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Photoreactions of the Triruthenium Cluster $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$. Isomerization of the Bridging Alkylidyne Ligand and Competing Ligand Substitutions

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Abstract: Irradiation of the title compound $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ (A) in hydrocarbon solution under CO leads to the formation of the bridging μ,η^2 acyl isomer $HRu_3(CO)_{10}(\mu,\eta^2\text{-}C(O)CH_3)$ (B). Quantum yields for isomerization ϕ_i were wavelength dependent ranging from $<10^{-5}$ at 405-nm excitation to about 0.05 at 313-nm excitation under P_{CO} 1.0 atm. In addition, over the range 0–1.0 atm, the ϕ_i values proved to be linearly dependent on P_{CO} despite the absence of a stoichiometric requirement for CO in the isomerization. A key observation was that photoisomerization of A ^{13}C labeled specifically at the bridging alkylidyne carbon, i.e., $HRu_3(CO)_{10}(\mu\text{-}^{13}COCH_3)$, gives B specifically labeled at the bridging acyl carbon, i.e., $HRu_3(CO)_{10}(\mu,\eta^2\text{-}^{13}C(O)CH_3)$, with no evidence of scrambling of the label with other carbons in the complex. Photolysis in the presence of ^{13}CO or other added ligands demonstrated the lability of the cluster coordinated carbonyls to photosubstitution reactions. The quantum yield for photosubstitution ϕ_s follows the same wavelength dependence as does ϕ_i, and it is proposed that the two processes result from competitive decay pathways of common intermediates. Limiting quantum yields for photosubstitution are about 0.25. A mechanism for these reactions related to that proposed previously for the photofragmentation of the parent triruthenium cluster $Ru_3(CO)_{12}$ is discussed. Prolonged 313-nm irradiation of $HRu_3(CO)_{10}(\mu,\eta^2\text{-}C(O)CH_3)$ under CO leads to cluster fragmentation and the formation of $Ru(CO)_5$ plus acetaldehyde.

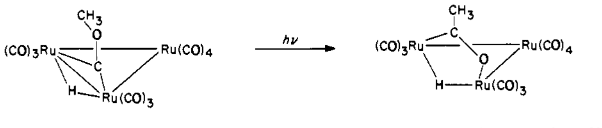
The possible involvement of multiple metal centers in ligand transformations and catalysis as well as analogies drawn to metal surfaces has fueled considerable interest in the chemistry of metal clusters. With regard to photochemistry, the clusters add dimensions not inherent to mononuclear metal complexes, namely electronic states involving orbitals delocalized over several metal centers as well as reaction pathways potentially leading to the homo- and heteronuclear cleavage of metal–metal bonds. These features as well as a long standing interest in the catalytic properties of such species have drawn the attention of this laboratory to the photoreactions of triangular ruthenium carbonyl clusters.[2,3] Related investigations by other laboratories have also been reported.[4-6]

The parent cluster $Ru_3(CO)_{12}$ displays an intense absorption band centered at 392 nm plus other, stronger absorptions at shorter wavelengths. Excitation of $Ru_3(CO)_{12}$ solutions in the presence of added ligands leads both to cluster photofragmentation[7] (e.g., eq 1) and to ligand photosubstitution[8] (e.g., eq 2), the former reaction being favored by excitation of the lower energy transitions and the latter by excitation of the higher energy bands.[3] As an

$$Ru_3(CO)_{12} + 3P(OCH_3)_3 \xrightarrow{h\nu} 3Ru(CO)_4P(OCH_3)_3 \tag{1}$$

$$Ru_3(CO)_{12} + P(OCH_3)_3 \xrightarrow{h\nu} Ru_3(CO)_{11}P(OCH_3)_3 + CO \tag{2}$$

extension of these investigations, the photochemistry of the triruthenium μ_2-methoxyalkylidyne derivative $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ (A) was surveyed with the goal of probing the possibility that linking two to the ruthenium sites with bridging ligands would perturb the fragmentation patterns. Indeed this proved to be the case, but instead of giving detectable diruthenium intermediates or products as projected, the result was an unprecedented oxygen-to-carbon migration of the CH_3 group of the bridging alkylidyne ligand.[9]



(3)

Oxygen-to-carbon methyl migration as shown in eq 3 has little precedent in organometallic chemistry, although an example has been described in the organic literature.[10] Such a transformation leading to the formation of carbon–carbon bonds has relevance to catalysis mechanisms, especially those involving the production of chemicals from C_1 compounds. For example, metal-based catalysts for the isomerization of methyl formate to acetic acid

$$HCO_2CH_3 \rightarrow CH_3CO_2H$$

have been reported,[11] but the conditions are extreme and the mechanisms are unknown. While eq 3 is the result of photochemical excitation, it does serve as the only known molecular model for such a transformation of a metal-coordinated ligand. Reported here is a detailed investigation of this reaction and other photochemical properties, including photosubstitution labilities of A and related metal clusters.

Experimental Section

Materials. The gases CO (CP grade), various CO/N_2 mixtures, ethylene, and hydrogen were purchased from Linde. These were purified prior to use by passing through an activated BASF Deox catalyst column or through a reduced chromium on silica column to remove dioxygen then through a drying column of molecular sieves and Drierite. Isotopically labeled ^{13}CO was obtained from Icon Services Inc.

Various solvents were purified prior to use as follows: Tetrahydrofuran (THF) was distilled from sodium benzophenone ketal under a blanket of N_2. Cyclohexane (Aldrich gold label) and benzene (ACS reagent grade) were distilled from lithium aluminum hydride under N_2. Methylene chloride was first washed with H_2SO_4 and water and then dried over calcium hydride before distillation from $LiAlH_4$ under N_2. Hexanes were dried with CaH_2 and then distilled under N_2. Acetonitrile (Burdick and Jackson) was dried over activated alumina and then vacuum distilled. Various alcohols were distilled from magnesium turnings under N_2. Deuteriated solvents were purchased from Aldrich and han-

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dled in the same manner as the perprotio analogues, although, when appropriate, $LiAlD_4$ was used.

Solvents used for spectroscopic measurements or for the preparation of solutions for photochemical experiments were further treated by freshly distilling from a Na/K melt (except for CH_3CN or CH_2Cl_2) on a vacuum line. Solvents used for these purposes were deaerated by repeated freeze–pump–thaw cycles and then vacuum distilled or transferred with syringe to the appropriate vessel for preparation of sample solutions. These solutions were then entrained with the desired gas mixtures. Crystallizations of air-sensitive compounds were also carried out using the vapor-diffusion technique with the glass speciality apparatus for this purpose described elsewhere.[12]

The triruthenium cluster $Ru_3(CO)_{12}$ was prepared from $RuCl_3$ (Johnson-Matthey) by literature procedures.[13] Bis(triphenylphosphoranylidene)ammonium chloride, [PPN]Cl (Aldrich), was dried in vacuo for 1 day prior to use. The salt $[PPN][CH_3CO_2]$ was prepared as described[14] as was sodium methoxide.[15] Trimethoxonium tetrafluoroborate (Alpha Inorganics) and trifluoromethanesulfonic acid (Aldrich) were used as received.

Syntheses. $\mathbf{[Et_3NH][HRu_3(CO)_{11}]}$: This was prepared via a modification of a previously described procedure.[16] A sample of $Ru_3(CO)_{12}$ (0.20 g, 0.313 mmol) was dissolved in THF (20 mL) under N_2 to give an orange solution to which was added a deaerated 50:50 mixture of Et_3N/H_2O (10 mL). As the reaction proceeds, the color changes first to brownish-red and then to bright red after 30 min. The product $[Et_3NH][HRu_3(CO)_{11}]$ was isolated by removing the solvent under reduced pressure to leave the red solid plus about 5 mL of water which was removed via pipet. Recrystallization was accomplished by dissolving the crude solid in a minimum of deaerated 2-ethoxyethanol and then slowly adding degassed water dropwise until crystallization was complete. The cation was exchanged with PPN^+ or Et_4N^+ by dissolving the cluster salt in a 2-ethoxyethanol solution containing a very large excess of the chloride salts of these cations followed by adding H_2O to precipitate the appropriate salt of the anionic cluster.

