can serve as a prototype for the photoreactivity of other such species.[1–13] It will be demonstrated that, in trinuclear clusters such as **1**, by careful choice of solvent and irradiation wavelength it is possible to prepare either photofragmentation or photosubstitution products. In addition, this perspective will show that cluster photochemistry has allowed the formation of a wide variety of versatile reagents a number of which are inaccessible by conventional synthetic techniques.

Photochemistry of Triruthenium Dodecacarbonyl

The electronic spectrum of $[Ru_3(CO)_{12}]$ **1** at 300 K exhibits two main bands at 390 and 238 nm with a shoulder at 320 nm. Extended-Hückel molecular orbital calculations have been performed on both the fragment $Ru(CO)_4$ and on **1** in an attempt to interpret this spectrum.[14] The calculations on the mononuclear species were performed assuming a C_{2v} molecular symmetry and show there to be three low-lying d orbitals relatively unaffected by the π bonding of carbonyl ligands, namely the d_{xy}, d_{yz} and d_{z^2}, as they are directed between the carbonyl ligands and are therefore of lowest energy. The d_{xz} orbital is of next highest energy as several lobes are directed towards the equatorial ligands. The $d_{x^2-y^2}$ orbital is directed towards the axial ligands and is of highest energy. It is this orbital that is involved in metal–metal bonding when the mononuclear $Ru(CO)_4$ unit trimerises to generate **1**. The results of these investigations are reproduced in Fig. 1.

From application of the selection rules governing electronic transitions, it has been concluded that for compound **1** there are three possible one-electron transitions from the d block of molecular orbitals to the LUMO (σ^*_{xz}) orbital, these being $\sigma_{xz} \longrightarrow \sigma^*_{xz}$ (${}^1A_1' \longrightarrow {}^1E'$), $\sigma^{*\prime}_{xz} \longrightarrow \sigma^*_{xz}$ (${}^1A_1' \longrightarrow {}^1E'$) and $a_1''(xz) \longrightarrow \sigma^*_{xz}$ (${}^1A_1' \longrightarrow {}^1A_2''$). By an in-depth comparison of the electronic spectrum of **1** and those of a number of closely related phosphine derivatives it has been deduced that the band observed at 390 nm for $[Ru_3(CO)_{12}]$ is due to a $\sigma_{xz} \longrightarrow \sigma^*_{xz}$ transition. The shoulder observed at 320 nm has been assigned to a $\sigma^{*\prime}_{xz} \longrightarrow \sigma^*_{xz}$ transition by comparison with the spectral data for **2**, a point which is discussed later. These results are confirmed by the fact that the A terms of these bands in the molecular circular dichroism spectrum show the excited states to be doubly degenerate.[14]

In covalent systems like $[Ru_3(CO)_{12}]$ **1** simple descriptions of photochemical transitions such as $\sigma \longrightarrow \sigma^*$ are of uncertain qualitative significance and molecular charge-density studies on **1** have been undertaken to aid further understanding of the photochemistry of the cluster.[15] The bonding changes have been monitored using difference electron-density maps, a process which involves multipolar potential calculations for each of the excited states then subtraction of the excited-state total density from the electron-density distribution in the ground state. These calculations have shown that $\sigma_{xz} \longrightarrow \sigma^*_{xz}$ excitation results in a decrease in electron density in the metal framework and it is therefore not surprising that, even though in clusters metal–metal bonding becomes significantly delocalised, fragmentation results from photolysis in this region.[1] It has also been demonstrated that $a_1''(xz) \longrightarrow \sigma^*_{xz}$ excitation, which is similar in energy to that of the $\sigma_{xz} \longrightarrow \sigma^*_{xz}$ transition, does not perturb the Ru–Ru bonding to such an extent but affects the Ru–CO bonding leading, in the excited state, to movement of electron density away from the metal into the CO π orbitals therefore facilitating a photodissociation process on irradiation.[14] The remaining transition, $\sigma^{*\prime}_{xz} \longrightarrow \sigma^*_{xz}$, results both in a decrease in bonding electron density in the metal framework and a movement of π-electron density towards the carbonyl groups.

The band observed at 238 nm in the electronic spectrum has been assigned to a metal–ligand charge-transfer transition (m.l.c.t.), as is expected in this region. This also may be predicted from the results of studies on $[Ru(CO)_5]$ **3** showing an m.l.c.t. band at 236 nm, since the energies of such transitions are determined, in the main, by the nature of the central metal atom, a factor that does not alter significantly on going from the mono- to the tri-nuclear case.

Although emphasis will be placed on the synthetic aspects of this subject, it is not possible to optimise the conditions of reaction or fully harness the potential of any reactive intermediates formed without a thorough understanding of the underlying mechanistic pathway. Indeed, the photochemist is often interested in the rates at which processes occur so the study of reaction kinetics is also often employed. For this reason the initial part of this study will focus on work undertaken to deduce the mechanistic pathways involved in the photolysis of $[Ru_3(CO)_{12}]$ **1** and discuss the factors effecting the distribution of photofragmentation and photosubstitution products.

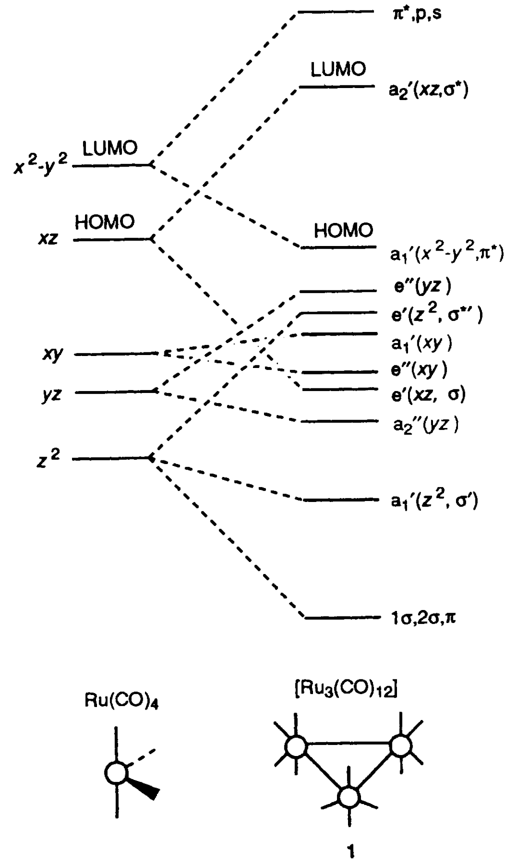

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Fig. 1 Molecular orbital schemes for $Ru(CO)_4$ and $[Ru_3(CO)_{12}]$ **1**. LUMO = Lowest unoccupied molecular orbital, HOMO = highest occupied molecular orbital

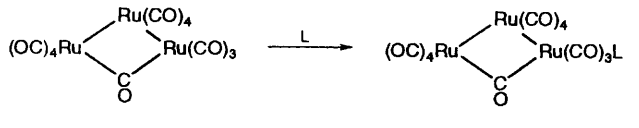
(*a*) *Photofragmentation*.—In 1974 Lewis and co-workers[2] reported that photolysis of a hydrocarbon solution of $[Ru_3(CO)_{12}]$ **1** under an atmosphere of CO causes fragmentation of the cluster to yield the mononuclear pentacarbonyl species $[Ru(CO)_5]$ **3**. Ever since these first investigations, the presence of π-acid donors such as CO, ethylene and tertiary phosphines has been recognised as leading to modest quantum yields of substituted mononuclear species in hydrocarbon solvents. In contrast, almost no photoactivity is observed with harder donors such as tetrahydrofuran (thf) or 2,5,8-trioxanonane (diglyme) when used as a solvent, and even at relatively low concentrations significant quenching of the photofragmentation pathway occurs when these reagents are added to hydrocarbon solutions. The quantitative behaviour of thf as a photoreaction quencher has been demonstrated by a linear Stern–Volmer type plot. These results have further stimulated interest into the quantitation of the cluster photofragmentation mechanism.[4]

It has been suggested that photofragmentation resulting from irradiation of compound **1** in the λ_{max} region (≈ 390 nm) may be as a result of cleavage of a single Ru–Ru bond to form a diradical species as the primary photoproduct (Scheme 1).[7] The postulation of a diradical species has been investigated by photolysis of **1** in the presence of chlorocarbons such as CCl_4.[4] If $[Ru_3(CO)_{12}]$ diradicals are formed it would be expected that they would be trapped to give chlorocarbonylruthenium products, as has been reported for a number of dimetallic metal–metal bonded systems. The photofragmentation quantum yield, Φ_f, of octane solutions of **1** in the presence of CCl_4 and equilibrated with CO is indistinguishable from that measured in the absence of the chlorocarbon, therefore it has been concluded that the principal photofragmentation pathway in hydrocarbon solvents does not proceed *via* the formation of a reactive diradical intermediate.[1,7]

Photolysis of compound **1** in cyclohexane under CO–N_2 atmospheres containing varying concentrations of CO has shown that there is an increase of the observed photochemical quantum yield, Φ_{obs}, with increasing [CO].[10] From this it has been suggested that the reactive intermediate or intermediates formed in the photolysis can either revert back to **1** or react further with CO to form **3**. Further experiments have confirmed that the reactive intermediate initially formed is still a triruthenium system. In addition, the quantum yields are independent of the intensity of absorbed light implying that fragmentation of **1** has not taken place by the time competitive attack by CO occurs since this would lead to a decrease of Φ_{obs} with increasing intensity of absorbed light.

It has been suggested that the solvent effects detailed above indicate a chemical selectivity on the part of the reactive intermediate rather than a photophysical selectivity.[10] This, together with the fact that the reaction quantum yields are affected only marginally by the presence of CCl_4 but significantly by the presence of weak Lewis bases, has led to the proposal that the mechanism for photofragmentation must involve the formation of a co-ordinatively unsaturated intermediate with the same composition as that of the starting cluster, therefore an isomeric form of **1**.[4,10] It is further postulated that this intermediate, **4**, is formed as a result of

Scheme 1



Scheme 2

heterolytic cleavage of a Ru–Ru bond with concomitant movement of a carbonyl group from a terminal to a bridging position. This would result in one of the ruthenium atoms in the system being electron deficient and able to co-ordinate a two-electron donor forming $[Ru_3(CO)_{12}L]$. This is represented in Scheme 2.

