

## PHOTOGENERATION OF REACTIVE ORGANOMETALLIC SPECIES

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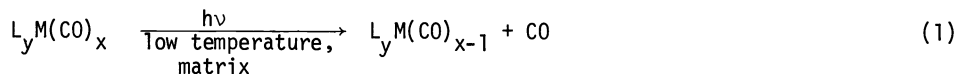
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**Abstract** - Dissociative loss of CO or H<sub>2</sub> or homolysis of metal-metal bonds can be the result of photoexcitation of organometallic molecules at low temperature. The resulting coordinatively unsaturated species are generally quite reactive. Recent studies of the chemistry resulting from photoexcitation of several organometallic systems at <25°C are summarized. Study of alkyl complexes such as ( $\eta^5$ -C<sub>5</sub>R'<sub>5</sub>)M(CO)<sub>3</sub>R and ( $\eta^5$ -C<sub>5</sub>R'<sub>5</sub>)M'(CO)<sub>2</sub>R (R' = H, CH<sub>3</sub>; M = Mo, W; M' = Fe, Ru; R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>,  $\eta$ -C<sub>5</sub>H<sub>11</sub>) shows that efficient dissociative loss of CO occurs as the only primary chemical result from photoexcitation. For the complexes having  $\beta$ -H's the 16-valence-electron species rapidly undergo  $\beta$ -H transfer to give an 18-valence-electron hydride. For the Mo and W species the spectroscopic observation of the 16-valence-electron species at low temperature is possible and conversion to the hydride can be monitored. Fe(CO)<sub>5</sub> and Fe<sub>3</sub>(CO)<sub>12</sub> are shown to yield extraordinarily active catalysts for alkene isomerization and hydrosilation, and low temperature irradiation yields infrared detectable intermediates believed to be important in the catalytic cycle. Study of R<sub>3</sub>SiCo(CO)<sub>4</sub> and related species, including  $(\text{S})-\text{O}-\text{SiCo}(\text{CO})_4$  ( $\text{S} \equiv \text{SiO}_2, \text{Al}_2\text{O}_3$ ), shows loss of CO to dominate the chemical decay paths following photoexcitation. Irradiation of the silyl-Co(CO)<sub>4</sub> yields catalytically active species for alkene hydrosilation having a turnover rate approaching that for thermal catalysis by Co<sub>2</sub>(CO)<sub>8</sub>. Photoexcitation of the hydrides H<sub>4</sub>M(DPPE)<sub>2</sub> (M = Mo, W; DPPE = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>), H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub>, H<sub>2</sub>Ru<sub>4</sub>(CO)<sub>13</sub>, H<sub>2</sub>Os<sub>3</sub>(CO)<sub>10</sub>, and H<sub>2</sub>Os<sub>3</sub>(CO)<sub>10</sub>(PPh<sub>3</sub>) accelerates the rate of reduction reactions, presumably via the generation of coordinatively unsaturated hydride intermediates.

## INTRODUCTION

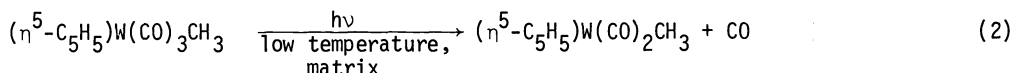
Photoexcited transition metal organometallic complexes often undergo dissociative type reactions leading to the production of reactive, coordinatively unsaturated intermediates (Ref. 1). In some cases the reaction that occurs from the thermally equilibrated excited state has a very low thermal barrier that allows observation of relatively efficient chemistry at low temperatures. The ability to prepare high concentrations of coordinatively unsaturated species at low temperature can be exploited to spectroscopically characterize species that could not be investigated by other means. The key is that with photoexcitation intermediates can sometimes be synthesized at sufficiently low temperatures that the subsequent thermal reactions are slow enough to allow studies of structure and reaction chemistry. Thermal generation of the same intermediate may be possible, but in many cases the temperatures and conditions required do not lead to even spectroscopically detectable concentrations.

Some of the best examples of the use of photochemistry to prepare reactive, coordinatively unsaturated complexes for structural characterization concern metal carbonyls that undergo dissociative loss of CO at low temperature in rigid matrices, eq. (1), (Ref. 2). A number



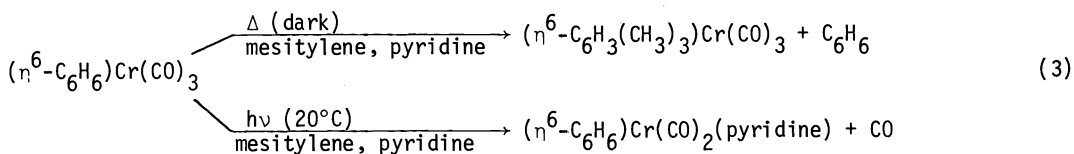
of photogenerated, coordinatively unsaturated species have now been characterized by various spectroscopies including infrared, Raman, and uv-vis absorption. While it is true that certain binary carbonyl systems can be prepared by metal atom/CO co-condensation, (Ref. 3 & 4) the rational synthesis of complexes containing both CO and other ligands by metal atom/CO/L co-condensation leads, at best, to mixtures, and in some cases it does not

appear that any synthesis other than photochemical is possible. For example, the photochemical generation of the product from the low temperature irradiation of  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{CH}_3$ , eq. (2) (Ref. 5), would seem to represent the only clean preparation of



the 16-valence-electron complex.

Coordinatively unsaturated organometallic species are important in stoichiometric and catalytic syntheses. The use of light to generate the key intermediates at low temperature can provide mechanistic insight into such synthetic procedures, since the intermediates can be structurally characterized. Further, the photochemical procedure may have practical advantages stemming from the ability to do the reaction at low temperature and from the fact that reaction begins from an excited electronic state, not the ground electronic state as in thermal reactions. The low temperature advantage is that thermally unstable products can be prepared and isolated, and in catalysis thermally unstable substrates could be used. Also, in catalysis the use of light to enter a catalytic cycle may change the rate limiting step from catalyst generation to a step that is closer to product formation. The advantage in reactions that begin from an excited electronic state is that processes can be observed that have no importance from the thermal activation of the ground electronic state. A simple illustration is the thermal chemistry vs. photochemistry of  $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$  in the presence of mesitylene and pyridine, eq. (3) (Ref. 1). The fundamental basis for such large



differences in the course of reaction from different electronic states is that the different electronic structures have associated unique physical, structural, and chemical properties that lead to substantial differences in reactivity patterns. A final advantage in photoactivation vs. thermal activation is the on-off control that is possible with photoactivation. Perhaps the best illustration is the use of photoinitiated polymerization reactions in the fabrication of microstructures in the electronics industry.

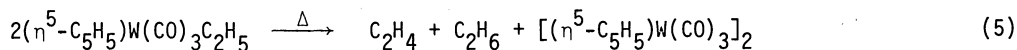
In this article we wish to summarize some of our results concerning the photogeneration of reactive organometallic species of importance in stoichiometric and catalytic syntheses. The results from the study of four systems will be summarized: (1)  $\beta$ -H transfer induced by irradiation of thermally inert, 18-valence-electron alkyl complexes where the role of light is to generate a 16-valence-electron alkyl by ligand dissociation; (2) photocatalysis of alkene isomerization and hydrosilylation by photoactivation of  $\text{Fe}(\text{CO})_5$  and  $\text{Fe}_3(\text{CO})_{12}$ ; (3) photochemistry and photocatalysis involving  $\text{R}_3\text{SiCo}(\text{CO})_4$  and related species; and (4) photoactivation of reduction processes by mononuclear and polynuclear polyhydride complexes. In every case irradiation promotes reaction at  $\leq 25^\circ\text{C}$  where thermal activation alone leads to little or no reaction. Primary photoprocesses involve dissociative loss of CO or  $\text{H}_2$  or cleavage of metal-metal bonds to yield the reactive coordinatively unsaturated species.

#### STUDY OF $\beta$ -HYDROGEN TRANSFER

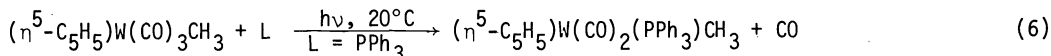
The catalytic reactions of many organic substrates involves the intermediacy of species having  $\beta$  C-H bonds. The  $\beta$ -H transfer process, illustrated by eq. (4) for the ethyl/ethylene



hydride system, has possible importance in many situations. Generally, it is believed that the  $\text{M-alkyl} \rightarrow \text{M(H)(alkene)}$  process requires an open coordination site on the metal. Hence, 18-valence-electron M-alkyl complexes can be inert with respect to  $\beta$ -H transfer chemistry if the ligands in the coordination sphere are inert with respect to dissociation from the metal. For example, species such as  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2\text{C}_2\text{H}_5$  are thermally inert at low temperatures, but elevated temperatures yield the formation of products according to eq. (5).



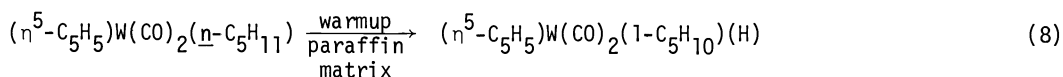
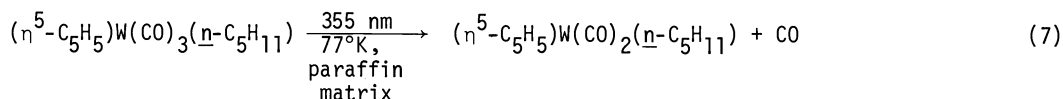
Inasmuch as photosubstitution of  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{CH}_3$  occurs at low temperature, eq. (6), (Ref. 6)



we felt that the dissociative loss of CO from the alkyl could be effected by photo-excitation at low temperature. Such should allow the study of the 16-valence-electron alkyl species  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2\text{R}$  ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ , etc.) at sufficiently low temperatures that intermediate(s) in the thermal chemistry represented by eq. (5) could be characterized. Presumably, the rate limiting step in the thermal chemistry is CO loss to give a 16-valence-electron species that then rapidly undergoes  $\beta\text{-H}$  transfer to give an intermediate alkene-hydride. At the temperatures required to extrude the CO the alkene-hydride is decomposed to form the observed products. The ability to photochemically extrude CO at low temperature can thus change the rate limiting step, possibly allowing the study of steps that would be "fast" under ordinary thermal activation conditions.

