

controls the observed redox potential.

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Transition-Metal Photocatalysis: Rhodium(I)-Promoted Hydrosilation Reactions

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Rhodium(I) complexes were found to be active photocatalyst precursors for the hydrosilation reaction. Substrates studied included Si-H and Si-vinyl functionalized siloxanes as well as simple terminal alkenes. Reaction rates dramatically increased when the mixtures were photolyzed in the presence of air or soluble oxidizing agents. Near-UV irradiation enhanced dissociation of the catalyst precursors and promoted oxidation of dissociated phosphine or phosphite ligands in $\text{ClRh}(\text{O}_2)(\text{PPh}_3)_3$ and the complexes formed between $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{P}(\text{OEt})_3$, and $\text{P}(\text{O}i\text{Bu})_3$. Efficiency of $\text{ClRh}(\text{PPh}_3)_2$ formation was shown to be the rate-determining criterion in the oxidized Rh-PPh₃ system. The positive oxygen dependence and unequivocally photocatalytic nature of hydrosilation in the presence of the Rh(I) compounds are unprecedented in Si-H addition catalysis. The previously studied $\text{Fe}(\text{CO})_5$ hydrosilation catalysts are completely inactive in air, and even in vacuo the lifetime of the active iron species subsequent to irradiation is exceedingly short compared to that of the Rh(I) intermediates described here.

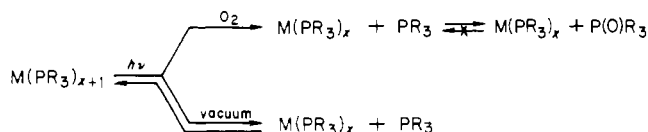
Introduction

The activation of alkenes toward addition and isomerization reactions by transition-metal complexes has received considerable attention in the recent literature.¹ Studies on metal-catalyzed hydrogenation, hydroformylation, and hydrosilation have defined a common ground between diverse areas of chemistry. Furthermore, since these reactions are crucial to process chemistry, such studies have created a useful interface between academia and industry.

Metal complexes in excited states can often decay via ligand extrusion or bond scission to produce reactive catalytic species otherwise unobtainable under ambient conditions.² The ground-state precursors to these intermediates may be classified as photoassistance or photocatalytic agents depending on their activity subsequent to irradiation. Photoassistance agents require continuous irradiation to maintain a catalytically viable species, while true photocatalysts produce thermally active decay products that continue to turn over substrate in the dark following initial irradiation. Even though many classes of low-valent transition-metal complexes and organometallics are photochemically active upon near-ultraviolet excitation, there has been surprisingly little work done in the area of light-generated catalysts.³

Practically all of the literature reports on photoinduced alkene chemistry deal with binary metal carbonyls and their simple substitution products as catalyst precursors.⁴⁻¹⁵ Loss

Scheme I



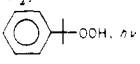
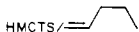
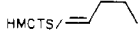
of CO from these complexes is almost 100% efficient upon irradiation into the appropriate ligand field bands. Other low-valent metal compounds containing noncarbonyl ligands also exhibit d-d transitions in the near-UV, and they should at least in theory give rise to similar photodissociative chemistry. Preferential loss of the nitrogen ligand from $\text{M}(\text{CO})_5\text{L}$ has been observed with good quantum efficiency for various mixed carbonyl-amine group 6B complexes,^{16,17} and it was very recently shown that $\text{W}[\text{P}(\text{OMe})_3]_6$ readily dissociates under mercury-lamp irradiation.¹⁸

When the labilized ligand is a phosphine or phosphite and the reaction is conducted in air, a secondary photoreaction can readily occur: oxidation of free ligand to phosphine oxide¹⁹ or phosphate-phosphonate mixtures,²⁰ respectively. Since the latter classes of P(V) compounds are less likely to strongly coordinate than their unoxidized P(III) counterparts,²¹ irradiation can conceivably generate high concentrations of coordinatively unsaturated centers in two ways: ligand dissociation and free ligand modification to prevent back-reaction (Scheme I). Previous qualitative observations have in fact indicated that oxygen is a cocatalyst for thermal processes built

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Table I

catalyst precursor	reaction conditions	substrates	$10^8 \Delta$, mol/min	ϕ_{355}
CIRh(PPh ₃) ₃	vacuum, dark	TMDS-DVTMDS	5.0	
CIRh(PPh ₃) ₃	O ₂ , dark	TMDS-DVTMDS	19.4	
CIRh(PPh ₃) ₃	O ₂ , h ν	TMDS-DVTMDS	41.7	1.0
CIRh(PPh ₃) ₃	 h ν	TMDS-DVTMDS	125	3.1
Rh(I)-P(OBu) ₃	O ₂ , h ν	HMCTS/ 	600	21
Rh(I)-PBu ₃	O ₂ , dark	TMDS-DVTMDS	600	
Rh(I)-PBu ₃	O ₂ , h ν	TMDS-DVTMDS	1450	21
Fe(CO) ₅	O ₂ , h ν	TMDS-DVTMDS	0.1	
Fe(CO) ₅	vacuum, h ν	TMDS-DVTMDS	3.2	0.08
Fe(CO) ₅	vacuum, h ν	HMCTS/ 	313	7.4

