(19) K. F. S. Luk, A. H. Maki, and R. J. Hoover, *J. Am. Chem. Soc.*, **97**, 1241 (1975).
(20) T. Yo Kono, S. Shimodawa, and S. Sohma, *J. Am. Chem. Soc.*, **97**, 5305 (1975).
(21) G. Kotowcyz and O. Suzuki, *Biochemistry*, **12**, 517, 3434, 5325 (1973).
(22) V. Wee, I. Feldman, P. Rose, and S. Gross, *J. Am. Chem. Soc.*, **96**, 103 (1974).
(23) P. J. Cozzone, P. J. Nelson, and O. Jardetzky, *Biochem. Biophys. Res. Commun.*, **60**, 341 (1974).
(24) J. R. De Memember and F. A. Wallace, *J. Am. Chem. Soc.*, **97**, 6240 (1975).
(25) I. A. G. Roos, A. J. Thomson, and S. Mansy, *J. Am. Chem. Soc.*, **96**, 6484 (1974).
(26) S. Mansy, B. Rosenbergy, and A. J. Thompson, *J. Am. Chem. Soc.*, **95**, 1663 (1973).
(27) T. J. Kistenmacher, P. J. Szalda, and L. G. Marzilli, *Inorg. Chem.*, **14**, 1686, 2623 (1975).
(28) P. de Meester, D. M. L. Goodgame, T. J. Jones, and A. C. Skapski, *Biochem. J.*, **139**, 791 (1974).
(29) R. W. Gellert and R. Bau, *J. Am. Chem. Soc.*, **97**, 7379 (1975).
(30) G. R. Clark and J. D. Orbel, *J. Chem. Soc., Chem. Commun.*, 139 (1974).
(31) M. J. Clarke, Ph.D. Thesis, Stanford University, 1974.
(32) M. J. Clarke and H. Taube, *J. Am. Chem. Soc.*, **97**, 1397 (1975).
(33) H. Sigel, *J. Am. Chem. Soc.*, **97**, 3209 (1975).
(34) K. Eriks, S. Edmonds, T. Hayden, and M. J. Clarke, to be submitted for publication.
(35) L. H. Vogt, J. L. Katz, and S. E. Wiberly, *Inorg. Chem.*, **4**, 1157 (1965).
(36) J. W. Jones and R. K. Robins, *J. Am. Chem. Soc.*, **85**, 193 (1963).
(37) R. F. Cookson, *Chem. Rev.*, **74**, 5 (1974).
(38) J. A. Lister, "Purines. The Chemistry of Heterocyclic Compounds", A. Weissberger and E. C. Taylor, Ed., Wiley-Interscience, New York, N.Y., 1971, p 493.
(39) G. Navon and N. Sutin, *Inorg. Chem.*, **13**, 2159 (1974).
(40) R. J. Sundberg, R. F. Bryan, I. F. Taylor, and H. Taube, *J. Am. Chem. Soc.*, **96**, 381 (1974).
(41) J. N. Armor, Ph.D. Thesis, Stanford University, 1970.
(42) A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, New York, N.Y., 1968, p 133.

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Photochemistry of Transition Metal Hydride Complexes. 2. $[RuClH(CO)(PPh_3)_3]$, $[RuH_2(CO)(PPh_3)_3]$, and $[RuClH(CO)_2(PPh_3)_2]$[1]

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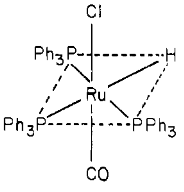
Ultraviolet irradiation of $[RuClH(CO)(PPh_3)_3]$ results in elimination of carbon monoxide and generation of the potent hydrogenation catalyst $[RuClH(PPh_3)_3]$. The reaction occurs with a 313-nm quantum yield of 0.06. The dicarbonyl complex $[RuClH(CO)_2(PPh_3)_2]$ is also formed in the photolysis through the separate reaction of $[RuClH(CO)(PPh_3)_3]$ with part of the photoreleased CO. Irradiation of $[RuH_2(CO)(PPh_3)_3]$ leads to elimination of molecular hydrogen, apparently generating transient $[Ru(CO)(PPh_3)_3]$, and irradiation under a CO atmosphere converts $[RuH_2(CO)(PPh_3)_3]$ quantitatively into $[Ru(CO)_3(PPh_3)_2]$. Photolysis of $[RuClH(CO)_2(PPh_3)_2]$ results in photoisomerization which is slowly reversed in the dark.

Introduction

Although transition metal hydride complexes are an important class of compounds in inorganic and organometallic chemistry, the photochemical properties of only a few have been investigated in detail.[2] We have initiated a systematic investigation into the photochemistry of hydride complexes in order to determine what effect the hydride ligand has on the excited-state properties and to determine if, as we now suspect,[2] photoinduced elimination of molecular hydrogen is a general property of di- and polyhydride complexes of all of the transition elements. In this paper we examine the previously well-characterized compounds $[RuClH(CO)(PPh_3)_3]$, **1**, $[RuH_2(CO)(PPh_3)_3]$, **2**, and $[RuClH(CO)_2(PPh_3)_2]$, **3**. Complexes **1** and **2** are ideally suited for comparison of their photochemistry since **2** is derived from **1** by simple substitution of chloride by hydride.



