Photochemistry and Photocatalytic Activity of $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ for Isomerization and Hydrogenation of Alkenes

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The tetranuclear complex $H_4Ru_4(CO)_{12}$ undergoes dissociative loss of CO upon near-uv, 355 nm, irradiation to give substitution products $H_4Ru_4(CO)_{11}L$ (L = $P(OMe)_3$, PPh_3) in the presence of L with a quantum yield of $\sim 5 \times 10^{-3}$. In the presence of an olefin $H_2Ru_4(CO)_{13}$ is the principal Ru-containing photoproduct and stoichiometric reduction of the olefin is observed, e.g. *cyclopentene gives cyclopentane. Presumably the intermediate $H_4Ru_4(CO)_{11}$ (olefin) gives alkane and the unsaturated $H_2Ru_4(CO)_{11}$ that rapidly reacts with CO to form $H_2Ru_4(CO)_{13}$. The $H_2Ru_4(CO)_{13}$ reacts slowly with H_2 to give $H_4Ru_4(CO)_{12}$ at 25 °C. Irradiation of $H_2Ru_4(CO)_{13}$ in the presence of an olefin such as 1-pentene accelerates the catalyzed isomerization and effects stoichiometric reduction of the olefin,* e.g. *n-pentane forms from 1-pentene at 25 °C under irradiation whereas no reduction occurs thermally at 25 °C.*

Introduction

Mononuclear hydrides and di- and trinuclear clusters have received considerable photochemical study, however few tetranuclear carbonyl clusters have been the object of detailed studies [1]. The $[Co_4(CO)_{12}]$ and $[HFeCo_3(CO)_{12-n}L_n]$ (L = PPh_3; n = 0, 2) species [2] undergo inefficient declusterification and $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ [3] undergoes metal-to-solvent charge-transfer oxidation upon optical excitation. Irradiation of $[H_4Re_4(CO)_{12}]$ [4] results in visible light emission, and photolysis of $[H_2MM'_3(CO)_{13}]$ (M, M′ = Fe, Ru, Os) [5] in the presence of PPh_3 yields the substitution product, $[H_2MM'_3(CO)_{12}PPh_3]$. Interesting photoreactions of $[H_4Os_4(CO)_{12}]$ [6] and $[Ir_4(CO)_{12}]$ [7] have been reported but the nature of the primary photoprocesses have not been established. These few studies demonstrate that various primary photoprocesses can occur, usually with low quantum efficiency, from the excited states of tetranuclear metal carbonyl clusters.

We have reported in a communication [8] on the photochemistry of $[H_4Ru_4(CO)_{12}]$. This cluster and its substituted derivatives are known catalyst precursors for olefin isomerization [9], hydrogenation [9a, 10], hydroformylation [9a, 11], water-gas shift [11, 12], and Fischer-Tropsch reactions [13]. The loss of CO from $[H_4Ru_4(CO)_{12}]$ is believed to produce an active catalyst for thermal olefin isomerization and hydrogenation reactions [9, 10]. Since the active catalyst may be only a step away from the precursor, $[H_4Ru_4(CO)_{12}]$, we began our work with the hope that photoactivation of $[H_4Ru_4(CO)_{12}]$ at 25 °C may produce an active catalyst directly *via* loss of CO. However, other primary photoprocesses such as metal–metal bond cleavage or loss of H_2 are possible and these could lead to different coordinatively unsaturated species which may also serve as active olefin isomerization and hydrogenation catalysts. It is of interest to see how photoactivation of this system may perturb the catalytic chemistry from that observed at elevated temperatures. In this article we summarize our earlier findings [8] and present results showing that $H_2Ru_4(CO)_{13}$ can effect olefin reduction upon irradiation at 25 °C.

Experimental

Materials

Olefins (99–99.9% purity) were obtained from Chemical Samples Co. or Phillips Petroleum Co. and passed through Al_2O_3 prior to use. All solvents were reagent grade and distilled under nitrogen from CaH_2 or sodium benzophenone ketyl. The n-hexane (99+%) was obtained from Aldrich Chemical Co. and distilled prior to use. The $[Ru_3(CO)_{12}]$ was obtained from Strem Chemical Co., Inc. and used as received. The PPh_3 and $P(OMe)_3$ were obtained from Aldrich Chemical Co. and purified by recrystallization and distillation, respectively. Commercial purity hydrogen, carbon monoxide, and ethylene were obtained from Matheson and used as received. The $[H_4Ru_4(CO)_{12}]$ [14] and $[H_2Ru_4(CO)_{13}]$ [15]

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were prepared according to known literature methods and characterized by standard spectroscopic techniques.