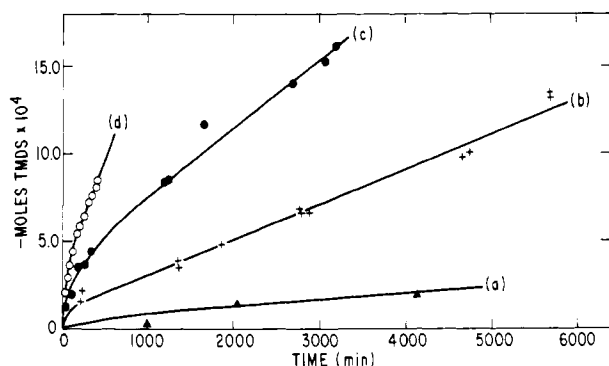


Figure 1. Disappearance of TMDS vs. time for the CIRh(PPh₃)₃ system under various conditions: (a) degassed CH₂Cl₂ solution ([Rh] = 2.77 × 10⁻³ M); (b) benzene solution prepared in air and kept in the dark ([Rh] = 1.16 × 10⁻³ M); (c) benzene solution prepared in air and irradiated (λ = 366 nm, [Rh] = 1.13 × 10⁻³ M); (d) oxygen-saturated cumene solution (irradiated, λ = 366 nm, [Rh] = 9.83 × 10⁻⁴ M). The initial substrate concentrations were [TMDS] = 0.068 M and [DVTMDS] = 0.30 M.

around phosphine-containing metal catalysts.²²⁻²⁴

With the above considerations in mind, we have studied Wilkinson's hydrogenation catalyst CIRh(PPh₃)₃²⁵ and several related complexes with regard to their hydrosilation activity in air and under the influence of near-UV irradiation.

Results

Even though rhodium-catalyzed hydrosilation has been extensively investigated,^{22,26-31} we felt that the effects of oxygen and irradiation mentioned above deserved further study. From a practical viewpoint, we also noted that siloxane substrates, the major raw materials of the silicone industry, were seldom used in simple hydrosilation experiments. Our model system except where otherwise noted consisted of a 1:4 molar ratio of *sym*-tetramethyldisiloxane (TMDS) and 1,3-divinyltetramethyldisiloxane (DVTMDS). These compounds are the smallest stable siloxanes commercially available that contain Si-H and Si-vinyl functionality.

Figures 1 and 2 illustrate disappearance profiles for the TMDS-DVTMDS system catalyzed by several rhodium complexes under various conditions. Dramatic differences are

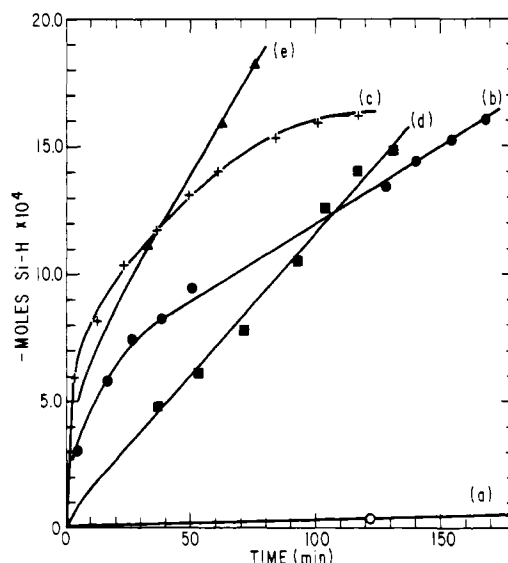


Figure 2. Disappearance of Si-H vs. time for Rh(I)-PR₃ systems: (a) tetradecane solution of HMCTS and 1-pentene (0.20 M) prepared in air containing CIRh[P(OPh)₃]₃ ([Rh] = 2.54 × 10⁻⁴ M, near-UV irradiated, λ = 300-450 nm); (b) benzene solution of TMDS (0.068 M) and DVTMDS (0.30 M) prepared in air containing Rh(I)-PBu₃ catalyst ([Rh] = 1.74 × 10⁻³ M, no irradiation); (c) repeat of (b) under 366 nm irradiation; (d) repeat of (b) using Rh(I)-P(OEt)₃ catalyst ([Rh] = 1.70 × 10⁻³ M, no irradiation); (e) repeat of (a) using Rh(I)-P(OBu)₃ catalyst under 366-nm irradiation ([Rh] = 4.75 × 10⁻³ M).

seen in the CIRh(PPh₃)₃ catalyzed addition reaction as the environment changes from airless through ambient-dark to ambient-irradiated. Introduction of a soluble oxidizing agent prior to irradiation gives the fastest disappearance of TMDS as shown in Figure 1. Figure 2 compares Si-H disappearance rates for rhodium(I) complexes ligated with PBu₃, P(OEt)₃, P(OBu)₃, and P(OPh)₃. Rate enhancement upon photolysis is observed for the alkylphosphine and alkyl phosphite containing complexes, but CIRh[P(OPh)₃]₃ is a poor catalyst at room temperature both in the dark and under UV irradiation.

Data in Figure 3 illustrate the photocatalytic nature of the CIRh(PPh₃)₃ system. In the presence of oxidizing agents we observe a continuing loss of TMDS following near-UV irradiation. Although the magnitude of TMDS disappearance decreases in both cases after photolysis, it still exceeds that of the nonirradiated control. Reaction continues to completion in the dark beyond the time frame of Figure 3. A true photocatalyst is also generated on irradiation of the Rh(I)-PBu₃ complex formed from RhCl₃·3H₂O and excess PBu₃ (vide infra). Disappearance quantum yields are on the order of 20 in this system vs. 3 in the CIRh(PPh₃)₃-2-phenyl-2-hydroperoxypropane reaction. Pentacarbonyliron by comparison fared poorly in catalyzing TMDS-DVTMDS addition. Disappearance data from these studies are given in Table I.