$\mathbf{HRu_3(CO)_{10}(\mu\text{-}COCH_3)}$: This was prepared by a modification of a published procedure.[17] The hydride salt $[Et_3NH][HRu_3(CO)_{11}]$ (0.21 g, 0.3 mmol) was dried under vacuum overnight in a Schlenk tube and then transferred to a 100-mL three-neck round-bottom flask fitted with Rotoflo stopcock attachments. This assembly was connected to the high-vacuum all-glass line and evacuated. Into this flask dry CH_2Cl_2 (15 mL) was vacuum distilled and the resulting mixture was stirred magnetically until all the solid had dissolved. To this mixture, solid $[(CH_3)_3O]BF_4$ (0.25 g, 1.7 mmol) was added while a constant flux of dry nitrogen was applied. The mixture was vigorously stirred for about 1 h, and then the solvent was removed under reduced pressure to give an orange-yellow solid with a crude yield of about 95%. This product was dissolved in cyclohexane and purified by thin-layer chromatography (TLC) on silica plate with cyclohexane as the elutant, followed by sublimation under vacuum and recrystallization (3×) from hot methanol.

$\mathbf{[Et_3NH][HRu_3(^{13}CO)_{11}]}$: A sample of $[Et_3NH][HRu_3(CO)_{11}]$ (0.21 g) was dissolved in THF in a Schlenk tube under a blanket of N_2 and the solution was degassed by repeated freeze–pump–thaw cycles. Into the tube was then introduced ^{13}CO (3 atm) and the solution was stirred at room temperature. The exchange between the coordinated and free carbon monoxide was monitored by IR spectroscopy and after about 20 min it was determined (from the shift in the bridging carbonyl frequency from 1730 to 1680 cm^{-1}) that the ^{13}C enrichment of the complex was >90%. The THF was removed by evaporation under reduced pressure and the label complex was used without further purification.

$\mathbf{HRu_3(^{13}CO)_{10}(\mu\text{-}^{13}COCH_3)}$: This was prepared, isolated, and purified in the same manner as was the unlabeled analogue (vida supra) but with $[Et_3NH][HRu_3(^{13}CO)_{11}$ as the starting complex. Isotopic labeling was examined by the IR spectrum and evaluated as being about 90% ^{13}C in the carbonyl and bridging alkylidine position. The proton-decoupled ^{13}C NMR spectrum (125 MHz) of this complex in benzene-d_6 displayed terminal carbonyl resonances at δ 202, 197, and 190 ppm (relative to tetramethylsilane), a resonance for the bridging alkylidyne C–O at 364 ppm, and a resonance for the alkylidyne methyl group at 77 ppm. The undecoupled spectrum was the same except that the methyl group resonance was split into a quartet with J_{CH} = 105 Hz. The monolabeled analogue $[HRu_3(CO)_{10}(\mu\text{-}^{13}COCH_3)]$ was prepared by heating a sample of $[HRu_3(^{13}CO)_{10}(\mu\text{-}^{13}COCH_3)]$ (0.065 g, 0.10 mmol) dissolved in cyclohexane in a Schlenck tube under unlabeled CO (1 atm) at 45 °C for 3 days. After isolation and purification by TLC and recrystallization from methanol, the product yield was determined to be approximately 35%. Examination of the ^{13}C NMR (125 MHz) and IR spectra indicated that only the bridging carbon remained substantially enriched.

$\mathbf{HRu_3(^{13}CO)_{10}(\mu\text{-}COCH_3)}$: This was prepared by heating a cyclohexane solution of $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ (0.060 g, 0.093 mmol) in a Schlenk tube under ^{13}CO (2 atm) at 45 °C for 3 days. After isolation and purification by TLC and recrystallization from methanol, the yield of product was 40%. The ^{13}C NMR and IR spectra showed the ^{13}C labels to reside only in the terminal carbonyls.

$\mathbf{HRu_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C(O)CH_3)}$: This was prepared by a modification of the reported procedure.[18] A solution was prepared by distilling THF (400 mL) from a K/Na mirror into a three-necked flask containing solid $Ru_3(CO)_{12}$ (1.0 g, 1.6 mmol) under argon. This was cooled to 195 K and methyllithium solution (Alfa, "low halide", 1.5 M) was added slowly with stirring to give a bright red solution after about 10 min. The temperature of the solution was allowed to rise to 250 K, $[PPN][CH_3CO_2]$ (2.0 g, 3.3 mmol) in dry, degassed methanol (2 mL) was added, and the resulting solution was stirred for 15 min. The solution was then cooled to 195 K and concentrated by evaporating the solvent under reduced pressure over approximately 6 h to a volume of 30 mL. At the same temperature, a stoichiometric quantity (1.6 mmol) of CF_3SO_3H was added dropwise to give a red-orange solution. The remainder of the solvent was then removed by evaporation under reduced pressure and the solid product purified by TLC (eluted with cyclohexane) and recrystallized from warm methanol. The overall yield was about 65%.

$\mathbf{HRu_3(CO)_{10-x}(P(OCH_3)_3)_x(\mu\text{-}COCH_3)}$: This was prepared by procedures similar to those described by Keister and co-workers.[19] A sample of $P(OCH_3)_3$ (19 μL for $x = 1$; twice that for $x = 2$) was added to a cyclohexane solution of $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ (30 mg, 0.047 mmol) and the mixture heated under N_2 for 2 days at 45 °C. The solvent was removed by evaporation under reduced pressure and the product purified by TLC (eluted with cyclohexane) and recrystallized from methanol. The triphenylphosphine complex $HRu_3(CO)_9(Ph_3P)(\mu\text{-}COCH_3)$ was prepared by a similar method. The IR spectra properties of these complexes agreed quantitatively with those published.[19]

Instrumentation. IR spectra were obtained as solutions in NaCl cells or as KBr pellets with Perkin-Elmer 683 or Digilab FTS-60 spectrophotometers. UV–vis spectra were obtained on Cary 118 spectrophotometers with quartz cells. NMR (^1H, ^{13}C, and ^{31}P) spectra were obtained on Nicolet Model NT300 or GE Model GN500 NMR spectrometers operating in a pulsed FT mode with deuterium lock.

Photochemical Procedures. Solutions for continuous photolysis reactions were prepared with use of Schlenk type vacuum line techniques. The reaction vessels were 1 cm quartz photolysis cells fitted with stopcocks and serum cap entry ports via quartz to Pyrex graded seals. Solutions were transferred to these vessels via syringe or prepared directly on the vacuum rack. Photolysis experiments were carried out with a high-pressure mercury lamp optical train (313, 334, 366, and 405 nm irradiation).[20] Photolysis reactions were monitored by recording the optical spectra directly in the photolysis cell or by removing aliquots periodically to record the IR spectra. Light intensities in the photolysis experiments were determined with the Actinochrome IR actinometer[21] ($\lambda_{irr} \leq 334$ nm), ferrioxalate actinometry[22] (313–405 nm), or Reinecke's ion actinometry[23] (>405 nm). Quantum yields were calculated according to equations described previously.[3]

Results

Photolysis of $\mathbf{HRu_3(CO)_{10}(\mu\text{-}COCH_3)}$ under CO. The electronic spectrum of $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ (A) in cyclohexane solution is dominated by a strong absorption maximum at 384 nm (ϵ_{384} = 6900 M^{-1} cm^{-1}) and a shoulder at 274 nm (ϵ_{274} = 18 000 M^{-1} cm^{-1}). When cyclohexane solutions of this cluster were photolyzed with 313-nm light under CO (P_{CO} = 1.0 atm) at 25 °C, the band at 384 nm was noted to decrease in intensity with corresponding increases in absorption at both longer and shorter wavelengths.