Instrumental

All vapor phase chromatography (vpc) was done with the use of Varian Series 1440 or 2440 gas chromatographs equipped with flame ionization detectors and a Hewlett Packard 3380S integrator. Separation of the olefins and their corresponding alkanes was accomplished on a 30′ X 1/8″ column of 20% propylene carbonate on Chromosorb P at 25 °C. All infrared spectra were recorded in matched pathlength (0.1 mm or 1.0 mm) NaCl solution cells with the use of a Perkin Elmer Model 180 grating infrared spectrometer. All electronic spectra were recorded with the use of a Cary 17. All ^{1}H NMR spectra were recorded with the use of a Varian T-60. A Bausch and Lomb Model SP200 high pressure mercury lamp served as a high intensity broad band light source. The light source for 355 nm (width at half-height is 15 nm) was two 15 W General Electric black light bulbs.

Photocatalyzed Olefin Isomerization Procedure

A toluene or benzene solution consisting of 5×10^{-4} *M* catalyst precursor, the appropriate concentration (0.1 *M*–2.0 *M*) of olefin, and the appropriate concentration of the internal standard, n-hexane, was prepared. Either 1 ml or 3 ml aliquots of this solution and 2 X 7 mm magnetic stir bars were placed into Pyrex test tubes (13 X 100 mm) with constrictions and degassed by five freeze-pump-thaw cycles, sealing hermetically. The samples were stirred and irradiated with the 355 nm light source. Thermal controls (foil wrapped ampules containing the catalysis solutions) were placed side by side with the photolyzed samples during the reaction, and all samples were air-cooled insuring they remained at room temperature. Light intensities incident on the samples were determined by ferrioxalate actinometry [16] and found to be $\sim 1.2 \times 10^{-6}$ ein/min. The solutions were analyzed *via* vpc following the photochemical or thermal reaction.

Photocatalyzed Olefin Hydrogenation Procedure

A benzene solution consisting of 5×10^{-4} *M* $[H_4Ru_4(CO)_{12}]$, the appropriate concentration (0.1 *M*–2.0 *M*) of olefin, and the appropriate concentration of the internal standard, n-hexane, was prepared. Three ml aliquots and 2 X 7 mm magnetic stir bars were placed into demountable Pyrex reaction tubes (12 mm diameter), each equipped with a Teflon valve. The samples were degassed by five freeze-pump-thaw cycles. The reaction tubes were transferred to a gas manifold which was evacuated and backfilled with H_2 five times. Then 10 psig H_2 was introduced to the reaction tube and allowed to saturate the solution. The solution was stirred and irradiated with the appropriate light source. A thermal control was prepared under identical conditions but the reaction tube was wrapped in foil and placed next to the photolyzed sample during irradiation. The samples were analyzed *via* vpc following the photochemical and thermal reactions.

Photolysis of $[H_4Ru_4(CO)_{12}]$

An isooctane solution 5×10^{-4} *M* in $[H_4Ru_4(CO)_{12}]$ was prepared. One ml aliquots of this solution were placed into Pyrex test tubes (13 X 100 mm) with constrictions and degassed by five freeze-pump-thaw cycles, sealing hermetically. The contents of an ampule were placed into a 1.0 mm pathlength NaCl infrared cell in a Vacuum Atmospheres dry box and irradiated with 355 nm light, monitoring the reaction by infrared spectrometry. Photolysis resulted in a slow decomposition of $[H_4Ru_4(CO)_{12}]$ to unidentifiable products, and the appropriate thermal control showed no reaction.

Photolysis of $[H_4Ru_4(CO)_{12}]$ with PPh_3 or $P(OMe)_3$

An isooctane solution 5×10^{-4} *M* in $[H_4Ru_4(CO)_{12}]$ and 0.1 *M* or 0.01 *M* in PPh_3 or $P(OMe)_3$ was prepared. Three ml aliquots of this solution were placed into Pyrex test tubes (13 X 100 mm) with constrictions and degassed by five freeze-pump-thaw cycles, sealing hermetically. The contents of an ampule were placed into a 1.0 mm NaCl infrared solution cell in a Vacuum Atmospheres dry box and irradiated with 355 nm light, monitoring the reaction by infrared spectrometry. Irradiation yields initially $H_4Ru_4(CO)_{11}L$ (L = PPh_3 or $P(OMe)_3$) [8]. The appropriate thermal control showed no reaction. The 366 nm and 436 nm reaction quantum yields were determined by irradiation of the ampules in a merry-go-round equipped [17] with a 450 W or 550 W Hanovia medium pressure mercury lamp filtered with Corning filters 0-52 and 7-37, isolating the 366 nm emission, or Corning filters 3-73 and 5-58, isolating the 436 nm emission. The light intensities ($\sim 10^7$ ein/min) were determined by ferrioxalate actinometry [16].