As noted in the Introduction, it is likely that UV irradiation not only promotes ligand dissociation from rhodium-pnicogen

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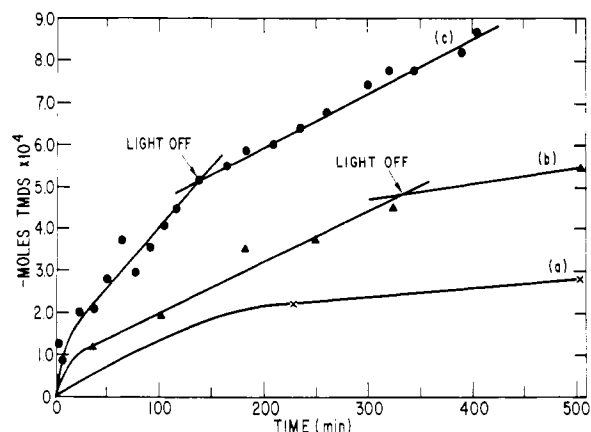


Figure 3. Photocatalytic behavior of $\text{ClRh}(\text{O}_2)(\text{PPh}_3)_3$: (a) $[\text{TMDS}] = 0.068 \text{ M}$ and $[\text{DVTMDS}] = 0.30 \text{ M}$ ($[\text{Rh}] = 1.16 \times 10^{-3} \text{ M}$ in benzene, no irradiation); (b) repeat of (a) under 366-nm irradiation ($[\text{Rh}] = 1.13 \times 10^{-3} \text{ M}$); (c) repeat of (b) in cumene ($[\text{Rh}] = 9.83 \times 10^{-4} \text{ M}$).

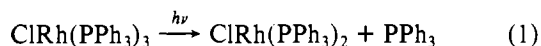
Table II. Quantum Yield Determinations for

$$\text{PR}_3 + \frac{1}{2}\text{O}_2 \xrightarrow[\text{CH}_2\text{Cl}_2]{h\nu} \text{P}(\text{O})\text{R}_3$$

R	ϕ	R	ϕ
Ph	3.3 ^a	Bu	3.3 ^b
OPh	0.0001 ^b	OBu	1.0 ^b

^a Reference 19. ^b $\lambda = 350\text{--}360 \text{ nm}$ (GE black light).

complexes but also accelerates free ligand oxidation to poorly coordinating $\text{P}(\text{O})\text{R}_3$ species. Experiments were conducted to estimate quantum yields for eq 1 and 2.



(R = Ph, Bu, OPh, OBU)

Thermal dissociation of $\text{ClRh}(\text{PPh}_3)_3$ undoubtedly takes place in solution, but there is little agreement on the magnitude of the equilibrium constant,^{25,32-34} especially when oxygen is present.³⁵ Electronic spectra of $\text{ClRh}(\text{PPh}_3)_3$ in degassed and oxygenated CH_2Cl_2 solution differ sharply as pointed out by Geoffroy and Keeney.³⁶ Irradiation of $\text{ClRh}(\text{PPh}_3)_3$ solutions containing Et_3SiH in air leads to $\text{HRhCl}(\text{PPh}_3)_2\text{SiEt}_3$ formation. The latter compound was prepared independently according to the procedure of Haszeldine et al.,²⁷ and its spectrum showed only a broad shoulder to the red of coordinated PPh_3 bands ($\lambda_{\text{max}} \approx 290 \text{ nm}$), tailing into the visible. Monitoring the disappearance of the original 366-nm band under UV vs. in the dark showed that the dissociation is photoaccelerated, although a thermal component is also present. We calculate the quantum yield for dissociation to be 0.09. Aerial photooxidation of phosphine and phosphite molecules proceeds with quantum efficiency of unity or greater for PBU_3 and $\text{P}(\text{OBU})_3$ (as well as for PPh_3),¹⁹ but virtually no oxidation of $\text{P}(\text{OPh})_3$ is detectable even under prolonged exposure to an unfiltered medium-pressure mercury lamp. These results are presented in Table II.

Since $\text{ClRh}(\text{PPh}_3)_3$ thermally or photochemically transforms to $\text{HRhCl}(\text{PPh}_3)_2\text{SiR}_3$ in degassed or aerated environments, we conducted experiments comparing the catalytic activity of

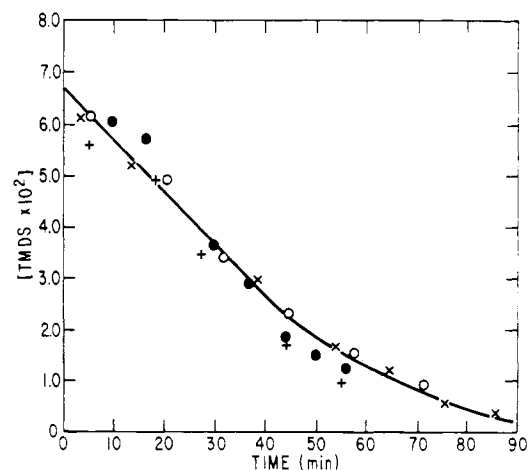


Figure 4. Disappearance of TMDS vs. time with $\text{HRhCl}(\text{PPh}_3)_2\text{SiMe}_2\text{Cl}$ catalyst in air: X, room temperature and dark ($[\text{Rh}] = 1.61 \times 10^{-3} \text{ M}$); O, 70 °C under 366-nm irradiation ($[\text{Rh}] = 1.64 \times 10^{-3} \text{ M}$); +, 70 °C and dark ($[\text{Rh}] = 1.70 \times 10^{-3} \text{ M}$); ●, $\text{ClRh}(\text{O}_2)(\text{PPh}_3)_3$ at 70 °C in the dark ($[\text{Rh}] = 1.00 \times 10^{-3} \text{ M}$).

$\text{ClRh}(\text{PPh}_3)_3$ to that of a preformed H-Rh-Si complex. Results hydrosilations that $\text{HRhCl}(\text{PPh}_3)_2\text{SiMe}_2\text{Cl}$ catalyst very readily interacts with the TMDS-DVTMDS system, giving disappearance rates superior to those seen for $\text{ClRh}(\text{PPh}_3)_3$. The rate is temperature independent between 25 and 70 °C as well as being insensitive to near-UV irradiation. As shown in Figure 4, a similar disappearance rate for TMDS is obtained at 70 °C with use of $\text{ClRh}(\text{PPh}_3)_3$.

