

Photosubstitution of Two Iron Pentacarbonyl CO's in Solution via a Single-Photon Process: Dependence on Dispersed Ligands and Role of Triplet Intermediates

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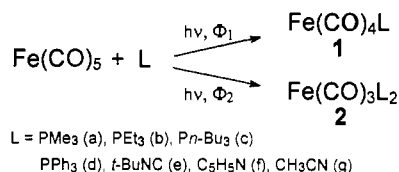
Photolysis of $\text{Fe}(\text{CO})_5$ in cyclohexane at 337 nm in the presence of PR_3 ($\text{R} = \text{Et}, \text{Me}, n\text{-Bu}, \text{Ph}$) pyridine, $\text{CNC}(\text{CH}_3)_3$, and CH_3CN was performed under conditions where secondary photolysis of photoproducts was negligible. Depending on the dispersed ligand, both **1** and **2** ($\text{Fe}(\text{CO})_4\text{L}$ and $\text{Fe}(\text{CO})_3\text{L}_2$, respectively) were formed. At low concentrations of dispersed ligand relative to $\text{Fe}(\text{CO})_5$, we report the first observation of quantum yields greater than unity for noncatalytic reactions leading to the formation of **1** and **2**. The mechanism of reaction is proposed to involve the formation of multinuclear species via the reaction of $\text{Fe}(\text{CO})_5$ with coordinatively-unsaturated intermediates. At high ligand concentrations, the formation of multinuclear species is inhibited and the total quantum yield is 0.8. When investigated for the specific case of PEt_3 , the product ratio of **2**/**1** did not change for 1-10% conversion of $\text{Fe}(\text{CO})_5$. It is concluded that, at high concentrations of dispersed ligand, a single-photon process produces **2**. The role of triplet intermediates was probed using triplet sensitizers and quenchers. The product ratio was unchanged when $\text{Fe}(\text{CO})_5$ was triplet-sensitized with xanthone in the presence of PEt_3 . Disubstituted product was formed when $\text{Fe}(\text{CO})_4\text{PEt}_3$ was triplet-sensitized with benzophenone in the presence of PEt_3 . Finally, the distribution of products was changed with the addition of triplet quenchers. It is proposed that $\text{Fe}(\text{CO})_5$ photolysis produces a triplet $\text{Fe}(\text{CO})_4$. Further reaction with L forms triplet $\text{Fe}(\text{CO})_4\text{L}$, which dissociates CO in competition with intersystem crossing to the ground state.

Introduction

Ligand dissociation from organometallic complexes is a common event following irradiation.¹ It provides a vacant site on the metal for the addition of a dispersed nucleophile and therefore can result in ligand substitution. It is a paradigm that only a single ligand dissociates per photon in solution and that multiple photosubstitutions are the result of multiphoton absorption.²⁻⁴ Thus it is noteworthy that disubstituted products were reported as single-photon products upon UV irradiation of $\text{Fe}(\text{CO})_5$.^{5,6} Early reports received little recognition perhaps because of limited experimental results or the yields of disubstituted products were low. In a preliminary communication, we reported an example where the quantum yield for disubstituted product (**2a**, Scheme 1) is not only high but is significantly greater than that for the monosubstituted product (**1a**).⁷ $\text{Fe}(\text{CO})_5$ appears to be the only documented case where two independent ligands substitute upon the absorption of a single photon. We have proposed that this unusual photochemistry may be attributed to the formation of a ground-state triplet intermediate, $^3\text{Fe}(\text{CO})_4$, which reacts with a dispersed ligand to form a triplet, $^3\text{Fe}(\text{CO})_4\text{L}$, that subsequently loses a CO, allowing the addition of a second ligand and the formation of $\text{Fe}(\text{CO})_3\text{L}_2$.⁷

In the current investigation, we present a full account of our results establishing the formation of the disubstituted product, **2**, as a single-photon process. The distribution of **1** and **2** for various ligands (Scheme 1) is reported, and we have found that disubstitution occurs in most cases (in addition to monosubstitution) but the distribution of **1** and **2** varies greatly. In addition, we have investigated the potential role of triplet species using triplet-quenching and -sensitization experiments. Finally, the

Scheme 1



first observation of quantum yields exceeding unity for the formation of **1** and **2** is reported. This is probably not a catalytic process and occurs when the concentration of dispersed ligand is low relative to that of $\text{Fe}(\text{CO})_5$.

Experimental Section

Materials. All chemicals and solvents (HPLC grade) were used as received from Aldrich unless otherwise indicated. 9,10-Dimethylanthracene (DMA) was purified by recrystallization from ethanol prior to use. *trans*-Azobenzene was recrystallized after refluxing in ethanol for 5 h. (*E*)-2-[1-(2,5-dimethyl-3-furanyl)ethylidene]-3-(1-methylethylidene)succinic anhydride (fulgide, Aberchrome 540) was obtained from Aberchromics, Ltd., and kept at -20°C until used. $\text{Fe}(\text{CO})_5$ (Strem Chemicals) was purified three times by trap-to-trap vacuum distillation prior to each use. Triphenylphosphine (Baker) was recrystallized from hot ethanol. Trimethylphosphine (97%) was refluxed with CaH_2 under argon and distilled prior to use for PAC experiments. Triethyl- and tributylphosphines (99%) were stored under argon until used. *tert*-Butylisocyanide was trap-to-trap distilled before use. Pyridine (Mallinckrodt, AR) was passed through an alumina column or distilled from KOH after refluxing for several hours. Cyclohexane was refluxed overnight with potassium and freshly distilled prior to use. Toluene (MCB or Fisher spectral grade) was distilled prior to use. Ethanol was obtained from Aper Alcohol and Chemical, and methanol was obtained from Mallinckrodt (HPLC). Benzophenone, biphenyl, ferrocene, and anthracene were vacuum-sublimed prior to use. Xanthone and azulene were used as received.

The syntheses of **1d**,⁸ **1f**,⁹ and potassium ferrioxalate followed published procedures and are described in the supplementary material.

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The NMR and IR spectra agree with those reported in the literature.¹⁰⁻¹⁵ The preparation and characterization of other iron complexes were described previously.¹⁶ All iron complexes were stored under argon at -20 °C until used.

Actinometry. The actinometric methods and apparatus have been described previously.¹⁶ Light from a xenon arc lamp (150-W Ushio UXL-151H, PTI A1010 lamp housing, and PTI LPS-220 power supply) was passed through a 10-cm water filter (PTI 02-A002), a neutral-density filter (10% transmission), a Schott filter (UG11, 100-nm bandwidth at 325 nm), and an interference filter (Corion P10F, 10-nm bandwidth at 337 nm) and focused on the sample cuvette with a 10 cm focal length lens. During irradiation, solutions in the cuvette were stirred with a Teflon stir bar and thermostatted at 25.0(1) °C. The light intensity was measured using a chemical actinometric method (*vide infra*) before and after each sample was irradiated. A pair of cuvettes, one for samples and one for chemical actinometers, were standardized against each other by irradiating the same chemical actinometer solution in each cuvette and determining the absorbed light intensities. The light intensity was also monitored during sample irradiation with a photodiode placed permanently in the light beam.