Photolysis of $[H_4Ru_4(CO)_{12}]$ in the Presence of 1-Pentene

An isooctane solution 5×10^{-4} *M* in $[H_4Ru_4(CO)_{12}]$ and 10^{-1} *M* in 1-pentene was prepared. Three ml aliquots of the solution were placed into Pyrex test tubes (13 X 100 mm) with constrictions and degassed by five freeze-pump-thaw cycles, sealing hermetically. The contents of an ampule were placed into a 1.0 mm NaCl infrared solution cell in a Vacuum Atmospheres dry box. The contents of the infrared cell were irradiated with the 355 nm light source, monitoring the reaction via infrared spectrometry. The ruthenium containing product was [$H_2Ru_4(CO)_{13}$] (ν_{CO} (isooctane) = 2078, 2066, 2054, 2034, 2022, and 2006 cm^{-1}) [18]. The appropriate thermal control showed no reaction.

Photolysis of [$H_4Ru_4(CO)_{12}$] in the Presence of Ethylene

A 150 ml isooctane solution that was ~5 × 10^{-4} *M* in [$H_4Ru_4(CO)_{12}$] was purged for 20 min with ethylene and then maintained the reaction mixture under 2 psig positive pressure of ethylene. The solution was stirred, irradiated with 355 nm light, and monitored *via* infrared spectrometry. [$H_2Ru_4(CO)_{12}$] and product(s) corresponding to infrared bands at 2099, 2072, 2060, 2047, 2038, 2032, 2016, 2009, and 1997 cm^{-1} grew in initially. These bands, possibly attributable to a Ru_4 olefin complex, decreased in intensity with continued irradiation while those of [$H_2Ru_4(CO)_{13}$] increased in intensity.

Reaction of [$H_2Ru_4(CO)_{13}$] with H_2

A 50 ml isooctane solution that was ~10^{-4} *M* in [$H_2Ru_4(CO)_{13}$] was purged with H_2 for 30 min and then maintained under 2 psig positive pressure of H_2. The solution was stirred at 25 °C and monitored with the use of infrared spectrometry. The product was [$H_4Ru_4(CO)_{12}$] (ν_{CO}(isooctane) = 2081, 2067, 2030, 2025, and 2008 cm^{-1}) [14]. Within 9 hours about half the [$H_2Ru_4(CO)_{13}$] had reacted and by 24 hours the reaction was complete. The reaction was accelerated upon near-UV, 355 nm, irradiation.

Reaction of [$H_2Ru_4(CO)_{13}$] with CO

A 50 ml isooctane solution ~10^{-4} *M* in [$H_2Ru_4(CO)_{13}$] was purged with CO for 30 min and then maintained under 2 psig positive pressure of CO. The solution was stirred at 25 °C and monitored with the use of infrared spectrometry. The ν_{CO} bands assignable to [$H_2Ru_4(CO)_{13}$] decreased in intensity and infrared bands grew in at 2061, 2031, and 2011 cm^{-1} (assigned to [$Ru_3(CO)_{12}$] [19] and at 2036 and 2001 cm^{-1} (assigned to [$Ru(CO)_5$]) [20]. After 12 h 85–90% of the [$H_2Ru_4(CO)_{13}$] had reacted and by 24 h the reaction was complete.