Discussion

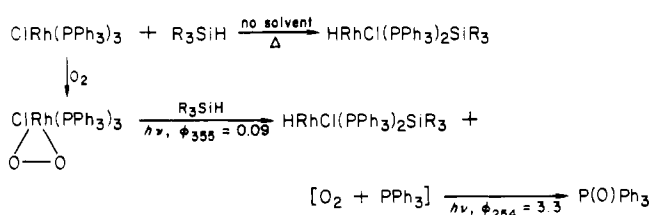
Catalysis of hydrosilation by rhodium(I)-phosphine or -phosphite complexes is strongly affected by reaction conditions as well as the nature of the catalyst. The hydrosilations described here are remarkable in their oxygen/oxidizing agent dependence. Spectral evidence supports the notion that the actual precursor to the active complex in the $\text{ClRh}(\text{PPh}_3)_3$ system is the soluble mononuclear oxide $\text{ClRh}(\text{O}_2)(\text{PPh}_3)_3 \cdot n\text{CH}_2\text{Cl}_2$ characterized by Bennett and Donaldson.³⁷ A second, more insoluble dimeric oxide $[\text{ClRh}(\text{O}_2)(\text{PPh}_3)_2 \cdot \text{CH}_2\text{Cl}_2]_2$ is a less likely component in homogeneous oxidized $\text{ClRh}(\text{PPh}_3)_3$ solutions.^{38,39} Ligand dissociation, the key first step in catalyst generation, appears to be more facile in rhodium-oxo complexes, considering molecular weight evidence³³ and enhanced hydrogenation rates over intentionally oxidized $\text{ClRh}(\text{PPh}_3)_3$.⁴⁰

The striking increases in hydrosilation rate observed upon $\text{ClRh}(\text{PPh}_3)_3$ irradiation in the presence of oxidizing agents underline the importance of both photochemical processes possible within this system. Rate increases in the dark under O_2 vs. in vacuo reflect the added facility of PPh_3 dissociation from $\text{ClRh}(\text{O}_2)(\text{PPh}_3)_3$ vs. $\text{ClRh}(\text{PPh}_3)_3$. Photogeneration of coordinatively unsaturated rhodium centers proceeds on top of this thermal dissociation with modest quantum efficiency while the secondary photoreaction involving free ligand oxidation ensures the high concentration of open coordination sites necessary for faster turnover by preventing the reverse reaction. Continued catalytic activity subsequent to irradiation can be rationalized in terms of the substrates (TMDS or DVTMDS) capturing photogenerated $\text{ClRh}(\text{PPh}_3)_2$. The quantity of $\text{ClRh}(\text{PPh}_3)_2$ groups tied up with vinyl or Si-H functionality ultimately determines the disappearance rate following irradiation. As it will be shown below, maximum conversion of $\text{ClRh}(\text{O}_2)(\text{PPh}_3)_3$ to an hydridorhodium intermediate via in-

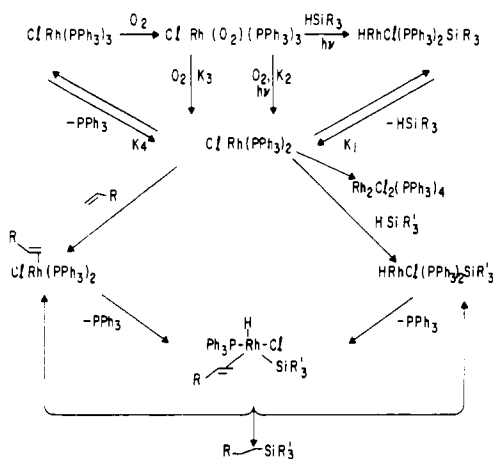
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Scheme II



Scheme III



teraction with TMDS is crucial in driving hydrosilation. The direct photoconversion of the oxorhodium complex to $\text{HRhCl}(\text{PPh}_3)_2\text{SiR}_3$ is partly responsible for the observed rate increases (Scheme II).

Quantum yield magnitudes for free ligand photooxidation correlate well with observed catalytic activity (Tables I and II). This is particularly obvious on comparing the $\text{ClRh}[\text{P}(\text{OPh})_3]_3$ and $\text{ClRh}(\text{PPh}_3)_3$ results. Since free $\text{P}(\text{OPh})_3$ from photoinduced dissociation is resistant to oxidation, it is likely that a re-coordinating back-reaction would lead again to $\text{ClRh}[\text{P}(\text{OPh})_3]_3$. Electronic spectra of $\text{ClRh}[\text{P}(\text{OPh})_3]_3$ and $\text{ClRh}(\text{PPh}_3)_3$ are rather similar for solutions prepared in air as illustrated in Figure 5. The 366-nm band in the $\text{ClRh}(\text{PPh}_3)_3$ spectrum has been assigned to the oxorhodium compound $\text{ClRh}(\text{O}_2)(\text{PPh}_3)_3 \cdot n\text{CH}_2\text{Cl}_2$.^{36,41} This band may indeed have d-d character as evidenced by a quantum yield of 0.09 for PPh_3 dissociation upon near-UV excitation of the complex in solution. In their experiments on the photodissociation of *trans*- $\text{ClRh}(\text{CO})(\text{PPh}_3)_2$ in solution in air, Geoffroy et al. observed that the reaction (yielding CO_2 , $\text{P}(\text{O})\text{Ph}_3$, and an oligomeric oxorhodium complex) was inhibited by excess PPh_3 , suggesting that photopromoted PPh_3 loss was a primary dissociation process.⁴² The lack of photocatalytic activity with $\text{ClRh}[\text{P}(\text{OPh})_3]_3$ suggests that ligand oxidation is more important than enhanced dissociation in these systems.