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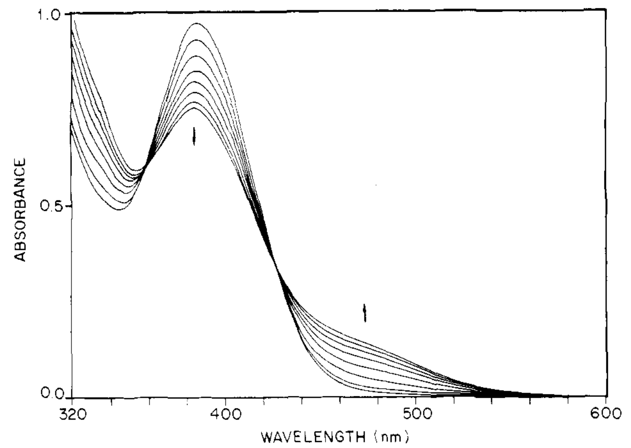


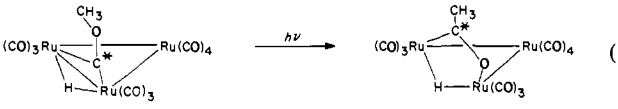
Figure 1. Changes in the electronic spectrum as the result of 313-nm photolysis of $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ in cyclohexane under CO (1.0 atm) at 25 °C.

Isosbestic points were noted at 358 and 436 nm (Figure 1), and these were unchanged for at least 65% reaction indicating that secondary photolysis was minor over this time frame. Surprisingly, the infrared spectrum in the carbonyl region displayed little change over the same photolysis period. However, both the changes in the electronic spectrum and the relatively little change in the IR spectra are fully consistent with the photolysis product being the bridging acyl cluster $HRu_3(CO)_{10}(\mu,\eta^2\text{-}C(O)CH_3)$ (B), the result of the photoisomerization indicated in eq 3. This conclusion was substantiated by comparison to the spectral properties of authentic samples of B synthesized by literature procedures[18] (Figure 2) and by the results of the NMR experiments described below.

Photolysis (313 nm) of A in tetrahydrofuran-d_8 solutions under CO (1 atm) induced substantial changes in the ^1H NMR and ^{13}C NMR (see below) spectra. The 500-MHz ^1H NMR spectrum of $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ in THF-d_8 displays singlet resonances at δ 3.641 ppm (alkylidyne methyl) and δ −14.895 ppm (bridging hydride) with an intensity ratio of 3/1. After photolysis representing roughly a 30% decrease in the concentration of the starting complex, only two new proton resonances were evident. These were singlets located at δ 2.066 ppm and at δ −13.984 ppm in a 3/1 ratio, consistent with the spectrum of B.

The ^{13}C NMR spectral changes (125 MHz) resulting from photolysis (λ_{irr} 313 nm) of the labeled complex $HRu_3(^{13}CO)_{10}(\mu\text{-}^{13}COCH_3)$ under natural abundance CO (1.0 atm) in benzene-d_6 demonstrated both that CO exchange (eq 4) accompanies the photoisomerization of A to B (eq 5) and that the isomerization indeed involves migration of the methyl group from the methoxyalkylidyne oxygen to the adjacent carbon of the same functional group (eq 5). The labilization of CO was demonstrated by the

$$HRu_3(^{13}CO)_{10}(\mu\text{-}^{13}COCH_3) + CO \xrightarrow{h\nu} HRu_3(CO)_{10}(\mu\text{-}^{13}COCH_3) + {}^{13}CO \quad (4)$$



(5)

observation that short-term photolysis of $HRu_3(^{13}CO)_{10}(\mu\text{-}^{13}COCH_3)$ under these conditions led to marked decreases in the ^{13}C NMR (125 MHz) resonances at 202, 197, and 190 ppm (assigned to the terminal CO's)[24] and a corresponding strong increase in the intensity of the resonance at 185 ppm corresponding to free CO. However, there was little or no change in the intensity of the resonance for the labeled bridging carbon of the alkylidyne ligand (364 ppm). In addition there was little change in the intensity of the methyl carbon resonance at 77 ppm (natural abundance ^{13}C) indicating that, although there had been considerable exchange of the terminal CO's with CO in solution (eq 4), little isomerization had yet occurred (quantum yield measurements are described below). Continued photolysis of this solution over a much longer term led to the disappearance of the 364- and 77-ppm ^{13}C resonances and the corresponding appearance of new resonances at 284 and 44 ppm (bridging acyl carbon and methyl carbon, respectively, of B). Comparisons of the intensities of acyl and methyl intensities in the product in comparison to unlabeled analogues, as well as comparing the intensities of the reactant and product labels during the course of these photoreaction experiments, demonstrated that the acyl carbon of the product retained the same fraction of the ^{13}C label (~90%) present in the alkylidyne carbon of the starting complex. An analogous experiment with the monolabeled starting material $HRu_3(CO)_{10}(\mu\text{-}^{13}COCH_3)$ photolyzed under natural abundance CO also gave the monolabeled product $HRu_3(CO)_{10}(\mu,\eta^2\text{-}^{13}C(O)CH_3)$. Thus, it was concluded that the photoisomerization depicted in eq 5 occurs with a very high degree of specificity.

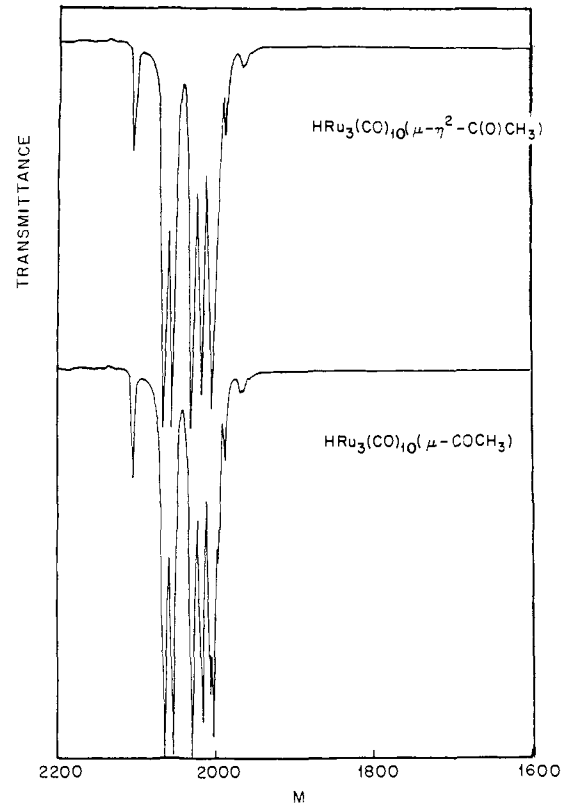


Figure 2. IR spectra in cyclohexane of $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ (lower) and $HRu_3(CO)_{10}(\mu,\eta^2\text{-}C(O)CH_3)$ (upper).

The quantum yields ϕ_i for the photoisomerization (eq 3) were determined spectrophotometrically by following the decreasing absorbance at the λ_{max} of A (384 nm) or the increasing absorbances at 460 nm. Values measured at the two monitoring wavelengths were identical. For solutions in 25 °C cyclohexane under CO at P_{CO} 1.0 atm, the quantum yield for 313-nm irradiation was determined to be 0.049 ± 0.005 mol/einstein. The quantum yields proved to be sensitive to a variety of solution parameters. Under CO (1.0 atm), ϕ_i was only modestly sensitive to the nature of the solvent but did prove to be strongly dependent on [CO] (Table I). For example, in cyclohexane, carbon tetrachloride, or 2,5-dimethyltetrahydrofuran (DMTHF), photolysis under CO gave ϕ_i's about 0.03 to 0.05 mol/einstein but under N_2 (P_{CO} = 0.00) gave immeasurably small values of ϕ_i (<10^{-5}). In THF solution under N_2, a significantly larger ϕ_i (1.4×10^{-3}) was found, although much smaller than under CO (Table I). Isomerization of A to B was also seen when ethylene (1.0 atm) was used as the blanketting gas, but the ϕ_i was much smaller (0.001) than under CO.