Alternatively, it has been suggested that fragmentation occurs *via* the sequential cleavage of two Ru–Ru bonds forming a mono- and a di-nuclear species, namely $[Ru(CO)_4]$, and $[Ru_2(CO)_8]$, however this is improbable since, by virtue of the independence of the fragmentation quantum efficiency with respect to irradiation intensity, the process must be irreversible, a fact that has been proven incorrect.[16]

A summary of the presently accepted mechanism for the photofragmentation of $[Ru_3(CO)_{12}]$ **1** is shown in Scheme 3.

$$\underset{\mathbf{1}}{[Ru_3(CO)_{12}]} \underset{k_d}{\overset{h\nu}{\rightleftharpoons}} [Ru_3(CO)_{12}]^* \tag{3}$$

$$[Ru_3(CO)_{12}]^* \xrightarrow{k_f} \underset{\mathbf{4}}{[Ru_3(CO)_{12}]^{**}} \tag{4}$$

$$\underset{\mathbf{4}}{[Ru_3(CO)_{12}]^{**}} \xrightarrow{k_1} \underset{\mathbf{1}}{[Ru_3(CO)_{12}]} \tag{5}$$

$$\underset{\mathbf{4}}{[Ru_3(CO)_{12}]^{**}} + L \underset{k_3}{\overset{k_2}{\rightleftharpoons}} [Ru_3(CO)_{12}L] \tag{6}$$

$$[Ru_3(CO)_{12}L] \xrightarrow{k_4} [Ru(CO)_4L] + [Ru_2(CO)_8] \tag{7}$$

$$[Ru_3(CO)_{12}L] \xrightarrow{k_5} [Ru_3(CO)_{11}L]^{**} + CO \tag{8}$$

$$[Ru_3(CO)_{12}L] \xrightarrow{k_6} [Ru_3(CO)_{12}] + L \tag{9}$$

$$\underset{\mathbf{4}}{[Ru_3(CO)_{12}]^{**}} + L' \underset{k_3'}{\overset{k_2'}{\rightleftharpoons}} [Ru_3(CO)_{12}L'] \tag{10}$$

$$[Ru_3(CO)_{12}L'] \xrightarrow{k_6'} [Ru_3(CO)_{12}] + L' \tag{11}$$

Scheme 3 The photofragmentation mechanism for $[Ru_3(CO)_{12}]$ **1**

Using this and assuming that both the rate of further reaction of $[Ru_3(CO)_{12}L]$ and the rate of generation of $[Ru_3(CO)_{12}]$ **1** from $[Ru_3(CO)_{12}L']$ are greater than that of regeneration of $[Ru_3(CO)_{12}]^{**}$ **4**, *i.e.* $(k_4 + k_6) \gg k_3$ and $k_6' \gg k_3'$, then Φ_{obs} may be expressed as in equation (12).[8]

$$\Phi_{obs} = \Phi_{max} \cdot \frac{k_2[L]}{k_1 + k_2[L] + k_2'[L']} \cdot \frac{k_4}{k_4 + k_6} \tag{12}$$

Much of the recent mechanistic insight into the photofragmentation pathway of compound **1** has been obtained by the use of flash-photolysis techniques.[4,6] A short-duration flash of light from either a discharge lamp or a laser initiates the photochemical reaction and any transient intermediates formed are monitored as a function of time. Recent developments make it possible to monitor reactions on the nano-, pico- and even femto-second time-scales.

Flash photolysis of $[Ru_3(CO)_{12}]$ **1** has gone some way to elucidating the nature and structure of the intermediates formed on photofragmentation of the cluster, studies showing that photolysis in the presence of argon, carbon monoxide and ethylene does not lead to the formation of any intermediates with lifetimes in excess of the dead-time of the apparatus (≈ 20 μs), with immediate formation of the reaction products in the case of CO and C_2H_4.[4] As there is no net photofragmentation in the reaction under argon, it has been concluded that the only pathway for decay of the activated system **3** in the absence of added ligand is the regeneration of $[Ru_3(CO)_{12}]$ [equation (5)]. Flash photolysis with PPh_3 and $P(OMe)_3$ leads to the formation of detectable transient intermediates, identified as $[Ru_3(CO)_{12}L]$ [equation (6)] which react further [equation (7)] to form mononuclear photofragmentation products, hence $k_4 \gg k_6$. This reaction has been shown to be rather non-selective although it is possible to correlate the rate of photofragmentation of $[Ru_3(CO)_{12}L]$ as a function of the ligand present, the fastest rates being observed with strong π-acceptor and weak σ-donor ligands.

Flash photolysis of a thf solution of compound **1** leads to little photofragmentation therefore the transient intermediates formed must decay *via* pathways other than those for the case of ligands such as CO, back to starting materials, hence $k_4 \ll k_6$ [equation (9)]. This is confirmed by the fact that the kinetics of this reaction is comparable to that in the absence of any added ligand. These results may be reinterpreted in terms of the original diradical formulation and it is possible that the diradical product is the immediate photoproduct, *i.e.* $[Ru_3(CO)_{12}]^*$, which forms $[Ru_3(CO)_{12}]^{**}$ **4** so rapidly that there is no significant opportunity for scavenging by chlorocarbons, even in pure carbon tetrachloride. Therefore, though the photokinetics of the processes may be controlled by the thermal chemistry of **4** and $[Ru_3(CO)_{12}L]$, the photophysics may be viewed in terms of the homolytic cleavage of a Ru–Ru bond. This interpretation is unlikely since, if **4** is a diradical, it is likely that $[Ru_3(CO)_{12}]^*$ is also a radical species. Although the flash-photolysis results would, to many extents, agree with this postulation, if **4** is also a radical it would be expected that this would react with chlorocarbons forming chlorocarbonylruthenium products, a process that is known not to occur. In addition, the photolysis of CCl_4 solutions of $[Ru_3(CO)_{12}]$ in the presence of trace amounts of CO leads to the formation of significant amounts of $[Ru(CO)_5]$. It would therefore be unexpected if the diradical **4**, a rather non-selective reactive intermediate, was to react selectively with the two-electron ligand to form $[Ru_3(CO)_{12}L]$ and not with the chlorocarbon, a known radical quencher. The simplest, but not the sole, interpretation of these results is that $[Ru_3(CO)_{12}]^{**}$ **4** is not itself a radical.[4]

(*b*) *Photosubstitution.*—Photosubstitution of $[Ru_3(CO)_{12}]$ occurs as a result of short-wavelength (≈ 310 nm) irradiation and, in the presence of a two-electron donor L, leads to the formation of the substituted cluster $[Ru_3(CO)_{11}L]$. As in the case of the photofragmentation studies, much of the mechanistic insight into the photosubstitution reaction has been obtained using flash photolysis.[4–6,9] In addition, matrix-isolation techniques have been employed and have allowed the structural elucidation of a number of key intermediates.[11] This involves the trapping of photochemically generated unstable intermediates in a large excess of an inert matrix, such as a noble gas, at very low temperatures. It is then possible to probe spectroscopically the unstable fragments generally by means of infrared or UV/VIS techniques.

Flash-photolysis studies (detection time 35 μs) of thf solutions of $[Ru_3(CO)_{12}]$ **1** at wavelengths greater in energy than that for photofragmentation under an atmosphere of CO show the formation of a transient species with a rate of decay dependent on [CO].[4] This has been interpreted in terms of an initial photochemical labilisation of CO forming the transient intermediate $[Ru_3(CO)_{11}]$ **5** followed by solvation to form $[Ru_3(CO)_{11}(solv)]$ then reaction with free CO to regenerate **1** as shown in Scheme 4.

Similar flash-photolysis investigations have been performed using hydrocarbon solvents but no long-living intermediates are observed, presumably because the reaction equivalent to (14) occurs too rapidly for the 35 μs dead-time of the apparatus

$$\underset{\mathbf{1}}{[Ru_3(CO)_{12}]} \xrightarrow{h\nu} \underset{\mathbf{5}}{[Ru_3(CO)_{11}]} + CO \qquad (13)$$

$$\underset{\mathbf{5}}{[Ru_3(CO)_{11}]} \underset{k_{-s}}{\overset{k_s}{\rightleftharpoons}} [Ru_3(CO)_{11}(solv)] \qquad (14)$$

$$\underset{\mathbf{5}}{[Ru_3(CO)_{11}]} + CO \xrightarrow{k_{co}} \underset{\mathbf{1}}{[Ru_3(CO)_{12}]} \qquad (15)$$

Scheme 4 The photosubstitution pathway

although, with the advent of nanosecond flash techniques, it has been possible to detect transient species.[9] In hydrocarbons, reaction with two-electron donors such as ethylene and CO is rapid although investigations point at a slight solvation of $[Ru_3(CO)_{11}]$, the rate constants being in the region of one order of magnitude smaller than the calculated diffusion limit. This point indicates a significant difference between the photofragmentation and substitution pathways. For photofragmentation, weakly co-ordinating solvents such as thf lead to efficient quenching of the photogenerated intermediates whereas in the case of photosubstitution, co-ordinating solvents actually prolong the life of the transients and correlate with a far greater selectivity in reaction.

