tetramer itself. The $LiClO_4$ data in Table X correspond to a somewhat different behavior in that while $1/\tau_{md\to d}$ is directly proportional to p_d/p_{md} for constant phenolate concentration, it is also dependent on the absolute concentration of phenolate. Furthermore, the reverse reaction is inversely proportional to p_d/p_{md} and is dependent on phenolate concentration. We postulate that the exchange reaction involves the intermediacy of monomeric lithium phenolate and involves a trimer as an intermediate (or transition state). There are therefore two pathways, depending on whether the "trimer" is derived from the dimer or mixed dimer as shown in eqs 6a and 6b, respectively. If only pathway 6a is

$$Li_2P^*X \rightleftharpoons LiP^* + LiX \qquad (6a)$$

$$Li_2P_2 + LiP^* \rightarrow [Li_3P_2P^*] \rightarrow Li_2PP^* + LiP$$

$$Li_2P_2^* \rightleftharpoons 2LiP^* \qquad (6b)$$

$$Li_2PX + LiP^* \rightarrow [Li_3P^*PX] \rightarrow LiP + Li_2P^*X$$

involved, the observed behavior would be similar to that of the Li_4E_4/Li_4E_3Cl system. Pathway 6b would give exactly the opposite result. The few available data in Table X suggest that for the $Li_2P_2/Li_2P(ClO_4)$ system in dioxolane both pathways contribute.

The very pronounced dependence of the nature of the anion is noteworthy. These findings suggest that the chloride mixed dimer exchanges with the dimer through pathway 6a. This is reasonable because dissociation is favored due to the stronger interaction of the chloride ion in the product LiCl compared to the analogous salts of the ClO_4^- and BPh_4^-. It is possible that the $LiBPh_4$ system involves only pathway 6b.

A further point in favor of the monomer as an intermediate is that, as was shown previously, this species can be directly observed in the case of lithium 2,4,6-tribromophenolate in THF, although it undergoes rapid exchange with the dimer above −100 °C. Clearly, a much more extensive study will be needed in order to establish these postulated pathways, and the full mechanistic picture should also take into account the solvent's direct role, if any, in affecting the dissociation of the dimeric species.

The observation that, for mixed dimers, exchange of anions is much more rapid than exchange of phenolate or lithium cations between dimer and mixed dimer or of lithium cations between mixed dimer and the added salt clearly implicates the intermediacy of a relatively free anion, which could be either a free ion or solvent-separated ion pair. This is certainly readily understood in terms of the structures **2** and **3**. The anion may also be somewhat more free in **1** since the ^{13}C chemical shifts, in all mixed dimers, indicate increased binding of Li^+ to oxygen, presumably as a consequence of decreased binding to the less basic, foreign anion.

Summary

(i) Lithium phenolates that are dimeric in weakly polar, aprotic solvents form mixed dimers (Li_2PX) with a number of lithium salts of strong acids.

(ii) The extent of mixed-dimer formation increases with the basicity of the phenolate ion.

(iii) Mixed-dimer formation is favored by decreased cation solvating power of the solvent.

(iv) There is no simple relation between the basicity of the anion of the added salt and mixed-dimer formation.

(v) The structures of the dimers can be regarded as dimeric ion pairs ($Li_2P^+X^-$) that may be contact or partially or fully solvent separated.

(vi) Interaggregate exchange appears to involve the intermediacy of monomeric lithium phenolate derived from the mixed aggregate and/or the dimeric phenolate.

Acknowledgment. We gratefully acknowledge support for this work by a grant (CHE 8801884) from the National Science Foundation. We also thank Rich Lawson for his assistance in developing software.

Photochemistry of a μ-Alkylidene Piano-Stool Dimer[1]

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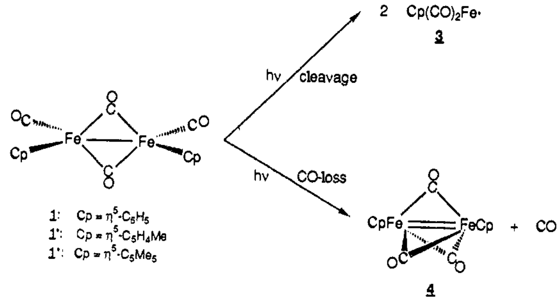
Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received June 14, 1990*

Abstract: Irradiation of the piano-stool dimer $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (**2**) results in the formation of a CO-loss intermediate as the only photochemical pathway available for this dimer. The CO-loss intermediate is proposed to have the structure $[CpFe]_2(\mu\text{-}CO)_2(\mu\text{-}CHCH_3)$ (**6a**). Thermal reactions of **6a** with a variety of species have been elucidated by laser flash photolysis (LFP) experiments. The kinetics and activation parameters for **6a** with a variety of reagents (CCl_4, CO, CH_3CN, and several phosphines) indicate that the reaction is an associative bimolecular process. Comparison of the reaction chemistry of **2** is discussed to that of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$ (**1**).

The past decade has seen a tremendous growth in the studies of the fundamental photoprocesses of organometallic compounds.[2] Such systems offer the potential for a diverse class of photochemical reagents wherein changing the metal–ligand combinations could lead to selective photochemistry.[3] To achieve this goal requires a concise picture of the factors that control the photochemical channels available to the molecule. In the case

Scheme I



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(1) Presented in part at the 198th National Meeting of the American Chemical Society, Miami Beach, FL, September 10-15, 1989; INOR 301.

(2) (a) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187. (b) Stiegman, A. E.; Tyler, D. R. *Acc. Chem. Res.* **1984**, *17*, 61. (c) Stiegman, A. E.; Tyler, D. R. *Coord. Chem. Rev.* **1985**, *63*, 217. (d) Geoffroy, G. L; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979. (e) Wrighton, M. S.; Graff, J. L.; Luong, J. C.; Reichel, C. L.; Robbins, J. L. In *Reactivity of Metal-Metal Bonds*; Chisholm, M. H., Ed.; ACS Symp. Ser. 155; American Chemical Society: Washington, DC, 1981; pp 85-110. (f) Poliakoff, M.; Weitz, E. *Adv. Organomet. Chem.* **1986**, *25*, 277.

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of dinuclear organometallic complexes, there are generally two very different photochemical pathways in competition, namely cleavage of the metal–metal bond, which produces mononuclear radicals, and ligand loss (usually CO) to yield a coordinatively unsaturated dinuclear intermediate:

$$\text{Cleavage:}\quad L_nM\text{-}ML_n \rightarrow 2L_nM^{\bullet}$$

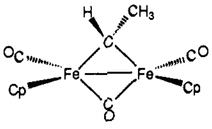
$$\text{Ligand loss:}\quad L_nM\text{-}ML_n \rightarrow L_{n-1}M\text{-}ML_n + L$$

For example, picosecond time scale studies of $Mn_2(CO)_{10}$ supports the formation of two different primary intermediates, $^{\bullet}Mn(CO)_5$ and $Mn_2(CO)_9$, but the primary photochemical event (or events) that controls the formation of these intermediates is not known.[4]

We have been interested in investigating the photochemical pathways available to diiron organometallics of the type $[CpFe]_2L_xL'_y$ (L = terminal ligand, L′ = bridging ligand, Cp = η^5-C_5H_5), so-called "piano-stool dimers", with $Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$ (**1**) being the most widely studied congener. Previous studies on **1** in the microsecond and nanosecond time regimes provide support for a competition between cleavage and CO-loss photoproducts (Scheme I).[2] A recent study of **1** on the picosecond time scale suggests that there are primary photochemical steps in the photolysis that prior studies did not reveal.[5] Clearly, a complete picture of the molecular dynamics of **1** upon photoexcitation has not been achieved.