The photolysis of A under CO (1.0 atm) in cyclohexane at longer wavelengths also gave photoisomerization, but the ϕ_i's

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Table I. ϕ_i Values Determined in Different Solvents[a]

$$HRu_3(CO)_{10}(\mu\text{-}COCH_3) \xrightarrow{h\nu} HRu_3(CO)_{10}(\mu,\eta^2\text{-}C(O)CH_3)$$

solvent	[CO]	ϕ_i
cyclohexane	0.0092[b]	4.9×10^{-2}
	0.0046	3.0×10^{-2}
	0.0023	1.3×10^{-2}
	0.0007	0.5×10^{-2}
	0.000[c]	$<10^{-5}$
hexanes	0.007[b]	4.6×10^{-2}
benzene	0.006[b]	3.2×10^{-2}
THF	0.0084[d]	7.5×10^{-2}
	0.000	1.4×10^{-3}
CCl_4	0.0089[b]	4.4×10^{-2}
	0.000	$<10^{-5}$
DMTHF[e]	0.0084[b,d]	4.4×10^{-2}
	0.000[c]	$<10^{-5}$

[a] $[HRu_3(CO)_{10}(\mu\text{-}COCH_3)] \sim 10^{-4}$ M; $\lambda_{irr} = 313$ nm; quantum yields in moles/einstein, average experimental uncertainties ca. ±5%. [b] $P_{CO} = 1.0$ atm, CO solubilities from ref 3. [c] $P_{CO} = 0.00$, $P_{N_2} = 1.0$ atm. [d] CO solubility estimated according to ref 27. [e] DMTHF = 2,5-dimethyltetrahydrofuran.

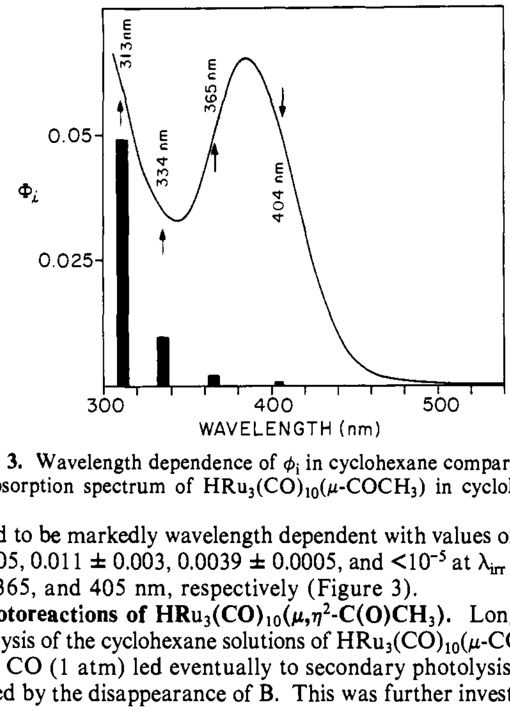
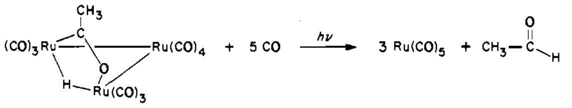


Figure 3. Wavelength dependence of ϕ_i in cyclohexane compared with the absorption spectrum of $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ in cyclohexane.

proved to be markedly wavelength dependent with values of 0.049 ± 0.005, 0.011 ± 0.003, 0.0039 ± 0.0005, and $<10^{-5}$ at λ_{irr} = 313, 334, 365, and 405 nm, respectively (Figure 3).

Photoreactions of $HRu_3(CO)_{10}(\mu,\eta^2\text{-}C(O)CH_3)$. Long-term photolysis of the cyclohexane solutions of $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ under CO (1 atm) led eventually to secondary photolysis as evidenced by the disappearance of B. This was further investigated briefly by preparing cyclohexane solutions of $HRu_3(CO)_{10}(\mu,\eta^2\text{-}C(O)CH_3)$ and probing the photoreactions at λ_{irr} = 313 nm. The electronic spectrum of B in cyclohexane displays a maximum at 380 nm (ϵ_{380} = 5800 M^{-1} cm^{-1}) with a shoulder at 425 nm 3100). Photolysis under CO (1.00 atm) led simply to the bleaching of these absorption bands to give a nearly colorless solution. The IR spectrum of these solutions showed the presence of $Ru(CO)_5$ (ν_{CO} = 2040 and 1998 cm^{-1}) plus acetaldehyde (1740 cm^{-1}), indicating that photolysis of B leads to cluster fragmentation (eq 6). The quantum yield for the photofragmentation was determined to be 0.0011 ± 0.0001.



(6)

Photoreactions of $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ with Other Added Ligands. Photolysis (λ_{irr} = 313 nm) of $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ in cyclohexane under N_2 had little effect on the electronic spectrum, but photolysis with added $P(OCH_3)_3$, $P(n\text{-}Bu)_3$, or pyridine gave marked changes indicating ligand photosubstitution processes (e.g., Figure 4). In each case the spectra showed progressive red shifts of the absorption maximum but not isosbestic points. Since the products of partial photolysis were stable in the dark, this pattern of spectral changes apparently reflects the operation of successive photolysis reactions, each having substantial quantum yields.

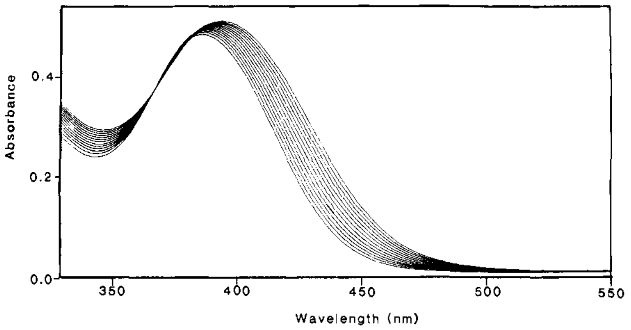


Figure 4. Electronic spectral changes during the early stages of 313-nm photolysis of $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ in cyclohexane under CO (1 atm) with added $P(OCH_3)_3$ (0.05 M).

When the solid obtained by evaporation of the solvent from a partially photolyzed cyclohexane solution of A with added $P(OCH_3)_3$ (0.05 M) (estimated 50% reaction according to spectral changes) was redissolved in CH_2Cl_2 and eluted with cyclohexane on a silica gel thin layer chromatography plate, four bands were observed. These bands were isolated from the TLC plates and the compounds extracted by washing with CH_2Cl_2. The first band was identified by its IR spectrum as unreacted A, while the second and fourth bands were identified as the substituted clusters $HRu_3(CO)_9(P(OCH_3)_3)(\mu\text{-}COCH_3)$ and $HRu_3(CO)_8(P(OCH_3)_3)_2(\mu\text{-}COCH_3)$, respectively, by comparing IR spectra to authentic samples.[19] The third band was a low-yield product that could not be isolated and identified under these conditions. When this reaction was examined by ^1H NMR in benzene-d_6, the two substituted clusters were the only products observable. However, when the 313-nm photolysis was carried at a lower $[P(OCH_3)_3]$ (0.005 M), the ^1H NMR techniques allowed detection of a third product with a methyl group at 2.2 ppm and a hydride at -13.5 ppm (singlets) consistent with the formation of the substituted η^2-acyl species $HRu_3(CO)_9(P(OCH_3)_3)(\mu,\eta^2\text{-}C(O)CH_3)$,[18] the product both of substitution and of isomerization via O-to-C migration of the alkylidyne methyl group (eq 7). The third product was formed with an efficiency about 1/25th that of simple photosubstitution (eq 8), and this ratio was roughly independent of the photolysis time, an indication that the two products are formed by competing pathways rather than sequentially.

