Photochemistry of η^4-Cyclopentadiene Iron Tricarbonyl Complexes: Transfer of the 5-Endo Substituent to the Iron Center Following Dissociative Loss of Carbon Monoxide

Chaofeng Zou, Mark S. Wrighton,* and Josephine Paw Blaha

*Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

Near-UV irradiation of the complexes (η^4-C$_5$H$_5$R^1)Fe(CO)$_3$ (R^1 = *exo*-H, Ia; *exo*-CH$_2$Ph (*exo*-Bz), Ib) and (η^4-C$_5$Me$_4$R^{1}R^2)Fe(CO)$_3$ (R^1 = *exo*-Me, R^2 = *endo*-Me, IIa; R^1 = *exo*-Me, R^2 = *endo*-H, IIb; R^1 = *exo*-Bz; R^2 = *endo*-Me, IIc) where R^1 and R^2 are on the doubly allylic carbon, C-5, in an exo and endo position, respectively, results in the dissociative loss of CO. For all complexes the prompt photoproduct is a coordinatively unsaturated, 16e (η^4-cyclopentadiene)Fe(CO)$_2$ that can be detected by IR at low temperature, ~77 K. Irradiation (λ > 420 nm) of the 16e species at low temperature (~77 K) results in transfer of the 5-endo substituent to form (η^5-cyclopentadienyl)Fe(CO)$_2$R^2 (R^2 = H, Me) products. Transfer of the 5-endo substituent can also occur thermally upon warmup, but the transfer of the 5-endo group is not very competitive with back-reaction of the 16e species and CO to regenerate the starting (η^4-cyclopentadiene)Fe(CO)$_3$ complexes. The 366-nm quantum yield (at 10^{-7} einstein/min) for CO loss at 298 K in alkane solution is ~0.1; the formation quantum yields for the (η^5-cyclopentadienyl)Fe(CO)$_2$H species are also ~0.1, but the formation quantum yields for the (η^5-cyclopentadienyl)Fe(CO)$_2$Me species are <10^{-2}. All results are consistent with thermal or light-activated transfer of the 5-endo substituent (H or Me) following light-induced loss of CO from the parent (η^4-cyclopentadiene)Fe(CO)$_3$. The thermal rate of the transfer of a 5-*endo*-Me vs. a 5-*endo*-H is much slower on the basis of the thermal rates of reactions of (η^4-C$_5$Me$_5$R^2)Fe(CO)$_2$(1-pentene) (R^2 = *endo*-H or *endo*-Me) which give (η^5-C$_5$Me$_5$)Fe(CO)$_2$R^2.

In this paper we wish to report our findings regarding the photochemistry of some (η^4-cyclopentadiene)Fe(CO)$_3$ complexes. Near-UV photoexcitation of various (η^4-cyclopentadiene)Fe(CO)$_3$ species, I and II, is found to induce dissociative loss of CO as the primary photochemical event followed by transfer of the 5-endo group, H or Me, to form η^5-cyclopentadienyl complexes.

Ia: R^1=H
  b: R^1=CH$_2$C$_6$H$_5$

IIa: R^1=R^2=Me
  b: R^1=Me; R^2=H
  c: R^1=CH$_2$C$_6$H$_5$; R^2=Me
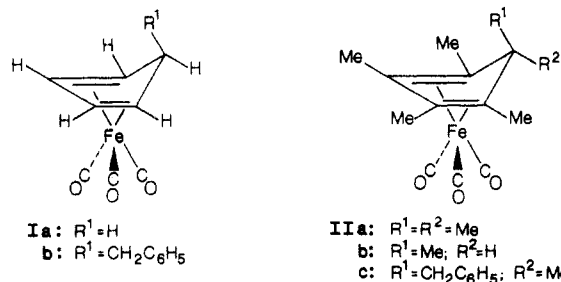
It is known that irradiation of (η^4-1,3-butadiene)Fe(CO)$_3$ at ambient temperatures leads to both loss of CO, eq 1, and η^4- → η^2-binding of the olefin, eq 2, as evidenced by

$$(\eta^4\text{-1,3-butadiene})Fe(CO)_3 \xrightarrow{h\nu}$$
$$(\eta^4\text{-1,3-butadiene})Fe(CO)_2 + CO \quad (1)$$

$$(\eta^4\text{-1,3-butadiene})Fe(CO)_3 \xrightarrow{h\nu}$$
$$(\eta^2\text{-1,3-butadiene})Fe(CO)_3 \quad (2)$$
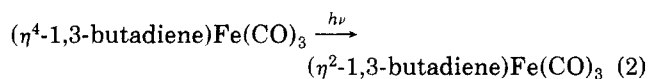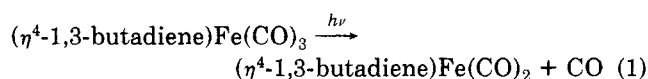
formation of both (η^4-1,3-butadiene)Fe(CO)$_2$L and (η^2-

diene)Fe(CO)$_3$L (L = P(OMe)$_3$) when the (η^4-1,3-butadiene)Fe(CO)$_3$ is irradiated in the presence of L.[1] The 366-nm quantum yields for CO loss are in the range 0.01-0.20 for a variety of (η^4-1,3-diene)Fe(CO)$_3$ complexes while the 366-nm quantum yield for the η^4- → η^2-binding of the olefin was reported to be much smaller, 0.001-0.007.[1] The low quantum efficiency for the η^4- → η^2-olefin binding was attributed to competition for the vacant coordination site between the uncoordinated double bond to regenerate the η^4-diene complex and the incoming P(OMe)$_3$ to yield the P(OMe)$_3$ substitution product. Both the CO loss product and the η^2-1,3-butadiene complexes from irradiation of (η^4-1,3-butadiene)Fe(CO)$_3$ have been observed in low-temperature matrices.[2] For example, (η^4-1,3-butadiene)Fe(CO)$_3$ yields both (η^4-1,3-butadiene)Fe(CO)$_2$ and η^2-1,3-butadiene)Fe(CO)$_3$ when irradiated in Ar or N$_2$ matrices at 10 K. For (η^4-2,3-diMe-1,3-butadiene)Fe(CO)$_3$, however, only the CO loss product was detected by IR. The difference in reactivity is attributed to the presence of the bulky Me groups which hinder rotation about the C$_2$-C$_3$ bond of the 2,3-dimethyl-1,3-butadiene ligand that is required for an s-cis-diene → s-trans-diene rearrangement, eq 3. For an η^2-1,3-diene complex to form, it is postulated that such a rearrangement must occur,[2] oth-

(1) Jaenicke, P.; Kerber, R. K.; Kirsch, P.; Koerner von Gustorf, E. A.; Rumin, R. *J. Organomet. Chem.* **1980**, *187*, 361.

(2) Ellerhorst, G.; Gerhartz, W.; Grevels, F. W. *Inorg. Chem.* **1980**, *19*, 67.