Alkyl complexes of Mo and W:  $(\eta^5\text{-C}_5\text{R}'_5)\text{M}(\text{CO})_3\text{R}$

A preliminary report on the low temperature photochemistry of  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3(\underline{n}\text{-C}_5\text{H}_{11})$  has appeared (Ref. 5), and the sequence represented by eq. (7) and (8) can be monitored by



infrared spectroscopy. Initially, the alkene-hydride is found in quantitative yield upon  $355 \text{ nm} \pm 15 \text{ nm}$  irradiation in alkane solution at  $20^\circ\text{C}$ , but at very low temperatures the 16-valence-electron alkyl precursor is the only detectable photoproduct. The photo-generated 16-valence-electron species  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2\text{R}$  ( $\text{R} = \text{CH}_3, \underline{n}\text{-C}_5\text{H}_{11}$ ), eq. (2) and (7), have nearly the same infrared absorption spectra in the CO stretching region in a low temperature paraffin matrix,  $\sim 1950$  and  $1865 \text{ cm}^{-1}$  in a 1:1 absorbance ratio, but the reactions for  $\text{R} = \text{CH}_3$  and  $\underline{n}\text{-C}_5\text{H}_{11}$  are very different. For  $\text{R} = \text{CH}_3$  the only detectable reaction upon warm-up is back reaction with CO to regenerate the 18-valence-electron starting material. For  $\text{R} = \underline{n}\text{-C}_5\text{H}_{11}$  the 16-valence-electron species yields the formation of the alkene-hydride upon warm-up, in addition to some regeneration of the starting material. Thus, the low temperature photochemistry of  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3(\underline{n}\text{-C}_5\text{H}_{11})$  yields two observable species that would not be observable in the thermolysis.

Warm-up of  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2\text{R}$  ( $\text{R} = \text{CH}_3, \underline{n}\text{-C}_5\text{H}_{11}$ ) in frozen alkane solutions containing  $\text{PPh}_3$  yields the formation of  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{PPh}_3)\text{R}$  ( $\nu_{\text{CO}} \approx 1935, 1860 \text{ cm}^{-1}$ ) consistent with the conclusion that the species associated with the  $\sim 1950, \sim 1865 \text{ cm}^{-1}$  absorptions is due to the 16-valence-electron species. Irradiation (355 nm) of  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{R}$  at  $20^\circ\text{C}$  in alkane solution containing  $\text{PPh}_3$  yields the same  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{PPh}_3)\text{R}$  species, though for  $\text{R} = \underline{n}\text{-C}_5\text{H}_{11}$  high concentrations of  $\text{PPh}_3$  are needed to compete with the  $\beta\text{-H}$  transfer to yield the alkene-hydride. The primary photoreaction of  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{R}$  is principally dissociative loss of CO, as previously concluded, but when  $\text{R} = \underline{n}\text{-C}_5\text{H}_{11}$  the  $\beta\text{-H}$  transfer can yield ultimate loss of the W-C sigma bond.

The photochemistry of the  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{R}$  species has been extended to the  $\text{R} = \text{C}_2\text{H}_5$  species and to Mo and  $(\eta^5\text{-C}_5(\text{CH}_3)_5)$  analogues (Ref. 7). The systems that have been investigated so far are summarized in Table 1. The quantum efficiency for CO loss in each case is in the

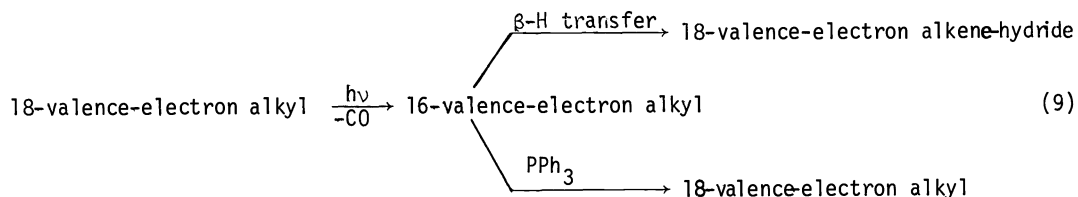
TABLE 1. Mo and W complexes investigated with respect to  $\beta$ -hydrogen transfer induced by photoexcitation,  $(\eta^5\text{-C}_5\text{R}'_5)\text{M}(\text{CO})_3\text{R}$  (Ref. 7).<sup>a</sup>

M	R'	R	Comments
W	H	$\underline{n}\text{-C}_5\text{H}_{11}$	355 nm irradiation yields <u>trans</u> - $(\eta^5\text{-C}_5\text{R}'_5)\text{-W}(\text{CO})_2(\text{alkene})(\text{H})$ with $\phi \approx 0.5$ at $25^\circ\text{C}$ . At
W	H	$\text{C}_2\text{H}_5$	$77^\circ\text{K}$ , primary photoproduct is $(\eta^5\text{-C}_5\text{R}'_5)\text{-W}(\text{CO})_2\text{R}$ .
Mo	H	$\underline{n}\text{-C}_5\text{H}_{11}$	355 nm irradiation yields $(\eta^5\text{-C}_5\text{R}'_5)\text{Mo}(\text{CO})_3\text{H}$ with $\phi \approx 0.5$ at $25^\circ\text{C}$ . At low temperature the primary photoproduct is $(\eta^5\text{-C}_5\text{R}'_5)\text{Mo}(\text{CO})_2\text{R}$ and warm-up yields <u>trans</u> - $(\eta^5\text{-C}_5\text{R}'_5)\text{Mo}(\text{CO})_2(\text{alkene})(\text{H})$ .
Mo	H	$\text{C}_2\text{H}_5$	
Mo	H	$\text{CH}_3$	355 nm yields photosubstitution with $\phi \approx$
W	H	$\text{CH}_3$	$0.5$ at $25^\circ\text{C}$ to form $(\eta^5\text{-C}_5\text{R}'_5)\text{M}(\text{CO})_2(\text{PPh}_3)\text{R}$ .

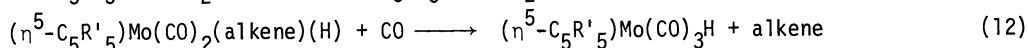
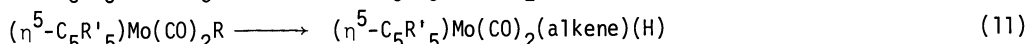
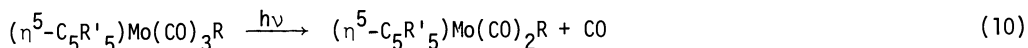
At low temperature primary photoproduct is  
 $(\eta^5\text{-C}_5\text{R}'_5)\text{M}(\text{CO})_2\text{R}$ .

<sup>a</sup>All reactions were carried out in deoxygenated alkane solution using  
 $355 \pm 15$  nm excitation.

vicinity of 0.5 at 25°C. For each system where R has  $\beta$ -H's we observe products from the  $\beta$ -H transfer reaction of the 16-valence-electron primary photoproduct from loss of CO, eq. (9). The formation of hydride products can be completely suppressed by the presence of a



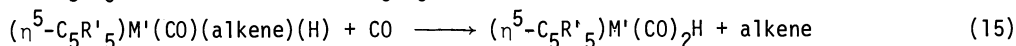
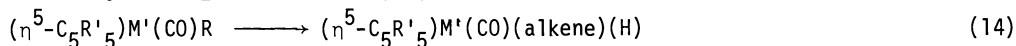
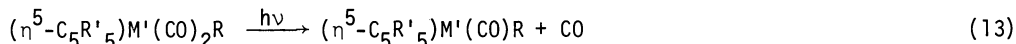
sufficient concentration of PPh<sub>3</sub>. For the Mo complexes the alkene-hydride is only detectable at low temperature. The Mo-containing product at 20°C in alkane solvent is  $(\eta^5\text{-C}_5\text{R}'_5)\text{Mo}(\text{CO})_3\text{H}$  formed via the sequence, eq. (10)-(12).



Interestingly, the infrared and <sup>13</sup>C nmr spectra of  $(\eta^5\text{-C}_5\text{R}'_5)\text{M}(\text{CO})_2(\text{alkene})(\text{H})$  are consistent with species being the trans isomer. Study of the rate of the  $\beta$ -H transfer reaction of the 16-valence-electron species as a function of temperature gives an activation energy in the vicinity of 40 kJ/mole. The activation energy for cis-trans isomerization in such complexes is ~40 kJ/mole (Ref. 8). Thus, the activation energy and the fact that the observed alkene-hydride complexes are trans isomers suggests that the  $\beta$ -H transfer first gives a cis-alkene-hydride that can then isomerize to give the trans isomer. The formation of the cis alkene-hydride may therefore be very fast and reversible, with cis + trans isomerization of the complex representing the rate determining step in observing the trans- $(\eta^5\text{-C}_5\text{R}'_5)\text{M}(\text{CO})_2(\text{alkene})(\text{H})$  species. Whatever the detailed mechanism, the formation of the alkene-hydride can be detected at fairly low temperatures; reaction half-times from the 16-valence-electron species can be as short as several minutes at ~150 K.