Results and Discussion

The new results reported here pertain mainly to the photochemistry of [$H_2Ru_4(CO)_{13}$] and its role in the photocatalysis of alkenes with [$H_4Ru_4(CO)_{12}$]. However, we first outline the results reported previously [8] concerning [$H_4Ru_4(CO)_{12}$]. The [$H_4Ru_4(CO)_{12}$] species consists of a tetrahedral Ru_4 core with twelve terminally bound CO ligands and four hydrides believed to bridge four edges of the tetrahedron [21]. Previous photochemical studies show that tetranuclear metal carbonyl clusters generally undergo quantum inefficient reactions upon photolysis [1–5]. Possible primary chemical results from the photolysis of [$H_4Ru_4(CO)_{12}$] are cleavage of a metal–metal bond giving a tethered diradical like that proposed in the photochemistry of [$Ru_3(CO)_9(PPh_3)_3$] [22] or metal–ligand bond cleavage resulting in loss of H_2 or CO. The yellow-orange $H_4Ru_4(CO)_{12}$ cluster exhibits an intense, near-UV absorption maximum at 362 nm (ϵ = 17,500 M^{-1} cm^{-1}) with a tail into the visible in hydrocarbon solvents. Near-UV irradiation 355 nm, at 25 °C of a deoxygenated isooctane solution that is 5 × 10^{-4} *M* in [$H_4Ru_4(CO)_{12}$] results in slow decomposition of [$H_4Ru_4(CO)_{12}$] to unidentified products. This decomposition becomes markedly slower as a function of time when the sample is sealed, presumably due to a thermal back reaction of the primary photoproduct with the photoejected CO. Irradiation in the presence of 0.1 *M* or 0.01 *M* L (L = PPh_3 or $P(OMe)_3$) in isooctane results in clean infrared spectral changes reflecting the formation of [$H_4Ru_4(CO)_{11}L$] [8]. The infrared bands in the CO stretching region that are associated with the product (L = PPh_3; ν_{CO}(isooctane) = 2094, 2067, 2057, 2027, 2014, and 2008 cm^{-1}) are identical with those previously reported for [$H_4Ru_4(CO)_{11}L$] [23]. Continued near-UV irradiation results in additional infrared spectral changes consistent with the further substitution of the cluster to form [$H_4Ru_4(CO)_{12-n}L_n$] (n = 2, 3, 4), but monosubstituted clusters can be generated essentially quantitatively before multiple substitution products appear [8]. The 366 nm and 436 nm quantum yield for the photosubstitution in eqn. (1) is 5 ± 1 × 10^{-3} for either $P(OMe)_3$ or PPh_3 at a concentration of L = 0.01 *M* or 0.1 *M*. No loss of H_2 occurs upon photolysis, a photoreaction generally observed with mononuclear polyhydride complexes [1, 24]. Presumably the bridging hydride ligands are not sufficiently labilized in the excited state(s) to be reductively eliminated as H_2 upon photoexcitation.

Dinuclear, metal–metal bonded carbonyl complexes generally undergo efficient metal–metal bond cleavage upon optical excitation [25], while trinuclear complexes may undergo efficient metal–metal bond cleavage but low quantum yields result from efficient recoupling of the radical centers [2, 19, 22, 26]. In the tetranuclear complexes where the lowest energy excitations involve transitions between orbitals delocalized over four metal atoms and where each metal atom is directly bonded to three others, it is less likely that complete metal–metal bond cleavage occurs. Here, optical excitation results in net ligand substitution as generally observed for mononuclear metal carbonyls having metal-centered lowest excited states [1a]. The question is whether this net CO substitution reaction occurs via cleavage of the metal–ligand bond or via metal–metal bond cleavage, generating a diradical followed by thermal substitution of PPh_3 for CO at one of the radical centers. We cannot rule out the ligand induced metal–metal bond cleavage pathway, but the disubstituted cluster arises from irradiation of the monosubstituted cluster, whereas substitution of two radical centers would give some of the disubstituted cluster as a primary photoproduct. The fact that *only* $[H_4Ru_4(CO)_{11}L]$ is observed as a primary photoproduct is compelling, but not unequivocal, evidence for photoinduced metal–ligand bond cleavage.

The photosubstitution of $[H_4Ru_4(CO)_{12}]$ is one of the few examples of the functionalization of a large cluster by photochemical means [5–7]. Such chemistry is important in understanding the photocatalytic activity of $[H_4Ru_4(CO)_{12}]$, detailed below. The first step in the thermal catalysis is loss of CO followed by substrate binding [9, 10]. Also, note that CO bonded to transition metal surfaces can be photodissociated and the CO loss is not necessarily only due to heating effects [27]. The clean CO photosubstitution of $[H_4Ru_4(CO)_{12}]$ may serve as a model for photodissociation of non-bridging CO from metal surfaces.

The following summarizes our preliminary findings for photocatalytic isomerization and hydrogenation [8]. Near-UV, 355 nm, irradiation of 5×10^{-4} *M* $[H_4Ru_4(CO)_{12}]$ in the presence of 1-pentene results in catalytic isomerization to *cis* and *trans*-2-pentene and slow, stoichiometric reduction to n-pentane. When the irradiation is carried out under the same conditions but also under 10 psi H_2 the reduction to n-pentane is catalytic. No thermal reaction is observed in the same timescale as the photochemical reaction at 25 °C. The $[H_4Ru_4(CO)_{12}]$ can effect the reduction of other olefins including internal alkenes, alkenes not possessing allylic hydrogens, and alkynes. Either stoichiometric or catalytic photoreduction of 2-pentyne initially yields principally *cis*-2-pentene; 1-pentyne initially yields principally 1-pentene. This indicates that once the conversion to the alkene takes place the product is exchanged for another alkyne molecule at a rate which is faster than the equilibration of the alkene product among its three isomers and faster than the subsequent reduction to the corresponding alkane. Large turnover numbers are found ($>10^3$ for isomerization; $>10^2$ for reduction). By using a higher light intensity turnover rates of >2000/h for isomerization and >60/h for hydrogenation of 2 *M* 1-pentene with 10 psig H_2 at 25 °C are observed.

