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PHOTOACTIVATION OF ORGANOMETALLIC CATALYSTS.(U)

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APR 79 M S WRIGHTON, J L GRAFF, C L REICHEL

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⁶ Photoactivation of Organometallic Catalysts.

by

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Photoactivation of Organometallic Catalysts

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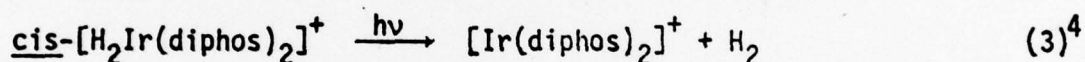
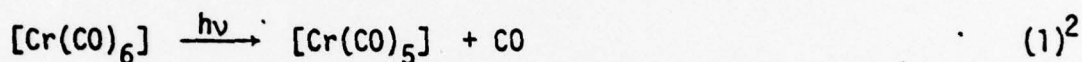
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Abstract

Photochemistry offers a technique to synthesize unique catalysts, control catalytic reactions, and perturb and better understand conventional catalytic cycles. Recent studies in the author's laboratory concerning photoinduced catalysis using mono-, di-, and trinuclear organometallic catalyst precursors are summarized. Specific systems considered here are $[M(CO)_nL_{5-n}]$ ($M = Fe, Ru$; $L = PPh_3$; $n = 5, 4, 3$), $[M_3(CO)_{12}]$ ($M = Fe, Ru, Os$), $[Ru_3(CO)_9(PPh_3)_3]$, and $[Co_2(CO)_6L_2]$ ($L = P(n-Bu)_3, P(OPh)_3$) used to effect catalytic chemistry of 1-pentene including isomerization, hydrogenation, and hydrosilation.

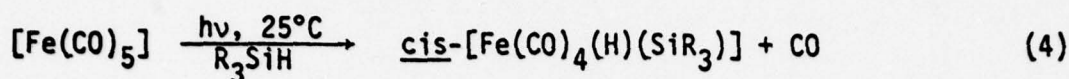
Introduction

Homogeneous catalysis often involves coordinatively unsaturated metal complexes as active intermediates. Optical irradiation of thermally inert metal complexes offers a way to produce unusual coordinatively unsaturated species.¹ At least three primary photoprocesses are known to lead to coordinatively unsaturated species with high efficiency and at low temperature: ligand dissociation, metal-metal bond cleavage, and reductive elimination, exemplified by the chemistry represented in equations (1)-(3).²⁻⁴ With the

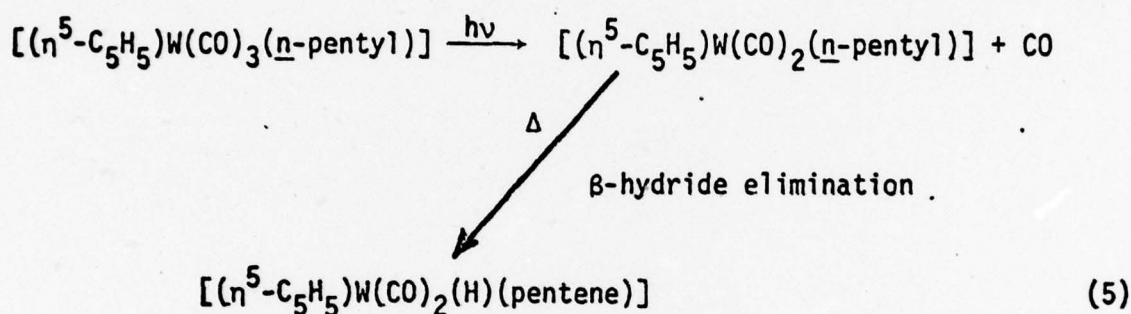


knowledge that such photoreactions exist, it appears plausible to generate active catalysts by photochemical means. Further, it would seem possible that any particular step in a catalytic cycle could be influenced by light, and by such effects, conventional catalytic cycles could be perturbed in order to accelerate overall rate, improve specificity, or to better understand the mechanism of the catalytic chemistry. Photochemistry offers a potential route to genuinely new catalysts or to improving and understanding known catalysts.

As a research tool in catalysis, photochemistry has untapped potential. For example, it is possible to photogenerate coordinatively unsaturated metal complexes at low temperatures in order to study the oxidative addition of substances like R_3SiH . The chemistry represented by equation (4),⁵ coupled with



the fact that $[\text{Fe}(\text{CO})_4]$ can be photogenerated from $[\text{Fe}(\text{CO})_5]$ at very low temperatures⁶ suggests that this is fertile territory for study. Likewise, a thermal process such as β -hydride elimination could be induced by ligand extrusion to open a vacant coordination site as in equation (5).⁷ The point

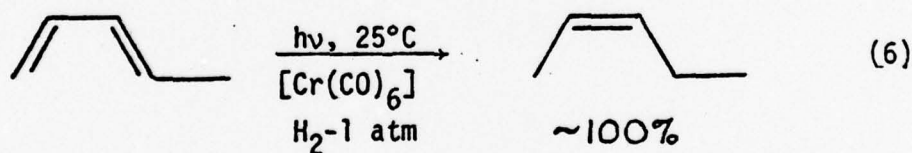


is that it may be possible to photogenerate the coordinative unsaturation at temperatures where there is not sufficient thermal activation available to effect the β -hydride elimination. Oxidative addition and β -hydride elimination are just two processes important to catalytic cycles which could be better studied in some systems by using light to generate coordinative unsaturation. These and other reactions are under study in our laboratory, in order to better understand the thermal processes in catalytic cycles. Generally, elaboration of the photochemistry of metal carbonyls, hydrides, alkyls, and olefin complexes should prove useful in identifying just what can be done in altering the course of events in catalytic cycles.

Thinking ahead to applications, it is noteworthy that photocatalyzed reactions can likely be turned off and on simply by turning the light off and on. Such instantaneous control is not possible in conventional thermal activation. The photocatalyzed reactions depend on two stimuli: light and

some minimum thermal activation energy. Xerography is a process depending on two stimuli (light and potential); photoinitiated polymerization likewise is a practical process depending on two stimuli (light and thermal activation). It is very intriguing to speculate on just what applications may be found for organometallic photocatalysis and whether two stimuli response and instantaneous on/off control can be exploited. For organometallics it is noteworthy that strong wavelength dependence can be found for primary photoprocesses, adding another dimension of control not commonly encountered with organic molecules.

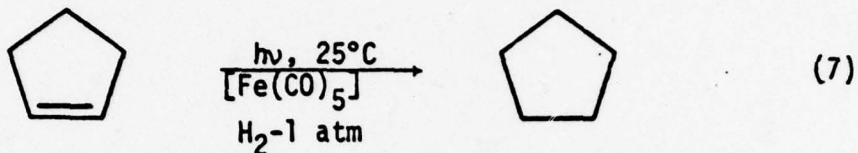
There have been a number of reports in recent years concerning the actual photogeneration of catalysts for polymerization,⁸ olefin isomerization,⁹⁻¹² hydrogenation,^{9,13,14} hydrosilation,^{11,12,15,16} metathesis,¹⁷ and olefin dimerization or oligomerization.¹⁸ These studies have demonstrated that it is possible to initiate catalytic transformations with light. In many instances the key advantage relates to the fact that the photocatalysis can be run at low temperatures whereas thermal activation of the same catalyst precursor requires high temperature. For example, the hydrogenation of trans-1,3-pentadiene can be carried out according to equation (6)¹² where the



primary photochemical event is likely that represented in equation (1).