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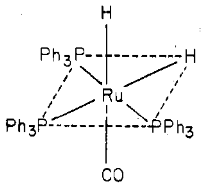

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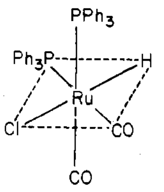

3

$[RuClH(CO)(PPh_3)_3]$ is a cream-colored solid and is easily prepared in high yield by the reaction of $RuCl_3{\cdot}xH_2O$ with PPh_3 and aqueous HCHO in boiling 2-methoxyethanol.[3] $[RuH_2(CO)(PPh_3)_3]$, a white solid, is prepared by a similar reaction in alcoholic KOH,[3] and $[RuClH(CO)_2(PPh_3)_2]$ derives from $[RuClH(CO)(PPh_3)_3]$ by treatment with CO.[4] The stereochemistry of the isomer of $[RuClH(CO)(PPh_3)_3]$ prepared in this manner, shown in **1**, is suggested by the demonstrated stereochemistry of $[RuClH(CO)(PMe_2Ph)_3]$,[5] by the published crystal structure of $[OsClH(CO)(PPh_3)_3]$,[6] and by the similarity of the infrared spectra of the ruthenium and osmium derivatives.[7] Infrared and NMR data have led to the assignment of the stereochemistries of $[RuH_2(CO)(PPh_3)_3]$[3,8] and $[RuClH(CO)_2(PPh_3)_2]$[4] shown in **2** and **3**. $[RuClH(CO)(PPh_3)_3]$ readily undergoes thermal substitution of the phosphine ligand trans to the hydride[9] and has also been shown[10] to be a catalyst for the isomerization of terminal olefins. Interestingly, $[RuH_2(CO)(PPh_3)_3]$ is apparently inert to substitution of the phosphine ligands.[11] Complexes **1**–**3** are relatively air stable in the solid state but solutions slowly decompose when exposed to air.

Experimental Section

The complexes $[RuClH(CO)(PPh_3)_3]$,[3] $[RuClD(CO)(PPh_3)_3]$,[12] $[RuClH(PPh_3)_3]$,[13] $[Ru(CO)_3(PPh_3)_2]$,[3] $[RuH_2(CO)(PPh_3)_3]$,[3] and $[RuClH(CO)_2(PPh_3)_2]$[4] were prepared by published procedures. Solvents used for measurement of spectra were MC & B Spectroquality, and all other solvents were purified by standard methods. All experiments and manipulations of compounds were conducted under vacuum or under a purified N_2 or Ar atmosphere, unless otherwise specified.

General Irradiation Procedures. Irradiations were conducted at 366 nm using a 450-W Hanovia medium-pressure Hg lamp equipped with Corning Glass 0-52 and 7-37 filters ($I \approx 10^{-8}$ einstein/min), at 313 nm using the same lamp in a Pyrex well with a K_2CrO_4 filter solution, or in a 350-nm Rayonet photoreactor. The complex to be studied was placed in an evacuable quartz UV cell or a Schlenk tube, and after degassing on a vacuum line the appropriate solvent was distilled onto the sample. Solutions for infrared studies were transferred in an inert-atmosphere glovebox to 0.5-mm NaCl solution infrared cells. Solutions were irradiated with the appropriate lamp, and electronic and infrared spectra were periodically recorded.

Samples for ^{31}P NMR spectra were similarly prepared and the NMR tubes sealed under vacuum. Lamp intensities were measured by ferrioxalate actinometry.

Photolysis of [$\mathrm{RuClH(CO)(PPh_3)_3}$]. Irradiation of degassed $\mathrm{CH_2Cl_2}$ and benzene solutions of [$\mathrm{RuClH(CO)(PPh_3)_3}$] with UV light induces a color change from pale yellow to purple. Evaporation of the solvent from a deep purple benzene solution initially 10^{-3} M in [$\mathrm{RuClH(CO)(PPh_3)_3}$] that had been irradiated for 2 h under an Ar purge yielded a purple solid which showed infrared bands (KBr) at 2040 and 1965 cm^{-1} ([$\mathrm{RuClH(CO)_2(PPh_3)_2}$]) and at 1925 cm^{-1} ([$\mathrm{RuClH(CO)(PPh_3)_3}$]) and a shoulder at 2020 cm^{-1} ([$\mathrm{RuClH(PPh_3)_3}$]), in addition to $\mathrm{PPh_3}$ bands at lower energy. The quantum yield of CO loss from [$\mathrm{RuClH(CO)(PPh_3)_3}$] was determined by 313-nm irradiation ($I = 5.08 \times 10^{-8}$ einstein/min) of thoroughly degassed $\mathrm{CH_2Cl_2}$ solutions of the complex placed in sealed UV cells. The photoreaction was monitored by measuring the increase in absorbance at 520 nm due to [$\mathrm{RuClH(PPh_3)_3}$].