Four different chemical actinometric methods were used to ensure the reliability of intensity measurements. These methods use DMA (1.7 mM in 1,1,2-trichloro-2,2,1-trifluoroethane),¹⁷ azobenzene (0.64 mM in methanol),¹⁸ fulgide (4–5 mM in toluene),¹⁹ and ferrioxalate (0.006 M in 0.1 N H₂SO₄).²⁰ In each case, the intensity was determined from the change in moles of reactant or product resulting from photolysis. For DMA, azobenzene, and fulgide the intensity entering the solution was determined from eq 1. ΔA is the change in the absorbance of the solution

$$I = ((\Delta A)V/\epsilon_{\lambda}d\tau\Phi) \quad (1)$$

at the monitoring wavelength (λ), V is the volume of irradiated solution (2–3 mL), ϵ_{λ} is the molar absorptivity at λ , d is the cuvette path length (1 cm), τ is the duration of irradiation in seconds, and Φ is the quantum yield of the actinometric reaction.

The loss of DMA was monitored at 324 nm. Since previous work indicates $\epsilon_{\lambda}\Phi$ varied only 3% when the irradiation wavelength was varied between 334 and 395 nm, $\epsilon_{\lambda}\Phi$ was assumed to be 627 for irradiation at 337 nm, the same as that for 334-nm irradiation.¹⁷ The conversion of *trans*-azobenzene to *cis*-azobenzene was monitored at 358 nm. In agreement with previous results, ϵ_{358} was found to be $1570 \pm 3 \text{ M}^{-1} \text{ cm}^{-1}$.¹⁸ For photolysis at 337 nm, Φ is 0.15. The product of fulgide irradiation was monitored at 494 nm, where ϵ_{494} is $8200 \text{ M}^{-1} \text{ cm}^{-1}$ and Φ is 0.20.¹⁹

The previously described method using potassium ferrioxalate was used.²⁰ Ferrioxalate (3 mL) was irradiated in a 10 mm path length cuvette. A 1-mL aliquot of the irradiated solution was diluted to the mark in a 10-mL flask containing 3 mL of 0.1% 1,10-phenanthroline and 0.5 mL of acetate buffer (0.6 M sodium acetate/0.36 N H₂SO₄). The formation of iron(II) phenanthroline was monitored by its absorbance at 510 nm after the solution had equilibrated for 30 min or more in the dark. The absorbance by a blank sample, prepared identically but without irradiation, was used to correct for background absorbance. The light flux absorbed by the sample was calculated from eq 2.

$$I = (\Delta A)V_1V_3/(\Phi\epsilon_{\lambda}V_2t) \quad (2)$$

ΔA is the change in absorbance at 510 nm compared to that of the blank sample, V_1 , V_2 , and V_3 are the respective volumes in liters of the irradiated solution (3 mL), the aliquot (1 mL), and the flask (10 mL), Φ is the

quantum yield for formation of iron(II) phenanthroline, ϵ_{λ} is the molar absorptivity of iron(II) phenanthroline at 510 nm, and t is the irradiation time (s).

The molar absorptivity of the iron(II) phenanthroline complex was determined using a standard Fe(II) solution prepared by dissolving ferrous ammonium sulfate (Aldrich, 99.997%) in 0.1 N H₂SO₄. An aliquot of the standard solution was diluted to the mark in a 10-mL flask containing 3 mL of 0.1% 1,10-phenanthroline and 0.5 mL of acetate buffer (0.6 M sodium acetate/0.36 N H₂SO₄), and the absorbance was measured at 510 nm. For our spectrometer, ϵ_{510} was determined to be $11098 \pm 134 \text{ M}^{-1} \text{ cm}^{-1}$.²⁰ The quantum yield used for 337-nm irradiation was 1.23.²⁰

Sample Preparation and Irradiation for Quantum Yield Measurements. The following procedures were typical for quantum yield measurements. In an N₂-purged glovebag, PPh₃ (1.3 g, 5 mmol) was added to a septum-sealed 50-mL flask previously purged with argon. The PPh₃ was diluted to the mark with cyclohexane, and the solution was purged with argon for 15 min. Fe(CO)₅ (12 mg, 0.06 mmol) was transferred with a syringe to a septum-sealed 10-mL volumetric flask (previously evacuated and filled with argon) and diluted with the PPh₃ solution by using a cannula. The resultant solution was mixed and purged with argon for 15 min. About 2 mL of this solution (6 mM Fe(CO)₅ and 0.1 M PPh₃) was transferred to a septum-sealed cuvette with a cannula and purged with argon for 5 min prior to irradiation.

In cases where a sample solution was saturated with CO, the solution in the cuvette was bubbled with CO for 10–15 min. The volume of the solution in the cuvette was determined by gravimetry and from the density of cyclohexane at 25 °C (0.7737 g/mL).²¹ The chemical actinometer was irradiated immediately before and after the sample irradiation. Irradiation times were generally 5–15 min at $(5-15) \times 10^{-10} \text{ einstein s}^{-1}$. The absorbances of sample solutions were greater than 2.5 to ensure that most of the light was absorbed, and the conversion of Fe(CO)₅ was kept below 10% to avoid photolysis of products.

The concentrations of photoproducts were determined by using FTIR spectroscopy. After irradiation, samples were protected from ambient light and temporarily stored in 1-mL vials. The solution was then transferred within an N₂-filled glovebag to a 0.5 or 1.0 mm path length NaCl IR cell previously calibrated by measuring the absorbance of a CO stretching peak at different concentrations of 1 and 2 in cyclohexane. The IR spectrum of the unphotolyzed solution was recorded for each run and subtracted from the IR spectrum of the photolyzed solutions. All spectra for quantum yield measurements were obtained within 3 h of irradiation. In triplet-sensitized or -quenching experiments, the procedures were the same as above except that sensitizers or quenchers were also dissolved in the ligand stock solution. The following expression was used to calculate the quantum yield

$$\Phi = \Delta m/(tI)$$

where Δm is the moles of product formed, t is irradiation time (s), and I is the light intensity absorbed by the sample (einstein s^{-1}). Measurements were made in triplicate using aliquots taken from the same Fe(CO)₅ stock solution. Independent experiments were made with different stock solutions.

Instrumentation. All IR spectra were obtained on a Mattson Galaxy or Polaris FTIR spectrometer, and NMR spectra were obtained on a Varian VXR 300 NMR spectrometer. UV-vis absorbance measurements were determined with a Guilford Response II spectrophotometer.