Table I. Spectroscopic Data for Relevant Compounds[a]

complex	temp, K	ν_{CO}, cm^{-1} (ϵ, M^{-1} cm^{-1} or rel abs)	λ_{max}, nm (ϵ, M^{-1} cm^{-1} or rel abs)
$(\eta^4\text{-}C_5H_6)Fe(CO)_3$ (Ia)	298	2047 (4600), 1980 (6000), 1972 (5400)	360 (sh), 280 (4100)
	77	2047 ($\sim$0.8), 1976 ($\sim$1.0), 1967 ($\sim$0.9)	
$(\eta^4\text{-}C_5H_5Bz)Fe(CO)_3$ (Ib)	298	2049 (7000), 1982 (9300), 1974 (7300)	345 (sh), 275 (7800)
	196	2045 ($\sim$0.8), 1981 ($\sim$1), 1972 ($\sim$0.9)	
	77	2043 ($\sim$0.8), 1976 ($\sim$1), 1965 (sh)	
$(\eta^4\text{-}C_5Me_5Bz)Fe(CO)_3$ (IIc)	298	2027 (4500), 1958 (7200)	300 (8080), 240 (29 230)
	196	2026 (0.8), 1956 (1.0)	
	77	2025 (0.8), 1954 (1.0)	
	77[b]	2023 (0.8), 1950 (1.0)	
$(\eta^4\text{-}C_5Me_6)Fe(CO)_3$ (IIa)	298	2029 (4200), 1958 (6800)	290 (6750), 230 (sh)
	196	2028 (0.8), 1957 (1.0)	
	77	2028 (0.8), 1956 (0.8)	
	77[b]	2023 (0.8), 1949 (1.0)	
$(\eta^4\text{-}C_5Me_5H)Fe(CO)_3$ (IIb)	298	2031 (4400), 1964 (5200), 1955 (4600)	
	77	2028 (0.9), 1958 (1.0), 1949 (0.8)	
$(\eta^5\text{-}C_5H_5)Fe(CO)_2H$	298	2024 ($\sim$1), 1967 ($\sim$1)	
	77	2018 ($\sim$1), 1959 ($\sim$1)	
$(\eta^5\text{-}C_5H_4Bz)Fe(CO)_2H$	298	2018 ($\sim$1), 1956 ($\sim$1)	330 (sh), 285
	196	2016 ($\sim$1), 1957 ($\sim$1)	
	77	2013 ($\sim$1), 1953 ($\sim$1)	
$(\eta^5\text{-}C_5Me_5)Fe(CO)_2H$	298	2002 ($\sim$1), 1944 ($\sim$1)	
	77	1998 ($\sim$1), 1939 ($\sim$1)	
$(\eta^4\text{-}C_5Me_5Bz)Fe(CO)_2$	77	1964 (1.0), 1900 (0.7)	480
$(\eta^4\text{-}C_5Me_6)Fe(CO)_2$	77	1965 (0.8), 1900 (1.0)	485
$(\eta^4\text{-}C_5Me_5H)Fe(CO)_2$	77	1968 (0.8), 1901 (1.0)	
$(\eta^4\text{-}C_5H_6)Fe(CO)_2$	77	1987 (0.9), 1922 (1.0)	
$(\eta^4\text{-}C_5Me_6)Fe(CO)_2(1\text{-pentene})$[b]	298	1976 (1.0), 1927 (0.7)	
	250	1976 (1.0), 1928 (0.7)	
	77	1968 (1.0), 1918 (0.8)	
$(\eta^4\text{-}C_5Me_5H)Fe(CO)_2(1\text{-pentene})$[b]	250	1980 (1.0), 1928 (1.0)	
	77	1973 (1.0), 1920 (0.9)	
$(\eta^4\text{-}C_5Me_5Bz)Fe(CO)_2(1\text{-pentene})$[b]	298	1977 (1.0), 1926 (0.7)	
	77	1966 (1.0), 1916 (0.8)	
$(\eta^4\text{-}C_5Me_5Bz)Fe(CO)_2(PPh_3)$	298	1955 (1.0), 1902 (0.8)	
$(\eta^4\text{-}C_5Me_6)Fe(CO)_2(PPh_3)$	298	1956 (1.0), 1903 (0.8)	
$(\eta^5\text{-}C_5Me_4Bz)Fe(CO)_2Me$	298	1995 (9720), 1941 (8840)	355 (1730), 285 (sh)
	196	1990 (1.0), 1938 (0.9)	
	77	1990 (1.0), 1936 (0.9)	
$(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me$	298	1992 (7700), 1938 (7750)	355 (880), 275 (sh)
	196	1990 (0.9), 1936 (1.0)	
	77	1990 (0.9), 1933 (1.0)	
$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$	298	2004 (3000), 1960 (6400) 1796 (6200)	520 (800), 409 (2100)
$(\eta^5\text{-}C_5H_4Bz)_2Fe_2(CO)_4$	298	1999 ((3100), 1955 (6500) 1781 (6250)	510 (850), 400 (2130)
$(\eta^5\text{-}C_5Me_4Bz)_2Fe_2(CO)_4$	298	1931 (12 500), 1762 (7500)	535 (1550), 420 (330), 362 (10 200)
$(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_4$	298	1929 (13 000), 1760 (7400)	533 (1500), 420 (3000), 362 (10 000)

[a] In methycyclohexane solvent unless noted otherwise. [b] In 1-pentene/MCH solvent.

erwise a back-reaction to the starting η^4-1,3-diene complex will dominate the reaction.

η^4-*s-cis*-diene η^2-*s-trans*-diene   (3)
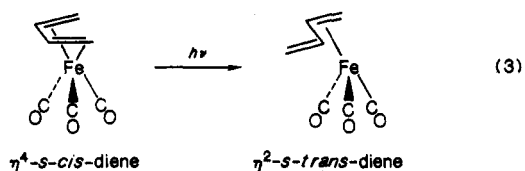
For dienes that are locked in the *s-cis* conformation, it appears that the only accessible photoprocess for $(\eta^4$-1,3-diene)$Fe(CO)_3$ is CO loss, as is observed in the photolysis of $(\eta^4$-1,3-cyclohexadiene)$Fe(CO)_3$ in solution.[3] Similarly, near-UV excitation of $(\eta^4$-5,5-R_2-$C_5H_4R_2)Fe(CO)_3$ (R = Me, Et) in an Ar or CH$_4$ matrix at 10 K yields only the 16e dicarbonyl and free CO.[4] Interestingly, further irradiation of the resulting dicarbonyl leads to growth of bands in the IR that are attributed to $(\eta^5$-$C_5H_4R)Fe(CO)_2R$. A light-induced transfer of the 5-*endo*-alkyl group to the metal center to form the metal alkyl has been proposed.[4] We

now wish to report the photochemistry of the molecules I and II in low-temperature organic glasses and in fluid solutions at higher temperature. Irradiation of species Ia has previously been shown to yield $(\eta^5$-$C_5H_5)Fe(CO)_2H$ at 298 K,[5] and preliminary results have been published[6] showing that photolysis of Ib yields $(\eta^5$-$C_5H_4Bz)Fe(CO)_2H$ at 77 K. The new results reported here show 16e intermediates that were proposed to form prior to the transfer of the 5-*endo*-H and the general finding that a 5-*endo*-Me group transfers much more slowly to the Fe center than does a 5-*endo*-H after photoejection of CO from $(\eta^4$-cyclopentadiene)$Fe(CO)_3$ complexes.

Experimental Section

Instruments and Equipment. UV–vis spectra were recorded by using a Cary 17 or Hewlett-Packard 8451A diode array spectrophotometer. IR spectra were recorded on a Nicolet 7199 or a Nicolet 60SX Fourier transform spectrometer. ^{1}H NMR spectra were recorded by using a Bruker 250 MHz or a Bruker 270 MHz Fourier transform spectrometer. Low-temperature UV–vis and IR spectra were recorded in deoxygenated methyl-

(3) Chaudhari, F. M.; Pauson, P. L. *J. Organomet. Chem.* **1966**, *5*, 73.
(4) Gerhartz, W.; Ellerhorst, G.; Dahler, P.; Eilbracht, P. *Liebigs Ann. Chem.* **1980**, 1296.
(5) Whitesides, T. H.; Shelley, *J. Organomet. Chem.* **1975**, *92*, 215.
(6) Blaha, J. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 2694.

cyclohexane solution samples held in a Specac Model P/N 21.000 variable-temperature cell with CaF$_2$ windows using either liquid N$_2$ or dry ice/organic solvents as coolant.