More detailed studies into the dissociative loss of CO from $[Ru_3(CO)_{12}]$ **1** have been made by broad-band photolysis in alkane glasses at 90 K and results show that the amount of free CO detected is consistent with the loss of one CO group per molecule of **1**.[11] This confirms the initial postulations that $[Ru_3(CO)_{11}]$ **5** is formed as a key photoproduct. Consistent with its formation, **5** reacts on warming up with triphenylphosphine to yield the substituted trinuclear cluster $[Ru_3(CO)_{11}(PPh_3)]$, although it has been demonstrated that in the presence of the photoejected CO, **5** shows some considerable selectivity for reaction with CO to regenerate **1** rather than with PPh_3, the reaction with carbon monoxide being about eight times faster than that with the phosphine. This result is consistent with a delocalised unsaturation in $[Ru_3(CO)_{11}]$, and it may be postulated that the structure of **5** has one carbonyl group bridging an edge of the metal triangle with formation of a multiple metal–metal bond, the observance of an infrared absorption at 1836 cm^{-1} confirming the presence of at least one bridging CO group. There has been keen discussion on the number of bridging carbonyl groups in **5** with two distinct arguments, but with the spectroscopic data recorded to date it is not possible unequivocally to draw conclusions on this point. It is possible to formulate **5** as $[Ru_3(CO)_{10}(\mu\text{-}CO)]$, with two co-ordinatively unsaturated metal centres and a metal–metal double bond between the two CO-bridged metal atoms.[5] Alternatively, based on results obtained from ^{13}CO-labelling experiments, it has been suggested that **5** has two bridging CO groups, where co-ordinative unsaturation is delocalised over two Ru–Ru bonds.[11] The two proposed forms of $[Ru_3(CO)_{11}]$ **5** are illustrated in Fig. 2.

In comparison to this, $[Os_3(CO)_{11}]$, formed in the photodissociation of $[Os_3(CO)_{12}]$ **2**, shows all the CO groups in terminal positions with an axial vacancy. With this in mind, rapid scan FTIR techniques have been employed to study the immediate photodissociation product from $[Ru_3(CO)_{12}]$ **1** in low-temperature glasses and it is found that the axially vacant terminal form of $[Ru_3(CO)_{11}]$ **5** is formed but interconverts rapidly into the bridging structural form as shown in Scheme 5.

The photosubstitution process is found to be highly wavelength dependent as compared to the case of photofragmentation, Φ_f being essentially wavelength independent whereas Φ_s, the photosubstitution quantum yield, increases dramatically with shortening wavelength.[5,9,11] This has been explained in terms of a direct reaction from an upper-level excited state prior to internal conversion into the state responsible for the fragmentation process. In addition, the wavelength dependence of Φ_s may be viewed in terms of the extent to which overlap of the transitions leading to substitution and other reactivities occurs.

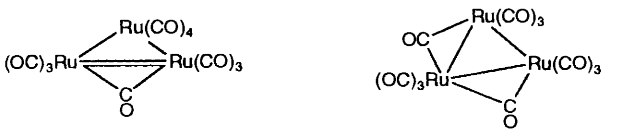
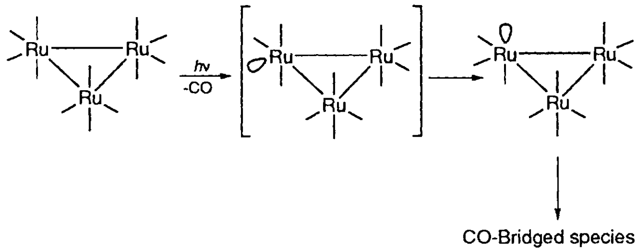


Fig. 2 The postulated structures for the intermediate $[Ru_3(CO)_{11}]$ **5**



Scheme 5 The mechanism for photolabilisation of CO in compound **1**

As stated earlier, photofragmentation of compound **1** in thf solutions under an atmosphere of CO leads to a reversible reaction, an intermediate **5** being formed which reacts with CO to regenerate the starting material. However, recent flash-photolysis experiments show that under high concentrations of CO this reversibility is lost.[5] The product mixture has been characterised by IR spectroscopy as being a 1:1 mixture of $[Ru_2(CO)_9]$ **6** and $[Ru(CO)_5]$ **3**, implying that the photogenerated intermediate $[Ru_3(CO)_{11}]$ reacts with a total of three CO groups [equation (16)]. Gradual conversion of **6** into **3** is

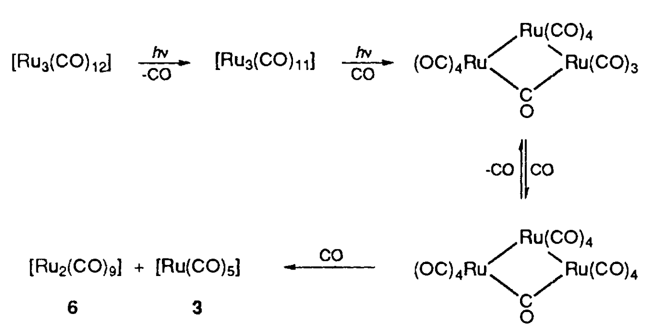
$$\underset{\mathbf{5}}{[Ru_3(CO)_{11}]} + 3CO \longrightarrow \underset{\mathbf{6}}{[Ru_2(CO)_9]} + \underset{\mathbf{3}}{[Ru(CO)_5]} \qquad (16)$$

seen on further reaction with CO over a few minutes to yield ultimately **3** as the sole product.[5] This is confirmed by the fact that conventional photolysis of **1** under an atmosphere of CO leads to the formation of nothing but the mononuclear pentacarbonyl **3**.

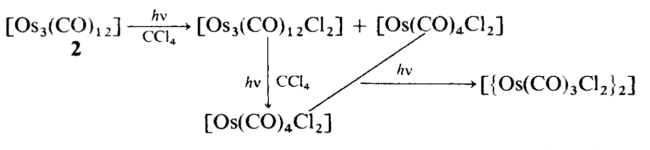
An in-depth study of the reaction of $[Ru_3(CO)_{11}]$ with CO shows the formation of a significant amount of a further intermediate compound which persists on the flash-photolysis time-scale.[5] Since **5** has potential co-ordination sites for reaction with ligands in the solution and when in high enough concentration two molecules of CO may react with this leading to the trinuclear intermediate $[Ru_3(CO)_{12}(\mu\text{-}CO)]$ which, upon further reaction with CO, may break down to form the mono- and di-nuclear products **3** and **6**. Further investigations have allowed the clear characterisation of $[Ru_3(CO)_{12}(\mu\text{-}CO)]$ by infrared spectroscopy. These results are illustrated in Scheme 6.

Photochemistry of Triosmium Dodecarbonyl

It is worth briefly comparing the photochemistry of $[Ru_3(CO)_{12}]$ **1** with that of the osmium analogue $[Os_3(CO)_{12}]$ **2**. Studies have demonstrated that, although structurally similar, the triruthenium and triosmium dodecacarbonyls are significantly different electronically.[14] The metal–metal orbital interactions are greater in **2** than in **1** leading to a greater bonding–antibonding energy splitting. Consequently the d_{z^2} antibonding molecular orbital moves above the d_{xz} bonding orbital with the result that, although in **1** the $\sigma_{xz} \longrightarrow \sigma^*_{xz}$ transition was assigned to the lowest-energy band, in **2** the $\sigma^{*\prime}_{xz} \longrightarrow \sigma^*_{xz}$ transition lies below the $\sigma_{xz} \longrightarrow \sigma^*_{xz}$. Unlike the triruthenium compound, $[Os_3(CO)_{12}]$ **2** reacts with chlorocarbons on photolysis to produce chlorocarbonylosmium compounds as summarised in Scheme 7, although these reactions proceed with much smaller quantum yields than those involving phosphine or olefin ligands.[13]



Scheme 6 Labilisation of CO and subsequent formation of $[Ru_3(CO)_{13}]$



Scheme 7 The photochemical reaction of $[Os_3(CO)_{12}]$ **2** with chlorocarbons

It has been concluded, as in the case of compound **1**, that reaction occurs *via* the generation of an isomeric form of **2**, a process which can be considered as the insertion of a carbonyl ligand into an Os–Os bond. There is no observable photochemical reaction between **2** and CO as compared to the formation of the mononuclear pentacarbonyl compound $[Ru(CO)_5]$ **3** in the case of **1** and this result, together with the chlorocarbon experiments, suggest that the photofragmentation of **2** is very inefficient. This is expected since, although the population of the lowest-energy excited level in **1** leads to metal–metal bond cleavage, in the case of **2** the metal–metal interaction is stronger and thus less affected on photochemical excitation of the molecule.

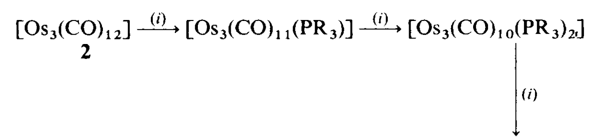
Reactions with phosphines readily occur leading to the formation of photosubstitution products as shown in Scheme 8, the Os_3 unit fragmenting only after substitution at each of the three metal centres, this being a very inefficient process. It is proposed that reaction takes place *via* a concerted dissociation of CO and reformation of the Os–Os bond broken in the formation of the intermediate $[Os_3(CO)_{11}(\mu\text{-}CO)]$, followed by attack by the phosphine moiety.[13]

In the case of reaction with olefins, significant fragmentation is observed forming $[Os(CO)_4(\text{olefin})]$, $[Os(CO)_4]$, $[Os_2(CO)_8]$ and $[Os_2(CO)_8(\text{olefin})]$ fragments, the unsaturated intermediates reacting with further molecules of olefin to form more stable substitution products. It is concluded that the photofragmentation process invokes an $[Os_3(CO)_{12}L]$ type intermediate as in the case of $[Ru_3(CO)_{12}]$ **1**, the main difference being that $[Ru_3(CO)_{12}L]$ undergoes only fragmentation whereas $[Os_3(CO)_{12}L]$ can undergo either fragmentation or substitution depending on the nature of the ligand, L. This rationalisation goes some way to explaining the relative inefficiency of photofragmentation in $[Os_3(CO)_{12}]$ **2**.

In general, it may be concluded that the photochemistry of triruthenium and triosmium dodecacarbonyls is qualitatively very similar, the main difference being that, in the case of **2**, olefins lead to fragmentation whereas phosphines lead to substitution, but for **1** addition of any of these ligands results in the fragmentation products.