#### Alkyl complexes of Fe and Ru: $(\eta^5\text{-C}_5\text{R}'_5)\text{M}'(\text{CO})_2\text{R}$

Complexes of the formula  $(\eta^5\text{-C}_5\text{R}'_5)\text{M}'(\text{CO})_2\text{R}$  (M' = Fe, Ru; R' = H, CH<sub>3</sub>; R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, n-C<sub>5</sub>H<sub>11</sub>) have also been subjected to irradiation (Ref. 9). In this set of complexes the possible alkene-hydride product from the R = C<sub>2</sub>H<sub>5</sub> and n-C<sub>5</sub>H<sub>11</sub> species must be cis. However, like the Mo species above, the alkene complexes are labile and alkene-hydride complexes are not observed as photoproducts at 25°C (Ref. 9, 10). Rather, the R = C<sub>2</sub>H<sub>5</sub> and n-C<sub>5</sub>H<sub>11</sub> species give the  $(\eta^5\text{-C}_5\text{R}'_5)\text{M}'(\text{CO})_2\text{H}$  complexes as the observed photoproduct, presumably via the sequence eq. (13)-(15) (Ref. 9). Support for the primary photoprocess represented by



eq. (13) comes from the substitution quantum yield data given in Table 2 for

TABLE 2. Quantum efficiency for photosubstitution of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_3$  to form  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{L})\text{CH}_3$ .<sup>a</sup>

L, M	$\phi \pm 5\%$
PPh <sub>3</sub> , $5.2 \times 10^{-3}$	0.71
PPh <sub>3</sub> , $4.9 \times 10^{-2}$	0.68
P(0- <u>o</u> -tolyl) <sub>3</sub> , $4.7 \times 10^{-3}$	0.72
P(0- <u>o</u> -tolyl) <sub>3</sub> , $5.1 \times 10^{-2}$	0.71
<sup>13</sup> CO, $\sim 5 \times 10^{-3}$	0.69

<sup>a</sup>All reactions carried out in deoxygenated alkane solution at 25° using

366 nm excitation (Ref. 9).

$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_3$ . The  $\sim 0.70$  quantum yield for substitution is independent of the entering group or its concentration. Even  $^{13}\text{CO}$  as an entering group is as good as the P-donor entering groups. The data tend to rule out "ring slippage",  $\eta^5 \rightarrow \eta^3\text{-C}_5\text{H}_5$ , as the pathway for photosubstitution. In fact, the  $^{13}\text{CO}$  quantum yield rules out the ring slippage unless it can be argued that the CO's in a species such as  $(\eta^3\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(^{13}\text{CO})\text{CH}_3$  are not equilibrated to give statistical loss of labelled and unlabelled CO when the  $\eta^3\text{-C}_5\text{H}_5$  relaxes back to  $\eta^5\text{-C}_5\text{H}_5$ .

Curiously, and unfortunately, the presumed 16-valence-electron intermediate  $(\eta^5\text{-C}_5\text{R}'_5)\text{M}'(\text{CO})\text{R}$  has not been observed upon irradiation of the parent dicarbonyl in low temperature matrices. However, the startling result is that  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{C}_2\text{H}_5$  does give  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{H}$  in inert matrices at temperatures as low as 10 K (Ref. 11). We have shown that the 77 K reaction is essentially completely suppressed by using a 1-pentene matrix which rules out the possibility that the elimination of the metal hydride is a unimolecular, single-step result of excited state decay. At 77 K in inert matrices the photogenerated intermediate leading to  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{H}$  from irradiation of the  $\text{-C}_2\text{H}_5$  species reacts completely in a half-time of less than 60 s. This shows that there is a low activation energy for both the  $\beta\text{-H}$  transfer and loss of alkene from the presumed alkene intermediate. Irradiation at low temperatures and in rigid media does not reveal any intermediates in the formation of the metal hydride, but it is attractive to conclude that a 16-valence-electron  $(\eta^5\text{-C}_5\text{R}'_5)\text{M}'(\text{CO})\text{R}$  intermediate is involved, since the evidence from the quantum yield data provide convincing evidence for the primary generation of such species in solutions at 25°C. Whatever the intermediate at low temperature, it is extraordinarily reactive.

Evidence for very labile alkene complexes of the  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{alkene})\text{R}$  type comes from irradiation of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_3$  in low temperature isooctane solution containing 1 M 1-pentene, (Ref. 9). At  $-90^\circ\text{C}$   $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{alkene})\text{CH}_3$  is detectable by infrared spectroscopy,  $\sim 1957\text{ cm}^{-1}$ , but upon warming to  $-20^\circ\text{C}$ , the  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_3$  is completely regenerated by reaction with the CO released in the primary photoreaction. Addition of  $\text{PPh}_3$  to solutions containing  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{alkene})\text{CH}_3$  rapidly gives  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{CH}_3$ . The point is that the  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{alkene})\text{R}$  is very labile and the system seems to voraciously seek even small concentrations of CO. These facts are consistent with  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{alkene})\text{H}$  as an intermediate in the conversion of the  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{R}$  to  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{H}$ . However, there is still no direct spectroscopic evidence for the alkene-hydride, and it is remarkable just how reactive the presumed intermediate actually is.

Consistent with the mechanistic proposal represented by eqs. (13)–(15), the irradiation of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{C}_2\text{H}_5$  in the presence of  $\text{PPh}_3$  yields both  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{C}_2\text{H}_5$  and  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{H}$ , in addition to  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{H}$ . The amount of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{C}_2\text{H}_5$  relative to the total of all hydride products formed depends on the concentration of  $\text{PPh}_3$ , Table 3, in a manner that is consistent with the sort of

TABLE 3.  $\text{PPh}_3$  concentration dependence on photochemical formation of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{C}_2\text{H}_5$  vs.  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{L})\text{H}$  from  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{C}_2\text{H}_5$  (Ref. 9).

[ $\text{PPh}_3$ ], M	Photoproducts <sup>a</sup>	
	% Substitution <sup>b</sup>	% Hydrides <sup>c</sup>
0	0	100
0.002	3.8	96.2
0.012	14.5	85.5
0.020	24.8	75.2
0.029	29.6	70.4
0.035	30.6	69.4
0.055	40.1	59.9

<sup>a</sup>Irradiation (355 nm at 25°C) of 0.01 M  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{C}_2\text{H}_5$  in deoxygenated isooctane containing variable amounts of  $\text{PPh}_3$ .

<sup>b</sup>%  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{C}_2\text{H}_5$ .

<sup>c</sup>%  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{H} + (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{H}$ .

competition suggested by eq. (9) where the 16-valence-electron primary photoproduct is either scavenged by the  $\text{PPh}_3$  or undergoes the unimolecular  $\beta\text{-H}$  transfer. With the knowledge that entering groups such as  $\text{PPh}_3$  can scavenge 16-valence-electron species with bimolecular rate constants in the vicinity of  $\sim 10^6\text{ M}^{-1}\text{s}^{-1}$  or greater (Ref. 12 & 13), we conclude that the unimolecular rate of  $\beta\text{-H}$  transfer could be greater than  $10^6\text{ s}^{-1}$  at 25°C. Flash photolysis studies are now in progress to measure this rate directly. The 16-valence-electron

$(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{R}$  ( $\text{M} = \text{Mo}, \text{W}$ ) species (Ref. 5 & 7) and other coordinatively unsaturated species (Ref. 2) are highly colored. Thus, it is reasonable that  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{R}$  would also be highly colored and kinetic flash experiments should be possible to measure the  $\beta\text{-H}$  transfer rates. Time-resolved Raman spectroscopy (Ref. 14) should also be applicable to these systems to gain molecular structural information for the intermediate(s).

#### Olefin isomerization and $\beta\text{-H}$ transfer

The photochemical studies of alkyl complexes clearly show that inert 18-valence-electron species can yield very reactive 16-valence-electron alkyl complexes. In some cases, both the 16-valence-electron alkyl and the 18-valence-electron alkene-hydride species from  $\beta\text{-H}$  transfer can be spectroscopically characterized. Aside from providing firm support for the mechanism of  $\beta\text{-H}$  transfer, the studies can provide direct insight into one of the mechanisms for alkene isomerization. For the  $n\text{-C}_5\text{H}_{11}$  complexes studied thus far we find that irradiation at  $25^\circ\text{C}$  ultimately yields  $n\text{-C}_5\text{H}_{12}$  and a mixture of the linear pentenes (Ref. 5,7, & 9). The production of a mixture of alkenes can occur via a reversible  $\beta\text{-H}$  transfer process. Previous work on the thermal isomerization of species such as  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(2\text{-C}_4\text{H}_9)$  to  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(n\text{-C}_4\text{H}_9)$  (Ref. 15) has been proposed to occur via dissociative loss of  $\text{PPh}_3$  as the rate limiting step followed by fast, reversible  $\beta\text{-H}$  transfer. The data showed that the terminal bonded alkyl is preferred (Ref. 15). Irradiation of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{C}_2\text{H}_5$  in the presence of 1-pentene does lead to some catalytic isomerization, but the extent conversion and the initial rate is low. The low extent conversion is likely due to the fact that the active hydride species eventually reduces alkene to alkane and yields  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  which does not catalyze 1-pentene isomerization thermally or photochemically at  $25^\circ\text{C}$  (Ref. 16). The low initial rate could be due to the low frequency for formation of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(2\text{-C}_5\text{H}_{11})$  from  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(1\text{-C}_5\text{H}_{10})(\text{H})$ . These studies are still in progress.

The Mo and W complexes could also yield alkene isomerization. The W-alkene-hydride complexes are too inert to give significant rates at  $25^\circ\text{C}$  but the Mo species are sufficiently labile so that isomerization could be effected. Again, however, net reduction of alkene to alkane with formation of inactive dinuclear complexes will ultimately lead to loss of catalytic activity.