Chemicals. All solvents were reagent grade and freshly distilled before use. Hexane and toluene were distilled from CaH$_2$ under Ar. Methylcyclohexane (MCH) was distilled from Na under Ar. Anhydrous Et$_2$O (Aldrich) was used as received. PPh$_3$ (Aldrich) was recrystallized three times from absolute EtOH. CH$_3$I (Aldrich) was passed through activated Al$_2$O$_3$ (Woelm Alumina, Akt. I; ICN Nutritional Biochemicals) and deoxygenated before use. Cyclopentadiene was obtained by cracking dicyclopentadiene (Aldrich) and stored at 0 °C. Pentamethylcyclopentadiene and n-BuLi (2.2 M in hexane) (Aldrich) were used as received. Al$_2$O$_3$ used for chromatography was activated alumina from MCB and used as received. (η^4-C$_5$H$_6$)Fe(CO)$_3$ (Ia), (η^4-C$_5$H$_5$Bz)Fe(CO)$_3$ (Ib), and (η^4-C$_5$Me$_5$Bz)Fe(CO)$_3$ (IIc) were available from previous syntheses.[6] IR and UV–vis data for these and other complexes are found in Table I. All reactions and manipulations of the organometallic reagents were carried out by using standard Schlenk techniques under an Ar atmosphere or in a Vac-Atmospheres drybox under Ar.

(η^4-C$_5$Me$_6$)Fe(CO)$_3$ (IIa) was obtained by refluxing 1.5 g (10 mmol) of C$_5$Me$_6$ (vide infra) with 3.6 g (10 mmol) of Fe$_2$(CO)$_9$ in Et$_2$O for 4 h. The reaction mixture was then stripped of the solvent under vacuum. The residue was extracted with hexanes; the hexane extract was concentrated to about 1 mL and chromatographed on Al$_2$O$_3$. Elution with hexanes yielded 1.5 g (5 mmol) of bright yellow, crystalline IIa. Elemental analysis (Schwarzkopf Microanalytical Laboratories) was satisfactory. Anal. Calcd (Found): C, 57.9 (58.10); H, 6.21 (6.53). ^{1}H NMR (C$_6$D$_6$) is as expected: δ 1.77 (s, 6 H), 1.21 (s, 3 H), 1.08 (s, 6 H), 0.43 (s, 3 H).

C$_6$Me$_6$ was prepared in the following manner. C$_5$Me$_5$H (20.4 g, 150 mmol) was deprotonated with 150 mmol of n-BuLi in hexane. The resulting C$_5$Me$_5$Li was filtered and washed with hexanes. This was suspended in Et$_2$O, and 28.6 g (200 mmol) CH$_3$I was added. The suspension was refluxed for 6 h, and the resulting LiI was removed by filtration. The solvent was removed by evaporation to yield a dark yellow oil. Reduced pressure distillation yielded 15 g (100 mmol) of a pale yellow oil at 36–37 °C (5 torr). ^{1}H NMR (C$_6$H$_6$): δ 1.74 (s, 12 H), 0.92 (s, 6 H).

(η^4-C$_5$Me$_5$H)Fe(CO)$_3$ (IIb) has been prepared previously by reaction of Fe$_3$(CO)$_{12}$ with PtCl$_2$(C$_5$Me$_5$H).[7] Our two methods to prepare IIb are as follows.

Method A. This method is analogous to that used to prepare IIa. C$_5$Me$_5$H (1.4 g, 10 mmol) and 3.7 g (10 mmol) of Fe$_2$(CO)$_9$ were refluxed in Et$_2$O for 5 h. The reaction mixture was then stripped of solvent under vacuum. The residue was extracted with hexanes, concentrated to about 1 mL, and chromatographed on Al$_2$O$_3$. Elution with hexanes, and the yellow band was collected. Hexane and a small amount of free ligand (C$_5$Me$_5$H) were removed under vacuum. Sublimation of the solid residue at 55 °C (2 torr) yielded pure product as a yellow, waxy solid. Elemental analysis (Schwarzkopf Microanalytical Laboratories) was satisfactory. Anal. Calcd (Found): C, 56.5 (56.8); H, 5.85 (5.78). ^{1}H NMR (C$_6$D$_6$): δ 0.27 (d, 3 H), 2.52 (q, 1 H), 1.26 (s, 6 H), 1.73 (s, 6 H).

Method B. Fe(CO)$_5$ (0.1 mL) and 30 mL of deoxygenated MCH were added to a Pyrex test tube and irradiated with a medium-pressure Hg lamp at 0 °C while C$_2$H$_4$ was bubbled through the solution. The reaction was monitored with IR until all Fe(CO)$_5$ was consumed. Three new peaks, due to Fe(CO)$_3$-(C$_2$H$_4$)$_2$,[8] grow in at 2060, 1988, and 1981 cm^{-1}. To this solution was added 0.3 mL of C$_5$Me$_5$H ($\sim$2 mmol), and the solution was stirred and purged with Ar at room temperature for 2 h. The solvent was removed from the resulting red-brown solution and residue extracted with hexane. Pure product was isolated from the extract in a manner as described in method A.

The IIb prepared from both methods shows only one set of ^{1}H NMR signals and was assigned as the isomer with the 5-H in an endo position as previously assigned.[7] No evidence of formation of the isomer with 5-H in an exo position was found. Previous

work[9] on the ^{1}H NMR for an *exo*- and *endo*-Me allow unambiguous assignment of IIb as the product from synthesis methods A and B used here.

Irradiations. A near-UV lamp consisting of two General Electric blacklight bulbs (355 ± 20 nm, 2 × 10^{-6} einstein min^{-1}) was used for room-temperature irradiations. A 500-W Hanovia medium-pressure Hg lamp was used for preparative photolyses. A Bausch and Lomb SP208 high-pressure Hg lamp (output filtered with Pyrex and $\sim$10 cm of H$_2$O to remove deep UV and IR light) was used for low-temperature irraditions. Samples (3.0 mL) of 0.01 M alkane solutions of (η^4-C$_5$R$_5$R')Fe(CO)$_3$ (with or without 0.1 M PPh$_3$) for quantum yields at 366 nm were freeze-pump-thaw-degassed (<10^{-5} torr, three cycles) in 13 × 100 Pyrex test tubes with constrictions and hermetically sealed. Irradiation was carried out in a merry-go-round.[10] The light source was a 500-W Hanovia medium-pressure Hg lamp equipped with Corning glass filters to isolate the 366-nm Hg emission. Ferrioxalate actinometry was used to determine the excitation rate which was typically $\sim$10^{-7} einstein min^{-1}.[11] Disappearance of starting material and formation of products were monitored quantitatively by FTIR to give quantum yield measurements with estimated error of ±15%. Products were measured and identified by comparison with authentic samples.