The FTIR spectrometers were calibrated with authentic samples of 1 and 2 before or after a quantum yield determination. In an N₂-filled glovebag, a stock solution of ligand was prepared by dissolving the ligand to a 25-mL flask with a microsyringe (or gravimetrically for solid samples) and diluting to the mark with cyclohexane. Pure 1 and 2 were weighed into a 10-mL volumetric flask, and the flask was sealed with a septum, evacuated, and filled with argon. A stock solution of products was prepared by diluting them to the mark with the ligand solution. To make several solutions for FTIR calibration, aliquots of the stock solution of products were transferred to 10-mL flasks using a microsyringe and diluted to the mark with the stock ligand solution. These solutions (0.04–0.5 mM in 1 and/or 2) spanned the concentrations of 1 and 2 generated during the quantum yield measurements and were used with the PLS-QUANT (Galaxy) or SQUANT (Polaris) software provided by Mattson. The same quantum yields were obtained when the calibration was performed manually by plotting the area under the IR peak versus the

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Table 1. Quantum Yields of Photosubstitution of $\text{Fe}(\text{CO})_5$ in the Presence of PEt_3 in Cyclohexane at 337 nm

$[\text{PEt}_3]$, mM	$[\text{Fe}(\text{CO})_5]$, mM	$[\text{PEt}_3]/[\text{Fe}(\text{CO})_5]$	n^a	Φ_1	Φ_2	$\Phi_1 + \Phi_2$	Φ_2/Φ_1
96	11	8.7	1	0.32(3)	0.45(1)	0.77	1.4
41	10.3	4.0	1	0.38(1)	0.49(5)	0.87	1.3
8.2	8.3	1.0	1	0.38(3)	0.420(4)	0.80	1.1
0.96	5.5	0.17	4	0.57(4)	0.30(5)	0.87	0.53
0.96	9.7	0.10	1	1.09(13)	0.31(9)	1.40	0.28
0.71	8.6	0.09	1	1.22(7)	0.26(7)	1.48	0.21
0.96	49	0.020	1	1.10(3)	0.060(4)	1.16	0.055
0.96	85	0.011	1	1.3(3)	0.092(5)	1.4	0.071
8.2	8.3	1.0	1	0.54(1)	0.28(1)	0.82	0.52 ^b
0.96	5.5–6.1	0.16–0.17	3	0.62(2)	0.07(3)	0.69	0.11 ^b
0.96	9.7	0.1	1	0.63(7)	0.037(7)	0.67	0.058 ^b
0.71	8.6	0.09	1	0.70(7)	0.085(22)	0.79	0.12 ^b
0.96	49	0.020	1	0.76(3)	0.024(6)	0.78	0.032 ^b
0.96	85	0.011	1	0.98(6)	0.052(3)	1.03	0.053 ^b

^a n indicates independent sets of experiments; errors are a standard deviation in the last digit. ^b CO-saturated solution.

Table 2. Quantum Yields for Photosubstitution of $\text{Fe}(\text{CO})_5$ in the Presence of PMe_3 in Cyclohexane at 337 nm

$[\text{PMe}_3]$, mM	$[\text{Fe}(\text{CO})_5]$, mM	$[\text{PMe}_3]/[\text{Fe}(\text{CO})_5]$	n^a	Φ_1	Φ_2	$\Phi_1 + \Phi_2$	Φ_2/Φ_1
32	9.7	3.3	1	0.32(1)	0.48(2)	0.80	1.5
10.6	9.9	1.1	1	0.34(5)	0.48(1)	0.82	1.4
1.0	9.7	0.10	1	0.650(3)	0.153(5)	0.80	0.22 ^b
1.0–1.1	9.7	0.10–0.11	2	0.80(8)	0.25(5)	1.05	0.31

^a $[\text{Fe}(\text{CO})_5] = 9.7$ mM. ^b CO-saturated solution.

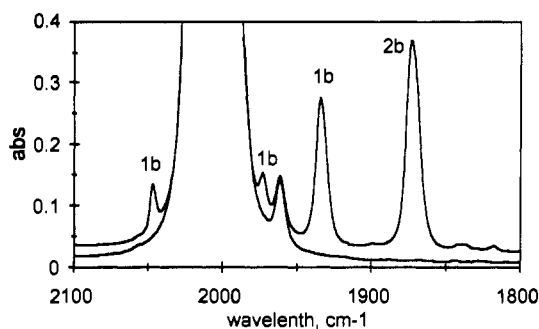


Figure 1. Infrared spectra of the CO stretching region before (lower spectrum) and after (upper spectrum) 337-nm photolysis for 10 min of 9.1 mM $\text{Fe}(\text{CO})_5$ with 102 mM PEt_3 in cyclohexane.

concentration of the standard solution. The autocorrelation values (R^2) for the calibration plots were usually better than 0.99.

The peaks near 1940 cm^{-1} (1) and 1870 cm^{-1} (2) were normally used for calibration. In benzene or neat pyridine, the solvent absorbs near 2000 cm^{-1} , and the $\text{Fe}(\text{CO})_5$ peaks near 2000 cm^{-1} are broadened. As a result, it was impossible to isolate the high-intensity peak of the $\text{Fe}(\text{CO})_4\text{Py}$ at 1940 cm^{-1} . So, the low-intensity peak at about 2050 cm^{-1} was used for calibration and the determination of the product concentration.

Results

Quantum Yields for Trialkylphosphines. In the presence of trialkylphosphine, 337-nm irradiation of $\text{Fe}(\text{CO})_5$ results in the formation of both mono- and disubstituted photoproducts. After irradiation of cyclohexane solutions of $\text{Fe}(\text{CO})_5$ with PEt_3 , new peaks appeared in the IR spectra (Figure 1). By comparison to the spectra of pure products in cyclohexane, the peaks were assigned to $\text{Fe}(\text{CO})_4\text{PEt}_3$ (**1b**: $1935, 1974, 2048\text{ cm}^{-1}$) and to $\text{Fe}(\text{CO})_3(\text{PEt}_3)_2$ (**2b**: 1874 cm^{-1}).^{22,23} The IR spectra were unchanged for up to 3 h after irradiation, demonstrating that the products are thermally stable on the time scale of the irradiation experiments. This result was confirmed in a separate experiment; in the absence of light, no **2b** was observed after **1b** and free PEt_3 were equilibrated overnight at room temperature in cyclohexane. The quantum yields for the formation of **1b** (Φ_{1b}) and **2b** (Φ_{2b})

are dependent on the concentrations of $\text{Fe}(\text{CO})_5$, PEt_3 , and CO (Table 1). When the concentration of PEt_3 is substantially lower than that of $\text{Fe}(\text{CO})_5$, the formation of **1b** is favored over that of **2b**, and $\Phi_{1b} + \Phi_{2b}$ exceeds unity. When the concentration of PEt_3 is greater than that of $\text{Fe}(\text{CO})_5$, the formation of **2b** is favored over that of **1b**. While the experimental error is high, it is clear that $\Phi_{1b} + \Phi_{2b}$ is ca. 0.8 as long as the concentration of PEt_3 (or added CO) is equal to or greater than that of $\text{Fe}(\text{CO})_5$. Furthermore, the ratio of Φ_{2b}/Φ_{1b} is independent of 1–10% conversion of $\text{Fe}(\text{CO})_5$, a 5-fold change in light intensity, and PEt_3 concentration. The concentration independence is more convincing when the results for PMe_3 in Table 2 are also considered. Photolysis of **1b** cannot be responsible for the formation of **2b** since the molar extinction coefficients at 337 nm for $\text{Fe}(\text{CO})_5$ and **1b** in cyclohexane were found to be 340 (20) and 350 (20) $\text{M}^{-1}\text{ cm}^{-1}$, respectively, and the quantum yield for formation of **2b** by direct photolysis of **1b** is $0.54(2)$.¹⁶ The presence of CO also affects the formation of products. For $[\text{PEt}_3]/[\text{Fe}(\text{CO})_5] \leq 0.1$, saturating the solutions with CO inhibits the formation of **1b** and, almost completely, the formation of **2b**. For $[\text{PEt}_3]/[\text{Fe}(\text{CO})_5] > 0.1$, saturating the solutions with CO increases **1b** apparently at the expense of **2b**.