One means of addressing the relationship between electronic structure and molecular reactivity for a series of piano-stool compounds is molecular modification.[6] For a generic piano-stool dimer $[CpM]_2L_xL'_y$, the $[CpM]_2$ framework can support a variety of hydrocarbyl bridging groups.[7] Studies from our laboratories and elsewhere have concluded that in complexes with π-acceptor ligands in the bridging position, the two CpM fragments of the dimer are held together by several interactions delocalized over the $[CpM]_2(\mu\text{-}L')_2$ metallacycle, rather than any direct metal–metal bond.[6b,7c-h] Thus, in **1**, the two Fe atoms are held in close proximity to one another by the bonding of the $[CpFe]_2(\mu\text{-}CO)_2$ core, rather than a direct Fe–Fe bond. By varying the π-acceptor ability of the bridging ligands, it should be possible to alter the strength of the interactions that hold the $[CpM]_2(\mu\text{-}L')_2$ metallacycle intact. This could have profound effects on the reaction chemistry exhibited and has led us to believe that the photochemical properties of these systems could be "tuned" by the judicious choice of ligand environment. We have therefore been undertaking a study of this possibility of electronic tuning by focussing on the photochemistry of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}L')$, in which one of the bridging carbonyls of **1** has been replaced by a hydrocarbyl ligand L′.

In this paper, we report laser flash photolysis (LFP) and preparative photochemical studies of the ethylidene-bridged dimer $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (**2**).[8] Synthetic studies originally performed by Pettit[9] and by Knox[10] suggest that the substitution photochemistry of **2** is analogous to **1**. Casey and Austin have proposed that a CO-loss intermediate from the related vinylidene-bridged piano-stool dimer $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$ facilitates the incorporation of ^{13}CO upon irradiation of the dimer in solution.[11] However, no spectroscopic evidence for the existence of a CO-loss intermediate analogous to **4** has been reported in the literature.[12] Here we will demonstrate that the irradiation of **2** leads to a CO-loss intermediate similar to that of **4**, although the ethylidene-bridged intermediate should differ from **4** in reactivity. Further, we demonstrate that **2** does *not* undergo photochemical cleavage into mononuclear radicals, at least under the conditions employed here.



2

Experimental Section

Materials. Mallinckrodt Spectrophotometric Grade toluene was used in all synthetic and kinetic studies and was distilled from either sodium metal or sodium/potassium alloy under nitrogen before use. Tetrahydrofuran (THF), acetonitrile (CH_3CN), hexanes, cyclohexane, xylenes, and carbon tetrachloride (CCl_4) (Mallinckrodt Analytical Reagent) were dried and distilled from calcium hydride (Aldrich) or potassium/benzophenone as dictated.[13] $Mn_2(CO)_{10}$ and $Cp^*{}_2Fe_2(CO)_2(\mu\text{-}CO)_2$ (**1***: Cp* = η^5-C_5Me_5) were obtained from Strem Chemical. $Cp^*{}_2Fe_2(CO)_2(\mu\text{-}CO)_2$ was used as received. $Mn_2(CO)_{10}$ was purified by sublimation. $Cp'_2Fe_2(CO)_2(\mu\text{-}CO)_2$ (**1′**: Cp′ = η^5-C_5H_4Me) was prepared by the reflux of methylcyclopentadiene dimer (Aldrich) and $Fe_2(CO)_9$ in xylenes.[14]

Tri-*n*-butylphosphine [$P(n\text{-}Bu)_3$], triphenylphosphine (PPh_3), trimethylphosphine (PMe_3; 1.0 M solution in toluene), and triphenyl phosphite [$P(OPh)_3$] were obtained from Aldrich. The PPh_3 was recrystallized twice from absolute ethanol. Tricyclohexylphosphine [$P(C_6H_{11})_3$] was obtained from Strem Chemical and used as received.

All synthetic manipulations and reactions were performed under an atmosphere of dry argon with Schlenk techniques. Argon for every experiment was purified by passing the gas through consecutive columns containing activated BTS catalyst and Drierite.[13] $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (**2**) was synthesized by the procedure of Pettit and co-workers.[9] For all kinetic studies, **2** was recrystallized twice from hexanes and stored in a Schlenk flask under argon and wrapped in aluminum foil to minimize exposure to light.

Irradiation Procedures. All synthetic manipulations requiring irradiation were performed in a quartz cell (28-mm diameter by 150-mm length) equipped with a sidearm for connection to the Schlenk line. The cell is sealed off at one end, with the other end tapered so it can be capped

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(3) The major impetus for early work in the area of inorganic photochemistry centers on the conversion of sunlight into electricity. However, recent advances in such diverse areas as photoconducting materials or photocatalysis offer much excitement and continued growth. For example, see: (a) *Chem. Eng. News* **1979**, *57*(36), 29. (b) *Photocatalysis: Fundamentals and Applications*; Serpone, N., Pelizzetti, E., Eds.; Wiley: New York, 1989. (c) Gratzel, M. *Heterogeneous Photochemical Electron Transfer*; CRC Press: Boca Raton, FL, 1989. (d) *Photochemistry and Photophysics of Coordination Compounds*; Yersin, H., Vogler, A., Eds.; Springer-Verlag: Heidelberg, 1987. (e) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, 1978.

(4) Rothberg, L. J.; Cooper, N. J.; Peters, K. S.; Vaida, V. *J. Am. Chem. Soc.* **1982**, *104*, 3536.

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(8) (a) Although compounds **1** and **2** are illustrated with the cyclopentadienyl groups in a cis orientation, these dimers exist in solution as a mixture of cis and trans isomers. (b) Dyke, A. F.; Knox, S. A. R.; Morris, M. J.; Naish, P. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1417. (c) Casey, C. P.; Woo, L. K.; Fagan, P. J.; Palermo, R. E.; Adams, B. R. *Organometallics* **1987**, *6*, 447. (d) Casey, C. P.; Meszaros, M. W.; Colborn, R. E.; Roddick, D. M.; Miles, W. H.; Gohdes, M. A. *Organometallics* **1986**, *5*, 1879.

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(11) Casey, C. P.; Austin, E. A. *J. Am. Chem. Soc.* **1988**, *110*, 7106.

(12) Recently, we have presented preliminary results on the similarities and differences in the photochemistry of the compounds $Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$, $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$, $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$, and $Cp_2Fe_2(CO)_2(\mu\text{-}CS)_2$. McKee, S. D.; Bursten, B. E.; Platz, M. S. Presented at the 21st Central Regional Meeting of the American Chemical Society, Cleveland, Ohio, May 31–June 2, 1989; Abstract 231.

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(14) Modified from the procedure reported by: Hepp, A. F.; Blaha, J. P.; Lewis, C.; Wrighton, M. S. *Organometallics* **1984**, *3*, 174.

Table I. Spectroscopic Values of Relevant Compounds[a]

compd	ν_{CO},[b] cm^{-1}	^{1}H δ_{Cp},[c] ppm
$Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$ (**1**)	1997, 1952, 1782	4.23
$Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (**2**)	1977, 1938, 1785	4.13[d]
$CpFe(CO)_2Cl$	2049, 2003	5.06[e]
$Cp'_2Fe_2(CO)_2(\mu\text{-}CO)_2$ (**1'**)	1995, 1950, 1780	4.18, 4.07[f]
$Cp^*_2Fe_2(CO)_2(\mu\text{-}CO)_2$ (**1***)	1925, 1758	1.61[g]
$CpCp'Fe_2(CO)_2(\mu\text{-}CO)_2$		4.27, 4.14, 4.03[h]
$CpCp^*Fe_2(CO)_2(\mu\text{-}CO)_2$		4.42, 1.53[g]
$Mn_2(CO)_{10}$	2045, 2010, 1981	
$Cp(CO)_2FeMn(CO)_5$[18]	2080, 2013, 1990 1984, 1974, 1944	3.99

[a] IR spectra were obtained on either a Perkin-Elmer Model 580B infrared spectrometer or a Model 1600 FT-IR instrument with KBr solution cells (1.0 mm). NMR spectra were obtained on a Bruker AM-250 FT NMR instrument with the deuterated solvents as the internal lock. Cp = η^5-C_5H_5, Cp' = η^5-$C_5H_4CH_3$, and Cp* = η^5-$C_5(CH_3)_5$. [b] All CO stretches reported in toluene solvent unless indicated. [c] All cyclopentadienyl resonances are singlets and measured in C_6D_6 solvent unless indicated. [d] Major isomer in solution. See ref 8b. [e] Spectrum measured in $CDCl_3$ solvent. [f] Cyclopentadienyl resonances of Cp' appear as triplets; CH_3 of Cp' is a singlet at 1.73 ppm. [g] CH_3 of Cp* are a singlet. See ref 8c. [h] Cp resonance at 4.27 is a singlet; Cp' resonances at 4.14 and 4.03 are triplets; CH_3 of Cp' is a singlet at 1.71 ppm. See ref 17.

with a septum. The cell underwent at least 5 evacuation–refill cycles before the addition of reagents. All irradiations were performed with a 450-W medium-pressure Hg lamp (Hanovia), with the lamp immersed in a quartz cooling jacket. The cell was positioned ca. 15 cm from the cooling jacket. Both the cell and the cooling jacket were immersed into a water temperature bath with the temperature controlled to 25 ± 5 °C during the photolysis experiment. For all product studies, the solvents were deoxygenated by bubbling argon through the solvent for at least 30 min.