Results

a. Irradiation of (η^4-Cyclopentadiene)Fe(CO)$_3$ Species at 77 K. Near-UV irradiation of $\sim$0.01 M samples of Ia and IIa–c in methylcyclohexane (MCH) or 3-methylpentane matrix at 77 K yields IR spectral changes as depicted in Figures 1 and 2 for these complexes. Spectral changes for Ib have been previously described.[6] In all cases examined there is loss of CO from the starting complex as shown by the appearance of a feature due to free CO at 2132 cm^{-1}.[12] The appearance of CO is quantitative;[12] one CO molecule is produced per starting molecule consumed. This result rules out any net loss of the hydrocarbon ligand or η^4- → η^2-olefin conversion found[1,2] for acyclic (1,3-diene)Fe(CO)$_3$ complexes. In all cases examined the 16e (η^4-cyclopentadiene)Fe(CO)$_2$ can be detected by IR. For complexes having an H at the 5-*endo* position, Ia,b and IIb, irradiation results in formation of 16e species and the subsequent H-transfer products, eq 4 and 5. For example, when IIb is irradiated at 77 K,
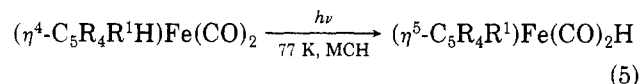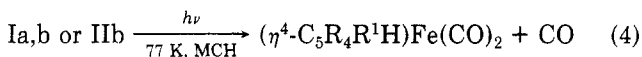
$$\text{Ia,b or IIb} \xrightarrow[\text{77 K, MCH}]{h\nu} (\eta^4\text{-C}_5\text{R}_4\text{R}^1\text{H})\text{Fe(CO)}_2 + \text{CO} \quad (4)$$

$$(\eta^4\text{-C}_5\text{R}_4\text{R}^1\text{H})\text{Fe(CO)}_2 \xrightarrow[\text{77 K, MCH}]{h\nu} (\eta^5\text{-C}_5\text{R}_4\text{R}^1)\text{Fe(CO)}_2\text{H} \quad (5)$$

Figure 1 (top), there is rapid decline of the starting material bands at 2028, 1960, and 1950 cm^{-1}, concomitant with growth of a band attributed to free CO at 2132 cm^{-1}. The presumed coordinatively unsaturated 16e (η^4-C$_5$Me$_5$H)-Fe(CO)$_2$ species is observed, as evidenced by growth of the low-energy absorption bands at 1968 and 1901 cm^{-1}. The 16e species are rapidly converted to (η^5-C$_5$Me$_5$)Fe(CO)$_2$H via light-activated transfer of the 5-*endo*-H from the cyclopentadiene ring to the Fe center, eq 5. The IR spectrum shows the growth of two bands at 1998 and 1939 cm^{-1} attributable to (η^5-C$_5$Me$_5$)Fe(CO)$_2$H as irradiation proceeds. Likewise, when Ia is irradiated at 77 K in MCH, the product observed is coordinatively unsaturated 16e

(7) Balakrishnan, P. V.; Maitlis, P. M. *J. Chem. Soc. A* **1971**, 1715.

(8) Wuu, Y.-M.; Bentsen, J. G.; Brinkley, C. G.; Wrighton, M. S. *Inorg. Chem.* **1987**, *26*, 530.
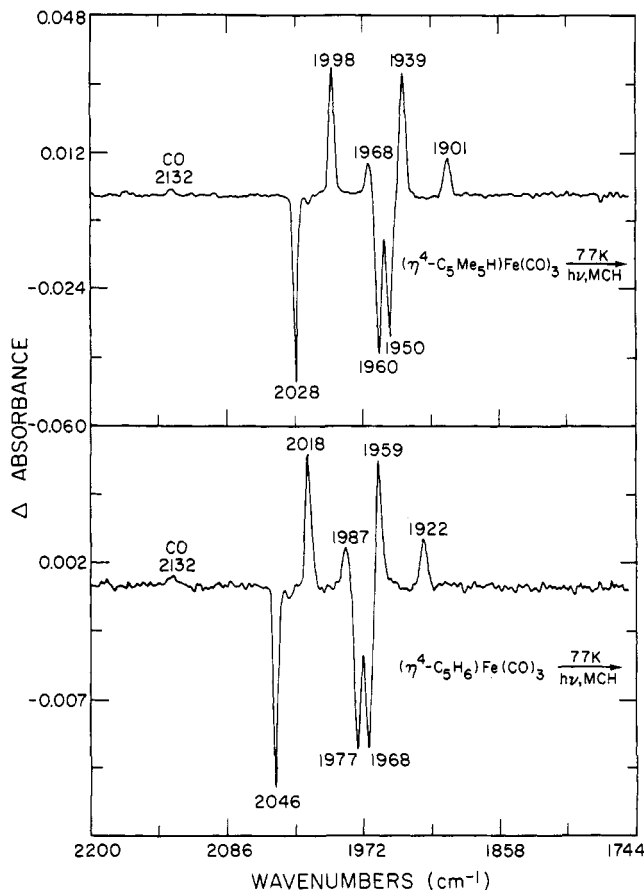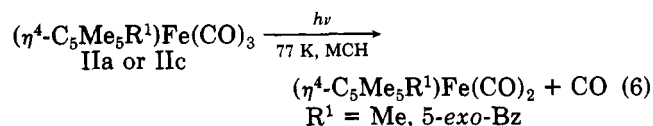
(9) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1969**, 2024 and references therein.

(10) Moses, F. G.; Liu, R. S. H.; Monroe, B. M. *Mol. Photochem.* **1969**, *1*, 245.

(11) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

(12) Pope, K. R.; Wrighton, M. S. *Inorg. Chem.* **1985**, *24*, 2792. The molar extinction coefficient of CO has been determined to be 400 M^{-1} cm^{-1} (±20%).

Figure 1. IR spectral changes (difference spectra) induced by near-UV excitation of 0.01 M complexes in a MCH matrix at 77 K after ~1 min of irradiation. Top: $(\eta^4$-$C_5Me_5H)Fe(CO)_3$; starting material bands at 2028, 1960, and 1950 cm^{-1} decline while bands due to $(\eta^4$-$C_5Me_5)Fe(CO)_2$ (1968, 1901 cm^{-1}) and $(\eta^4$-$C_5Me_5)$-$Fe(CO)_2H$ (1998, 1939 cm^{-1}) grow. Bottom: $(\eta^4$-$C_5H_6)Fe(CO)_3$; starting material bands at 2046, 1977, and 1968 cm^{-1} decline while bands due to $(\eta^4$-$C_5H_6)Fe(CO)_2$ (1987, 1922 cm^{-1}) and $(\eta^5$-$C_5H_5)Fe(CO)_2H$ (2018, 1959 cm^{-1}) grow.

$(\eta^4$-$C_5H_6)Fe(CO)_2$ and $(\eta^5$-$C_5H_5)Fe(CO)_2H$ is a secondary photoproduct. However, the concentration of the 16e species reaches a maximum within 5 min of irradiation. Upon further irradiation, the concentrations of 16e species remain constant for about 5 min and then start to diminish. This is caused by an efficient, but secondary, photoprocess to form metal carbonyl hydride, eq 5.

Assignment of the ultimate 77 K photoproducts from Ia,b and IIb is based on comparison of IR band positions and intensities of authentic samples of $(\eta^5$-$C_5R_4R^1)Fe$-$(CO)_2H$ and on reaction chemistry upon warming irradiated samples to 298 K. The $(\eta^5$-$C_5R_4R^1)Fe(CO)_2H$ species thermally yield the known $(\eta^5$-$C_5R_4R^1)_2Fe_2(CO)_4$ complexes. In addition, the UV–vis spectral changes upon irradiation at 77 K accord well with the spectral properties, λ_{max} = 330 nm, of authentic $(\eta^5$-$C_5R_4R^1)Fe(CO)_2H$. Thus, the hydride products are unambiguously identified.