Synthetic Ruthenium Photochemistry

The synthetic potential of photochemistry in the preparation of substituted mono- and tri-nuclear species from $[Ru_3(CO)_{12}]$ **1** was first realised by Lewis and co-workers[2] in 1974 when it was demonstrated that, on broad-band photolysis of **1** in the presence of a two-electron donor, it is possible to form a number of substituted mononuclear complexes rather than, in the case of thermal reaction, complexes of the form $[Ru_3(CO)_9L_3]$. Following these initial investigations, there has been significant interest both in the preparation and stabilisation of these and other complexes and in the synthetic potential of the reactive mononuclear species in the generation of further mononuclear and also higher-nuclearity products. In addition, a number of the photogenerated species show potential as catalysts for a variety of industrially and synthetically important processes. It is the aim of this section to discuss the photochemical synthesis and subsequent reactivity of a variety of mono- and tri-nuclear complexes, then investigate the reported catalytic potential of a number of these species.



Scheme 8 The photochemical reaction of $[Os_3(CO)_{12}]$ **2** with phosphines. (*i*) $h\nu$, PR_3

The majority of the photochemical studies on $[Ru_3(CO)_{12}]$ **1** have involved the generation and subsequent reactivity of mononuclear η^2-olefin complexes and it is on this area that attention will be focused.

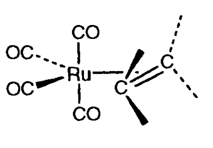
(*a*) *Photochemical Preparation of* η^2-*Olefin Complexes*.—As explained previously, irradiation of a hydrocarbon solution of compound **1** in the presence of an excess of olefin leads quantitatively to the corresponding $[Ru(CO)_4(\eta^2\text{-olefin})]$ complex, the reaction taking place *via* a photofragmentation mechanism,[2] *e.g.* equation (17). The majority of the olefin

$$\underset{\mathbf{1}}{[Ru_3(CO)_{12}]} \xrightarrow[C_2H_4]{h\nu} \underset{\mathbf{7}}{[Ru(CO)_4(C_2H_4)]} \qquad (17)$$

complexes prepared are unstable at room temperature, decomposing to regenerate the starting material **1**, although a number have been isolated as white crystalline solids by application of low-temperature crystallisation techniques and using olefins containing electron-withdrawing groups such as acrylonitrile ($H_2C{=}CHCN$).[16,17] The relative substitution lability of the olefin moiety allows use of η^2-olefin complexes as controlled sources of the highly reactive $Ru(CO)_4$ fragment and this has proven useful in the generation of a number of novel complexes as illustrated later.

It has recently been demonstrated that both the rate of formation and the stability of the η^2-olefin complexes can be greatly increased by performing the reaction at low temperature using dichloromethane as a solvent in the place of hydrocarbons such as hexane.[18] In addition, it is possible to generate far higher concentrations of the intermediates using dichloromethane as compared to hexane and this solvent system offers greater flexibility in the number of potential reagents available for reaction with any photogenerated complexes since polar and charged species, which are insoluble in hexane, are often solvated in the chlorocarbon solvent.

The η^2-olefin complexes exhibit four bands in the carbonyl region of the infrared spectrum, consistent with an equatorial olefin in a trigonal-bipyramidal system, although in the case of certain olefins such as ethylene and pent-1-ene the two central bands overlap. An equatorial olefin position is also predicted by frontier-orbital calculations taking into account the nature of the bonding, the rotational barriers and the conformational preferences of the olefin.[19] In addition, it is calculated that, for a d^8 metal system, the olefin will prefer an orientation perpendicular to the axial ligands in the olefin complex as compared to a parallel arrangement.



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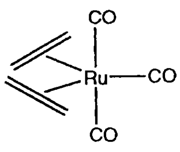

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In addition to the mono-olefin complexes, [$Ru(CO)_4(\eta^2$-olefin)], a number of bis- and tris-substituted mononuclear ruthenium η^2-olefin complexes have been prepared. Near-UV irradiation of hydrocarbon solutions of [$Ru(CO)_4(C_2H_4)$] **7** in the presence of ethylene leads to the formation of [$Ru(CO)_3(C_2H_4)_2$] **8** in high yields.[3] Low-temperature matrix-isolation studies (55 K) show that the bis(ethylene) complex is formed *via* photolabilisation of a carbonyl group in **7** leading to the formation of the co-ordinatively unsaturated intermediate [$Ru(CO)_3(C_2H_4)$] which, on warming to 90 K and in the presence of ethylene, reacts with an olefin group forming **8**. The bis complex **8** shows three bands in the carbonyl-stretching region of the infrared spectrum consistent with a diequatorial arrangement of the olefin groups as predicted from molecular orbital calculations and energetics.[20]

Similar bis-substituted complexes have been prepared using substituted olefins, one of the most stable being the methyl acrylate derivative [$Ru(CO)_3(H_2C{=}CHCO_2Me)_2$] of which the crystal and molecular structure have been determined, confirming the diequatorial arrangement of the olefin moieties in such complexes.[17]

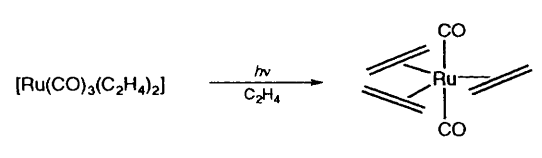
Further irradiation of ethylene-saturated alkane solutions of compound **7** at low temperature leads to the formation of the tris-substituted olefin complex [$Ru(CO)_2(C_2H_4)_3$] **9** showing a single product absorption in the carbonyl region of the infrared spectrum, therefore indicating an all-equatorial arrangement of the olefin groups as shown in Scheme 9.[3]

Recently a novel case of olefin bonding has been observed.[18] If a solution of [$Ru(CO)_4(C_2H_4)$] **7** is irradiated in the presence of acetonitrile it is possible to prepare the disubstituted mononuclear compound [$Ru(CO)_3(C_2H_4)(MeCN)$] **10** which is found to have both substituents in axial positions. To reach the diaxial arrangement reported, a rearrangement of the ethylene group from an equatorial to a less-favourable axial co-ordination site is required, a process of current research interest.

As in the case of the monosubstituted olefin complex **7**, the photogenerated [$Ru(CO)_3(C_2H_4)_2$] **8**, [$Ru(CO)_2(C_2H_4)_3$] **9** and [$Ru(CO)_3(C_2H_4)(MeCN)$] **10** provide potential sources of the highly reactive '$Ru(CO)_3$' and '$Ru(CO)_2$' intermediates due to the extreme lability of the substituent olefin and acetonitrile groups, therefore in principle allowing the preparation of compounds which are particularly thermally and photochemically sensitive.

In addition to the alkene complexes it has been possible to prepare a number of η^2-alkyne-containing mononuclear compounds but starting from the mononuclear pentacarbonyl compound [$Ru(CO)_5$] **3** rather than trinuclear substrates. Photolysis of a hydrocarbon solution of ruthenium pentacarbonyl with acetylene and bis(trimethylsilyl)acetylene leads to the formation of the η^2-alkyne complexes [$Ru(CO)_4(C_2H_2)$] **11** and [$Ru(CO)_4\{C_2(SiMe_3)_2\}$] **12** respectively.[21,22] These compounds are structurally analogous to the alkene complexes with the substituent occupying an equatorial position of a trigonal bipyramid and conform to the electronic site preference arguments presented by Hoffmann and Rossi.[20]

More recently, by using modified conditions, it has been possible to prepare monosubstituted acetylene complexes in high yields from [$Ru_3(CO)_{12}$] **1**.[23]



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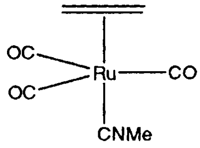
Scheme 9



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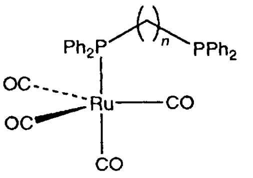
(*b*) *Synthetic Potential of Photogenerated Mononuclear Ruthenium Complexes*.—Of all the mononuclear ruthenium complexes discussed, the most synthetically exploited is [$Ru(CO)_4(C_2H_4)$] **7** which has been used in the generation of both mononuclear and cluster compounds. Addition of any tertiary phosphine to a solution of **7** leads quantitatively to the monophosphine compounds [$Ru(CO)_4(PR_3)$].[18] This has proven a rapid and high-yielding route to this class of mononuclear compounds with selective formation of the monosubstituted phosphine product whereas, *via* direct photolysis of [$Ru_3(CO)_{12}$] in the presence of the free phosphine, a 2:1 mixture of the mono- and bis-substituted products [$Ru(CO)_4(PR_3)$] + [$Ru(CO)_4(PR_3)_2$] is formed.[2,24]

The ruthenium complexes are considerably more reactive than their iron analogues [$Fe(CO)_4(PR_3)$]. This results from more favourable enthalpies of activation and parallels the enhanced susceptibility of the iron and ruthenium tricarbonyl derivatives of cyclooctenediyl towards loss of CO.[24] This enhanced reactivity is illustrated by the photolysis of a solution of [$Ru(CO)_4(PPh_3)$] **13** in the presence of a further equivalent of free phosphine which leads, in almost quantitative yield, to the formation of the *trans* disubstituted complex [$Ru(CO)_3(PPh_3)_2$] **14** as is the case when a solution of PR_3 is added to the olefin–acetonitrile complex [$Ru(CO)_3(C_2H_4)(MeCN)$] **10**.[2,18,24] This synthetic transformation is of particular importance due to the reported catalytic activity of [$Ru(CO)_3(PPh_3)_2$] **14** in the hydroformylation and hydrogenation of olefins.[25] A recent study has suggested also that mononuclear ruthenium complexes like **14** show great potential in the efficient catalytic addition of aromatic carbon–hydrogen bonds to olefins.[26]

Reaction of [$Ru(CO)_4(C_2H_4)$] **7** with 1 equivalent of a bidentate diphenylphosphine leads to the formation of mononuclear complexes of the class [$Ru(CO)_4\{Ph_2P(CH_2)_nPPh_2\}$] where the phosphine is monodentate (see below).[27,28] It has been observed that, to a general rule, the



longer the carbon backbone the faster the complex is formed. This is expected due to the fact that the steric requirements of the large PPh_2 groups at each end of the molecule are less in the systems with larger backbones. It was also found that the nature of the carbon backbone greatly affected the rate of formation. With 1,2-bis(diphenylphosphino)acetylene (dppa), containing a C≡C unit, the reaction was considerably slower than with 1,2-bis(diphenylphosphino)ethane (dppe), the alkane analogue.