We have demonstrated that the oxidation product of $\text{ClRh}(\text{PPh}_3)_3$ gives rise to a truly photocatalytic system by following TMDS disappearance through many additional turnovers after irradiation. If neither oxygen nor 2-phenyl-2-hydroperoxypropane takes part in actual coordination to an unsaturated intermediate, we can ascribe the observed disappearance rate differences to the magnitudes of K_2 and K_3 in Scheme III. Comparison of $\text{ClRh}(\text{PPh}_3)_3$ catalysis to that of metal carbonyl promoted hydrosilation is of interest. The latter precursors require air-free conditions for successful initiation.^{11,13,14} Although photocatalysis was claimed for Cr-

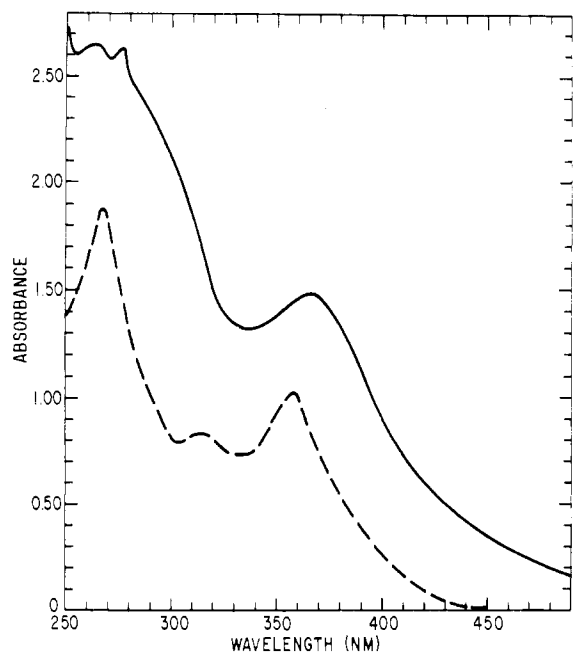


Figure 5. Electronic spectra of $\text{ClRh}(\text{PPh}_3)_3$ (—) and $\text{ClRh}[\text{P}(\text{OPh})_3]_3$ (---) in aerated in CH_2Cl_2 solution ($[\text{Rh}-\text{PPh}_3] = 7.86 \times 10^{-5} \text{ M}$, $[\text{Rh}-\text{P}(\text{O})\text{Ph}_3] = 2.20 \times 10^{-4} \text{ M}$).

(CO)₆,¹¹ $\text{Fe}(\text{CO})_5$,^{13,14} and the iron triad trinuclear dodecacarbonyls,¹⁴ in only one case were data presented illustrating minor increases of product following small $h\nu$ -induced conversions on holding previously irradiated samples in the dark.¹¹ Quantum yields exceeding unity for reactant consumption were given as evidence for photocatalysis, although photoassistance agents could also give this result. Interestingly, $\text{Fe}(\text{CO})_5$ proved to be a poor catalyst for TMDS-DVTMDS addition even in vacuo. Experiments conducted with $\text{Fe}(\text{CO})_5$ -TMDS-DVTMDS (molar ratios of 1:10:10) partially explained this anomaly in that TMDS disappearance rapidly commenced on irradiation up to a point where between 2 and 3 mol of TMDS/mol of $\text{Fe}(\text{CO})_5$ were lost. Further irradiation induced practically no more loss of TMDS or DVTMDS. We are currently examining the nature of the highly air-sensitive products of this reaction, but it is quite evident that they are not efficient hydrosilation catalysts. In a less complicated evaluation $\text{Fe}(\text{CO})_5$ promoted the addition of heptamethylcyclotetrasiloxane $(\text{Me}_2\text{SiO})(\text{SiMe}_2\text{O})_2(\text{SiMeHO})$ (HMCTS) to 1-pentene with good quantum efficiency as long as the system was continuously irradiated. Cessation of irradiation immediately quenched reactant disappearance (Table I).

Our experiments with rhodium(I) catalyst precursors other than the well-characterized $\text{ClRh}(\text{PPh}_3)_3$ ²⁵ and $\text{ClRh}[\text{P}(\text{OPh})_3]_3$ ⁴³ gave interesting results while raising questions about the fundamental nature of the catalysts. While $\text{ClRh}[\text{P}(\text{OPh})_3]_3$ was a poor catalyst under all conditions (O_2 , vacuum, dark, $h\nu$), the complexes of Rh(I) with PBu_3 , $\text{P}(\text{OEt})_3$, and $\text{P}(\text{OBu})_3$ actively catalyzed hydrosilation. Reactions of the last three ligands with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ or $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ led to various products depending on which Rh parent was used, the Rh:P molar ratio, and reaction conditions. For example, the Rh(III) adducts formed between PBu_3 and $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ ⁴⁴ can be converted to multinuclear Rh(I) complexes by heating with excess phosphine. These presently incompletely characterized compounds were used in the experiments described herein, giving faster hydrosilation rates than the known Rh(III)- PBu_3

(41) Reference 36 assigns the 366-nm band to $[\text{RhCl}(\text{O}_2)(\text{PPh}_3)_2]_2 \cdot 2\text{CH}_2\text{Cl}_2$. It was later shown that the more soluble species in $\text{ClRh}(\text{PPh}_3)_3$ oxidation is indeed the monomer.³⁷