For complexes having a Me group in the 5-endo-position, IIa,c, the only prompt photoproduct is a 16e species, Figure 2, eq 6. Upon photolysis there are decreases of the starting

$$(\eta^4\text{-}C_5Me_5R^1)Fe(CO)_3 \xrightarrow[\text{77 K, MCH}]{h\nu}$$
IIa or IIc

$$(\eta^4\text{-}C_5Me_5R^1)Fe(CO)_2 + CO \quad (6)$$
$$R^1 = Me, 5\text{-}exo\text{-}Bz$$

material bands for both IIa (2028, 1956 cm^{-1} and IIc (2025, 1954 cm^{-1}) along with growth of absorption due to free CO (2132 cm^{-1}). Continued broad-band irradiation leads to
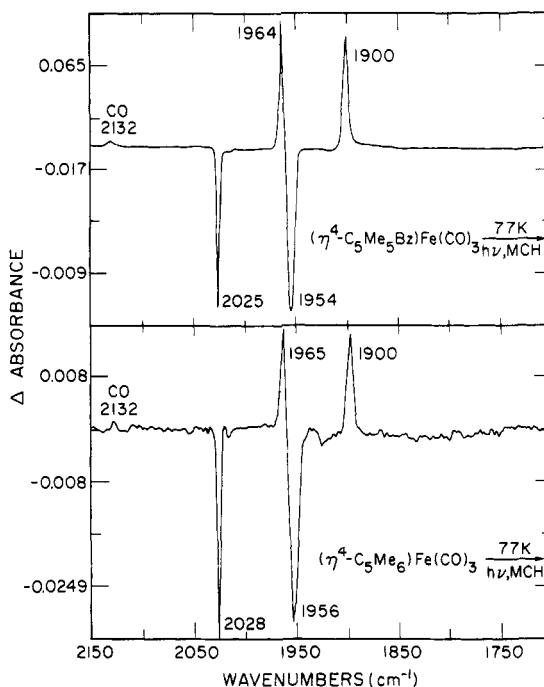

Figure 2. IR spectral changes (difference spectra) induced by near-UV excitation of 0.01 M complexes in MCH matrix at 77 K after ~2 min of irradiation. Top: $(\eta^4$-$C_5Me_5Bz)Fe(CO)_3$; starting material bands at 2025 and 1954 cm^{-1} decline while bands due to $(\eta^4$-$C_5Me_5Bz)Fe(CO)_2$ grow at 1964 and 1900 cm^{-1}. Bottom: $(\eta^4$-$C_5Me_6)Fe(CO)_3$; starting material bands at 2028 and 1956 cm^{-1} decline while bands due to $(\eta^4$-$C_5Me_6)Fe(CO)_2$ grow at 1965 and 1900 cm^{-1}.

secondary photoproducts: the Me-transfer products $(\eta^5$-$C_5Me_4R^1)Fe(CO)_2Me$ are detected by IR. The secondary photolysis of the 16e complexes having a 5-endo-Me proceeds much more slowly than for the 16e species having a 5-endo-H. Accordingly, clean conversion of IIa,c to the 16e species is possible, Figure 2, without apparent formation of the ultimate $(\eta^5$-$C_5Me_4R^1)Fe(CO)_2Me$ complexes. As illustrated in Figure 1, irradiation of Ia,c and IIb always yields a mixture of the 16e species and $(\eta^5$-$C_5R_4R^1)Fe(CO)_2H$.

The 16e species from irradiation of starting tricarbonyl complexes are assigned on the basis of positions and intensities of IR absorptions for other 16e $(\eta^4$-1,3-diene)Fe-$(CO)_2$ species.[1,2,4] Since the low-temperature photolysis yields one CO per molecule reacted, the product must be a dicarbonyl. That the dicarbonyl is coordinatively unsaturated is consistent with reaction chemistry upon further photolysis or warming and also with the UV–vis spectral changes. Figure 3 shows the UV–vis changes following photoexcitation of IIc at 77 K. Trace 0 shows the optical spectrum of the starting IIc. Traces 1 and 2 show the UV–vis changes after irradiation. The growth of a well-defined, low-energy first absorption band at 480 nm is attributed to the 16e dicarbonyl seen by IR. This is consistent with the formulation of the dicarbonyl as a coordinatively unsaturated species. Generally, coordinatively unsaturated 16e photofragments have a lower energy first absorption than their 18e parents, due to the stabilization of the lowest unoccupied molecular orbital when a 2e donor ligand is extruded from the coordination sphere.[13] We observe UV–vis spectral changes similar to those of IIc upon irradiation of IIa, with the growth of a distinct first absorption band at 485 nm.

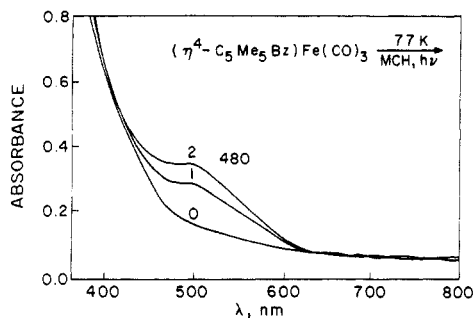(13) Geoffroy, G. O.; Wrighton, M. S. *Organometallic Photochemistry*; Academic: New York, 1979.

Figure 3. UV–vis spectral changes that accompany the near-UV-induced dissociative loss of CO from 0.01 M $(\eta^4\text{-}C_5Me_5Bz)\text{-}Fe(CO)_3$ in a MCH matrix at 77 K. The path length in the cell is ~0.1 mm. Trace 0 is the optical spectrum before photolysis while traces 1 and 2 represent the optical spectra after 5 (~50% conversion) and 10 min (~90% conversion) of irradiation, respectively. The low-energy band at ~480 nm is assigned to the 16e $(\eta^4\text{-}C_5Me_5Bz)Fe(CO)_2$ species.

Photolysis of $(\eta^4$-cyclopentadiene)$Fe(CO)_3$ complexes in a 1-pentene matrix at 77 K leads to the formation of 1-pentene-substituted products. For example, for $(\eta^4$-$C_5Me_5H)Fe(CO)_3$ (IIb) there is decline of the IR bands due to the starting material, growth of a band attributed to free CO, and two bands at 1973 and 1920 cm^{-1} attributed to $(\eta^4$-$C_5Me_5H)Fe(CO)_2$(1-pentene). However, upon prolonged irradiation two other bands due to the H-transfer product $(\eta^5$-$C_5Me_5)Fe(CO)_2H$ at 1995 and 1934 cm^{-1} also appear. For complexes having a 5-*endo*-Me group only 1-pentene-substituted dicarbonyl complexes are formed upon irradiation in 1-pentene matrices at 77 K. The formulation of the products as 1-pentene substitution products is consistent with the differences in the IR spectral changes compared to MCH matrices (higher CO stretching frequencies in 1-pentene) and with chemistry upon warming the samples. Warmup (ultimately to 298 K) of the 1-pentene-substituted dicarbonyls results in >99% regeneration of starting material. There is essentially no conversion to H- or Me-transfer products; apparently R^2 group migration is a relatively slow process compared to back-reaction with CO at low temperatures.