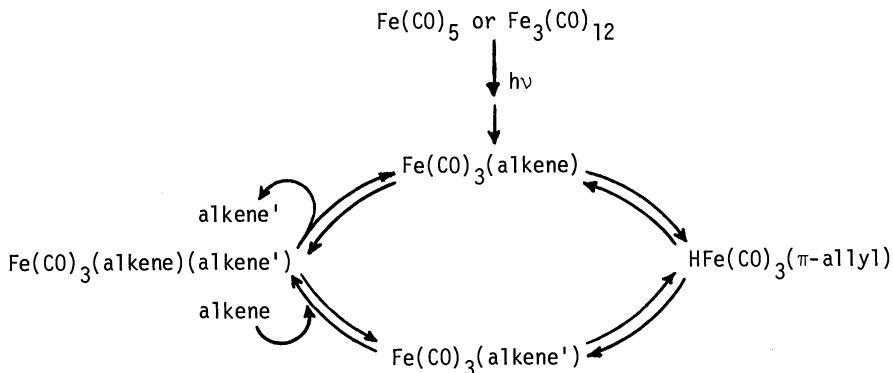
#### LASER LIGHT ACTIVATION OF IRON CARBONYL CATALYSTS

Light-induced loss of CO from  $\text{Fe}(\text{CO})_5$ , eq. (16), is one of the oldest known photoreactions of



transition metal organometallics (Ref. 17). This process is undoubtedly the first step in the photochemical formation of a very active catalyst for the isomerization, hydrogenation, and hydrosilation of alkenes (Ref. 18). Activation of  $\text{Fe}(\text{CO})_5$  requires near-ultraviolet light, since the  $\text{Fe}(\text{CO})_5$  does not absorb strongly in the visible. However, it appears that visible light irradiation of  $\text{Fe}_3(\text{CO})_{12}$ , which does absorb strongly throughout most of the visible, yields the same active catalyst as ultraviolet excitation of  $\text{Fe}(\text{CO})_5$  (Ref. 19). While we are also currently pursuing the nature of the various intermediates using low temperature techniques, we have recently characterized the catalytic activity of  $\text{Fe}(\text{CO})_5$  and  $\text{Fe}_3(\text{CO})_{12}$  when subjected to very intense irradiation from a visible or ultraviolet laser (Ref. 20). The basic issue addressed in this study is whether the excitation rate of the catalyst precursor can ever be so large that the rate of isomerization actually becomes rate limiting.

The isomerization of alkenes, for example, is believed to occur via a  $\pi$ -allyl-hydride intermediate generated by the sequence indicated in Scheme I. Since the  $\text{Fe}(\text{CO})_4(\text{alkene})$  is



**Scheme I.** Catalytic cycle for alkene isomerization. Alkene and alkene' represent isomers.

not significantly thermally active as an isomerization catalyst and it is the dominant species in alkene solutions of  $\text{Fe}(\text{CO})_5$  or  $\text{Fe}_3(\text{CO})_{12}$  under illumination, it is possible that the rate of loss of CO from this species limits the rate of product formation. Excitation rate can thus be limiting product formation rate even when the quantum yield for product formation significantly exceeds unity. That is, once  $\text{Fe}(\text{CO})_3$ alkene is photogenerated many molecules of alkene can be isomerized before inert  $\text{Fe}(\text{CO})_4$ alkene forms, but more isomerized alkene can be formed per unit time if the steady state concentration of  $\text{Fe}(\text{CO})_3$ alkene can be increased by an increased excitation rate. At some high light intensity it should be impossible to raise the steady-state concentration to a higher value. When this is the case, the true turnover rate of the photoactivated catalyst can be equated to the rate of product formation divided by the  $\text{Fe}(\text{CO})_3$ alkene concentration.

Table 4 summarizes some data for  $\text{Fe}(\text{CO})_5$  and  $\text{Fe}_3(\text{CO})_{12}$  photocatalyzed alkene isomerization

TABLE 4.  $\text{Fe}(\text{CO})_5$  and  $\text{Fe}_3(\text{CO})_{12}$  photocatalyzed isomerization of 1-pentene.<sup>a</sup>

Catalyst Precursor, $\underline{M}$	Irrdn Source, (time, s)	% Conv. to 2-pentenes	$\phi^b$	Turnover Rate, <sup>c</sup> $\text{min}^{-1}$
$\text{Fe}(\text{CO})_5$ , $8 \times 10^{-3}$	2.5W-333,351,364 nm			
	(5)	27	68	3700
	(10)	35	44	2400
$\text{Fe}_3(\text{CO})_{12}$ , $5 \times 10^{-3}$	1.3W-514.5 nm			
	(10)	7	11	700
	(30)	24	13	900

<sup>a</sup>Ar ion laser excitation at indicated wavelength and power. Starting substrate is neat 1-pentene, 9.14  $\underline{M}$  (Ref. 20).

<sup>b</sup>Observed quantum yield for 1-pentene consumption.

<sup>c</sup>Observed # of 2-pentene molecules formed per min per Fe initially added.

using laser light activation. The data show that no light intensity used is sufficiently high that the isomerization rate is limited by the actual turnover rate of the catalyst, since the observed quantum yields still exceed unity. The data do allow a lower limit to be placed on the turnover rate, and we find that the system exhibits an extraordinarily high turnover rate for alkene isomerization. In fact, the data place the iron carbonyl systems among the fastest homogeneous catalysts for alkene isomerization.

Interestingly, photocatalyzed hydrosilation of 1-pentene by  $\text{HSiEt}_3$  using either  $\text{Fe}(\text{CO})_5$  or  $\text{Fe}_3(\text{CO})_{12}$  also reveals the Fe systems to be extraordinarily active catalysts, Table 5. Again,

TABLE 5.  $\text{Fe}(\text{CO})_5$  and  $\text{Fe}_3(\text{CO})_{12}$  photocatalyzed hydrosilation of 1-pentene by  $\text{HSiEt}_3$ .<sup>a</sup>

Catalyst Precursor, $\underline{M}$	Irrdn Source (time, s)	% Consumption of 1-pentene <sup>b</sup>	$\phi^c$	Turnover Rate, <sup>d</sup> $\text{min}^{-1}$
$\text{Fe}(\text{CO})_5$ , $1 \times 10^{-2}$	2.5W-333,351,364 nm			
	(5)	42	42	1700
	(10)	50	24	1000
$\text{Fe}_3(\text{CO})_{12}$ , $5 \times 10^{-3}$	7.5 W-514.5 nm			
	(10)	42	5	1800
	(20)	59	3	1300

<sup>a</sup>Substrates are 3.66  $\underline{M}$  1-pentene, 3.66  $\underline{M}$   $\text{HSiEt}_3$ . Deoxygenated systems are excited using an Ar ion laser at the wavelength and power indicated (Ref. 20).

<sup>b</sup>~25% of the products are 2-pentenes; ~75% of the products are  $n\text{-C}_5\text{H}_{12}$ , ( $n\text{-pentyl}$ )- $\text{SiEt}_3$  and ( $\text{pentenyl}$ ) $\text{SiEt}_3$ .

<sup>c</sup>Observed quantum yield for 1-pentene consumption.

<sup>d</sup>Observed turnover rate, # of 1-pentene molecules consumed per min per Fe initially added.

the turnover rates given represent lower limits, since the observed quantum yields exceed

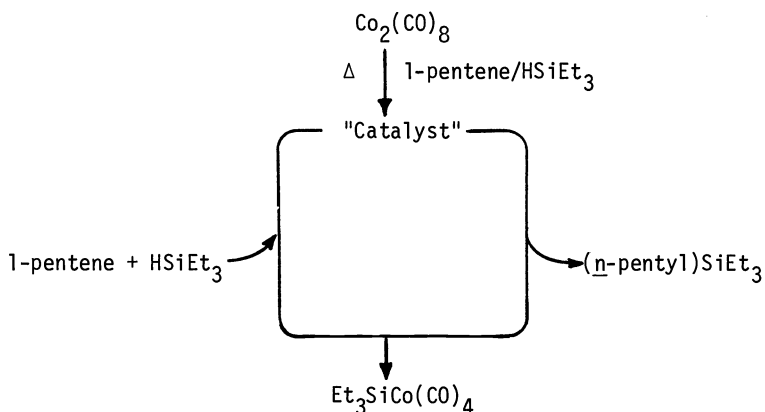
unity. For the same 1/1 1-pentene/HSiEt<sub>3</sub> substrate mixture we find that the photocatalyzed reaction using Fe(CO)<sub>5</sub> or Fe<sub>3</sub>(CO)<sub>12</sub> is faster than the thermal hydrosilation catalyzed by Co<sub>2</sub>(CO)<sub>8</sub>. The hydrosilation of alkenes by H<sub>2</sub>PtCl<sub>6</sub> likely exceeds the rate of photocatalyzed reaction and the Pt system will likely tolerate a larger range of functional groups, but this point requires further investigation.

The catalytic data in Tables 4 and 5 establish the Fe carbonyl catalysts formed by irradiation to be very reactive at 25°C. Previously (Ref. 18) it has been shown that irradiation of Fe(CO)<sub>5</sub> in neat 1-pentene at 77 K yields very active species, since warm-up in the dark of such irradiated samples leads to extensive isomerization of the 1-pentene. Infrared analysis of such irradiated solutions after warm-up gives evidence for only the formation of Fe(CO)<sub>4</sub>(pentene) that is not a very active catalyst for alkene isomerization at 25°C. However, the irradiated solutions at low temperature are blue in color, while the Fe(CO)<sub>4</sub>(pentene) is colorless to yellow. Thus, it would appear that the low temperature irradiation should allow the spectroscopic characterization of Fe carbonyl species that participate in the catalytic cycle given in Scheme I.