Catalytic Hydrogenation by Photogenerated [$\mathrm{RuClH(PPh_3)_3}$]. The catalytic hydrogenation experiments were conducted using a vacuum line equipped with a gas-measuring buret. A 60-mL benzene solution 10^{-3} M in [$\mathrm{RuClH(CO)(PPh_3)_3}$] and 3×10^{-2} M in 1-hexene was thoroughly degassed and the vacuum line and gas buret assembly placed under an $\mathrm{H_2}$ atmosphere. The solution was vigorously stirred and the system allowed to reach equilibrium. No hydrogen uptake occurred over a period of several hours, but when irradiated with 366 nm the solution turned purple and hydrogen uptake commenced and proceeded at a rate of approximately 10 mL/h. Identical electronic absorption spectra were obtained for solutions of [$\mathrm{RuClH(CO)(PPh_3)_3}$] with and without 1-hexene present, indicating that 1-hexene does not replace $\mathrm{PPh_3}$ to any significant extent in [$\mathrm{RuClH(CO)(PPh_3)_3}$] and that [$\mathrm{RuClH(CO)(PPh_3)_3}$] rather than [$\mathrm{RuClH(CO)(PPh_3)_2(1\text{-}C_6H_{12})}$] was the light absorber in this experiment.

Photolysis of [$\mathrm{RuClH(CO)_2(PPh_3)_2}$]. Photolysis of degassed benzene and $\mathrm{CH_2Cl_2}$ solutions of [$\mathrm{RuClH(CO)_2(PPh_3)_2}$] with 366 nm induces a slow change from colorless to yellow. The color change and the accompanying infrared and electronic absorption spectral changes can be reversed by storage of irradiated solutions for several days in the dark. No inhibition of the spectral changes was observed when a solution containing a 10-fold molar excess of $\mathrm{PPh_3}$ was irradiated, and identical spectral changes were obtained upon photolysis of [$\mathrm{RuClD(CO)_2(PPh_3)_2}$]. Evaporation of solvent from a $\mathrm{CH_2Cl_2}$ solution that had been irradiated for a prolonged period gave a yellow solid which showed infrared bands (KBr) at 2040, 2000, 1965, and 1890 cm^{-1}. Separation of the initial complex and the photoproduct by recrystallization was not successful because of similar solubilities in the solvents tried.

Photolysis of [$\mathrm{RuH_2(CO)(PPh_3)_3}$]. Photolysis of degassed benzene solutions of [$\mathrm{RuH_2(CO)(PPh_3)_3}$] with UV light induces a color change from colorless to yellow. Mass spectral analysis of the gases above irradiated solutions showed substantial quantities of $\mathrm{H_2}$ but no CO. Evaporation of the solvent from irradiated solutions gave an amorphous yellow solid which in the infrared spectrum (KBr) showed a broad band at 1895 cm^{-1} with a strong shoulder at 1930 cm^{-1}. The $\mathrm{PPh_3}$ bands at lower energy were broad and a three-band pattern at 1545, 1557, and 1570 cm^{-1} and a weak band at 710 cm^{-1} were observed. The spectrum of [$\mathrm{RuH_2(CO)(PPh_3)_3}$] does not show the 710-cm^{-1} band and shows a two-band pattern at 1558 and 1572 cm^{-1}. Irradiation of a benzene solution of [$\mathrm{RuH_2(CO)(PPh_3)_3}$] under a CO purge produced [$\mathrm{Ru(CO)_3(PPh_3)_2}$] quantitatively as evidenced by the infrared spectrum showing only a single carbonyl vibration at 1895 cm^{-1}.

Reaction of [$\mathrm{RuClH(CO)(PPh_3)_3}$] with Carbon Monoxide. Admission of carbon monoxide to a stirred benzene solution of [$\mathrm{RuClH(CO)(PPh_3)_3}$] induces a rapid change from pale yellow to colorless. Evaporation of solvent from a solution stirred for 0.5 h under CO yielded a white solid which showed infrared bands at 2040 and 1965 cm^{-1} assignable[4] to [$\mathrm{RuClH(CO)_2(PPh_3)_2}$]. The reaction is quantitative as evidenced by the absence of the carbonyl vibration of [$\mathrm{RuClH(CO)(PPh_3)_3}$] at 1925 cm^{-1}. Addition of CO to a solution of [$\mathrm{RuClD(CO)(PPh_3)_3}$] gave [$\mathrm{RuDCl(CO)_2(PPh_3)_2}$].

Spectral Measurements. Infrared spectra were recorded on a Perkin-Elmer 621 grating infrared spectrophotometer using KBr disks prepared from IR Spectroquality powder (MC & B) or 0.5-mm path length NaCl solution infrared cells. Electronic absorption spectra were recorded with a Cary 17 spectrophotometer using 1-cm quartz spectrophotometer cells. Mass spectra were recorded with an AEI MS 902 mass spectrometer. ^{31}P NMR spectra were recorded with a JEOL PS-100 FT Fourier transform NMR spectrometer equipped with a Nicolet 1080 computer using a benzene-d_6 internal lock and were referenced to external 85% $\mathrm{H_3PO_4}$. Downfield chemical shifts are reported as positive.

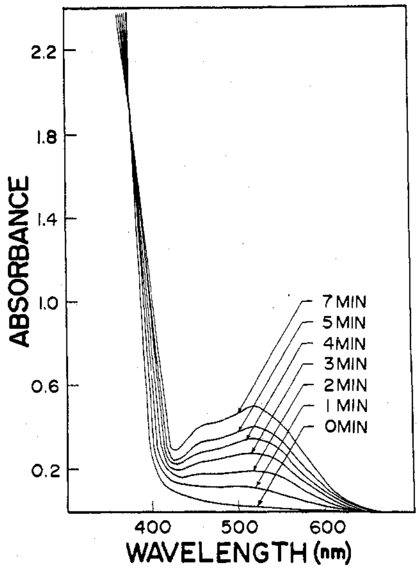

Figure 1. Electronic absorption spectral changes resulting from 366-nm irradiation of a 10^{-3} M $\mathrm{CH_2Cl_2}$ solution of [$\mathrm{RuClH(CO)(PPh_3)_3}$].