$$HRu_3(CO)_{10}(\mu\text{-}COCH_3) + P(OCH_3)_3 \xrightarrow{h\nu} HRu_3(CO)_9(P(OCH_3)_3)(\mu,\eta^2\text{-}C(O)CH_3) + CO \quad (7)$$

$$HRu_3(CO)_{10}(\mu\text{-}COCH_3) + L \xrightarrow{h\nu} HRu_3(CO)_9L(\mu\text{-}COCH_3) + CO \quad (8)$$

$$(L = P(OCH_3)_3,\ PBu_3 \text{ or pyridine})$$

The same photoreactions were also followed by recording the solution FTIR spectra during the course of the reaction. Difference spectra demonstrated that, over the first 10% of the photoreaction (λ_{irr} = 313 nm), the only observable products were the monosubstituted complexes (eq 8). Quantum yields for photosubstitution ϕ_s were determined over this time frame by assuming eq 8 to be the exclusive photoreaction. Values of ϕ_s so determined for L $\neq$ ^{13}CO were independent of whether electronic or IR spectral differences were used for these calculations. Quantum yields for CO exchange ϕ_{ex} between unlabeled A and ^{13}CO (P_{CO} = 1.0 atm) in cyclohexane were determined via the IR technique; ϕ_{ex}'s determined by NMR techniques were consistent with these values. Long-term photolysis under these conditions led to >75% incorporation of ^{13}CO into the terminal CO sites as determined from FTIR and ^{13}C NMR spectral observations with no apparent incorporation of ^{13}C into either the bridging alkylidyne of A or the bridging acyl of B eventually formed by the less efficient photoisomerization pathway (eq 3).

Table II. ϕ_s Values Determined for Various L in Cyclohexane[a]

$$HRu_3(CO)_{10}(\mu\text{-}COCH_3) + L \xrightarrow{h\nu} HRu_3(CO)_9(L)(\mu\text{-}COCH_3) + CO$$

L	λ_{irr} (nm)	ϕ_s[b]
$P(OCH_3)_3$	313	0.24
	334	0.048
	366	0.019
	405	$<10^{-5}$
$P(n\text{-}Bu)_3$	313	0.17
NC_5H_5	313	0.16
^{13}CO	313	0.25[c]
^{12}CO	313	0.25[c]

[a] Photolysis conditions: $[HRu_3(CO)_{10}(\mu\text{-}COCH_3)] \approx 10^{-4}$ M, [L] = 0.05 M except for L = CO or ^{13}CO, which were determined for P_{CO} = 1.0 atm. All other experiments carried out under N_2. [b] Quantum yield in moles/einstein, average experimental uncertainty ±5%. [c] Average experimental uncertainty ±10%.

Table III. ϕ_s Values in Cyclohexane for Various $[P(OCH_3)_3]$ under Different CO/N_2 Gas Mixtures[a]

$[P(OCH_3)_3]$ (M)	ϕ_s[b,c] 0%, CO	10%, CO	75%, CO	100%, CO
0.00424	0.153	0.138		0.075
0.00624	0.196	0.174	0.110	0.10
0.00848	0.201	0.183	0.134	0.122
0.0165	0.220	0.211		0.145
0.050	0.232	0.227	0.200	0.187
0.10	0.244	0.238		0.194

[a] [A] ~ 10^{-4} M at 25 °C, λ_{irr} = 313 nm. [b] ϕ_s in moles/einsteins, experimental uncertainties ±5%. [c] Gas mixtures CO/N_2 at 1.0 atm total; % CO in mixture listed.

Table IV. Effect of Added THF on the Photosubstitution Quantum Yields ϕ_s for the $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ plus $P(OCH_3)_3$ in Cyclohexane

[THF]	ϕ_s[b]	[THF]	ϕ_s[b]
0.00	0.23	0.10	0.16
0.02	0.22	0.20	0.14
0.03	0.20	0.30	0.12
0.05	0.18		

[a] $[HRu_3(CO)_{10}(\mu\text{-}COCH_3)] = 10^{-4}$ M, $[P(OCH_3)_3]$ = 0.034 M at 25 °C, λ_{irr} = 313 nm. [b] Quantum yield in moles/einstein, experimental uncertainty ±5%.

Table V. ϕ_s for the Photoreaction of $HRu_3(CO)_9(P(OCH_3)_3)(\mu\text{-}COCH_3)$ with $P(OCH_3)_3$ in Cyclohexane[a]

$$HRu_3(CO)_9L(\mu\text{-}COCH_3) + L \xrightarrow{h\nu} HRu_3(CO)_8L_2(\mu\text{-}COCH_3) + CO$$

$[P(OCH_3)_3]$ (M)	ϕ_s[b]	$[P(OCH_3)_3]$ (M)	ϕ_s[b]
0.00424	0.02	0.05	0.076
0.00624	0.04	0.10	0.079
0.00848	0.048	0.10[c]	0.11[c]
0.0165	0.059		

[a] $[HRu_3(CO)_9(\mu\text{-}COCH_3)(P(OCH_3)_3)] = 10^{-4}$ M, P_{CO} = 1 atm in cyclohexane, except where noted. [b] ϕ_s in moles/einstein, experimental uncertainty about ±5%. [c] Under N_2.

The quantum yield for CO exchange was also determined by following the photoreaction of $HRu_3(^{13}CO)_{10}(\mu\text{-}^{13}COCH_3)$ under a blanket of natural abundance CO (1.0 atm) (see above); there were no differences in the ϕ_{ex} values determined by the two methods.

Table II summarizes the photosubstitution quantum yields ϕ_s for various L measured for 0.05 M [L] as well as the photoexchange quantum yields ϕ_{ex} determined at λ_{irr} = 313 nm under N_2. Notably, under these conditions the photosubstitution quantum yields proved to be rather independent of the nature of L. The ϕ_s values for L = $P(OCH_3)_3$ (0.050 M) at various λ_{irr} are also summarized in Table II. Clearly, the efficiency of this photoreaction proved to be strongly dependent on λ_{irr}, falling off to very low values at longer wavelengths. Table III summarizes ϕ_s values determined for L = $P(OCH_3)_3$ at different concentrations of $P(OCH_3)_3$ in cyclohexane and under varying P_{CO}. From these data, it can be seen that, under N_2, ϕ_s proved to be substantial even for $[P(OCH_3)_3]$ as low as 0.0042 M, although a 60% increase in ϕ_s was observed on a 20-fold increase in concentration of the ligand. For all [L] the quantum yields for photosubstitution were smaller under CO than under N_2. The introduction of THF to the cyclohexane solutions also suppressed the photosubstitution by $P(OCH_3)_3$ (Table IV).

When the photolysis (313 nm) of $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ in cyclohexane was carried out under dihydrogen (1.0 atm), both the IR and electronic spectral changes were consistent with the formation of the trihydride alkylidyne complex $H_3Ru_3(CO)_9(\mu\text{-}COCH_3)$ reported by previous workers (eq 9).[19] The reaction was quite clean with an isosbestic point at 446 nm holding for >80% of the reaction. The quantum yield at this wavelength was measured as 0.060 ± 0.004, and qualitative observations indicated that the quantum yield was much smaller at longer λ_{irr}.

$$HRu_3(CO)_{10}(\mu\text{-}COCH_3) + H_2 \xrightarrow{h\nu} H_3Ru_3(CO)_9(\mu\text{-}COCH_3) + CO \quad (9)$$