Irradiation (355 nm) of Fe(CO)<sub>5</sub> in 1-pentene at 77 K first yields the formation of Fe(CO)<sub>4</sub>(1-pentene) 2082, ~2020, ~2000, and 1971 cm<sup>-1</sup>. The Fe(CO)<sub>4</sub>(1-pentene) is subsequently photolyzed to give a new absorption at 1924 cm<sup>-1</sup> that can be logically attributed to Fe(CO)<sub>3</sub>(1-pentene)<sub>2</sub>. Sequential loss of CO is confirmed by the appearance of a feature at 2133 cm<sup>-1</sup> due to CO in the matrix. The Fe(CO)<sub>3</sub>(alkene)<sub>2</sub> species is relatively photoinert. Warm-up of the system to the softening point of the 1-pentene matrix results in rapid infrared spectral changes such that a strong feature at 1973 cm<sup>-1</sup> and weaker absorption at 2050 cm<sup>-1</sup> grow. We believe that this infrared spectral change is accompanied by a change in the uv-vis-nir spectrum from a feature at ~800 nm to one at ~520 nm, giving the solution a red color. Warm-up to 298 K from this point leads to the formation of the Fe(CO)<sub>4</sub>(pentene) as the principal metal carbonyl product, while the species absorbing at ~1973 cm<sup>-1</sup> disappears. During this time extensive 1-pentene isomerization to the 2-pentenes is detectable by infrared. Further studies will be required in order to identify the red ~1973 cm<sup>-1</sup> species, but we believe that it is one of the species in the catalytic cycle. These preliminary data establish that irradiation at low temperature can reveal intermediates of importance in the catalytic chemistry resulting from activation of Fe<sub>3</sub>(CO)<sub>12</sub> and Fe(CO)<sub>5</sub>.

#### PHOTOACTIVATION OF COBALT CARBONYL CATALYSTS

Many thermal catalyst systems have limited turnover numbers because there is a pathway out of the cycle that leads to an inert complex. In some cases it may be possible to re-enter the catalytic cycle by photoexcitation of the inert species. One system that we have investigated from this point of view is the Co<sub>2</sub>(CO)<sub>8</sub>-catalyzed hydrosilation of alkenes, Scheme II. After several hundred turnovers for the 1/1 1-pentene/HSiEt<sub>3</sub> substrate mixture



Scheme II. Catalytic cycle for hydrosilation.

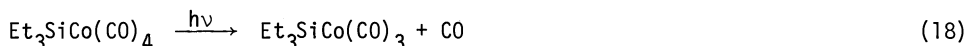
at 25°C we find that catalytically inert Et<sub>3</sub>SiCo(CO)<sub>4</sub> accounts for >80% of the Co originally added as Co<sub>2</sub>(CO)<sub>8</sub> (Ref. 21). Consequently, we undertook an investigation of the photochemistry of Et<sub>3</sub>SiCo(CO)<sub>4</sub> and related species with the hope that catalysis could be re-activated by irradiation and with an interest in establishing certain mechanistic features of the catalysis.

One direct photochemical entry into the catalytic cycle would seemingly be via the light-induced homolysis of the Si-Co bond to give ·Co(CO)<sub>4</sub>, eq. (17), since the metal-centered

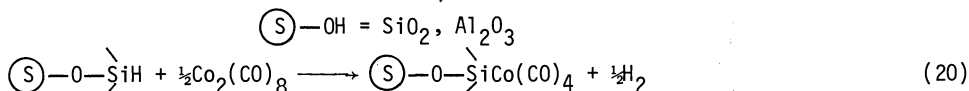




radical could couple to form  $\text{Co}_2(\text{CO})_8$ . However, the primary photoprocess is not Si-Co bond homolysis. Rather, loss of CO, eq. (18), would appear to represent the primary chemical

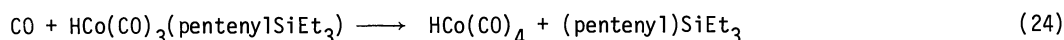
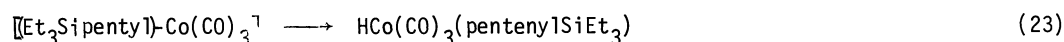
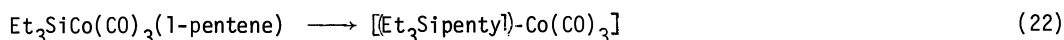
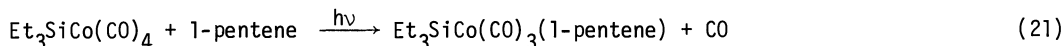


result of photoexcitation. Irradiation of  $\text{Et}_3\text{SiCo}(\text{CO})_4$  in the presence of  $\text{P}(\text{OPh})_3$  leads to clean, quantum efficient substitution to form  $\text{Et}_3\text{SiCo}(\text{CO})_3\text{P}(\text{OPh})_3$ , consistent with dissociative loss of CO, eq. (18), as the primary photoreaction (Ref. 21). Further, we have anchored  $-\text{Co}(\text{CO})_4$  to high surface area  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  via eq. (19) and (20) to establish the



primary photoreaction of the  $\text{R}_3\text{SiCo}(\text{CO})_4$  species (Ref. 22 & 23). Irradiation of the  $\textcircled{\text{S}}-\text{O}-\overset{\text{H}}{\underset{|}{\text{Si}}}\text{Co}(\text{CO})_4$  powder under an atmosphere of  $^{13}\text{CO}$  (>10-fold excess of  $^{13}\text{CO}$ ) leads to rapid, clean formation of  $\textcircled{\text{S}}-\overset{\text{H}}{\underset{|}{\text{Si}}}\text{Co}(^{13}\text{CO})_4$  via the intermediate substitution products as monitored by Fourier transform infrared photoacoustic spectroscopy (Ref. 23). Importantly, there is no significant loss of  $-\text{Co}(\text{CO})_4$  species and no detectable  $\text{Co}_2(\text{CO})_n(^{13}\text{CO})_{8-n}$  is formed. Irradiation of suspensions of the  $\textcircled{\text{S}}-\text{O}-\overset{\text{H}}{\underset{|}{\text{Si}}}\text{Co}(\text{CO})_4$  powder in isoctane/ $\text{P}(\text{OPh})_3$  solutions yields the generation of  $\textcircled{\text{S}}-\text{O}-\overset{\text{H}}{\underset{|}{\text{Si}}}\text{Co}(\text{CO})_3(\text{P}(\text{OPh})_3)$  (Ref. 22). These results all point toward dissociative loss of CO as the dominant primary photoreaction.

Several results, however, seem to support the conclusion that prompt Si-Co bond cleavage, eq. (17), has some importance. For example, irradiation of  $\text{Et}_3\text{SiCo}(\text{CO})_4$  in isoctane solution gives  $\text{Co}_2(\text{CO})_8$  and  $\text{Co}_4(\text{CO})_{12}$  as products; ultimately these two binary carbonyls account for >80% of the Co (Ref. 21). However, the quantum yield is only ~0.01 whereas photosubstitution by  $\text{P}(\text{OPh})_3$  has a quantum yield of ~0.3. Irradiation of  $\text{Et}_3\text{SiCo}(\text{CO})_4$  in the presence of 1-pentene, though, gives  $\text{Co}_2(\text{CO})_8/\text{Co}_4(\text{CO})_{12}$  with good chemical and quantum yields. In this case, the Si-containing product has been quantitated and determined to be (pentenyl)SiEt<sub>3</sub>, accounting for >90% of the Si. The formation of the alkenylsilane could occur via the sequence represented by eq. (21)-(25), but none of the intermediates are inert at 25°C.



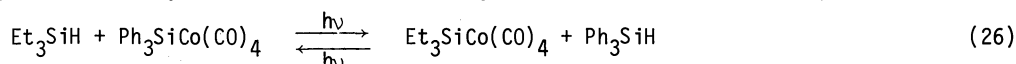
Low temperature irradiation of  $\text{Et}_3\text{SiCo}(\text{CO})_4$  (Ref. 21) or  $\textcircled{\text{S}}-\text{O}-\overset{\text{H}}{\underset{|}{\text{Si}}}\text{Co}(\text{CO})_4$  (Ref. 23) in the presence of alkene supports the first step of the above sequence: infrared spectroscopy reveals an inert  $\text{Et}_3\text{SiCo}(\text{CO})_3(\text{1-pentene})$  complex ( $\nu_{\text{CO}} = 1960 \text{ cm}^{-1}$ ) when 0.01 M  $\text{Et}_3\text{SiCo}(\text{CO})_4$  is irradiated (355 nm) at -78°C in isoctane containing 1 M 1-pentene. Addition of  $\text{P}(\text{OPh})_3$  to the -78°C solution of  $\text{Et}_3\text{SiCo}(\text{CO})_3(\text{1-pentene})/1\text{-pentene}$  followed by warm-up to 25°C yields  $\text{Et}_3\text{SiCo}(\text{CO})_3(\text{P}(\text{OPh})_3)$ , consistent with the conclusion that the alkene complex is substitution labile. Warm-up of the  $\text{Et}_3\text{SiCo}(\text{CO})_3(\text{1-pentene})/1\text{-pentene}$  in the absence of any additives leads to decomposition, regeneration of  $\text{Et}_3\text{SiCo}(\text{CO})_4$  and the formation of  $\text{Co}_4(\text{CO})_{12}$ . Thus, the low temperature technique allows the spectroscopic characterization of the alkene complex, whereas it is too labile to be observed at 25°C. Apparently, the insertion of the 1-pentene into the Si-Co bond, eq. (22), is the slow step in the formation of the (pentenyl)SiEt<sub>3</sub>, since no new species builds to a significant concentration during the warm-up of  $\text{Et}_3\text{SiCo}(\text{CO})_3(\text{1-pentene})$ .