Results

Electronic Absorption Spectra. None of the three complexes examined in this work exhibit well-resolved electronic absorption spectra. No absorption feature with $\lambda > 280$ nm was discernible in the spectrum of [$\mathrm{RuClH(CO)_2(PPh_3)_2}$], and each of the complexes [$\mathrm{RuClH(CO)(PPh_3)_3}$] and [$\mathrm{RuH_2(CO)(PPh_3)_3}$] shows only a single shoulder on a rising UV absorption at 335 nm (ϵ 2800) and 325 nm (ϵ 15 000), respectively.

Photolysis of [$\mathrm{RuClH(CO)(PPh_3)_3}$]. Irradiation of a thoroughly degassed 10^{-3} M benzene solution of [$\mathrm{RuClH(CO)(PPh_3)_3}$] with 366 nm results in the electronic absorption spectral changes shown in Figure 1. As the irradiation proceeds, the color of the solution changes from yellow to purple and new absorption bands appear and increase in intensity at 520 and 470 nm. The final spectrum shown in Figure 1 is identical with that of an authentic sample of [$\mathrm{RuClH(PPh_3)_3}$] prepared by the reaction of [$\mathrm{RuCl_2(PPh_3)_4}$] with $\mathrm{Et_3N}$ and $\mathrm{H_2}$[13] and suggests that the photochemical reaction expressed in eq 1 occurs. Similar spectral changes

$$[\mathrm{RuClH(CO)(PPh_3)_3}] \xrightarrow{h\nu} \mathrm{CO} + [\mathrm{RuClH(PPh_3)_3}] \qquad (1)$$

obtain in degassed toluene and dichloromethane solutions, but irradiation in the presence of oxygen leads to rapid decomposition due to the air sensitivity of [$\mathrm{RuClH(PPh_3)_3}$].

Confirmation of the photogeneration of [$\mathrm{RuClH(PPh_3)_3}$] comes from a catalysis experiment. [$\mathrm{RuClH(PPh_3)_3}$] has been reported[8] to be the most efficient of all known homogeneous catalysts for the hydrogenation of terminal olefins. A deoxygenated benzene solution 10^{-3} M in [$\mathrm{RuClH(CO)(PPh_3)_3}$] and 3×10^{-2} M in 1-hexene under an $\mathrm{H_2}$ atmosphere showed no $\mathrm{H_2}$ uptake prior to irradiation, but upon photolysis with 366 nm hydrogen uptake commenced and proceeded at a rapid rate.

The infrared spectral changes which occur during photolysis of [$\mathrm{RuClH(CO)(PPh_3)_3}$], however, indicate that the overall reaction is not as simple as that expressed in eq 1. As shown in Figure 2A, irradiation of a deoxygenated $\mathrm{CH_2Cl_2}$ solution of [$\mathrm{RuClH(CO)(PPh_3)_3}$] results in a progressive decrease in

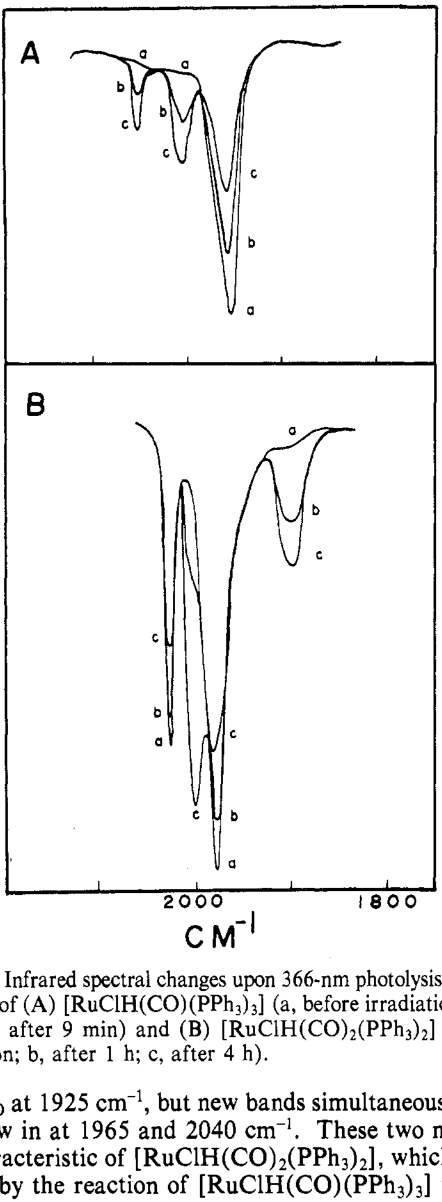

Figure 2. Infrared spectral changes upon 366-nm photolysis of CH_2Cl_2 solutions of (A) $[RuClH(CO)(PPh_3)_3]$ (a, before irradiation; b, after 3 min; c, after 9 min) and (B) $[RuClH(CO)_2(PPh_3)_2]$ (a, before irradiation; b, after 1 h; c, after 4 h).