Photolysis of the Substituted Alkylidyne Cluster $HRu_3(CO)_9(P(OCH_3)_3)(\mu\text{-}COCH_3)$. When a sample of $HRu_3(CO)_9(P(OCH_3)_3)(\mu\text{-}COCH_3)$ in cyclohexane was irradiated (λ_{irr} = 313 nm) no net photoreactions were observed under either N_2 or CO (1.0 atm). Even when the solutions were irradiated for very long periods, no measureable changes in the IR and UV/vis spectra were detectable. Hence, it was concluded that photoisomerization in analogy to eq 3 is at most a very low yield process. In contrast, the complexes were markedly photoactive when irradiated in the presence of added $P(OCH_3)_3$. This was indicated by spectral shifts, disappearance of the absorption maximum at 392 nm (ϵ = 8000 M^{-1} cm^{-1}), and appearance of a new band centered at 414 nm (7900 M^{-1} cm^{-1}) characteristic of the disubstituted cluster $HRu_3(CO)_8(P(OCH_3)_3)_2(\mu\text{-}COCH_3)$.[19] An isobestic point at 398 nm was observed through most of the photolysis. Thus, simple substitution for CO (eq 10) appears to be the principal photoreaction. Quantum yields for eq 10 proved to be sensitive to both $[P(OCH_3)_3]$ and P_{CO} (Table V).

$$HRu_3(CO)_9(P(OCH_3)_3)(\mu\text{-}COCH_3) + P(OCH_3)_3 \xrightarrow{h\nu} HRu_3(CO)_8(P(OCH_3)_3)_2(\mu\text{-}COCH_3) + CO \quad (10)$$

Discussion

In evaluating a possible mechanism for the photoisomerization of A to B (eq 3) the following experimental observations must be interpreted:

(1) The reaction is highly specific. There is no exchange apparent of the bridging alkylidyne carbon either with the terminal carbonyls of the cluster or with free CO in solution.

(2) The photoisomerization quantum yields are linearly dependent on P_{CO} over the range 0–1.0 atm, despite the absence of a stoichiometric requirement for CO for isomerization. Under N_2 in cyclohexane or 2,5-dimethyltetrahydrofuran (DMTHF), ϕ_i was immeasurably small, but significant isomerization was noted in the presence of two-electron donors such as solvent THF or added ethylene or $P(OCH_3)_3$ in cyclohexane.

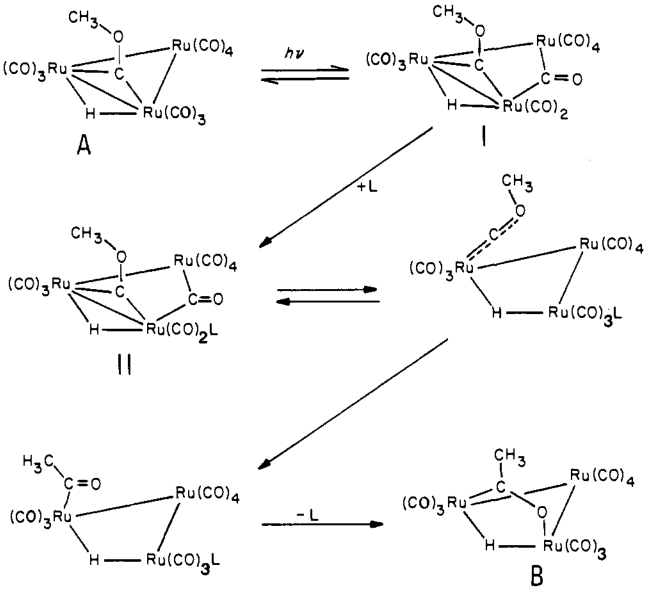
(3) The absence of any effect from using CCl_4 as the solvent argues against the role of trapable radicals in the mechanism.

(4) The ϕ_i values were sharply higher at shorter wavelengths of irradiation.

(5) Photosubstitution of L for a CO on A occurs readily at 313-nm irradiation and shows a λ_{irr} dependence for ϕ_s which closely parallels that seen for ϕ_i.

The mechanism proposed in Scheme I addresses the first two of these points. The first intermediate (I) in this speculative sequence is analogous to that proposed for the mechanism of the photofragmentation on the parent triruthenium cluster $Ru_3(CO)_{12}$,[2,5] while II is similar to the second intermediate in the $Ru_3(CO)_{12}$ photofragmentation mechanism. Conclusions regarding the nature of the second intermediate in the latter mechanism find support in the results of flash photolysis (fluid solutions)[3] and IR spectral (low temperature glasses) studies.[4]

Scheme I



Preliminary flash photolysis studies[25] of $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ are also consistent with the formation of a species such as II. A long-lived transient is formed in THF solution, but no transient with a lifetime longer than the flash (20 μs) is seen under analogous conditions in cyclohexane.

The photosubstitution reaction can be accommodated by an extension of this mechanism as indicated in Scheme II. For this generalized scheme, photolysis in the absence of donor ligands would lead simply to regeneration of A, either by nonradiative deactivation of A* (k_n) or by relaxation of I (k_a), which is formed with the efficiency $\phi_I = k_i/(k_n + k_i)$. If CO is added, then II′ (II from Scheme I with L = CO) would be formed with the efficiency

$$\phi_{II}' = \frac{k_{CO}[CO]\phi_I}{k_a + k_{CO}[CO]} \qquad (11)$$

For the case where $k_a > k_{CO}[CO]$, ϕ_{II}' would be strongly dependent on [CO] as would be the quantum yield for formation of B

$$\phi_i = \frac{k_b'\phi_{II}'}{(k_a' + k_b')} \qquad (12)$$

Furthermore, if II′ is sufficiently longlived for the CO's to undergo positional scrambling, reformation of A via the k_a' pathway would lead to CO exchange with an efficiency

$$\phi_{ex} = \frac{k_a'\phi_{II}'}{k_a' + k_b'} \qquad (13)$$

Under P_{CO} = 1.0 atm, the quantum yield ratio of exchange to isomerization ϕ_{ex}/ϕ_i is about 5, which in the context of Scheme II suggests a k_a'/k_b' ratio of about 5.

In the presence of another ligand L, the intermediate II″ (II with L ≠ CO) would be formed with the ligand dependent efficiency

$$\phi_{II}'' = \frac{k_L[L]\phi_I}{k_a + k_{CO}[CO] + k_L[L]} \qquad (14)$$

Four competitive paths from II″ would lead respectively to A, the bridging acyl isomer B, the substituted bridging acyl species C, or the substituted bridging alkylidine product D. Stable substitution products are not formed when L = THF, and the only pathway leading to net reaction is isomerization to B with the overall efficiency $\phi_i = (k_b''\phi_{II}'')/(k_a'' + k_b'')$. As was noted above, photolysis in THF under N_2 gave measurable yields of B ($\phi_i = 1.4 \times 10^{-3}$) which, while smaller than in cyclohexane, DMTHF, or THF under CO, were much larger than in the nondonors cyclohexane or DMTHF under N_2.

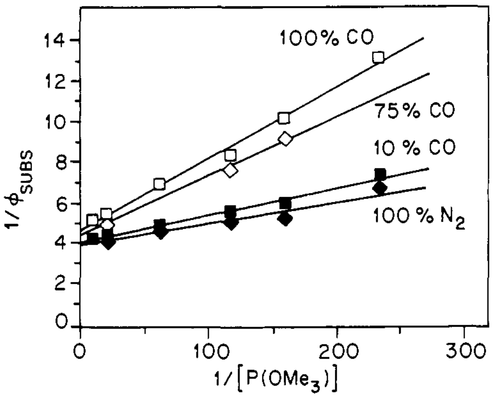


Figure 5. Plots of ϕ_s^{-1} vs $[P(OCH_3)_3]^{-1}$ under different CO/N_2 compositions at 1.0 atm. The lines are least-squares fits of the experimental data.

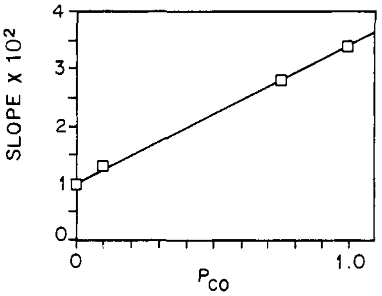


Figure 6. Plot of the slopes of the lines from Figure 5 vs the different concentrations of CO for which these were obtained.