Flash Photolysis Studies. All transient optical density spectra were obtained using an E. G. & G. Princeton Applied Research Corporation Optical Multichannel Analyzer (OMA). The OMA and the laser flash photolysis (LFP) experiments were performed with equipment previously described.[15]

Samples for the LFP experiments were prepared in the following manner. The toluene was distilled before use and deoxygenated by bubbling argon for at least 1 h. A stock solution of **2** (ca. 1.75 × 10^{-4} M) was prepared in a 100-mL volumetric flask. The flask was first washed with concentrated sulfuric acid, water, acetone and finally the solvent to be used in the LFP experiment. It was then oven-dried (>150 °C) and flushed with argon for at least 1 h. An appropriate amount of **2** was added to the flask under a stream of Ar, the flask was sealed with a septum, and solvent was added by syringe. The stock solution flask was wrapped in aluminum foil to keep the solution from being exposed to light. Solutions prepared in this manner showed no visible signs of decomposition after 2–4 h.

In a typical LFP trial, a 1-cm^2 suprasil quartz cell was rinsed with 1.00 mL of the stock solution and sealed with a septum. The cell was charged with 2.00 mL of the stock solution and the appropriate amount of quenching reagent with use of a gastight syringe. The cell was further deoxygenated by bubbling with high-purity nitrogen for an additional 2 min. The $P(n\text{-}Bu)_3$ and $P(OPh)_3$ quenching agents were added neat, PPh_3 was added as a 0.30 M solution, $P(C_6H_{11})_3$ was added as a 1.00 M solution, and PMe_3 was added as a 1.0 M solution. All solutions were in toluene solvent. Determination of rate constants was accomplished by a linear least-squares analysis. In all cases, the pseudo-first-order decay (k_{obs}) was linear over 2 half-lives. Plots of k_{obs} versus quencher concentration were linear with the slope equal to the bimolecular rate constant. Typically four k_{obs} values were measured for each sample prepared in this manner. No averaging of multiple shots was used for any data analysis. The second-order rate constants were obtained from multiple (5–7) static samples that varied over a 10-fold concentration range of quenching agent. All rate constants and activation parameters reported here were the result of at least two independent measurements.

Irradiation of 2 with CCl_4. **2** (ca. 0.015 g; 4.3 × 10^{-5} mol) was added under a backflow of argon to the purged quartz photolysis tube. After several additional evacuation-refill cycles with argon, 40 mL of deoxygenated toluene was syringed into the cell. CCl_4 (500 μL) was added to the solution by syringe. The solution was then irradiated for 30 min, with aliquots of the solution removed (typically every 5 min) for NMR and/or IR analysis. A flocculent white insoluble solid was observed with prolonged photolysis.[16] This procedure was followed for other solvents (THF and cyclohexane) and was performed both with and without argon purge during irradiation. Chemical shifts and carbonyl stretches for $CpFe(CO)_2Cl$ were verified by comparison to an authentic sample (Table I).

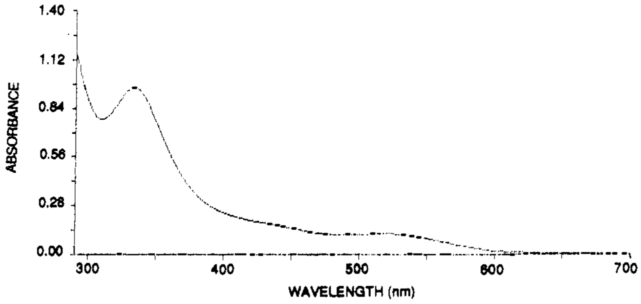
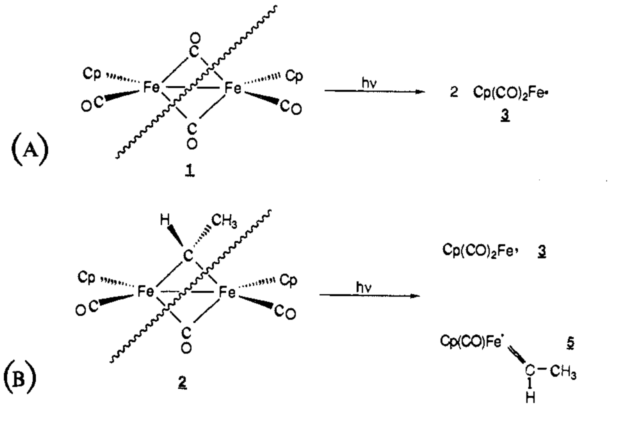


Figure 1. The electron absorption spectrum of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (**2**) in toluene at room temperature (10^{-4} M, 1 cm path length).

Scheme II



Irradiation of 2 with $Mn_2(CO)_{10}$, 1', and 1*. The cell was prepared in the manner outlined above. Under a backflow of argon, equimolar amounts of **2** (ca. 0.017 g; 4.8 × 10^{-5} mol) and the other dimer were added to the cell. After additional evacuation-refill cycles with argon to the cell, the solid was dissolved in 40 mL of deoxygenated toluene. The solution was irradiated for 75 min, with aliquots removed periodically (10 to 15 minute intervals) for NMR and/or IR analysis. This procedure was followed for other solvents (THF and cyclohexane) and performed with or without argon purge during irradiation. Argon purge during irradiation increased the amount of dimer decomposition. Chemical shifts for $CpCp'Fe_2(CO)_2(\mu\text{-}CO)_2$, $CpCp^*Fe_2(CO)_2(\mu\text{-}CO)_2$, and $Cp(CO)_2FeMn(CO)_5$ (Table I) were determined from the appropriate crossover reaction of **1** with **1'**, **1***, and $Mn_2(CO)_{10}$, performed as a separate reaction under conditions identical with those described above.

Irradiation of 2 with CH_3CN. The cell was prepared in the manner outlined above. Under a backflow of argon, 0.10 g (2.8 × 10^{-4} mol) of **2** was added to the cell. After additional evacuation-refill cycles with argon, 50 mL of deoxygenated CH_3CN was syringed into the cell. The solution was irradiated under a vigorous argon purge, with aliquots removed after 4 and 8 h for IR analysis. The IR cell must be sufficiently purged with argon in order to prevent sample decomposition. After irradiation for 4 h, the solution exhibits an obvious color change from red-orange to deep brown.

Results and Discussion

The infrared and NMR spectroscopic studies of **2** in toluene at room temperature are consistent with its previously reported

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(15) (a) Soundararajan, N.; Platz, M. S.; Jackson, J. E.; Doyle, M. P.; Oon, SuMin; Liu, M. T. H.; Anand, S. M. *J. Am. Chem. Soc.* **1988**, *110*, 7143. (b) Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1988**, *110*, 5595.

(16) One of the referees questioned the lack of the use of cutoff filters in the irradiation of **2** with CCl_4. Initially, no cutoff filters were employed in any of the product studies. We have since found that the use of either a Pyrex filter or a 355-nm band pass filter (Oriel No. 51810) does not alter the experimental results reported.

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(18) (a) Pope, K. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 4545. (b) Johnston, P.; Hutchings, G. J.; Denner, L.; Boeyens, J. C. A.; Coville, N. J. *Organometallics* **1987**, *6*, 1292.