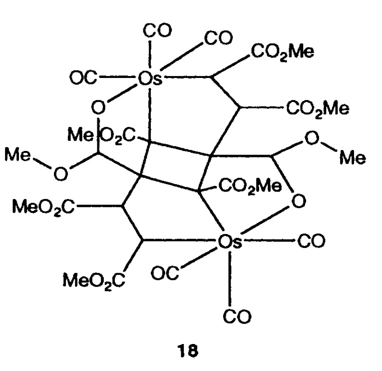
This again is expected since the two CH_2 groups in dppe are better electron donors than is the C≡C moiety in dppa, thus making dppe and other systems with simple hydrocarbon backbones more nucleophilic and therefore more reactive towards the mononuclear ruthenium system than in the case of dppa.

In the absence of air the monodentate diphosphine complexes have a considerable lifetime before producing a number of trinuclear ruthenium complexes of which the main products are $[Ru_3(CO)_{12}]$ **1** and $[Ru_3(CO)_{10}\{Ph_2P(CH_2)_nPPh_2\}]$. In general it is observed that the complexes containing phosphines with long carbon backbones have longer lifetimes than those with shorter backbones, this being due to chelation being more energetically favourable for bidentate phosphines such as dppe, which forms a six-membered ring on chelation as compared to the case of the hexane backbone analogue dpph which would form a ten-membered ring on co-ordination.

The photochemically prepared η^2-ethylene complexes can be used in the synthesis of metallacyclic compounds since they are excellent starting materials for ligand-exchange reactions with other olefins and for C–C coupling reactions with alkenes or alkynes.[29] In addition, metallacycloalkane compounds of the transition-metal elements are important organometallic substrates and find uses in key organic transformations such as olefin carbonylations, oligomerisations and metathesis reactions.[30]

Several osmium metallacycles have been prepared and are well characterised. Irradiation of $[Os_3(CO)_{12}]$ **2** in the presence of a large excess of methyl acrylate results in the formation of both the η^2-olefin complex $[Os(CO)_4(CH_2CHCO_2Me)]$ **15** and of the dinuclear osmacyclobutane $[Os_2(CO)_8(CH_2CHCO_2Me)]$ **16**.[31] The Os–Os bond length in **16** is 2.885 Å, typical for a Os–Os single bond and the length of the μ-ethane-1,2-diyl bridge is that of a single C–C bond. The four-membered ring is puckered presumably to relieve the steric strain of the $Os(CO)_4$ moieties resultant from a planar, eclipsed, conformation. More recently the diosmacycles $[Os_2(CO)_8(\mu\text{-}\eta^1:\eta^1\text{-}MeO_2CCCCO_2Me)]$ **17** and $[Os_2(CO)_6(MeO_2CCCCO_2Me)_4]$ **18** have been prepared by long-wavelength irradiation of **2** with acetylenedicarboxylic acid dimethyl ester.[32] The formation of **18** represents a novel coupling of alkynes, the compound being considered to arise from the condensation of two tricarbonylosmacyclopentadiene fragments by means of a [2 + 2] cycloaddition. This is followed by end-on co-ordination of an oxygen atom from a carboxylate group on an adjacent osmacyclopentene ring to yield the product.

Ruthenium differs from osmium quite considerably in the nature of any metallacyclic complexes formed. Whereas osmium forms a variety of metal–metal bonded dimetallic species, owing to the decreased strength of the Ru–Ru bond in the majority of cases ruthenium forms either mononuclear or non-metal–metal bonded dinuclear complexes. The initial stages of the synthesis of ruthenacyclic complexes often involves the reaction of tetracarbonyl(η^2-ethylene)ruthenium **7** with activated alkenes or alkynes to generate substitution products. In this way, the η^2-ethylene complex is acting as a source of the reactive '$Ru(CO)_4$' fragment and, as in the case of reaction with phosphines, substitution products can be prepared, the mild conditions and high yields obtained making this ligand-exchange reaction a viable alternative to common synthetic methods.



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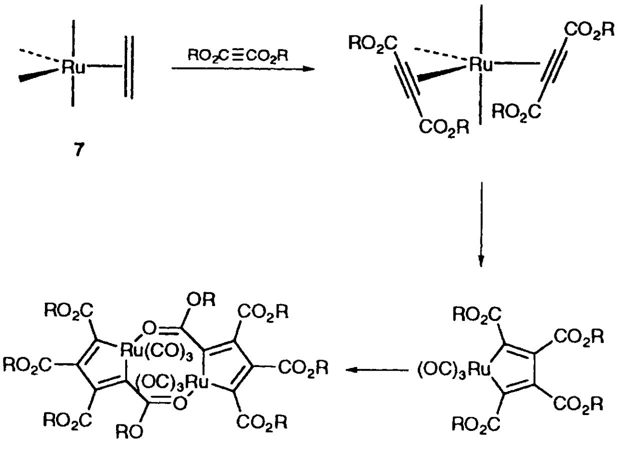
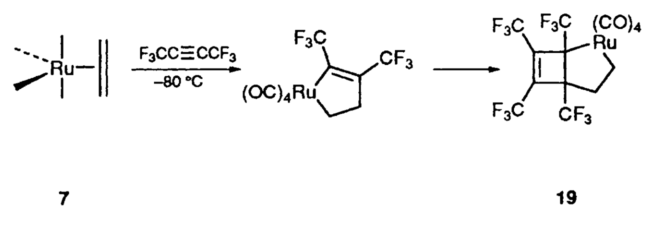
Reaction of $[Ru(CO)_4(C_2H_4)]$ **7** with acetylenedicarboxylic acid dimethyl ester or diethyl ester at 20 °C results in the formation of the tricyclic systems shown in Scheme 10.[29] These compounds are prepared by substitution of the labile ethylene group and a CO ligand by a molecule of the alkyne substrate, formation of a C–C bond to yield a co-ordinatively unsaturated ruthenacyclopentadiene then a dimerisation to form the non-metal–metal bonded diruthenium product. These products are catalysts for the cyclotrimerisation of acetylene-dicarboxylic and -monocarboxylic acid dialkyl esters, yielding the corresponding benzene-hexacarboxylic and -tricarboxylic acid hexaalkyl esters. In addition, the diruthenium tricyclic systems react with CO to form mononuclear ruthenacyclopentadienes due to facile cleavage of the Ru–O donor bond.

Reaction of $[Ru(CO)_4(C_2H_4)]$ **7** with hexafluorobut-2-yne at −80 °C leads to the formation of a ruthenabicyclo[3.2.0]-heptene product **19** (Scheme 11).[29] This is in contrast to the behaviour of the η^2-ethylene complex with the acetylenedicarboxylate esters since in this case it reacts like a metallacyclopropane. The alkyne is inserted into a Ru–C bond of **7** with the formation of a ruthenacyclopentene which, in turn, reacts with a second molecule of the alkyne in a [2 + 2] cycloaddition reaction to yield the product **19**.

Both ruthenium and osmium η^2-ethylene complexes have been used in the synthesis of a number of organic substrates by generation and subsequent reaction of metallacycles.[33,34] Heating a toluene solution of tetracarbonylruthenacyclobutane to 80 °C results in a reductive elimination reaction yielding cyclopropane. This is in contrast to the formation of ethylene in the case of the corresponding nickela- and pallada-cyclobutane systems. In the case of tetracarbonylruthenacyclopentane and hexane, heating leads to two distinct product sets. Buta-1,3-diene and penta-1,4-diene are formed from the pentane and hexane complexes respectively by way of a β-hydrogen-elimination pathway. Alternatively *cis*- and *trans*-but-2-ene and pent-2-ene are formed by way of a ring rearrangement or *via*



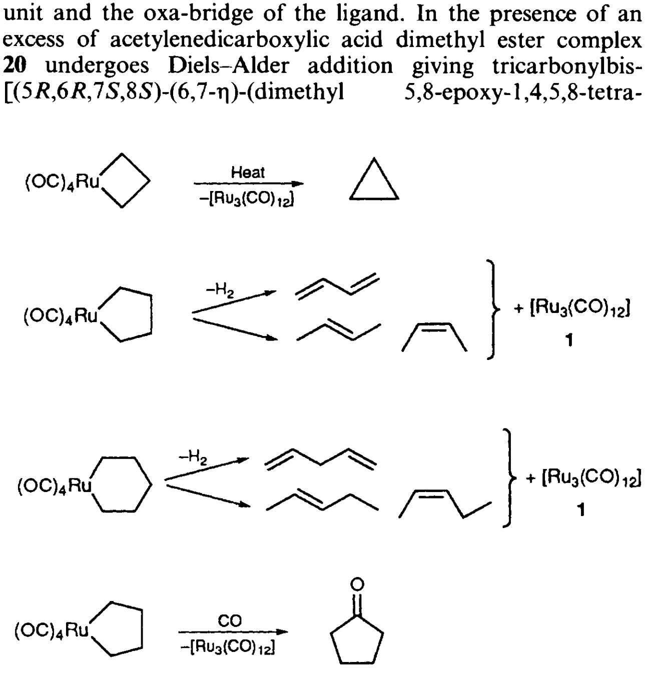
Scheme 10 Reaction of $[Ru(CO)_4(C_2H_4)]$ **7** with activated alkynes (R = Me or Et)



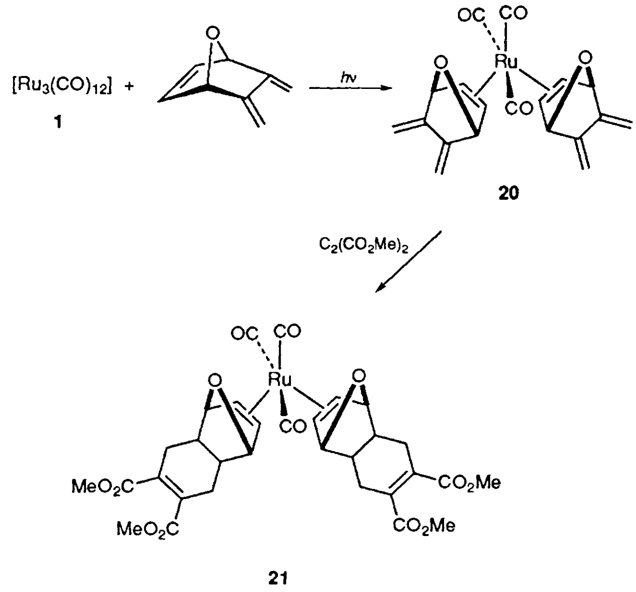
Scheme 11 Reaction of $[Ru(CO)_4(C_2H_4)]$ **7** with hexafluorobut-2-yne

an allylic intermediate. In the presence of carbon monoxide, insertion of CO into a M–C bond of the ruthenacycloalkane is possible to form the corresponding ruthenacycloalkanone which then undergoes reductive elimination to yield the free cycloalkanone. These reactions of these ruthenacycloalkanes are summarised in Scheme 12.