We have reported similar results for photolysis of $\text{Fe}(\text{CO})_5$ with PMe_3 in a communication (Table 2).⁷ The results with $\text{P-}n\text{-Bu}_3$ are distinctly different in two ways (Table 3). First, the ratio of $[\text{P-}n\text{-Bu}_3]/[\text{Fe}(\text{CO})_5]$ must be much higher before $\Phi_1 + \Phi_2$ is below unity, and second, Φ_{2b}/Φ_{1b} is much greater than that observed for any other ligand studied except when $[\text{P-}n\text{-Bu}_3]/[\text{Fe}(\text{CO})_5]$ is very high or low.

Quantum Yields for Other Ligands. Upon photolysis of 4.9 mM $\text{Fe}(\text{CO})_5$ with 0.1 M PPh_3 in cyclohexane, new peaks were observed at $2050, 1978, \text{ and } 1943\text{ cm}^{-1}$ (**1d**) and 1888 cm^{-1} (**2d**). While accurate quantum yields were difficult to obtain, it was clear that the quantum yield of **1d** was at least 0.6. More interestingly, from the relative peak heights and literature extinction coefficients⁵ we determined that **1d** exceeded **2d** by at least a factor of 10. The formation of **1d** as the dominant photosubstitution product in isooctane has been reported previously.⁵

For other ligands the product distribution is also different from that observed for trialkylphosphines. Photolysis of 9.9 mM $\text{Fe}(\text{CO})_5$ with 0.05 M pyridine produced peaks at $2051, 1965, \text{ and } 1940\text{ cm}^{-1}$ in cyclohexane and at $2048, 1959, \text{ and } 1936\text{ cm}^{-1}$ in

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Table 3. Quantum Yields for Photosubstitution of Fe(CO)₅ in the Presence of P-*n*-Bu₃ in Cyclohexane at 337 nm

[P- <i>n</i> -Bu ₃], mM	[Fe(CO) ₅], mM	[P- <i>n</i> -Bu ₃]/[Fe(CO) ₅]	<i>n</i> ^a	Φ ₁	Φ ₂	Φ ₁ + Φ ₂	Φ ₂ /Φ ₁
neat ^a	9.9	404	1	0.33(2)	0.39(3)	0.72	1.2
804	9.9	81	1	0.177(5)	0.65(4)	0.83	3.7
502	9.7	52	1	0.195(7)	0.79(4)	0.99	4.1
50	9.9	5.1	1	0.190(3)	0.96(3)	1.15	5.1
50	9.9	5.1	1	0.22(1)	0.51(2)	0.72	2.3 ^b
20	9.7	2.1	1	0.187(5)	0.93(10)	1.02	5.0
10	9.7	1.0	1	0.242(3)	0.974(4)	1.21	4.0
1.0	9.7–9.9	0.10	3	1.09(19)	0.30(4)	1.39	0.28
1.0	9.7	0.10	2	0.68(11)	0.059(11)	0.74	0.09 ^c

^a [P-*n*-Bu₃] = 4 M. ^b Benzene was used as a solvent instead of cyclohexane. ^c CO-saturated solution.

benzene. These peaks are the same as those observed for pure **1f** in these solvents. Quantum yields were found to be 0.77(4) and 0.67(6), respectively. No IR peaks due to **2f** were observed. The result was the same for 1% pyridine in THF. Only when 9.9 mM Fe(CO)₅ was irradiated in neat pyridine was a peak observed that was assignable to **2f** (br 1873 cm⁻¹, lit.²⁴ 1876/1867 cm⁻¹). The Φ_{1f} was 0.4(1), and the peak at 1936 cm⁻¹ was at least an order of magnitude larger than the peak at 1873 cm⁻¹. In any event, **2f** is a minor product, assuming the extinction coefficients of **1f** and **2f** are comparable. In a related experiment, 2.5 mM **1f** with 0.15 M pyridine in cyclohexane was photolyzed in an IR cell, and the IR spectrum was monitored after 5, 15, and 45 min of irradiation. The only new peaks observed were at 2020 and 1998 cm⁻¹, corresponding to Fe(CO)₅.

After 5-min photolysis of 3 mM Fe(CO)₅ in the presence of 0.1 M *t*-BuNC in cyclohexane, new peaks appeared at 2245, 1964, and 1930 cm⁻¹, consistent with formation of **1e** (2245 and 1964 cm⁻¹) and **2e** (1930 cm⁻¹).²⁵ A peak due to **1e** near 1992 cm⁻¹ was obscured by the Fe(CO)₅ peaks. Contrary to what was observed for high phosphine concentrations, the ratio of peaks for **1e** and **2e** varied with irradiation time.²⁶ In an experiment with brief irradiation, only **1e** peaks were observed; thus we estimate Φ₂/Φ₁ is less than 0.1 for a single-photon process.

Photolysis of 8 mM Fe(CO)₅ with 0.96 M acetonitrile in cyclohexane or neat acetonitrile produces a peak at 2029 cm⁻¹ and a much larger and broader peak at 1951 cm⁻¹ (a slight shoulder also appeared at 1970 cm⁻¹). These peaks are assigned to **1g**. No peak between 1900 and 1940 cm⁻¹ attributable to **2g** was observed.

Phosphine Reaction with Fe₂(CO)₉. While no peaks due to Fe₂(CO)₉ were observed during any of the photolysis experiments, this did not rule out the possibility that it was a transient intermediate. Using typical experimental conditions in the absence of light at room temperature, Fe₂(CO)₉ (3.64 mg, 0.1 mmol) and PEt₃ (150 μL, 1 mmol) were dispersed in 10 mL of cyclohexane or THF. Prior to addition of phosphine, additional peaks (within 15 min) were observed at 2022 and 1997 cm⁻¹ due to Fe(CO)₅. After phosphine addition, new peaks at 2048, 1974, 1935, and 1872 cm⁻¹ due to Fe(CO)₄PEt₃ and Fe(CO)₃(PEt₃)₂ were observed, and the peaks for Fe(CO)₅ increased. The ratio of **2** to **1** was approximately 1/3, consistent with previous reports.²⁷

Experiments with Triplet Quenchers or Sensitizers. Fe(CO)₅ was photolyzed in the presence of triplet quenchers. In these experiments, argon-purged solutions were irradiated directly in an IR cell. The ratio of the peaks areas (not concentrations) for **2b** (1874 cm⁻¹) and **1b** (1935 cm⁻¹) are reported in Table 4. Except for oxygen, whose quenching energy is the lowest of those quenchers investigated, the effect is small. In other experiments, Fe(CO)₅ (9.74 mM) was photosensitized with xanthone (0.49–0.63 mM, ε₃₃₇ = 8600 M⁻¹ cm⁻¹) in the presence of PEt₃ (11–30 mM) in cyclohexane. Unlike those of the quenching experiments,

Table 4. Effect of Triplet Quenchers on the Photosubstitution of Fe(CO)₅ with PEt₃ in Cyclohexane at 337 nm^a

Q	[Q], M	[PEt ₃], mM	E _T , ^b kcal/mol	ratio ^c 2/1
biphenyl	0	44	66	1.64
	0.026	44		1.56
	0.11	44		1.64
ferrocene	satd	44	40 ^d	1.40
	0.21	9.5		1.28
azulene	0.01	9.5	30	1.24
	0.43	9.5		1.32
O ₂	satd	9.5	23	0.86 ^e

^a [Fe(CO)₅] = 10.6 mM. ^b Energies of triplet quenchers.⁵⁹ ^c Ratio of peak areas. ^d Reference 60. ^e In this case an additional peak at 1917 cm⁻¹ with peak area 2.5 times greater than the area due to disubstituted product was observed.