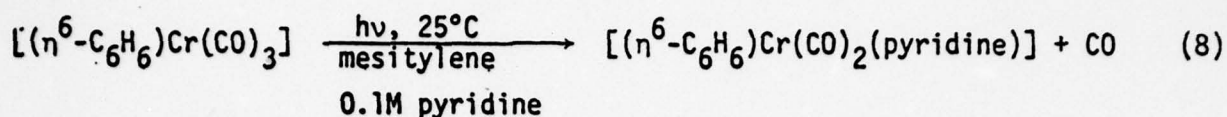
Thermal hydrogenation with essentially the same specificity using $[\text{Cr}(\text{CO})_6]$ could likely be effected but only at high temperatures where generation of the actual catalyst is possible. Thermal generation of the actual catalyst from a different precursor is possible, and we and others have shown that thermally labile sources of " $[\text{Cr}(\text{CO})_3]$ " such as $[\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3]$ ¹⁹ or $[(\eta^6\text{-arene})\text{Cr}(\text{CO})_3]$ ²⁰

can be used at low temperature to effect hydrogenation of 1,3-dienes with essentially the same specificity as with the low temperature photochemical activation of $[\text{Cr}(\text{CO})_6]$. In other instances low temperature thermal routes to the same catalyst produced photochemically may prove difficult. For example, hydrogenation of alkenes can be effected according to equation (7)⁹ using



$[\text{Fe}(\text{CO})_5]$ as the catalyst precursor. Thermally labile precursors to the coordinatively unsaturated, mononuclear $[\text{Fe}(\text{CO})_n]$ species are capable of ultimately yielding the cluster $[\text{Fe}_3(\text{CO})_{12}]$ which is essentially not active at 25°C . Any $[\text{Fe}_3(\text{CO})_{12}]$ formed in the photochemical procedure is degraded to mononuclear, catalytically active iron species by the light.¹¹ However, the chemistry represented by equation (7) is not sufficiently specific or unique to make photocatalyzed hydrogenation the synthetic procedure of choice.

In realistically assessing the practical aspects of photochemistry in catalytic chemistry it is appropriate to consider what is unique about excited state, compared to ground state, reactions of potential catalyst precursors. Are there any reactions at all that can be said to be genuinely unique to excited compared to ground state molecules? The answer to this question is subject to some interpretation; it is probably true that any reaction is possible from any electronic state, but what matters is the relative rate of the various competing reaction pathways. Thus, for practical purposes it is true that certain reactions will be found to only occur for a given electronic state. Within the framework of the examples already given, $[(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3]$ is known to undergo photoreaction chemistry as represented in equation (8)²¹ whereas



thermal activation produces only arene group exchange and no CO substitution.²² Accordingly, since "[Cr(CO)₃]" generation seems essential to the hydrogenation of 1,3-dienes, we²³ were unsuccessful in our attempts to effect the 25°C hydrogenation of 1,3-dienes by photoactivation of $[(\eta^6\text{-C}_6\text{H}_6)\text{Cr(CO)}_3]$. Selective loss of a particular ligand is therefore an example of a reaction where the excited state may do something not found in the ground state. Since the ligands in the coordination sphere during the actual catalytic chemistry may control the product specificity, selective ligand extrusion by photochemical means represents a powerful advantage. No doubt other unique aspects of excited state chemistry exist, but for now, selective ligand loss is the most clearly defined unique chemistry possible by photoexcitation as it relates to catalysis.

Metal-metal bonded complexes comprise a large class of organometallics, and at least for such species having two^{3,24} or three metal atoms,²⁵ metal-metal bond cleavage is believed to represent an important component of the excited state chemistry. In many cases it is conceivable that the metal-ligand and metal-metal dissociation energies are in the same range. Thermal activation would then give a mixture of products resulting from metal-ligand and metal-metal dissociation. For a large number of dinuclear metal-metal bonded complexes, the only detectable photoproducts derive from metal-metal bond cleavage as the primary photoprocess.^{3,24} While the general view might be one where metal-metal bond cleavage is another example of selective ligand extrusion, we distinguish metal-metal and metal-ligand cleavage from one another. Generally, the selective metal-ligand cleavage reactions have involved the

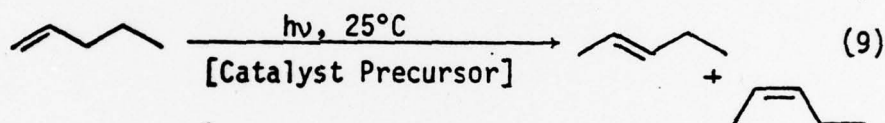
photogeneration of 16-valence-electron intermediates whereas metal-metal bond cleavage yields 17-valence-electron intermediates. Since cluster complexes may play an important role in some important catalytic syntheses, examination of the photochemistry of such systems is interesting.

In the sections below we outline some of the highlights of our recent photochemical research using mononuclear, dinuclear, and trinuclear organometallic catalyst precursors. In the several cases studied, 1-pentene isomerization, hydrogenation, or hydrosilation have been the probe catalytic reactions.

Results and Discussion

a. Comparison of Mononuclear and Trinuclear Iron and Ruthenium Organometallic Catalyst Precursors for Alkene Isomerization

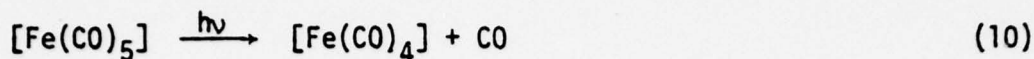
The species $[M(CO)_n(PR_3)_{5-n}]$ and $[M_3(CO)_n(PR_3)_{12-n}]$ ($M = Fe, Ru$) for certain values of n and certain PR_3 are thermally inert at $25^\circ C$ with respect to catalytic chemistry of 1-pentene.¹⁰ In particular, some of these systems show no thermal activity toward 1-pentene as isomerization catalysts at $25^\circ C$. Optical excitation in many cases, though, does produce isomerization activity at $25^\circ C$ according to equation (9).¹⁰ By examining the initial ratio



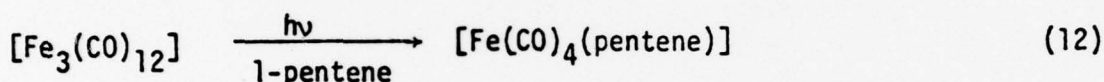
of products and defining the primary photoprocesses in the various catalyst precursors studied, we have been able to draw some important conclusions concerning these photocatalytic systems. Detecting variation in the initial distribution of catalytic products evidences variation in the nature of the catalyst; reaction according to (9) has proven to be very sensitive to the nature of the catalyst precursor.

1. Systems Chosen for Study and Primary Photoprocesses. One question to which we have sought an answer concerns whether cluster precursors offer any advantages over mononuclear precursors to catalysts in photochemical systems. To begin answering this question we have studied $[Fe(CO)_5]$ relative to $[Fe_3(CO)_{12}]$ and $[Ru(CO)_4PPh_3]$ relative to $[Ru_3(CO)_9(PPh_3)_3]$. Aside from being a pair of systems where there is one mononuclear species and one cluster species of the same metal, these two systems are related in an important way by their primary photoprocesses. It has been known for some time that $[Fe(CO)_5]$ undergoes

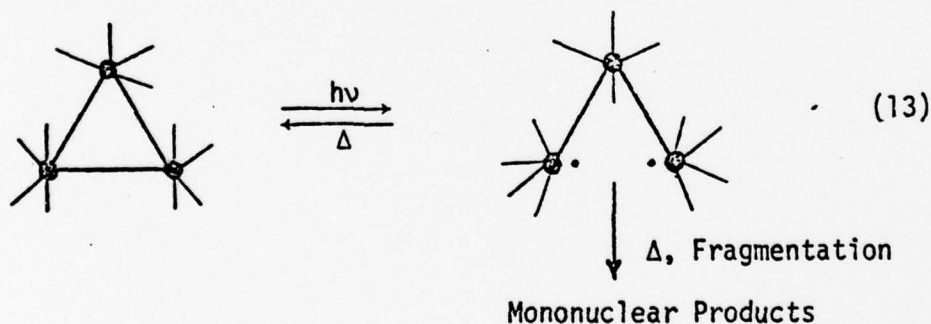
dissociative loss of CO according to equation (10) with high quantum efficiency.²⁶



What is noteworthy is that the photoproduct $[\text{Fe}(\text{CO})_4]$ and the cluster $[\text{Fe}_3(\text{CO})_{12}]$ have the same simplest formula. Further, we have found that visible irradiation of $[\text{Fe}_3(\text{CO})_{12}]$ under CO or in the presence of 1-pentene proceeds according to equations (11) and (12).¹¹ The disappearance quantum yield for the cluster is



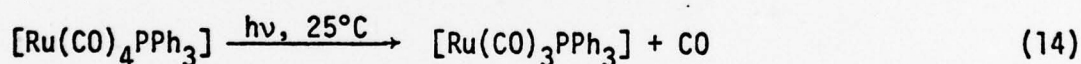
$\sim 10^{-2}$ for 550 nm excitation. While it is possible that irradiation of $[\text{Fe}_3(\text{CO})_{12}]$ ultimately yields $[\text{Fe}(\text{CO})_4]$ intermediates which are scavenged by CO or 1-pentene, the primary chemical result of photoexcitation is likely Fe-Fe bond cleavage, equation (13). A question with respect to the catalytic