X-ray structure.[9,19] The electronic absorption spectrum for **2**, shown in Figure 1, is similar to those of other dinuclear organometallic systems.[2] Following the assignments of Abrahamson et al. for **1**, the two weak bands of lowest energy in the spectrum of **2** are assigned to the $d\pi \rightarrow \sigma^*$ transitions.[2,20] Similarly, the intense UV band at 337 nm is assigned to the $\sigma \rightarrow \sigma^*$ transition.

Radical Formation Studies. Photolysis of dinuclear metal carbonyl compounds invariably leads to the formation of mononuclear metal carbonyl radicals.[2] For **1**, homolytic cleavage results in the formation of the 17-electron metal radical $Cp(CO)_2Fe^\bullet$ (**3**, Scheme IIA). If we envision a similar homolytic process for **2**, two different mononuclear metal centered radicals would be produced (Scheme IIB). Evidence to support radical formation could be obtained by trapping the radical species **3** or **5** with a suitable chemical trap. For example, the irradiation of **1** in the presence of CCl_4 leads to the formation of $CpFe(CO)_2Cl$, apparently consistent with the intermediacy of the $Cp(CO)_2Fe^\bullet$ radical **3** abstracting $Cl^\bullet$ from CCl_4.[21]

Irradiation of a toluene solution containing **2** and excess CCl_4 results in the formation of $CpFe(CO)_2Cl$ (eq 1). There is no NMR evidence for the formation of a second cyclopentadienyl containing

$$\underset{\mathbf{2}}{Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)} \xrightarrow{h\nu\,/\,CCl_4} CpFe(CO)_2Cl \qquad (1)$$

species, nor is a second metal–carbonyl containing species indicated by infrared spectroscopy. Prolonged irradiation leads to extensive decomposition, analogous to that previously reported for the irradiation of **1** in CCl_4 or $CHCl_3$.[16,22]

A possible interpretation of the results of irradiating **2** with CCl_4 is that homolytic cleavage of **2** yields **3** and **5** but that CCl_4 is not an effective trap for **5**. However, the reaction of a dinuclear complex with CCl_4 to yield mononuclear chlorides cannot be taken as unequivocal proof of radical formation (vide infra).[2] We have therefore also investigated photochemical crossover reactions of **2** with other dinuclear complexes. Wrighton and co-workers have demonstrated that the irradiation of two different homobimetallic metal carbonyls can be an efficient method to form heterobimetallic metal carbonyls.[23] Thus, $Cp(CO)_2FeMn(CO)_5$ can be synthesized by irradiating **1** and $Mn_2(CO)_{10}$ (eq 2). The crossover product is consistent with the coupling of mononuclear 17-electron metal radicals that are produced upon irradiation (equation 3).

$$\underset{\mathbf{1}}{Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2} + Mn_2(CO)_{10} \xrightarrow{h\nu} Cp(CO)_2FeMn(CO)_5 \qquad (2)$$

$$\underset{\mathbf{3}}{Cp(CO)_2Fe^\bullet} + {}^\bullet Mn(CO)_5 \longrightarrow Cp(CO)_2FeMn(CO)_5 \qquad (3)$$

When equimolar amounts of **2** and $Mn_2(CO)_{10}$ are irradiated, the expected $Cp(CO)_2FeMn(CO)_5$ crossover product is *not* observed by either NMR or IR spectroscopy. The use of excess $Mn_2(CO)_{10}$ does not alter this result. These experiments seem to indicate that the $Cp(CO)_2Fe^\bullet$ radical **3** is not formed by irradiating **2**. Similarly, no crossover reaction was observed when **2** was irradiated with equimolar amounts of either **1′** or **1***. These latter crossover reactions are particularly informative, for they offer the possibility of trapping the ethylidene radical **5** to form the μ-ethylidene compounds $CpCp'Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ and $CpCp^*Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ respectively, in addition to the expected $CpCp'Fe_2(CO)_2(\mu\text{-}CO)_2$ and $CpCp^*Fe_2(CO)_2(\mu\text{-}CO)_2$ crossover products (Scheme III). The complete lack of crossover products involving either radical fragment **3** or **5** is strong evidence supporting the absence of radical formation during the irradiation of **2**.

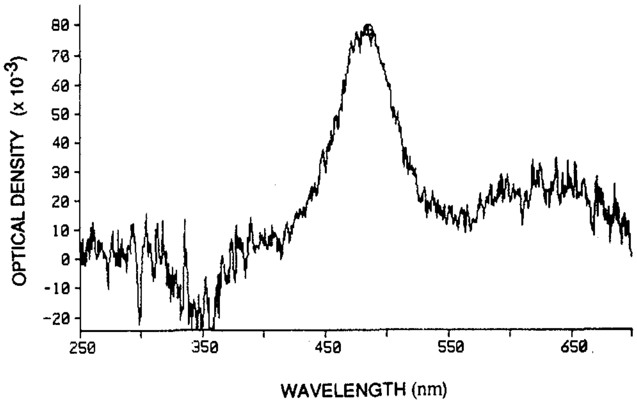
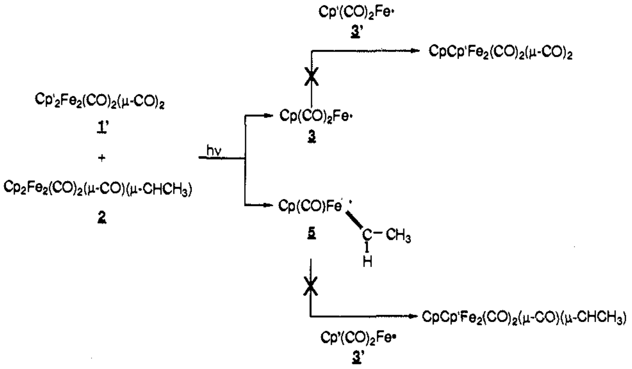


Figure 2. OMA spectrum for $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ in toluene solvent (10^{-4} M; taken 3 μs after 351 nm laser pulse).

Scheme III



We believe that the lack of radical formation upon irradiation of **2**, as compared to the readily formed mononuclear radicals upon irradiation of **1**, is a direct result of the replacement of the bridging carbonyl group in **1** with a bridging ethylidene. Whereas carbonyl ligands do not exhibit a pronounced preference for bridging or terminal coordination, alkylidene ligands in low-valent complexes show a preponderance for bridging coordination.[24] The radical **5**, which contains a terminal ethylidene ligand, is apparently inaccessible under photolysis conditions. In support of this notion, the radical species $Cp(CO)(C{=}CH_2)Fe^\bullet$ is not observed upon irradiation of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$ or upon treatment of the same dinuclear complex with tetracyanoethylene.[12,25]

Flash Photolysis Studies. For the dinuclear metal carbonyl systems that have been previously studied, there is a CO-loss pathway that competes with radical formation.[2] The fact that **2** undergoes photochemistry with CCl_4 in spite of not forming mononuclear radicals strongly suggests the formation of a CO-loss intermediate from **2**. We have therefore undertaken LFP studies of this compound in an effort to elucidate the nature of any intermediate(s) formed upon irradiation. A transient spectrum (OMA, see Experimental Section) for **2** in toluene solvent is shown in Figure 2. The spectrum, taken 3 μs after a 351 nm laser pulse,

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(19) (a) Meyer, B. B.; Riley, P. E.; Davis, R. E. *Inorg. Chem.* **1981**, *20*, 3024. (b) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1983**, 1427.

(20) (a) Abrahamson, H. B.; Palazzotto, M. C.; Reichel, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 4123. (b) Harris, D. C.; Gray, H. B. *Inorg. Chem.* **1975**, *14*, 1215.

(21) For example: Wuu, Yee-Min; Zou, C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5861.

(22) Giannotti, C.; Merle, G. *J. Organomet. Chem.* **1976**, *105*, 97.

