A Mechanistic Study of the Photochemistry of $(C_5H_5)CoMe_2PPh_3$, Including Unimolecular and Bimolecular Excited-State Chemistry[1]

Anna Becalska and Ross H. Hill*

Contribution from the Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6. *Received September 6, 1988*

Abstract: Photolysis of $(C_5H_5)CoMe_2PPh_3$ in benzene solution by 432-nm light leads to intramolecular reductive elimination of ethane from the lowest singlet excited state with a quantum yield of 0.004. The resultant photoproduct then undergoes subsequent thermal chemistry to produce the stable radical, $(C_5H_5)CoMePPh_3$, and under prolonged photolysis $(C_5H_5)Co(PPh_3)_2$. The lowest triplet state was also studied and found to undergo bimolecular reactions with PPh_3 and C_2Ph_2. In the case of the reaction in the presence of PPh_3 the net reaction products were $(C_5H_5)CoMePPh_3$, methane, and under prolonged photolysis $(C_5H_5)Co(PPh_3)_2$. The quantum yield for this process is dependent on the concentration of PPh_3 and is given by $[PPh_3]/(3 + [PPh_3])$. For reaction with C_2Ph_2 the observed products were $(C_5H_5)Co(C_4Ph_4)PPh_3$ and 2,3-diphenyl-1-butene and the quantum yield is given by $[C_2Ph_2]/(0.3 + [C_2Ph_2])$.

Herein we report the results of our study on the mechanism of the photochemical reactions of $CpCoMe_2PPh_3$ ($Cp = C_5H_5$) in benzene. This report deals with its reactions in the absence of free ligands and in the presence of $2e^-$ ligands. In contrast with the well-studied thermal reactions of metal alkyl groups,[2] very few mechanistic studies have been conducted on the photochemical reactions of transition-metal alkyls. The bulk of this work indicates that photolysis initiates homolytic cleavage of the metal alkyl bond.[3,4] This is in contrast with the photochemistry of metal dihydrides which are known to undergo reductive elimination of dihydrogen upon irradiation.[4]

Although systems are known in which reductive elimination and homolytic cleavage are competitive processes, the only case we are aware of in which reductive elimination is the dominant process is in the photochemistry of $Pt_2(dppm)_2Me_3^+$.[5] Under a variety of conditions, reductive elimination was shown to be induced photochemically; however, it is not apparent if this reaction is a result of a primary photochemical step. The data were also consistent with elimination from an intermediate resultant from a primary photochemical process such as metal-metal bond cleavage.

In order to investigate further photochemical reductive elimination to form carbon-carbon bonds we chose to study $CpCoMe_2PPh_3$. This molecule forms a convenient basis for study as its thermal chemistry has been investigated primarily by Bergman et al. and is known to decompose producing methyl radicals on thermolysis.[6]

During the course of the investigation of the photochemical elimination of ethane from $CpCoMe_2PPh_3$ we also found some interesting chemistry resulting from bimolecular reactions of its triplet excited state.

Results

Characterization of the Products. The photolysis ($\lambda > 400$ nm) of degassed benzene solutions of $CpCoMe_2PPh_3$ ($Cp = C_5H_5$) in sealed NMR tubes was monitored by ^1H NMR and ESR spectroscopy. Initially, all we observed in the ^1H NMR were decreasing signals due to starting material and an apparent increase in the signals due to benzene-d_5 and ethane. Measurement of the T_1 for benzene indicated that this was an artifact of the relaxation rate increasing as radical production occurred. The spectra were then repeated with longer relaxation delays, 60 s, and a smaller pulse angle. With these acquisition parameters and the use of C_5H_{10} as an internal standard, it was possible to monitor the reaction quantitatively. Initially a decrease in the resonances due to $CpCoMe_2PPh_3$ and the production of ethane and broad resonances at 8.1 and 6.9 ppm (line width 30 Hz) were observed. In order to observe other signals attributed to the radical product we collected spectra over a spectral width of 5 kHz (on 100 MHz instrument), with very short acquisition times and no relaxation delay. Under these conditions the ^1H NMR shows the presence of broad absorption peaks at −20 ppm (line width 1100 Hz) and 5.7 ppm (line width 450 Hz). The positions of these peaks are temperature dependent, shifting toward higher field as the sample is cooled. The ^1H NMR is consistent with the formulation of the product as paramagnetic $CpCoMePPh_3$. Photolysis of the complex $CpCo(CD_3)_2PPh_3$ gives rise to an identical spectrum. On the basis of this experiment we assign the resonance at −20 ppm as due to the Cp ring protons and the resonances at 8.1, 6.9, and 5.7 ppm as due to the ring protons on the PPh_3. Unfortunately we have been unable to observe the protons on the methyl group.

The complex $CpCoMePPh_3$ has also been characterized by its ESR spectrum. In either benzene or toluene solution a single featureless signal is observed: the isotropic shift is $g = 2.141$, and the line width is 120 G, Figure 1a.[7] Under these conditions the lack of observation of hyperfine coupling in the spectrum of the radical is presumably due to relaxation effects. The anisotropic spectrum obtained in a toluene glass at −140 °C does however indicate some hyperfine interaction. Analysis of this was aided by obtaining the ESR spectra of both the $CpCoCH_3PPh_3$ and $CpCoCD_3PPh_3$ derivative, Figure 1b. Both spectra display approximate axial symmetry. The spectra of $CpCoCD_3PPh_3$ are better resolved although the most intense lines are visible in either complex. The predominant feature is the hyperfine coupling due to both ^{59}Co, 25 G, and ^{31}P, 198 G, being observed about g_1. An eight-line component, due to coupling with ^{59}Co, $S = 3.5$, is further split into a doublet due to ^{31}P, $S = 0.5$, hyperfine coupling. The observation of phosphorus hyperfine coupling causing a doublet unambiguously establishes that the radical is ligated by only one phosphorus donor. The other two components are g_2 centered about 2.001 with a hyperfine coupling due to Co, 27 G, and P, 87 G, and g_3 at 2.007 also showing hyperfine coupling due to Co, 23 G, and P, 77 G. Unfortunately due to the overlap of signals

---

[1] Hill, R. H.; Becalska, A. Presented at the 70th Canadian Chemical Conference, Sainte-Foy, Quebec, June 1987; paper ING-14-A2.

[2] Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic: New York, 1978. Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1978.

[3] Pourreau, D. B.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1985**, *24*, 249.

[4] Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic: New York, 1979.

[5] Hill, R. H.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1472. Azam, K. A.; Hill, R. H.; Puddephatt, R. J. *Can. J. Chem.* **1984**, *62*, 2029.

[6] Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 3973.

[7] Photolysis of $CpCoMe_2PPh_3$ with $\lambda > 310$ nm in the presence of PPh_3 yielded a different result. In this case, in addition to the signal described in the text, a second ESR signal at $g = 2.022$, $\Delta pp = 45$ G was observed. This particular reaction was not investigated further.