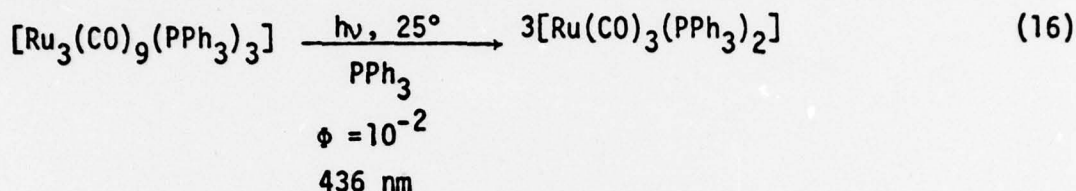
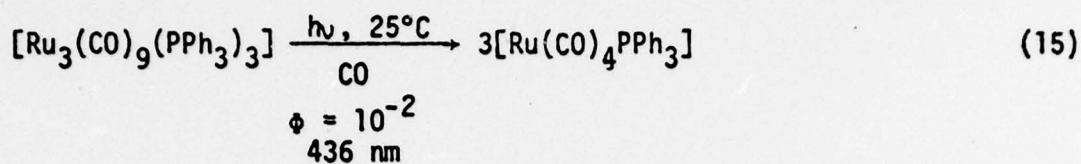
properties would concern whether the fragmentation is dissociative or associative in character. Fast reformation of the metal-metal bond would account for the modest quantum efficiency for reactions (11) and (12). The fact that the $[\text{Fe}_3(\text{CO})_{12}]$ disappearance quantum yield is about the same for neat 1-pentene

solution as for the isooctane solutions exposed to 1 atm. CO suggests that associative contributions to the fragmentation efficiency are small. However, this does not rule out catalysis at the diradical stage without fragmentation. Generation of $[\text{Fe}(\text{CO})_4]$ is thus possible from $[\text{Fe}(\text{CO})_5]$ or $[\text{Fe}_3(\text{CO})_{12}]$; if such is the only route to catalytically active species the ratio of catalytic products should be independent of whether $[\text{Fe}(\text{CO})_5]$ or $[\text{Fe}_3(\text{CO})_{12}]$ is used. We assume here that if the diradical in equation (13), or any other photogenerated cluster intermediate such as $[\text{Fe}_3(\text{CO})_{11}]$, is catalytically active it will give a different distribution of initial products than that found for the mononuclear species. Thus, the relationship of $[\text{Fe}(\text{CO})_5]$ and $[\text{Fe}_3(\text{CO})_{12}]$ in their primary photoprocesses should enable a conclusion as to whether the cluster and mononuclear species yield the same catalyst, provided cluster catalysts do yield a different ratio of products compared to the mononuclear catalysts.

The two Ru species are related to each other in the same way that $[\text{Fe}(\text{CO})_5]$ and $[\text{Fe}_3(\text{CO})_{12}]$ are related. Photoexcitation of $[\text{Ru}(\text{CO})_4\text{PPh}_3]$ occurs according to equation (14),¹⁰ since irradiation in the presence of $\text{P}(\text{OMe})_3$ produces



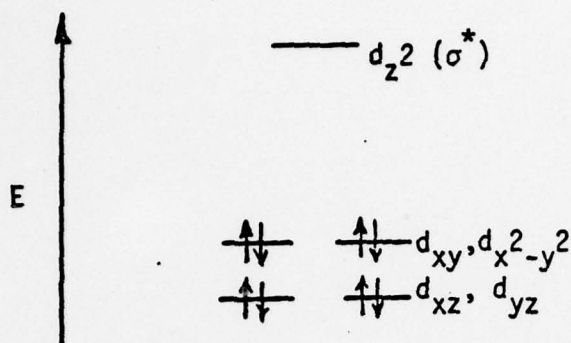
$[\text{Ru}(\text{CO})_3(\text{PPh}_3)(\text{P}(\text{OMe})_3)]$ with a 355 nm quantum yield of ~0.3. The $[\text{Ru}(\text{CO})_3\text{PPh}_3]$ has the same simplest formula as $[\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3]$. Reaction according to equation (14) is an example of selective loss of a ligand; here CO is extruded completely selectively. The relative efficiency for CO vs. PPh_3 extrusion could not have been predicted, unfortunately. Interestingly, $[\text{Fe}(\text{CO})_4\text{PPh}_3]$ also gives essentially exclusively CO extrusion as the primary photoprocess.¹² Photoexcitation of the cluster $[\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3]$ under CO or in the presence of PPh_3 results in chemistry as represented in equations (15) and (16), raising the same sort of



questions surrounding the fragmentation of $[\text{Fe}_3(\text{CO})_{12}]$. Again, it is likely that the primary chemical result of photoexcitation is rupture of one of the Ru-Ru bonds. If the products formed under CO or in the presence of PPh_3 actually form via $[\text{Ru}(\text{CO})_3\text{PPh}_3]$ as their stoichiometry suggests, $[\text{Ru}(\text{CO})_4\text{PPh}_3]$ and $[\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3]$ may yield the same catalyst in the presence of alkene.

The electronic structure of the mononuclear and trinuclear species certainly differ. The lowest excited states for the mononuclear complexes are ligand field states where the one-electron levels in Scheme I are appropriate. Examination of Scheme I shows that all ligand field excited states involve population of the d_{z^2} orbital. This orbital is σ -antibonding with respect to all ligands in the coordination sphere but particularly for the ligands on the z-axis. For $[\text{Fe}(\text{CO})_5]$ we would assume that it is one of the CO's on the z-axis that is extruded, and for $[\text{Ru}(\text{CO})_4\text{PPh}_3]$ the CO trans to the PPh_3 is likely the labilized ligand.²⁷ But as noted above we could not have predicted that the loss of CO would occur exclusively.

The trinuclear species exhibit one-electron excited states at low energy which involve the population of orbitals which are strongly σ -antibonding with respect to the metal-metal bond.²⁸ Such states also have antibonding character



Scheme 1. One-Electron Orbital Diagram for D_{3v} , d^8 , $[M(CO)_5]$ or C_{3v} , d^8
 $[M(CO)_4L]$ ($M = Fe, Ru$).

with respect to metal-ligand bonding. But there is no evidence to suggest that the primary photoprocess is any other than metal-metal bond rupture. One obvious point of relevance is that the clusters absorb lower energy light than do the mononuclear species. Provided that the low energy absorptions can actually yield catalytically active material, the lower energy absorption of clusters represents a general advantage compared to mononuclear species where the same catalyst may result. A comparison of some of the relevant optical absorption spectra are given in Figure 1, and spectral data are given in Table I. The clusters may prove useful as photochemical precursors using visible light where many potential substrates are transparent; many functionalized organic materials absorb too strongly in the near-uv to allow use of the mononuclear catalyst precursors.

2. Photocatalyzed 1-Pentene Isomerization With Mono- and Trinuclear Iron and Ruthenium Precursors. Table II summarizes the findings relating to the use of $[Fe(CO)_5]$, $[Fe_3(CO)_{12}]$, $[Ru(CO)_4PPh_3]$, and $[Ru_3(CO)_9(PPh_3)_3]$ as the catalyst precursor for the 1-pentene isomerization represented in equation (9). First,

all of the species used are effectively thermally inert under conditions where photoactivation yields efficient isomerization. Second, all of the photoactivated systems ultimately yield a mixture of the linear pentenes which is very close to that expected at thermodynamic equilibrium.²⁹ Third, all of the catalyst precursors give "observed" quantum yields for 1-pentene disappearance which are high and typically exceed unity. Finally, the two cluster precursors are in fact active upon visible irradiation with wavelengths completely transmitted by the mononuclear catalyst precursors.

The 1-pentene is transparent to the near-uv or visible irradiation. The high quantum yields, thermodynamic ratios at long irradiation times, and the large number of pentene molecules reacted per molecule of catalyst initially added allow the conclusion that light activates efficient catalysis in each case.