Photochemistry has been used for the chemo- and stereoselective co-ordination of 5,6-dimethylene-7-oxabicyclo[2.2.1]hept-2-ene to mononuclear ruthenium complexes which, once generated, have been used to investigate the Diels–Alder reactivity of dienes perturbed by remote olefin complexation.[35] Irradiation of $[Ru_3(CO)_{12}]$ in the presence of the bicycloheptene leads to the formation of the bis(η^2-olefin) complex **20** with the ligand attached to the ruthenium *via* the endocyclic double bond rather that the exocyclic diene (Scheme 13). This compound is formed in high yield and the chemoselectivity is thought to be due to the fact that there is an interaction between one of the axial CO groups of the $M(CO)_4$ unit and the oxa-bridge of the ligand. In the presence of an excess of acetylenedicarboxylic acid dimethyl ester complex **20** undergoes Diels–Alder addition giving tricarbonylbis-[(5*R*,6*R*,7*S*,8*S*)-(6,7-η)-(dimethyl 5,8-epoxy-1,4,5,8-tetrahydronaphthylene-2,3-dicarboxylate)]ruthenium **21**. The rate of reaction is approximately 250 times faster than that of the ligand itself therefore illustrating how the Diels–Alder reactivity of the exocyclic diene moiety in the bicycloheptene can be significantly enhanced by co-ordination of the homoconjugated, endocyclic double bond to a low-valent d^8-metal system. The increased activity may be explained in terms of the attractive interaction between the oxa-bridge of the ligand and a terminal carbonyl group in the metal complex reducing the strain between the olefin and oxa-bridge moieties in the ligand therefore making the cycloaddition more exothermic and, consequently, faster than in the case of the uncomplexed triene.



Scheme 12 Reactions of ruthenacycloalkanes



Scheme 13

In addition to the formation of novel ruthenium mono- and di-nuclear complexes, photochemically generated intermediates have been used to generate cluster complexes. The mononuclear ethylene complex $[Ru(CO)_4(C_2H_4)]$ **7** has been used in the preparation of a variety of heterometallic products. Reaction with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ $[HB(pz)_3$ = hydrotris(pyrazol-1-yl)borate$]$ in a 3:1 molar ratio yields the tetranuclear product $[WRu_3(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_{11}\{HB(pz)_3\}]$ **22** as the only product.[36] A similar reaction with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_5H_5)]$ yields the corresponding triruthenium alkylidyne complex $[WRu_3(\equiv CC_6H_4Me\text{-}4)(CO)_{11}(\eta^5\text{-}C_5H_5)]$ **23**. If the reaction between **7** and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_5H_5)]$ is performed using a 1:2 molar ratio the product formed is the trinuclear $[W_2Ru\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta^5\text{-}C_5H_5)_2]$ **24** in high yield.

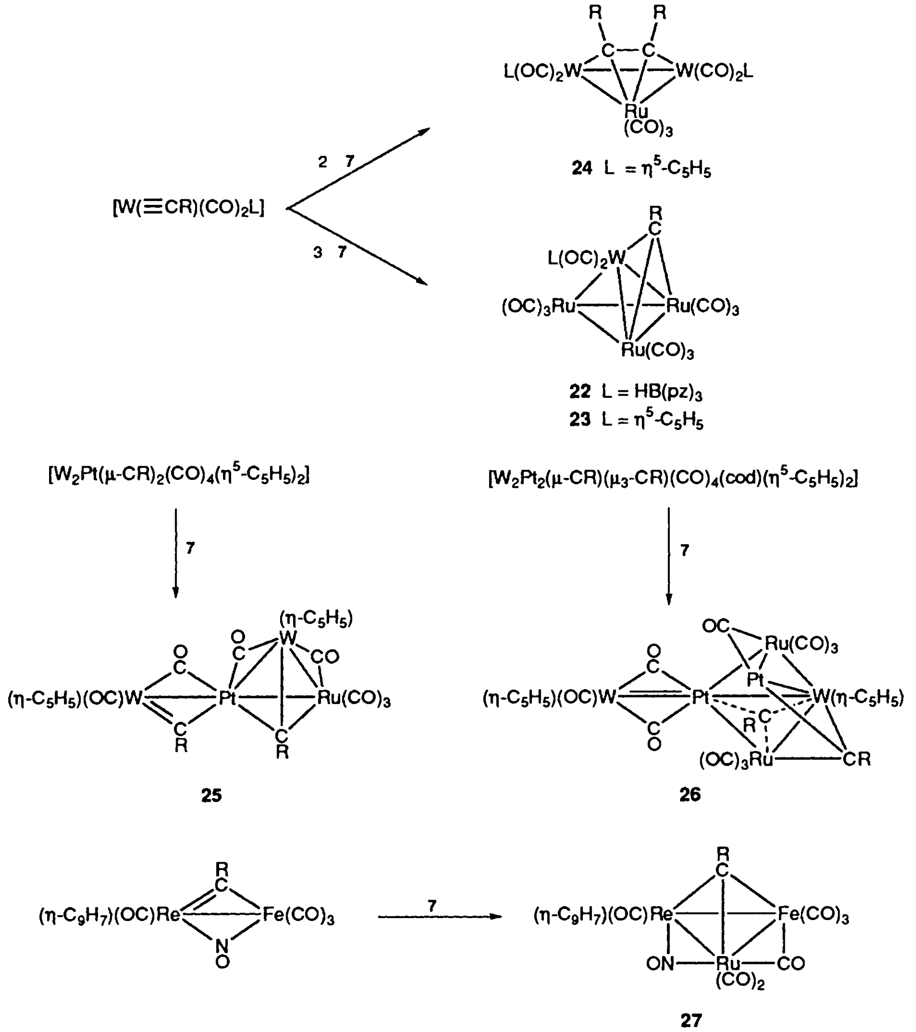
The ready availability of the photogenerated mononuclear intermediate **7** has allowed many further aspects of this chemistry to be exploited with the preparation of molecules with backbones consisting of a number of heterometallic atoms. As examples of this, reactions with $[W_2Pt(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta^5\text{-}C_5H_5)_2]$ and $[W_2Pt_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4\text{-}Me\text{-}4)(CO)_4(cod)(\eta^5\text{-}C_5H_5)_2]$ (cod = cycloocta-1,5-diene) yield the tetra- and hexa-nuclear clusters $[W_2RuPt(\mu\text{-}CC_6H_4\text{-}Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_7(\eta^5\text{-}C_5H_5)_2]$ **25** and $[W_2Ru_2Pt_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)_2]$ **26** respectively.[37]

In addition, $[Ru(CO)_4(C_2H_4)]$ **7** has been used to add an '$Ru(CO)_3$' group to $[FeRe(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}NO)(CO)_4(\eta^5\text{-}C_9H_7)]$ in order to form the trimetallatetrahedrane complex $[FeReRu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}NO)(\mu\text{-}CO)(CO)_6(\eta^5\text{-}C_9H_7)]$ **27**.[38] This is an example of an interesting class of trimetal compounds in which an alkylidyne group triply bridges three different transition metals.

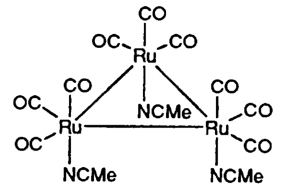
The reactions of compound **7** with mixed-metal clusters are summarised in Scheme 14.

In recent years there has been considerable interest in the generation of mixed transition metal–non-metal clusters, these compounds often being unsaturated, a property important in the studies of the cluster–surface analogy and related to both the increase and poisoning of the catalytic activity of systems. Owing to the ease of synthesis and high reactivity, photochemically generated ruthenium intermediates such as **7** have been used in the synthesis of novel transition metal–chalcogen carbonyl compounds. Tellurium has been noted for its ability to bridge between small metal aggregates to form larger clusters. Addition of mono- and poly-nuclear metal carbonyl fragments occurs readily across the Te–Te bond of $[Fe_2(CO)_6(\mu\text{-}Te_2)]$ and reaction with **7** yields the cluster $[Fe_2Ru(CO)_9(\mu_3\text{-}Te)_2]$ **28**.[39] Further addition of **7** to **28** yields the diruthenium cluster compound $[Fe_2Ru_2(CO)_{11}(\mu_4\text{-}Te)_2]$ **29** which is structurally analogous to the tetrairon cluster $[Fe_4(CO)_{11}(\mu_4\text{-}Te)_2]$ containing one bridging and two semi-bridging carbonyl ligands.