(23) (a) Abrahamson, H. B.; Wrighton, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 5510. (b) Abrahamson, H. B.; Wrighton, M. S. *Inorg. Chem.* **1978**, *17*, 1003. (c) van Dijk, H. K.; Haar, J.; Syufkens, D. J.; Oskam, A. *Inorg. Chem.* **1989**, *28*, 75. (d) Reinking, M. K.; Kullberg, M. L.; Cutler, A. R.; Kubiak, C. P. *J. Am. Chem. Soc.* **1985**, *107*, 3517. (e) Heterobimetallic metal carbonyl dimers can also be prepared from the homobimetallic dimers in refluxing benzene. See: Madach, T.; Vahrenkamp, H. *Chem. Ber.* **1980**, *113*, 2675. The thermal reaction between **2** and $Mn_2(CO)_{10}$ in toluene failed to yield $Cp(CO)_2FeMn(CO)_5$.

(24) (a) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159. (b) Herrmann, W. A. *Pure Appl. Chem.* **1982**, *54*, 62.

(25) (a) Etienne, M.; Toupet, L. *J. Organomet. Chem.* **1988**, *344*, C19. (b) We have not attempted any ESR experiments to detect the production of radicals upon irradiation. However, similar crossover studies with $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$ support the absence of radical photochemistry for this dimer. Homolytic cleavage of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$ by photolysis would yield the radicals $Cp(CO)(C{=}CH_2)Fe^\bullet$ and $Cp(CO)_2Fe^\bullet$, analogous to Scheme IIB for **2**. (c) Austin, E. A. Ph.D. Dissertation, The University of Wisconsin—Madison, 1987.

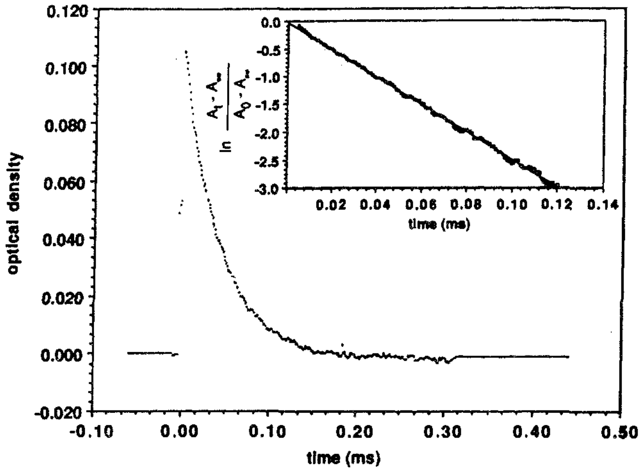
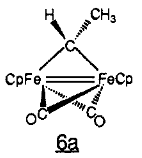


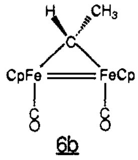
Figure 3. A representative pseudo-first-order decay of **6a** in a CO-saturated toluene solution. The inset figure is the first-order fit of the data over 3 half-lives.

has a strong absorbance with λ_{max} at 485 nm and a weaker absorbance at 625 nm. These features decay with time, and quenching studies attribute both absorption bands as belonging to the same intermediate. The intermediate is fully formed within the time resolution of the LFP experiment (<20 ns) and is formed by a monophotonic process. Both of these results are analogous to those previously observed in our studies of the CO-loss product for **1**.[12] The transient spectrum of **1** has a strong absorbance at 515 nm, which is assigned to the coordinatively unsaturated species **4**. Caspar and Meyer attribute the 400-nm absorption to the short-lived radical species **3**.[26,27] The transient spectrum of **2** shows no analogous absorption band at 400 nm, which we take as spectroscopic evidence to further support our conclusion that no mononuclear radicals are formed upon irradiation of **2**. While we have not been able to determine the lifetime of the transient species in Figure 2 with great accuracy, we can establish an upper limit of ca. 1 ms, which is much shorter than the lifetime of **4**.[26,28]

Because the LFP experiment uses UV-vis detection, it is difficult to extract direct structural information about the intermediate.[2f] By analogy to **4**, we propose that the intermediate is a CO-loss product that possesses one of the static structures **6a** or **6b**. There is ample precedent for either of these structures in the chemistry of known alkylidene-bridged compounds.[24] For example, Herrmann has shown that diazoalkanes add across the Rh-Rh double bond of Cp*Rh(μ-CO)$_2$RhCp*. The structure and stability of the product is dependent on the substituents introduced by the diazo precursor. With bulky groups, the isolated compound, [Cp*Rh]$_2$(μ-CO)$_2$(μ-CRR′), has two bridging carbonyls. For less bulky substituents, the isolated product is [Cp*Rh(CO)]$_2$(μ-CRR′), with terminal carbonyl ligands. Both structures **6a** and **6b** are consistent with the general observation that, when a CO ligand is ejected from a dinuclear metal carbonyl compound, the number of bridging CO ligands changes by ±1.[29] Previous studies have shown that most CO-loss intermediates from dinuclear carbonyl complexes contain bridging or semibridging carbonyls (assuming that the precursor complex contains two or more CO ligands).[14,30] This observation, in conjunction with the similarity in the transient spectrum of the intermediate from **2** with that observed for **4**, leads us to favor the bridging form **6a** of the intermediate.

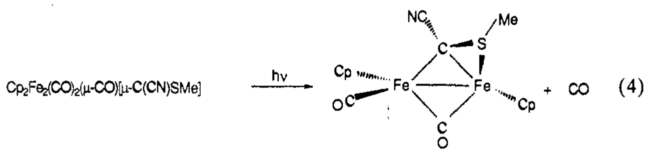


6a



6b

Further support for a CO-loss intermediate from irradiation of an alkylidene complex comes from the work of Busetto et al.[31] They found that irradiation of the dimer Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-C(CN)SMe) results in the formation of Cp$_2$Fe$_2$(CO)(μ-CO)(μ-η^1-η^2-C(CN)SMe), where the bridging unit (μ-C(CN)SMe) has remained intact (eq 4). Formation of this product implies that the CO-loss intermediate is trapped through an intramolecular reaction with the thio ligand. Casey et al. report a similar trapping upon irradiation of the vinylcarbene complex Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-(E)-CHCMe=CHMe) to form the CO-loss product Cp$_2$Fe$_2$(CO)(μ-CO)(μ-η^1-η^3-(E)-CHCMe=CHMe).[8c]



(4)

Intermediate **6a** is isostructural to the known compound [Cp*Co]$_2$(μ-CO)$_2$(μ-CHCH$_3$), although **6a** would contain a formal Fe–Fe double bond.[32] Thus, **6a** represents another example of an unsaturated 32-electron species. Preliminary matrix IR studies of the photochemistry of **2** provide further support for structure **6a**.[33]

Intermediate **6a** is also isostructural to **4**, a species that is unusual in that because of its high symmetry, it possesses a triplet ground state.[30f] By contrast, the lower symmetry of **6a** dictates that it should have a singlet ground state.[34] Inasmuch as the spin state of a compound can play a role in its reaction chemistry, we believe that the difference in spin ground state of intermediates **4** and **6a** may be evident in their chemistry.[35]

Reactions of the CO-Loss Intermediate. As we have done previously for **4**, we have used LFP to probe the kinetics of the thermal reaction of **6a** with a variety of substrates.[12,36] Consistent

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(26) Meyer, T. J.; Caspar, J. V. *J. Am. Chem. Soc.* **1980**, *102*, 7794.

(27) Under identical experimental conditions (3 μs after 351 nm laser pulse), **1** shows an absorbance at 400 nm and a strong absorbance at 515 nm in toluene solvent. The species at 400 nm has a very short lifetime and is assigned to the radical Cp(CO)$_2$Fe$^\bullet$ (**3**) whereas the species at 515 nm is very long lived and is assigned to CpFe(μ-CO)$_3$FeCp (**4**).

(28) (a) Moore, B. D.; Simpson, M. B.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1984**, 972. (b) Dixon, A. J.; Healy, M. A.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1986**, 994.

(29) Haynes, A.; Poliakoff, M.; Turner, J. J.; Bender, B. R.; Norton, J. R. *J. Organomet. Chem.* **1990**, *383*, 497.