Irradiation is required in order to sustain olefin isomerization; that is, when the light is turned off isomerization essentially stops. This is consistent with the finding that the isomerization quantum yields are high, but finite. For example, with $[\text{Fe}(\text{CO})_5]$ a minimum of one photon per hundred or so isomerizations is needed. Such may be consistent with the fact that the reactions are carried out in hermetically sealed ampules where CO recombination with the coordinatively unsaturated intermediates deactivates their catalytic activity. Under steady state illumination there is some steady state concentration of active species which declines upon termination of irradiation or as the metal complexes are irreversibly decomposed in side reactions.

Perhaps the most significant findings concern the initial product ratio (trans-2-pentene/cis-2-pentene). As seen in Table II the ratio of isomerization products depends on the catalyst precursor in the $[\text{Ru}(\text{CO})_4\text{PPh}_3]$ vs. $[\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3]$ comparison but the ratio is the same

for $[\text{Fe}(\text{CO})_5]$ and $[\text{Fe}_3(\text{CO})_{12}]$. The different ratio for the Ru species allows the conclusion that the cluster behaves differently than the mononuclear species. A different catalytically active species is formed giving different relative rates of cis- and trans-2-pentene production. Since $[\text{Ru}(\text{CO})_4\text{PPh}_3]$ logically produces a mononuclear catalyst, we conclude that the cluster yields a catalytically active species retaining some sort of cluster framework. What cannot be assessed is to what extent a mononuclear catalyst might be contributing to the activity found for the cluster. But the differing product ratios do evidence the viability of doing photocatalysis with clusters and the catalytically active species may have different properties compared to an appropriate mononuclear species.

The fact that the same product ratio is found for $[\text{Fe}(\text{CO})_5]$ and $[\text{Fe}_3(\text{CO})_{12}]$ is consistent with the conclusion that the dominant catalytically active species is the same and is mononuclear. However, it is true that different catalysts could be involved and not give a very different ratio of products. That is, all iron carbonyl-centered catalysts may give the same product ratio. That iron carbonyl-centered catalysts can yield differing isomerization product ratios is proven by the data given in Table III.¹² These data have been used to establish that irradiated phosphine-polymer anchored $[\text{Fe}(\text{CO})_n]$ ($n = 3, 4$) in fact remain anchored via the triarylphosphine groups during photocatalysis.¹² Here the point is that very selective CO loss obtains from $[\text{Fe}(\text{CO})_4\text{PPh}_3]$ and $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]$ leaving behind a coordination sphere which significantly influences the ratio of initial catalysis products. This evidence still does not prove that the catalyst from $[\text{Fe}(\text{CO})_5]$ and $[\text{Fe}_3(\text{CO})_{12}]$ is the same, but we shall assume that there is no reason for them not to give a detectably different ratio of products had different catalysts been generated. It is worth noting that the second

row metal-metal bond systems are generally more stable than the first row metal-metal bonded system, consistent with cluster retention in the second row Ru_3 system.

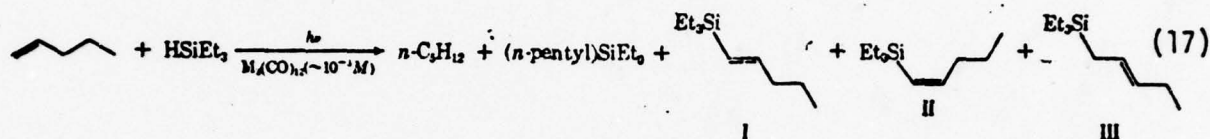
The nature of the photogenerated catalyst in the mononuclear case is logically one involving a mononuclear, π -allyl hydride species as the isomerization intermediate. Such a species likely first forms from the irradiation of an alkene complex resulting in CO extrusion followed by reversible internal oxidative addition to form the π -allyl hydride.⁹

The nature of the catalyst resulting from the $[\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3]$ is not clear; we have not detected substantial yields of any olefin complex in the experiments carried out thus far. Experiments aimed at elucidating the nature of the cluster catalyst and structure-activity relationships are underway in our laboratory.

3. Conclusions. On the basis of the primary photoprocesses and the photocatalyzed 1-pentene isomerization we can conclude that clusters have at least the advantage of being activated with lower energy light than mononuclear species. Further, the data allow the conclusion that clusters can remain intact upon photoactivation and yield different product ratios. Finally, the various mononuclear iron carbonyls in Table III illustrate the importance of selective ligand loss to leave behind a coordination sphere having specific structure-activity parameters. Such would be particularly valuable in designing photochemical precursors for specific processes depending on the ligands in the coordination sphere such as asymmetric hydrogenation.³⁰

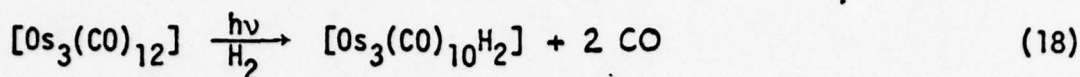
b. $[M_3(CO)_{12}]$ (M = Fe, Ru, Os) Photocatalyzed Reaction of Alkenes with Trialkylsilanes.

The foregoing section describes photocatalytic activity of trinuclear catalyst precursors with respect to alkene isomerization. The trinuclear, binary carbonyls of Fe, Ru, and Os are quite effective photocatalysts for alkene hydrosilation, equation (17), as has been previously



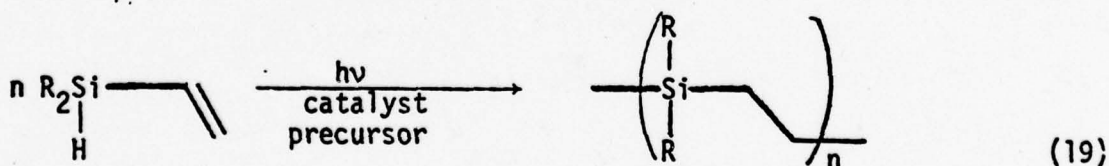
demonstrated in this laboratory.¹¹ Presumably, the primary photoprocess is still rupture of a metal-metal bond. Like alkene isomerization, hydrosilation chemistry involving alkenes gives an initial ratio of products which does not depend on whether the precursor is $[\text{Fe}(\text{CO})_5]$ or $[\text{Fe}_3(\text{CO})_{12}]$, Table IV. However, as Table V shows, there is a substantial difference in the product distribution depending on M when $[M_3(\text{CO})_{12}]$ is the catalyst precursor. Further, there is a qualitative difference in the behavior of $[\text{Os}_3(\text{CO})_{12}]$ compared to the Fe and Ru analogues in that the ratio of alkyl-/alkenyl-silanes is very different for the Os precursor. The qualitative difference in the Os cluster compared to the Fe and Ru species can be extended to the alkene isomerization reaction as well in that the isomerization occurs only slowly upon photoactivation of the Os cluster, whereas isomerization is rapid for M = Fe or Ru.

The distinction of $[\text{Os}_3(\text{CO})_{12}]$ may be correlated to the fact that the Os_3 unit is rugged and resists breakdown even under photochemical conditions where the Fe and Ru species can be light driven to mononuclear products.¹¹ Under H_2 , for example, photoreaction according to equation (18) obtains³¹ and

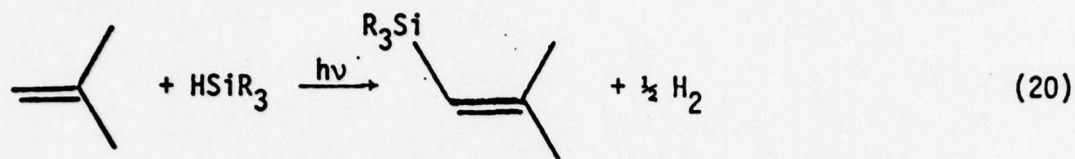


the resulting dihydride is a known catalyst for hydrogenation³² and alkene isomerization.³³ Preliminary findings³¹ in our laboratory show that photo-excitation of the dihydride in the presence of alkene at 25° yields a different ratio of catalytic products (hydrogenation vs. isomerization and ratio of isomeric products) compared to what obtains thermally under the same conditions. Irradiation of the dihydride appears to selectively accelerate thermal processes in such a way that catalytic products differ. Further elaboration of this important finding is underway.