the $\nu_{C\equiv O}$ at 1925 cm^{-1}, but new bands simultaneously appear and grow in at 1965 and 2040 cm^{-1}. These two new bands are characteristic of $[RuClH(CO)_2(PPh_3)_2]$, which must be formed by the reaction of $[RuClH(CO)(PPh_3)_3]$ with photoreleased CO, eq 2. In separate experiments we have indeed

$$[RuClH(CO)(PPh_3)_3] + CO \rightarrow [RuClH(CO)_2(PPh_3)_2] + PPh_3 \qquad (2)$$

observed a rapid thermal reaction of $[RuClH(CO)(PPh_3)_3]$ with carbon monoxide. Admission of CO to a stirred solution of $[RuClH(CO)(PPh_3)_3]$, for example, gives an immediate change from light yellow to colorless, and evaporation of the solvent yields a white solid with the infrared spectrum of $[RuClH(CO)_2(PPh_3)_2]$. A similar reactivity has been reported for $[RuClH(PPh_3)_3]$.[4]

Formation of the dicarbonyl complex during the photolysis has thus far limited the synthetic utility of the reaction. We had originally aimed to develop a convenient and high-yield synthesis of the potent catalyst $[RuClH(PPh_3)_3]$ through irradiation of easily prepared $[RuClH(CO)(PPh_3)_3]$. The purple solid isolated after photolysis, however, invariably showed infrared bands due to the dicarbonyl complex as well as bands due to $[RuClH(PPh_3)_3]$ and unreacted $[RuClH(CO)(PPh_3)_3]$. Unfortunately, $[RuClH(CO)_2(PPh_3)_2]$ does not lose carbon monoxide under thermal or photochemical conditions (see below), and its formation thus decreases the maximum yield of $[RuClH(PPh_3)_3]$. Various experiments designed to prevent formation of the dicarbonyl complex have been conducted. These included photolysis of solutions under a brisk inert-gas purge and irradiation in the presence of excess PPh_3, since the mechanism of the reaction of $[RuClH(CO)(PPh_3)_3]$ with CO likely involves thermal dissociation of PPh_3. None of the experiments were completely effective in preventing formation of the dicarbonyl complex, and the maximum yield of $[RuClH(PPh_3)_3]$ which we have been able to achieve under these experimental conditions is approximately 85%. When the photolysis of $[RuClH(CO)(PPh_3)_3]$ is conducted in a sealed vessel from which the photoreleased CO cannot escape, such as an infrared cell, approximately equal amounts of $[RuClH(PPh_3)_3]$ and $[RuClH(CO)_2(PPh_3)_2]$ are formed. The two complexes have similar solubilities in common solvents and purification by recrystallization was not successful. Chromatographic separation was not attempted.

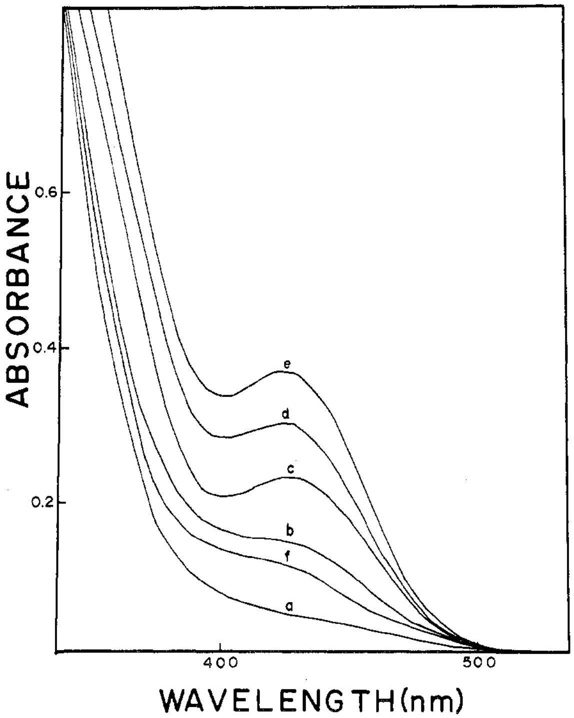

Figure 3. Electronic absorption spectral changes resulting from 366-nm irradiation of a 10^{-3} M CH_2Cl_2 solution of $[RuClH(CO)_2(PPh_3)_2]$: a, before irradiation; b, after 35 min; c, after 1 h, d, after 1.5 h; e, after 2.5 h; f, after storage in the dark for 105 h.

The quantum yield measured at 313 nm for the reaction expressed in eq 1 is 0.06 ± 0.02. Due to the air sensitivity of $[RuClH(PPh_3)_3]$, the yield was determined by irradiating a CH_2Cl_2 solution of $[RuClH(CO)(PPh_3)_3]$ in a degassed and sealed UV cell. Since the reaction vessel was sealed, back-reaction with CO was not prevented, and the measured quantum yield must be considered as a lower limit.