(30) (a) Creaven, B. S.; Dixon, A. J.; Kelly, J. M.; Long, C.; Poliakoff, M. *Organometallics* **1987**, *6*, 2600. (b) Dixon, A. J.; Firth, S.; Haynes, A.; Poliakoff, M.; Turner, J. J.; Boag, N. M. *J. Chem. Soc., Dalton Trans.* **1988**, 1501. (c) Yesaka, H.; Kobayashi, T.; Yasufuku, K.; Nagakura, S. *J. Am. Chem. Soc.* **1983**, *105*, 6249. (d) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 5934. (e) Pope, K. R.; Wrighton, M. S. *Inorg. Chem.* **1987**, *26*, 2321. (f) Blaha, J. P.; Bursten, B. E.; Dewan, J. C.; Frankel, R. B.; Randolph, C. L.; Wilson, B. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 4561. (g) Hooker, R. H.; Mahmoud, K. A.; Rest, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1022. (h) Turner, J. J.; Poliakoff, M.; Healy, M. A. *Pure Appl. Chem.* **1989**, *61*, 787.

(31) Busettto, L.; Bordoni, S.; Zanotti, V.; Albano, V. G.; Braga, D. *Gazz. Chim. Ital.* **1988**, *118*, 667.

(32) (a) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 464. (b) Herrmann, W. A.; Huggins, J. M.; Bauer, C.; Smischek, M.; Pfisterer, H.; Ziegler, M. L. *J. Organomet. Chem.* **1982**, *226*, C59.

(33) Bursten, B. E.; McKee, S. D. Presented in part at the 200th National Meeting of the American Chemical Society, Washington, DC, August 26–31, 1990; INOR 126. Preliminary matrix isolation studies of **2** in 90% methylcyclohexane and 10% 3-methylpentane show the growth of two carbonyl bands at 1832 and 1795 cm^{-1} as well as the production of free CO (2132 cm^{-1}) upon irradiation of the sample. These results support the assignment of structure **6a** as the CO-loss product. The experiments also suggest no cis/trans isomer dependence on the formation of the intermediate.

(34) (a) Fenske–Hall calculations for either [CpFe]$_2$(μ-CO)$_2$(μ-CH$_2$) or [CpFe(CO)]$_2$(μ-CH$_2$) support the idea of a singlet ground state. Bursten, B. E.; McKee, S. D. Unpublished results. (b) The bridging/terminal isomerization for Cp$_2$Rh$_2$(CO)$_2$(μ-CH$_2$) has been addressed theoretically. See: Pinhas, A. R.; Albright, T. A.; Hoffman, P.; Hoffmann, R. *Helv. Chim. Acta* **1980**, *63*, 29.

(35) (a) Seder, T. A.; Ouderkirk, A. J.; Weitz, E. *J. Chem. Phys.* **1986**, *85*, 1977. (b) Bogdan, P. L.; Weitz, E. *J. Am. Chem. Soc.* **1989**, *111*, 3163. (c) Bogdan, P. L.; Weitz, E. *J. Am. Chem. Soc.* **1990**, *112*, 639. (d) Atwood, J. D. *J. Organomet. Chem.* **1990**, *383*, 59.

(36) Bursten, B. E.; McKee, S. D.; Platz, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 3428.

with the formation of a CO-loss intermediate, **6a** readily reacts with CO to reform **2**. Figure 3 shows the pseudo-first-order decay of **6a** in a CO-saturated solution.[37] The pseudo-first-order plot was linear over 3 half-lives. By using the concentration of CO in toluene under the experimental conditions employed, a second-order rate constant of 3.4 ± 0.4 × 10^6 M^{-1} s^{-1} is obtained for the reaction **6a** + CO → **2**. This value is two orders of magnitude larger than the reaction for **4** with CO (6 × 10^4 M^{-1} s^{-1} in cyclohexane).[38] While we have not experimentally determined either the ground state of **6a** or the effect of the spin ground state on the magnitude of the rate constants for these reactions, the comparatively slower value for the reaction of **4** with CO is likely due to the spin-forbidden nature of the reaction.[2a,38] For comparison, the reaction of $Mn_2(CO)_9$ with CO has a second-order rate constant of 1.2 × 10^6 M^{-1} s^{-1}.[39] $Mn_2(CO)_9$ has a singlet ground state with a semibridging CO group.

The LFP kinetic experiments also clarify the photochemical reactivity of **2** toward halogenated hydrocarbons, reactivity that is often associated with the formation of mononuclear metal-centered radicals (vide supra). The dinuclear CO-loss intermediate readily reacts with CCl_4 to form $CpFe(CO)_2Cl$ (eq 5). The reaction follows pseudo-first-order kinetics in toluene solvent. The

$$(5)\quad \underset{\underline{\mathbf{6a}}}{[CpFe]_2(\mu\text{-}CO)_2(\mu\text{-}CHCH_3)} \xrightarrow{CCl_4} CpFe(CO)_2Cl \qquad (5)$$

variation of the observed rate constant (k_{obs}) with CCl_4 concentration yields an overall second-order rate constant of 6.9 ± 0.9 × 10^3 M^{-1} s^{-1}. This value is similar to the value of 4 × 10^3 M^{-1} s^{-1} reported by Caspar and Meyer for the reaction of **4** with CCl_4.[26] Additionally, Kobayashi and co-workers have shown that $Mn_2(CO)_9$ reacts with CCl_4.[30c] Thus, it is clear that *the observed formation of a metal chloride by irradiation of a dinuclear complex in the presence of* CCl_4 *should not be used as absolute proof of the formation of a radical species.*

The formation of $CpFe(CO)_2Cl$ from **6a** (eq 5) naturally leads to the question of the fate of the remaining "$CpFe(CHCH_3)$" fragment. We have thus far been unable to isolate any alkylidene-containing products from the photoreaction of **2** with CCl_4, and it seems likely that the alkylidene is incorporated into the ill-defined decomposition products. This point is under investigation.[2a,40]

In light of the difference in reaction rate of **4** and **6a** with CO, we find it puzzling that these two intermediates react with CCl_4 at essentially the same rate. This points to the need to study the reactivity of these intermediates with a variety of quenching agents that have a range of steric and electronic properties. Our hope is that we will observe differences in the reactivity that might be related to the differences in the spin ground state.

Table II. Rate Constants and Activation Parameters[a]

phosphine	k, M^{-1} s^{-1}	$\Delta H^\ddagger$, kJ mol^{-1}	$\Delta S^\ddagger$, J mol^{-1} K^{-1}
PMe_3[b]	>10^8		
$P(n\text{-}Bu)_3$	1.7 ± 0.1 × 10^6	13.5 ± 1.4	−82.6 ± 4.1
PPh_3	6.4 ± 0.5 × 10^5	13.0 ± 1.7	−89.5 ± 4.3
$P(OPh)_3$	7.5 ± 0.6 × 10^5		
$P(C_6H_{11})_3$[b]	<10^4		

[a] All rate constants are in toluene solution and measured at 22 ± 2 °C. The activation parameters were obtained by an Eyring plot over a temperature range of 50 °C. For $P(n\text{-}Bu)_3$, the temperatures were −20 to +35 °C and 0 to +50 °C for PPh_3. [b] The results for PMe_3 and $P(C_6H_{11})_3$ are from a single experiment.

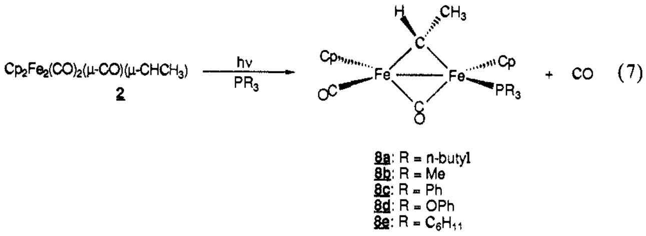
The LFP experiment allows us to study the photosubstitution kinetics of **2** with simple 2-electron donor ligands other than CO. For example, Labinger and Madhaven have shown that irradiation of **1** in CH_3CN leads to the formation of the unstable product $Cp_2Fe_2(CO)(\mu\text{-}CO)_2(NCCH_3)$.[41] Likewise, irradiation of **2** in CH_3CN solvent forms the unstable product $Cp_2Fe_2(CO)(\mu\text{-}CO)(\mu\text{-}CHCH_3)(NCCH_3)$ (**7**). Support for the formation of this product comes from the observed changes in the IR spectrum on irradiation of **2** in CH_3CN to yield new CO stretches at 1925 and 1745 cm^{-1}. These values compare favorably with those for the bands we observe at 1940 and 1741 cm^{-1} for the irradiation of **1** in CH_3CN under the same experimental conditions.[33,41] For $Cp_2Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)(NCCH_3)$, Knox reports two strong CO stretches at 1935 and 1755 cm^{-1} in CH_3CN.[42] Attempts to isolate and further characterize **7** lead to only the starting material and an insoluble brown solid. An interesting aspect of this reaction chemistry is that when CCl_4 is added to a previously irradiated solution of **2** in CH_3CN, $CpFe(CO)_2Cl$ is obtained, and the carbonyl stretches for **7** disappear.