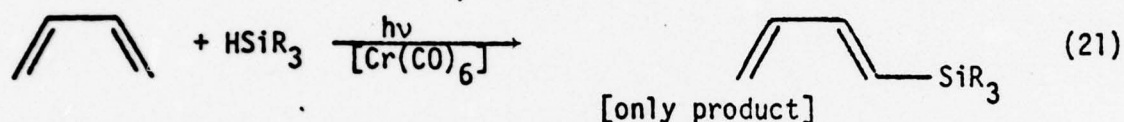
The data in Table V, and the more recent findings concerning $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$ allow the conclusion that metal-metal bonded catalyst precursors can lead to oxidative addition of H_2 or $\text{H-Si} \equiv$ and subsequent transfer to olefinic substrates. Synthetic importance for photo-catalyzed hydrosilation has not yet materialized, but it is interesting to speculate on whether photopolymerization according to chemistry as in equation (19) might be useful. Further, for the Fe or Ru precursors, it is



worth noting that a catalytic synthesis of vinylsilanes for which there is no acetylenic precursor is possible, e.g. equation (20).¹⁶ So far, the



specificity associated with the Fe, Ru, or Os systems has not yet equalled the $[\text{Cr}(\text{CO})_6]$ photocatalyzed hydrosilation 1,3-dienes, equation (21), where

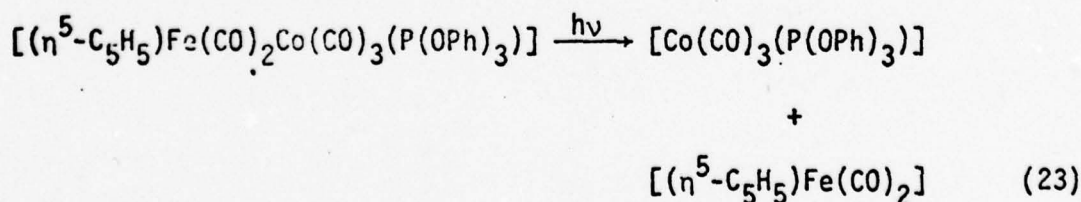
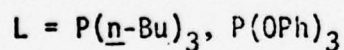


only 1,4-addition is found and only the cis-alkene is formed which does not undergo subsequent isomerization or hydrosilation.¹⁵ Finally, it is worth noting that photoinduced free radical chain processes are ruled out by the specificity of processes like that represented in equation (21) and the lack of reaction of the alkene and the formation of significant, but metal dependent, amounts of vinylsilane products with the Fe, Ru, Os catalysts starting with an alkene.

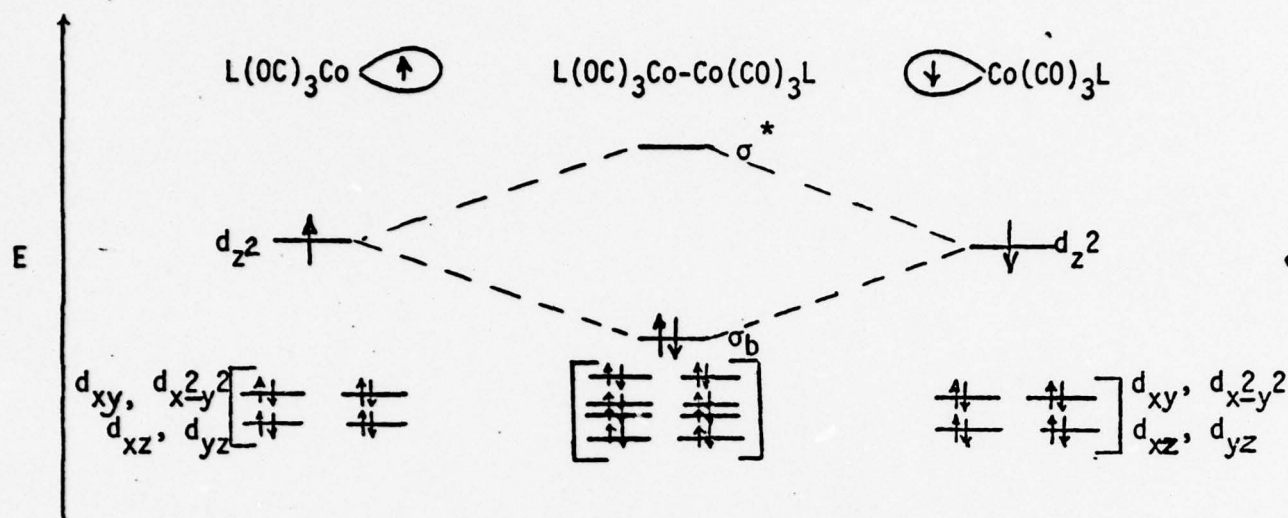
c. Photoactivation of Mononuclear Cobalt Carbonyl Catalysts Using Dinuclear, Metal-Metal Bonded Precursors.

Certain dinuclear cobalt carbonyl species are known hydroformylation catalysts.³⁴ We initially set out to photoactivate such organometallics, since metal-metal bond cleavage is an efficient photoprocess, and it is believed that mononuclear species are the actual catalytically active species.³⁴ Here we outline our findings for $[\text{Co}_2(\text{CO})_6\text{L}_2]$ ($\text{L} = \text{P}(\underline{n}\text{-Bu})_3$, $\text{P}(\text{OPh})_3$) and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Co}(\text{CO})_3\text{P}(\text{OPh})_3]$ as photochemical precursors to catalysts in the presence of Et_3SiH and 1-pentene.³⁵ The central question here concerns whether photogenerated 17-valence-electron species lead to catalytic activity. The cobalt-centered systems are a reasonable starting point here, but we have already noted that metal-metal bond cleavage is a very common, efficient, and clean photoreaction.^{3,24} Photoinitiated radical polymerizations⁸ are already known and dinuclear complexes absorbing much of the visible spectrum can be found.²⁴

1. Primary Photoprocesses.³⁵ Near-ultraviolet and visible irradiation of the metal-metal bonded complexes considered here proceeds according to equations (22) and (23). In all cases the 355 nm quantum yield exceeds 0.1, and



the homolytic cleavage appears to be clean.



Scheme II. One-Electron Orbital Scheme for $[\text{Co}_2(\text{CO})_6\text{L}_2]$.

Scheme II shows the one-electron orbital diagram for $[\text{Co}_2(\text{CO})_6\text{L}_2]$.

Figure 2 shows the optical spectra for the

three cobalt radical precursors, and Table I includes relevant optical spectral data. For $[\text{Co}_2(\text{CO})_6\text{L}_2]$ all low lying absorptions correspond to transitions terminating in an orbital strongly σ -antibonding with respect to the metal-metal bond. The orbital scheme for $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Co}(\text{CO})_3\text{L}]$ is similar but obviously the two photofragments are not identical and the d^7 , 17-valence-electron Fe-centered radical gives rise to one other relatively low-lying unoccupied orbital other than the σ^* orbital. The intense feature at ~360 nm in the optical spectra, Figure 2, is the $\sigma_b \rightarrow \sigma^*$ absorption in each case, and in one-electron terms such a transition can reduce the M-M or M-M' bond order to zero, consistent with the efficient photoinduced cleavage reactions found in such systems.²⁴

2. Photocatalysis Results.³⁵ Irradiation of the $[\text{Co}(\text{CO})_3\text{L}]$ radical sources under certain conditions leads to catalytic activity involving 1-pentene. Irradiation of the various precursors in the presence of 1-pentene alone leads to only very slow 1-pentene isomerization, Table VI. For $\text{L}=\text{P}(\text{OPh})_3$ there is definite activity beyond that associated with dark reaction under the same conditions, but the rate is extremely modest compared to the systems summarized in Tables II and III under essentially the same conditions. These results suggest that the radicals are not too reactive towards simple alkenes. Indeed, the $[\text{Co}_2(\text{CO})_6\text{L}_2]$ species can be recovered from irradiated solutions containing 1-pentene. The $[(\eta^3\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_3]$ radical, which might be regarded as comparable to the $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$, is, by comparison, fairly active as an alkene isomerization catalyst.³⁶

Irradiation of the $[\text{Co}(\text{CO})_3\text{L}]$ sources in the presence of 1-pentene and equimolar amounts of Et_3SiH results in rapid alkene isomerization and the production of small, but significant, amounts of n-pentane, Table VII. Small amounts of Si-containing products have also been detected but not analyzed quantitatively. The $[\text{Co}_2(\text{CO})_6(\text{P}(\text{n-Bu})_3)_2]$ complex is qualitatively less active than the two precursors to $[\text{Co}(\text{CO})_3\text{P}(\text{OPh})_3]$. Actually, the study of the $\text{P}(\text{OPh})_3$ complex was prompted by the finding that the addition of small amounts of $\text{P}(\text{OR})_3$ ($\text{R}=\text{Me}, \text{Ph}$) to the solutions containing $[\text{Co}_2(\text{CO})_6(\text{P}(\text{n-Bu})_3)_2]$ results in significantly enhanced photocatalysis rates. Qualitatively, the heterodinuclear $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Co}(\text{CO})_3(\text{P}(\text{OPh})_3)]$ is just as effective as the homodinuclear source of $[\text{Co}(\text{CO})_3(\text{P}(\text{OPh})_3)]$. The $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$ is qualitatively less active in these experiments, since irradiation of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4]$, a photochemical source of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$, results in essentially no reaction on the same time scale as found when $[\text{Co}(\text{CO})_3(\text{P}(\text{OPh})_3)]$ is generated at the same rate. The main distinction between $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Co}(\text{CO})_3(\text{P}(\text{OPh})_3)]$ and $[\text{Co}_2(\text{CO})_6(\text{P}(\text{OPh})_3)_2]$ is that the heterodinuclear species is less thermally active than the homodinuclear species with respect to the catalytic chemistry.