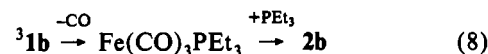
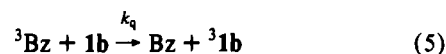
Table 5. Quantum Yields of Benzophenone-Sensitized Photosubstitution of Fe(CO)₄PEt₃ with PEt₃^a

[Fe(CO) ₄ PEt ₃], mM	[Bz], M	time, min	Φ	Φ _{Bz}
1.41	0.087	10	0.089	0.07
2.20	0.104	30	0.131	0.11
4.41	0.104	20	0.241	0.21
6.61	0.104	20	0.320	0.28
8.81	0.104	20	0.325	0.28

^a [PEt₃] = 47 mM, λ = 337 nm.

quantum yields were determined by photolyzing samples in a quartz cuvette as described in the Experimental Section. The ratio of Φ_{2b}/Φ_{1b} was unchanged by the absence of xanthone.

³Fe(CO)₄PEt₃ was generated by triplet sensitization of **1b** with benzophenone (Bz), and the quantum yield of **2b** was determined (Table 5). The high concentration of **1b** required to quench benzophenone resulted in some direct photolysis of **1b**. Benzophenone-sensitized and direct photosubstitutions of **1b** are described by eqs 3–8, from which eq 9 can be derived.



$$\Phi = \chi_{\text{1b}} \Phi_{\text{1b}} + \chi_{\text{Bz}} \Phi_{\text{Bz}} =$$

$$\chi_{\text{1b}} \Phi_{\text{1b}} + \frac{\chi_{\text{Bz}} \Phi_{\text{1b}} k_q [{}^3\text{Bz}][\text{1b}]}{(k_{\text{ISC}}[{}^3\text{Bz}] + k_q[{}^3\text{Bz}][\text{1b}])} \quad (9)$$

(24) van Dijk, H. K.; Stufkens, D. J.; Oskam, A. *J. Organomet. Chem.* **1988**, *340*, 227.

(25) The peak due to the ((CH₃)₂CNC)₂Fe(CO)₃ complex is reported at 1927 cm⁻¹ in CCl₄; Cotton, F. A.; Parish, R. V. *J. Chem. Soc.* **1960**, 1440.

(26) The extinction coefficient for (*t*-BuNC)Fe(CO)₄ was 450 M⁻¹ cm⁻¹.

(27) Bratnam, P. S.; Wallace, W. J. *J. Organomet. Chem.* **1971**, *30*, C17.

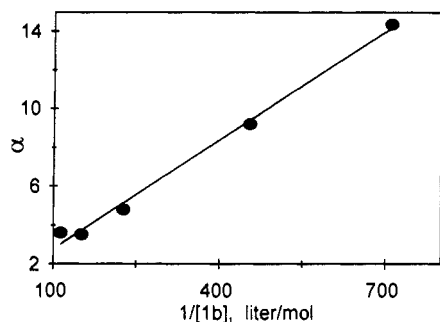


Figure 2. Plot of α versus $1/[1b]$ for triplet sensitization of **1b** with benzophenone in cyclohexane at 337 nm.

$$\Phi_{Bz} = (\Phi - \chi_{1b}\Phi_{1b})/\chi_{Bz} \quad (10)$$

$$\alpha = \frac{\chi_{Bz}}{\Phi - \chi_{1b}\Phi_{1b}} = \frac{k_{ISC}}{\Phi_{1b}k_q[1b]} + \frac{1}{\Phi_{1b}} \quad (11)$$

Φ is the observed quantum yield, χ_{1b} and χ_{Bz} are the fractions of photons absorbed by **1b** and by benzophenone (extinction coefficients for benzophenone, **1b**, and **2b** are 116, 310, and 350 $M^{-1} cm^{-1}$, respectively, at 337 nm), and Φ_{1b} is the quantum yield for direct photolysis of **1b**.²⁸ Rearrangement of eq 9 yields eq 10, and the sensitized photosubstitution may be calculated (see Table 5). From eq 9 it can be seen that increasing **1b** will increase the quenching of benzophenone by **1b** and the upper limit of Φ_{Bz} equals Φ_{1b} . In practice, absorbance by **1b** occurs before this is achieved. Alternatively, eq 9 may be rearranged to give eq 11. A linear plot of α versus $1/[1b]$, shown in Figure 2, demonstrates that eqs 3–8 are consistent with the observed results.

Discussion

While previous studies make it clear that UV photolysis of $Fe(CO)_5$ leads to CO dissociation and the formation of $Fe(CO)_4$,^{4,29} there is some doubt about the spin state of $Fe(CO)_4$ and the path of its subsequent reactions. Quantum yield studies provide important information about both of these issues. The quantum yields were determined for the formation of **1** and **2** from $Fe(CO)_5$. When the ratio of $[PR_3]/[Fe(CO)_5]$ was varied, we noted that the product yields and distribution were distinctly different for low ($PR_3/Fe(CO)_5 < 1$) and high ratios (≥ 1 , Tables 1–3). While **1** and **2** were the only products observed for any ratio studied, the mechanistic pathways are probably very different at extreme ratios. The results can be explained, in part, by the reactions of $Fe(CO)_4$ with PR_3 (high ratio) and with $Fe(CO)_5$ (low ratio).

In the absence of PR_3 , $Fe_2(CO)_9$ is produced upon photolysis of $Fe(CO)_5$.¹ As the ratio $[PR_3]/[Fe(CO)_5]$ decreases, $Fe(CO)_5$ will compete with PR_3 for $Fe(CO)_4$, and more $Fe_2(CO)_9$ will form. At a low value for $[PR_3]/[Fe(CO)_5]$ (near 0.1), Φ_2/Φ_1 is independent of R ($\Phi_2/\Phi_1 = 0.2(1)$; R = Me, Et, *n*-Bu), suggesting that in each case the same reaction is responsible for the products formed. This reaction is probably between PR_3 and $Fe_2(CO)_9$. Other potential intermediates are $Fe_2(CO)_8$, $Fe_2(CO)_8PR_3$, and $Fe_3(CO)_{12}$.^{30–33} Our results for the thermal reaction of PEt_3 with $Fe_2(CO)_9$ in cyclohexane demonstrate that both **1b** and **2b** can be formed from $Fe_2(CO)_9$. Analogous results have been described

previously for the reaction of $Fe_2(CO)_9$ with $P(p-C_6H_4CH_3)_3$ in toluene.³⁴ Likewise, heating $Fe_2(CO)_9$ and $P(CF_3)_3$ yields both $Fe(CO)_4(P(CF_3)_3)$ and $Fe(CO)_3(P(CF_3)_3)_2$.³⁰ The reaction of a dinuclear complex with a Lewis base could form two mononuclear products. This may explain the observation of total quantum yields that exceed unity (Table 1–3). While detailed mechanisms could be proposed for reactions of multinuclear species, we have no direct evidence to distinguish them, and further work in this area is beyond the scope of this study.