The conclusions drawn from irradiation of low temperature solutions of  $\text{Et}_3\text{SiCo}(\text{CO})_4/1\text{-pentene}$  are supported by results for  $\textcircled{\text{S}}-\text{O}-\overset{\text{H}}{\underset{|}{\text{Si}}}\text{Co}(\text{CO})_4$  irradiated at -50°C in the presence of gas phase alkenes such as ethylene, propylene, and isobutylene (Ref. 23). At -50°C clean photo-substitution to give a surface-anchored alkene complex is formed, whereas the same experiment at 25°C leads to the loss of all surface-anchored Co-carbonyl species. Likewise, warm-up of  $\textcircled{\text{S}}-\text{O}-\overset{\text{H}}{\underset{|}{\text{Si}}}\text{Co}(\text{CO})_3(\text{alkene})$  to 25°C yields decomposition, presumably via the alkene insertion reaction. The  $\textcircled{\text{S}}-\text{O}-\overset{\text{H}}{\underset{|}{\text{Si}}}\text{Co}(\text{CO})_4$  photosubstitution involving alkene entering groups was

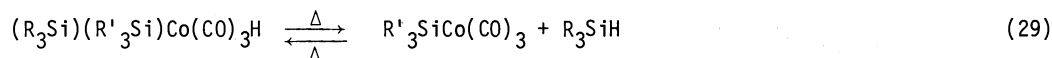
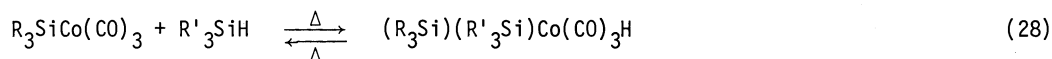
monitored by Fourier transform infrared photoacoustic spectroscopy. Preliminary results also show that persistent coordinatively unsaturated, surface-confined species can be photogenerated when the irradiation is carried out under vacuum at  $-50^{\circ}\text{C}$ . Additional studies are in progress to characterize the structure and reactivity of the surface-confined, unsaturated species.

The Fourier transform infrared photoacoustic spectroscopy is a new technique that allows the determination of vibrational spectra of surface-confined species without sample manipulation (Ref. 23). Interfacial, solid/gas reactions can be monitored, as we have done in the case of the alkene substitutions. Another reaction illustrates that the technique can be very useful in monitoring the production of gas phase products as well. Irradiation of  $(\text{S})-\text{O}-\text{SiCo}(\text{CO})_4$  in the presence of an  $\text{O}_2$  atmosphere results in the generation of gas phase  $\text{CO}_2$  along with  $\text{CO}$  as all metal carbonyl absorptions decline. The Co product is an oxide (Ref. 23). Similarly, irradiation of  $\text{Ph}_3\text{SiCo}(\text{CO})_4$  as a pure solid in the presence of  $\text{O}_2$  results in the formation of  $\text{CO}_2$  and  $\text{CO}$ . Low temperature studies may reveal an intermediate  $\text{O}_2$  complex and such studies are currently in progress.

One remaining photoreaction of  $\text{R}_3\text{SiCo}(\text{CO})_4$  deserves discussion. Irradiation of  $\text{R}_3\text{SiCo}(\text{CO})_4$  in the presence of  $\text{R}'_3\text{SiH}$  results in the exchange reaction represented by eq. (26) (Ref. 21).



The exchange reaction has high quantum efficiency,  $\sim 0.3$ , but it is completely suppressed by the addition of a sufficient quantity of  $\text{P}(\text{OPh})_3$  leading to  $\text{R}_3\text{SiCo}(\text{CO})_3(\text{P}(\text{OPh})_3)$  as the only detectable product beginning with  $\text{R}_3\text{SiCo}(\text{CO})_4$ . Thus, it would appear that exchange occurs via eq. (27)-(30). Consistently, the irradiation of suspensions of  $(\text{S})-\text{O}-\text{SiCo}(\text{CO})_4$



in isooctane/ $\text{HSiEt}_3$  solution leads to the clean formation of  $\text{Et}_3\text{SiCo}(\text{CO})_4$  and presumably  $(\text{S})-\text{O}-\text{SiH}$  (Ref. 22).

The conclusion from all of the studies of  $\text{R}_3\text{SiCo}(\text{CO})_4$  and  $(\text{S})-\text{O}-\text{SiCo}(\text{CO})_4$  is that dissociative loss of  $\text{CO}$  is the dominant result following photoexcitation. The only chemical result that is not consistent with this being the exclusive mode of chemical decay is that irradiation in isooctane alone leads to  $\text{Co}_2(\text{CO})_8/\text{Co}_4(\text{CO})_{12}$ , albeit with low quantum yield. The  $\text{Co}_4(\text{CO})_{12}$  is logically a photoproduct from irradiation of  $\text{Co}_2(\text{CO})_8$  or a product from the intermediate(s) responsible for  $\text{Co}_2(\text{CO})_8$  formation. The  $\text{Co}_2(\text{CO})_8/\text{Co}_4(\text{CO})_{12}$  products could be due to low level olefin impurities in the alkane, since addition of alkene has been shown to facilitate the  $\text{Co}_2(\text{CO})_8/\text{Co}_4(\text{CO})_{12}$  formation via the intermediacy of a labile  $\text{R}_3\text{SiCo}(\text{CO})_3$ - (alkene) species. In any event, there is only minor importance for Si-Co bond homolysis relative to Co-CO bond cleavage.

Returning now to the question of photoactivation of the hydrosilation catalysis using  $\text{R}_3\text{SiCo}(\text{CO})_4$ , we have found that alkene isomerization, hydrosilation, and hydrogenation can be effected by the irradiation of  $\text{R}_3\text{SiCo}(\text{CO})_4$  or  $(\text{S})-\text{O}-\text{SiCo}(\text{CO})_4$  in the presence of 1-pentene/ $\text{HSiEt}_3/\text{H}_2$  mixtures. Despite the fact that Co-CO bond cleavage is the dominant primary photo-process it is apparent that the photoactivation yields the same catalysis as found using the thermal precursor  $\text{Co}_2(\text{CO})_8$  (Ref. 24). Table 6 summarizes some data comparing the  $\text{Co}_2(\text{CO})_8$  thermal system and the photoactivated  $(\text{S})-\text{O}-\text{SiCo}(\text{CO})_4$  system for 1-pentene isomerization and hydrosilation. Like the photoactivated  $\text{Fe}(\text{CO})_5$ ,  $\text{Fe}_3(\text{CO})_{12}$  systems summarized above, the photoactivated silyl-Co( $\text{CO})_4$  systems exhibit a light intensity (excitation rate) dependence on the product formation rate. Thus, the turnover rates given in Table 6 for the photoactivated Co system represent lower limits. What is noteworthy is that the photoactivated system comes close to the product formation rate that can be achieved with the thermal system. Note also that the thermal system ultimately gives a smaller number of product molecules per Co, since thermally inert  $\text{Et}_3\text{SiCo}(\text{CO})_4$  forms (Ref. 21). Irradiation does

TABLE 6. Comparison of  $\text{Co}_2(\text{CO})_8$ -catalyzed and  $(\text{S})-\text{O}-\text{SiCo}(\text{CO})_4$ -photo-catalyzed hydrosilation and isomerization of 1-pentene.<sup>a</sup>

Catalyst Precursor, $\underline{M}$	Time h, hv or $\Delta$	Product (% Conversion)	Turnover Rate, $\text{h}^{-1b}$
$\text{Co}_2(\text{CO})_8, 2 \times 10^{-3}$	24 ( $\Delta$ )	2-pentenes (54.4)	1100
	54 ( $\Delta$ )	2-pentenes (82.0)	750
	96 ( $\Delta$ )	( <i>n</i> -pentyl)SiEt <sub>3</sub> (12.3)	125
	237 ( $\Delta$ )	( <i>n</i> -pentyl)SiEt <sub>3</sub> (15.5)	60
$(\text{S})-\text{O}-\text{SiCo}(\text{CO})_4, 4 \times 10^{-3}$ <sup>c</sup>	56 (hv)	2-pentenes (21.0)	180
		( <i>n</i> -pentyl)SiEt <sub>3</sub> (4.0)	35
	91 (hv)	2-pentenes (47.3)	250
		( <i>n</i> -pentyl)SiEt <sub>3</sub> (22.2)	120

<sup>a</sup>Substrates are 3.66  $\underline{M}$  each 1-pentene, HSiEt<sub>3</sub>. Thermal catalysis ( $\Delta$ ) was done at 25°C and photocatalysis (hv) was done using a 450 W Hanovia Hg lamp as the excitation source (Ref. 22).

<sup>b</sup># of product molecules formed per hour per Co initially added.

<sup>c</sup>Suspension added to substrate,  $(\text{S}) = \text{Al}_2\text{O}_3$ ; the  $4 \times 10^{-3}$   $\underline{M}$  refers to the molar concentration of anchored  $-\text{Co}(\text{CO})_4$  groups.

re-activate the  $\text{Co}_2(\text{CO})_8$  system. Finally, it is worth pointing out that the  $(\text{S})-\text{O}-\text{SiCo}(\text{CO})_4$  system involves the photochemical formation of solution Co-carbonyl species. The bulk of the photocatalysis does not involve the surface-confined species, since the irradiation is in the presence of 1-pentene and Et<sub>3</sub>SiH both of which will lead to cleavage of the surface-Si-Co bond to release Co species into solution that can be subsequently photo-activated to effect the catalysis (Ref. 22).

#### PHOTOACTIVATION OF MONONUCLEAR AND POLYNUCLEAR POLYHYDRIDES

Many mononuclear, polyhydride complexes are known to undergo photoinduced reductive elimination of H<sub>2</sub>, eq. (31) (Ref. 25). The resulting coordinatively unsaturated species



may be active as a catalyst, especially if hydride ligands remain in the coordination sphere. Such a species can straightforwardly effect alkene isomerization and participate in catalytic cycles for hydrogenation, hydroformylation, and hydrosilation. In this section we outline preliminary results for the activation of the polyhydrides  $\text{H}_4\text{M}(\text{DPPE})_2$  ( $\text{M} = \text{Mo}, \text{W}$ ; DPPE  $\equiv$  1,2-bis(diphenylphosphino)ethane);  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ ;  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ ;  $\text{H}_2\text{Os}_3(\text{CO})_{10}$ ; and  $\text{H}_2\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)$ .