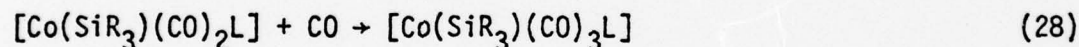
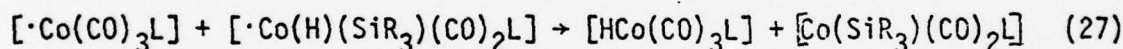
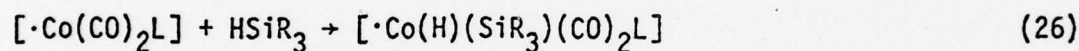
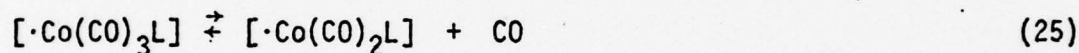
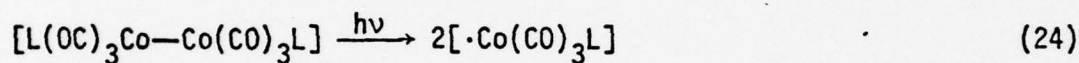
Spectral changes accompanying the photocatalysis obtain, and it has been determined that photocatalytic activity continues even after all metal-metal bonded complexes have been consumed. Further, while catalytic activity does persist in the dark after the catalyst has been photogenerated, light further accelerates the rate of the catalytic activity. These results are consistent with the photogeneration of mononuclear cobalt complexes which can be further excited with near-ultraviolet light to accelerate the catalysis.

The metal-metal bonded complexes exhibit thermal catalytic activity on a time scale long compared to that associated with the photocatalysis. The thermal products roughly correspond to what is found from the photocatalysis experiments. In both photocatalytic and thermal experiments there are modest amounts of n-pentane compared to the isomerization. The isomerization appears to result in very high initial trans- to cis-2-pentene ratios thermally or photochemically. Finally, the effect of the Et_3SiH is similar for both thermal and photocatalytic experiments. These various findings suggest that the thermally activated catalysis proceeds via the same mechanism as in the photocatalytic experiments. That the Fe-Co system is slower than the Co-Co complex, thermally, is consistent with the conclusion that the metal-metal bond is stronger in the Fe-Co case. Presumably, a completely thermally inert $[\geq \text{M-Co}(\text{CO})_3\text{L}]$ system would give no thermal catalysis corresponding to what we have found.

The formation of n-pentane, the small quantities of Si-containing products, and the strong effect from Et_3SiH all point to the conclusion that the catalytically active mononuclear Co-containing species is a hydride. The Et_3SiH is logically the hydride source from reaction of the photogenerated cobalt fragments. It is known that various metal-metal bonded carbonyls give hydride species when irradiated in the presence of silicon hydrides!³⁷ The detailed mechanism of formation of the hydride species is not clear at the present time, but it is well known that cobalt-carbonyl hydrides are capable of alkene isomerization,³⁸ and reduction to the alkane is not an unexpected result

given that such obtains under hydroformylation conditions. Use of H_2 as a hydride source has been attempted with our systems and alkane formation and alkene isomerization do obtain, but at 2 atm. H_2 the photocatalyzed isomerization rate is slower than found using $1M$ Et_3SiH under the same conditions. It is probably true that Et_3SiH is the better hydride source since the Si-H bond is weaker than the H-H bond. Further, it is likely that Si-Co bonded species also form and the Co-Si bond is likely stronger than the Co-H bond.

While the details of how cobalt-hydrides are formed are not clear, a plausible mechanism is represented by equations (24)-(28). The key steps



are the thermal loss of CO to form a 15-valence-electron species from the 17-valence-electron photofragment, equation (25) and the subsequent oxidative addition of $HSiR_3$. The intermediacy of 15-valence-electron species from 17-valence-electron photofragments has precedence in the formation of $[HM(CO)_5]$ ($M = Mn, Re$) via photolysis of $[M_2(CO)_{10}]$ in the presence of H_2 .³⁹ Further, oxidative addition of R_3SiH to such metal-metal bonded complexes³⁷ is also a known process and also likely proceeds via the mechanism outlined for H_2 . Substitution labile 17-valence-electron fragments seem to be common^{3,37,39-4} and such lability is crucial to their catalytic activity.

3. Conclusions. Dinuclear photochemical precursors to $[\text{Co}(\text{CO})_3(\text{P}(\text{OPh})_3)]$ give rise to catalytic activity under near-ultraviolet irradiation in the presence of a hydride source and alkene. The primary photofragments, 17-valence-electron species, do not themselves appear to be catalytic; rather such species likely react with the hydride source to form cobalt-hydrides which may then effect alkene isomerization or reduction to alkane. The findings allow the conclusion that the reactivity of photogenerated fragments varies considerably, $[\text{Co}(\text{CO})_3(\text{P}(\text{OPh})_3)] > [\text{Co}(\text{CO})_3(\text{P}(\text{n-Bu})_3)] > [(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$, but just what electronic/structural features are essential remain to be determined. Thermal activation at 25°C of the same catalytic chemistry can be found on a long time scale compared to photoactivation; strong M-Co bonds in $[\text{M-Co}(\text{CO})_3\text{L}]$ systems should prove generally less thermally active while weak M-Co bonds should promote greater thermal activity at 25°C.

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Table I. Electronic Spectral Features of Various Photochemical Catalyst Precursors.^a

Catalyst Precursors	Absorption Maxima, nm, (ϵ)	Catalyst Precursors	Absorption Maxima, nm, (ϵ)
$[\text{Fe}(\text{CO})_5]$	285 (3800) 240 (40,000)	$[\text{Co}_2(\text{CO})_6(\text{P}(\underline{n}\text{-Bu}_3))_2]$	367 (26,300) 278 (15,600)
$[\text{Fe}(\text{CO})_4(\text{PPh}_3)]$	273 (6400) 265 (7300)	$[\text{Co}_2(\text{CO})_6(\text{P}(\text{OPh})_3)_2]$	368 (21,300) 284 (13,200) (in 96% isooctane 4% benzene)
$[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]$	275 (7500) 248 (28,000)	$[\text{FeCp}(\text{CO})_2\text{Co}(\text{CO})_3(\text{P}(\text{OPh})_3)]$	554 (680) 369 (8240) (in 96% isooctane 4% benzene)
$[\text{Fe}_3(\text{CO})_{12}]$	603 (2900) 440 (2400) 315 (12,400) 275 (17,700) 192 (>70,000)		
$[\text{Ru}(\text{CO})_4(\text{PPh}_3)]$	273 (7500) 266 (8800) 259 (9400)		
$[\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3]$	506 (14,400) 388 (13,600) 302 (33,000) 262 (40,000)		

^aMeasurements in alkane at 25°C unless noted otherwise.