LFP studies indicate that **6a** reacts with CH_3CN in toluene solvent (eq 6) in a bimolecular process with k = 1.3 ± 0.1 × 10^7 M^{-1} s^{-1}. For the reaction of **4** with CH_3CN, we have measured

$$\underset{\underline{\mathbf{6a}}}{[CpFe]_2(\mu\text{-}CO)_2(\mu\text{-}CHCH_3)} \xrightarrow{CH_3CN} \underset{\underline{\mathbf{7}}}{Cp_2Fe_2(CO)(\mu\text{-}CO)(\mu\text{-}CHCH_3)(NCCH_3)} \qquad (6)$$

a rate constant of 3.1 ± 0.3 × 10^5 M^{-1} in toluene.[36] As observed with CO, the reaction of **6a** with CH_3CN is faster than the reaction of **4** with CH_3CN, but just as interesting is the observation that the reactivity of **6a** with CH_3CN is faster than that with CO. A similar trend has been observed with the CO-loss intermediates $Mn_2(CO)_9$ and **4**.[30c,38,39]

Because the photochemistry of **2** appears to parallel the photochemistry of **1** with respect to CO loss, it is not surprising that irradiation of the ethylidene dimer in the presence of phosphines leads to formation of the substitution product **8** (eq 7).[43] Pettit



and co-workers have reported IR and NMR data for the substitution product **8a**.[9,44] An interesting aspect of their work was the report of the lack of either a photochemical or a thermal reaction of **2** with triphenylphosphine. We have been successful in isolating and characterizing **8a** and the trimethylphosphine

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(37) **CO Sparge procedure**: The CO experiment is performed with a slight modification of the given experimental discussion. The septum sealed suprasil cell is charged with 2.00 mL of the stock solution and deoxygenated with bubbling dinitrogen through the solution for 2 min. The solution is then treated with vigorously bubbling CO for ca. 2 min before flashing. Time-dependent absorbances following flash photolysis at 22 ± 2 °C were analyzed by a least-squares fit of ΔOD versus time over 3 half-lives. The first-order rate constant is divided by the concentration of CO (6.9 × 10^{-3} M) to obtain the second-order rate constant. All analyses of the first-order data gave linear least-squares correlations of 0.998 or better. The value of the rate constant represents the average of 6 experiments. Longer CO bubbling times produced little deviation from the given rate constant. This procedure has been previously used. See: (a) Herrick, R. S.; Peters, C. H.; Duff, R. R. *Inorg. Chem.* **1988**, *27*, 2214. (b) Wink, D. A.; Ford, P. C. *J. Am. Chem. Soc.* **1987**, *109*, 436. (c) DiBenedetto, J. A.; Rybe, D. W.; Ford, P. C. *Inorg. Chem.* **1989**, *28*, 3503.

(38) Dixon, A. J.; Healy, M. A.; Hodges, P. M.; Moore, P. D.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; West, M. A. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2083.

(39) Church, S. P.; Hermann, H.; Grevels, F. W.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1984**, 785.

(40) This reaction is analogous to

$$CpFe(\mu\text{-}CO)_3FeCp \xrightarrow{CCl_4} CpFe(CO)_2Cl + \text{“}CpFe(CO)\text{”} + {}^\bullet CCl_3$$

See: Davis, R.; Khazaal, N. M. S.; Maistry, V. *J. Chem. Soc., Chem. Commun.* **1986**.

(41) Labinger, J. A.; Madhavan, S. *J. Organomet. Chem.* **1977**, *134*, 381.

(42) Lewandos, G. S.; Doherty, N. M.; Knox, S. A. R.; MacPherson, K. A.; Orpen, A. G. *Polyhedron* **1988**, *7*, 837.

(43) (a) Haines, R. J.; Du Preez, A. L. *Inorg. Chem.* **1969**, *8*, 1459. (b) Tyler, D. R.; Schmidt, M. A.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 6018.

(44) We have recently determined the X-ray crystal structure for **8a**. Bursten, B. E.; Deng, H. B.; McKee, S. D. Unpublished results.

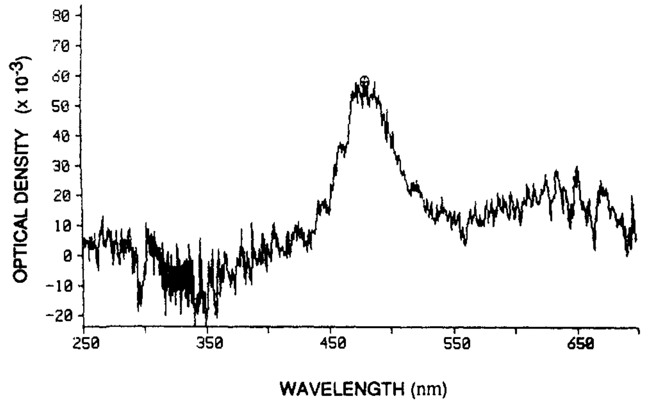


Figure 4. OMA spectrum for $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ in THF solvent (10^{-4} M; taken 3 μs after 351 nm laser pulse).

compound **8b**.[12] In addition, we have isolated the impure products **8c** and **8d** by the irradiation of **2** in the presence of PPh_3 and $P(OPh)_3$, respectively. In fact, our LFP studies indicate that **6a** reacts with all of the phosphines that we have investigated. Rate

$$\underset{\mathbf{6a}}{[CpFe]_2(\mu\text{-}CO)_2(\mu\text{-}CHCH_3)} \xrightarrow{PR_3} \underset{\mathbf{8}}{Cp_2Fe_2(CO)(\mu\text{-}CO)(\mu\text{-}CHCH_3)(PR_3)} \quad (8)$$

constants and activation parameters for eq 8 with various phosphines are listed in Table II.

The associative nature of the reaction in eq 8 is supported by the large negative values for the entropies of activation values (Table II). The overall associative bimolecular process for the reaction of **6a** with phosphines is remarkably similar to the reaction of **4** with phosphines as reported by Poliakoff et al. and in our studies of the reaction of **4** with alkynes.[28,36] It is interesting to note that the ΔH^* values reported here for phosphine substitution are 10–15 kJ/mol smaller than those reported previously for the reactions of **4** with the same phosphines.[28] The origin of this larger activation barrier for the reaction of **4** with phosphines has been attributed to the spin-forbidden nature of the reaction.[38] It is our belief that the smaller ΔH^* values measured here for the reaction of **6a** with phosphines reflects the conservation of spin state upon going from reactant to product.