Mixed-chalcogen clusters such as $[Fe_2Ru(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)]$ **30** and $[Fe_2Ru_2(CO)_{11}(\mu_4\text{-}Se)(\mu_4\text{-}Te)]$ **31** have also been prepared by the simple addition of **7** to the diiron cluster $[Fe_2(CO)_6(\mu\text{-}SeTe)]$.[40]



Scheme 14 Reactions of $[Ru(CO)_4(C_2H_4)]$ **7** with mixed-metal clusters. R = C_6H_4Me-4



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Photochemically generated mononuclear ruthenium complexes have been used to generate cluster compounds a number of which have been synthetically inaccessible by other methods to date. If the light source is removed from a solution of the ethylene–acetonitrile intermediate $[Ru(CO)_3(C_2H_4)(MeCN)]$ **10** it is possible to generate the highly reactive tris(acetonitrile) triruthenium cluster $[Ru_3(CO)_9(MeCN)_3]$ **32**.[18] This result is of significance since, as well as this being the first tris(acetonitrile) complex reported, **32** has potential as a starting material for the synthesis of crowded trinuclear clusters, as is observed on reaction with bulky ligands, and for cluster build-up processes. Reaction of **32** with a variety of mono- and bi-dentate phosphines and nitrogen heterocycles lead to the formation of the sterically crowded substitution products $[Ru_3(CO)_9L_3]$ in the case of mononuclear ligands and $[Ru_3(CO)_9(L\text{–}L)_2]$ in the case of bidentate ligands.[18,23]

Photochemistry of Substituted Triruthenium Clusters

The aim of this section is to discuss briefly the photochemistry of substituted triruthenium carbonyl clusters, in particular the tris(phosphine) cluster $[Ru_3(CO)_9(PPh_3)_3]$ **33**. Like $[Ru_3(CO)_{12}]$ **1** the phosphine-substituted clusters $[Ru_3(CO)_9(PR_3)_3]$ show a band in the electronic spectrum near 390 nm but in addition there is a band at approximately 500 nm. Since phosphine substitution occurs at an equatorial plane to the Ru_3 cluster framework, it is the d_{xz} orbital which is primarily perturbed on going from the binary carbonyl **1** to the tris(phosphine) adduct, this orbital being made less antibonding.[14] As a result the d_{z^2} antibonding orbital is higher in energy than the d_{xz} bonding orbital, decreasing the energy of the $\sigma^{*\prime} \longrightarrow \sigma^*$ transition in passing from **1** to $[Ru_3(CO)_9(PR_3)_3]$.

As in the case of $[Ru_3(CO)_{12}]$ **1** there is scope for both photosubstitution and photofragmentation processes in phosphine-substituted clusters.[41] However, studies show that, independent of the phosphine, photosubstitution of CO for L is negligible and photofragmentation follows the same stoichiometry as in the case of **1**, the irradiation of $[Ru_3(CO)_9(PPh_3)_3]$ **33** yielding $[Ru(CO)_4(PPh_3)]$ **13** and $[Ru(CO)_3(PPh_3)_2]$ **14** in the presence of CO and PPh_3 respectively.[4,42]

Mono- and bis-substituted complexes give fragmentation quantum yields (Φ_f) comparable to that for $[Ru_3(CO)_{12}]$ **1**, but those for tris-substituted clusters are significantly smaller, the relative differences in Φ_f between $[Ru_3(CO)_{10}(PR_3)_2]$ and $[Ru_3(CO)_9(PR_3)_3]$ being greater the more bulky the R group becomes. The photofragmentation process is mechanistically similar to that for **1**, the observed changes in Φ_f for $[Ru_3(CO)_9(PR_3)_3]$ being consistent with the formulation of a photogenerated co-ordinatively unsaturated carbonyl-bridged trinuclear intermediate (*cf.* **3**), the corresponding phosphine-substituted system being considerably less reactive owing to the bulky phosphine groups on the metal centres.[42]

Alternatively it is suggested that, from a consideration of the molecular orbital approach discussed above, ligand substitution leads to a reversal of the order of the energy levels to an extent that the nature of the excited state responsible for the photofragmentation of compound **1** is different to that for the substituted clusters. On consideration, this explanation is unlikely in the light of the smooth progression in λ_{max} of the dominant lowest-energy absorption band from **1** to the tris-substituted compound but the significant discontinuity in Φ_f between the bis- and tris-substituted systems.[4]

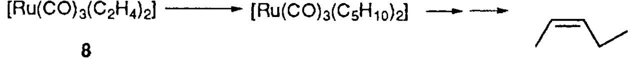
Use of Ruthenium Cluster Photochemistry in Catalysis

The photogeneration of catalysts from homogeneous organometallic precursors has become a topic of some considerable interest over recent years and it is widely recognised that photochemistry offers an effective means of avoiding the use of elevated temperatures and pressures. One of the largest areas of study in the field of ruthenium photocatalysis has been the isomerisation of alkenes, $[Ru_3(CO)_{12}]$ **1** being a useful catalyst precursor for this process. The mechanism of reaction has been investigated by studying the chemistry of the η^2-olefin complexes $[Ru(CO)_3(C_2H_4)_2]$ **8** and $[Ru(CO)_2(C_2H_4)_3]$ **9** generated in hydrocarbon solution by photolysis of **1** in the presence of ethylene at low temperatures.[3] The bis(ethylene) compound **8** readily undergoes alkene exchange with pent-1-ene to yield the bis(pent-1-ene) system $[Ru(CO)_3(C_5H_{10})_2]$ **34** as shown in Scheme 15. On warming to above 260 K pent-1-ene undergoes alkene isomerisation to the *cis*- and *trans*-pent-2-enes with turnover rates in excess of 250. These results are of significance since this points towards the role of substantially labile $[Ru(CO)_3(alkene)_2]$ and even $[Ru(CO)_2(alkene)_3]$ complexes in the photochemical activity of $[Ru_3(CO)_{12}]$ **1** in photoisomerisation, these compounds providing an entrance to the catalytic cycle. The turnover rate is found to decrease with reaction time with the formation of, in the case of pent-1-ene, penta-1,3-diene and monosubstituted olefin complexes $[Ru(CO)_3(C_5H_8)]$ **35** and $[Ru(CO)_4(C_5H_{10})]$ **36** respectively. The latter complex **36** may be expected since catalyst decomposition releases CO which can react with the bis-substituted complex $[Ru(CO)_3(C_5H_{10})_2]$ giving the monoolefin product by loss of dihydrogen. The formation of the pentadiene complex **35** is not so easily rationalised.

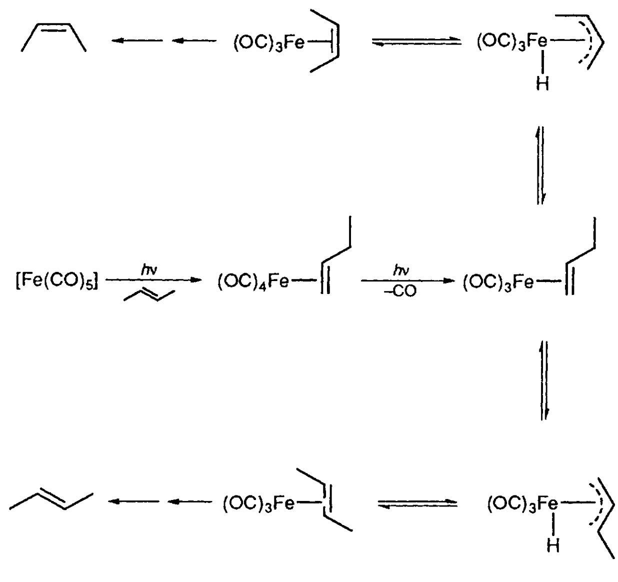
The mechanism for the isomerisation process may be further understood by considering the corresponding catalytic activity of $[Fe(CO)_5]$.[43] It has been determined that an allyl complex $[FeH(CO)_3(\eta^3\text{-allyl})]$ is intimately involved in the reaction and may be the essential intermediate in the catalytic cycle, the product being determined by whether a *syn*- or *anti*-allyl hydride is formed. The proposed mechanism for the reaction in the case of iron is summarised in Scheme 16.

Recently, studies in methylpentane glasses at 90 K have allowed for the identification of the analogous $[RuH(CO)_3(\eta^3\text{-allyl})]$ species on photolysis of $[Ru(CO)_4(C_5H_{10})]$ but, beyond the involvement of the $[Ru(CO)_3(C_5H_{10})_2]$ species, it is not possible to speculate further on the exact mechanism of photoisomerisation in the case of $[Ru_3(CO)_{12}]$ **1**.[3]

It is well established that the ligands in the co-ordination sphere of a metal-centred catalyst can influence the rate and product distribution of a reaction due both to steric and electronic effects. Phosphines are useful in this way as stabilising ligands in catalytic processes and it is possible to optimise reaction conditions since there are a vast number of phosphorus ligands each exhibiting unique steric and electronic properties.[42] With this in mind, studies have been undertaken to investigate the photocatalytic isomerism of pent-1-ene using phosphine-substituted triruthenium cluster precursors.[42] As in the case of **1**, one of the key steps in the reaction is the photofragmentation of the substituted trinuclear clusters to co-ordinatively unsaturated $[Ru(CO)_3(PR_3)]$ fragments which, under the correct conditions, may react with a molecule of the substrate alkene to form the bis-substituted complex $[Ru(CO)_3(PR_3)(alkene)]$, the geometry of which is not fully characterised. The nature of the phosphorus donor can effect significantly the photochemistry of these systems, perhaps the most important result being that the initial ratio of *trans*- to *cis*-pent-2-ene depends on the nature of the phosphine in the catalyst precursor, bulky ligands favouring a *cis* arrangement, although the kinetically controlled initial distribution of products often differs from that of the ultimate thermodynamic equilibrium. As in the case of the catalysis of alkenes using $[Ru_3(CO)_{12}]$ **1**, after dissociation of $[Ru_3(CO)_{12}(PR_3)_3]$ and co-ordination of an alkene moiety, it is proposed that carbonyl loss occurs to yield an allyl hydride species as a precursor to the isomerised products.



Scheme 15 Isomerisation of pent-1-ene using mononuclear ruthenium fragments



Scheme 16 A mechanism for the isomerisation of alkenes using $[Fe(CO)_5]$

The neutral mononuclear ruthenium complexes $[Ru(CO)_4(PPh_3)]$ **13**, $[Ru(CO)_3(PPh_3)_2]$ **14** and $[RuCl(CO)_2(NO)(PPh_3)_2]$ **37** have been used in the photochemical carbonylation of benzene and in the hydrogenation of benzaldehyde.[44] It is suggested that the principal catalyst precursor is the monophosphine complex **13**, the other two starting materials being converted into this before entering the catalytic cycle. The key photochemical step is proposed to be dissociation of CO to generate the unsaturated $[Ru(CO)_3(PPh_3)]$ compound which then either adds free CO to regenerate **13** or co-ordinates benzene in a η^2 mode. The benzene activation proceeds by oxidative addition of a phenyl C–H bond to generate a phenyl hydride species which subsequently undergoes insertion of CO and reductive elimination to yield the product.