0002-7863/89/1511-4346$01.50/0

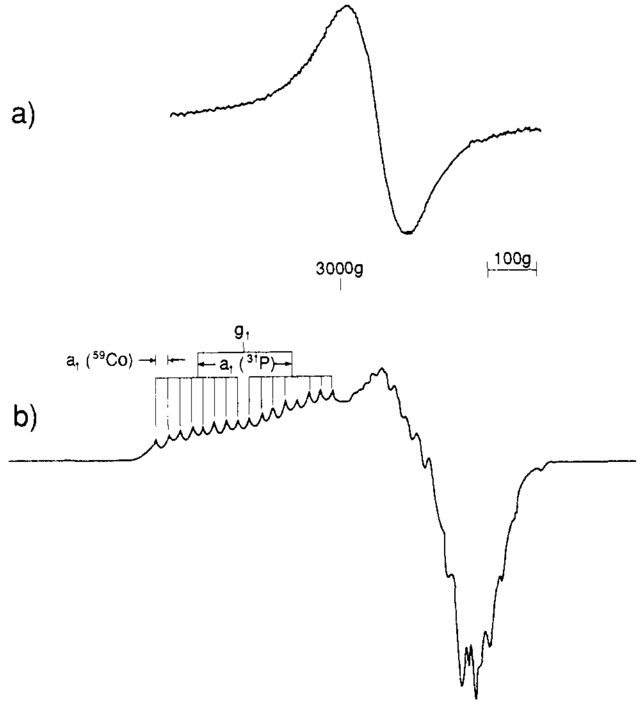

Figure 1. ESR spectrum of the complex $CpCoCD_3PPh_3$ at room temperature (a) and at −130 K (b) in toluene.

and the poor resolution in the high field region the assignment of g_1, g_2 and the magnitude of the hyperfine coupling about these positions are uncertain. The major conclusion however, that the radical contains a Co center ligated by one PPh_3, is established.

In order to measure the yield of the radical the integral of the ESR signal was compared with that of degassed standard solutions of $Ti(acac)_3$. The yield of paramagnetic product in the beginning of the reaction (up to 15% of the reaction) was found to be 100% (calculated on reacted starting material) by both NMR and ESR techniques. The maximum yield of the radical based on starting material was found to be 65% by NMR and 68% by ESR, when 98% of the starting material has been consumed.

In order to complete the characterization of $CpCoMePPh_3$ we prepared a derivative of it. A sample containing $CpCoMe_2PPh_3$ and PPh_3 was photolyzed as above. The reaction was stopped when the radical accounted for 58% of the total Co. The sealed NMR tube was then opened, under nitrogen, and CHI_3 was added to the solution. The ESR spectra of the resultant solution showed no signal. The ^1H NMR of this solution however showed the appearance of new resonances in both the Cp (4.45 ppm) and methyl (2.00 ppm; $^3J(PH) = 8$ Hz) regions with relative intensities of 5 to 3. These signals were shown to be due to the known complex $CpCoMeIPPh_3$ by comparing the NMR with that of an authentic sample prepared by a known route.[8] Using the relative intensity of the NMR signal the yield of $CpCoMeIPPh_3$ was found to be 50% based on total cobalt or 85% based on radical concentration prior to CHI_3 addition. The observed reaction is consistent with simple trapping of the radical by an iodine atom, eq 1. The high yield of this product conclusively estalishes that the radical must have a methyl group and is hence $CpCoMePPh_3$.

$$CpCoMePPh_3 \xrightarrow{CHI_3} CpCoMeIPPh_3 \qquad (1)$$

Further photolysis of solutions containing $CpCoMePPh_3$ gave rise to ^1H NMR signals due to methane at 0.22 ppm and two new cyclopentadiene resonances at 4.51 (triplet, JH–P = 1.2 Hz) and 4.48 ppm. The cyclopentadiene resonance at 4.51 ppm was identified as being due to $CpCo(PPh_3)_2$ by comparison with an authentic sample prepared independently by a known route.[9] This assignment was confirmed by the $^{31}P\{^1H\}$ NMR spectrum which contained a singlet at 69.1 ppm for both the authentic sample and our photolyzed solution. We have no evidence for the ultimate fate of the second product containing a cyclopentadiene group other than a ^1H NMR signal at 4.48 ppm, although the ^{31}P NMR spectrum indicates that this product has no PPh_3 substituent. It is worth noting that $CpCo(C_6H_6)_n$ (n = 1,2) have been reported. The characterization was based on mass spectral data; however, no other spectroscopic data was provided.[10] By comparison with the internal standard the spectroscopic yield was determined to be 43% for $CpCo(PPh_3)_2$ and 40% for $CpCo(C_6H_6)_n$. Throughout the photolysis the sum of the concentration of starting material, $CpCo(PPh_3)_2$, $CpCo(C_6H_6)_n$, calculated from the NMR, and $CpCoMePPh_3$ calculated from ESR were within error (~20%) of accounting for 100% of the Co. In synthetic scale reactions the yield of recrystallized $CpCo(PPh_3)_2$ was 40% based on Co or 80% based on the limiting reagent, PPh_3.

Reactions were also monitored by visible absorption spectroscopy. Early in the reaction an isobestic point is observed at 425 nm which is lost at longer photolysis times. If the gases produced are analyzed early in the reaction the amount of ethane formed corresponds to 0.48 mol per mol of $CpCoMe_2PPh_3$ decomposed, with only trace amounts of methane detected. Analysis of the resultant solutions produced by exhaustive photolysis of $CpCoMe_2PPh_3$, after the isobestic point is lost, indicated the formation of ethane, 0.38 equiv, and methane, 0.85 equiv. The overall equation for the photodecomposition of $CpCoMe_2PPh_3$ is then given by eq 2. It should be noted that both steps, the formation of $CpCoMePPh_3$ and its decomposition, are light induced. The photolysis of the solution containing paramagnetic species, together with other products but no starting material, results in decrease of the intensity of the ESR and NMR signals associated with $CpCoMePPh_3$ and concomitant increase of the intensity of NMR signals due to methane, ethane, and other products. If stored in the dark at room temperature solutions containing $CpCoMePPh_3$ are stable for periods exceeding 1 year, as monitored by ESR spectroscopy. The methane formed arose from radical abstraction of ^1H from solvent as shown by isotopic labeling experiments (see later).

$$CpCoMe_2PPh_3 \xrightarrow{h\nu} \tfrac{1}{2}CpCo(PPh_3)_2 + CH_4 + \tfrac{1}{2}C_2H_6 + \tfrac{1}{2}CpCo(C_6H_6)_n \qquad (2)$$

The photolysis ($\lambda > 400$ nm) of $CpCoMe_2PPh_3$ in the presence of equimolar PPh_3 was also monitored by ^1H NMR and ESR spectroscopy. The initial product was again found to be the paramagnetic species (up to 5% of the reaction). The ESR spectrum at ambient temperature showed a single resonance $g = 2.137$, $\Delta pp = 120$ G for which no fine structure was resolved. This absorption is clearly due to the radical $CpCoMePPh_3$ identified earlier. The ^1H NMR and low-temperature ESR were also obtained and are identical with those found for $CpCoMePPh_3$. Spectroscopic conversions to $CpCoMePPh_3$ as high as 35%, based on total cobalt, were obtained under these conditions. Further photolysis leads to the growth of the signals due to ethane, methane, and $CpCo(PPh_3)_2$. In no case were signals due to ring deuterated toluene observed. The spectroscopic yield of $CpCo(PPh_3)_2$ following exhaustive photolysis was 100% from NMR.