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adducts. Studies on the synthesis and structure of the new complexes will be reported in due course. Similar reactions with alkylphosphites give rise to Rh(I)-Rh(III) mixtures. We were unable to purify products from $P(OEt)_3$ or $P(OBu)_3$ reactions with either $RhCl_3 \cdot 3H_2O$ or $Rh_2(CO)_4Cl_2$, but preliminary electronic spectral data support the notion of dinuclear metal-metal bonded frameworks.⁴⁵ Larock et al. have recently noted that rhodium(I) phosphine or phosphite catalysts for internal cyclization of unsaturated aldehydes are best prepared by adding 4 equiv of PR_3 to $Rh_2(C_8H_{14})_4Cl_2$ in situ.⁴⁶ This stoichiometry suggests the intermediacy of a chloro-bridged rhodium(I) dimer in solution. Similarity in catalytic activity between the PBu_3 and alkyl phosphite complexes argues for similar initial structure and mechanism of breakdown, possibly involving radical species from metal-metal bond homolysis.⁴⁷

The complexes $HRhCl(PPh_3)_2SiR_3$ arising from thermolysis of $ClRh(PPh_3)_3$ in $HSiR_3$ have been well studied over the past 15 years.^{22,27,30} Reductive elimination of $HSiR_3$ is facile in the presence of CO or PF_3 , and dimeric $Rh_2(PPh_3)_4Cl_2$ is formed along with $HSiR_3$ on heating in the absence of addends. Our data indicate that preformed $HRhCl(PPh_3)_2SiMe_2Cl$ readily enters into hydrosilation cycles, probably via elimination of $HSiMe_2Cl$ and coordination of vinylsiloxane (DVTMDS) or oxidative addition of hydro-siloxane (TMDS) followed by further PPh_3 labilization. It is interesting to note that TMDS-DVTMDS addition catalyzed by $HRhCl(PPh_3)_2SiMe_2Cl$ is temperature and irradiation independent, besides being similar in rate to the $ClRh(PPh_3)_3$ system at 70 °C (Figure 4). This result suggests that clean generation of $ClRh(PPh_3)_2$ is the rate-limiting process and that our measurements with different oxidizing agents under irradiation or in the dark simply define an efficiency series for obtaining useful concentrations of this highly reactive unsaturated intermediate (Scheme III). The relative ordering of rate constants is $K_1 > K_2 > K_3 > K_4$. We also point out that oxygen must play a role in rate enhancement subsequent to $ClRh(PPh_3)_2$ formation, as earlier work in vacuo found no change in the slow rate of Et_3SiH addition to 1-hexene on substituting $HRhCl(PPh_3)_2SiEtCl_2$ catalyst for $ClRh(PPh_3)_3$.²⁷

Experimental Section

A. General Data. Syntheses of rhodium complexes were carried out with use of Schlenk apparatus under nitrogen. Catalytic runs were conducted in sealed test tubes under air or in vacuo on 1.0–3.0-mL aliquots of solutions prepared as described below. Samples were analyzed on a Varian 3700 gas chromatograph equipped with flame ionization detectors and either a 2-m $1/8$ in. diameter stainless-steel column packed with 10% OV 101 on 80/100 mesh Chrom W-HP or a 4-m $1/8$ in. diameter stainless-steel column containing 10% Carbowax 1540 on the same support. Chromatographic data were integrated through an SP 4000 central processor. Electronic spectra were recorded on a Varian 219 instrument, and infrared spectra were taken on a Perkin-Elmer 598 recording spectrometer. Irradiations were performed with use of either two 15-W GE black lights ($\lambda_{max} = 355$ nm with width at half-height ≈ 25 nm)¹⁴ or a 450-W Hanovia medium-pressure mercury lamp (either unfiltered or equipped with appropriate Corning filters to isolate the near-UV region or the 366-nm emission line). Light intensities were measured via ferrioxalate actinometry⁴⁸ or by the measurement of $Mn_2(CO)_{10}$ disappearance upon irradiation in alkane- CCl_4 solutions ($\phi_{366} = 0.41$).⁴⁹

Silicon reagents were purchased from Silar Labs, Inc., and checked for purity via GLC prior to use. Strem Chemicals, Inc., or Alfa-

Ventron were the sources of $RhCl_3 \cdot 3H_2O$, $Rh_2(CO)_4Cl_2$, and $ClRh(PPh_3)_3$. Phosphine and phosphite ligands were acquired from various commercial sources including Strem, Aldrich, and Eastman Kodak, and these reagents were routinely distilled before use.

B. Quantum Yield Determinations. Following distillation of $P(OPh)_3$, PBu_3 , and $P(OBu)_3$, the compounds were quantitatively dissolved in CH_2Cl_2 and sealed into test tubes in air. The samples were irradiated either in a merry-go-round apparatus using the medium-pressure mercury lamp or in close contact to the GE black-light bulbs under a cooling air stream. Extinction coefficients were calculated for $P=O$ bands in pure samples of $P(O)(OPh)_3$, $P(O)(OBu)_3$, and $P(O)Bu_3$ [λ , cm^{-1} (ϵ , $L mol^{-1} cm^{-1}$): 1300 (390), 1250 (140), 1160 (270), respectively]. Conversions to product were kept below 20%. Solutions of 10^{-4} – 10^{-5} M $ClRh(O_2)(PPh_3)_3$ were prepared by dissolving $ClRh(PPh_3)_3$ in CH_2Cl_2 containing 0.5 M Et_3SiH in air followed by sealing measured aliquots in test tubes under air. Samples were irradiated on the GE black light along with thermal controls wrapped in aluminum foil. Disappearance of the 366-nm band was monitored over low conversions to $HRhCl(PPh_3)_2SiEt_3$.