When L is $P(n\text{-}Bu)_3$, $P(OCH_3)_3$, or pyridine, the most prominent photoreaction of A is substitution of L for CO to give the substituted bridging alkylidyne derivative D. At least for L = $P(OCH_3)_3$, formation of C is a minor competing pathway with a quantum yield about 1/25th that of photosubstitution. According to Scheme II, the quantum yield ratio ϕ_d/ϕ_c would be equal to k_d/k_c and equals approximately 25. No B was found under these conditions; thus, k_b'' must be small relative to the other pathways by which II″ decays.

In the context of the above definition of ϕ_{II}'', photosubstitution quantum yields should follow the relationship

$$\phi_d = C''\left(\frac{k_L[L]}{k_a + k_{CO}[CO] + k_L[L]}\right) = \phi_s \qquad (15)$$

where $C'' = (k_d''\phi_I)/(k_a'' + k_b'' + k_c'' + k_d'')$. Qualitatively, this indicates that intermediate I can be intercepted either by CO (to

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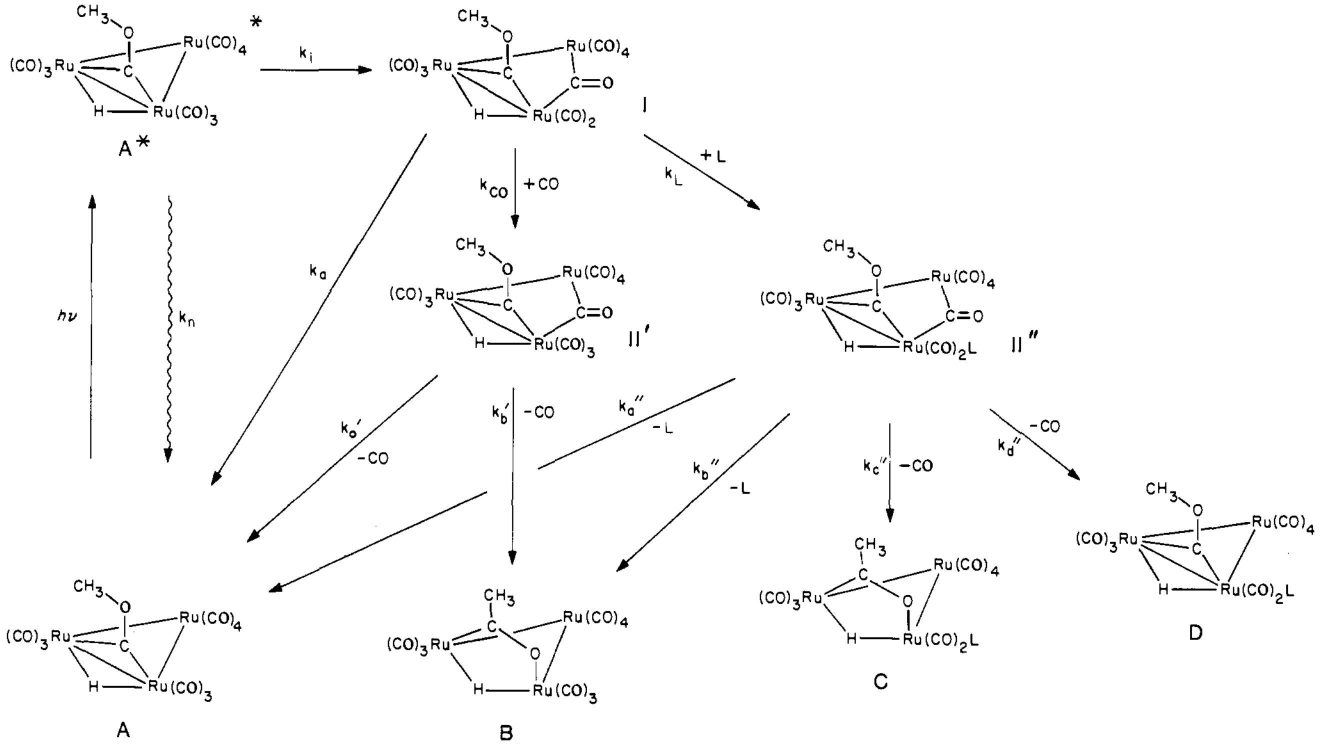
(25) Kyle, K.; Friedman, A. E.; Ford, P. C., studies in progress.

(26) Some quantitative comparisons can be drawn from these analyses of the quantum yield data according to Scheme II. For example, the slope to intercept ratio of the plot in Figure 6 is k_{CO}/k_a and equals 250 M^{-1}. Similarly, the slope to intercept ratio of the plot of ϕ_s^{-1} vs [THF] for the data in Table IV is k_{THF}/k_a and gives the value 3.3 M^{-1}. Thus, these data lead to the ratio k_{CO}/k_{THF} = 76, indicating that the ability of THF to capture intermediate I is considerably less than that of CO. In the same context, the slope to intercept ratios of the plots in Figure 5 equal $[k_{CO}[CO] + k_a]/k_L$. Use of the data for [CO] = 0.00 (dinitrogen atmosphere) gives a k_L/k_a ratio of 400 M^{-1} for L = $P(OCH_3)_3$, thus a k_{CO}/k_L ratio of about 0.63. Alternatively, if the data for P_{CO} 1.0 atm ([CO] = 0.0092 M) are used along with the relationship k_{CO} = (250 M^{-1})k_a, the k_{CO}/k_L ratio is calculated to be 0.57, fully in agreement with the above. Although the quantitative values of these ratios are subject to the errors inherent to calculations based on such extrapolations, they do clearly indicate that the reactivity order of various ligands with the proposed intermediate I would follow the order $P(OCH_3)_3$ > CO ≫ THF. Furthermore, by taking into account the relationships $k_a' = 5k_b'$ and k_{CO} = (250 M^{-1})k_a, the concentration of CO in cyclohexane at 1.0 atm [0.0092 M), and the quantum yield for CO exchange under these conditions (0.25), eq 11 and 13 can be used to estimate the quantum yield ϕ_I for formation of intermediate I as 0.31 mol/einstein. This and the limiting ϕ_s (about 0.22–0.25 from the intercepts in Figure 5) indicate that the principal decay pathway for intermediate II″ is loss of CO to give the substitution product D rather than loss of L to reform A.

Scheme II



give II′) or by L (to give II″), thus ϕ_s will be enhanced by increasing [L] but inhibited by increasing [CO]. The reciprocal of eq 15 is

$$(\phi_s)^{-1} = (C'')^{-1}\left(1 + \frac{k_{CO}[CO] + k_a}{k_L[L]}\right) \qquad (16)$$

Equation 16 predicts that plots of $(\phi_s)^{-1}$ vs $[L]^{-1}$ should be linear with a constant nonzero intercept $(C'')^{-1}$ and slopes of $(k_{CO}[CO] + k_a)/(C''k_L)$. Figure 5 shows such plots for the data in Table III, and from these it is seen that the results are consistent with this prediction. Furthermore, a plot of these slopes vs [CO] should also be linear (slope = $k_{CO}/(C''k_L)$) with a nonzero intercept ($k_a/(C''k_L)$). This prediction is also borne out (Figure 6).[26]

In a similar vein, ligands such as THF may also intercept I, hence inhibit formation of II″, therefore, of the photosubstitution products. If the intermediate formed by trapping I with THF largely decays to A, then a relationship such as indicated in eq 15 and 16 (with k_{THF}[THF] appearing rather than k_{CO}[CO] in the equation) should hold true. This is indicated qualitatively by the data in Table IV and by the demonstration that a plot of $(\phi_s)^{-1}$ vs [THF] in cyclohexane is linear for a constant concentration of L ($[P(OCH_3)_3]$ = 0.034 M) as predicted by such equations.[26]