Gas chromatographic analysis of the product mixture indicated the production of ~1 mol of methane and traces of ethane per mol of $CpCoMe_2PPh_3$ decomposed under these conditions. The initial reaction is hence given by eq 3. When the solutions were photolyzed for an extended period, an additional equivalent of methane was produced.

$$CpCoMe_2PPh_3 \xrightarrow[PPh_3]{h\nu} CpCoMePPh_3 + CH_4 \qquad (3)$$

Photolysis of degassed benzene solutions of $CpCoMe_2PPh_3$ and C_2Ph_2 were monitored by ^1H NMR spectroscopy. Once again photolysis ($\lambda > 400$ nm) resulted in loss at the resonances asso-

---

(8) Yamazaki, H.; Hagihara, N. *J. Organomet. Chem.* **1970**, *21*, 431.

(9) Yamazaki, H.; Hagihara, N. *Bul. Chem. Soc. Jpn.* **1971**, *44*, 2260.

(10) Lee, W. S.; Koola, J. D.; Brintzinger, H. H. *J. Organomet. Chem.* **1981**, *206*, C4.

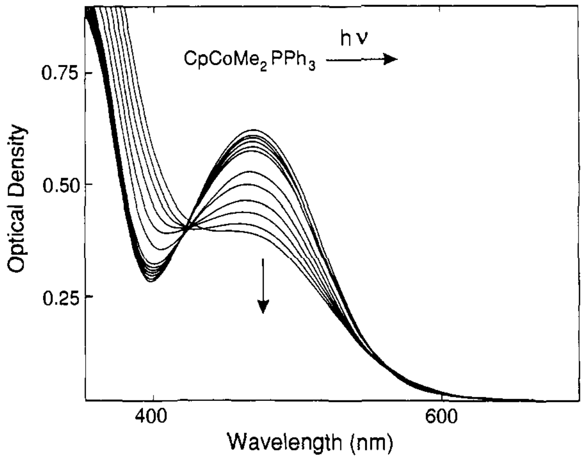

Figure 2. Electronic spectral changes accompanying the 436-nm photolysis of $(C_5H_5)CoMe_2PPh_3$ in benzene.

ciated with $CpCoMe_2PPh_3$; however, in this case no paramagnetic product was observed. ^1H NMR spectra showed new resonances which were assigned to the known compounds $CpCo(C_4Ph_4)PPh_3$ and 2,3-diphenyl-1-butene. The formation of $CpCo(C_4Ph_4)PPh_3$ was confirmed by its ^{31}P NMR spectrum which exhibited a signal at 52.5 ppm. Both, the metal containing and the organic products, had identical spectra as authentic samples prepared thermally.[9,11] The equation for the reaction in the presence of C_2Ph_2 is hence given by eq 4. In addition to these products, weak resonances due to ethane and methane were observed in the NMR spectra. The spectroscopic yield of $CpCo(C_4Ph_4)PPh_3$ was measured to be 75% based on initial Co content.

$$CpCoMe_2PPh_3 + 3C_2Ph_2 \xrightarrow{h\nu} CpCo(C_4Ph_4)PPh_3 + PhC(CH_2)CH(Me)(Ph) \quad (4)$$

Isotope Labeling Studies. Two different types of labeling studies were undertaken. The first was done in order to determine the hydrogen source in the production of methane, whereas the second was done to determine whether ethane was formed in an inter- or intramolecular process.

Unfortunately in the absence of any additives the relative amounts of hydrogen atom abstraction from the solvent could not be determined due to the low amounts of methane formed under these conditions. In the presence of PPh_3, however, the methane formed is primarily a result of hydrogen atom abstraction from the solvent with less than 30% resulting from other sources. This was shown by analysis of the gas formed from photolysis in benzene-d_6. Photolysis of $CpCo(CD_3)_2PPh_3$ in benzene led to the production of less than 5% CD_4 indicating that the methyl groups on the complex are not a major source of hydrogen atoms.

In order to study the ethane production, similar experiments were done in which samples containing both $CpCo(CH_3)_2PPh_3$ and $CpCo(CD_3)_2PPh_3$ were degassed and irradiated. Using low light intensities, to inhibit coupling of the methyl radicals formed, the sample was irradiated, and the ethane produced was analyzed by mass spectroscopy. The result indicated that less than 12% of the ethane formed consists of $C_2H_3D_3$. This shows that the ethane produced in dilute solution, under the conditions of quantum yield determinations, is formed primarily by an intramolecular process.

Quantum Yield Determination. The quantum yield for ethane formation from $CpCoMe_2PPh_3$ at 436 nm was measured by monitoring samples irradiated under N_2. The concentration was set such that the optical density of $CpCoMe_2PPh_3$ was in excess of 1 and the reaction was monitored to less than 10% conversion. Under these conditions we can approximate that the light is absorbed entirely by the starting material. The yield of ethane produced was quantitated by gas chromatography. A plot of ethane production vs einsteins absorbed yields a quantum yield for ethane formation of 0.004 ± 0.001.

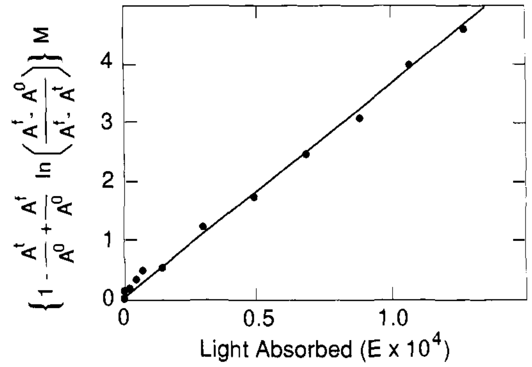

Figure 3. Plot of the kinetic factor, $[1 - A^t/A^0 + (A^f/A^0)\ln\{(A^f - A^0)/(A^f - A^t)\}]M$ vs quanta absorbed for the photochemical reaction of $(C_5H_5)CoMe_2PPh_3$ in benzene.

Table I. Quantum Yields[a] for $CpCoMe_2PPh_3$ Decomposition

λ	$[PPh_3]$	Φ
436	0.0468	0.0235
	0.0486	0.0254
	0.100	0.0422
	0.196	0.0780
	0.380	0.146
	1.23	0.382
460	0.065	0.0263
	0.137	0.051
	0.27	0.108
	0.38	0.139
λ	**$[C_2Ph_2]$**	**Φ**
436	0.0044	0.022
	0.0119	0.045
	0.0201	0.062
	0.0445	0.108
	0.0635	0.186
	0.2949	0.486
	0.7077	0.668

[a] Relative errors are approximately 0.002 although the absolute error is presumably larger.