Photolysis of $[RuClH(CO)_2(PPh_3)_2]$. Only one of the geometrical isomers of $[RuClH(CO)_2(PPh_3)_2]$ has been reported, and it has been assigned[4] the structure shown in **3**. The complex is photosensitive and the spectral changes detailed below suggest that reversible photoisomerization occurs. Irradiation of a 10^{-3} M thoroughly degassed CH_2Cl_2 solution of $[RuClH(CO)_2(PPh_3)_2]$ results in the electronic absorption spectral changes shown in Figure 3. The initially colorless solution changes to a deep yellow during the photolysis, and a new absorption band appears and grows in at 430 nm. The reversibility of the reaction is suggested by spectrum f in Figure 3 which obtains after storage of the irradiated solution in the dark and by the observation that the light-dark spectral changes can be cycled repeatedly. Further evidence comes from the infrared spectral changes shown in Figure 2B. When a CH_2Cl_2 solution of $[RuClH(CO)_2(PPh_3)_2]$ is irradiated with 366 nm, the two carbonyl vibrations at 1965 and 2040 cm^{-1} smoothly decrease in intensity and two new bands appear and

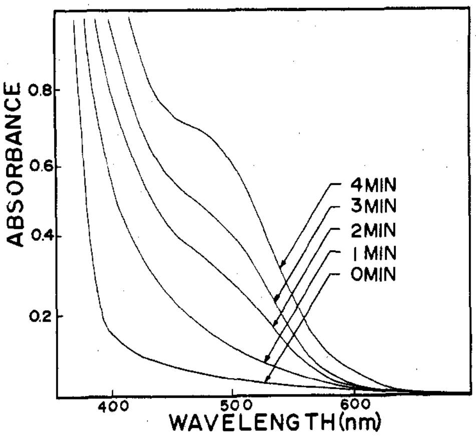

Figure 4. Electronic absorption spectral changes resulting from 366-nm irradiation of a 10^{-3} M benzene solution of $[RuH_2(CO)(PPh_3)_3]$.

grow in at 2000 and 1890 cm^{-1}. Storage of the irradiated solutions in the dark reverses the infrared changes, and the 1965- and 2040-cm^{-1} bands return to their original intensity. Identical spectral changes obtain upon photolysis of $[RuClD(CO)_2(PPh_3)_2]$ and indicate that the 2000- and 1890-cm^{-1} bands are both carbonyl vibrations.

The lack of evidence for the formation of $[RuClH(PPh_3)_3]$ when $[RuClH(CO)_2(PPh_3)_2]$ is irradiated for prolonged periods in the presence of excess PPh_3 strongly indicates that $[RuClH(CO)_2(PPh_3)_2]$ does not lose CO upon photolysis. Further, the observation that excess PPh_3 does not at all inhibit the electronic absorption spectral changes rules out photoinduced expulsion of PPh_3. The only reasonable candidate for the photoreaction is then reversible photoisomerization, as is known[14,15] to occur for an extensive series of $[RuX_2(CO)_2L_2]$ complexes. The complexes previously studied, however, isomerize from cis to trans isomers when irradiated, whereas the infrared changes which obtain on photolysis of $[RuClH(CO)_2(PPh_3)_2]$, showing the appearance of *two* new carbonyl vibrations, suggest conversion from one *cis*-dicarbonyl isomer to another. We have been unable to isolate pure samples of the photoisomer, and the spectral properties of the two isomers have thus far precluded quantum yield measurements. Qualitatively, however, the photoisomerization is much less efficient than the reaction expressed in eq 1.

Photolysis of $[RuH_2(CO)(PPh_3)_3]$. Irradiation of a thoroughly degassed benzene solution of $[RuH_2(CO)(PPh_3)_3]$ results in the electronic absorption spectral changes shown in Figure 4. As the irradiation proceeds, the solutions change from colorless to yellow, and a shoulder appears and increases in intensity at 400 nm. The photolysis could not be monitored in the infrared spectrum in benzene solution because of solvent absorption in the carbonyl region. The infrared and electronic spectral changes observed upon irradiation of degassed CH_2Cl_2 solutions were quite complex and implied reaction with solvent. Mass spectral analysis of the gases above an irradiated degassed benzene solution showed substantial amounts of molecular hydrogen and no evidence of CO, suggesting that irradiation of $[RuH_2(CO)(PPh_3)_3]$ leads to photoinduced elimination of H_2, eq 3. Similar photoinduced elimination

$$[RuH_2(CO)(PPh_3)_3] \xrightarrow{h\nu} H_2 + [Ru(CO)(PPh_3)_3] \qquad (3)$$

has been shown[18] to readily occur from a series of di- and trihydride complexes of iridium. The primary photoproduct expected from H_2 loss, $[Ru(CO)(PPh_3)_3]$, should be extremely reactive. Evaporation of solvent from a degassed benzene solution of $[RuH_2(CO)(PPh_3)_3]$ that had been irradiated for 5 h gave an amorphous yellow solid. This material in the infrared region showed a broad band at 1895 cm^{-1} with a strong shoulder at 1930 cm^{-1}. The 1930-cm^{-1} shoulder is the $\nu_{C\equiv O}$ of unreacted $[RuH_2(CO)(PPh_3)_3]$, and the 1895-cm^{-1} band presumably is the carbonyl stretch of the photoproduct. The three-band pattern at 1545, 1557, and 1570 cm^{-1} and the new weak band at 710 cm^{-1} suggest[2,16,17] formation of an ortho-metalated derivative.