Table II. Comparison of Photocatalyzed 1-Pentene Isomerization Using Mono- and Trinuclear Catalyst Precursors.^a

Catalyst Precursor	Irrdn, λ (nm)	% Convn	ϕ	<u>trans/cis</u>
$[\text{Ru}(\text{CO})_4\text{PPh}_3]^b$	355	5.7	3.1	2.3
		14.9	2.7	2.0
$[\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3]$	355	5.3	0.6	4.3
		10.0	0.9	3.4
	436	6.7	1.2	3.0
		13.7	1.9	2.9
$[\text{Fe}(\text{CO})_5]^b$	550	6.9	---	3.3
		12.0	---	3.5
	355	6.2	91	2.8
		14.1	107	2.8
$[\text{Fe}_3(\text{CO})_{12}]$	355	7.3	27	3.0
		13.4	26	2.8
	436	8.5	41	2.9
		17.0	33	2.8
	550	8.7	---	3.0
		13.9	---	2.9

^aData from ref. 10. All experiments were carried out at 298 K in a degassed 1.76 M 1-pentene-benzene solution containing 1×10^{-3} M catalyst precursor. Quantum yields, ϕ , are $\pm 20\%$, and the ratio of trans- to cis-2-pentene products (trans/cis) is $\pm 5\%$. Irradiation at 550 or 436 nm was carried out using an appropriately filtered 550-W Hanovia Hg lamp and at 355 nm using a GE Blacklite. Light intensities at 436 or 355 nm were in the range of 1×10^{-6} to 1×10^{-7} einstein/min. All analyses were carried out using vapor-phase chromatography and each entry represents the average of at least two analyses.

^bNote that for these species 1×10^{-3} M does not completely absorb all incident photons at 355 nm in the 1.0 cm path-length ampules used to contain the samples. The ϕ 's have not been corrected in any way to account for this transmission of incident light. We take ϕ to be the number of 1-pentene molecules isomerized per incident photon. These are thus "observed" quantum yields.

Table III. Comparison of Photocatalyzed 1-Pentene Isomerization Using Various Mononuclear Fe-Centered Species.^a

Catalyst Precursor	% Conversion (Irrdn Time, min)	Observed ϕ^b	(trans/cis) ^c
[Fe(CO) ₅]	6.2 (2)	117	2.92
	11.9 (4)	112	2.93
	31.5 (15)	96	3.29
[Fe(CO) ₄ PPh ₃]	7.8 (5)	71	1.11
	12.7 (10)	58	1.20
	16.3 (15)	50	1.32
	19.8 (21)	43	1.43
	36.2 (60)	28	2.12
[Fe(CO) ₃ (PPh ₃) ₂]	8.6 (15)	12	0.56
	11.2 (30)	7.7	0.57
	18.4 (60)	7.7	0.58

^aData from ref. 12. All reactions are carried out in hermetically sealed, degassed ampules at 25°C. For the homogeneous precursors the concentration was $2 \times 10^{-3} \text{ M}$ in neat 1-pentene as solvent except for Fe(CO)₃(PPh₃)₂ which was 5.0 M 1-pentene in benzene as solvent.

^b ϕ is the number of 1-pentene molecules isomerized per photon incident on the sample. The irradiation source was a GE Black Lite, 355 nm.

^cRatio of trans-2- and cis-2-pentene products.

Table IV. Comparison of $[\text{Fe}(\text{CO})_5]$ and $[\text{Fe}_3(\text{CO})_{12}]$
Photocatalyzed Reaction of 1-Pentene and $\text{HSiEt}_3^{\text{a}}$.

Catalyst Precursor	Irrdn. λ (nm) ^b	% Conv.	Product Distribution			
			(n-pentyl)- SiEt ₃	(pentenyl)SiEt ₃ ^c		
				<u>I</u>	<u>II</u>	<u>III</u>
$[\text{Fe}(\text{CO})_5]$	355	2	16.5	21.3	52.3	9.9
		>80	17.5	16.1	51.2	15.2
$[\text{Fe}_3(\text{CO})_{12}]$	355	2	6.1	20.2	62.9	10.9
		30	9.1	20.3	58.9	11.7
		80	15.9	17.2	51.7	15.1
$[\text{Fe}_3(\text{CO})_{12}]$	550	1	4.8	17.5	66.2	11.5
		4	6.5	18.6	64.3	10.6
		26	8.2	20.7	60.4	10.6

^aData from ref. 11. One mL samples of 10^{-3}M catalyst precursor in degassed 1:1 mole ratio of 1-pentene and HSiEt_3 .

^b355-nm irradiation was with a GE Black Lite and the 550 nm irradiation was with a filtered 550-W Hanovia medium pressure Hg lamp.

^cFor identity of I, II, III, see text.

Table V. Metal Dependence of $[M_3(CO)_{12}]$ Photocatalyzed Reaction of 1-Pentene and $HSiEt_3$ ^a.

Catalyst Precursor	Irrdn. Time	% Conv	% $n-C_5H_{12}$	% (n-pentyl)- SiEt ₃	% (pentenyl)SiEt ₃ ^b		
					I	II	III
$[Fe_3(CO)_{12}]$	5 min	2	49.0	4.2	8.8	33.0	4.9
	1 hr	15	47.4	4.5	9.2	33.6	5.3
	18 hr	80	44.4	8.9	9.6	28.8	8.4
$[Ru_3(CO)_{12}]$	1 hr	15	48.4	3.5	42.8	4.6	~0.6
	2 hr	30	48.7	3.2	40.8	5.7	1.5
	24 hr	96	46.1	2.8	45.2	4.3	1.5
$[Os_3(CO)_{12}]$	1 hr	24	13.4	69.8	13.9	2.9	<1
	24 hr	>99	15.0	63.2	17.7	4.1	<1

^aData are from ref. 11. Neat, 1:1 mole ratio of 1-pentene and $HSiEt_3$.
One mL degassed solutions of $10^{-3}M [M_3(CO)_{12}]$ irradiated with GE Black Lite at 298°K.

^bSee text for identity of I, II, III.

Table VI. Comparison of Photocatalyzed 1-Pentene Isomerization Using Precursors to $[\text{Co}(\text{CO})_3\text{L}]$.

Catalyst Precursor, (conc.)	Conditions ^a	Irrdn Time, h	Analysis, % ^b		
			n-pentane	1-pentene	trans-2-pentene cis-2-pent
$[\text{Co}_2(\text{CO})_6(\text{P}(\text{n-Bu})_3)_2]$ ($2.64 \times 10^{-3}\text{M}$)	3.6M 1-pentene in n-octane	0	---	99.7	0.20
		94	---	99.7	0.23
		[thermal control]	---	99.7	0.21
$[\text{Co}_2(\text{CO})_6(\text{P}(\text{OPh})_3)_2]$ ($8.97 \times 10^{-4}\text{M}$)	1.0M 1-pentene in benzene	0	---	99.3	0.28
		76	0.28	92.0	5.05
		[thermal control]	---	99.3	0.40

^aAll experiments run at 25° C using 1.0 ml samples freeze-pump-thaw degassed in at least four cycles and hermetically sealed in Pyrex ampules. Irradiation was with a GE Blacklite with principal output at 355 nm $\pm$ 15 nm providing 1.6×10^{-6} ein/min incident on the sample.

^bAnalysis of C_5 mixture by vpc against n-hexane as an internal standard.

Table VII. Photocatalyzed Reactions of 1-Pentene in the Presence of Et_3SiH Using Precursors to $[\text{Co}(\text{CO})_3\text{L}]^a$.