b. Chemistry of $(\eta^4$-Cyclopentadiene)$Fe(CO)_2$ at Low Temperature. The photogenerated 16e fragments $(\eta^4$-cyclopentadiene)$Fe(CO)_2$ are inert at 77 K. There are no changes of absorption bands due to 16e species in the dark during a 3-h period. Warming of the matrix to just 100 K results in rapid (<5 min) back-reaction of the 16e species with CO to regenerate the starting tricarbonyls. Thermal transfer of an H or a Me group at 77 K is not observed. Interestingly, irradiation of the 16e species at 77 K with λ > 420 nm light, where the starting tricarbonyls do not absorb significantly, leads to loss of the bands attributed to the 16e dicarbonyl and formation of H- or Me-transfer products $(\eta^5$-$C_5R_4R^1)Fe(CO)_2R^2$ and regeneration of starting tricarbonyl. Back-reaction with the photoejected CO is competitive with the intramolecular transfer of the 5-endo group to the Fe center. Figure 4 shows the IR changes associated with the visible light excitation of $(\eta^4$-$C_5Me_5H)Fe(CO)_2$ from IIb and $(\eta^4$-$C_5H_6)Fe(CO)_2$ from Ia. The IR bands for the 16e species decline with irradiation time. At the same time, bands due to the H-transfer product (top, 1998, 1939 cm^{-1}) (bottom, 2018, 1959 cm^{-1}) grow with the time, as well as bands due to starting tricarbonyls (for IIb, 2028, 1960, 1950 cm^{-1}; for Ia, 2046, 1977, 1968 cm^{-1}). These results not only unambiguously identify the 16e species as precursors to the metal hydride but also show that photochemical formation of the H-transfer products from the parent tricarbonyl
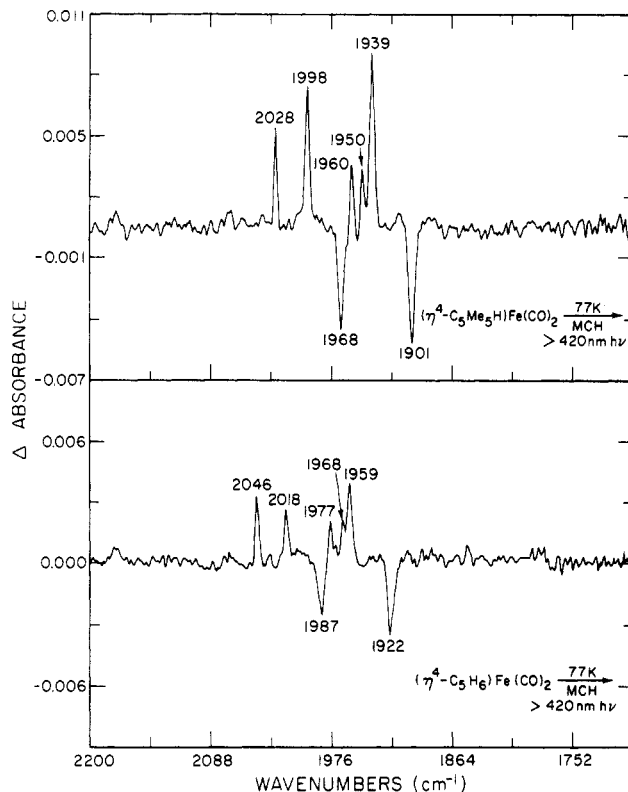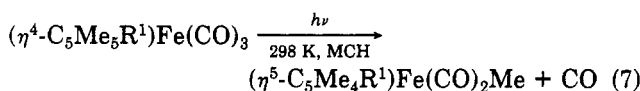

Figure 4. IR spectral changes (difference spectra) induced by visible light (λ > 420 nm) excitation of the photogenerated 16e fragments at 77 K in MCH matrix for 2 min. Top: $(\eta^4$-$C_5Me_5H)Fe(CO)_2$; peaks observed at 2028, 1960, and 1950 cm^{-1} correspond to $(\eta^4$-$C_5Me_5H)Fe(CO)_3$ while those at 1998 and 1939 cm^{-1} correspond to $(\eta^5$-$C_5Me_5)Fe(CO)_2H$. Bottom: $(\eta^4$-$C_5H_6)$-$Fe(CO)_2$; peaks observed at 2046, 1977, and 1968 cm^{-1} are due to $(\eta^4$-$C_5H_6)Fe(CO)_3$ while those at 2018 and 1959 cm^{-1} correspond to $(\eta^5$-$C_5H_5)Fe(CO)_2H$.

species can be due to secondary irradiation of the primary photogenerated 16e species. IR spectral change upon visible light excitation of 16e complexes having an *endo*-Me group show that conversion to the $(\eta^5$-$C_5Me_4R^1)Fe(CO)_2Me$ also occurs photochemically at 77 K, Figure 5. Since H and Me transfer from the cyclopentadiene ring to the Fe do not occur thermally at 77 K, our results provide examples of photoactivated *endo*-H and -Me transfer. Previous results[14] from this laboratory show that photolysis of Fe-$(CO)_4(\eta^2$-$C_3H_6)$ at 77 K yields IR spectral changes consistent with prompt formation of HFe(CO)$_3(\eta^3$-$C_3H_5)$. In this case, H transfer via a thermal reaction appears to be so fast that it is not possible to observe the 16e intermediate Fe(CO)$_3(\eta^2$-$C_3H_6)$ at 77 K.

c. Photochemistry of $(\eta^4$-Cyclopentadiene)$Fe(CO)_3$ Complexes in Fluid Solution at 250 and 298 K. Near-UV irradiation of 0.01 M I and IIb in alkane solution at 298 K leads to initial formation of $(\eta^5$-$C_5R_4R^1)Fe(CO)_2H$ and subsequent thermal and photochemical formation of the dimer $(\eta^5$-$C_5R_4R^1)_2Fe_2(CO)_4$. The 366-nm quantum yield for formation of the hydrides is ~0.1. For the tricarbonyl complexes having a 5-*endo*-Me quantitative formation of the iron alkyls $(\eta^5$-$C_5Me_5)Fe(CO)_2Me$ (from IIa) and $(\eta^5$-$C_5Me_4Bz)Fe(CO)_2Me$ (from IIc) is observed, eq 7, but the 366-nm appearance quantum yields are only

$$(\eta^4\text{-}C_5Me_5R^1)Fe(CO)_3 \xrightarrow[\text{298 K, MCH}]{h\nu}$$
$$(\eta^5\text{-}C_5Me_4R^1)Fe(CO)_2Me + CO \quad (7)$$

(14) Mitchener, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983,** *105,* 1065.
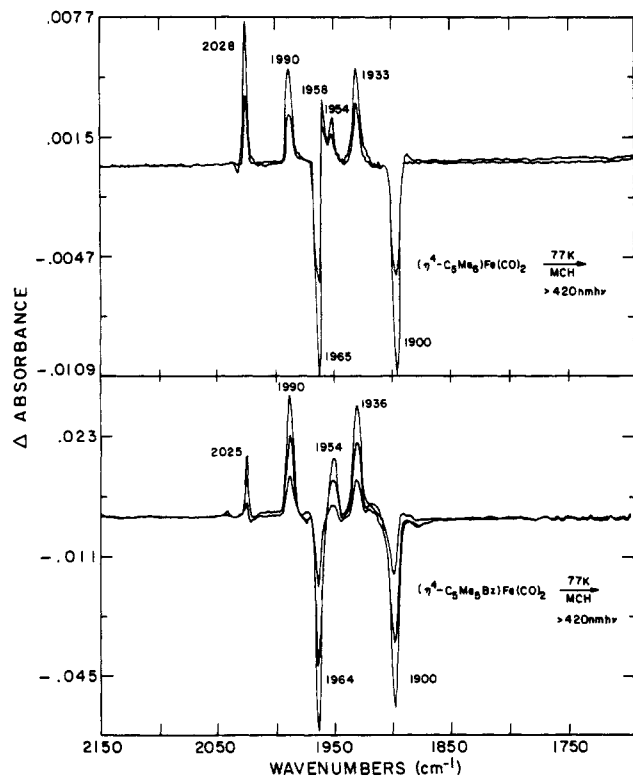
Figure 5. IR spectral changes (difference spectra) induced by visible light ($\lambda > 420$ nm) excitation of the photogenerated 16e fragments at 77 K in MCH matrix. Top: $(\eta^4\text{-}C_5Me_6)Fe(CO)_2$; after 2 and 4 min of irradiation, peaks observed at 2028, 1958 and 1954 cm^{-1} correspond to $(\eta^4\text{-}C_5Me_6)Fe(CO)_3$ while those at 1990 and 1933 cm^{-1} correspond to $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me$. Bottom: $[(\eta^4\text{-}C_5Me_5(5\text{-}exo\text{-}Bz)]Fe(CO)_2$; after 4, 8 and 12 min of irradiation, peaks observed at 2025 and 1954 cm^{-1} are due to $[(\eta^4\text{-}C_5Me_5(5\text{-}exo\text{-}Bz)]Fe(CO)_3$ while those at 1990 and 1936 cm^{-1} correspond to $(\eta^5\text{-}C_5Me_4Bz)Fe(CO)_2Me$.