#### Photoactivation of $\text{H}_4\text{M}(\text{DPPE})_2$

The photochemistry of  $\text{H}_4\text{Mo}(\text{DPPE})_2$  has been investigated previously (Ref. 25 & 26) and is believed to result in the stepwise loss of two H<sub>2</sub> molecules. Photoexcitation of  $\text{H}_4\text{M}(\text{DPPE})_2$  in the presence of alkenes results in the stoichiometric reduction of the alkene, Table 7

TABLE 7. Reduction of alkenes by photoexcitation of  $\text{H}_4\text{M}(\text{DPPE})_2$  (Ref. 27).<sup>a</sup>

A. Stoichiometric Reductions				
M	Irrdn. Time, h	Substrate, $\underline{M}$	Product, % <sup>b</sup>	$\phi^c$
Mo	0.28	1-pentene, 0.1	<i>n</i> -pentane, 50	0.06
	0.77	1-pentene, 0.1	<i>n</i> -pentane, 100	0.05
	28.3	<i>cis</i> -2-pentene, 0.1	<i>n</i> -pentane, 13	---
	1.3	3,3-dimethyl-1-pentene, 0.1	3,3-dimethylpentane, 87	---
	24	cyclopentene, 0.1	cyclopentane, 90	---
W	3	1-pentene, 0.1	<i>n</i> -pentane, 29	0.004
	48	1-pentene, 0.1	<i>n</i> -pentane, 87	0.001

42	3,3-dimethyl-1-pentene, 0.1	3,3-dimethyl-1-pentane, 99	---
44	cyclopentene, 0.1	cyclopentane, 78	---

B. Catalytic Reductions Under 10 psi H<sub>2</sub>

M	Irrdn. Time, h	Substrate, M	Product	Turnover Number <sup>d</sup>
Mo	15.5	1-pentene, 5.0	<u>n</u> -pentane	150
W	23.5	1-pentene, 0.1	<u>n</u> -pentane	3.2

<sup>a</sup>All experiments for 10<sup>-3</sup> M H<sub>4</sub>M(DPPE)<sub>2</sub> in deoxygenated toluene. Photoexcitation was at 355 ± 15 nm, 1.2 × 10<sup>-6</sup> ein/min.

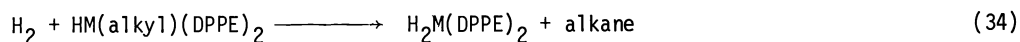
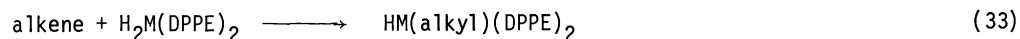
<sup>b</sup>Based on the assumption that H<sub>4</sub>M(DPPE)<sub>2</sub> can provide two molecules of H<sub>2</sub>.

<sup>c</sup># of product molecules per photon incident.

<sup>d</sup># of product molecules per H<sub>4</sub>M(DPPE)<sub>2</sub> initially added.

(Ref. 27). Remarkably, when beginning with 1-pentene or with cis-2-pentene there is no detectable isomerization of the olefin, while reduction to alkane occurs. The reduction of the terminal alkenes occurs faster than the internal alkenes, and the Mo complex has about an order of magnitude higher quantum yield than the W complex.

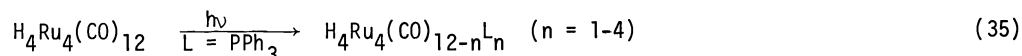
Irradiation of H<sub>4</sub>M(DPPE)<sub>2</sub> under H<sub>2</sub> in the presence of alkene results in catalytic hydrogenation (Ref. 27). We propose the tentative mechanism represented by eq. (32)-(34). The



lack of isomerization is quite unusual for a species that hydrogenates alkenes. The lack of isomerization may be attributable to the steric encumbrance about the central metal. Whatever the mechanism, the data in Table 7 establish that photoexcitation can significantly alter the reactivity of a hydride species with respect to olefin reactions.

Photoactivation of H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub> and H<sub>2</sub>Ru<sub>4</sub>(CO)<sub>13</sub>

Polynuclear complexes containing three or more metals typically give quantum inefficient photochemistry, while dinuclear complexes often undergo very efficient net photoreaction to form metal-centered radicals (Ref. 28). We have found that H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub> undergoes clean, but quantum inefficient ( $\phi \approx 5 \times 10^{-3}$ ) photosubstitution according to eq. (35) (Ref. 29.) The



finding of clean photosubstitution suggests that we should be able to accelerate olefin reactions known to be thermally catalyzed by H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub> (Ref. 30-32). The thermal catalysis is believed to be initiated by dissociative loss of CO to form H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>11</sub>. Thus, the light-induced loss of CO should allow the catalysis to be effected at lower temperatures.

Irradiation (355 nm) of H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub> at 25°C in the presence of an olefin such as alkene or alkyne leads to stoichiometric reduction reactions with modest rates (Ref. 29), Table 8.

TABLE 8. Olefin reductions from photoexcitation of H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub> (Ref. 29).<sup>a</sup>

Olefin	Stoichiometric			Catalytic, 10 psi H <sub>2</sub>		
	Irrdn. Time, h	% Conv. <sup>b</sup>	Product(s), %	Irrdn. Time, h	T.O.# <sup>c</sup>	Product(s), %
1-pentene	7	69	<u>n</u> -pentane, 100 <sup>d</sup>	24	84	<u>n</u> -pentane, 100 <sup>d</sup>
cyclopentene	13	51	cyclopentane, 100	24	206	cyclopentane, 100
3,3-diMe-1-pentene	7	80	3,3-diMe-pentane, 100	24	127	3,3-diMe-pentane, 100
1-pentyne	23	74	1-pentene, 73 <u>cis</u> -2-pentene, 10 <u>trans</u> -2-pentene, 13 <u>n</u> -pentane, 4	24	11	1-pentene, 66 <u>cis</u> -2-pentene, 13 <u>trans</u> -2-pentene, 10 <u>n</u> -pentane, 11
2-pentyne	23	60	1-pentene, 24 <u>cis</u> -2-pentene, 75 <u>trans</u> -2-pentene, 1 <u>n</u> -pentane, <1	24	137	1-pentene, 2 <u>cis</u> -2-pentene, 19 <u>trans</u> -2-pentene, 73 <u>n</u> -pentane, 6

<sup>a</sup>All data for 0.1 M olefin/ $5 \times 10^{-4}$  M  $H_4Ru_4(CO)_{12}$  in deoxygenated  $C_6H_6$  solution irradiated at  $355 \pm 15$  nm at  $\sim 1.2 \times 10^{-6}$  ein/min.

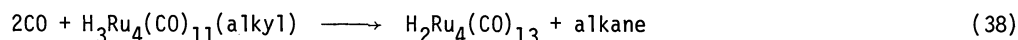
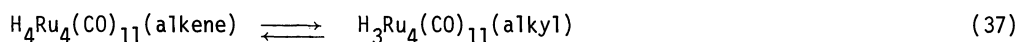
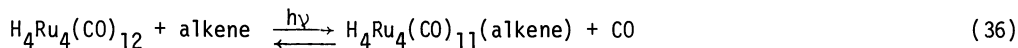
<sup>b</sup>Assuming  $H_4Ru_4(CO)_{12}$  can transfer two molecules of  $H_2$ .

<sup>c</sup># of reduced molecules per  $H_4Ru_4(CO)_{12}$  initially added.

<sup>d</sup>1-pentene to 2-pentene competes with hydrogenation. At these times the pentenes are at the thermodynamic ratio:  $\sim 3\%$  1-pentene;  $\sim 80\%$  trans-2-pentene;  $\sim 17\%$  cis-2-pentene.

Under 10 psi  $H_2$  catalytic hydrogenation occurs. No thermal reduction chemistry occurs at  $25^\circ C$ . Isomerization of 1-pentene is also accelerated by photoexcitation of  $H_4Ru_4(CO)_{12}$ . The photocatalysis products suggest that all steps after CO release have sufficiently low activation barriers that reaction can proceed at  $25^\circ C$ .

The irradiation of  $H_4Ru_4(CO)_{12}$  in the presence of 1-pentene leads to the initial formation of  $H_2Ru_4(CO)_{13}$  as the principal metal carbonyl product. The reaction presumably proceeds via the sequence represented by eq. (36)-(38). Processes (37) and (38) can account for the



generation of isomerized alkene and alkane, respectively. Like  $H_4Ru_4(CO)_{12}$ , the  $H_2Ru_4(CO)_{13}$  is a thermal catalyst for alkene isomerization (Ref. 33). We find that irradiation of  $H_2Ru_4(CO)_{13}$  accelerates alkene isomerization at  $25^\circ C$  and leads to reduction of the alkane and unidentified Ru-containing products. Under  $H_2$ , the 355 nm irradiation of  $H_2Ru_4(CO)_{13}$  leads to  $H_4Ru_4(CO)_{12}$  presumably via dissociative loss of CO. The dissociative loss of CO from  $H_2Ru_4(CO)_{13}$  also accounts for the photocatalyzed alkene isomerization and light-induced, stoichiometric reduction of alkene to alkane. A detailed study of the photochemistry of  $H_2Ru_4(CO)_{13}$  and related species has confirmed the conclusion that CO dissociation is the most likely chemical result from photoexcitation (Ref. 34).

Our studies of the  $H_4Ru_4(CO)_{12}$  and  $H_2Ru_4(CO)_{13}$  systems establish that photoinduced loss of CO from polynuclear polyhydrides can lead to the generation of stoichiometrically and catalytically active reagents at  $25^\circ C$ . It should be possible in these particular systems to gain further insight into the mechanisms of reduction reactions by monitoring such reactions at temperatures below  $25^\circ C$ , as we have done in the systems described above.