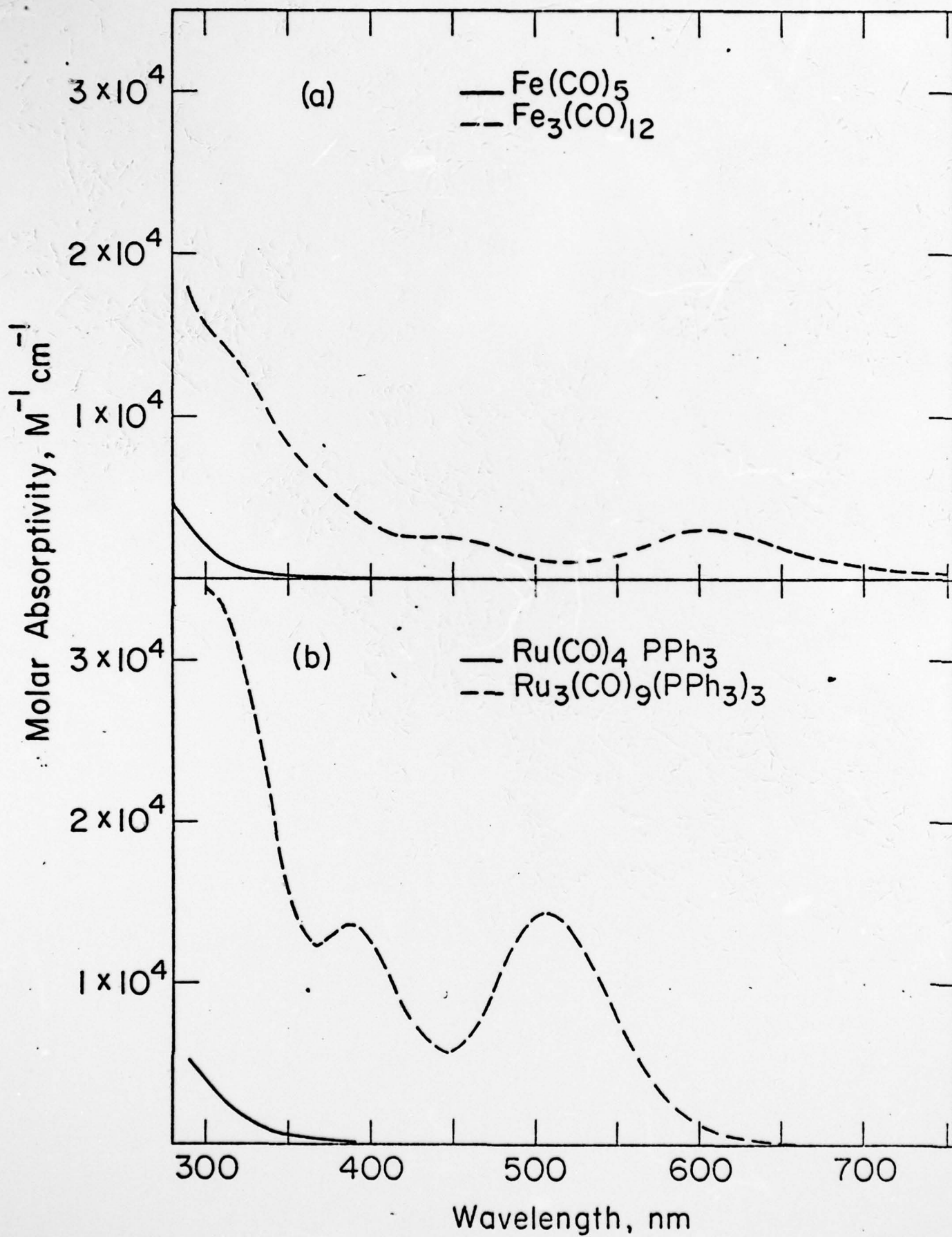
Catalyst Precursor, (conc.)	Conditions	Irrdn Time, h	Analysis, %			
			n-pentane	1-pentene	trans-2-pentene	cis-2-pentene
$[\text{Co}_2(\text{CO})_6(\text{P}(\underline{n}\text{-Bu})_3)_2]$ ($2.65 \times 10^{-3}\text{M}$)	1.0M HSiEt_3 1.0M 1-pentene in n-octane	0	---	99.7	0.20	0.03
		52	0.93	94.0	3.61	1.51
$[\text{Co}_2(\text{CO})_6(\text{P}(\text{OPh})_3)_2]$ ($8.97 \times 10^{-4}\text{M}$)	1.0M HSiEt_3 1.0M 1-pentene in benzene	0	---	99.6	0.28	0.20
		5	3.07	46.0	37.0	13.9
		[thermal control]	0.12	97.8	1.29	0.78
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{-Co}(\text{CO})_3(\text{P}(\text{OPh})_3)]$ ($1.79 \times 10^{-3}\text{M}$)	1.0M HSiEt_3 1.0M 1-pentene in benzene	0	---	99.6	0.22	0.20
		7	2.74	7.46	76.2	13.6
		[thermal control]	0.02	99.1	0.65	0.22
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4]$ ($2.65 \times 10^{-3}\text{M}$)	3.6M HSiEt_3 3.6M 1-pentene (neat)	0	0.04	99.6	0.19	0.14
		96	0.77	98.3	0.60	0.35
		[thermal control]	0.04	99.3	0.41	0.25

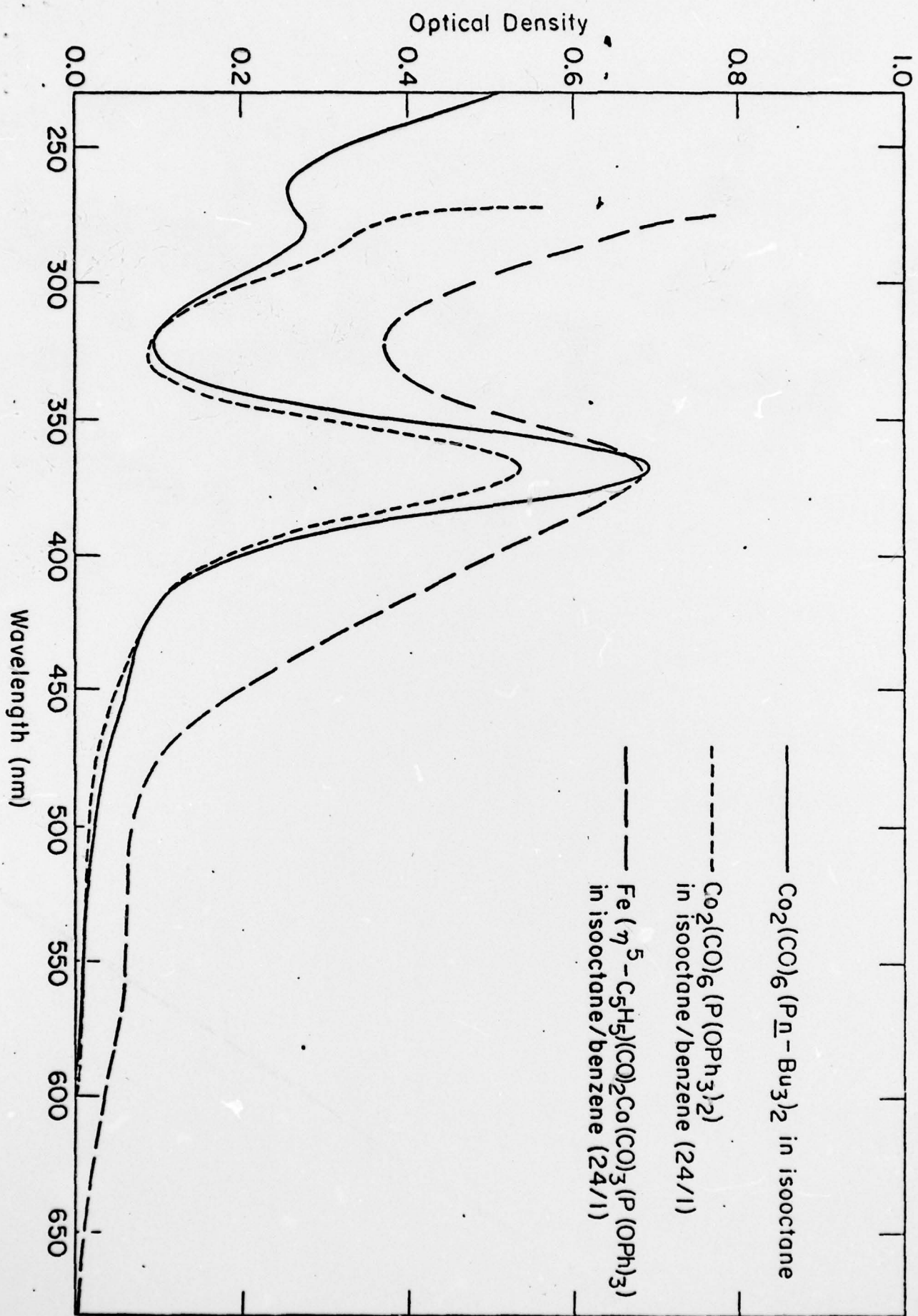
^aSee notes for Table VI. Data from ref. 35.

Figure Captions

Figure 1. Electronic absorption spectra at 25°C in alkane solvent;
for absorptivities and band maxima see Table I.

Figure 2. Electronic absorption spectra at 25°C; for absorptivities
and band maxima see Table I.





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