The results for photosubstitution with $P-n-Bu_3$ are unique among our studies and are the most complex observed. It is unlikely that impurities are responsible for its behavior since proton and carbon NMR spectra show $P-n-Bu_3$ to be as pure as the other phosphines. A quantum yield greater than unity at all but the highest phosphine concentrations again is an indication that multinuclear intermediates are formed. The details are unclear, and we can only speculate that a steric effect may result in a slower reaction with $P-n-Bu_3$, so that the formation of multinuclear species occurs at higher $[PR_3]/[Fe(CO)_5]$. It is somewhat surprising that the substitution of the ethyl by butyl would have such a pronounced effect on the chemistry; nevertheless, a steric effect from this subtle change is not unprecedented. As an example, the quantum yields for photosubstitution of **1b** and **1c** are significantly different.¹⁶ Furthermore a steric effect has been observed previously for CO dissociation from **1b** and **2b**.¹⁶

As L increases, the formation of multinuclear species (such as $Fe_2(CO)_9$) will be inhibited; **2** is still formed in addition to **1**. The results are consistent with the substitution of two CO's via a single-photon process. No other complex is known to undergo substitution of two independent ligands per photon in solution.³⁵ Multiligand photosubstitution has been observed previously in solution, but this is only after extended photolysis in which a monosubstituted product, produced by the first photon, absorbs a second photon to make the disubstituted product.³⁶ This is not the case in the current study, where we have limited the amount of product formed, so that direct photolysis of monosubstituted product was insignificant. Even with only 1% conversion of $Fe(CO)_5$, $\Phi_2/\Phi_1 = 1.4$ for L = PEt_3 .

The results from the present study, as well as those from others, suggest that the quantum yield for CO dissociation to produce solvent-separated $Fe(CO)_4$ and CO is about 0.8. We find in the absence of multinuclear reactions (*i.e.*, high $[L]/[Fe(CO)_5]$) that the sum of the quantum yields at 337 nm for the formation of **1** and **2** from trialkylphosphines is 0.79(4). On the basis of our results at 337 nm without corrections for inner-filter effects and those of Schroeder and Wrighton in isoctane at 366 nm,⁵ the lower limit for the total quantum yield for photosubstitution with triphenylphosphine is about 0.7. Similar results have been obtained for the photosubstitution at 302 nm with $P(OCH_3)_3$.³⁷ For pyridine, negligible disubstitution occurs, but the quantum yield of **1f** formation is 0.77(3). For photosubstitution with (*Z*)-cyclooctene in *n*-hexane at 304 nm, the yield of $Fe(CO)_4(\eta^2-(Z)-C_8H_{14})$ is 0.80(1), and the formation of disubstituted product is reported to be low.⁶ Thus the total quantum yields are very similar and independent of ligand structure or product distribution, indicating that an initial common intermediate is formed with a quantum yield of 0.8. We suggest that this intermediate is most likely $Fe(CO)_4$.

We consider four possible mechanisms for the formation of a disubstituted product in the absence of multinuclear reactions. In each mechanism the formation of $Fe(CO)_4$ is assumed since

(28) A similar derivation has been presented previously: Nasielski, J.; Colas, A. *Inorg. Chem.* **1978**, *17*, 237.

(29) Church, S. P.; Grevels, F.-W.; Hermann, H.; Kelly, J. M.; Klotzbücher, W. E.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1985**, 594.

(30) Burg, A. *Inorg. Chem.* **1986**, *25*, 4751. Sun photolysis of nearly equimolar $Fe(CO)_5$ and $P(CF_3)_3$ gives a high yield of $Fe_2(CO)_9$ in addition to $Fe(CO)_4(P(CF_3)_3)$ and $Fe(CO)_3(P(CF_3)_3)_2$.

(31) Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1974**, 2276.

(32) Poliakoff, M.; Turner, J. J. *J. Chem. Soc. A* **1971**, 2404.

(33) Burkinshaw, P. M.; Dixon, D. T.; Howell, J. A. S. *J. Chem. Soc. Dalton Trans.* **1980**, 999.

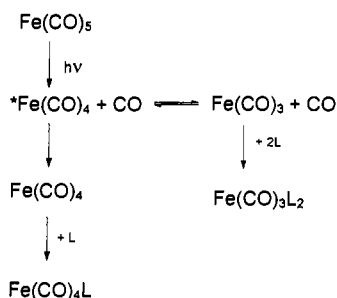
(34) Braterman, P. S.; Wallace, W. J. *J. Organomet. Chem.* **1971**, *30*, C17.

(35) We would not consider X and Z to be independent in $M(X)(Z)$ if elimination forms the single molecule XZ.

(36) Moggi, L.; Juris, A.; Sandrini, D.; Manfrin, M. F. *Rev. Chem. Intermed.* **1981**, *4*, 171.

(37) Angermund, H.; Bandyopadhyay, A. K.; Grevels, F.-W.; Mark, F.; Schappert, K. *Abstract of Papers*, Eighth International Symposium on the Photochemistry and Photophysics of Coordination Compounds, Santa Barbara, CA, Aug 1989.

Scheme 2

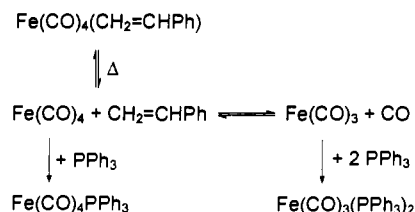


matrix isolation and flash photolysis studies have demonstrated that Fe(CO)_4 is the initial intermediate formed upon photolysis of Fe(CO)_5 in condensed phases.⁴ The first mechanism involves the addition of Fe(CO)_4 to Fe(CO)_5 to yield $\text{Fe}_2(\text{CO})_9$. This reaction is known to occur,¹ and we have shown that phosphines will react with $\text{Fe}_2(\text{CO})_9$ to form **1** and **2**. Three observations exclude a photochemical mechanism involving $\text{Fe}_2(\text{CO})_9$ at high $[\text{PR}_3]/[\text{Fe(CO)}_5]$. First, the ratio $[\mathbf{2}]/[\mathbf{1}]$ is about 0.3 for the thermal reaction of $\text{Fe}_2(\text{CO})_9$ with 100 mM PEt_3 (*vide supra*) while it is 1.4 for the photolysis of Fe(CO)_5 with 96 mM PEt_3 (Table 1). Second, at high $[\text{PR}_3]/[\text{Fe(CO)}_5]$, reaction of Fe(CO)_4 should be faster with PR_3 than with Fe(CO)_5 and little or no $\text{Fe}_2(\text{CO})_9$ should form. Third, at low $[\text{PR}_3]/[\text{Fe(CO)}_5]$, reaction of Fe(CO)_4 should be faster with Fe(CO)_5 than with PR_3 , $\text{Fe}_2(\text{CO})_9$ will form, and the product distribution be due to the reactions of $\text{Fe}_2(\text{CO})_9$. Since the ratio $[\mathbf{2}]/[\mathbf{1}]$ is different at high and low $[\text{PR}_3]/[\text{Fe(CO)}_5]$, it seems unlikely that formation and reactions of $\text{Fe}_2(\text{CO})_9$ are responsible for the product distribution observed at high $[\text{PR}_3]/[\text{Fe(CO)}_5]$.