The photocatalytic hydrogenation of benzaldehyde to benzoic acid also involves the generation of $[Ru(CO)_3(PPh_3)]$ which, on reaction with dihydrogen, forms the dihydride

$[RuH_2(CO)_3(PPh_3)]$. Interaction with the benzaldehyde moiety is proposed to be *via* co-ordination through the carbonyl bond paralleling the η^2 co-ordination of the arene in the oxidative addition above.

Photochemically generated $[Ru(CO)_3(PPh_3)]$ has also been utilised in the hydroformylation of ethylene and propylene.[45]

The compound $[Ru_3(CO)_{12}]$ **1** has been used in the catalytic hydrosilylation of acetone, involving initial photofragmentation followed by photodissociation of a CO group then co-ordination of the ketone *via* the carbonyl moiety.[46] It has been found that the catalytic process is very sensitive to the structure of the carbonyl substrate and indeed the hydrosilylation of heptan-2-one using ruthenium complexes is considerably less effective than in the case of acetone.

Photochemistry of Tetranuclear Ruthenium Clusters

So far, this article has focused on the photochemistry of trinuclear clusters and on the reaction chemistry of the resultant mononuclear fragments formed. It is the aim of this final section to summarise the photochemistry of tetranuclear ruthenium clusters.

Compared to trinuclear ruthenium systems, the photochemistry of tetranuclear carbonyl clusters has been the object of far fewer detailed studies. The tetrahydridotetraruthenium cluster $[Ru_4H_4(CO)_{12}]$ **38** has a tetrahedral metal core with twelve terminally bound CO ligands and four edge-bridging hydrides and is a catalyst precursor for a number of industrially important processes including olefin isomerisation, hydrogenation, hydroformylation, water-gas shift and Fischer–Tropsch reactions. Consequently there is interest in the photogeneration of the active catalytic compounds.[47]

Compound **38** exhibits an intense absorption maximum at 362 nm with a tail into the visible region in hydrocarbon solvents. Tetranuclear clusters often undergo quantum-inefficient reactions upon irradiation and, by comparison with $[Ru_3(CO)_{12}]$ **1**, it is postulated that the possible primary photochemical processes are cleavage of a metal–metal bond to form a co-ordinatively unsaturated intermediate or metal–ligand bond cleavage resulting in loss of either H_2 or CO. Irradiation of a hydrocarbon solution of **38** leads to decomposition products, but irradiation in the presence of a potential co-ordinating ligand, L, such as PPh_3 results in the formation of the monosubstituted cluster $[Ru_4H_4(CO)_{11}L]$. Continued irradiation leads to further substitution yielding $[Ru_4H_4(CO)_{12-n}L_n]$ (n = 1–4) although, in the case of PPh_3, the monosubstituted cluster can be prepared quantitatively and isolated before multiple substitution occurs.

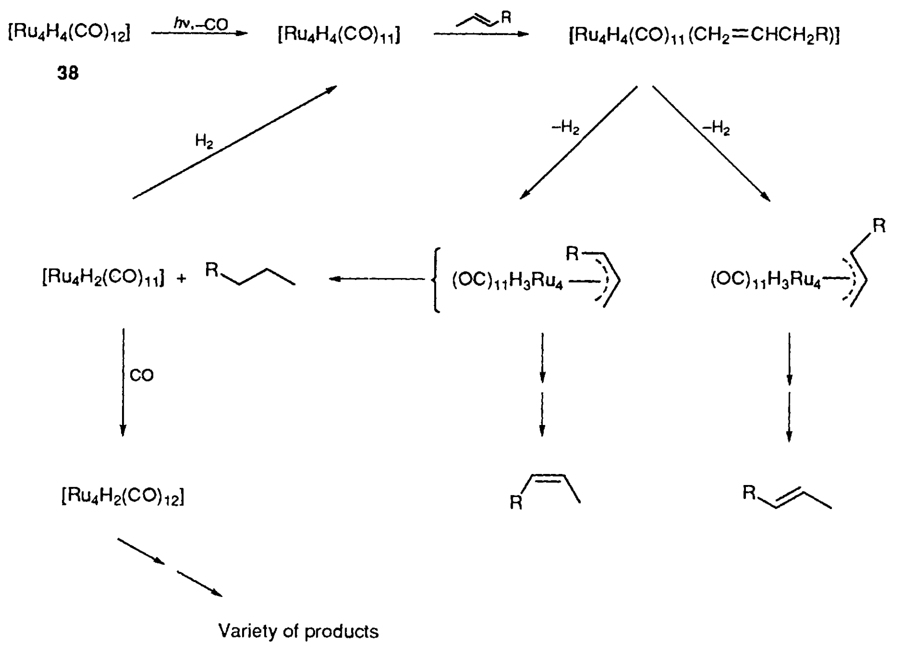
The generation of photosubstitution rather than fragmentation products is explained by the increased delocalisation over the metal framework and it is unlikely that metal–metal bond cleavage will occur. In drawing this conclusion it is important not to exclude entirely the possibility that cleavage does indeed occur, but with either substitution at the co-ordinatively unsaturated site followed by metal–metal bond reformation or else inhibition of net fragmentation by the remaining metal–metal bonds in the cluster.

In comparison, it has been demonstrated that, upon irradiation, photofragmentation of $[Ru_4H_2(CO)_{13}]$ **39** and $[FeRu_3H_2(CO)_{13}]$ **40** occurs in the presence of CO [equations (18) and (19)] but with very low quantum efficiency and it is

$$\underset{\mathbf{39}}{[Ru_4H_2(CO)_{13}]} \xrightarrow[L]{h\nu} \underset{\mathbf{1}}{[Ru_3(CO)_{12}]} + \underset{\mathbf{3}}{[Ru(CO)_5]} \quad (18)$$

$$\underset{\mathbf{40}}{[FeRu_3H_2(CO)_{13}]} \xrightarrow[L]{h\nu} \underset{\mathbf{1}}{[Ru_3(CO)_{12}]} + [Fe(CO)_5] \quad (19)$$

often the case that competing thermal reactions are much more rapid.[48] As with **38**, photolysis of $[Ru_4H_2(CO)_{13}]$ **39** in the presence of donor ligands results in the formation of photosubstituted products, although with PPh_3 only the mono- and bis-substituted clusters are generated. Compound **39** also reacts with dihydrogen on irradiation to yield the tetrahydrido cluster **38**. The formation of photosubstitution rather than photofragmentation products in the case of tetranuclear clusters has been supported by kinetic studies which show that, if **38** or **39** undergoes metal–metal bond cleavage on irradiation to yield a 'butterfly' cluster intermediate, either dissociation of CO from the cluster intermediate or competitive addition of CO or ligand to the intermediate would be required.[48] The former process is somewhat improbable since a cluster that is already electron deficient is unlikely to dissociate a CO group to yield an even more co-ordinatively unsaturated species. Additional evidence against metal–metal bond cleavage is found in the lack of a dependence of the quantum yield for substitution on the ligand-concentration. If photolysis were to induce metal–metal bond



Scheme 17 A mechanism for the isomerisation and hydrogenation of alkenes

cleavage, the intermediate formed could either react with the added ligand followed by loss of CO to effect substitution, or regenerate the metal–metal bond to return to the starting material. The relative efficiency of the former process, together with the observed high quantum yield, would be expected to increase with increasing concentration of added ligand and since this does not occur it is concluded that metal–metal bond cleavage is not the primary photoprocess although it must occur at some stage since it is the only pathway by which the low-yield CO-induced fragmentation of the tetranuclear clusters can occur.

As already stated, tetranuclear clusters have found application in catalytic processes and it is the objective of this final part to discuss the photocatalysis of organic substrates using $[Ru_4H_4(CO)_{12}]$. Addition of pent-1-ene to a solution of compound **38** at 70 °C results in isomerisation to *cis*- and *trans*-pent-2-ene. It has been found that the rate of isomerisation is greatly increased on near-UV irradiation and effects the stoichiometric reduction of pent-1-ene to pentane.[47] It has been concluded that the catalytically active species is $[Ru_4H_4(CO)_{11}]$ **41**, formed by photochemical loss of CO from **38**, the isomerisation process taking place either by a reversible hydride transfer or by a π-allyl–hydride mechanism. The only detectable ruthenium-containing product from the irradiation of $[Ru_4H_4(CO)_{12}]$ in the presence of pent-1-ene is $[Ru_4H_2(CO)_{13}]$. Comparing this with the case of osmium, if $[Os_4H_4(CO)_{12}]$ is irradiated in the presence of a terminal alkene $RCHCH_2$, the cluster $[Os_4H_3(CO)_{11}(RCHCH_2)]$ is formed and is relatively stable.[49,50] It may be proposed that an analogous compound is formed in the case of ruthenium although characterisation of the $[Ru_4H_4(CO)_{11}(\text{olefin})]$ cluster proves difficult due to the increased lability of the system.

A mechanism for the catalytic isomerisation and subsequent hydrogenation of alkenes is shown in Scheme 17.

Conclusion

This article has highlighted the use of inorganic photochemistry in the synthesis of both mononuclear and higher-nuclearity compounds. Photochemistry offers a very selective tool, it being possible judiciously to labilise one group over another. In trinuclear clusters such as $[Ru_3(CO)_{12}]$ **1**, by careful choice of solvent and irradiation wavelength, it is possible to prepare either photofragmentation or photosubstitution products. In addition, due to the selectivity of this method, photochemistry leads to high product yields and often just one product as compared to mixed products using conventional synthetic techniques. Photochemistry also offers a route to catalytically active species and has allowed the elucidation of the mechanism for a number of important catalytic processes such as olefin isomerisation.

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