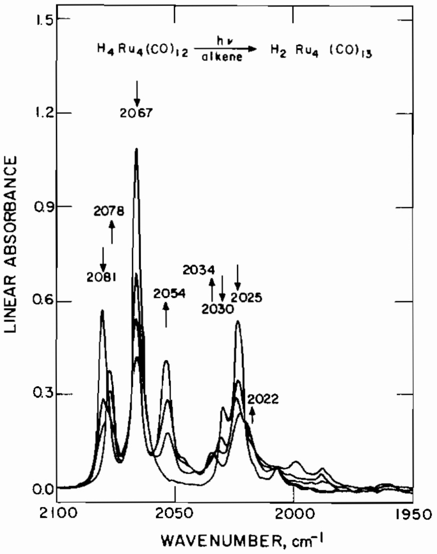

Fig. 1. Infrared spectral changes accompanying near-UV (355 nm) irradiation of $[H_4Ru_4(CO)_{12}]$ ($\sim 5 \times 10^{-4}$ *M*) in the presence of 1-pentene ($\sim 10^{-1}$ *M*) in isooctane at 25 °C. Bands at 2081, 2067, 2030, 2025, and 2008 cm^{-1} are due to $[H_4Ru_4(CO)_{12}]$ and those growing with irradiation at 2078, 2066, 2054, 2034, and 2022 cm^{-1} are due to $[H_2Ru_4(CO)_{13}]$.

Photochemical loss of CO logically leads to catalytically active ruthenium species. At 2 *M* 1-pentene the observed quantum yield for alkene isomerization is ~1.6 whereas photosubstitution by phosphines is occurring with a quantum yield of only 5×10^{-3}, consistent with the generation of a thermally, catalytically active species. The ratio of isomerization to photosubstitution quantum yields indicates that each catalytically active species turns over ~300 times before another photon is needed to reactivate catalysis. At 0.1 *M* 1-pentene the isomerization quantum yield is only 0.3, presumably because the active species may be competitively scavenged by the photoejected CO. Irradiation of $[H_4Ru_4(CO)_{12}]$ in the presence of 1-pentene under 10 psig CO results in *no* isomerization or reduction of 1-pentene. The suppression of catalytic activity by CO is consistent with the belief that photochemical CO loss is the key step in the photoactivation of $[H_4Ru_4(CO)_{12}]$. The mechanism of the alkene reaction is therefore likely to be first photosubstitution to form a labile olefin complex followed by hydride transfer and then reductive elimination to form the reduced olefin. Isomerization of alkenes may occur by a reversible hydride transfer or by a π-allyl-hydride mechanism.

As shown in Fig. 1, the only infrared detectable ruthenium containing product from the irradiation of $[H_4Ru_4(CO)_{12}]$ in the presence of 1-pentene is $[H_2Ru_4(CO)_{13}]$, obtained in up to 67% yield. Product identity was confirmed by comparison with authentic $[H_2Ru_4(CO)_{13}]$ prepared by known literature methods [15]. This result is similar to known thermal reactions of $[H_4Ru_4(CO)_{12}]$ with olefins

TABLE I. Catalytic 1-Pentene Isomerization Using $[H_2Ru_4(CO)_{13}]$ at 25 °C.[a]

Rxn. Time, h	% Reduction[b] to n-pentane	% Isomerization[c] to 2-pentenes	(t/c)[d]
A. Thermal Catalysis			
7	2	7.40	1.92
17.5	<1	10.16	1.75
40	1	16.89	2.24
67	2	28.04	2.38
90.5	<1	46.09	2.47
B. Photoinduced Catalysis			
4	10	13.34	1.48
7	15	16.54	2.12
17.5	28	31.70	2.64
40	48	51.79	2.92

[a] All experiments were carried out in deoxygenated, dry toluene solutions of 5×10^{-4} *M* $[H_2Ru_4(CO)_{13}]$ and 0.1 *M* 1-pentene. [b] Based on the assumption that $[H_2Ru_4(CO)_{13}]$ can transfer one molecule of H_2. [c] % Conversion of 1-pentene to 2-pentenes. [d] (t/c) is the ratio of *trans*- to *cis*-2-pentene isomerization products.