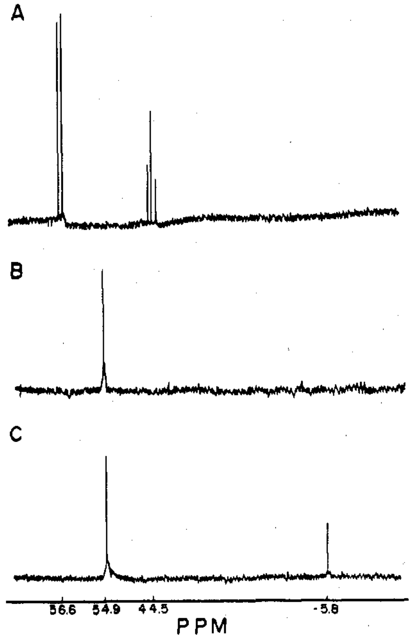

Figure 5. ^{31}P NMR spectra of benzene solutions of (A) $[RuH_2(CO)(PPh_3)_3]$, (B) $[Ru(CO)_3(PPh_3)_2]$, and (C) the product resulting from 366-nm photolysis of $[RuH_2(CO)(PPh_3)_3]$ under a CO purge.

Although we have not been able to isolate and characterize a pure product from photolysis of $[RuH_2(CO)(PPh_3)_3]$ in benzene, we have been able to trap the proposed intermediate by irradiation under a carbon monoxide atmosphere. When irradiation is done under CO, a smooth decrease in the 1930-cm^{-1} $\nu_{C\equiv O}$ of $[RuH_2(CO)(PPh_3)_3]$ occurs, and a sharp band at 1895 cm^{-1} grows in. This 1895-cm^{-1} band is characteristic[3] of $[Ru(CO)_3(PPh_3)_2]$ and suggests its formation. Confirmation of the production of $[Ru(CO)_3(PPh_3)_2]$ comes from a ^{31}P NMR experiment. The ^{31}P NMR spectrum of $[RuH_2(CO)(PPh_3)_3]$, Figure 5A, shows a doublet at 56.6 ppm due to the trans phosphines and a triplet at 44.5 ppm due to the phosphine trans to hydride. $[Ru(CO)_3(PPh_3)_2]$ shows only a single resonance at 54.9 ppm, Figure 5B. The solution resulting from 1-h irradiation of $[RuH_2(CO)(PPh_3)_3]$ under a carbon monoxide atmosphere gave the spectrum shown in Figure 5C. The resonance at 54.9 ppm clearly indicates the production of $[Ru(CO)_3(PPh_3)_2]$, and the resonance at −5.8 ppm is that of uncoordinated PPh_3. Indeed, the intensity ratio of the 54.9- and −5.8-ppm resonances is approximately 2:1, exactly as required for conversion of a tris(phosphine) complex into a bis(phosphine) complex and uncoordinated PPh_3, eq 4.

$$[RuH_2(CO)(PPh_3)_3] \xrightarrow[CO]{h\nu} H_2 + [Ru(CO)_3(PPh_3)_2] + PPh_3 \qquad (4)$$

The infrared and ^{31}P NMR spectra indicate that the production of $[Ru(CO)_3(PPh_3)_2]$ is virtually quantitative, and the product can be precipitated pure by concentration of solvent.

Discussion

Three ruthenium hydride complexes have been examined in this work and each has been observed to show a different photochemistry. Irradiation of $[RuClH(CO)(PPh_3)_3]$ leads to loss of CO, $[RuH_2(CO)(PPh_3)_3]$ undergoes photoinduced reductive elimination of molecular hydrogen, and $[RuClH(CO)_2(PPh_3)_2]$ photoisomerizes. Unfortunately, the electronic absorption spectra of the three complexes are not well resolved and reveal little as to the nature of the excited states which lead to the three different reactivities.

The only spectrum which is readily interpretable is that of [RuClH(CO)$(PPh_3)_3$] which shows a distinct shoulder at 335 nm with ϵ 2800. This band can be logically assigned as a ligand field (LF) transition which derives from the octahedral $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. This assignment accords well with the interpretation[19] of the spectra of a series of [RuX_2(diphos)$_2$] complexes showing bands which are similar but which are at lower energy due to the overall decrease in ligand field strengths of the ligands. Photoinduced loss of CO is not unexpected from an LF excited state. Indeed, Adamson's rules[20] predict CO loss from [RuClH(CO)$(PPh_3)_3$] since CO is the strong field ligand on the weakest ligand field axis.

Although [RuH_2(CO)$(PPh_3)_3$] also displays a clear shoulder near 325 nm in its absorption spectrum, the large ϵ suggests that this band is not an LF transition. Because of the very high position of hydride in the spectrochemical series, substitution of a hydride ligand for chloride is expected to move LF transitions to much higher energy. Although the 325-nm band cannot be assigned with certainty, it is attractive to view the active excited state leading to H_2 elimination as population of an orbital which is antibonding between ruthenium and H_2, in accordance with the molecular orbital scheme previously proposed[2] for the series of iridium hydrides which readily eliminate H_2 upon photolysis.

The spectrum of [RuClH$(CO)_2(PPh_3)_2$] is virtually featureless down to 280 nm where the PPh_3 ligands begin to absorb. Although a number of six-coordinate transition metal complexes have been shown[14,15] to photoisomerize, there has been no thorough study of the nature of the excited states which give rise to isomerization. It is likely, however, that the states have an LF origin. For example, the photoisomerization of the complexes *mer*-[$IrCl_3(PR_3)_3$] to *fac*-[$IrCl_3(PR_3)_3$] were among the first reported examples,[14] and an examination of the electronic absorption spectra of the series of *mer*-[$IrCl_3(PR_3)_3$] complexes reported by Grim and Ference,[21] each of which shows a band between 428 and 440 nm with ϵ 60–100, strongly suggests that the lowest transition is LF. The poor spectral features of [RuClH$(CO)_2(PPh_3)_2$] allow us to make no contribution to an understanding of the photoisomerization excited states, although this is clearly an area which warrants further study.