0.009 and 0.007, respectively. Irradiation of 0.01 M alkane solutions of IIa with 0.05 M PPh$_3$ leads to quantitative formation of the substitution product $(\eta^4\text{-}C_5Me_6)Fe(CO)_2PPh_3$ (1956, 1903 cm^{-1}) with a 366-nm quantum yield of 0.15. Similarly, for IIc irradiation of the 0.01 M solutions in the presence of 0.05 M PPh$_3$ leads to quantitative formation of $(\eta^4\text{-}C_5Me_5Bz)Fe(CO)_2PPh_3$ (1955, 1902 cm^{-1}) with a 366 nm quantum yield of 0.12. The conclusion from these results is that PPh$_3$ intercepts the efficiently photogenerated $(\eta^4\text{-}C_5R_4R^1Me)Fe(CO)_2$ prior to Me transfer. The low quantum yields for photoreactions according to eq 7 are consistent with the low temperature result that the Me migration is a slow process and that back-reaction with photoejected CO is a competitive process. All quantum yields have been measured at less than 10% conversion and at the same excitation rate, $\sim 10^{-7}$ einstein/min^{-1}, in order to make comparisons from system to system. The low quantum yield for the room-temperature reaction to form the Me-transfer products is thus due to rapid (compared to Me transfer) back-reaction of the 16e intermediate with photogenerated CO.

The results of quantum yield determinations described to this point are consistent with the conclusion that thermal transfer of a 5-*endo*-H is much faster compared with the thermal transfer of a 5-*endo*-Me group subsequent to photoextrusion of CO from a tricarbonyl. Regarding CO back-reaction with the 16e species, we would expect that the 16e species with a 5-*endo*-H would react with CO faster than would the 16e species with a 5-*endo*-Me due to larger steric constraint in the Me case. Hence, the quantum yield for the hydride formation would be expected to be smaller than for Me complex formation if the
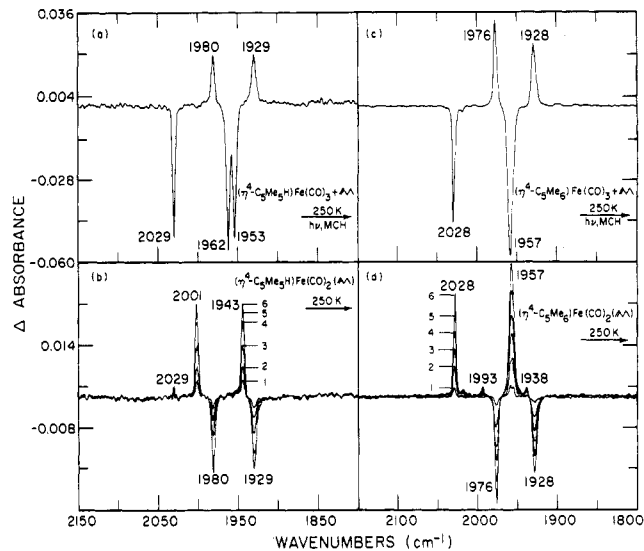

Figure 6. IR spectral changes (difference spectra) associated with the photogeneration of $(\eta^4\text{-}C_5Me_5R^2)Fe(CO)_2(1\text{-pentene})$ (R^2 = H or Me) and the subsequent thermal chemistry in 1-pentene/MCH solution at 250 K. (a) After 1 min of irradiation, peaks at 1980 and 1929 cm^{-1} correspond to $(\eta^4\text{-}C_5Me_5H)Fe(CO)_2(1\text{-pentene})$. (b) Peaks due to $(\eta^4\text{-}C_5Me_5H)Fe(CO)_2(1\text{-pentene})$ decline thermally while the peaks due to $(\eta^5\text{-}C_5Me_5)Fe(CO)_2H$ at 2001 and 1943 cm^{-1} grow at 0.5, 1, 2, 4, 7, and 10 min. The peak at 2029 cm^{-1} is due to the starting tricarbonyl. (c) After 1 min of irradiation, peaks at 1976 and 1928 cm^{-1} correspond to $(\eta^4\text{-}C_5Me_6)$-Fe(CO)$_2$(1-pentene). (d) Peaks due to $(\eta^4\text{-}C_5Me_6)Fe(CO)_2(1\text{-pentene})$ decline thermally while the peaks due to $(\eta^4\text{-}C_5Me_6)$-Fe(CO)$_3$ (2028 and 1957 cm^{-1}) and to $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me$ (1993 and 1938 cm^{-1}) grow at 3, 26, 34, 48, 60, and 70 min.

H and Me transfer have the same rates. Instead we find the quantum yield for formation of hydride to be much greater than that for formation of Me-transfer products. This difference in quantum yield can, therefore, only be attributed to the faster thermal rate of H transfer vs. Me transfer following extrusion of CO from the tricarbonyls I and II.

When 0.01 M solutions of $(\eta^4\text{-}C_5Me_5R^2)Fe(CO)_3$ (R^2 = 5-*endo*-H (IIb) and 5-*endo*-Me (IIa)) in MCH solution containing 0.1 M 1-pentene are photolyzed at 250 K, the 1-pentene substitution products $(\eta^4\text{-}C_5Me_5R^2)Fe(CO)_2(1\text{-pentene})$ are observed, Figure 6. The photogenerated 1-pentene complexes are labile at 250 K. Upon standing in the dark at 250 K, significant regeneration of the starting tricarbonyl IIa and a very small amount of formation of the Me-transfer product $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me$ occurs from reaction of $(\eta^4\text{-}C_5Me_6)Fe(CO)_2(1\text{-pentene})$. For the substituted complex with an H in the 5-endo-position, $(\eta^4\text{-}C_5Me_5H)Fe(CO)_2(1\text{-pentene})$, rapid conversion to the H-transfer product $(\eta^5\text{-}C_5Me_5)Fe(CO)_2H$ is the only observed reaction. There is no regeneration of the starting tricarbonyl IIb. Figure 6b shows the IR spectral changes accompanying the thermal chemistry of $(\eta^4\text{-}C_5Me_5H)Fe$-(CO)$_2$(1-pentene) in a 1-pentene/MCH solution. Note the decline of the dicarbonyl (1980, 1929 cm^{-1}) and growth of the H-transfer product $(\eta^5\text{-}C_5Me_5)Fe(CO)_2H$ (2001, 1943 cm^{-1}) over a time period of 10 min. By comparison (Figure 6d) the consumption of $(\eta^4\text{-}C_5Me_6)Fe(CO)_2(1\text{-pentene})$ (1976, 1928 cm^{-1}) generates two species, starting tricarbonyl (2028, 1957 cm^{-1}) and Me-transfer products (1993, 1938 cm^{-1}) over a longer time period. Thus, like PPh$_3$, 1-pentene is able to trap the 16e precursors to the H and Me transfer, but the rates of subsequent H and Me transfer at the same temperature are substantially different. The 5-*endo*-H transfer is apparently too fast to allow CO back-reaction to regenerate the starting tricarbonyls, whereas the rate