in which $[H_2Ru_4(CO)_{13}]$ is produced in ~10–30% yields as well as various Ru_3 or Ru_4 complexes containing organic ligands [15]. No evidence was observed for the formation of similar Ru complexes bearing organic ligands upon photolysis of $[H_4Ru_4(CO)_{12}]$ in the presence of 1-pentene. Infrared bands possibly attributable to $[H_4Ru_4(CO)_{11}\text{alkene}]$ are observed at short irradiation times, *vide infra*. Recall that $[H_4Ru_4(CO)_{12}]$ does not lead to identifiable products in the absence of olefin or other potential ligands. Thus, the 1-pentene appears to serve as a hydride acceptor, and the resulting $[H_2Ru_4(CO)_{11}]$ fragment scavenges CO yielding $[H_2Ru_4(CO)_{13}]$.

The $[H_2Ru_4(CO)_{13}]$ species is reported to isomerize 1-pentene at 70 °C [28]. We find that it slowly isomerizes 1-pentene even at 25 °C. Near-UV, 355 nm, irradiation accelerates the rate of isomerization of 1-pentene and effects the stoichiometric reduction of 1-pentene to n-pentane. Data are shown in Table I. The $[H_2Ru_4(CO)_{13}]$ complex remains unchanged in the thermal catalytic reaction, but the photoinduced catalysis yields a ruthenium containing product which remains to be identified. An investigation of the reaction chemistry of $[H_2Ru_4(CO)_{13}]$ uncovered reactions (2) and (3). These reactions are accelerated by near-UV, 355 nm, irradiation. The reaction with H_2 has been previously reported but at elevated temperatures [14]. The facile generation of $[H_4Ru_4(CO)_{12}]$ evidences the presence of a labile CO ligand in $[H_2Ru_4(CO)_{13}]$. The reaction chemistry of $[H_2Ru_4(CO)_{13}]$ is more complex than simple CO dissociation, since the reaction with CO fragments the cluster yielding $[Ru(CO)_5]$ and $[Ru_3(CO)_{12}]$, reaction (3). Geoffroy and co-workers [29] have determined that H_2 is produced as well. Geoffroy and co-workers find no thermal reaction of $[H_2Ru_4(CO)_{13}]$ with PPh_3, a surprising result in view of the reactions with H_2, CO, and 1-pentene at 25 °C, but optical excitation yields $[H_2Ru_4(CO)_{13-n}(PPh_3)_n]$ (n = 1, 2). Thus, two different reaction pathways, one involving metal–metal bond cleavage and the other ligand dissociation, have been proposed [5]. Generation of a coordinatively unsaturated species that may bind olefins can occur by either pathway in the thermal and photoinduced catalytic olefin reactions. We are not in a position to support either mechanism since no infrared detectable loss of $[H_2Ru_4(CO)_{13}]$ is evident during the thermal catalysis, and the photoinduced catalysis yields unidentified ruthenium carbonyl-containing products. Although the mechanism of the thermal and photochemical catalytic reactions is unclear and the reaction chemistry is complex, $[H_2Ru_4(CO)_{13}]$ is a reactive cluster capable of catalyzing olefin isomerization thermally and photochemically at 25 °C. The important finding for $[H_2Ru_4(CO)_{13}]$ is that photoexcitation at 25 °C does lead to olefin reduction whereas none is detected thermally. Further, as seen from the data in Table I the initial *trans/cis* ratio of the 2-pentenes formed from 1-pentene is different upon thermal and photoactivation implicating different catalytically active species in the two schemes.

$$[H_2Ru_4(CO)_{13}] \xrightarrow[25\ ^\circ C]{H_2\ (2psig)} [H_4Ru_4(CO)_{12}] \qquad (2)$$

$$H_2Ru_4(CO)_{13}] \xrightarrow[25\ ^\circ C]{Co\ (2psig)} [Ru(CO)_5] + [Ru_3(CO)_{12}] \qquad (3)$$

Characterization and isolation of the presumed $[H_4Ru_4(CO)_{11}(\text{olefin})]$ complex from the photolysis of $[H_4Ru_4(CO)_{12}]$ in the presence of 1-pentene has proven difficult. The irradiation routinely yields a weak infrared band at ~2097 cm^{-1} that may be attributable to the alkene complex, but this species has not been produced in sufficient concentration to allow characterization. Irradiation in the presence of ethylene, that should be more firmly bound, gives infrared spectral changes consistent with the formation of $[H_2Ru_4(CO)_{13}]$, but other infrared bands also grow in at 2099, 2072, 2060, 2047, 2038, 2032, 2016, 2009, and 1997 cm^{-1}. With continued irradiation these bands decrease in intensity and those of $[H_2Ru_4(CO)_{13}]$ increase in intensity. These unassigned infrared bands may be attributable to Ru_4 olefin species, however, the photochemistry is complex and the identity of the species has not been determined. Contrasting our results on $[H_4Ru_4-$