The remainder of the quantum yields were determined as decomposition quantum yields. Irradiation of an oxygen free benzene solution of $CpCoMe_2PPh_3$ at 436 nm, with known amounts of light, was accomplished with a calibrated PTI Quanta count. The extent of reaction was monitored by visible spectroscopy. A typical set of spectra are shown in Figure 2. Early in the reaction an isobestic point is evident at λ = 422 nm which is lost at high conversions. In lower concentration studies the isobestic point is retained to ~100% completion; however, small amounts of sample decomposition during preparation made these studies less reliable for quantum yield determinations. The decomposition quantum yield derived from the slope of a plot of $[1 - A^t/A^0 + (A^f/A^0) \ln \{(A^f - A^0)/(A^f - A^t)\}]M$ vs quanta absorbed, Figure 3 (see Appendix for explanation of the quantities plotted), was $\Phi^{436} = 0.0084 \pm 0.0020$. Similar experiments yielded decomposition quantum yields, at a variety of wavelengths, to be $\Phi^{400} = 0.012 \pm 0.002$ and $\Phi^{460} = 0.0062 \pm 0.0020$.

Quantum yields were also determined at 436 and 460 nm in the presence of PPh_3. The quantum yield was found to increase in a nonlinear fashion as a function of PPh_3 concentration (Table I). The efficiency was not strongly wavelength dependent; quantum yields at 460 nm were slightly lower than at 436 nm but were within error of being identical. At the end of the reaction the amount of ethane produced was measured, and the light absorbed by the starting material was calculated. The quantum yield for ethane formation was found to be 0.0048 ± 0.002, based on an average of six determinations, independent of PPh_3 concentration over the range from 0.011 to 0.11 M. Similarly quantum yields for $CpCoMe_2PPh_3$ decomposition in the presence of C_2Ph_2 were determined. The calculated quantum yields and corresponding C_2Ph_2 concentrations are included in Table I. The

---

(11) Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 3237.

quantum yields increase in a nonlinear fashion with increasing C_2Ph_2 concentration. Once again gas chromatography was done on the resultant product mixtures, and the quantum yield of ethane formation determined to be 0.0048 ± 0.002, on the average of seven determinations, independent of C_2Ph_2 concentration over the range from 0.022 to 0.668 M.

Proof of the Bimolecular Nature of the Reaction Producing the $CpCoMePPh_3$. If photolysis of a sample of $CpCoMe_2PPh_3$ was immediately followed by obtaining the ESR and the sample was then allowed to sit in the dark, the ESR signal due to $CpCoMePPh_3$ was observed to increase, corresponding to a change in concentration of the radical, from 0.0040 to 0.0042 M after 2 days. This indicated that the initially formed product reacted with something else to produce the radical, $CpCoMePPh_3$. The reaction was also monitored by NMR, and the decrease of signals due to $CpCoMe_2PPh_3$ indicated that the change in concentration from 0.00028 to 0.00013 M observed coincided with the production of $CpCoMePPh_3$. This is consistent with ~0.0001 M of an unsaturated intermediate abstracting a methyl group from an equivalent number of mol of $CpCoMe_2PPh_3$ to produce 0.0002 M $CpCoMePPh_3$. Further evidence for the bimolecular nature of this secondary reaction was obtained by the following low-temperature experiment: A solution of the $CpCoMe_2PPh_3$ in toluene was cooled in the cavity of an ESR spectrometer. The solution was frozen and photolyzed for 17 h. During this time no signal due to the radical product was observed. Warming of the solution resulted in the appearance of an ESR signal identical with that obtained for the room temperature photolysis of $CpCoMe_2PPh_3$. This experiment also demonstrates that no $CpCoMePPh_3$ is formed directly via photochemical methyl radical loss from starting material.

Discussion

Mechanism of the Reductive Elimination of Ethane. Photolysis of $CpCoMe_2PPh_3$ in benzene leads to the initial production of $CpCoMePPh_3$, ethane, and eventually $CpCo(PPh_3)_2$, methane, and $CpCo(C_6H_6)_n$. The intramolecular nature of the ethane formation is most consistent with initial reductive elimination of ethane, eq 5. The photogenerated $CpCoPPh_3$ fragment then

$$CpCoMe_2PPh_3 \xrightarrow{h\nu} CpCoPPh_3 + C_2H_6 \qquad (5)$$

abstracts a methyl group from the starting material to produce our initially observed organometallic photoproduct, $CpCoMePPh_3$. The related complex, $CpCo(CPhCHPh)PPh_3$, has been reported previously by Yamazaki and Hagihara.[8] Although $CpCoMePPh_3$ degrades under photolysis, we have found that in air-free benzene solution it is stable for periods exceeding 1 year at room temperature.

One of the questions we wished to answer concerns the intimate details of the reductive-elimination step. The possibility of phosphine loss followed by elimination from a thermal intermediate was considered, as the bulk of precedent in thermal studies has shown reductive elimination to be enhanced by ligand loss. For example, the elimination of ethane from $LAuMe_3$[12] and L_3PtMe_3[13] (L = phosphine) are thought to occur following initial phosphine loss, eq 6 and 7. In order to probe this question the reductive

$$LAuMe_3 \rightleftharpoons L + AuMe_3 \rightarrow C_2H_6 + LAuMe \qquad (6)$$

$$L_2PtMe_3I \rightleftharpoons L + LPtMe_3I \rightarrow C_2H_6 + L_2PtMeI \qquad (7)$$

elimination of ethane was monitored in the presence of PPh_3. In this case if photochemical ethane elimination was the result of phosphine loss, eq 8, the presence of excess phosphine should trap

$$CpCoMe_2PPh_3 \xrightarrow{h\nu} CpCoMe_2 + PPh_3 \rightarrow C_2H_6 + CpCo(C_6H_6)_n \qquad (8)$$

the photogenerated $CpCoMe_2$ fragment producing the starting material. This would lead to an observation of a reduction in quantum yield for ethane production as the concentration of free PPh_3 was increased. The elimination quantum yield for ethane was found to be invariant over a wide range of PPh_3 concentrations indicating no such dissociation was initiating the reductive elimination. During this set of experiments we did find an increase in the quantum yield for methane production and $CpCoMe_2PPh_3$ disappearance.

Initially, the observed product of the reaction is the radical, $CpCoMePPh_3$. This is formed via a methyl group extraction by the unsaturated $CpCoPPh_3$ from a second equivalent of starting material. This leads to the production of two molecules of the organometallic product per effective photon, eq 9. The quantum

$$CpCoPPh_3 + CpCoMe_2PPh_3 \rightarrow 2CpCoMePPh_3 \qquad (9)$$

yield for decomposition varies only slightly with irradiation wavelength and is within error of being independent of wavelength over the range from 400 to 460 nm. The measured quantum yield for decomposition, 0.0084, is approximately twice that observed for ethane formation, 0.004. This is consistent with one photon leading to the elimination of one molecule of ethane but resulting in the decomposition of a second molecule of $CpCoMe_2PPh_3$ via a subsequent thermal process.

The second observation which must be accounted for is the production of methyl radicals and eventually methane upon extended photolysis. This is a result of the subsequent photolysis of the radical product and not a competing process for the starting materials (in the absence of free phosphine). Consistent with this interpretation is the observation that the production of methane continued during the photolysis of the sample containing paramagnetic $CpCoMePPh_3$ together with other products but no starting material. The production of methyl radicals must then proceed from the photolysis of $CpCoMePPh_3$.