While the above analysis of the effects of [CO], [L], and [THF] on the photosubstitution quantum yields is fully consistent with the mechanism shown in Scheme II, an alternative mechanism, namely the simple photodissociation of one CO (eq 17–19), should be considered. Indeed, this is the commonly accepted mechanism for the photosubstitutions of other mononuclear and polynuclear metal carbonyls.

$$HRu_3(CO)_{10}(\mu\text{-}COCH_3) \xrightarrow{h\nu} \underset{\text{III}}{HRu_3(CO)_9(\mu\text{-}COCH_3)} + CO \qquad (17)$$

$$\text{III} + CO \xrightarrow{k_{18}} HRu_3(CO)_{10}(\mu\text{-}COCH_3) \qquad (18)$$

$$\text{III} + L \xrightarrow{k_{19}} HRu_3(CO)_9L(\mu\text{-}COCH_3) \qquad (19)$$

According to this scheme, the photosubstitution yield would be determined by

$$\phi_s = \phi_{III}\left(\frac{k_{19}[L]}{k_{18}[CO] + k_{19}[L]}\right) \qquad (20)$$

where ϕ_{III} is the efficiency of forming intermediate III. The reciprocal of eq 20 would be

$$(\phi_s)^{-1} = (\phi_{III})^{-1}\left(1 + \frac{k_{14}[CO]}{k_{15}[L]}\right) \qquad (21)$$

This equation also predicts that plots of $(\phi_s)^{-1}$ vs $[L]^{-1}$ should be linear with a constant nonzero intercept as seen in Figure 5. However, the slopes of these plots would be simply $k_{18}[CO]/(\phi_{III}k_{19})$, and a plot of the slopes vs [CO] should be linear as in Figure 6, *but with a zero intercept* in contrast to that figure. Furthermore, the presence of THF should not inhibit the photosubstitution reaction according to this mechanism since THF trapping of III would give $HRu_3(CO)_9(\mu\text{-}COCH_3)(THF)$, which would react subsequently with L to give the photosubstitution product. *Thus, the mechanism described in Scheme II is much more consistent with the quantum yield data for the substitution reactions than is the alternative described by eq 17–19.*

The photoreaction of A with dihydrogen described by eq 9 can also be rationalized in terms of Scheme II. The preparation of an open coordination site either by an isomerization to give a species such as I or by ligand dissociation as in eq 17 allows reaction of the metal cluster with H_2 to give the trihydride, perhaps via the initial formation of a dihydrogen complex. Similar oxidative addition of dihydrogen to triruthenium clusters has been shown to be activated by nucleophiles that add to coordinated carbonyls to give nucleophile–carbonyl adducts and substantially enhance the lability of the remaining carbonyls.[27]

Comparison to the $Ru_3(CO)_{12}$ photochemistry[3,4] is in order. For this system also, two photoreaction modes, cluster fragmentation and ligand substitution (eq 1 and 2), were observed; however, a critical difference is that the two originate from different states and display markedly different dependences on the irradiation wavelength.[3] Indeed, quantum yield,[3] flash photolysis,[3] and low-temperature FTIR[4] data clearly point to CO dissociation as the principal mechanism for ligand photosubstitution on $Ru_3(CO)_{12}$. The formation of a photoisomer analogous to I and a subsequent adduct analogous to II along the cluster fragmentation photoreaction coordinate is also supported by quantum yield,[3] flash photolysis,[3] and low-temperature FTIR[4] data. Notably, when

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[27] Taube, D. J.; Rokicki, A.; Anstock, M.; Ford, P. C. *Inorg. Chem.* **1987**, *26*, 526–530.

methylcyclohexane solutions of $Ru_3(CO)_{12}$ containing PPh_3 were irradiated at low temperature (195 K) with the longer wavelengths for which cluster photofragmentation is the characteristic reaction in ambient solutions, an adduct with a bridging CO and a composition believed to be $Ru_3(CO)_{12}(PPh_3)$ (IV) was observed by FTIR.[4] Although the nearly exclusive net photoreaction in ambient temperature solutions with this excitation wavelength would be cluster fragmentation, warming these low-temperature solutions of the adduct led in part to the formation of the photosubstitution product $Ru_3(CO)_{11}(PPh_3)$ in a pathway presumably analogous to the k_d'' path in Scheme II. Thus, there appears to be a fine balance between the different pathways by which an intermediate such as IV will decay.

The competitive photosubstitutions and photofragmentations of the triosmium cluster $Os_3(CO)_{12}$ in the presence of various ligands have similarly been proposed to be the result of intermediates analogous to II and IV.[28] In the present case, the bridging alkylidyne and hydride ligands (i.e., for II′ and II″) may serve to inhibit cluster fragmentation, leaving the loss of CO or L as the principal decay routes but isomerization of the bridging alkylidyne ligand as an additional pathway unique to the μ-methoxyalkylidyne cluster.

There is one puzzling difference between the photochemistries of $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ and $Ru_3(CO)_{12}$. Although the electronic absorption spectra of these two clusters are qualitatively similar (both display strong, broad absorption bands of similar intensities at about 390 nm), the wavelength dependencies of their photoreactions are quite different. In particular, the photofragmentation reactions of $Ru_3(CO)_{12}$ were noted to occur as the result of excitation of this long wavelength absorption band, but A appears to be essentially inert to excitation at these wavelengths. Both photosubstitution and photoisomerization appear to be nearly exclusively the result of excitation of the shorter wavelength absorptions. Since the formation of similar intermediates is postulated for the photoisomerization of A and the photofragmentation of $Ru_3(CO)_{12}$, the different wavelength dependencies would imply that the seemingly similar longer wavelength absorption bands of A and $Ru_3(CO)_{12}$ may not have the same orbital parentages. In this context, it is notable that earlier workers have concluded that simple substitution of other ligands for one or more CO's of $Ru_3(CO)_{12}$ may indeed lead to reversals in the ordering of the lower energy excited states.[29]

In summary, the photolysis of $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ in various solvents has been demonstrated to lead both to "simple" photosubstitutions for the coordinated CO's and to an unprecedented O-to-C migration of the methyl group on the bridging alkylidyne ligand. The wavelength dependences of both photoprocesses are the same implying that both occur from common excited state(s) and/or intermediates. Such intermediates are proposed to be the unsaturated cluster I formed by photoinduced rearrangement of A and the subsequent ligand adduct II (Scheme I). Loss of CO or L from II competitive with rearrangement followed by ligand loss leads to regeneration of A, photosubstitution, or isomerization to the μ,η^2-acyl products (e.g., B), respectively.

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Registry No. A, 71737-42-3; B, 80800-53-9; C (L = $P(OCH_3)_3$), 117582-69-1; D (L = $P(OCH_3)_3$), 117582-67-9; D (L = PPh_3), 98065-38-4; D (L = PBu_3), 117582-70-4; D (L = Py), 117582-71-5; $Ru_3(CO)_{12}$, 15243-33-1; $[PPN][CH_3CO_2]$, 59386-05-9; $[Et_3NH][HRu_3(CO)_{11}]$, 117308-29-9; $[Et_3NH][HRu_3(^{13}CO)_{11}]$, 117582-65-7; $HRu_3(^{13}CO)_{10}(\mu\text{-}^{13}COCH_3)$, 117582-66-8; $HRu_3(CO)_{10}(\mu\text{-}^{13}COCH_3)$, 117605-91-1; $HRu_3(^{13}CO)_{10}(\mu\text{-}COCH_3)$, 117582-66-8; $HRu_3(CO)_8(P(OCH_3)_3)_2(\mu\text{-}COCH_3)$, 98065-61-3; $HRu_3(CO)_{10}(\mu,\eta^2\text{-}^{13}C(O)CH_3)$, 117582-68-0; $Ru(CO)_5$, 16406-48-7; CH_3CHO, 75-07-0; $H_3Ru_3(CO)_9(\mu\text{-}COCH_3)$, 71562-47-5.

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