It is not completely clear whether steric or electronic effects dominate the rate of reaction of phosphines with **6a**. For the phosphines in which we have obtained rate data (Table II), the rate constant decreases with increasing cone angle [$PMe_3 > P(n\text{-}Bu)_3 > PPh_3 > P(C_6H_{11})_3$].[45] It is notable that the ordering of the reaction rates for $P(n\text{-}Bu)_3$ and PPh_3 is the reverse of that observed by Poliakoff et al. for the reaction of these phosphines with **4** in cyclohexane.[28] Although $P(OPh)_3$ has a smaller cone angle than $P(n\text{-}Bu)_3$, $P(OPh)_3$ reacts with **6a** more slowly than $P(n\text{-}Bu)_3$. It may be that the decreased basicity of phosphites as compared to alkyl phosphines inhibits the reaction rate of the former with **6a**.[46]

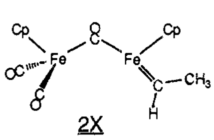
Given the reactivity of the CO-loss intermediate toward other donor ligands, the situation with L = THF is rather surprising. It has been shown that **4** in either a glass matrix or solution fails to react with THF.[14,28,30f] Similarly, our experiments indicate that **6a** does not react with THF. An interesting observation on the role of solvent warrants further comment. In both THF and cyclohexane, the OMA spectra of **6a** are virtually identical with that obtained in toluene (Figures 2 and 4). These observations are very different from our results with **1** in these solvents.[12] The transient spectrum for the intermediate **4** in THF is much weaker than in the other solvents. One possible explanation for this observation rests on the solvent dependence of the cis/trans ratio for **1**.[47] Because the CO-loss intermediate **4** is formed exclusively from the trans isomer of **1**, the isomer ratio would profoundly effect the amount of **4** produced.[14,30f,g] Studies on the cis/trans isomerization of **2** suggest a similar solvent effect.[8b] Whether there is a similar isomer dependence on the formation of the CO-loss intermediate **6a** is currently under study.[33]

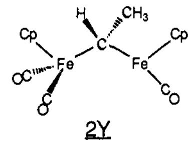
Concluding Comments

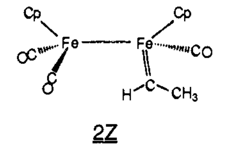
In this paper, we have attempted to detail the possible photoproducts and photochemical reactions of **2**. At the outset, we believed that because the electronic structure of **2** was similar to that of **1**, the photochemistry may also be similar.[6b] The results indicate this is not entirely the case.

UV photolysis of **2** does not produce mononuclear metal centered radicals. This result is quite different from those observed in other dinuclear systems that formally possess a single metal–metal bond.[2,23] Clearly, the nature of the bridging ligand influences the photochemical pathways available to piano-stool dimers. In the case of the ethylidene-bridged dimer **2**, formation of metal centered radicals by homolytic cleavage would result in the formation of the mononuclear fragment $Cp(CO)(CHCH_3)Fe^\bullet$ (**5**), a species that we believe to be very unstable and probably energetically inaccessible. Mononuclear cyclopentadienyl–iron–alkylidene cations with the formula $CpL_2Fe{=}CHR^+$ are known, but they have been shown to have varying stability that is highly dependent on L and R.[48] It may be possible to generate a species similar to **5** with selective tuning of either the cyclopentadienyl or alkylidene substituent. While it is generally believed that metal centered radical species are highly energetic and very reactive, they have been shown to be isolated with suitable trapping agents.[2,49] The fact that proven traps for $Cp(CO)_2Fe^\bullet$ (**3**) fail to indicate the presence of this species upon irradiation of **2** strongly suggests the absence of a radical pathway.

We believe that a primary role of the bridging ethylidene group in **2** is to maintain the integrity of the $Fe_2(\mu\text{-}CHCH_3)$ dinuclear unit. If our original assertion that the photochemistry is "LUMO-controlled" is valid, the excitation from the HOMO into the LUMO should weaken the $Fe_2(\mu\text{-}CHCH_3)$ metallacycle.[6b] Thus, a 16 electron/18 electron dinuclear intermediate **2X** could


2X


2Y


2Z

be plausible. However, if the ethylidene group maintains its bonding to both metals, intermediate **2Y** is equally plausible. Both intermediates **2X** and **2Y** are similar to the intermediate proposed for the substitution photochemistry of **1** by Tyler, Schmidt, and Gray.[43b] Additionally, it is important to note that the cis/trans isomerization for $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ has been proposed to follow a different mechanism than the Cotton–Adams bridge-to-terminal mechanism for cis/trans isomerization in **1**.[50] Rather, the isomerization is proposed to go through an intermediate similar to **2Y**, in which the methylidene bridge is maintained. Knox and co-workers have suggested that an un-

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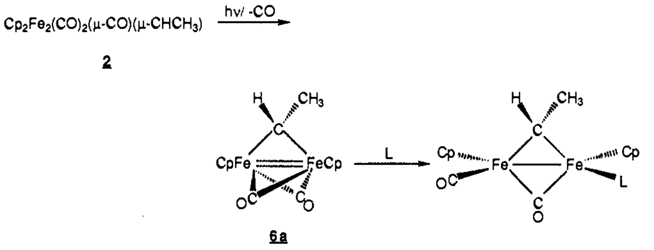
J. Am. Chem. Soc. 1991, 113, 1217-1225

Scheme IV



bridged intermediate analogous to **2Z** is involved in the cis/trans isomerization of **2** and Cp$_2$Ru$_2$(CO)$_2$(μ-CO)(μ-CMe$_2$); Bergman and Theopold favor a similar intermediate for the cis/trans isomerization in Cp$_2$CoRh(CO)$_2$(μ-CH$_2$).[8b,32a,51]

While **2X** and **2Y** would be equally possible substitution intermediates, LFP studies support formation of a CO-loss species that we propose to be isostructural to **4**. Given the similarity in the electronic structures of **1** and **2**, we think it is quite plausible that the photochemistry of the two would be similar, except for the apparent absence of a radical pathway. Indeed, the dinuclear substitution photochemistry is similar, suggesting a mechanism for **2** entirely parallel to that for **1** (Scheme IV). The major difference between the two starting dimers is that the CO-loss product for **2** would possess a singlet ground state. The implication of the difference in the spin state of the intermediate is currently under investigation.

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Surface-Enhanced Resonance Raman Scattering from Cytochromes P-450 Adsorbed on Citrate-Reduced Silver Sols

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Abstract: Four mammalian liver microsomal cytochrome P-450 enzymes were adsorbed onto citrate-reduced silver colloidal particles, and the active site of each was studied by surface-enhanced resonance Raman scattering (SERRS) spectroscopy. There were differences in the spin states of the heme groups in each protein. Methylcholanthrene-induced rat liver cytochrome P-450 IA2 was approximately 90% high spin. Phenobarbital-induced rat liver cytochromes P-450 IIB1 (90% low spin) and P-450 IIB2 (mixed high and low spin) and rabbit liver cytochrome P-450 IIB4 (100% low spin) were shown to be biologically active while adsorbed on the metal surface by following benzphetamine-induced low- to high-spin-state conversion of the heme prosthetic group. On formation of the mixed low- and high-spin-state P-450 IIB4 benzphetamine complex, the low-spin-state marker band ν_{10} shifts down by 3 cm^{-1}. It is suggested that reorganization of the water molecules in the pocket upon binding of the benzphetamine is responsible. P-450 proteins are readily denatured at a sol surface, and the protein/sol preparation described in this paper is carefully controlled so that the surface of the sol is "biocompatible". The ability of this particular sol to support an active enzyme is due to a layer of citrate ions that form a coating on the sol surface of the enzyme, providing a spacer between the silver and the protein and protecting it from silver-induced reactions. In addition, the heme group is not on the surface of the protein. This fact and the effect of the citrate layer are sufficient to preserve the integrity of the active site, and yet the distance between the silver and the heme is close enough for SERRS. If the sol is carefully prepared, no denaturation involving changing spin states is observed, although denaturation to P-420 can be forced with acid or alkali. Surface selection rules suggest that the heme orientation is less flat relative to the surface of the metal particle than is heme in cytochrome *c*. Thus, a "biocompatible sol" has been prepared and reactions of the immobilized enzymes at the metal surface have been examined in situ in contact with aqueous media by using only a few nanograms of sample.

Introduction

The intensity amplification gained from specially prepared silver surfaces along with the inherent selectivity of the chromophores associated with natural pigments enables surface-enhanced resonance Raman scattering (SERRS) spectroscopy[1] to provide information on the orientation, adsorption, and activity of adsorbed enzymes.[2] Since very small amounts of protein can be observed by SERRS and since contact can be maintained between the protein adsorbed onto the particle surface and the aqueous media or buffer, reactions of adsorbed proteins with substrates can be probed in situ. Thus, the SERRS technique could be of considerable value in the study of reactions of immobilized proteins,

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