of Me transfer is slow enough that there is competitive back-reaction with CO to regenerate the starting material. At low temperature (vide supra), the rate of CO back-reaction vs. Me transfer is too fast to allow significant formation of the Me-transfer products due to the difference in activation energies for the CO back-reaction compared to Me transfer. At 250 K there is enough thermal energy to provide the activation energy required for the Me transfer. The thermal chemistry of $(\eta^4\text{-}C_5Me_5R^2)Fe(CO)_2(1\text{-pentene})$ thus shows that the transfer of 5-*endo*-H is more facile than the 5-*endo*-Me. With the assumption that the thermal chemistry proceeds via dissociative loss of 1-pentene and that this rate is the same for $(\eta^4\text{-}C_5Me_6)Fe(CO)_2(1\text{-pentene})$ and $(\eta^4\text{-}C_5Me_5H)Fe(CO)_2(1\text{-pentene})$, the transfer of the 5-*endo*-H occurs at least 10^2 times faster than the transfer of the 5-*endo*-Me.

Discussion

Results reported above demonstrate that the mechanism for all photoreactions of $(\eta^4\text{-cyclopentadiene})Fe(CO)_3$ begins with quantum-efficient, light-induced loss of CO. The quantum yield for CO loss is at least 0.1 at 366 nm. The resulting 16e fragments can be scavenged by photoejected CO or by added ligands such as 1-pentene or PPh_3, provided transfer of the 5-*endo* group is sufficiently slow. The transfer of 5-*endo* group (H or Me) does not occur thermally at 77 K. For the 5-*endo*-H species the transfer of the H to form a metal hydride and the back-reaction with photoejected CO are too fast to allow observation of the 16e fragment at temperatures above 100 K. For the 5-*endo*-Me species the transfer of the Me, eq 8, is so slow

$$(\eta^4\text{-}C_5Me_5R^1)Fe(CO)_2 \xrightarrow[\Delta]{k_8} (\eta^5\text{-}C_5Me_4R^1)Fe(CO)_2Me \quad (8)$$
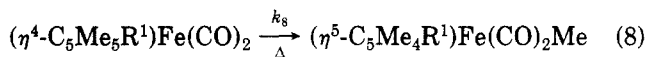
that Fe–Me formation is only barely competitive with the back-reaction of the 16e species with photoejected CO, eq 9, at 298 K and low light intensity (where steady-state

$$(\eta^4\text{-}C_5Me_5R^1)Fe(CO)_2 + CO \xrightarrow[\Delta]{k_9} (\eta^4\text{-}C_5Me_5R^1)Fe(CO)_3 \quad (9)$$
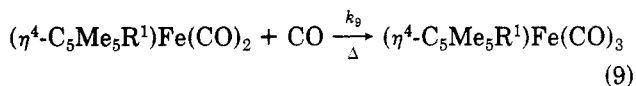
concentration of CO and the 16e species are low). While the rate of the reaction represented by eq 8 is too slow to give large quantum yields, this does not mean that the value of k_8 is, in absolute terms, small. The bimolecular rate constant k_9 is conservatively 10^6 M^{-1} s^{-1}, judging from measured values for other cases of CO reaction with coordinatively unsaturated compounds.[15] Flash photolysis studies will be required to determine k_8 (and k_9). The studies of the 250 K thermal reaction of the $(\eta^4\text{-}C_5Me_5R^2)Fe(CO)_2(1\text{-pentene})$ (R^2 = H, Me) complexes, Figure 6, clearly show that the transfer of a 5-*endo*-H is faster than the 5-*endo*-Me by at least 10^2. Thus, the Me transfer rate constant at 298 K may be fairly large in absolute terms, but H transfer is much faster. A difference in rate for C–C and C–H bond-breaking reactions is commonplace in organometallic chemistry. The fact that Me transfer is observed at all is clearly associated with the special geometric and electronic situation in the complexes studied.

It is interesting to point out that the photochemical alkyl transfer we observe is the reverse of a thermal reaction involving the migration of a R group from a metal center to the 5-endo position of the cyclopentadiene ring following the attack of a metal center by a ligand.[16] Also, Brookhart et al. proposed[17] a mechanism involving metal-to-ring migration to account for the result of methylation of the cyclohexadiene ring when [(cyclohexadiene)Mn(CO)$_3$]$^-$ was treated with CH$_3$I. More recently, Brookhart et al. have reported an entering group induced transfer of an alkyl group, R, in $(C_6H_6)Mn(CO)_2R$.[18] There are now many well-documented cases[19] where alkene–metal, polyenyl–metal hydride, or metal–alkyl complexes adopt an agostic structure in which the M–H–C bond is a three-center, two-electron bond rather than the classic terminal hydride structure. It is possible that such agostic complexes are isolable intermediates in ring-to-metal or metal-to-ring R group migration processes upon loss of ligand or attack by the entering group. However, the 16e species that we observe from loss of CO from I and II do not appear to be agostic complexes, based on UV–vis and IR.

The final noteworthy point concerning the 5-*endo*-R^2 group transfer (R^2 = H, Me) concerns the fact that irradiation of the 16e species leads to transfer of the R^2 group at 77 K. The quantum yields for R^2 group transfer have not been measured, but it is obvious that the quantum yields for the H transfer are much higher than for the Me transfer. This conclusion follows from the ability to essentially quantitatively form the 16e species before observing significant amount of the $(\eta^5\text{-}C_5Me_4R^1)Fe(CO)_2Me$. In comparison, $(\eta^5\text{-}C_5R_4R^1)Fe(CO)_2H$ forms as soon as the 16e species are observed. The photoreactions of photogenerated 16e complexes have been studied previously with the main process being loss of 2e donor ligands, uptake of an extruded ligand, or reorientation of the fragment in a matrix.[20] Light-activated R group transfer from an organic ligand to a metal center is uncommon, and the mechanism of these processes is still unclear at this stage, but the results here and earlier[4] suggest that optical energy can be channeled to give chemical reactions that require thermal activation energy. Other important photochemical reactions of interest in this connection include oxidative addition of alkanes to photoexcited atoms in low-temperature matrices.[21] In the case at hand there remains the interesting question of whether the light-activated R group transfer occurs in the excited state or is the result of crossing to upper vibrational levels of the ground state. The 16e $(\eta^4\text{-cyclopentadiene})Fe(CO)_2$ species might be good systems to investigate with IR laser activation to determine whether the R group transfer can be induced by pumping the group state to upper vibrational levels.

(15) (a) Kelly, J. M.; Bent, D. V.; Hermann, H.; Schulte-Frohlinde, D.; Koerner von Gustorf, E. *J. Organomet. Chem.* **1974**, *69*, 259. (b) Bonneau, R.; Kelly, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 1220.

(16) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324.

(17) Lamanna, W.; Brookhart, M. *J. Am. Chem. Soc.* **1981**, *103*, 989.

(18) (a) Rush, P. K.; Hoh, S. K.; Brookhart, M. *Organometallics* **1986**, *5*, 1745. (b) Brookhart, M.; Pinhas, A. R.; Kukacs, A. *Organometallics* **1982**, *1*, 1730.

(19) Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 1443 and references therein.

(20) Turner, J. J.; Poliakoff, M. *ACS Symp. Ser.* **1983**, *No. 211*, 35.

(21) (a) Billups, W. E.; Konarski, M. M.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 7394. (b) Ozin, G. A.; McIntosh, D. F.; Mitchell, S. A. *J. Am. Chem. Soc.* **1981**, *103*, 1574.