The overall reaction is given by eq 2. Initially intramolecular reductive elimination of ethane, without prior PPh_3 loss (eq 5), to produce $CpCoPPh_3$ occurs. This is followed by the thermal reaction of $CpCoPPh_3$ with $CpCoMe_2PPh_3$ to produce two $CpCoMePPh_3$ radicals (eq 9), which then undergo photodecomposition producing two methyl radicals, and the observed metal-containing products, $CpCo(PPh_3)_2$ and $CpCo(C_6H_6)_n$.[14]

The methyl radicals then presumably abstract hydrogen from solvent to produce methane. Interestingly we find that no toluene is formed despite the presence of free methyl radicals in solution.

This photochemistry is in contrast with the thermolysis of $CpCoMe_2PPh_3$ reported by Evitt and Bergman. They report that the thermal reaction occurs at 70 °C ($t_{1/2}$ = 12 h) to yield methane and ethane in a 6:1 ratio.[15] It should be noted that the ground state of this complex undergoes facile reductive elimination of acetone following insertion of carbon monoxide.[16] This indicates that the energy required for the concerted elimination from the ground and first excited states may only differ by a small amount.

Bimolecular Chemistry of Excited-State $CpCoMe_2PPh_3$. In the presence of PPh_3 the major photoproducts are $CpCoMePPh_3$, identified by its characteristic ^1H NMR and ESR, and CH_4, identified by GC and ^1H NMR. The reaction equation is hence given by eq 10.

$$CpCoMe_2PPh_3 \xrightarrow[PPh_3]{h\nu} CpCoMePPh_3 + CH_3^{\bullet} \qquad (10)$$

Under the low concentration and irradiation intensities utilized in this study the ultimate fate of the methyl radicals is primarily hydrogen atom abstraction from solvent to produce methane. Once again no detectable amounts of toluene appear to be formed via addition to benzene. This may indicate that under low radical concentrations the addition to benzene by methyl radicals is re-

---

(12) Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255.

(13) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E. *J. Chem. Soc., Dalton Trans.* **1974**, 2457.

(14) Although we have not conducted a complete study of this second reaction, the following observation indicates phosphine dissociation occurs initially. The photostability of $CpCoMePPh_3$ is greatly affected by phosphine: in the absence of phosphine, the radical undergoes decomposition following 5 days of photolysis, whereas, in the presence of 0.01 M PPh_3, solutions of the radical decay less than 15% under identical conditions.

(15) See footnote 10 in ref 6.

(16) Bergman, R. G. *Acc. Chem. Res.* **1980**, *13*, 113.

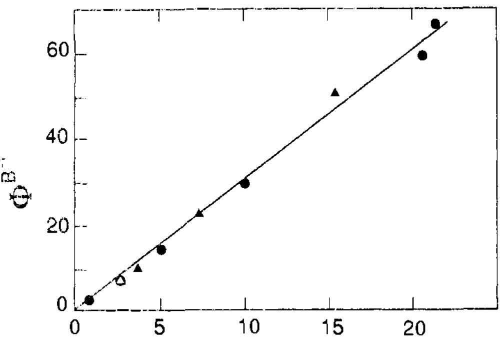

Figure 4. A plot of the reciprocal of the quantum yield for the bimolecular excited state reaction between $(C_5H_5)CoMe_2PPh_3$ and PPh_3 for 436 (●) and 460 (▲) nm photolysis vs reciprocal phosphine concentration.

versible. In addition, hydrogen atom abstraction from either the Cp or methyl groups of $CpCoMe_2PPh_3$ is a minor process. This result is in contrast to the methane derived from $MeMn(CO)_5$ where the majority of the methane is a result of abstraction from the methyl group of starting material.[17] The abstraction, other than from solvent, must be primarily from free PPh_3.

The reaction between PPh_3 and $CpCoMe_2PPh_3$ must originate from an excited state lower than the state responsible for the reductive-elimination reaction, since this process does not quench the elimination of ethane. We assign the state undergoing reaction, in the presence of added ligands, as the lowest triplet since the state undergoing the elimination is presumably the lowest singlet.

The observed increase in the quantum yield for decomposition of $CpCoMe_2PPh_3$ with increasing ligand concentration indicates that this new reaction must occur as a result of a bimolecular reaction between PPh_3 and an excited state of $CpCoMe_2PPh_3$. If this is true the overall decomposition quantum yield, Φ^D, is expected to follow eq 11 where Φ^0 is the quantum yield for de-

$$\Phi^D = \Phi^0 + \Phi^{ISC}\frac{k_b[L]}{k_D + k_b[L]} \qquad (11)$$

composition in the absence of PPh_3, Φ^{ISC} is the quantum yield for intersystem crossing into the state reacting with free ligand, k_D is the rate constant for decay to the ground state, L is PPh_3, and k_b is the rate constant for the bimolecular reaction of the excited state with PPh_3. Rearrangement and substitution of Φ^B, the quantum yield for the bimolecular reaction, for $\Phi^D - \Phi^0$ yields eq 12. This indicates that a plot of $1/\Phi^B$ vs $1/[PPh_3]$ should be

$$\frac{1}{\Phi^B} = \frac{1}{\Phi^{ISC}}\left\{1 + \frac{k_D}{k_b[L]}\right\} \qquad (12)$$

linear. Such a plot is shown in Figure 4. The intercept is approximately 1 indicating Φ^{ISC} is within error of 1. The slope of the line then gives the ratio k_D/k_b as 3.0 ± 0.2. The quantum yield data are hence consistent with a bimolecular reaction between excited state $CpCoMe_2PPh_3$ and PPh_3. Before we consider the nature of this interaction it is useful to discuss the reaction with C_2Ph_2.

The photochemical reaction of $CpCoMe_2PPh_3$ with C_2Ph_2 leads to the production of $PhC(CH_2)CH(CH_3)(Ph)$ and $CpCo(C_4Ph_4)PPh_3$. These products have been identified previously in the thermal reaction of $CpCoMe_2PPh_3$ with C_2Ph_2.[11] As in the case of added PPh_3, the upper state reaction forming methane and ethane was not quenched by the C_2Ph_2. Once again the quantum yield dependence on additive concentration fits the form of eq 12 where L = C_2Ph_2 as illustrated by Figure 5. The value of Φ^{ISC} is once again observed to be ~1, and the ratio of k_D/k_b is given by 0.33 ± 0.03. This value allows us to estimate the maximum rate for k_D. If the reaction with C_2Ph_2 is diffusion-controlled, then k_b is ~1.6×10^{10} m^{-1} s^{-1} (calculated from the modified Debye Huckel equation); hence k_D would be on the order of 5×10^9 s^{-1}. This value represents an upper limit for k_D; if the rate of reaction with C_2Ph_2 is smaller than the diffusion limit, then the inherent decay rate of the excited state will be correspondingly increased.

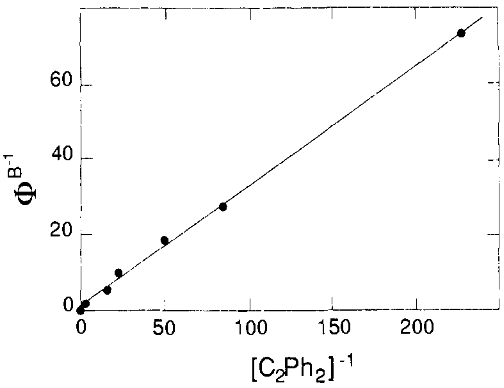

Figure 5. A plot of the reciprocal quantum yield for the excited state reaction between $(C_5H_5)CoMe_2PPh_3$ and C_2Ph_2 for 436-nm photolysis vs reciprocal C_2Ph_2 concentration.