The second mechanism is depicted in Scheme 2 with the dissociation of the second CO from a vibrationally excited Fe(CO)_4 . **2** is formed by the addition of two L's to Fe(CO)_3 . At 337 nm, there is sufficient energy to dissociate two CO's, and indeed, in the gas phase, two or more CO's have been shown to dissociate stepwise.^{2,3,38} However, after the dissociation of the first CO, the available energy will be 40 kcal/mol lower (the $\text{Fe(CO)}_4\text{-CO}$ bond energy),³⁹ the excess driving force for dissociation will be reduced, and the rate of the second dissociation will be slower than the first. For photolysis of metal carbonyls near 337 nm, the rate of dissociation of the second CO is slow ($10^7\text{--}10^8 \text{ s}^{-1}$)^{2,3,40,41} compared to the rate of thermal relaxation in solution (10^{10} s^{-1}).^{3,42,43} Thus only a single CO dissociates in solution, and Scheme 2 is inconsistent with the reaction dynamics of metal carbonyls in solution.⁴⁴

A third possible mechanism for the formation of **2** would be identical to that in Scheme 2 except Fe(CO)_4 is thermally equilibrated with the solvent before a second CO dissociates. A similar mechanism was previously proposed to account for the thermal substitution of $\text{Fe(CO)}_4(\text{CH}_2=\text{CHPh})$ with triphenylphosphine at 50 °C in toluene (Scheme 3).⁴⁵ The dependence of the product distribution on dispersed CO and phosphine is analogous to that observed for our photochemical results with phosphines. For example, the ratio of **2**/**1** was independent of

Scheme 3



the phosphine concentration (and the extent of reaction) when $[\text{PPh}_3]/[\text{Fe(CO)}_4(\text{CH}_2=\text{CHPh})] > 5$. In addition, low phosphine concentrations favored a lower ratio of **2**/**1**, just as we observed. These results suggest that **2** can form from Fe(CO)_4 without originating from a photolytically excited species and that the thermal and photolytic processes have one or more common intermediates. Nevertheless, Scheme 3 is inconsistent with at least two observations. First, according to Scheme 3, the product ratio should be dependent on the concentration of phosphine and this is not the case thermally or photolytically. Second, the reaction between Fe(CO)_4 and phosphine is rapid ($>10^8 \text{ s}^{-1}$),⁴⁶ so CO dissociation from Fe(CO)_4 would require an exceedingly weak Fe-CO bond to compete with the reaction of Fe(CO)_4 with phosphine. On the contrary, the $\text{Fe(CO)}_3\text{-CO}$ bond energy is of moderate strength (28 kcal/mol).⁴⁷

We propose Scheme 4 as a possible mechanism for the formation of **1** and **2** via a single-photon process. The production of Fe(CO)_4 as a ground-state triplet has been proposed previously and is supported by MCD and gas-phase studies of Fe(CO)_4 .^{4,48} Attack of ${}^3\text{Fe(CO)}_4$ by L initially yields $\text{Fe(CO)}_4\text{L}$ in the triplet state instead of the ground-state singlet because of spin conservation. According to this scheme, the formation of **2** is the result of CO dissociation from ${}^3\text{Fe(CO)}_4\text{L}$. Furthermore, the product distribution is determined by the competition of two unimolecular processes involving ${}^3\text{Fe(CO)}_4\text{L}$: intersystem crossing and CO dissociation. The ratio of $[\mathbf{2}]/[\mathbf{1}]$ (Φ_2/Φ_1) is determined by the ratio of the rates of formation of **1** and **2**:

$$d[\mathbf{1}]/dt = k_{\text{ISC}}[{}^3\text{Fe(CO)}_4\text{L}] \quad (12)$$

$$d[\mathbf{2}]/dt = k_4[{}^3\text{Fe(CO)}_3\text{L}][\text{L}] \quad (13)$$

Using the steady-state assumption for ${}^3\text{Fe(CO)}_3\text{L}$

$$d[\mathbf{2}]/dt = \frac{k_3 k_4 [{}^3\text{Fe(CO)}_4\text{L}][\text{L}]}{k_{-3}[\text{CO}] + k_4[\text{L}]} \quad (14)$$

For $k_4[\text{L}] > k_{-3}[\text{CO}]$

$$d[\mathbf{2}]/dt = k_3[{}^3\text{Fe(CO)}_4\text{L}] \quad (15)$$

Dividing eq 15 by eq 12 gives

$$[\mathbf{2}]/[\mathbf{1}] = k_3/k_{\text{ISC}} \quad (16)$$

Thus the product distribution would be independent of ligand concentration (until L drops to a low concentration where Fe(CO)_5 can react with Fe(CO)_4 or $\text{Fe(CO)}_3\text{L}$), consistent with the experimental results.⁴⁹ On the other hand, k_3/k_{ISC} , and hence Φ_2/Φ_1 , ought to be affected by the structure of L. Indeed we

(38) Venkataraman, B. K.; Bandukwalla, G.; Zhang, Z.; Vernon, M. *J. Chem. Phys.* **1989**, *90*, 5510.

(39) Smith, G. P. *Polyhedron* **1988**, *7*, 1605.

(40) Rayner, D. M.; Ishikawa, Y.; Brown, C. E.; Hackett, P. A. *J. Chem. Phys.* **1991**, *94*, 5471.

(41) Seder, T. A.; Ouderkirk, A. J.; Weitz, E. *J. Chem. Phys.* **1986**, *85*, 1977.

(42) Heilweil, E. J.; Cavanagh, R. R.; Stephenson, J. C. *Chem. Phys. Lett.* **1987**, *134*, 181.

(43) Yu, S.-C.; Xu, X.; Lingle, R., Jr.; Hopkins, J. B. *J. Am. Chem. Soc.* **1990**, *112*, 3668.

(44) Photolysis in the gas phase is much different. Multiple ligand substitutions are common since infrequent collisions with intermediates allow retention of thermal energy that can disrupt further metal-ligand bonds. See ref 4.

(45) Cardaci, G. *Inorg. Chem.* **1974**, *13*, 2974.

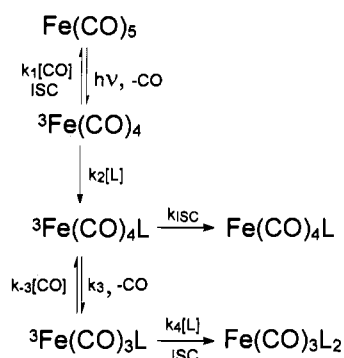
(46) Nayak, S.; Burkey, T. J. Unpublished result.

(47) Sunderlin, L. S.; Wang, D.; Squires, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 2788.

(48) Barton, T. J.; Grinter, R.; Thomson, A. J.; Davies, B.; Poliakov, M. *J. Chem. Soc., Chem. Commun.* **1977**, 841.

(49) For the formation of **2** in the ground state we believe intersystem crossing occurs subsequent to the addition of the second L and likewise for the formation Fe(CO)_5 from ${}^3\text{Fe(CO)}_4$ and CO. We have no evidence that indicates the sequence of intersystem crossing and addition of the Lewis base.