#### Photoactivation of $H_2Os_3(CO)_{10}$ and $H_2Os_3(CO)_{10}PPh_3$

Like  $H_4Ru_4(CO)_{12}$ ,  $H_2Os_3(CO)_{10}$  is a known thermal catalyst for the isomerization and hydrogenation of olefins (Ref. 35). Near-uv irradiation of  $H_2Os_3(CO)_{10}$  in the presence of alkene accelerates the rate of isomerization and reduction to alkane (Ref. 36), Table 9.

TABLE 9. Photoactivation of  $H_2Os_3(CO)_{10}$  for 1-pentene isomerization and reduction. (Ref. 36).<sup>a</sup>

Irrdn. $\lambda$ , nm (time)	% <u>n</u> -Pentane <sup>b</sup>	% isom. <sup>c</sup>	t/c <sup>d</sup>	$\phi_{\text{red.}}$ <sup>e</sup>
355 (3 h)	6.0	18.0	1.97	$0.4 \times 10^{-3}$
(5 h)	25.4	32.1	1.99	$1.0 \times 10^{-3}$
(18.5 h)	66.1	63.7	2.85	$1.0 \times 10^{-3}$
Dark (6 h)	0.0	7.7	1.35	-----
(9 h)	0.0	10.2	1.44	-----
(18 h)	0.0	22.0	1.53	-----
(48 h)	0.0	51.3	1.60	-----
(146 h)	0.0	81.5	1.81	-----

<sup>a</sup>Photocatalysis and dark catalysis were carried out in  $10^{-3}$  M  $H_2Os_3(CO)_{10}$ /0.2 M 1-pentene in deoxygenated  $C_6H_6$  solution.

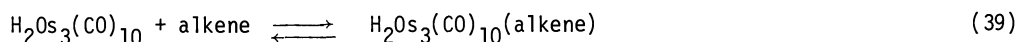
<sup>b</sup>Assuming  $H_2Os_3(CO)_{10}$  can transfer one  $H_2$  molecule.

<sup>c</sup>Based on consumption of the 0.2 M 1-pentene.

<sup>d</sup>Ratio of trans-2- to cis-2-pentene products.

<sup>e</sup># of n-pentane molecules formed per photon absorbed.

However, unlike the  $H_4Ru_4(CO)_{12}$  system described above where the same initial trans/cis ratio of the 2-pentenes is formed thermally and photocatalytically, we find that photoactivation of  $H_2Os_3(CO)_{10}$  gives a different ratio of isomeric products. This indicates that photoexcitation of  $H_2Os_3(CO)_{10}$  does not give the same catalytically active species. In the thermal catalysis it is possible that the crucial step is the addition of the alkene to the coordinatively unsaturated  $H_2Os_3(CO)_{10}$ . It is not obvious that photoexcitation of the complex will promote the binding of alkene in any significant way. The absorption spectrum of the purple  $H_2Os_3(CO)_{10}$  in hydrocarbon solvents is not significantly altered by the addition of alkene, supporting the suggestion that ligand binding is a crucial step. We believe that the equilibrium represented by eq. (39) lies far to the left and is not



significantly influenced by light.

The fact that photoexcitation yields a different initial ratio of trans- and cis-2-pentene from 1-pentene suggests that the photogenerated catalyst is not the same as that obtained by thermal activation. We also note that photoexcitation into the lowest absorption by irradiation at 632.8 nm with the same intensity as at 355 nm leads to no acceleration of alkene isomerization or alkane formation. Given that both CO loss and Os-Os bond cleavage are known to occur upon photoexcitation of  $Os_3$  species (Ref. 37) we are not certain of the primary photoreaction in  $H_2Os_3(CO)_{10}$ . Since we do observe photoproduction of alkane in the presence of alkene, we tend to rule out loss of  $H_2$  as the result of photoexcitation. The generation of a coordinatively unsaturated species by either loss of CO or Os-Os bond cleavage could result in sufficient enhancement of the reactions of the hydride to give increased catalysis rates at 25°C. Irradiation (355 nm) of the  $H_2Os_3(CO)_{10}$  in the presence of alkene under  $H_2$  does yield catalytic hydrogenation, but we have not determined whether the catalytically active species is the same as that generated thermally. However, it is very apparent that photoexcitation changes the relative rate of hydrogenation vs. isomerization such that hydrogenation at 25°C is quite competitive with isomerization whereas only isomerization is observed at 25°C using thermal activation alone. This change in relative importance for hydrogenation vs. isomerization could be attributed to either a different catalyst or to merely changing the rate limiting step in the catalytic cycle. This issue is still under investigation.

The coordinatively saturated species  $H_2Os_3(CO)_{10}(PPh_3)$ , prepared by adding  $PPh_3$  to  $H_2Os_3(CO)_{10}$ , also gives accelerated alkene isomerization and reduction when subjected to 355 nm irradiation. As for  $H_2Os_3(CO)_{10}$ , the  $H_2Os_3(CO)_{10}PPh_3$  gives alkene isomerization but not reduction at 25°C. Product ratios suggest that the  $PPh_3$  is retained in the coordination sphere under illumination. Again whether CO is lost or Os-Os bond cleavage occurs is unclear.

Study of the irradiation of  $H_2Os_3(CO)_{10}$  in the presence of halocarbons give the interesting result that irradiation of the hydride can result in reduction of the halocarbon, Table 10.

TABLE 10. Photoreduction of halocarbons by  $H_2Os_3(CO)_{10}$  (Ref. 36).<sup>a</sup>

Halocarbon, <u>M</u>	Irrdn. Time, h	Product (% Conversion) <sup>b</sup>	$\phi^c$
$CCl_4$ , neat	20	$CHCl_3$ (75)	---
$CHCl_3$ , neat	20	$CH_2Cl_2$ (100)	---
3-I-pentane, 0.1	4.5	<u>n</u> -pentane (100)	---
1-I-pentane, 0.1	1	<u>n</u> -pentane (8.1)	$2.4 \times 10^{-3}$
	2	(29.6)	$4.5 \times 10^{-3}$
	4	(81.8)	$6.3 \times 10^{-3}$
1-Br-pentane, 0.1	5.1	<u>n</u> -pentane (10.3)	$0.7 \times 10^{-3}$
	55.1	(78.0)	$0.5 \times 10^{-3}$
1-Cl-pentane, 0.1	6.8	<u>n</u> -pentane (9.8)	$0.5 \times 10^{-3}$
	54	(45.0)	$0.3 \times 10^{-3}$

<sup>a</sup>Irradiation with  $355 \pm 15$  nm,  $\sim 1.2 \times 10^{-6}$  ein/min in deoxygenated solution of neat halocarbon or  $C_6H_6$  solution containing  $10^{-2} - 10^{-3}$  M  $H_2Os_3(CO)_{10}$ .

<sup>b</sup>% based on assumption that two RX can be reduced to two RH per  $H_2Os_3(CO)_{10}$ .

<sup>c</sup># Product molecules per photon incident.

Similar enhanced reactivity of the  $\text{H}_2\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)$  occurs under 355 nm irradiation. The quantum yields for the reduction of RX appear to be about the same as for the stoichiometric reduction of alkenes, Table 9, suggesting that the same photoprocess leads to an active reductant in each system. For  $\text{CCl}_4$  we find by infrared and  $^1\text{H}$  nmr that the initial Os-containing species is  $(\text{H})(\text{Cl})\text{Os}_3(\text{CO})_{10}$ . Ultimately, mononuclear Os-carbonyl chloride species are generated, presumably as a secondary photoreaction. The retention of the  $\text{Os}_3$  core establishes that the cluster can remain intact during the photocatalysis of alkene reactions, but this still does not resolve the issue of whether CO loss or Os-Os bond cleavage is the primary chemical result from photoexcitation of  $\text{H}_2\text{Os}_3(\text{CO})_{10}$ . It should be emphasized that  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  is inert with respect to RX reduction in the dark. The photoactivation of RX reduction by irradiation of metal hydrides is a new reaction that will receive continued study in this laboratory.

#### SUMMARY

A large number of thermally inert organometallic complexes can be photoactivated for stoichiometric and catalytic reactions using visible or ultraviolet light. In favorable cases, low temperature irradiation leads to the generation of spectroscopically detectable intermediates, e.g.  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2\text{C}_2\text{H}_5$  or  $\text{Fe}(\text{CO})_n(\text{alkene})_{5-n}$ , that likely participate in catalytic cycles at higher temperatures where the steady state concentration is too low to detect. The dissociative process of CO or  $\text{H}_2$  loss and metal-metal bond rupture can lead to the coordinatively unsaturated intermediates that pervade homogeneous and heterogeneous catalytic systems. In some cases the same catalyst as generated thermally at high temperature can be prepared photochemically at low temperature using the same precursor, as in the case of  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  where loss of CO thermally or photochemically produces an active species. In other situations different catalysis results, as reflected in product ratios, when photoexcitation is used compared to thermal activation as in hydrogenation vs. isomerization using  $\text{H}_2\text{Os}_3(\text{CO})_{10}$ . New spectroscopic techniques such as Fourier transform infrared photoacoustic spectroscopy will become important in the *in situ* analysis of heterogenized catalyst precursors, such as the case of  $(\text{S})-\text{O}-\text{SiCo}(\text{CO})_4$ , ( $\text{S} \equiv \text{Al}_2\text{O}_3$  or  $\text{SiO}_2$ ) where gas/solid interfacial photoreactions can be monitored.

**Acknowledgement** - This work was supported in part by the Office of Naval Research, the National Science Foundation, and the Dow Chemical Company. RJK acknowledges support as an NSF Predoctoral Fellow, 1978-1981.

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