In both the reactions of $CpCoMe_2PPh_3$ with PPh_3 and C_2Ph_2 the data indicate a bimolecular excited state reaction. The simplest scheme is that the reductive elimination occurs from the lowest excited singlet state and that the bimolecular reaction proceeds from the lowest triplet state. The intersystem crossing quantum yield then represents the efficiency of conversion from the singlet to triplet state. This bimolecular reaction is consistent with a simple associative process forming intermediates of the type $CpCoMe_2PPh_3L$ (L = PPh_3, C_2Ph_2).[18] The initially formed species may be transition states. An alternate possibility is that these represent true intermediates, albeit with low thermal stability. If the latter is true it is most likely that the structure is best represented by the ring-slipped geometry, $(\eta^3\text{-}C_5H_5)CoMe_2PPh_3L$. Unfortunately our data does not allow us to distinguish between these possibilities.

The initial reaction is, in the case of PPh_3, the formation of $CpCoMe_2(PPh_3)_2$. This product then decomposes via methyl radical loss to generate $CpCoMe(PPh_3)_2$ which is not observed. This intermediate then loses PPh_3 to produce the observed product, $CpCoMePPh_3$, and regenerate free PPh_3.

The reaction with C_2Ph_2 must result in initial formation of a molecule of stoichiometry, $CpCoMe_2(C_2Ph_2)PPh_3$. This may occur either by coordination of C_2Ph_2 or by direct insertion of C_2Ph_2 into the cobalt-methyl bond. Unfortunately our experiments cannot distinguish between these two possibilities. The result of either process must eventually be the inserted species. This then presumably undergoes subsequent rearrangements discussed previously in Bergman and Evitt's study of the thermal chemistry of $CpCoMe_2PPh_3$ with C_2Ph_2.[11] The main difference between the thermal and photochemical processes is that the thermal chemistry is thought to arise from an unsaturated $CpCoMe_2$ fragment, whereas the photochemistry is an associative reaction. The only other significant difference is that the thermal reaction produces some (*Z*)-2,3-diphenyl-2-butene (7%) via dis-

---

(17) Gismondi, T. E.; Rausch, M. D. *J. Organomet. Chem.* **1985**, *284*, 59.

(18) An initial electron transfer to $CpCoMe_2PPh_3{}^*$ is ruled out by the following observations. If the reaction was initiated by an electron transfer the rate would be affected by the thermodynamics of the transfer. The reduction potential of $CpCoMe_2PPh_3$ (~ +0.32 V vs SCE) minus the excitation energy of ~2.7 V gives an excited state reduction potential of ~ −2.4 V. The oxidation potentials of PPh_3 and C_2Ph_2 are ~1.3 and ~2.2 V vs SCE indicating a reductive electron transfer to $CpCoMe_2PPh_3{}^*$ to be energetically favorable by ~1.1 V (~25 kcal) and ~0.2 V (~5 kcal) in the cases of PPh_3 and C_2Ph_2, respectively. The relative rates for these processes would be predicted, on energetic grounds, to be $PPh_3 > C_2Ph_2$. The slopes of Figure 4 and 5 give the rate constant ratio k_D/k_b for these systems. The deactivation rate constant k_D should be invarient as it is associated only with the properties of the excited state hence the relative rates for k_b are 1:10 for PPh_3:C_2Ph_2. As this is not the ordering of rate constants expected for a reductive electron-transfer reaction we rule out electron transfer. The details of the electrochemical measurements are in the Experimental Section.

sociation from an intermediate in the reaction. Photochemically we observe none of this product, presumably since the rate of this dissociation is slow at room temperature.

The possibility that the reaction with C_2Ph_2 occurs by dissociation of PPh_3 and reaction with PPh_3 is associative is unlikely because both reactions approach a limiting quantum yield of one. This behavior indicates a common mechanism for the two reactions.

Conclusions

The photochemistry of $CpCoMe_2PPh_3$ alone and in the presence of ligands has been elucidated. In the absence of ligands the excited state molecule reductively eliminates ethane, and the unsaturated fragment then reacts with a molecule of starting material yielding $CpCoMePPh_3$. Photolysis of the radical eventually yields $CpCo(PPh_3)_2$, "CpCo", presumably as its benzene solvate, and methyl radicals. The initially formed excited state can undergo intersystem crossing to yield triplet state $CpCoMe_2PPh_3{}^*$. It is this triplet state molecule which undergoes bimolecular reactions with incoming ligands. In the case of PPh_3 the ultimate product is the radical $CpCoMePPh_3$, whereas with C_2Ph_2 the metal-containing product is $CpCo(C_4Ph_4)PPh_3$.

Bimolecular excited state chemistry as described here is well-known in organic photochemistry (i.e., the 2 + 2 cycloadditions of olefins[19]); however, it has rarely been observed for inorganic systems except in cases involving initial electron transfer.[20] Photochemically induced oxidative addition reactions of alkyl halides to square-planar metal centers have been shown to be initiated through a bimolecular step; however, this may be through an initial electron-transfer step.[21] We are only aware of a few other associative reactions of organometallic excited states not involving electron transfer. The photosubstitution of CO by PPh_3 in $Mn(NO)(CO)_4$ was reported by Keeton and Basolo[22] to occur by both an associative and a dissociative pathway. Associative excited state chemistry has also been reported to occur in low-temperature matrix isolation experiments. Photolysis of $CpCo(CO)_2$ in a CO matrix indicated the production of $(\eta^3\text{-}C_5H_5)Co(CO)_3$.[23] Similarly photolysis of Cp_2ReH in a CO matrix led to, among other things, $Cp_2ReH(CO)$.[24]

Of the bimolecular reactions described here the reaction with PPh_3 is particularly intriguing as it represents catalysis of an excited state reaction by the PPh_3.

Experimental Section

$[CpCoMe_2PPh_3]$ was obtained by published procedures[25,26] and identified by ^1H and ^{31}P NMR spectra. Benzene was purified by distillation from Na. $Ti(acac)_3$ was obtained by published procedure.[27]

^1H and ^{31}P NMR spectra were recorded with a Bruker SY100 or a Bruker WM400 spectrometer. Chemical shifts are reported relative to TMS (^1H) or H_3PO_4 (^{31}P). UV-vis spectra were measured with a Beckman D.B. or a Cary 17 spectrophotometer. ESR spectra were recorded with a Varian E4.

Analysis of methane and ethane by gas chromatography was carried out with a Varian 1400 with a Porapak Q column at ambient temperature. Isotope analysis was done by means of a HP 5985 GC MS.

Standard samples for ESR were prepared by dissolving known amounts (6 samples, 0.0023–0.0106 g) of $Ti(acac)_3$ in benzene (0.5 mL). Solutions were degassed and flame sealed in 5 mm NMR tubes.