Scheme 4



observed Φ_2/Φ_1 is greater than 1 for $\text{L} = \text{PEt}_3, \text{PMe}_3, \text{and P-}n\text{-Bu}_3$ and is less than 1 for $\text{L} = \text{PPh}_3, \text{pyridine}, (\text{CH}_3)_3\text{CNC}, \text{and CH}_3\text{CN}$. In a previous study with $\text{L} = (E)\text{-cyclooctene}$, $\Phi_2/\Phi_1 < 1$.⁵⁰ The dependence of the product distribution on L may be understood in terms of the electronic energies of ${}^3\text{Fe(CO)}_4\text{L}$, which will change with different L 's. While the exact orbital energies are not known, it is a reasonable expectation that the relative energy barriers, and thus rates of CO dissociation and intersystem crossing, will change with the related orbital energies. Although solvent effects were not investigated in detail, Scheme 4 is also consistent with a change in product distribution with solvent. Scheme 4 also explains why added CO decreases Φ_2/Φ_1 : ${}^3\text{Fe(CO)}_3\text{L}$ is converted back to ${}^3\text{Fe(CO)}_4\text{L}$ and limits the formation of **2** and increases the formation of **1**. Assuming that $k_{-3}[\text{CO}] > k_4[\text{L}]$ in eq 14, $[2]/[1] = k_3k_4[\text{L}]/k_{-3}k_{\text{ISC}}[\text{CO}]$, so increasing $[\text{CO}]$ will decrease $[2]/[1]$. Finally, added CO did not decrease the total quantum yield, which means that the CO concentration (9 mM at 25 °C)⁵¹ was too low for CO addition to compete with phosphine addition to ${}^3\text{Fe(CO)}_4$ (*i.e.*, $k_1[\text{CO}] < k_2[\text{L}]$). These results indicate that the kinetic preference of ${}^3\text{Fe(CO)}_4$ for PR_3 over CO is greater than that of ${}^3\text{Fe(CO)}_3\text{L}$ ⁵² (*i.e.*, $k_2[\text{L}]/k_1[\text{CO}] > k_3k_4[\text{L}]/k_{-3}k_{\text{ISC}}[\text{CO}]$ where $[\text{L}]/[\text{CO}]$ is the same for both terms). A possible explanation may be that the metal center of ${}^3\text{Fe(CO)}_4$ is not as electron rich as ${}^3\text{Fe(CO)}_3\text{L}$ and prefers the electron-rich donor.

If triplet species are intermediates in the photosubstitution of Fe(CO)_5 , independent formation of these species should produce the same products in the same distribution. ${}^3\text{Fe(CO)}_4$ was generated via triplet sensitization of Fe(CO)_5 with xanthone in the presence of PEt_3 . Under the conditions of the experiments, xanthone absorbed essentially all the light, and the quenching of the xanthone triplet led to ${}^3\text{Fe(CO)}_4$ via CO dissociation from ${}^3\text{Fe(CO)}_5$. **1b** and **2b** were produced in the same ratio as that observed without sensitizer, implicating ${}^3\text{Fe(CO)}_4$ directly and ${}^3\text{Fe(CO)}_4(\text{PEt}_3)$ indirectly as intermediates of the direct photolysis.

Experiments with **1b** and benzophenone generated ${}^3\text{Fe(CO)}_4\text{-PEt}_3$ directly and, in the presence of PEt_3 , produced **2b** in high yield (Table 5). Intersystem crossing by ${}^3\text{Fe(CO)}_4\text{PEt}_3$ is undetected since it regenerates **1b**. This establishes that ${}^3\text{Fe(CO)}_4\text{PEt}_3$ and PEt_3 can form **2b**. We also attempted to quench ${}^3\text{Fe(CO)}_4\text{PEt}_3$ with triplet quenchers during the photolysis of Fe(CO)_5 . This should decrease the ratio of **2b/1b**, since quenching ${}^3\text{Fe(CO)}_4\text{PEt}_3$ will increase intersystem crossing (**1b** formation)

and consequently decrease the extent of CO dissociation (**2b** formation). This is consistent with our findings that **2b/1b** decreased 20% for azulene and about 50% in the case of oxygen. Complete quenching at 337 nm was limited by the lack of solubility and direct photolysis of quenchers. The results suggest that the triplet energy of ${}^3\text{Fe(CO)}_4\text{PEt}_3$ is between 40 and 23 kcal/mol (ferrocene and oxygen, respectively) and that ${}^3\text{Fe(CO)}_4\text{PEt}_3$ is a possible intermediate in the formation of **1b** and **2b**. The interpretation of quenching experiments is not without ambiguity, since the quencher may reduce the formation of **2** by intercepting $\text{Fe(CO)}_3\text{PEt}_3$. It should also be noted that the formation of ${}^1\text{-Fe(CO)}_4$ in addition to ${}^3\text{Fe(CO)}_4$ cannot be excluded, even though our results and those of previous studies strongly support the role of ${}^3\text{Fe(CO)}_4$ as an important intermediate in Fe(CO)_5 photochemistry.^{2,4,53-57} If the singlet is present, it seems likely that it plays a minor role. In any event, it is not clear how ${}^1\text{Fe(CO)}_4$ could account for the formation of **2**.

The question arises as to why CO dissociation from ${}^3\text{Fe(CO)}_4\text{PR}_3$ is facile at room temperature. ${}^3\text{Fe(CO)}_4\text{PEt}_3$ is electronically excited, and electron density in an antibonding orbital will weaken the Fe-CO bond. The observation that **1b** is stable in the presence of PEt_3 overnight establishes that CO does not dissociate from ground-state **1b** at room temperature. In fact, we recently showed that the $\text{Fe(CO)}_3\text{PEt}_3\text{-CO}$ bond energy is at least 38 kcal/mol,¹⁶ a value that is consistent with the activation enthalpy (42.5(12) kcal/mol) for dissociative CO substitution for $\text{Fe(CO)}_4\text{PPh}_3$.⁵⁸ It is clear that a labile intermediate must undergo the loss of the second CO.

Conclusions. UV photolysis of Fe(CO)_5 leads to CO dissociation with a quantum yield of 0.8 and the formation of ${}^3\text{Fe(CO)}_4$. At phosphine concentrations comparable to or lower than that of Fe(CO)_5 , the sum of the quantum yields for mono- and disubstitution exceeds unity. This result is attributed to the reaction of coordinatively-unsaturated intermediates (Fe(CO)_4 or $\text{Fe(CO)}_3\text{PR}_3$) with Fe(CO)_5 to give multinuclear iron carbonyls that go on to react with phosphines to yield stable mononuclear products. Multinuclear processes are inhibited at high phosphine concentrations (relative to Fe(CO)_5), and a single-photon process forms both mono- and disubstitution products. Overall substitution of two CO's can be explained by a labile triplet intermediate, ${}^3\text{Fe(CO)}_4\text{L}$, that competitively loses CO and intersystem-crosses to the ground-state singlet. The relative rates of these processes will change with the structure of L and the ratio of mono- to disubstituted products.

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Supplementary Material Available: Synthetic procedures for **1d-1f** and potassium ferrioxalate (2 pages). Ordering information is given on any current masthead page.

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