One of the more important aspects of this research is the photogeneration of the potent hydrogenation catalyst, [RuClH$(PPh_3)_3$]. Although [RuClH$(PPh_3)_3$] has been reported[8] to be the most active of all known homogeneous hydrogenation catalysts for terminal olefins, it has not been as much studied or used as other systems, presumably due to the extreme air sensitivity of the complex. The photochemical reaction expressed in eq 1 offers a convenient and easy method of generating solutions containing the potent catalyst from the air-stable and very easily prepared [RuClH(CO)$(PPh_3)_3$]. The carbonyl complex can be prepared in high yield and high purity in minutes by heating commercial $RuCl_3 \cdot xH_2O$ with HCHO and PPh_3 in 2-methoxyethanol. The complex is not air sensitive in the solid state and can be stored indefinitely without noticable decomposition. To generate the hydrogenation catalyst, it is only necessary to dissolve [RuClH(CO)$(PPh_3)_3$] in the appropriate solvent in the presence of substrate and deaerate either by vacuum degassing or by N_2 or H_2 purging. Irradiation of the solution with 366-nm light rapidly yields the catalyst. Further, the catalytic reaction can be stopped at any moment by admission of CO to the vessel resulting in formation of catalytically inactive [RuClH$(CO)_2(PPh_3)_2$]. However, once [RuClH$(CO)_2(PPh_3)_2$] is formed, the catalyst cannot again be regenerated because of the inability of the dicarbonyl complex to lose CO.

The apparent limitations of the catalytic system are twofold. First, the system cannot be used with a light-sensitive substrate or in a 366-nm absorbing solvent and, second, the catalyst cannot be generated quantitatively, at least in our hands, from [RuClH(CO)$(PPh_3)_3$] because of the tendency to form [RuClH$(CO)_2(PPh_3)_2$] as a side product. However, since the dicarbonyl complex is itself catalytically inactive under the conditions in which [RuClH$(PPh_3)_3$] would normally be used, its presence should not interfere with the catalytic behavior of the system.

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Registry No. **1**, 61521-25-3; **2**, 22337-78-6; **3**, 52555-05-2; [RuClH$(PPh_3)_3$], 19631-00-6; [$Ru(CO)_3(PPh_3)_2$], 14741-36-7; ^{31}P, 7723-14-0.

References and Notes

(1) A preliminary report of this work has appeared: G. L. Geoffroy and M. G. Bradley, *J. Chem. Soc., Chem. Commun.*, 20 (1976).
(2) G. L. Geoffroy and R. Pierantozzi, *J. Am. Chem. Soc.*, **98**, 8054 (1976), and references therein.
(3) N. Ahmad, J. J. Levison, S. D. Robinson, and M. F. Uttley, *Inorg. Synth.*, **15**, 48 (1974).
(4) B. R. James, L. D. Markham, B. C. Hui, and G. L. Rempel, *J. Chem. Soc., Dalton Trans.*, 2247 (1973).
(5) J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *J. Chem. Soc. A*, 1787 (1966).
(6) P. L. Orioli and L. Vaska, *Proc. Chem. Soc., London*, 333 (1962).
(7) L. Vaska, *J. Am. Chem. Soc.*, **88**, 4100 (1966).
(8) P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc. A*, 3143 (1968).
(9) P. G. Douglas and B. L. Shaw, *J. Chem. Soc. A*, 1556 (1970).
(10) D. Bingham, D. E. Webster, and P. P. Wells, *J. Chem. Soc., Dalton Trans.*, 1519 (1974).
(11) We observed, for example, that a CH_2Cl_2 solution of [RuH_2(CO)$(PPh_3)_3$] stirred at 25 °C under a CO atmosphere for 6 h gave no formation of [$RuH_2(CO)_2(PPh_3)_2$] and quantitative recovery of [RuH_2(CO)$(PPh_3)_3$]. This contrasts sharply to the behavior of [RuHCl(CO)$(PPh_3)_3$] under similar conditions.
(12) L. Vaska, *Proc. Int. Conf. Coord. Chem., 8th, 1964*, 99 (1964).
(13) R. A. Schunn and E. R. Wonchoba, *Inorg. Synth.*, **13**, 131 (1972).
(14) P. B. Brooks and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 919 (1968).
(15) C. F. J. Barnard, J. A. Daniels, J. Jeffery, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 953 (1976).
(16) M. A. Bennett and D. L. Milner, *J. Am. Chem. Soc.*, **91**, 6983 (1969).
(17) B. Longato, F. Morandini, and S. Bresadola, *J. Organomet. Chem.*, **88**, C7 (1975).
(18) G. L. Geoffroy, H. B. Gray, and G. S. Hammond, *J. Am. Chem. Soc.*, **97**, 3933 (1975).
(19) D. M. Klossen and G. A. Crosby, *J. Mol. Spectrosc.*, **25**, 398 (1968).
(20) A. W. Adamson, *J. Phys. Chem.*, **71**, 798 (1967).
(21) S. O. Grim and R. A. Ference, *J. Coord. Chem.*, **2**, 225 (1973).