All samples were handled under N_2 unless otherwise specified.

Photolysis of $[CpCoMe_2PPh_3]$. A solution of $CpCoMe_2PPh_3$ (0.005 g) in benzene-d_6 (0.6 mL) was degassed and flame sealed in a 5 mm NMR tube. The sample was then photolyzed with the filtered (5.0 cm of H_2O in Pyrex and bandpass $\lambda > 413$) output of a focused xenon lamp held 30 cm from the sample. During photolysis the sample was cooled by immersion in a water bath at 4 °C. The ^1H NMR and ESR spectra were monitored. C_5H_{10} was used as an internal standard for ^1H NMR spectra. The concentration of the radical was measured by comparison of the integrals of the ESR signal with that of standard solutions of $Ti(acac)_3$.

Upon photolysis ^1H NMR signals due to $CpCoMe_2PPh_3$ were observed to decrease. The appearance and continual increase of the ESR signal due to $CpCoMePPh_3$ and ^1H NMR signals due to CH_4, C_2H_6, $CpCo(PPh_3)_2$; and $CpCo(C_6H_6)_n$ were monitored. At completion, when ^1H NMR signals due to $CpCoMe_2PPh_3$ and the ESR signal were no longer observed, the peaks due to $CpCo(PPh_3)_2$ accounted for 43% of the original compound. The ^{31}P NMR confirmed the production of $CpCo(PPh_3)_2$ ($\delta = 69.1$ ppm).

Experiments were conducted in toluene using the procedure above as were experiments with $CpCo(CD_3)_2PPh_3$.

A solution of $CpCoMe_2PPh_3$ (0.0895 g) was prepared in a benzene (1 mL) hexane (4 mL) mixed solvent. This was degassed and photolyzed with the filtered (5.0 cm H_2O, and band pass $\lambda > 413$) output of a focused 150 W xenon lamp for 11 days. The solvents were removed under reduced pressure, and the resultant residue was dissolved in 2 mL of hexane. The solution was cooled to 277 K, and over 2 h red crystals precipitated. These crystals were filtered, washed twice with cold hexane, and dried under vacuum (yield 0.036 g, 40% based on Co). The crystals were identified as $CpCo(PPh_3)_2$ by their ^1H and ^{31}P NMR spectra which were obtained in benzene-d_6. No other products were isolated from the reaction mixture.

Photolysis of $CpCoMe_2PPh_3$ at 153 K. A solution of $CpCoMe_2PPh_3$ (0.0033 g) in toluene-d_8 (0.6 mL) was degassed and flame sealed in a NMR tube. The sample was photolyzed for 17 h with the filtered output of the xenon lamp at 153 K. The ESR spectra were run prior, during, and after photolysis at 153 K. No signal due to the paramagnetic product, $CpCoMePPh_3$, was observed. The solution was then warmed to room temperature, kept at room temperature for 3 min, and subsequently cooled to 153 K where an additional ESR spectrum was obtained. This spectrum showed a signal due to $CpCoMePPh_3$.

Reaction of $CpCoMePPh_3$ with CHI_3. A sample of $CpCoMe_2PPh_3$ in benzene-d_6 was photolyzed until the ESR signal indicated a 58% conversion to $CpCoMePPh_3$. At this point the sample tube was opened, CHI_3 was added to the solution, and the NMR and ESR were obtained. The ESR indicated no $CpCoMePPh_3$ remained. The NMR indicated the production of $CpCoMeIPPh_3$. The yield for this reaction was 50% based on total cobalt and 85% based on $CpCoMePPh_3$.

Photolysis of $[CpCoMe_2PPh_3]$ in the Presence of PPh_3. A solution containing $CpCoMe_2PPh_3$ (0.010 g) and PPh_3 (0.07 g) in benzene-d_6 (0.5 mL) was degassed and flame sealed in a 5 mm NMR tube. This sample was then photolyzed with the filtered output of a xenon lamp. The ESR indicated the production of $CpCoMePPh_3$. In this case NMR signals due to C_2H_6, CH_4, and $CpCo(PPh_3)_2$ were observed. At long photolysis times the signal due to $CpCo(PPh_3)_2$ accounted for 100% of the starting material. At this point the ESR spectrum was obtained and showed no signal.

An experiment was conducted in which a solution containing $CpCoMe_2PPh_3$, PPh_3, and benzene-d_6 was prepared as above. This sample was photolyzed with $\lambda > 310$ nm. In this case $CpCo(PPh_3)_2$ accounted for less than 10% of the starting material. The ESR was recorded and showed two signals: $g = 2.137$, $\Delta pp = 120$ G and $g = 2.022$, $\Delta pp = 45$ G.

Photolysis of $[CpCoMe_2PPh_3]$ and C_2Ph_2. In a similar experiment $CpCoMe_2PPh_3$ (0.007 g), C_2Ph_2 (0.015 g), and benzene-d_6 (0.05 mL) were degassed and hermetically sealed in an NMR tube. Photolysis as above caused loss of $CpCoMe_2PPh_3$ and production of $CpCo(C_4Ph_4)PPh_3$, 2,3-diphenyl-1-butene, and a small amount of methane and ethane as monitored by ^1H NMR.

Quantum Yield Determinations. Irradiations were carried out with a PTI QUANTA COUNT system equipped with either a 150 W or 75 W xenon lamp. The instrument was calibrated at 366, 406, and 436 nm with Actinochrome R (obtained from PTI), and 460 nm was calibrated by an extrapolation of this calibration. (Typical band width used was 4 nm).

In a typical experiment, 4.0 mL of a stock solution of $CpCoMe_2PPh_3$ (0.0052 g) in benzene (20.0 mL) was degassed by three freeze-pump-thaw cycles, each cycle to a maximum residual pressure of 5×10^{-5} Torr at 77 K. The sample was then flame sealed in a 1 cm quartz cuvette and irradiated such that a known amount of light was absorbed by the solution. The extent of the reaction was monitored by the change in optical density at 460 nm (Figure 2). The kinetic factor, $[1 - A^t/A^0 + (A^f/A^0)\ln\{(A^f - A^0)/(A^f - A^t)\}]M$, was plotted against light absorbed, I, yielding the decomposition quantum yield as the slope (for details on the derivation of the kinetic factor see the Appendix).

Studies of Gas Evolution. A solution of $CpCoMe_2PPh_3$ (3.51×10^{-6} mol) and C_2Ph_2 (4.7×10^{-5} mol) in benzene (4.0 mL) was degassed and

---

(19) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978.

(20) Sutin, N.; Creutz, C. *J. Chem. Educ.* **1983**, *60*, 809.

(21) Hill, R. H.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1218.

(22) Keeton, D. B.; Basolo, K. *Inorg. Chim. Acta.* **1972**, *6*, 33.

(23) Crichton, O.; Rest, A. J.; Taylor, D. J. *J. Chem. Soc., Dalton Trans.* **1980**, 167.

(24) Chetwynd-Talbot, J.; Grebenik, P.; Perutz, R. N.; Powell, M. H. A. *Inorg. Chem.* **1983**, *22*, 1675.

(25) King, R. B. *Inorg. Chem.* **1966**, *5*, 82.

(26) Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 7003.