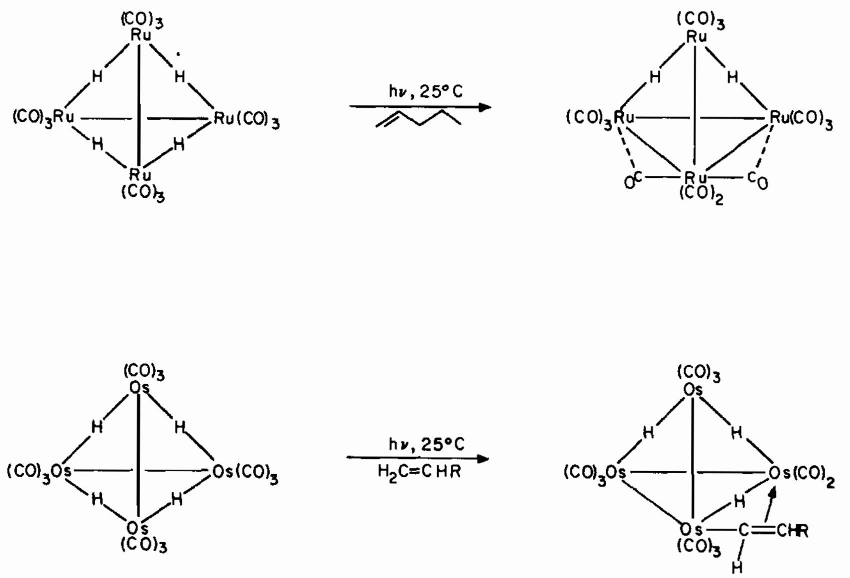

Fig. 2. Principal metal-containing products formed upon photolysis of $[H_4M_4(CO)_{12}]$ (M = Ru, Os) in the presence of olefins.

$(CO)_{12}]$, Lewis, Johnson, and co-workers [6] report that irradiation of $[H_4Os_4(CO)_{12}]$ in the presence of $RCH{=}CH_2$ yields $[H_3Os_4(CO)_{11}(HC_2HR)]$, as shown in Fig. 2. Presumably this forms via initial photoinduced loss of CO, however, the loss of two H atoms also occurs and it has not been established as to whether they form H_2 or reduced olefin. It would appear that if a similar species is produced from $[H_4Ru_4(CO)_{12}]$ and 1-pentene, it is far more labile than the osmium analogue since the main product observed, $[H_2Ru_4(CO)_{13}]$, contains no hydrocarbon ligands.

Although the details of the light-induced chemistry remain to be elucidated, catalytic chemistry of olefins can be induced at lower temperatures than needed thermally using $[H_4Ru_4(CO)_{12}]$. In fact, the photochemical reaction of $[H_4Ru_4(CO)_{12}]$ with 1-pentene produces $[H_2Ru_4(CO)_{13}]$ which catalyzes olefin isomerization in the dark at 25 °C. Previous studies show that $[H_4Ru_4(CO)_{12}]$ and its substituted derivatives are thermal catalysts for alkene isomerization and hydrogenation, but the temperatures used are at least in the 70–80 °C range [9, 10], no thermal chemistry occurs on the same time scale as the photoreactions at 25 °C. The initial *trans*- to *cis*-2-pentene ratio from 1-pentene produced photocatalytically is near that found thermally [9c], and the principal formation of 1-pentene from 1-pentyne and *cis*-2-pentene from 2-pentyne at low extent conversions parallels findings from the thermal catalysis [10b,c]. Added CO suppresses both the thermal and photochemical olefin reactions [9c, d, 10d]. It appears that the same catalyst is involved thermally and photochemically, thus photoinduced ejection of CO from $[H_4Ru_4(CO)_{12}]$ is contributory to achieving the catalytically active species, as proposed in the thermal chemistry [9, 10]. The data do not constitute unequivocal proof that the Ru_4 core remains intact during the catalytic reaction, since undetectable amounts of very active mononuclear catalysts may be present. However, photosubstitution of CO does take the system a step closer to the catalyst at lower temperatures than ordinarily needed. Further, for both $[H_4Ru_4(CO)_{12}]$ and $[H_2Ru_4(CO)_{13}]$ reduction of olefins can be effected photochemically at 25 °C whereas thermal activation does not yield reduction.