C. Catalytic Runs. Samples consisted of either neat mixtures of the reactants or, preferably, portions diluted with solvents such as tetradecane, benzene, or toluene. Most experiments were run on solutions containing 0.068 M TMDS and 0.30 M DVTMDS. Catalysts were predissolved in reactants whenever possible, but for $ClRh(O_2)(PPh_3)_3$ minimal amounts of CH_2Cl_2 were necessary to add the complex homogeneously. Catalyst levels were on the order to 10^{-3} M (see figure captions). To ensure that TMDS disappearance was indeed linked to DVTMDS disappearance, we conducted several experiments with reverse molar excesses (1:4 DVTMDS to TMDS), and consistent results were obtained. For runs conducted on HMCTS and 1-pentene, equimolar quantities were used (ca. 0.20 M), and formation of the adduct was monitored along with disappearance of HMCTS. Iron carbonyl containing samples were prepared by introducing 5 μL of $Fe(CO)_5$ per 25.00 mL of total reaction mixture (0.0015 M) just prior to aliquot transfer and thorough degassing. Experiments with 2-phenyl-2-hydroperoxypropane were conducted in oxygenated cumene solvent; i.e., the soluble oxidant was generated in situ. All irradiations were conducted as indicated in the quantum yield section above.

D. Synthesis. The complexes $ClRh[P(OPh)_3]_3$ ⁴³ and $HRhCl(PPh_3)_2SiMe_2Cl$ ²⁷ were prepared via literature procedures. Reaction of $RhCl_3 \cdot 3H_2O$ (1.00 g, 3.80 mmol) and PBu_3 (2.80 mL, 11.24 mmol) at room temperature in methanol produced $Rh(PBu_3)_3Cl_3$ ⁴⁴ in 48% yield (1.49 g) on removal of the solvent in vacuo after 3 h. Repeating the reaction with 7.60 mmol of $RhCl_3 \cdot 3H_2O$ and excess PBu_3 (44.2 mmol) yielded 0.85 g (19%) of a new complex analyzing as $Rh_2Cl_4(PBu_3)_4$. Anal. Calcd: C, 53.09; H, 10.02; P, 11.41; Rh, 18.95. Found: C, 52.98; H, 10.08; P, 11.66; Rh, 18.20. This compound formed the known Rh(III) complex $Rh_2Cl_6(PBu_3)_4$ on direct chlorination in heptane solution.

Repeating the above procedure with $P(OEt)_3$ and $P(OBu)_3$ produced intractable air-sensitive oils. For the $P(OEt)_3$ reaction, 2.00 g (7.60 mmol) of $RhCl_3 \cdot 3H_2O$ were mixed with 4.7 mL of the freshly distilled phosphite in 40 mL acetone. No reaction was apparent at room temperature. All reactants dissolved on reflux, and the orange-red solution turned yellow. Solvent stripping left a yellow oil that was separated into two components by pentane extraction. Neither the residue nor the alkane-soluble material gave reasonable microanalyses. Catalytic runs were made with use of the more soluble component. Similar results were found on reaction of $RhCl_3 \cdot 3H_2O$ with $P(OBu)_3$. An attempt was made to obtain a more tractable product in the $P(OBu)_3$ system by slowly adding 4 equiv of $P(OBu)_3$ to a heptane solution of 0.50 g of $Rh_2(CO)_4Cl_2$. Gas evolution was immediate, and on stripping of the solvent in vacuo, an orange oil remained that showed similar catalytic activity to the $RhCl_3 \cdot 3H_2O-P(OBu)_3$ product.

Concluding Remarks

We have shown that noncarbonyl metal complexes can act as photocatalysts for hydrosilation. Our findings include the first unequivocal examples of photocatalytic rather than photoassisted Si-H addition. Furthermore, the systems defined here require the presence of aerial O_2 or other oxidants for facile catalyst formation rather than the usual rigorous exclusion of air. Iron pentacarbonyl was shown to be non-functional under these conditions as well as only marginally

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useful even in vacuo for siloxanes substrates with appreciable concentrations of $\text{Si}(\text{H})\text{R}_2\text{OSi}(\text{H})\text{R}_2$ units.

Our data indicate that the intermediacy of $\text{ClRh}(\text{PPh}_3)_2$ is paramount of catalytic success. Relatively high concentrations of this intermediate are conveniently generated by photolysis of $\text{ClRh}(\text{O}_2)(\text{PPh}_3)_3$ or via reductive elimination from $\text{HRhCl}(\text{PPh}_3)_2\text{SiR}_3$ at room temperature. The photolytic route works by enhancing $\text{Rh}-\text{PPh}_3$ cleavage and by promoting $\text{P}(\text{O})\text{Ph}_3$ formation via free-radical oxidation of dissociated

ligand.

Registry No. TMDS, 3277-26-7; DVTMDS, 2627-95-4; HMCTS, 15721-05-8; 1-pentene, 109-67-1; $\text{ClRh}(\text{PPh}_3)_3$, 14694-95-2; $\text{ClRh}[\text{P}(\text{O})\text{Ph}_3]_4$, 21481-16-3; $\text{ClRh}(\text{O}_2)(\text{PPh}_3)_3$, 15709-77-0; $\text{HRhCl}(\text{PPh}_3)_2\text{SiMe}_2\text{Cl}$, 25931-65-1; $\text{Fe}(\text{CO})_5$, 13463-40-6; $\text{Rh}_2\text{Cl}_4(\text{PBU}_3)_4$, 76466-42-7; $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, 13876-89-6; $\text{Rh}_2(\text{CO})_4\text{Cl}_2$, 14523-22-9; $\text{P}(\text{O})\text{Ph}_3$, 101-02-0; PBU_3 , 998-40-3; $\text{P}(\text{OBU})_3$, 102-85-2; $\text{P}(\text{OEt})_3$, 122-52-1; O_2 , 7782-44-7; 2-phenyl-2-hydroperoxypropane, 80-15-9; $\text{P}(\text{O})(\text{OPh})_3$, 115-86-6; $\text{P}(\text{O})(\text{OBu})_3$, 126-73-8; $\text{P}(\text{O})\text{Bu}_3$, 814-29-9.