(27) Lo, G. Y.-S.; Brubaker, C. H. *J. Inorg. Nucl. Chem.* **1972**, *34*, 2375.

irradiated such that the quantum yield for decomposition was determined to be 0.045. A sample of the liquid was then removed and injected into the GC. Comparison of the peaks observed in a GC with those produced by identically contained samples containing benzene (4.0 mL) and known amounts of methane and ethane indicated that $3.4 \pm 0.4 \times 10^{-7}$ mol ethane and $7.0 \pm 1 \times 10^{-7}$ mol methane had been produced. The quantum yield for ethane formation in hence calculated as 4.3×10^{-3} and methane as 9.0×10^{-3}. Similar experiments were done in the presence of a variey of C_2Ph_2 and PPh_3 concentrations.

In the absence of additives $CpCoMe_2PPh_3$ (7.21×10^{-6} mol) in benzene (4.0 mL) under N_2 was photolyzed to less than 10% conversion, and the ethane production was monitored by GC, calibrated as before. A plot of ethane produced vs quanta absorbed gave a quantum yield for ethane formation of 0.0040 ± 0.0005. It was found that methane production could not be measured in this way due to a small amount of decomposition during repeated sampling (the amount of methane, though not reproducible, was less than 5% of the ethane). If solutions were prepared and flame sealed into a cuvette and then irradiated, as above ethane was found, yet only trace amounts of methane were observed.

A sample (4.0 mL) prepared from $CpCoMe_2PPh_3$ (0.0053 g) in benzene (20 mL) was degassed by three freeze-pump-thaw cycles and flame sealed in a cuvette. The sample was then irradiated with the filtered (5.0 cm of H_2O in Pyrex and band pass $\lambda > 413$) output of a xenon lamp until no further change in the absorption spectra was evident. Gas analysis was then conducted, and ethane (0.38 mol/mol Co) and methane (0.85 mol/mol Co) were identified. A second aliquot (4.0 mL) was added to PPh_3 (0.2 g), degassed, and photolyzed to completion. Analysis of the gas indicated the production of 0.98 mol methane per mol $CpCoMe_2PPh_3$.

Mass Spectral Studies. A degassed solution containing $CpCoMe_2PPh_3$ (0.0022 g) in benzene-d_6 (10 mL) was photolyzed with 436 nm light, obtained from a 100 W Hg lamp directed through a water filter and a monochromator, for 13 days. The sample was then frozen in liquid N_2, and the gas admitted directly into the mass spectrometer (ionization 12 eV). Peaks were observed at *m/e* 15 (3.6), *m/e* 16 (23.3), and *m/e* 17 (43.3). This result was not reproducible; in a separate experiment the result was 25:100:50.

In a similar experiment $CpCoMe_2PPh_3$ (0.0026 g) and PPh_3 (0.0165 g) in benzene-d_6 (10 mL) was photolyzed for 7 days. Analysis, as above, yielded *m/e* 15 (4.4), *m/e* 16 (38.2), and *m/e* 17 (100).

Similarly, a sample of $CpCo(CD_3)_2PPh_3$ was photolyzed in benzene. The relative intensity of *m/e* 20 to *m/e* 19 was 2:45, 2:39, and 1:59 in three separate experiments.

In a similar experiment a mixture of $CpCo(CH_3)_2PPh_3$ (0.0016 g) and $CpCo(CD_3)_2PPh_3$ (0.0016 g) was degassed in benzene (10 mL). The sample was photolyzed as above, except a 21% transmission filter was used to reduce the light intensity. Sampling of the gasses produced yielded *m/e* 36 (56), *m/e* 33 (12), *m/e* 32 (87), *m/e* 31 (6), *m/e* 30 (91), *m/e* 29 (9), and *m/e* 28 (100). Standard samples containing ethane indicated that under these conditions the ratio of ethane to ethylene observed as a result of fragmentation was 3:5. Correcting the observed *m/e* 28 and 30 by this yields an intensity of 160 due to C_2H_6. For the C_2D_6 the intensity is 140. This leaves an intensity of 42 due to $C_2H_3D_3$. This indicates that 12% of the ethane formed is $C_2H_3D_3$. The experiment was repeated yielding *m/e* 36 (26), *m/e* 33 (4.7), *m/e* 32 (100), *m/e* 31 (3.1), *m/e* 30 (46.2), *m/e* 29 (5.1), and *m/e* 28 (89). This yields less than 5% $C_2H_3D_3$.

Electrochemical Measurements. Solutions of $CpCoMe_2PPh_3$, PPh_3, and C_2Ph_2 were prepared in distilled acetonitrile with 0.1 M TEAP as a supporting electrolyte. Cyclic voltammograms were recorded using a Princeton Applied Research Model 173 potentiostat and Model 175 programmer with a platinum electrode and a Ag/AgCl reference electrode. The oxidations were found to be in all cases irreversible at 0.32 V, $CpCoMe_2PPh_3$, 1.3 V, PPh_3, and 2.2 V, C_2Ph_2 vs SCE.

Acknowledgment. We thank Dr. Gregg A. Lane and Dr. Steven Holdcroft for electrochemical measurements, Joanne Johnson and Patrick Rowe for preliminary experiments, and the Natural Sciences and Engineering Research Council of Canada for research support.

Appendix

The quantum yield, Φ, is generally given by eq A-I where B is the number of mol of product and I' is the light absorbed by the starting complex. In our experimental setup the measured

$$\frac{\mathrm{d}B}{\mathrm{d}I'} = \Phi \qquad \text{(A-I)}$$

parameter is not the light absorbed by the starting complex, I', but the light absorbed by both starting complex and the product, I. The quantities I' and I can be related by the ratio of $\epsilon^A A$ to $\epsilon^A A + \epsilon^B B$ as in eq A-II where ϵ^x is the extinction coefficient of

$$I' = I\,\frac{\epsilon^A A}{\epsilon^A A + \epsilon^B B} \qquad \text{(A-II)}$$

x and A is the number of mol of starting material (eq A-II). The final relation required is that the total number of mol of cobalt remains invariant hence the initial number of moles, M, equals the sum $A + B$ at any time. Substituting for all A terms then combining A-I and A-II yields A-III.

$$\mathrm{d}B = \Phi\,\mathrm{d}I\,\frac{\epsilon^A(M-B)}{\epsilon^A(M-B) + (\epsilon^B B)} \qquad \text{(A-III)}$$

Rearrangement of A-III yields A-IV which when integrated from the initial conditions $I = 0$, $B = 0$ yields A-V.

$$\left\{1 + \frac{\epsilon^B B}{\epsilon^A(M-B)}\right\}\mathrm{d}B = \Phi\mathrm{d}I \qquad \text{(A-IV)}$$

$$\Phi x I = B + \frac{\epsilon^B}{\epsilon^A}\left\{-B + M\ln\frac{M}{M-B}\right\} \qquad \text{(A-V)}$$

$$\Phi x I/M = 1 - \frac{A^t}{A^0} + \frac{A^f}{A^0}\ln\left\{\frac{A^f - A^0}{A^f - A^t}\right\} \qquad \text{(A-VI)}$$

Substituting absorption terms into A-V leads to eq A-VI where A^x is the optical density at time X.