To conclude, we regard the photocatalysis to be represented by the processes illustrated in Fig. 3. Beginning with $[H_4Ru_4(CO)_{12}]$ it is possible to extrude CO thermally (above 25 °C) or photochemically to enter cycles for alkene isomerization or reduction. We believe that the thermal catalysis and photocatalysis for alkene isomerization is the same at this stage. Further, formation of alkane must be slow compared to the isomerization because quantum yields for the photocatalyzed isomerization can exceed unity whereas alkane formation quantum yields are well below unity. When alkane is formed, however, a new catalytic cycle for alkene reactions may be entered that can be entered independently from the thermal activation or photoactivation of $[H_2Ru_4(CO)_{13}]$. In the first cycle for isomerization, the similarity in initial *trans*/*cis* 2-pentene ratios in the thermal catalysis and photocatalysis suggests common catalysts in the two systems. However, irradiation of $[H_2Ru_4(CO)_{13}]$ does not give the same initial product ratio as does thermal activation, despite the

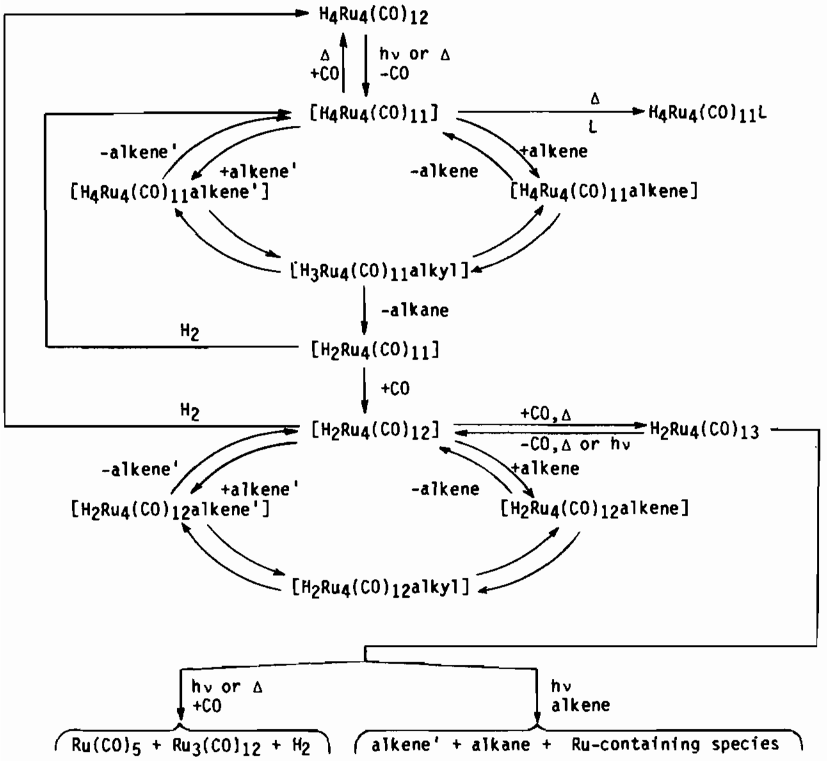

Fig. 3. Representation of possible mechanisms for alkene isomerization, alkene ←→ alkene', and alkene reduction to form alkane. A similar set of mechanisms could be written for the isomerization employing π-allyl hydride intermediates instead of the alkyl. The alkyl intermediates, however, would best account for the formation of alkane.

knowledge [5] that CO loss is a key photoreaction of $[H_2Ru_4(CO)_{13}]$ which would be a logical first step in thermal catalysis with $[H_2Ru_4(CO)_{13}]$. The differing initial product ratio and the formation of alkane only under illumination demands yet a third cycle entered by irradiation of $[H_2Ru_4(CO)_{13}]$ yielding reduction of alkene and isomerization of the starting alkene. In principle, the role of light in $[H_2Ru_4(CO)_{13}]$ could be transform one of the intermediates in the catalytic cycle. This seems unlikely in view of the fact that $[H_2Ru_4(CO)_{13}]$ is the only detected light absorbing species in the system. In view of the fact that reaction of $[H_2Ru_4(CO)_{13}]$ with CO, eqn. (3), is accelerated by light, it is not illogical to conclude that irradiation of $[H_2Ru_4(CO)_{13}]$ in the presence of a CO-like ligand such as alkene will lead to mononuclear, catalytically active species. Future studies will include irradiation at low temperature to attempt to spectroscopically identify photogenerated intermediates implicated by our findings to date.

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