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Electrophilic Attack at Metal Carbonyls. Kinetics of Reactions of Halogens with Some Trisubstituted Nonacarbonyltriruthenium Clusters

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The kinetics have been studied of the reactions in cyclohexane of $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ with iodine, bromine, and iodine chloride and of $\text{Ru}_3(\text{CO})_9(\text{P}-n\text{-Bu}_3)_3$ and $\text{Ru}_3(\text{CO})_9[\text{P}(\text{O})\text{Ph}_3]_3$ with I_2 and Br_2 . Apart from the reaction of ICl all the reactions proceed in two kinetically observable stages to form $\text{Ru}(\text{CO})_3\text{LX}_2$. Spectroscopic titration studies suggest that the second stage involves reaction of the Ru-Ru-bonded species $\text{Ru}_2(\text{CO})_6\text{L}_2\text{X}_2$. The kinetics are governed by quite complex rate dependence on $[\text{X}_2]$ in some cases, and there is clear kinetic, and in one case spectroscopic, evidence for the formation of adducts between the complex and one or more halogen molecules. Even in some cases where simple second-order kinetics are observed, first order in both $[\text{complex}]$ and $[\text{X}_2]$, it can be shown that this probably arises from reaction of X_2 with a completely formed adduct, $\text{complex} \cdot \text{X}_2$. It is suggested that the electrophilic nature of the halogens weakens the Ru-Ru bonds by an inductive effect transmitted through the CO ligands to the HOMOs that bind the metal atoms together.

Introduction

Reactions of halogens with metal-metal-bonded carbonyls have long been known as a means of producing mononuclear metal carbonyl halides.¹ Studies of the kinetics of reactions of iodine^{2,3} and bromine⁴ with a series of substituted dinuclear carbonyls of manganese and rhenium have shown^{2,4} that reactions proceed via the rapid preformation of a series of adducts, $\text{complex} \cdot n\text{X}_2$, which can contain up to four halogen molecules. These adducts then undergo relatively slow intramolecular electron transfer and metal-metal bond fission to form mononuclear products in high yield. The rates of these reactions are very sensitive to the σ basicity of the substituents, and it was concluded that the reactions proceeded by electrophilic attack at the O atoms of the CO ligands. Studies of reactions of Br_2 and Cl_2 with $\text{Os}_3(\text{CO})_{12}$ had previously shown⁵ that $\text{complex} \cdot \text{X}_2$ adducts were formed in those cases as well. Since reactions of this sort can provide systematic and quantitative estimates of the stability of such clusters toward fragmentation by electrophilic attack, we have made studies of the kinetics of the reactions in cyclohexane of some halogens with the complexes $[\text{Ru}(\text{CO})_3\text{L}]_3$ where $\text{L} = \text{PPh}_3$, $\text{P}-n\text{-Bu}_3$, and $\text{P}(\text{O})\text{Ph}_3$.

Experimental Section

The ruthenium complexes were those used in a previous study⁶ and were kindly provided by Dr. S. K. Malik. Resublimed I_2 (Baker Chemical Co.) and Br_2 (Baker analyzed grade) were used as received. Iodine chloride was prepared as described in the literature⁷ ($\lambda_{\text{max}} = 460 \text{ nm}$, $\epsilon = 150 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). Cyclohexane (AnalaR grade, BDH

Chemicals Ltd.) was dried over molecular sieves.

Solutions of the complexes $[\text{Ru}(\text{CO})_3\text{PPh}_3]_3$ and $[\text{Ru}(\text{CO})_3\text{P}(\text{O})\text{Ph}_3]_3$ were prepared by dissolving weighed amounts in a little dichloromethane which was subsequently removed under reduced pressure after addition of cyclohexane. $[\text{Ru}(\text{CO})_3\text{PBU}_3]_3$ was much more soluble, and solutions for reaction in cyclohexane were prepared by dilution of a 0.01 M stock solution in decalin. All manipulations of the solutions were carried out in dim light. Reactions of the complexes with oxygen were shown to be much slower than any of the reactions with halogens so that no attempts were made to exclude air from the reaction solutions.

Unless otherwise indicated all the reactions were followed at $25.0 \pm 0.1^\circ \text{C}$. Reactions with half-lives up to ca. 20 s were followed in a "Canterbury" stopped-flow spectrophotometer,⁴ and slower reactions were followed in 10-mm silica cells in the thermostated cell compartment of a Cary 16K spectrophotometer set to the continuous drive mode. Wavelengths were chosen so as to monitor the eventual disappearance of the absorption bands in the near-UV which can be assigned to transitions involving metal cluster molecular orbitals.⁸ In general the overall reaction proceeded in two stages, but the difference in rates between them was always sufficiently large that no difficulty was encountered in estimating values of the absorbance or transmission at the end of a given reaction. Absorbance changes during a reaction were generally ≤ 0.1 units so that plots of $\log(T_\infty - T)$ against time obtained from the stopped-flow data were equivalent to plots of $\log(A - A_\infty)$ ($T = \text{percent transmission}$, $A = \text{absorbance}$).⁴ Rate plots were generally linear for ca. 2 half-lives.

Reactions were followed over wide ranges of $[\text{X}_2]$ and, where possible, over quite wide ranges of initial concentration, c_0 , of complex. The rate equations were initially derived by graphical analysis of the dependence of the pseudo-first-order rate constants, k_{obsd} , on $[\text{X}_2]$ after which the various individual constants in the rate equation were evaluated by computer analysis using least-squares procedures described previously.^{2,4} Unless otherwise indicated the uncertainties quoted are estimates of the standard deviations that have been corrected for the number of degrees of freedom so that 95% confidence limits can be obtained by doubling them.

The final products of all the reactions were characterized in solution by IR and UV-vis spectroscopy, and the IR spectra of the products

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